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

(Final Report)

Edgar Flores¹, Joëlle Viallon¹, Faraz Idrees¹, Philippe Moussay¹, Uehara Shinji², Dariusz Cieciora³, Francesca Rolle⁴, Michela Sega⁵, Oh Sang-Hyub⁶, Tatiana Macé⁶, Christophe Sutour⁶, Celine Pascale⁷, Tiqiang Zhang⁸, Defa Wang⁸, Hushu Guo⁸, Qian Han⁹, Damian Smeulders⁵, Mudalo Jozela¹⁰, Napo Godwill Ntasa¹⁰, James Tshilongo¹⁰, Tshepiso Mphamo¹⁰, Sivan Van Aswegen¹¹, Paul Brewer¹¹, Miroslava Valkova¹², Viliam Stovcik¹², Tanul Tarhan¹³, Olga Efremova¹⁴, Leonid Konopelko¹⁴, Iris de Krom¹⁵, Stefan Persijn¹⁵ and Adriaan van der Veen¹⁵.

¹ Bureau International des Poids et Mesures, Pavillon de Breteuil, F-92312 Sèvres Cedex, France.
² Chemicals Evaluation and Research Institute (CERI), Japan, 1600 Shimotakano,Sagito-machi, Kitakatsushika-gun,Saitama 345-0043, Japan.
³ Central Office of Measures, Główny Urząd Miar (GUM), Elektoralna 2; 00-139 Warsaw; Poland.
⁴ Istituto Nazionale di Ricerca Metrologica (INRIM), Strada delle Cacce 91, I-10135 Torino, Italy
⁵ KRISS,1 Doryong-Dong, Yuseong-Gu, Daejeon 305-340, Republic of Korea
⁶ Laboratoire National de métrologie et d’Essais (LNE), 1, rue Gaston Boissier, 75724 Paris Cedex 15, France
⁷ Federal Office of Metrology (METAS), Gas Analysis Laboratory, Lindenweg 50, 3003 Bern-Wabern, Switzerland
⁸ National Institute of Metrology (NIM), China, No.18, Bei-San-Huan Dong Str., Beijing 100013, China.
⁹ National Measurement Institute Australia (NMIA), 36 Bradfield Rd, Lindfield NSW 2070, Australia.
¹⁰ National Metrology Institute of South Africa (NMISA), CSIR, Building 4 West, Meiring Naude Road Brummeria, 0184, Pretoria, South Africa
¹¹ National Physical Laboratory (NPL), Hampton Road, Teddington, Middlesex, TW11 0LW, UK.
¹² Slovak Institute of Metrology (SMU), Karloveská 63, SK-842 55 Bratislava, Slovak Republic
¹³ Gas Metrology Laboratory - TÜBİTAK (UME), Baris Mah. Dr. Zeki Acar Cad. No:1, 41470 Gebze / Kocaeli Turkey
¹⁴ D.I. Mendeleev Institute for Metrology (VNIIM), 19 Moskovsky pr., St. Petersburg, 190005 Russia.
¹⁵ Dutch National Metrology Institute - Van Swinden Laboratory (VSL), Thijssseweg 11 2629 JA Delft The Netherlands.

Coordinating laboratory:
Bureau International des Poids et Mesures (BIPM)

Study coordinator: Edgar Flores (BIPM)
Correspondence to be addressed to: Edgar Flores edgar.flores@bipm.org
(Tel: +33 1 45 07 70 92)

Field: Amount of substance

Organizing Body: CCQM
Index

1 EXECUTIVE SUMMARY 3
2 QUANTITIES AND UNITS 4
3 SCHEDULE 4
4 STANDARDS PREPARATION AND MEASUREMENTS OF PARTICIPANTS 4
4.1 Summary of participants’ reports 4
4.2 Participants’ submitted results 9
5 BIPM MEASUREMENT RESULTS 16
5.1 Analysis of trace components 16
5.2 Loss of NO₂ versus time 34
6 COMPARISON RESULTS 35
6.1 The Key Comparison Reference Value 35
6.2 Participants’ values at the date of the KCRVs 36
   6.2.1 No decay was observed 36
   6.2.2 A decay was observed 36
6.3 Degrees of equivalence 38
7 RESULTS ANALYSIS 41
7.1 Comparison with CCQM-K74 (2009) results 42
8 ‘HOW FAR THE LIGHT SHINES’ STATEMENT 43
ANNEX I- PARTICIPANTS’ VALUES AT THE DATE OF THE KCRVS 44
ANNEX II- HNO₃ AND OFFSET VS BIPM REFERENCE VALUES 48
ANNEX III- BIPM VALUE ASSIGNMENT PROCEDURE 51
ANNEX IV- ABB LIMAS ANALYSER RESULTS 64
ANNEX V- ABB LIMAS ANALYSER RESULTS AND OFFSET VS BIPM REFERENCE VALUES 68
ANNEX VI- CHARACTERISTIC SPECTRA OF THE ANALYSED MIXTURES 71
ANNEX VII - MEASUREMENT REPORTS OF PARTICIPANTS 74
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 ($\text{NO}_2$) 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 participant are plotted next to each other's.](image-url)
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 \(\mu\)mol 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 \(\mu\)mol mol\(^{-1}\))

3 Schedule

The revised schedule for the project was as follows:

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

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 NO₂ standards, CCQM-K74.2009 had highlighted the potential presence of HNO₃ in the gas mixtures and the importance of a correct estimation of its amount fraction to accurately determine NO₂ amount fractions. Therefore, the analytical technique used by participants to perform NO₂ measurements after preparation of the standards is a key information, as well as the quantification of HNO₃.

In Table 1 we can observe that seven laboratories of fourteen used Chemiluminescence (CLD) analysers, which measure NOₓ rather than NO₂ only, including HNO₃. Three laboratories used Non-Dispersive Ultraviolet (ND-UV) analysers (NPL, NMISA and VSL), which can measure exclusively NO₂. Three laboratories used Fourier Transformed InfraRed (FT-IR) analysers (LNE, NMIA and VNIIM) which can measure both NO₂ and HNO₃ independently. Among these three laboratories, only LNE and VNIIM reported HNO₃ amount fractions measured in their gas mixtures.

VSL measured HNO₃ by Cavity Ring Down Spectroscopy (CRDS) and NMISA used FT-IR to measure the HNO₃ 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.

<table>
<thead>
<tr>
<th>Lab</th>
<th>Standards for pre BIPM stability values</th>
<th>Date of prep.</th>
<th>Standards for post BIPM stability values</th>
<th>Date of prep.</th>
<th>Analytical instrument</th>
<th>Responds to</th>
<th>Preparation method</th>
<th>Impurities detected in submitted Standard 1</th>
<th>Impurities detected in submitted Standard 2</th>
<th>Submitted cylinder type</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>GUM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CLD Thermo 42i</td>
<td>NOx</td>
<td>NO + O2 reaction</td>
<td></td>
<td></td>
<td></td>
<td>Al with coated layers</td>
</tr>
<tr>
<td>INRIM</td>
<td>3 standards same as sent 7-11 ppm</td>
<td></td>
<td>with NPL QC standard</td>
<td></td>
<td>CLD Thermo 42i-HL</td>
<td>NOx</td>
<td>NO + O2 reaction</td>
<td>HNO3 (below LoD)</td>
<td></td>
<td>Al</td>
<td>Traceability to NPL NO in N2 mixtures at 100ppm</td>
</tr>
<tr>
<td>KRISS</td>
<td>4 PRMs</td>
<td></td>
<td></td>
<td></td>
<td>FT-IR</td>
<td>NO2</td>
<td>NO + O2 reaction</td>
<td>HNO3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPL</td>
<td>Reference gas</td>
<td></td>
<td></td>
<td></td>
<td>UV LIMAS 11 NO2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LNE</td>
<td>Dynamic dilution high amount fraction NO2</td>
<td></td>
<td></td>
<td></td>
<td>FT-IR</td>
<td>NO2</td>
<td>NO + O2 reaction</td>
<td>HNO3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMISA</td>
<td>NO2 10-100ppm multipoint</td>
<td></td>
<td></td>
<td></td>
<td>UV LIMAS NO2</td>
<td>NO2</td>
<td>NO + O2 reaction</td>
<td>HNO3 (below LoD)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CERI</td>
<td>1 Fresh NO2 standard</td>
<td>At each stability measurement</td>
<td>1 Fresh NO2 standard</td>
<td>At each stability measurement</td>
<td>CLD Thermo 42i-HL</td>
<td>NOX including HNO3</td>
<td>NO + O2 reaction.</td>
<td>NO 20 ppb at 3rd stability measurement</td>
<td>NO 20 ppb at 3rd stability measurement</td>
<td>Al</td>
<td></td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol⁻¹
<table>
<thead>
<tr>
<th>Lab</th>
<th>Standards for pre BIPM stability values</th>
<th>Date of prep.</th>
<th>Standards for post BIPM stability values</th>
<th>Date of prep.</th>
<th>Analytical instrument</th>
<th>Responds to</th>
<th>Preparation method</th>
<th>Impurities detected in submitted Standard 1</th>
<th>Impurities detected in submitted Standard 2</th>
<th>Submitted cylinder type</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMIA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>FT-IR</td>
<td>NO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Moisture in regulators</td>
</tr>
<tr>
<td>NIM</td>
<td>1 Fresh NO₂ standard</td>
<td>At each stability measurement</td>
<td>1 Fresh NO₂ standard</td>
<td>At each stability measurement</td>
<td>CLD Thermo 42i-HL</td>
<td>NOₓ including HNO₃</td>
<td>NO + O₂ reaction</td>
<td></td>
<td></td>
<td></td>
<td>Cylinder heated and exposed to 100 ppm NO₂ for 2 days, 0.2 ppm H₂O in N₂</td>
</tr>
<tr>
<td>SMU</td>
<td>3 standards 10-15 ppm</td>
<td>3 standards 10-15 ppm</td>
<td>CLD Thermo 42c NOₓ including HNO₃</td>
<td>NO + O₂ reaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Aculife IV surface</td>
</tr>
<tr>
<td>UME</td>
<td>single point calibration</td>
<td></td>
<td>Single point calibration</td>
<td></td>
<td>CLD Thermo 42i</td>
<td>NOₓ including HNO₃</td>
<td>NO + O₂ reaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>METAS</td>
<td>Dynamic preparation with a new PERM TUBE for each measurement</td>
<td>Dynamic preparation with a new PERM TUBE for each measurement</td>
<td>CLD Thermo 42i-TL NOₓ including HNO₃</td>
<td>VSL standard NO + O₂ reaction</td>
<td></td>
<td></td>
<td>Trace level analyser used at the 50-100 ppb range for NO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VNIIM</td>
<td>6 series were carried out for APEX614632 cylinder and 5 – for cylinder № 5603778</td>
<td></td>
<td>FT-IR NO₂ NO + O₂ reaction HNO₃ correction applied to NO₂ HNO₃ correction applied to NO₂</td>
<td></td>
<td>4.8 m FT-IR</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 µmol mol⁻¹
<table>
<thead>
<tr>
<th>Lab</th>
<th>Standards for pre BIPM stability values</th>
<th>Date of prep.</th>
<th>Standards for post BIPM stability values</th>
<th>Date of prep.</th>
<th>Analytical instrument</th>
<th>Responds to</th>
<th>Preparation method</th>
<th>Impurities detected in submitted Standard 1</th>
<th>Impurities detected in submitted Standard 2</th>
<th>Submitted cylinder type</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>VSL</td>
<td>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} NO₂ in N₂</td>
<td>Less than 12 months before analysis</td>
<td>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} NO₂ in N₂</td>
<td>Less than 12 months before analysis</td>
<td>LIMAS</td>
<td>NO₂</td>
<td>NO + O₂ reaction</td>
<td>HNO₃ correction applied to NO₂</td>
<td>HNO₃ correction applied to NO₂</td>
<td>10 litre aluminium cylinder with Alpha Tech NO₂ passivation</td>
<td>The gravimetric amount fraction has been corrected for the HNO₃ amount fraction, according to analysis, and the N₂O₄ amount fraction calculated based on literature</td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol⁻¹
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
- **\(x_{\text{NMI}}\)** the NO\(_2\) amount fraction in the standard assigned by the NMI;
- **\(u(x_{\text{NMI}})\)** 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 (\(u(x_{\text{NMI}})= 0.016 \, \mu\text{mol mol}^{-1}\)) and the largest (\(u(x_{\text{NMLA}})= 0.30 \, \mu\text{mol mol}^{-1}\)) submitted uncertainties. The average standard uncertainty value was 0.074 \(\mu\text{mol mol}^{-1}\).

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 \(\mu\text{mol mol}^{-1}\) and 0.17 \(\mu\text{mol mol}^{-1}\) (see Table 3).
Table 2. $NO_2$ amount fraction reported by participants for each of their six measurements. – No measurements available.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>Date of measurement by the NMI</th>
<th>Assigned NO$<em>2$ amount fraction $x</em>{NMI}$ (μmol mol$^{-1}$)</th>
<th>Assigned standard uncertainty $u(x_{NMI})$ (μmol mol$^{-1}$)</th>
<th>NMI</th>
<th>Cylinder</th>
<th>Date of measurement by the NMI</th>
<th>Assigned NO$<em>2$ amount fraction $x</em>{NMI}$ (μmol mol$^{-1}$)</th>
<th>Assigned standard uncertainty $u(x_{NMI})$ (μmol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMI</td>
<td>CPB 25961</td>
<td>15/01/2018</td>
<td>10.098</td>
<td>0.041</td>
<td>06/02/2018</td>
<td>10.526</td>
<td>0.117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>CPB 25961</td>
<td>16/02/2018</td>
<td>10.052</td>
<td>0.040</td>
<td>07/03/2018</td>
<td>10.619</td>
<td>0.107</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>CPB 25961</td>
<td>12/03/2018</td>
<td>10.022</td>
<td>0.040</td>
<td>10/04/2018</td>
<td>10.906</td>
<td>0.118</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>CPB 25961</td>
<td>10/04/2019</td>
<td>9.798</td>
<td>0.039</td>
<td>04/04/2019</td>
<td>10.446</td>
<td>0.119</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>CPB 25961</td>
<td>23/05/2019</td>
<td>9.742</td>
<td>0.039</td>
<td>16/05/2019</td>
<td>10.355</td>
<td>0.126</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>CPB 25961</td>
<td>12/07/2019</td>
<td>9.792</td>
<td>0.039</td>
<td>10/07/2019</td>
<td>10.399</td>
<td>0.143</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>CPB 18969</td>
<td>15/01/2018</td>
<td>10.088</td>
<td>0.041</td>
<td>06/02/2018</td>
<td>10.535</td>
<td>0.117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>CPB 18969</td>
<td>16/02/2018</td>
<td>10.074</td>
<td>0.041</td>
<td>07/03/2018</td>
<td>10.604</td>
<td>0.108</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>CPB 18969</td>
<td>12/03/2018</td>
<td>10.044</td>
<td>0.040</td>
<td>10/04/2019</td>
<td>10.827</td>
<td>0.117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>CPB 18969</td>
<td>10/04/2019</td>
<td>9.770</td>
<td>0.039</td>
<td>04/04/2019</td>
<td>10.159</td>
<td>0.117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>CPB 18969</td>
<td>23/05/2019</td>
<td>9.748</td>
<td>0.039</td>
<td>16/05/2019</td>
<td>10.134</td>
<td>0.124</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>CPB 18969</td>
<td>12/07/2019</td>
<td>9.772</td>
<td>0.039</td>
<td>10/07/2019</td>
<td>9.989</td>
<td>0.142</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>P27787/D247449</td>
<td>01/12/2017</td>
<td>10.090</td>
<td>0.065</td>
<td>17/05/2018</td>
<td>10.030</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>P27787/D247449</td>
<td>29/01/2018</td>
<td>9.900</td>
<td>0.065</td>
<td>18/05/2018</td>
<td>10.050</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>P27787/D247449</td>
<td>26/04/2018</td>
<td>9.840</td>
<td>0.065</td>
<td>19/05/2018</td>
<td>10.040</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>P27787/D247449</td>
<td>18/04/2019</td>
<td>10.100</td>
<td>0.065</td>
<td>20/08/2018</td>
<td>10.050</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>P27787/D247449</td>
<td>13/05/2019</td>
<td>9.910</td>
<td>0.060</td>
<td>22/08/2019</td>
<td>10.050</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>P27787/D247449</td>
<td>21/06/2019</td>
<td>10.110</td>
<td>0.075</td>
<td>18/09/2019</td>
<td>10.060</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>INRIM</td>
<td>01/12/2017</td>
<td>10.360</td>
<td>0.065</td>
<td>17/05/2018</td>
<td>10.030</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>INRIM</td>
<td>29/01/2018</td>
<td>10.240</td>
<td>0.065</td>
<td>18/05/2018</td>
<td>10.020</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>INRIM</td>
<td>26/04/2018</td>
<td>10.210</td>
<td>0.065</td>
<td>19/05/2018</td>
<td>10.030</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>INRIM</td>
<td>18/04/2019</td>
<td>10.080</td>
<td>0.050</td>
<td>20/08/2018</td>
<td>10.030</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>INRIM</td>
<td>13/05/2019</td>
<td>10.150</td>
<td>0.050</td>
<td>22/08/2019</td>
<td>10.040</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI</td>
<td>INRIM</td>
<td>21/06/2019</td>
<td>10.250</td>
<td>0.065</td>
<td>18/09/2019</td>
<td>10.050</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol$^{-1}$
<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>Date of measurement by the NMI</th>
<th>Assigned NO$<em>2$ amount fraction $N</em>{\text{NMI}}$ ($\mu$mol mol$^{-1}$)</th>
<th>Assigned standard uncertainty $u(N_{\text{NMI}})$ ($\mu$mol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNE</td>
<td>1191</td>
<td>28/02/2018 10.100 0.065</td>
<td>28/03/2018 10.020 0.065</td>
<td>27/04/2018 9.960 0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14/05/2019 9.600 0.060</td>
<td>20/06/2019 9.570 0.060</td>
<td>12/07/2019 9.620 0.060</td>
</tr>
<tr>
<td></td>
<td>1183</td>
<td>28/02/2018 10.090 0.065</td>
<td>28/03/2018 10.010 0.065</td>
<td>27/04/2018 9.970 0.060</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14/05/2019 9.700 0.060</td>
<td>20/06/2019 9.690 0.060</td>
<td>12/07/2019 9.740 0.060</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>26/01/2018 9.936 0.017</td>
<td>02/03/2018 9.904 0.017</td>
<td>26/03/2018 9.890 0.017</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24/05/2019 9.769 0.017</td>
<td>28/06/2019 9.806 0.017</td>
<td>24/07/2019 9.785 0.017</td>
</tr>
<tr>
<td></td>
<td>L62804125</td>
<td>26/01/2018 9.947 0.017</td>
<td>02/03/2018 9.909 0.017</td>
<td>26/03/2018 9.896 0.017</td>
</tr>
<tr>
<td></td>
<td></td>
<td>29/05/2019 9.737 0.017</td>
<td>28/06/2019 9.759 0.017</td>
<td>24/07/2019 9.748 0.017</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23/03/2018 9.930 0.155</td>
<td>17/04/2018 9.670 0.130</td>
<td>23/05/2018 9.840 0.045</td>
</tr>
<tr>
<td></td>
<td></td>
<td>04/06/2019 9.500 0.030</td>
<td>03/07/2019 9.250 0.060</td>
<td>15/08/2019 9.560 0.105</td>
</tr>
<tr>
<td>METAS</td>
<td></td>
<td>26/03/2018 9.970 0.045</td>
<td>05/04/2018 9.970 0.045</td>
<td>06/04/2018 9.950 0.085</td>
</tr>
<tr>
<td></td>
<td></td>
<td>05/08/2019 9.850 0.300</td>
<td>06/08/2019 10.010 0.110</td>
<td>06/08/2019 10.020 0.120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>05/04/2018 10.270 0.100</td>
<td>05/04/2018 10.220 0.045</td>
<td>05/08/2019 10.020 0.120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>06/04/2018 10.220 0.075</td>
<td>05/08/2019 10.020 0.120</td>
<td>06/08/2019 10.020 0.120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>06/08/2019 10.010 0.120</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 $\mu$mol mol$^{-1}$
<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>Date of measurement by the NMI</th>
<th>Assigned NO₂ amount fraction (x_{NMI}) (μmol mol(^{-1}))</th>
<th>Assigned standard uncertainty (u(x_{NMI})) (μmol mol(^{-1}))</th>
<th>NMI</th>
<th>Date of measurement by the NMI</th>
<th>Assigned NO₂ amount fraction (x_{NMI}) (μmol mol(^{-1}))</th>
<th>Assigned standard uncertainty (u(x_{NMI})) (μmol mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMISA</td>
<td>D62 6618</td>
<td>12/03/2018</td>
<td>9.958</td>
<td>0.072</td>
<td></td>
<td></td>
<td>19/04/2018</td>
<td>10.020</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15/04/2018</td>
<td>10.029</td>
<td>0.072</td>
<td></td>
<td></td>
<td>03/05/2018</td>
<td>9.990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>07/05/2018</td>
<td>9.948</td>
<td>0.082</td>
<td></td>
<td></td>
<td>16/05/2018</td>
<td>10.020</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25/04/2019</td>
<td>10.020</td>
<td>0.045</td>
<td></td>
<td></td>
<td>08/05/2019</td>
<td>9.820</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27/05/2019</td>
<td>10.010</td>
<td>0.059</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25/07/2019</td>
<td>10.000</td>
<td>0.051</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>19/04/2018</td>
<td>10.020</td>
<td>0.035</td>
<td></td>
<td></td>
<td>19/04/2018</td>
<td>10.040</td>
</tr>
<tr>
<td></td>
<td></td>
<td>03/05/2018</td>
<td>9.990</td>
<td>0.035</td>
<td></td>
<td></td>
<td>03/05/2018</td>
<td>10.010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16/05/2018</td>
<td>10.020</td>
<td>0.035</td>
<td></td>
<td></td>
<td>16/05/2018</td>
<td>10.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>08/05/2019</td>
<td>9.820</td>
<td>0.050</td>
<td></td>
<td></td>
<td>08/05/2019</td>
<td>9.750</td>
</tr>
<tr>
<td></td>
<td></td>
<td>03/06/2019</td>
<td>9.880</td>
<td>0.050</td>
<td></td>
<td></td>
<td>03/06/2019</td>
<td>9.880</td>
</tr>
<tr>
<td></td>
<td></td>
<td>08/07/2019</td>
<td>9.810</td>
<td>0.050</td>
<td></td>
<td></td>
<td>08/07/2019</td>
<td>9.810</td>
</tr>
<tr>
<td>SMU</td>
<td>D62 6554</td>
<td>08/03/2018</td>
<td>9.938</td>
<td>0.068</td>
<td></td>
<td></td>
<td>S357</td>
<td>19/04/2018</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15/04/2018</td>
<td>9.943</td>
<td>0.084</td>
<td></td>
<td></td>
<td>03/05/2018</td>
<td>10.010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>07/05/2018</td>
<td>9.856</td>
<td>0.069</td>
<td></td>
<td></td>
<td>16/05/2018</td>
<td>10.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25/04/2019</td>
<td>10.007</td>
<td>0.046</td>
<td></td>
<td></td>
<td>08/05/2019</td>
<td>9.750</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27/05/2019</td>
<td>9.985</td>
<td>0.058</td>
<td></td>
<td></td>
<td>08/05/2019</td>
<td>9.880</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25/07/2019</td>
<td>9.999</td>
<td>0.056</td>
<td></td>
<td></td>
<td>08/07/2019</td>
<td>9.810</td>
</tr>
<tr>
<td></td>
<td>MY9742</td>
<td>29/01/2018</td>
<td>10.180</td>
<td>0.105</td>
<td></td>
<td></td>
<td>PSM499783</td>
<td>17/01/2018</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27/02/2018</td>
<td>10.130</td>
<td>0.105</td>
<td></td>
<td></td>
<td>21/02/2018</td>
<td>9.790</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28/03/2018</td>
<td>10.110</td>
<td>0.105</td>
<td></td>
<td></td>
<td>21/03/2018</td>
<td>9.819</td>
</tr>
<tr>
<td></td>
<td></td>
<td>09/04/2019</td>
<td>10.130</td>
<td>0.130</td>
<td></td>
<td></td>
<td>28/05/2019</td>
<td>9.717</td>
</tr>
<tr>
<td></td>
<td></td>
<td>02/05/2019</td>
<td>10.140</td>
<td>0.115</td>
<td></td>
<td></td>
<td>27/06/2019</td>
<td>9.748</td>
</tr>
<tr>
<td></td>
<td></td>
<td>05/06/2019</td>
<td>10.130</td>
<td>0.120</td>
<td></td>
<td></td>
<td>25/07/2019</td>
<td>9.745</td>
</tr>
<tr>
<td></td>
<td>UME</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MY9728</td>
<td>29/01/2018</td>
<td>10.050</td>
<td>0.115</td>
<td></td>
<td></td>
<td>PSM499791</td>
<td>17/01/2018</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27/02/2018</td>
<td>10.050</td>
<td>0.110</td>
<td></td>
<td></td>
<td>21/02/2018</td>
<td>10.123</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28/03/2018</td>
<td>10.060</td>
<td>0.110</td>
<td></td>
<td></td>
<td>21/03/2018</td>
<td>10.109</td>
</tr>
<tr>
<td></td>
<td></td>
<td>09/04/2019</td>
<td>9.870</td>
<td>0.115</td>
<td></td>
<td></td>
<td>28/05/2019</td>
<td>10.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>02/05/2019</td>
<td>9.880</td>
<td>0.115</td>
<td></td>
<td></td>
<td>27/06/2019</td>
<td>10.033</td>
</tr>
<tr>
<td></td>
<td></td>
<td>05/06/2019</td>
<td>9.830</td>
<td>0.150</td>
<td></td>
<td></td>
<td>25/07/2019</td>
<td>10.024</td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol\(^{-1}\)
<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>Date of measurement by the NMI</th>
<th>Assigned NO₂ amount fraction $x_{NMI}$ (μmol mol⁻¹)</th>
<th>Assigned standard uncertainty $u(x_{NMI})$ (μmol mol⁻¹)</th>
<th>NMI</th>
<th>Cylinder</th>
<th>Date of measurement by the NMI</th>
<th>Assigned NO₂ amount fraction $x_{NMI}$ (μmol mol⁻¹)</th>
<th>Assigned standard uncertainty $u(x_{NMI})$ (μmol mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>20/03/2018</td>
<td>9.890</td>
<td>0.070</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>04/04/2018</td>
<td>9.950</td>
<td>0.070</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18/04/2018</td>
<td>9.890</td>
<td>0.070</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>16/07/2019</td>
<td>9.810</td>
<td>0.075</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>28/08/2019</td>
<td>9.750</td>
<td>0.075</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17/09/2019</td>
<td>9.740</td>
<td>0.075</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>VSL105804</td>
<td>05/01/2018</td>
<td>9.875</td>
<td>0.070</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>01/03/2018</td>
<td>9.856</td>
<td>0.070</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>28/03/2018</td>
<td>9.903</td>
<td>0.070</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>VSL105806</td>
<td>21/05/2019</td>
<td>9.785</td>
<td>0.070</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25/06/2019</td>
<td>9.850</td>
<td>0.070</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>VSL105804</td>
<td>25/07/2019</td>
<td>9.834</td>
<td>0.070</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol⁻¹
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).

<table>
<thead>
<tr>
<th>NMI</th>
<th>Number of Cylinder</th>
<th>Date</th>
<th>$x_{\text{HNO}_3(1)}$ (µmol mol$^{-1}$)</th>
<th>$\sigma_{x_{\text{HNO}_3(1)}}$ (µmol mol$^{-1}$)</th>
<th>Date</th>
<th>$x_{\text{HNO}_3(2)}$ (µmol mol$^{-1}$)</th>
<th>$\sigma_{x_{\text{HNO}_3(2)}}$ (µmol mol$^{-1}$)</th>
<th>Date</th>
<th>$x_{\text{HNO}_3(3)}$ (µmol mol$^{-1}$)</th>
<th>$\sigma_{x_{\text{HNO}_3(3)}}$ (µmol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNE</td>
<td>1191</td>
<td>28/02/2018</td>
<td>9.00E-03</td>
<td>4.50E-04</td>
<td>28/03/2018</td>
<td>3.20E-02</td>
<td>2.00E-03</td>
<td>27/04/2018</td>
<td>4.10E-02</td>
<td>2.00E-03</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>28/02/2018</td>
<td>4.00E-03</td>
<td>2.00E-04</td>
<td>28/03/2018</td>
<td>3.90E-02</td>
<td>2.00E-03</td>
<td>27/04/2018</td>
<td>5.20E-02</td>
<td>3.00E-03</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6554</td>
<td>08/05/2018</td>
<td>1.70E-01</td>
<td>6.00E-03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>18/04/2018</td>
<td>1.08E-01</td>
<td>1.80E-02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>19/04/2018</td>
<td>5.00E-02</td>
<td>9.00E-03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>17/01/2018</td>
<td>7.00E-02</td>
<td>6.00E-03</td>
<td>28/02/2018</td>
<td>7.80E-02</td>
<td>7.00E-03</td>
<td>29/03/2018</td>
<td>1.13E-01</td>
<td>1.00E-02</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>17/01/2018</td>
<td>8.00E-02</td>
<td>7.00E-03</td>
<td>28/02/2018</td>
<td>8.10E-02</td>
<td>7.00E-03</td>
<td>29/03/2018</td>
<td>1.13E-01</td>
<td>1.00E-02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NMI</th>
<th>Number of Cylinder</th>
<th>Date</th>
<th>$x_{\text{HNO}_3(4)}$ (µmol mol$^{-1}$)</th>
<th>$\sigma_{x_{\text{HNO}_3(4)}}$ (µmol mol$^{-1}$)</th>
<th>Date</th>
<th>$x_{\text{HNO}_3(5)}$ (µmol mol$^{-1}$)</th>
<th>$\sigma_{x_{\text{HNO}_3(5)}}$ (µmol mol$^{-1}$)</th>
<th>Date</th>
<th>$x_{\text{HNO}_3(6)}$ (µmol mol$^{-1}$)</th>
<th>$\sigma_{x_{\text{HNO}_3(6)}}$ (µmol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNE</td>
<td>1191</td>
<td>14/05/2019</td>
<td>7.00E-02</td>
<td>3.50E-03</td>
<td>20/06/2019</td>
<td>6.60E-02</td>
<td>3.00E-03</td>
<td>12/7/2019</td>
<td>4.30E-02</td>
<td>2.00E-03</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>14/05/2019</td>
<td>1.02E-01</td>
<td>5.10E-03</td>
<td>20/06/2019</td>
<td>1.07E-01</td>
<td>5.00E-03</td>
<td>12/7/2019</td>
<td>9.50E-02</td>
<td>5.00E-03</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6554</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>31/05/2019</td>
<td>1.38E-01</td>
<td>1.20E-02</td>
<td>23/08/2019</td>
<td>1.41E-01</td>
<td>1.30E-02</td>
<td>28/08/2019</td>
<td>1.43E-01</td>
<td>1.30E-02</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>31/05/2019</td>
<td>1.41E-01</td>
<td>1.30E-02</td>
<td>23/08/2019</td>
<td>1.51E-01</td>
<td>1.30E-02</td>
<td>28/08/2019</td>
<td>1.44E-01</td>
<td>1.30E-02</td>
</tr>
</tbody>
</table>

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

\[ x_{\text{BIPM},i} \]

is the \( i \)th measurement result by the BIPM (\( i = 1 \) to 3);

\[ u(x_{\text{BIPM},i}) \]

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 \( \mu \)mol 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\(_2\)O (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 HNO₃ (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 HNO₃ amount fraction measured in the VSL standards was also observed in other standards, with some exceptions. The gain in HNO₃ amount fractions is plotted versus the loss in NO₂ 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\textsubscript{2} amount fraction measurements.

<table>
<thead>
<tr>
<th>NMI and BIPM internal cylinder code (1 or 2)</th>
<th>Cylinder</th>
<th>Measurement date</th>
<th>1st BIPM NO\textsubscript{2} amount fraction measurement</th>
<th>Standard uncertainty</th>
<th>Measurement date</th>
<th>2nd BIPM NO\textsubscript{2} amount fraction</th>
<th>Standard uncertainty</th>
<th>Measurement date</th>
<th>3rd BIPM NO\textsubscript{2} amount fraction</th>
<th>Standard uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERI.1</td>
<td>CPB 25961</td>
<td>12/07/2018</td>
<td>9.782 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>21/11/2018</td>
<td>9.764 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>15/01/2019</td>
<td>9.735 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>CERI.2</td>
<td>CPB 18969</td>
<td>20/07/2018</td>
<td>9.806 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>11/12/2018</td>
<td>9.748 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>06/02/2019</td>
<td>9.819 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>GUM.1</td>
<td>No D298386_1</td>
<td>12/07/2018</td>
<td>10.330 (μmol mol\textsuperscript{-1})</td>
<td>0.039</td>
<td>29/11/2018</td>
<td>10.367 (μmol mol\textsuperscript{-1})</td>
<td>0.039</td>
<td>30/01/2019</td>
<td>10.324 (μmol mol\textsuperscript{-1})</td>
<td>0.039</td>
</tr>
<tr>
<td>GUM.2</td>
<td>No D298387_1</td>
<td>27/07/2018</td>
<td>10.142 (μmol mol\textsuperscript{-1})</td>
<td>0.039</td>
<td>12/12/2018</td>
<td>10.168 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>06/02/2019</td>
<td>10.161 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>INRIM.1</td>
<td>D247448</td>
<td>13/07/2018</td>
<td>9.566 (μmol mol\textsuperscript{-1})</td>
<td>0.030</td>
<td>29/11/2018</td>
<td>9.594 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>05/02/2019</td>
<td>9.651 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>INRIM.2</td>
<td>P27787/D247449</td>
<td>26/07/2018</td>
<td>9.349 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>18/12/2018</td>
<td>9.355 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>07/02/2019</td>
<td>9.318 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>KRISS.1</td>
<td>D59 6882</td>
<td>17/07/2018</td>
<td>9.344 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>05/12/2018</td>
<td>9.198 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>30/01/2019</td>
<td>9.127 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>KRISS.2</td>
<td>D59 6920</td>
<td>25/07/2018</td>
<td>9.267 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>06/12/2018</td>
<td>9.130 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>07/02/2019</td>
<td>9.055 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>LNE.1</td>
<td>1191</td>
<td>13/07/2018</td>
<td>9.558 (μmol mol\textsuperscript{-1})</td>
<td>0.030</td>
<td>22/11/2018</td>
<td>9.532 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>06/02/2019</td>
<td>9.554 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>LNE.2</td>
<td>1183</td>
<td>19/07/2018</td>
<td>9.628 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>06/12/2018</td>
<td>9.557 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>07/02/2019</td>
<td>9.488 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>METAS.1</td>
<td>10918</td>
<td>17/07/2018</td>
<td>9.707 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>03/12/2018</td>
<td>9.739 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>21/01/2019</td>
<td>9.703 (μmol mol\textsuperscript{-1})</td>
<td>0.039</td>
</tr>
<tr>
<td>METAS.2</td>
<td>10919</td>
<td>26/07/2018</td>
<td>9.728 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>17/12/2018</td>
<td>9.754 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>04/02/2019</td>
<td>9.725 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>NIM.1</td>
<td>L62804125</td>
<td>10/07/2018</td>
<td>9.786 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>29/11/2018</td>
<td>9.764 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>17/01/2019</td>
<td>9.756 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>NIM.2</td>
<td>L62804135</td>
<td>25/07/2018</td>
<td>9.779 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>06/12/2018</td>
<td>9.776 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>04/02/2019</td>
<td>9.746 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>NMIA.1</td>
<td>MK0806</td>
<td>16/07/2018</td>
<td>9.524 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>03/12/2018</td>
<td>9.509 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>15/01/2019</td>
<td>9.480 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>NMIA.2</td>
<td>MK0807</td>
<td>25/07/2018</td>
<td>9.561 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>17/12/2018</td>
<td>9.514 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>08/02/2019</td>
<td>9.449 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>NMISA.1</td>
<td>D62 6618</td>
<td>16/07/2018</td>
<td>9.572 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>05/12/2018</td>
<td>9.559 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>17/01/2019</td>
<td>9.525 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>NMISA.2</td>
<td>D62 6554</td>
<td>20/07/2018</td>
<td>9.559 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>12/12/2018</td>
<td>9.548 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>11/02/2019</td>
<td>9.494 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>NPL.1</td>
<td>2448</td>
<td>13/07/2018</td>
<td>4.961 (μmol mol\textsuperscript{-1})</td>
<td>0.063</td>
<td>03/12/2018</td>
<td>9.689 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>30/01/2019</td>
<td>9.635 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>NPL.2</td>
<td>S357</td>
<td>20/07/2018</td>
<td>8.228 (μmol mol\textsuperscript{-1})</td>
<td>0.039</td>
<td>11/12/2018</td>
<td>9.611 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
<td>08/02/2019</td>
<td>9.556 (μmol mol\textsuperscript{-1})</td>
<td>0.038</td>
</tr>
<tr>
<td>NMI and BIPM internal cylinder code (1 or 2)</td>
<td>Cylinder</td>
<td>Measurement date</td>
<td>1st BIPM assigned NO\textsubscript{2} amount (μmol mol\textsuperscript{-1})</td>
<td>Standard uncertainty (μmol mol\textsuperscript{-1})</td>
<td>Measurement date</td>
<td>2nd BIPM assigned NO\textsubscript{2} amount (μmol mol\textsuperscript{-1})</td>
<td>Standard uncertainty (μmol mol\textsuperscript{-1})</td>
<td>Measurement date</td>
<td>3rd BIPM assigned NO\textsubscript{2} amount (μmol mol\textsuperscript{-1})</td>
<td>Standard uncertainty (μmol mol\textsuperscript{-1})</td>
</tr>
<tr>
<td>------------------------------------------</td>
<td>------------</td>
<td>------------------</td>
<td>-------------------------------------------------</td>
<td>-----------------</td>
<td>------------------</td>
<td>-------------------------------------------------</td>
<td>-----------------</td>
<td>------------------</td>
<td>-------------------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>SMU.1</td>
<td>MY9742</td>
<td>10/07/2018</td>
<td>9.749</td>
<td>0.038</td>
<td>22/11/2018</td>
<td>9.714</td>
<td>0.038</td>
<td>15/01/2019</td>
<td>9.698</td>
<td>0.038</td>
</tr>
<tr>
<td>SMU.2</td>
<td>MY9728</td>
<td>27/07/2018</td>
<td>9.175</td>
<td>0.038</td>
<td>18/12/2018</td>
<td>9.128</td>
<td>0.038</td>
<td>08/02/2019</td>
<td>9.060</td>
<td>0.038</td>
</tr>
<tr>
<td>UME.1</td>
<td>PSM499791</td>
<td>10/07/2018</td>
<td>9.291</td>
<td>0.038</td>
<td>21/11/2018</td>
<td>9.226</td>
<td>0.038</td>
<td>21/01/2019</td>
<td>9.175</td>
<td>0.039</td>
</tr>
<tr>
<td>UME.2</td>
<td>PSM499783</td>
<td>17/07/2018</td>
<td>8.930</td>
<td>0.038</td>
<td>05/12/2018</td>
<td>8.873</td>
<td>0.039</td>
<td>12/02/2019</td>
<td>8.780</td>
<td>0.039</td>
</tr>
<tr>
<td>VNIIM.1</td>
<td>614632</td>
<td>16/07/2018</td>
<td>9.324</td>
<td>0.038</td>
<td>22/11/2018</td>
<td>9.457</td>
<td>0.038</td>
<td>21/01/2019</td>
<td>9.419</td>
<td>0.039</td>
</tr>
<tr>
<td>VNIIM.2</td>
<td>5603778</td>
<td>19/07/2018</td>
<td>9.577</td>
<td>0.038</td>
<td>11/12/2018</td>
<td>9.515</td>
<td>0.038</td>
<td>11/02/2019</td>
<td>9.479</td>
<td>0.038</td>
</tr>
<tr>
<td>VSL.1</td>
<td>VSL105804</td>
<td>12/07/2018</td>
<td>9.717</td>
<td>0.038</td>
<td>21/11/2018</td>
<td>9.718</td>
<td>0.038</td>
<td>17/01/2019</td>
<td>9.710</td>
<td>0.038</td>
</tr>
<tr>
<td>VSL.2</td>
<td>VSL105806</td>
<td>19/07/2018</td>
<td>9.701</td>
<td>0.038</td>
<td>12/12/2018</td>
<td>9.716</td>
<td>0.038</td>
<td>11/02/2019</td>
<td>9.668</td>
<td>0.038</td>
</tr>
</tbody>
</table>

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

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

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

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

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

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

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol$^{-1}$
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. HNO₃ 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.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>Measurement date</th>
<th>$x_{\text{HNO}_3(1)}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{HNO}_3(1)})$ (μmol mol$^{-1}$)</th>
<th>Measurement date</th>
<th>$x_{\text{HNO}_3(2)}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{HNO}_3(2)})$ (μmol mol$^{-1}$)</th>
<th>Measurement date</th>
<th>$x_{\text{HNO}_3(3)}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{HNO}_3(3)})$ (μmol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERI</td>
<td>CPB 25961</td>
<td>12/07/2018</td>
<td>0.154</td>
<td>0.022</td>
<td>21/11/2018</td>
<td>0.209</td>
<td>0.023</td>
<td>15/01/2019</td>
<td>0.226</td>
<td>0.023</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 18969</td>
<td>20/07/2018</td>
<td>0.126</td>
<td>0.021</td>
<td>11/12/2018</td>
<td>0.169</td>
<td>0.022</td>
<td>06/02/2019</td>
<td>0.182</td>
<td>0.022</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298386_1</td>
<td>12/07/2018</td>
<td>0.046</td>
<td>0.020</td>
<td>29/11/2018</td>
<td>0.051</td>
<td>0.020</td>
<td>30/01/2019</td>
<td>0.063</td>
<td>0.020</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298387_1</td>
<td>27/07/2018</td>
<td>0.026</td>
<td>0.020</td>
<td>12/12/2018</td>
<td>0.043</td>
<td>0.020</td>
<td>06/02/2019</td>
<td>0.052</td>
<td>0.020</td>
</tr>
<tr>
<td>INRIM</td>
<td>D247448</td>
<td>13/07/2018</td>
<td>0.197</td>
<td>0.023</td>
<td>29/11/2018</td>
<td>0.253</td>
<td>0.024</td>
<td>05/02/2019</td>
<td>0.219</td>
<td>0.023</td>
</tr>
<tr>
<td>INRIM</td>
<td>P27787/D247449</td>
<td>26/07/2018</td>
<td>0.250</td>
<td>0.024</td>
<td>18/12/2018</td>
<td>0.281</td>
<td>0.025</td>
<td>07/02/2019</td>
<td>0.290</td>
<td>0.025</td>
</tr>
<tr>
<td>KRIS</td>
<td>D59 6882</td>
<td>17/07/2018</td>
<td>0.170</td>
<td>0.022</td>
<td>05/12/2018</td>
<td>0.361</td>
<td>0.028</td>
<td>30/01/2019</td>
<td>0.369</td>
<td>0.028</td>
</tr>
<tr>
<td>KRIS</td>
<td>D59 6920</td>
<td>25/07/2018</td>
<td>0.261</td>
<td>0.024</td>
<td>06/12/2018</td>
<td>0.404</td>
<td>0.029</td>
<td>07/02/2019</td>
<td>0.442</td>
<td>0.031</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>13/07/2018</td>
<td>0.011</td>
<td>0.020</td>
<td>22/11/2018</td>
<td>0.048</td>
<td>0.020</td>
<td>06/02/2019</td>
<td>0.034</td>
<td>0.020</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>19/07/2018</td>
<td>0.042</td>
<td>0.020</td>
<td>06/12/2018</td>
<td>0.044</td>
<td>0.020</td>
<td>07/02/2019</td>
<td>0.041</td>
<td>0.020</td>
</tr>
<tr>
<td>METAS</td>
<td>10918</td>
<td>17/07/2018</td>
<td>0.083</td>
<td>0.020</td>
<td>03/12/2018</td>
<td>0.089</td>
<td>0.021</td>
<td>21/01/2019</td>
<td>0.100</td>
<td>0.021</td>
</tr>
<tr>
<td>METAS</td>
<td>10919</td>
<td>26/07/2018</td>
<td>0.044</td>
<td>0.020</td>
<td>17/12/2018</td>
<td>0.056</td>
<td>0.020</td>
<td>04/02/2019</td>
<td>0.072</td>
<td>0.020</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>10/07/2018</td>
<td>0.070</td>
<td>0.020</td>
<td>29/11/2018</td>
<td>0.063</td>
<td>0.020</td>
<td>17/01/2019</td>
<td>0.111</td>
<td>0.021</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>25/07/2018</td>
<td>0.075</td>
<td>0.020</td>
<td>06/12/2018</td>
<td>0.073</td>
<td>0.020</td>
<td>04/02/2019</td>
<td>0.070</td>
<td>0.020</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0806</td>
<td>16/07/2018</td>
<td>0.052</td>
<td>0.020</td>
<td>03/12/2018</td>
<td>0.134</td>
<td>0.021</td>
<td>15/01/2019</td>
<td>0.103</td>
<td>0.021</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0807</td>
<td>25/07/2018</td>
<td>0.117</td>
<td>0.021</td>
<td>17/12/2018</td>
<td>0.151</td>
<td>0.022</td>
<td>08/02/2019</td>
<td>0.176</td>
<td>0.022</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6618</td>
<td>16/07/2018</td>
<td>0.198</td>
<td>0.023</td>
<td>05/12/2018</td>
<td>0.241</td>
<td>0.024</td>
<td>17/01/2019</td>
<td>0.260</td>
<td>0.024</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6554</td>
<td>20/07/2018</td>
<td>0.222</td>
<td>0.023</td>
<td>12/12/2018</td>
<td>0.272</td>
<td>0.025</td>
<td>11/02/2019</td>
<td>0.287</td>
<td>0.025</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>13/07/2018</td>
<td>0.229</td>
<td>0.023</td>
<td>03/12/2018</td>
<td>0.185</td>
<td>0.022</td>
<td>30/01/2019</td>
<td>0.192</td>
<td>0.022</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>20/07/2018</td>
<td>0.340</td>
<td>0.027</td>
<td>11/12/2018</td>
<td>0.189</td>
<td>0.022</td>
<td>08/02/2019</td>
<td>0.221</td>
<td>0.023</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9742</td>
<td>10/07/2018</td>
<td>0.079</td>
<td>0.020</td>
<td>22/11/2018</td>
<td>0.121</td>
<td>0.021</td>
<td>15/01/2019</td>
<td>0.157</td>
<td>0.022</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9728</td>
<td>27/07/2018</td>
<td>0.202</td>
<td>0.023</td>
<td>18/12/2018</td>
<td>0.242</td>
<td>0.024</td>
<td>08/02/2019</td>
<td>0.268</td>
<td>0.025</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>10/07/2018</td>
<td>0.177</td>
<td>0.022</td>
<td>21/11/2018</td>
<td>0.244</td>
<td>0.024</td>
<td>21/01/2019</td>
<td>0.112</td>
<td>0.021</td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol$^{-1}$
<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>Measurement date</th>
<th>$x_{\text{HNO}_3(1)}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{HNO}_3(1)})$ (μmol mol$^{-1}$)</th>
<th>Measurement date</th>
<th>$x_{\text{HNO}_3(2)}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{HNO}_3(2)})$ (μmol mol$^{-1}$)</th>
<th>Measurement date</th>
<th>$x_{\text{HNO}_3(3)}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{HNO}_3(3)})$ (μmol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>17/07/2018</td>
<td>0.177</td>
<td>0.022</td>
<td>05/12/2018</td>
<td>0.217</td>
<td>0.023</td>
<td>12/02/2019</td>
<td>0.211</td>
<td>0.023</td>
</tr>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>16/07/2018</td>
<td>0.368</td>
<td>0.028</td>
<td>22/11/2018</td>
<td>0.512</td>
<td>0.034</td>
<td>21/01/2019</td>
<td>0.548</td>
<td>0.035</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>19/07/2018</td>
<td>0.109</td>
<td>0.021</td>
<td>11/12/2018</td>
<td>0.162</td>
<td>0.022</td>
<td>11/02/2019</td>
<td>0.189</td>
<td>0.022</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>12/07/2018</td>
<td>0.100</td>
<td>0.021</td>
<td>21/11/2018</td>
<td>0.074</td>
<td>0.020</td>
<td>17/01/2019</td>
<td>0.121</td>
<td>0.021</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>19/07/2018</td>
<td>0.116</td>
<td>0.021</td>
<td>12/12/2018</td>
<td>0.120</td>
<td>0.021</td>
<td>11/02/2019</td>
<td>0.135</td>
<td>0.021</td>
</tr>
</tbody>
</table>
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. \( \text{H}_2\text{O} \) 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 $\Delta x_{HNO_3}$ values against loss in $\Delta x_{NO_2}$ 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 NO₂ versus time

The NO₂ 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 NO₂ in each cylinder was calculated after linear regression of the $x_{BIPM}$ (Table 4) versus the time. The NO₂ 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 NO₂ 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 NO₂ amount fractions in cylinders.

![Figure 22: Loss rate of NO₂ 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.](image-url)

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’ NO₂ 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 NO₂ amount fractions submitted by participants. Calculated decay rates faster than -10⁻⁴ μmol mol⁻¹/day were taken to indicate a cylinder in which NO₂ was decreasing.

#### 6.2.1 No decay was observed

In this case the participants’ value \( x_{\text{NMI}} \), is a constant estimated from the average of the six measurements performed by the participant. The standard uncertainty \( u(x_{\text{NMI}}) \) 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 NO₂ 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 NO₂ amount fractions at the KCRV dates, and a decreasing power function ending with constant NO₂ amount fractions. The value \( x_{\text{NMI}} \) at a specific date was therefore estimated from the average of two values:

- \( x_{\text{NMI, LinPred}} \), the value predicted at that date by the linear regression of the participants’ results;
- \( \bar{x}_{\text{NMI,3Last}} \), the average of the last three participants’ results;

The standard uncertainty of the participant’s value, \( u(x_{\text{NMI}}) \), is estimated from a rectangular distribution delimited by the upper value \( x_{\text{NMI, LinPred}} \) plus its expanded uncertainty and the lower value \( \bar{x}_{\text{NMI,3Last}} \) minus its expanded uncertainty:

\[
u(x_{\text{NMI}}) = \frac{(x_{\text{NMI, LinPred}} + U(x_{\text{NMI, LinPred}}) - \bar{x}_{\text{NMI,3Last}} + U(\bar{x}_{\text{NMI,3Last}}))/(2\sqrt{3})}{(2\sqrt{3})}
\]  

In which:

\( u(x_{\text{NMI, LinPred}}) \) is the median of the standard uncertainties submitted by the participant for all its six measurements;
\( u(x_{\text{NMI}_3\text{Last}}) \) is the median of the three standard uncertainties submitted by the participant for its last three measurements;

The values \( x_{\text{NMI}_\text{LinPred}}, x_{\text{NMI}_3\text{Last}} \) 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} \text{ \( \mu \text{mol mol}^{-1} \)/day}. No uncertainty is provided as the values do not impact the comparison’s results. * are those cylinders that do not meet this criterion.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>Intercept</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \mu \text{mol mol}^{-1} )</td>
<td>( \mu \text{mol mol}^{-1}/\text{day} )</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 25961</td>
<td>10.0740</td>
<td>-5.97\times10^{-4}</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 18969</td>
<td>10.0857</td>
<td>-6.47\times10^{-4}</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298386_1</td>
<td>10.6912</td>
<td>-5.99\times10^{-4}</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298387_1</td>
<td>10.6867</td>
<td>-1.25\times10^{-3}</td>
</tr>
<tr>
<td>INRIM</td>
<td>P27787/D247449*</td>
<td>9.9462</td>
<td>1.51\times10^{-4}</td>
</tr>
<tr>
<td>INRIM</td>
<td>D247448</td>
<td>10.2879</td>
<td>-2.43\times10^{-4}</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6920*</td>
<td>10.0938</td>
<td>2.90\times10^{-3}</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6882*</td>
<td>10.0264</td>
<td>2.92\times10^{-3}</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>10.0547</td>
<td>-9.71\times10^{-4}</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>10.0436</td>
<td>-7.07\times10^{-4}</td>
</tr>
<tr>
<td>METAS</td>
<td>10918</td>
<td>9.8332</td>
<td>-8.32\times10^{-4}</td>
</tr>
<tr>
<td>METAS</td>
<td>10919</td>
<td>9.8524</td>
<td>-9.20\times10^{-4}</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>9.9283</td>
<td>-3.49\times10^{-4}</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>9.9179</td>
<td>-2.55\times10^{-4}</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0806*</td>
<td>9.8865</td>
<td>1.37\times10^{-4}</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0807</td>
<td>10.2368</td>
<td>-4.51\times10^{-4}</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6618*</td>
<td>9.9772</td>
<td>7.05\times10^{-4}</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6554*</td>
<td>9.9090</td>
<td>1.88\times10^{-4}</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>10.0168</td>
<td>-5.11\times10^{-4}</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>10.0217</td>
<td>-5.00\times10^{-4}</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9742*</td>
<td>10.1422</td>
<td>-2.25\times10^{-5}</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9728</td>
<td>10.0658</td>
<td>-4.45\times10^{-4}</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>10.0882</td>
<td>-1.25\times10^{-4}</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>9.8487</td>
<td>-2.15\times10^{-4}</td>
</tr>
<tr>
<td>VNIM</td>
<td>614632</td>
<td>9.9153</td>
<td>-2.89\times10^{-4}</td>
</tr>
<tr>
<td>VNIM</td>
<td>5603778</td>
<td>9.9484</td>
<td>-3.64\times10^{-4}</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>9.8806</td>
<td>-1.04\times10^{-4}</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>9.8692</td>
<td>-1.75\times10^{-4}</td>
</tr>
</tbody>
</table>
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:

\[ D = x_{\text{NMI}} - x_{\text{KCRV}} \]  \hspace{1cm} (2)

where \( x_{\text{NMI}} \) denotes the estimation of the \( \text{NO}_2 \) amount fraction in the participants’ standards at the date of the KCRVs and \( x_{\text{KCRV}} \) 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:

\[ u(D) = \sqrt{u(x_{\text{NMI}})^2 + u(x_{\text{KCRV}})^2} \]  \hspace{1cm} (3)

and the expanded uncertainty, at 95 % confidence level

\[ U(D) = k \cdot u(D) \]  \hspace{1cm} (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** is the identification code of the cylinder sent by the participating laboratory;
- \( x_{\text{NMI}} \) is the participants value estimated at the time of the KCRV as explained in section 6.2.
- \( u(x_{\text{NMI}}) \) is the uncertainty of the participants value estimated at the time of the KCRV as explained in section 6.2.
- \( x_{\text{KCRV}} \) is the KCRV measured by the BIPM explained in section 6.1.
- \( u(x_{\text{KCRV}}) \) is the uncertainty of the KCRV described in ANNEX III- BIPM Value assignment procedure.
- **\( D \)** is the degree of equivalence; and
- **\( U(D) \)** is 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.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>$D_1$</th>
<th>$U(D_1)$</th>
<th>$D_2$</th>
<th>$U(D_2)$</th>
<th>$D_3$</th>
<th>$U(D_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(μmol mol⁻¹)</td>
<td>(μmol mol⁻¹)</td>
<td>(μmol mol⁻¹)</td>
<td>(μmol mol⁻¹)</td>
<td>(μmol mol⁻¹)</td>
<td>(μmol mol⁻¹)</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 25961</td>
<td>0.091</td>
<td>0.214</td>
<td>0.069</td>
<td>0.173</td>
<td>0.082</td>
<td>0.156</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 18969</td>
<td>0.058</td>
<td>0.221</td>
<td>0.070</td>
<td>0.171</td>
<td>-0.020</td>
<td>0.153</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298386_1</td>
<td>0.169</td>
<td>0.404</td>
<td>0.090</td>
<td>0.357</td>
<td>0.114</td>
<td>0.336</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298387_1</td>
<td>0.141</td>
<td>0.503</td>
<td>0.029</td>
<td>0.405</td>
<td>0.001</td>
<td>0.365</td>
</tr>
<tr>
<td>INRIM</td>
<td>P27787/D247449</td>
<td>0.631</td>
<td>0.185</td>
<td>0.586</td>
<td>0.173</td>
<td>0.521</td>
<td>0.165</td>
</tr>
<tr>
<td>INRIM</td>
<td>D247448</td>
<td>0.643</td>
<td>0.151</td>
<td>0.637</td>
<td>0.151</td>
<td>0.674</td>
<td>0.151</td>
</tr>
<tr>
<td>KRIS</td>
<td>D59 6920</td>
<td>0.689</td>
<td>0.309</td>
<td>0.835</td>
<td>0.309</td>
<td>0.906</td>
<td>0.309</td>
</tr>
<tr>
<td>KRIS</td>
<td>D59 6882</td>
<td>0.780</td>
<td>0.309</td>
<td>0.917</td>
<td>0.310</td>
<td>0.992</td>
<td>0.309</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>0.202</td>
<td>0.333</td>
<td>0.164</td>
<td>0.265</td>
<td>0.105</td>
<td>0.224</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>0.199</td>
<td>0.284</td>
<td>0.221</td>
<td>0.230</td>
<td>0.267</td>
<td>0.205</td>
</tr>
<tr>
<td>METAS</td>
<td>10918</td>
<td>-0.120</td>
<td>0.346</td>
<td>-0.210</td>
<td>0.281</td>
<td>-0.195</td>
<td>0.259</td>
</tr>
<tr>
<td>METAS</td>
<td>10919</td>
<td>-0.145</td>
<td>0.357</td>
<td>-0.238</td>
<td>0.282</td>
<td>-0.231</td>
<td>0.257</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>0.023</td>
<td>0.133</td>
<td>0.021</td>
<td>0.111</td>
<td>0.020</td>
<td>0.104</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>0.050</td>
<td>0.116</td>
<td>0.036</td>
<td>0.102</td>
<td>0.059</td>
<td>0.096</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0806</td>
<td>0.396</td>
<td>0.233</td>
<td>0.411</td>
<td>0.233</td>
<td>0.440</td>
<td>0.233</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0807</td>
<td>0.541</td>
<td>0.372</td>
<td>0.555</td>
<td>0.335</td>
<td>0.608</td>
<td>0.321</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6618</td>
<td>0.422</td>
<td>0.151</td>
<td>0.435</td>
<td>0.151</td>
<td>0.469</td>
<td>0.151</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6554</td>
<td>0.402</td>
<td>0.147</td>
<td>0.407</td>
<td>0.147</td>
<td>0.461</td>
<td>0.147</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>-</td>
<td>-</td>
<td>0.171</td>
<td>0.163</td>
<td>0.210</td>
<td>0.148</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>-</td>
<td>-</td>
<td>0.247</td>
<td>0.176</td>
<td>0.288</td>
<td>0.161</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9742</td>
<td>0.388</td>
<td>0.233</td>
<td>0.423</td>
<td>0.233</td>
<td>0.439</td>
<td>0.233</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9728</td>
<td>0.748</td>
<td>0.347</td>
<td>0.763</td>
<td>0.311</td>
<td>0.819</td>
<td>0.298</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>0.752</td>
<td>0.161</td>
<td>0.809</td>
<td>0.152</td>
<td>0.856</td>
<td>0.149</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>0.843</td>
<td>0.175</td>
<td>0.885</td>
<td>0.160</td>
<td>0.971</td>
<td>0.152</td>
</tr>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>0.500</td>
<td>0.248</td>
<td>0.348</td>
<td>0.228</td>
<td>0.378</td>
<td>0.219</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>0.255</td>
<td>0.262</td>
<td>0.291</td>
<td>0.233</td>
<td>0.316</td>
<td>0.221</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>0.125</td>
<td>0.199</td>
<td>0.117</td>
<td>0.191</td>
<td>0.122</td>
<td>0.188</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>0.103</td>
<td>0.208</td>
<td>0.076</td>
<td>0.195</td>
<td>0.119</td>
<td>0.190</td>
</tr>
</tbody>
</table>
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 \(x_{\text{BIPM+HNO}_3}\) 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 be 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.
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 NO₂ 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 HNO₃ measurements in NO₂ standard development;
b) Development of best practice procedure for NO₂ 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 NO₂ 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 NO₂ in nitrogen mixtures in the range from 10 -1000 µmol mol⁻¹, provided the impact of dimerization to N₂O₄ 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 $x_{\text{NMI}}$, is a constant estimated from the average of the six measurements performed by the participant. The standard uncertainty $u(x_{\text{NMI}})$ is the median of the six reported standard uncertainties, as reported below.

Table 8. Participants’ values for cylinders without decay.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>$\bar{x}_{\text{NO}_2}$</th>
<th>$u(x_{\text{NMI}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(µmol mol$^{-1}$)</td>
<td>(µmol mol$^{-1}$)</td>
</tr>
<tr>
<td>INRIM</td>
<td>P27787/D247449</td>
<td>9.992</td>
<td>0.065</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6882</td>
<td>10.033</td>
<td>0.150</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6920</td>
<td>10.047</td>
<td>0.150</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0806</td>
<td>9.920</td>
<td>0.110</td>
</tr>
<tr>
<td>NMISA</td>
<td>MK0806</td>
<td>9.920</td>
<td>0.110</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9742</td>
<td>10.137</td>
<td>0.110</td>
</tr>
</tbody>
</table>

A decay was observed

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

- $x_{\text{NMI LinPred}}$, the value predicted at that date by the linear regression of the participants’ results
- $\bar{x}_{\text{NMI 3Last}}$, the average of the last three participants’ results;

The standard uncertainty of the participant’s value, $u(x_{\text{NMI}})$, is estimated from a rectangular distribution delimited by the upper value $x_{\text{NMI LinPred}}$ plus its expanded uncertainty and the lower value $\bar{x}_{\text{NMI 3Last}}$ minus its expanded uncertainty, equation 1.

The values $x_{\text{NMI LinPred}}$, $\bar{x}_{\text{NMI 3Last}}$ 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 \((\overline{x}_{NMI-3Last}, u(x_{NMI-3Last}))\), 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.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>(\overline{x}_{NMI-3Last}) (μmol mol(^{-1}))</th>
<th>(u(x_{NMI-3Last})) (μmol mol(^{-1}))</th>
<th>(x_{NMI_{LinPred}}) (μmol mol(^{-1}))</th>
<th>(u(x_{NMI_{LinPred}})) (μmol mol(^{-1}))</th>
<th>(x_{NMI,1}) (μmol mol(^{-1}))</th>
<th>(u(x_{NMI,1})) (μmol mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERI</td>
<td>CPB 25961</td>
<td>9.777</td>
<td>0.039</td>
<td>9.968</td>
<td>0.040</td>
<td>9.873</td>
<td>0.100</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 18969</td>
<td>9.763</td>
<td>0.039</td>
<td>9.965</td>
<td>0.040</td>
<td>9.864</td>
<td>0.104</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298386.1</td>
<td>10.400</td>
<td>0.126</td>
<td>10.598</td>
<td>0.119</td>
<td>10.499</td>
<td>0.198</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298387.1</td>
<td>10.094</td>
<td>0.124</td>
<td>10.473</td>
<td>0.117</td>
<td>10.283</td>
<td>0.248</td>
</tr>
<tr>
<td>INRIM</td>
<td>D247448</td>
<td>10.160</td>
<td>0.050</td>
<td>10.234</td>
<td>0.065</td>
<td>10.197</td>
<td>0.088</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>9.597</td>
<td>0.060</td>
<td>9.924</td>
<td>0.060</td>
<td>9.760</td>
<td>0.164</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>9.710</td>
<td>0.060</td>
<td>9.944</td>
<td>0.060</td>
<td>9.827</td>
<td>0.137</td>
</tr>
<tr>
<td>METAS</td>
<td>10918</td>
<td>9.437</td>
<td>0.060</td>
<td>9.737</td>
<td>0.083</td>
<td>9.587</td>
<td>0.169</td>
</tr>
<tr>
<td>METAS</td>
<td>10919</td>
<td>9.423</td>
<td>0.060</td>
<td>9.742</td>
<td>0.083</td>
<td>9.583</td>
<td>0.174</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>9.748</td>
<td>0.017</td>
<td>9.871</td>
<td>0.017</td>
<td>9.809</td>
<td>0.055</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>9.787</td>
<td>0.017</td>
<td>9.872</td>
<td>0.017</td>
<td>9.829</td>
<td>0.044</td>
</tr>
<tr>
<td>NIMIA</td>
<td>MK0807</td>
<td>10.017</td>
<td>0.120</td>
<td>10.187</td>
<td>0.110</td>
<td>10.102</td>
<td>0.182</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>9.820</td>
<td>0.050</td>
<td>9.972</td>
<td>0.035</td>
<td>9.897</td>
<td>0.093</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>9.813</td>
<td>0.050</td>
<td>9.976</td>
<td>0.043</td>
<td>9.895</td>
<td>0.100</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9728</td>
<td>9.860</td>
<td>0.115</td>
<td>9.986</td>
<td>0.115</td>
<td>9.925</td>
<td>0.169</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>10.020</td>
<td>0.050</td>
<td>10.066</td>
<td>0.049</td>
<td>10.043</td>
<td>0.071</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>9.737</td>
<td>0.049</td>
<td>9.810</td>
<td>0.051</td>
<td>9.773</td>
<td>0.079</td>
</tr>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>9.767</td>
<td>0.075</td>
<td>9.881</td>
<td>0.073</td>
<td>9.824</td>
<td>0.118</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>9.760</td>
<td>0.075</td>
<td>9.905</td>
<td>0.070</td>
<td>9.832</td>
<td>0.126</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>9.823</td>
<td>0.070</td>
<td>9.861</td>
<td>0.070</td>
<td>9.842</td>
<td>0.092</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>9.776</td>
<td>0.070</td>
<td>9.831</td>
<td>0.070</td>
<td>9.804</td>
<td>0.097</td>
</tr>
</tbody>
</table>
Table 10. Value predicted at the second KCRV date by the linear regression of the participants' results $x_{\text{NMI LinPred}}$, associated uncertainty $u(x_{\text{NMI LinPred}})$, and resulting participants' values $x_{\text{NML2}}$ and associated standard uncertainty $u(x_{\text{NML2}})$.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>$x_{\text{NMI LinPred}}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{NMI LinPred}})$ (μmol mol$^{-1}$)</th>
<th>$x_{\text{NML2}}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{NML2}})$ (μmol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERI</td>
<td>CPB 25961</td>
<td>9.889</td>
<td>0.040</td>
<td>9.833</td>
<td>0.078</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 18969</td>
<td>9.872</td>
<td>0.040</td>
<td>9.818</td>
<td>0.077</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298386 1</td>
<td>10.514</td>
<td>0.119</td>
<td>10.457</td>
<td>0.174</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298387 1</td>
<td>10.300</td>
<td>0.117</td>
<td>10.197</td>
<td>0.199</td>
</tr>
<tr>
<td>INRIM</td>
<td>D247448</td>
<td>10.200</td>
<td>0.065</td>
<td>10.180</td>
<td>0.078</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>9.795</td>
<td>0.060</td>
<td>9.696</td>
<td>0.127</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>9.845</td>
<td>0.060</td>
<td>9.777</td>
<td>0.108</td>
</tr>
<tr>
<td>METAS</td>
<td>10918</td>
<td>9.621</td>
<td>0.083</td>
<td>9.529</td>
<td>0.135</td>
</tr>
<tr>
<td>METAS</td>
<td>10919</td>
<td>9.609</td>
<td>0.083</td>
<td>9.516</td>
<td>0.136</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>9.821</td>
<td>0.017</td>
<td>9.785</td>
<td>0.040</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>9.838</td>
<td>0.017</td>
<td>9.812</td>
<td>0.034</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0807</td>
<td>10.121</td>
<td>0.110</td>
<td>10.069</td>
<td>0.163</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>9.900</td>
<td>0.035</td>
<td>9.860</td>
<td>0.072</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>9.904</td>
<td>0.043</td>
<td>9.858</td>
<td>0.079</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9728</td>
<td>9.922</td>
<td>0.115</td>
<td>9.891</td>
<td>0.151</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>10.050</td>
<td>0.049</td>
<td>10.035</td>
<td>0.066</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>9.779</td>
<td>0.051</td>
<td>9.758</td>
<td>0.070</td>
</tr>
<tr>
<td>VNIIM</td>
<td>6146532</td>
<td>9.844</td>
<td>0.073</td>
<td>9.805</td>
<td>0.107</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>9.852</td>
<td>0.070</td>
<td>9.806</td>
<td>0.110</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>9.847</td>
<td>0.070</td>
<td>9.835</td>
<td>0.088</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>9.807</td>
<td>0.070</td>
<td>9.792</td>
<td>0.090</td>
</tr>
</tbody>
</table>
Table 11. value predicted at the third KCRV date by the linear regression of the participants’ results $x_{\text{NMI LinPred}}$, associated uncertainty $u(x_{\text{NMI LinPred}})$, and resulting participants’ values $x_{\text{NMI3}}$ and associated standard uncertainty $u(x_{\text{NMI3}})$.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>$x_{\text{NMI LinPred}}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{NMI LinPred}})$ (μmol mol$^{-1}$)</th>
<th>$x_{\text{NMI3}}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{NMI3}})$ (μmol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERI</td>
<td>CPB 25961</td>
<td>9.856</td>
<td>0.040</td>
<td>9.817</td>
<td>0.068</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 18969</td>
<td>9.835</td>
<td>0.040</td>
<td>9.799</td>
<td>0.066</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298386 1</td>
<td>10.477</td>
<td>0.119</td>
<td>10.438</td>
<td>0.163</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298387 1</td>
<td>10.230</td>
<td>0.117</td>
<td>10.162</td>
<td>0.178</td>
</tr>
<tr>
<td>INRIM</td>
<td>D247448</td>
<td>10.183</td>
<td>0.065</td>
<td>10.172</td>
<td>0.073</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>9.722</td>
<td>0.060</td>
<td>9.659</td>
<td>0.105</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>9.800</td>
<td>0.060</td>
<td>9.755</td>
<td>0.095</td>
</tr>
<tr>
<td>METAS</td>
<td>10918</td>
<td>9.580</td>
<td>0.083</td>
<td>9.508</td>
<td>0.124</td>
</tr>
<tr>
<td>METAS</td>
<td>10919</td>
<td>9.564</td>
<td>0.083</td>
<td>9.494</td>
<td>0.123</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>9.804</td>
<td>0.017</td>
<td>9.776</td>
<td>0.035</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>9.823</td>
<td>0.017</td>
<td>9.805</td>
<td>0.030</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0807</td>
<td>10.097</td>
<td>0.110</td>
<td>9.939</td>
<td>0.156</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>9.871</td>
<td>0.035</td>
<td>9.845</td>
<td>0.064</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>9.874</td>
<td>0.043</td>
<td>9.844</td>
<td>0.071</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9728</td>
<td>9.899</td>
<td>0.115</td>
<td>9.879</td>
<td>0.144</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>10.042</td>
<td>0.049</td>
<td>10.031</td>
<td>0.064</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>9.765</td>
<td>0.051</td>
<td>9.751</td>
<td>0.065</td>
</tr>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>9.827</td>
<td>0.073</td>
<td>9.797</td>
<td>0.102</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>9.829</td>
<td>0.070</td>
<td>9.795</td>
<td>0.104</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>9.841</td>
<td>0.070</td>
<td>9.832</td>
<td>0.086</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>9.797</td>
<td>0.070</td>
<td>9.787</td>
<td>0.087</td>
</tr>
</tbody>
</table>
ANNEX II- HNO₃ 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 HNO₃ 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 NOₓ species and the BIPM system reports only NO₂, 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 NO₂ and HNO₃ were added to obtain $x_{\text{BIPM+HNO}_3}$. 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 HNO₃ 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.
Table 12. Results interpolated from participants’ measurements $x_{NMI\text{Pred}}$ 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 $\mu$mol mol$^{-1}$. * are the mixtures without decay. For further details see section and Table 9.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>$D'_{i1}$</th>
<th>$U(D'_{i1})$</th>
<th>$D'_{i2}$</th>
<th>$U(D'_{i2})$</th>
<th>$D'_{i3}$</th>
<th>$U(D'_{i3})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(μmol mol$^{-1}$)</td>
<td>(μmol mol$^{-1}$)</td>
<td>(μmol mol$^{-1}$)</td>
<td>(μmol mol$^{-1}$)</td>
<td>(μmol mol$^{-1}$)</td>
<td>(μmol mol$^{-1}$)</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 25961</td>
<td>-0.063</td>
<td>0.219</td>
<td>-0.140</td>
<td>0.179</td>
<td>-0.144</td>
<td>0.163</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 18969</td>
<td>-0.068</td>
<td>0.225</td>
<td>-0.099</td>
<td>0.177</td>
<td>-0.202</td>
<td>0.159</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298386_1</td>
<td>0.123</td>
<td>0.406</td>
<td>0.039</td>
<td>0.359</td>
<td>0.051</td>
<td>0.338</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298387_1</td>
<td>0.115</td>
<td>0.505</td>
<td>-0.014</td>
<td>0.407</td>
<td>-0.051</td>
<td>0.367</td>
</tr>
<tr>
<td>INRIM</td>
<td>P27787/D247449*</td>
<td>0.434</td>
<td>0.191</td>
<td>0.333</td>
<td>0.180</td>
<td>0.302</td>
<td>0.171</td>
</tr>
<tr>
<td>INRIM</td>
<td>D247448</td>
<td>0.393</td>
<td>0.158</td>
<td>0.356</td>
<td>0.159</td>
<td>0.384</td>
<td>0.159</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6920*</td>
<td>0.519</td>
<td>0.313</td>
<td>0.474</td>
<td>0.314</td>
<td>0.537</td>
<td>0.314</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6882*</td>
<td>0.519</td>
<td>0.313</td>
<td>0.513</td>
<td>0.315</td>
<td>0.550</td>
<td>0.316</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>0.191</td>
<td>0.335</td>
<td>0.116</td>
<td>0.268</td>
<td>0.071</td>
<td>0.228</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>0.157</td>
<td>0.287</td>
<td>0.177</td>
<td>0.233</td>
<td>0.226</td>
<td>0.209</td>
</tr>
<tr>
<td>METAS</td>
<td>10918</td>
<td>-0.203</td>
<td>0.349</td>
<td>-0.299</td>
<td>0.284</td>
<td>-0.295</td>
<td>0.263</td>
</tr>
<tr>
<td>METAS</td>
<td>10919</td>
<td>-0.189</td>
<td>0.359</td>
<td>-0.294</td>
<td>0.285</td>
<td>-0.303</td>
<td>0.261</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>-0.047</td>
<td>0.139</td>
<td>-0.042</td>
<td>0.118</td>
<td>-0.091</td>
<td>0.112</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>-0.025</td>
<td>0.123</td>
<td>-0.037</td>
<td>0.110</td>
<td>-0.011</td>
<td>0.105</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0806*</td>
<td>0.344</td>
<td>0.236</td>
<td>0.277</td>
<td>0.237</td>
<td>0.337</td>
<td>0.236</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0807</td>
<td>0.424</td>
<td>0.374</td>
<td>0.404</td>
<td>0.337</td>
<td>0.432</td>
<td>0.324</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6618*</td>
<td>0.224</td>
<td>0.158</td>
<td>0.194</td>
<td>0.158</td>
<td>0.209</td>
<td>0.159</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6554*</td>
<td>0.180</td>
<td>0.154</td>
<td>0.135</td>
<td>0.155</td>
<td>0.174</td>
<td>0.155</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>-</td>
<td>-</td>
<td>-0.014</td>
<td>0.169</td>
<td>0.018</td>
<td>0.155</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>-</td>
<td>-</td>
<td>0.058</td>
<td>0.182</td>
<td>0.067</td>
<td>0.168</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9742*</td>
<td>0.388</td>
<td>0.233</td>
<td>0.302</td>
<td>0.237</td>
<td>0.282</td>
<td>0.237</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9732</td>
<td>0.748</td>
<td>0.347</td>
<td>0.521</td>
<td>0.314</td>
<td>0.551</td>
<td>0.302</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>0.752</td>
<td>0.161</td>
<td>0.565</td>
<td>0.159</td>
<td>0.612</td>
<td>0.157</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>0.843</td>
<td>0.175</td>
<td>0.668</td>
<td>0.166</td>
<td>0.760</td>
<td>0.159</td>
</tr>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>0.500</td>
<td>0.248</td>
<td>-0.164</td>
<td>0.238</td>
<td>-0.170</td>
<td>0.230</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>0.255</td>
<td>0.262</td>
<td>0.129</td>
<td>0.237</td>
<td>0.127</td>
<td>0.226</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>0.125</td>
<td>0.199</td>
<td>0.043</td>
<td>0.196</td>
<td>0.001</td>
<td>0.193</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>0.103</td>
<td>0.208</td>
<td>-0.044</td>
<td>0.199</td>
<td>-0.016</td>
<td>0.194</td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 $\mu$mol mol$^{-1}$
ANNEX III- BIPM Value assignment procedure

The BIPM-NO₂ primary gas facility has been described in detail elsewhere²-⁵. For completeness reasons a summary of the value assignment procedure is presented as follows.

The BIPM-NO₂ 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 NO₂ 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 (NO₂ 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 \( x_{\text{BIPM}} \) in this document or \( x_{\text{NO₂}} \) in this section, are calculated by the expression below:

\[
x_{\text{NO₂}} = \left( \frac{P \times V_m}{q_v \times M_{\text{NO₂}}} \right) - \left( \frac{M_{\text{HNO₃}} \times x_{\text{HNO₃}}}{M_{\text{NO₂}}} \right) - \sum \left( \frac{M_{\text{imp}} \times x_{\text{imp}}}{M_{\text{NO₂}}} \right)
\]

(5)

where:

- \( x_{\text{NO₂}} \) is the NO₂ amount fraction in µmol mol⁻¹;
- \( P \) is the NO₂ permeation rate (mass lost rate) in ng min⁻¹;
- \( V_m = 22.4038 \text{ L mol}^{-1} \) is the molar volume of air/N₂ at standard conditions (273.15 K, 101.3 kPa);
- \( M_{\text{NO₂}} = 46.0055 \text{ g mol}^{-1} \) is the molar mass of NO₂;
- \( q_v \) is the total flow rate of N₂ given by the sum of carrier nitrogen (\( q_{\text{v molbloc2}} \)) and the diluent nitrogen (\( q_{\text{v molbloc1}} \)) flow rates in mL min⁻¹ at standard conditions (273.15 K, 101.325 kPa);
- \( x_{\text{HNO₃}} \) is the HNO₃ amount fraction in µmol mol⁻¹ measured by FT-IR spectroscopy (anchored to HITRAN 2012);
- \( M_{\text{HNO₃}} = 63.013 \text{ g mol}^{-1} \) is the molar mass of HNO₃;
- \( x_{\text{imp}} \) are the amount fractions in µmol mol⁻¹ of other impurities measured by FT-IR Spectroscopy (anchored to HITRAN 2012); and
- \( M_{\text{imp}} \) are the molar mass of the impurities in g mol⁻¹;

Uncertainties associated with each NO₂ amount fraction \( x_{\text{NO₂}} \) in gas mixtures produced by permeation of nitrogen dioxide, \( u(x_{\text{NO₂}}) \), are calculated by means of the software GUM Workbench V.2.3⁶. An example of the uncertainty budget is listed below:
Table 13. Uncertainty budget for a NO₂ / N₂ primary mixture generated with the BIPM facility.

Note: the molar masses $M_{N₂O₄}$, $M_{N₂O₃}$, $M_{N₂O₅}$, $M_{HONO}$, $M_{HO₂NO₂}$ were not included in this budget as they represent negligible uncertainty contributions.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Estimate</th>
<th>Assumed distribution</th>
<th>Standard uncertainty $u(x_i)$</th>
<th>Sensitivity coefficient $c_i = \frac{\sigma_{x_{NO2}}}{\sigma_x}$</th>
<th>Uncertainty contribution $u(y)$ mol·mol⁻¹</th>
<th>Index %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>11.1239</td>
<td>Normal</td>
<td>4.18 10⁻⁶ g·min⁻¹</td>
<td>0.95</td>
<td>4.0 10⁻⁹</td>
<td>1.7</td>
</tr>
<tr>
<td>$V_m$</td>
<td>22.4038</td>
<td>Normal</td>
<td>340.00 10⁻⁶ L·mol⁻¹</td>
<td>480</td>
<td>160 10⁻¹²</td>
<td>0.0</td>
</tr>
<tr>
<td>$q_{molbloc1}$</td>
<td>511 10⁻³ L·min⁻¹</td>
<td>Normal</td>
<td>455.21 10⁻⁶ L·min⁻¹</td>
<td>-21</td>
<td>-9.5 10⁻⁹</td>
<td>9.6</td>
</tr>
<tr>
<td>$M_{NO2}$</td>
<td>46.0055</td>
<td>Normal</td>
<td>1.40 10⁻³ g·mol⁻¹</td>
<td>-230</td>
<td>-320 10⁻¹²</td>
<td>0.0</td>
</tr>
<tr>
<td>$x_{HNO3}$</td>
<td>0.176 10⁻⁶ mol·mol⁻¹</td>
<td>Normal</td>
<td>0.021 10⁻⁶ mol·mol⁻¹</td>
<td>-1.4</td>
<td>-29 10⁻⁹</td>
<td>88.1</td>
</tr>
<tr>
<td>$x_{N2O4}$</td>
<td>0 mol·mol⁻¹</td>
<td>Normal</td>
<td>866 10⁻¹² mol·mol⁻¹</td>
<td>-2.0</td>
<td>-1.7 10⁻⁹</td>
<td>0.3</td>
</tr>
<tr>
<td>$x_{N2O3}$</td>
<td>0 mol·mol⁻¹</td>
<td>Normal</td>
<td>307 10⁻¹² mol·mol⁻¹</td>
<td>-1.7</td>
<td>-510 10⁻¹²</td>
<td>0.0</td>
</tr>
<tr>
<td>$x_{N2O5}$</td>
<td>0 mol·mol⁻¹</td>
<td>Normal</td>
<td>360 10⁻¹² mol·mol⁻¹</td>
<td>-2.3</td>
<td>-850 10⁻¹²</td>
<td>0.0</td>
</tr>
<tr>
<td>$x_{HONO}$</td>
<td>0 mol·mol⁻¹</td>
<td>Normal</td>
<td>520 10⁻¹² mol·mol⁻¹</td>
<td>-1.0</td>
<td>-530 10⁻¹²</td>
<td>0.0</td>
</tr>
<tr>
<td>$x_{HO2NO2}$</td>
<td>0 mol·mol⁻¹</td>
<td>Normal</td>
<td>572 10⁻¹² mol·mol⁻¹</td>
<td>1.7</td>
<td>-980 10⁻¹²</td>
<td>0.1</td>
</tr>
<tr>
<td>$M_{HNO3}$</td>
<td>63.013 g·mol⁻¹</td>
<td>Normal</td>
<td>1.17 10⁻³ g·mol⁻¹</td>
<td>-3.8</td>
<td>-6.5 10⁻¹²</td>
<td>0.0</td>
</tr>
</tbody>
</table>

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 HNO₃ uncertainty contribution to the combined uncertainty is significant. This was the subject of specific workshop held in 2010 by the GAWG and of further publications by the BIPM (see references²-⁵).

An additional uncertainty contribution due to possible NO₂ losses, when analyzing cylinders with the BIPM facility, $u(x_{NO2.losses})$, 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, \(u(x_{\text{NO}_2,j}, x_{\text{NO}_2,i})\) 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:

\[
u(x_{\text{NO}_2,j}, x_{\text{NO}_2,i}) = \gamma \left[ u(x_{\text{NO}_2,i}) \right]^2.
\]

Where \(u(x_{\text{NO}_2,i})\) is the standard uncertainty of the more concentrated mixture as given by equation 10.

\[
\gamma = \frac{q_j}{q_i}
\]

is the dilution factor of the total gas flow rates \(q_j\) and \(q_i\) (with \(q_i < q_j\)). Note that as the \(\text{NO}_2\) 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 \(u(x_{\text{NO}_2,i})\)^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 \(\text{NO}_2\) 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 $\sim 1 \times 10^4$ peak-peak from (2400-4700) cm$^{-1}$. By comparison the main NO$_2$ peak had absorbance in the range (0.04–0.16) abs$^{-1}$.

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 $\sim 400$ 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 $\Omega$ 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 $\sim 750$ mL and the sample flows at $\sim 400$ 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 $\pm 0.2%$ $^{13}$);
- CO$_2$: 2300 to 2400 cm$^{-1}$
- N₂O: 2100 to 2300 cm⁻¹
- H₂O: 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 HNO₃, Table 15 for H₂O, Table 16 for CO₂, Table 17 for N₂O, 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 is 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 \( j \) \((j=1, 2 \text{ or } 3)\); and

\( u(x_{i,j}) \) is 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: HNO₃ at an amount fraction \( (x) \) ranging from 100 nmol mol⁻¹ to 250 nmol mol⁻¹; CO₂ at an amount fraction \( (x) \) ranging from 10 nmol mol⁻¹ to 300 nmol mol⁻¹; N₂O 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 HNO₃ measured amount fraction values:

\[
u(x_{HNO₃}) = \sqrt{(0.02)^2 + (0.017x)^2 + (0.05x)^2}
\]  (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.

<table>
<thead>
<tr>
<th>Uncertainty</th>
<th>HNO₃</th>
<th>CO₂</th>
<th>N₂O</th>
<th>H₂O</th>
<th>HONO</th>
<th>NOCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>/μmol mol⁻¹</td>
<td>μmol mol⁻¹</td>
<td>μmol mol⁻¹</td>
<td>μmol mol⁻¹</td>
<td>μmol mol⁻¹</td>
<td>μmol mol⁻¹</td>
</tr>
<tr>
<td>Type A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Instrument stability</td>
<td>0.020</td>
<td>0.010</td>
<td>0.010</td>
<td>0.003</td>
<td>0.020</td>
<td>0.025</td>
</tr>
<tr>
<td>Type B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MALT</td>
<td>0.017x</td>
<td>0.015x</td>
<td>0.015x</td>
<td>0.017x</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>HITRAN</td>
<td>0.05x</td>
<td>0.03x</td>
<td>0.03x</td>
<td>0.05x</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Reference spectra</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1x</td>
<td>0.1x</td>
</tr>
<tr>
<td>Area measurement</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5x</td>
<td>0.5x</td>
</tr>
</tbody>
</table>
Table 15. $H_2O$ amount fraction measured in cylinder gas standards by the BIPM using FT-IR spectroscopy.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>Measurement date</th>
<th>$x_{H2O(1)}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{H2O(1)})$ (μmol mol$^{-1}$)</th>
<th>Measurement date</th>
<th>$x_{H2O(2)}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{H2O(2)})$ (μmol mol$^{-1}$)</th>
<th>Measurement date</th>
<th>$x_{H2O(3)}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{H2O(3)})$ (μmol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERI</td>
<td>CPB 25961</td>
<td>12/07/2018</td>
<td>0.678</td>
<td>0.107</td>
<td>21/11/2018</td>
<td>0.210</td>
<td>0.102</td>
<td>15/01/2019</td>
<td>0.242</td>
<td>0.102</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 18969</td>
<td>20/07/2018</td>
<td>0.937</td>
<td>0.113</td>
<td>11/12/2018</td>
<td>0.364</td>
<td>0.103</td>
<td>06/02/2019</td>
<td>0.392</td>
<td>0.103</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298386_1</td>
<td>12/07/2018</td>
<td>0.469</td>
<td>0.104</td>
<td>29/11/2018</td>
<td>0.230</td>
<td>0.102</td>
<td>30/01/2019</td>
<td>0.484</td>
<td>0.104</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298387_1</td>
<td>27/07/2018</td>
<td>1.017</td>
<td>0.114</td>
<td>12/12/2018</td>
<td>0.867</td>
<td>0.111</td>
<td>06/02/2019</td>
<td>1.023</td>
<td>0.115</td>
</tr>
<tr>
<td>INRIM</td>
<td>D247448</td>
<td>13/07/2018</td>
<td>0.631</td>
<td>0.106</td>
<td>29/11/2018</td>
<td>0.142</td>
<td>0.101</td>
<td>05/02/2019</td>
<td>0.575</td>
<td>0.106</td>
</tr>
<tr>
<td>INRIM</td>
<td>P27787/D247449</td>
<td>26/07/2018</td>
<td>0.596</td>
<td>0.106</td>
<td>18/12/2018</td>
<td>0.496</td>
<td>0.104</td>
<td>07/02/2019</td>
<td>0.471</td>
<td>0.104</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6882</td>
<td>17/07/2018</td>
<td>0.572</td>
<td>0.105</td>
<td>05/12/2018</td>
<td>0.606</td>
<td>0.106</td>
<td>30/01/2019</td>
<td>0.659</td>
<td>0.107</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6920</td>
<td>25/07/2018</td>
<td>1.150</td>
<td>0.118</td>
<td>06/12/2018</td>
<td>0.790</td>
<td>0.109</td>
<td>07/02/2019</td>
<td>0.785</td>
<td>0.109</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>13/07/2018</td>
<td>0.172</td>
<td>0.101</td>
<td>22/11/2018</td>
<td>0.227</td>
<td>0.102</td>
<td>06/02/2019</td>
<td>0.092</td>
<td>0.101</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>19/07/2018</td>
<td>0.000</td>
<td>0.101</td>
<td>06/12/2018</td>
<td>0.178</td>
<td>0.101</td>
<td>07/02/2019</td>
<td>0.212</td>
<td>0.102</td>
</tr>
<tr>
<td>METAS</td>
<td>10918</td>
<td>17/07/2018</td>
<td>0.581</td>
<td>0.106</td>
<td>03/12/2018</td>
<td>0.210</td>
<td>0.102</td>
<td>21/01/2019</td>
<td>0.296</td>
<td>0.102</td>
</tr>
<tr>
<td>METAS</td>
<td>10919</td>
<td>26/07/2018</td>
<td>0.302</td>
<td>0.102</td>
<td>17/12/2018</td>
<td>0.000</td>
<td>0.101</td>
<td>04/02/2019</td>
<td>0.326</td>
<td>0.103</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>10/07/2018</td>
<td>2.129</td>
<td>0.151</td>
<td>29/11/2018</td>
<td>0.008</td>
<td>0.101</td>
<td>17/01/2019</td>
<td>0.138</td>
<td>0.101</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>25/07/2018</td>
<td>0.233</td>
<td>0.102</td>
<td>06/12/2018</td>
<td>0.123</td>
<td>0.101</td>
<td>04/02/2019</td>
<td>0.128</td>
<td>0.101</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK8086</td>
<td>16/07/2018</td>
<td>0.076</td>
<td>0.101</td>
<td>03/12/2018</td>
<td>0.001</td>
<td>0.101</td>
<td>15/01/2019</td>
<td>0.027</td>
<td>0.101</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK8087</td>
<td>25/07/2018</td>
<td>0.001</td>
<td>0.101</td>
<td>17/12/2018</td>
<td>0.000</td>
<td>0.101</td>
<td>08/02/2019</td>
<td>0.074</td>
<td>0.101</td>
</tr>
<tr>
<td>NMISSA</td>
<td>D62 6618</td>
<td>16/07/2018</td>
<td>0.160</td>
<td>0.101</td>
<td>05/12/2018</td>
<td>0.000</td>
<td>0.101</td>
<td>17/01/2019</td>
<td>0.040</td>
<td>0.101</td>
</tr>
<tr>
<td>NMISSA</td>
<td>D62 6554</td>
<td>20/07/2018</td>
<td>0.002</td>
<td>0.101</td>
<td>12/12/2018</td>
<td>0.039</td>
<td>0.101</td>
<td>11/02/2019</td>
<td>0.000</td>
<td>0.101</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>13/07/2018</td>
<td>261.204</td>
<td>13.795</td>
<td>03/12/2018</td>
<td>0.345</td>
<td>0.103</td>
<td>30/01/2019</td>
<td>0.440</td>
<td>0.104</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>20/07/2018</td>
<td>200.657</td>
<td>10.597</td>
<td>11/12/2018</td>
<td>0.278</td>
<td>0.102</td>
<td>08/02/2019</td>
<td>0.327</td>
<td>0.103</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9742</td>
<td>10/07/2018</td>
<td>0.334</td>
<td>0.103</td>
<td>22/11/2018</td>
<td>0.525</td>
<td>0.105</td>
<td>15/01/2019</td>
<td>0.544</td>
<td>0.105</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9728</td>
<td>27/07/2018</td>
<td>0.401</td>
<td>0.103</td>
<td>18/12/2018</td>
<td>0.483</td>
<td>0.104</td>
<td>08/02/2019</td>
<td>0.550</td>
<td>0.105</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>10/07/2018</td>
<td>0.526</td>
<td>0.105</td>
<td>21/11/2018</td>
<td>0.524</td>
<td>0.105</td>
<td>21/01/2019</td>
<td>0.512</td>
<td>0.105</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>17/07/2018</td>
<td>0.040</td>
<td>0.101</td>
<td>05/12/2018</td>
<td>0.435</td>
<td>0.104</td>
<td>12/02/2019</td>
<td>0.483</td>
<td>0.104</td>
</tr>
<tr>
<td>NMI</td>
<td>Cylinder</td>
<td>Measurement date</td>
<td>$x_{\text{H}_2\text{O}(1)}$ (μmol mol$^{-1}$)</td>
<td>$u(x_{\text{H}_2\text{O}(1)})$ (μmol mol$^{-1}$)</td>
<td>Measurement date</td>
<td>$x_{\text{H}_2\text{O}(2)}$ (μmol mol$^{-1}$)</td>
<td>$u(x_{\text{H}_2\text{O}(2)})$ (μmol mol$^{-1}$)</td>
<td>Measurement date</td>
<td>$x_{\text{H}_2\text{O}(3)}$ (μmol mol$^{-1}$)</td>
<td>$u(x_{\text{H}_2\text{O}(3)})$ (μmol mol$^{-1}$)</td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>------------------</td>
<td>-----------------------------------------------</td>
<td>-----------------------------------------------</td>
<td>------------------</td>
<td>-----------------------------------------------</td>
<td>-----------------------------------------------</td>
<td>------------------</td>
<td>-----------------------------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>16/07/2018</td>
<td>12.080</td>
<td>0.646</td>
<td>22/11/2018</td>
<td>10.182</td>
<td>0.547</td>
<td>21/01/2019</td>
<td>10.727</td>
<td>0.575</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>19/07/2018</td>
<td>0.640</td>
<td>0.107</td>
<td>11/12/2018</td>
<td>0.892</td>
<td>0.111</td>
<td>11/02/2019</td>
<td>0.799</td>
<td>0.110</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>12/07/2018</td>
<td>0.231</td>
<td>0.102</td>
<td>21/11/2018</td>
<td>0.159</td>
<td>0.101</td>
<td>17/01/2019</td>
<td>0.194</td>
<td>0.102</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>19/07/2018</td>
<td>0.067</td>
<td>0.101</td>
<td>12/12/2018</td>
<td>0.160</td>
<td>0.101</td>
<td>11/02/2019</td>
<td>0.134</td>
<td>0.101</td>
</tr>
</tbody>
</table>
Table 16. CO₂ amount fraction measured in cylinder gas standards by the BIPM using FT-IR spectroscopy.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>Measurement date</th>
<th>(x_{\text{CO}_2(1)}) (μmol mol⁻¹)</th>
<th>(u(x_{\text{CO}_2(1)})) (μmol mol⁻¹)</th>
<th>Measurement date</th>
<th>(x_{\text{CO}_2(2)}) (μmol mol⁻¹)</th>
<th>(u(x_{\text{CO}_2(2)})) (μmol mol⁻¹)</th>
<th>Measurement date</th>
<th>(x_{\text{CO}_2(3)}) (μmol mol⁻¹)</th>
<th>(u(x_{\text{CO}_2(3)})) (μmol mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERI</td>
<td>CPB 25961</td>
<td>12/07/2018</td>
<td>0.018</td>
<td>0.017</td>
<td>21/11/2018</td>
<td>0.033</td>
<td>0.017</td>
<td>15/01/2019</td>
<td>0.036</td>
<td>0.017</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 18969</td>
<td>20/07/2018</td>
<td>0.020</td>
<td>0.017</td>
<td>11/12/2018</td>
<td>0.047</td>
<td>0.017</td>
<td>06/02/2019</td>
<td>0.051</td>
<td>0.017</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298386_1</td>
<td>12/07/2018</td>
<td>0.000</td>
<td>0.017</td>
<td>29/11/2018</td>
<td>0.019</td>
<td>0.017</td>
<td>30/01/2019</td>
<td>0.022</td>
<td>0.017</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298387_1</td>
<td>27/07/2018</td>
<td>0.010</td>
<td>0.017</td>
<td>12/12/2018</td>
<td>0.024</td>
<td>0.017</td>
<td>06/02/2019</td>
<td>0.025</td>
<td>0.017</td>
</tr>
<tr>
<td>INRIM</td>
<td>D247448</td>
<td>13/07/2018</td>
<td>0.010</td>
<td>0.017</td>
<td>29/11/2018</td>
<td>0.018</td>
<td>0.017</td>
<td>05/02/2019</td>
<td>0.017</td>
<td>0.017</td>
</tr>
<tr>
<td>INRIM</td>
<td>P27787/D247449</td>
<td>26/07/2018</td>
<td>0.003</td>
<td>0.017</td>
<td>18/12/2018</td>
<td>0.019</td>
<td>0.017</td>
<td>07/02/2019</td>
<td>0.019</td>
<td>0.017</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6882</td>
<td>17/07/2018</td>
<td>0.000</td>
<td>0.017</td>
<td>05/12/2018</td>
<td>0.027</td>
<td>0.017</td>
<td>30/01/2019</td>
<td>0.028</td>
<td>0.017</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6920</td>
<td>25/07/2018</td>
<td>0.022</td>
<td>0.017</td>
<td>06/12/2018</td>
<td>0.002</td>
<td>0.017</td>
<td>07/02/2019</td>
<td>0.024</td>
<td>0.017</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>13/07/2018</td>
<td>0.000</td>
<td>0.017</td>
<td>22/11/2018</td>
<td>0.004</td>
<td>0.017</td>
<td>06/02/2019</td>
<td>0.005</td>
<td>0.017</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>19/07/2018</td>
<td>0.000</td>
<td>0.017</td>
<td>06/12/2018</td>
<td>0.004</td>
<td>0.017</td>
<td>07/02/2019</td>
<td>0.001</td>
<td>0.017</td>
</tr>
<tr>
<td>METAS</td>
<td>10918</td>
<td>17/07/2018</td>
<td>0.015</td>
<td>0.017</td>
<td>03/12/2018</td>
<td>0.010</td>
<td>0.017</td>
<td>21/01/2019</td>
<td>0.012</td>
<td>0.017</td>
</tr>
<tr>
<td>METAS</td>
<td>10919</td>
<td>26/07/2018</td>
<td>0.024</td>
<td>0.017</td>
<td>17/12/2018</td>
<td>0.013</td>
<td>0.017</td>
<td>04/02/2019</td>
<td>0.014</td>
<td>0.017</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>10/07/2018</td>
<td>0.000</td>
<td>0.017</td>
<td>29/11/2018</td>
<td>0.015</td>
<td>0.017</td>
<td>17/01/2019</td>
<td>0.016</td>
<td>0.017</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>25/07/2018</td>
<td>0.013</td>
<td>0.017</td>
<td>06/12/2018</td>
<td>0.015</td>
<td>0.017</td>
<td>04/02/2019</td>
<td>0.018</td>
<td>0.017</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0806</td>
<td>16/07/2018</td>
<td>0.007</td>
<td>0.017</td>
<td>03/12/2018</td>
<td>0.015</td>
<td>0.017</td>
<td>15/01/2019</td>
<td>0.018</td>
<td>0.017</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0807</td>
<td>25/07/2018</td>
<td>0.012</td>
<td>0.017</td>
<td>17/12/2018</td>
<td>0.021</td>
<td>0.017</td>
<td>08/02/2019</td>
<td>0.021</td>
<td>0.017</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6618</td>
<td>16/07/2018</td>
<td>0.000</td>
<td>0.017</td>
<td>05/12/2018</td>
<td>0.003</td>
<td>0.017</td>
<td>17/01/2019</td>
<td>0.002</td>
<td>0.017</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6554</td>
<td>20/07/2018</td>
<td>0.000</td>
<td>0.017</td>
<td>12/12/2018</td>
<td>0.003</td>
<td>0.017</td>
<td>11/02/2019</td>
<td>0.004</td>
<td>0.017</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>13/07/2018</td>
<td>0.002</td>
<td>0.017</td>
<td>03/12/2018</td>
<td>0.003</td>
<td>0.017</td>
<td>30/01/2019</td>
<td>0.007</td>
<td>0.017</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>20/07/2018</td>
<td>0.010</td>
<td>0.017</td>
<td>11/12/2018</td>
<td>0.013</td>
<td>0.017</td>
<td>08/02/2019</td>
<td>0.014</td>
<td>0.017</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9742</td>
<td>10/07/2018</td>
<td>0.000</td>
<td>0.017</td>
<td>22/11/2018</td>
<td>0.013</td>
<td>0.017</td>
<td>15/01/2019</td>
<td>0.013</td>
<td>0.017</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9728</td>
<td>27/07/2018</td>
<td>0.002</td>
<td>0.017</td>
<td>18/12/2018</td>
<td>0.022</td>
<td>0.017</td>
<td>08/02/2019</td>
<td>0.024</td>
<td>0.017</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>10/07/2018</td>
<td>0.007</td>
<td>0.017</td>
<td>21/11/2018</td>
<td>0.031</td>
<td>0.017</td>
<td>21/01/2019</td>
<td>0.009</td>
<td>0.017</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>17/07/2018</td>
<td>0.035</td>
<td>0.017</td>
<td>05/12/2018</td>
<td>0.058</td>
<td>0.017</td>
<td>12/02/2019</td>
<td>0.059</td>
<td>0.017</td>
</tr>
<tr>
<td>NMI</td>
<td>Cylinder</td>
<td>Measurement date</td>
<td>$x_{\text{CO}_2(1)}$ (μmol mol$^{-1}$)</td>
<td>$u(x_{\text{CO}_2(1)})$ (μmol mol$^{-1}$)</td>
<td>Measurement date</td>
<td>$x_{\text{CO}_2(2)}$ (μmol mol$^{-1}$)</td>
<td>$u(x_{\text{CO}_2(2)})$ (μmol mol$^{-1}$)</td>
<td>Measurement date</td>
<td>$x_{\text{CO}_2(3)}$ (μmol mol$^{-1}$)</td>
<td>$u(x_{\text{CO}_2(3)})$ (μmol mol$^{-1}$)</td>
</tr>
<tr>
<td>---------</td>
<td>----------</td>
<td>-----------------</td>
<td>--------------------------------------</td>
<td>------------------------------------------</td>
<td>-----------------</td>
<td>--------------------------------------</td>
<td>------------------------------------------</td>
<td>-----------------</td>
<td>--------------------------------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>16/07/2018</td>
<td>0.007</td>
<td>0.017</td>
<td>22/11/2018</td>
<td>0.020</td>
<td>0.017</td>
<td>21/01/2019</td>
<td>0.021</td>
<td>0.017</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>19/07/2018</td>
<td>0.002</td>
<td>0.017</td>
<td>11/12/2018</td>
<td>0.015</td>
<td>0.017</td>
<td>11/02/2019</td>
<td>0.018</td>
<td>0.017</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>12/07/2018</td>
<td>0.000</td>
<td>0.017</td>
<td>21/11/2018</td>
<td>0.011</td>
<td>0.017</td>
<td>17/01/2019</td>
<td>0.011</td>
<td>0.017</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>19/07/2018</td>
<td>0.003</td>
<td>0.017</td>
<td>12/12/2018</td>
<td>0.011</td>
<td>0.017</td>
<td>11/02/2019</td>
<td>0.011</td>
<td>0.017</td>
</tr>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>16/07/2018</td>
<td>0.007</td>
<td>0.017</td>
<td>22/11/2018</td>
<td>0.020</td>
<td>0.017</td>
<td>21/01/2019</td>
<td>0.021</td>
<td>0.017</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>19/07/2018</td>
<td>0.002</td>
<td>0.017</td>
<td>11/12/2018</td>
<td>0.015</td>
<td>0.017</td>
<td>11/02/2019</td>
<td>0.018</td>
<td>0.017</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>12/07/2018</td>
<td>0.000</td>
<td>0.017</td>
<td>21/11/2018</td>
<td>0.011</td>
<td>0.017</td>
<td>17/01/2019</td>
<td>0.011</td>
<td>0.017</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>19/07/2018</td>
<td>0.003</td>
<td>0.017</td>
<td>12/12/2018</td>
<td>0.011</td>
<td>0.017</td>
<td>11/02/2019</td>
<td>0.011</td>
<td>0.017</td>
</tr>
</tbody>
</table>

Table 17. $\text{N}_2\text{O}$ amount fraction measured in cylinder gas standards by the BIPM using FT-IR spectroscopy.
<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>Measurement 1</th>
<th>$u(x_{N2O(1)})$</th>
<th>Measurement 2</th>
<th>$u(x_{N2O(2)})$</th>
<th>Measurement 3</th>
<th>$u(x_{N2O(3)})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$x_{N2O(1)}$</td>
<td>(μmol mol$^{-1}$)</td>
<td>$x_{N2O(2)}$</td>
<td>(μmol mol$^{-1}$)</td>
<td>$x_{N2O(3)}$</td>
<td>(μmol mol$^{-1}$)</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>13/07/2018</td>
<td>0.000</td>
<td>0.015</td>
<td>22/11/201</td>
<td>0.008</td>
<td>0.015</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>19/07/2018</td>
<td>0.000</td>
<td>0.015</td>
<td>06/12/201</td>
<td>0.007</td>
<td>0.015</td>
</tr>
<tr>
<td>META</td>
<td>10918</td>
<td>17/07/2018</td>
<td>0.008</td>
<td>0.015</td>
<td>03/12/201</td>
<td>0.010</td>
<td>0.015</td>
</tr>
<tr>
<td>META</td>
<td>10919</td>
<td>26/07/2018</td>
<td>0.007</td>
<td>0.015</td>
<td>17/12/201</td>
<td>0.011</td>
<td>0.015</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>10/07/2018</td>
<td>0.000</td>
<td>0.015</td>
<td>29/11/201</td>
<td>0.014</td>
<td>0.015</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>25/07/2018</td>
<td>0.012</td>
<td>0.015</td>
<td>06/12/201</td>
<td>0.014</td>
<td>0.015</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0806</td>
<td>16/07/2018</td>
<td>0.020</td>
<td>0.015</td>
<td>03/12/201</td>
<td>0.023</td>
<td>0.015</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0807</td>
<td>25/07/2018</td>
<td>0.037</td>
<td>0.015</td>
<td>17/12/201</td>
<td>0.040</td>
<td>0.015</td>
</tr>
<tr>
<td>NMIS</td>
<td>D62 6618</td>
<td>16/07/2018</td>
<td>0.000</td>
<td>0.015</td>
<td>05/12/201</td>
<td>0.008</td>
<td>0.015</td>
</tr>
<tr>
<td>NMIS</td>
<td>D62 6554</td>
<td>20/07/2018</td>
<td>0.009</td>
<td>0.015</td>
<td>12/12/201</td>
<td>0.009</td>
<td>0.015</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>13/07/2018</td>
<td>0.012</td>
<td>0.015</td>
<td>03/12/201</td>
<td>0.016</td>
<td>0.015</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>20/07/2018</td>
<td>0.018</td>
<td>0.015</td>
<td>11/12/201</td>
<td>0.020</td>
<td>0.015</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9742</td>
<td>10/07/2018</td>
<td>0.005</td>
<td>0.015</td>
<td>22/11/201</td>
<td>0.043</td>
<td>0.015</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9728</td>
<td>27/07/2018</td>
<td>0.045</td>
<td>0.015</td>
<td>18/12/201</td>
<td>0.046</td>
<td>0.015</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>10/07/2018</td>
<td>0.020</td>
<td>0.015</td>
<td>21/11/201</td>
<td>0.010</td>
<td>0.015</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>17/07/2018</td>
<td>0.008</td>
<td>0.015</td>
<td>05/12/201</td>
<td>0.011</td>
<td>0.015</td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol$^{-1}$
Table 18. NOCl amount fraction measured in cylinder gas standards by the BIPM using FT-IR spectroscopy.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>Measurement date</th>
<th>$x_{\text{NOCl}(1)}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{NOCl}(1)})$ (μmol mol$^{-1}$)</th>
<th>Measurement date</th>
<th>$x_{\text{NOCl}(2)}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{NOCl}(2)})$ (μmol mol$^{-1}$)</th>
<th>Measurement date</th>
<th>$x_{\text{NOCl}(3)}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{NOCl}(3)})$ (μmol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>16/07/2018</td>
<td>0.007</td>
<td>0.015</td>
<td>22/11/201</td>
<td>0.009</td>
<td>0.015</td>
<td>21/01/201</td>
<td>0.011</td>
<td>0.015</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>19/07/2018</td>
<td>0.000</td>
<td>0.015</td>
<td>11/12/201</td>
<td>0.009</td>
<td>0.015</td>
<td>11/02/201</td>
<td>0.009</td>
<td>0.015</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>12/07/2018</td>
<td>0.000</td>
<td>0.015</td>
<td>21/11/201</td>
<td>0.010</td>
<td>0.015</td>
<td>17/01/201</td>
<td>0.002</td>
<td>0.015</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>19/07/2018</td>
<td>0.008</td>
<td>0.015</td>
<td>12/12/201</td>
<td>0.010</td>
<td>0.015</td>
<td>11/02/201</td>
<td>0.011</td>
<td>0.015</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>Measurement date</th>
<th>$x_{\text{HONO(1)}}$ (μmol mol$^{-1}$)</th>
<th>$u(x_{\text{HONO(1)}}$) (μmol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPL</td>
<td>2448</td>
<td>13/07/2018</td>
<td>0.101</td>
<td>0.055</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>20/07/2018</td>
<td>0.028</td>
<td>0.025</td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol$^{-1}$
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 NO₂ 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 NO₂.

The difference is defined as:

\[ D'' = x_{NMI} - x_{UV} \]  \hspace{1cm} (9)

where \( x_{NMI} \) denotes the estimation of the NO₂ amount fraction in the participants’ standards at the date of the KCRVs according sections 6.2.1 and 6.2.2 criteria and \( x_{UV} \) 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:

\[ u(D'') = \sqrt{u(x_{NMI})^2 + u(x_{UV})^2} \]  \hspace{1cm} (10)

and the expanded uncertainty, at 95 % confidence level

\[ U(D'') = k \cdot u(D'') \]  \hspace{1cm} (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.
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 $\mu$mol mol$^{-1}$.* are the mixtures without decay.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>$D''_i$</th>
<th>$U(D''_i)$</th>
<th>$D''_a$</th>
<th>$U(D''_a)$</th>
<th>$D''_b$</th>
<th>$U(D''_b)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(μmol mol$^{-1}$)</td>
<td>(μmol mol$^{-1}$)</td>
<td>(μmol mol$^{-1}$)</td>
<td>(μmol mol$^{-1}$)</td>
<td>(μmol mol$^{-1}$)</td>
<td>(μmol mol$^{-1}$)</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 25961</td>
<td>0.010</td>
<td>0.231</td>
<td>0.043</td>
<td>0.184</td>
<td>0.101</td>
<td>0.198</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 18969</td>
<td>0.097</td>
<td>0.239</td>
<td>0.024</td>
<td>0.179</td>
<td>0.100</td>
<td>0.168</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298386_1</td>
<td>0.089</td>
<td>0.406</td>
<td>-0.058</td>
<td>0.366</td>
<td>0.141</td>
<td>0.360</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298387_1</td>
<td>0.247</td>
<td>0.535</td>
<td>0.113</td>
<td>0.436</td>
<td>-0.104</td>
<td>0.416</td>
</tr>
<tr>
<td>D247448</td>
<td>D247448</td>
<td>0.564</td>
<td>0.227</td>
<td>0.510</td>
<td>0.193</td>
<td>0.645</td>
<td>0.178</td>
</tr>
<tr>
<td>P27787/D247449</td>
<td>P27787/D247449*</td>
<td>0.601</td>
<td>0.170</td>
<td>0.752</td>
<td>0.176</td>
<td>0.614</td>
<td>0.160</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6882*</td>
<td>0.496</td>
<td>0.316</td>
<td>1.088</td>
<td>0.359</td>
<td>0.838</td>
<td>0.315</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6920*</td>
<td>0.688</td>
<td>0.361</td>
<td>0.890</td>
<td>0.336</td>
<td>0.939</td>
<td>0.347</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>0.244</td>
<td>0.358</td>
<td>0.117</td>
<td>0.295</td>
<td>0.366</td>
<td>0.243</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>0.587</td>
<td>0.347</td>
<td>0.168</td>
<td>0.240</td>
<td>0.269</td>
<td>0.256</td>
</tr>
<tr>
<td>METAS</td>
<td>10918</td>
<td>-0.311</td>
<td>0.353</td>
<td>-0.144</td>
<td>0.289</td>
<td>-0.216</td>
<td>0.280</td>
</tr>
<tr>
<td>METAS</td>
<td>10919</td>
<td>-0.155</td>
<td>0.363</td>
<td>-0.244</td>
<td>0.292</td>
<td>-0.123</td>
<td>0.269</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>0.062</td>
<td>0.178</td>
<td>-0.008</td>
<td>0.146</td>
<td>-0.030</td>
<td>0.104</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>0.035</td>
<td>0.147</td>
<td>-0.118</td>
<td>0.141</td>
<td>0.101</td>
<td>0.152</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0806*</td>
<td>0.373</td>
<td>0.239</td>
<td>0.542</td>
<td>0.237</td>
<td>0.564</td>
<td>0.241</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0807</td>
<td>0.567</td>
<td>0.374</td>
<td>0.641</td>
<td>0.343</td>
<td>10.057</td>
<td>0.312</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6618*</td>
<td>0.432</td>
<td>0.186</td>
<td>0.509</td>
<td>0.171</td>
<td>0.286</td>
<td>0.197</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6554*</td>
<td>0.454</td>
<td>0.158</td>
<td>0.576</td>
<td>0.220</td>
<td>0.367</td>
<td>0.171</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>-</td>
<td>-</td>
<td>0.221</td>
<td>0.166</td>
<td>0.162</td>
<td>0.185</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>-</td>
<td>-</td>
<td>0.147</td>
<td>0.217</td>
<td>9.844</td>
<td>0.142</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9742*</td>
<td>0.444</td>
<td>0.262</td>
<td>0.383</td>
<td>0.256</td>
<td>0.490</td>
<td>0.250</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9728</td>
<td>0.749</td>
<td>0.379</td>
<td>0.717</td>
<td>0.343</td>
<td>9.879</td>
<td>0.288</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>0.744</td>
<td>0.187</td>
<td>0.775</td>
<td>0.162</td>
<td>0.750</td>
<td>0.174</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>9.773</td>
<td>0.157</td>
<td>0.985</td>
<td>0.184</td>
<td>0.999</td>
<td>0.180</td>
</tr>
<tr>
<td>VNIM</td>
<td>614632</td>
<td>0.481</td>
<td>0.281</td>
<td>0.317</td>
<td>0.247</td>
<td>0.422</td>
<td>0.232</td>
</tr>
<tr>
<td>VNIM</td>
<td>5603778</td>
<td>0.577</td>
<td>0.266</td>
<td>0.312</td>
<td>0.258</td>
<td>0.334</td>
<td>0.251</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>0.176</td>
<td>0.225</td>
<td>0.085</td>
<td>0.221</td>
<td>0.122</td>
<td>0.200</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>0.069</td>
<td>0.232</td>
<td>0.089</td>
<td>0.214</td>
<td>0.117</td>
<td>0.277</td>
</tr>
</tbody>
</table>
Table 21. Measurements by the ABB Limas 11 analyzer.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>x_{UV1} (μmol mol^{-1})</th>
<th>u(x_{UV1}) (μmol mol^{-1})</th>
<th>x_{UV2} (μmol mol^{-1})</th>
<th>u(x_{UV2}) (μmol mol^{-1})</th>
<th>x_{UV3} (μmol mol^{-1})</th>
<th>u(x_{UV3}) (μmol mol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERI</td>
<td>CPB 25961</td>
<td>9.863</td>
<td>0.057</td>
<td>9.790</td>
<td>0.050</td>
<td>9.716</td>
<td>0.072</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 18969</td>
<td>9.767</td>
<td>0.059</td>
<td>9.794</td>
<td>0.046</td>
<td>9.699</td>
<td>0.052</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298386 1</td>
<td>10.410</td>
<td>0.044</td>
<td>10.515</td>
<td>0.056</td>
<td>10.297</td>
<td>0.076</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298387 1</td>
<td>10.036</td>
<td>0.099</td>
<td>10.084</td>
<td>0.090</td>
<td>10.266</td>
<td>0.107</td>
</tr>
<tr>
<td>INRIM</td>
<td>D247448</td>
<td>9.633</td>
<td>0.072</td>
<td>9.670</td>
<td>0.057</td>
<td>9.527</td>
<td>0.051</td>
</tr>
<tr>
<td>INRIM</td>
<td>P27787/D247449</td>
<td>9.391</td>
<td>0.055</td>
<td>9.240</td>
<td>0.059</td>
<td>9.378</td>
<td>0.047</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6882</td>
<td>9.537</td>
<td>0.049</td>
<td>8.945</td>
<td>0.099</td>
<td>9.195</td>
<td>0.048</td>
</tr>
<tr>
<td>KRISS</td>
<td>D59 6920</td>
<td>9.359</td>
<td>0.100</td>
<td>9.157</td>
<td>0.076</td>
<td>9.108</td>
<td>0.087</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>9.516</td>
<td>0.073</td>
<td>9.579</td>
<td>0.076</td>
<td>9.293</td>
<td>0.060</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>9.240</td>
<td>0.107</td>
<td>9.609</td>
<td>0.052</td>
<td>9.486</td>
<td>0.085</td>
</tr>
<tr>
<td>METAS</td>
<td>10918</td>
<td>9.898</td>
<td>0.051</td>
<td>9.673</td>
<td>0.050</td>
<td>9.724</td>
<td>0.066</td>
</tr>
<tr>
<td>METAS</td>
<td>10919</td>
<td>9.738</td>
<td>0.051</td>
<td>9.760</td>
<td>0.053</td>
<td>9.617</td>
<td>0.055</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>9.747</td>
<td>0.070</td>
<td>9.793</td>
<td>0.061</td>
<td>9.806</td>
<td>0.038</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>9.794</td>
<td>0.059</td>
<td>9.930</td>
<td>0.062</td>
<td>9.704</td>
<td>0.070</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0806</td>
<td>9.547</td>
<td>0.047</td>
<td>9.378</td>
<td>0.044</td>
<td>9.356</td>
<td>0.049</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0807</td>
<td>9.535</td>
<td>0.043</td>
<td>9.428</td>
<td>0.054</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6618</td>
<td>9.562</td>
<td>0.066</td>
<td>9.485</td>
<td>0.055</td>
<td>9.708</td>
<td>0.074</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6554</td>
<td>9.501</td>
<td>0.048</td>
<td>9.379</td>
<td>0.090</td>
<td>9.588</td>
<td>0.058</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>5.866</td>
<td>0.517</td>
<td>9.639</td>
<td>0.041</td>
<td>9.683</td>
<td>0.067</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>8.395</td>
<td>0.480</td>
<td>9.711</td>
<td>0.074</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9742</td>
<td>9.693</td>
<td>0.071</td>
<td>9.754</td>
<td>0.065</td>
<td>9.647</td>
<td>0.059</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9728</td>
<td>9.174</td>
<td>0.085</td>
<td>9.174</td>
<td>0.082</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>9.299</td>
<td>0.061</td>
<td>9.260</td>
<td>0.047</td>
<td>9.281</td>
<td>0.059</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>0.000</td>
<td>0.000</td>
<td>8.773</td>
<td>0.060</td>
<td>8.752</td>
<td>0.062</td>
</tr>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>9.343</td>
<td>0.076</td>
<td>9.488</td>
<td>0.061</td>
<td>9.375</td>
<td>0.054</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>9.255</td>
<td>0.044</td>
<td>9.494</td>
<td>0.067</td>
<td>9.461</td>
<td>0.071</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105804</td>
<td>9.666</td>
<td>0.065</td>
<td>9.750</td>
<td>0.067</td>
<td>9.710</td>
<td>0.051</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL105806</td>
<td>9.735</td>
<td>0.064</td>
<td>9.703</td>
<td>0.058</td>
<td>9.670</td>
<td>0.108</td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol^{-1}
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 HNO3 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:

$$D''' = x_{NMI} - x_{UV+HNO3}$$

where $x_{NMI}$ denotes the estimation of the NO2 amount fraction in the participants’ standards at the date of the KCRVs (see sections 6.2.1 and 6.2.2) and $x_{UV+HNO3}$ 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 HNO3 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:

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

and the expanded uncertainty, at 95 % confidence level

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

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 $x_{\text{NMI,red}}$ and calibrated values of the AAB LIMAS UV analyzer $x_{\text{BPM,UV}}$ adding the HNO₃ 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.

<table>
<thead>
<tr>
<th>NMI</th>
<th>Cylinder</th>
<th>$D''_{\text{1}}$</th>
<th>$U(D''_{\text{1}})$</th>
<th>$D''_{\text{2}}$</th>
<th>$U(D''_{\text{2}})$</th>
<th>$D''_{\text{3}}$</th>
<th>$U(D''_{\text{3}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERI</td>
<td>CPB 25961</td>
<td>-0.144</td>
<td>0.219</td>
<td>-0.166</td>
<td>0.179</td>
<td>-0.125</td>
<td>0.163</td>
</tr>
<tr>
<td>CERI</td>
<td>CPB 18969</td>
<td>-0.029</td>
<td>0.225</td>
<td>-0.145</td>
<td>0.177</td>
<td>-0.082</td>
<td>0.159</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298386_1</td>
<td>0.043</td>
<td>0.406</td>
<td>-0.109</td>
<td>0.359</td>
<td>0.078</td>
<td>0.338</td>
</tr>
<tr>
<td>GUM</td>
<td>No D298387_1</td>
<td>0.221</td>
<td>0.505</td>
<td>0.070</td>
<td>0.407</td>
<td>-0.156</td>
<td>0.367</td>
</tr>
<tr>
<td>INRIM</td>
<td>P27787/D247449*</td>
<td>0.367</td>
<td>0.191</td>
<td>0.257</td>
<td>0.180</td>
<td>0.426</td>
<td>0.171</td>
</tr>
<tr>
<td>INRIM</td>
<td>D247448</td>
<td>0.351</td>
<td>0.158</td>
<td>0.471</td>
<td>0.159</td>
<td>0.324</td>
<td>0.159</td>
</tr>
<tr>
<td>KRSS</td>
<td>D59 6920*</td>
<td>0.326</td>
<td>0.313</td>
<td>0.727</td>
<td>0.314</td>
<td>0.469</td>
<td>0.314</td>
</tr>
<tr>
<td>KRSS</td>
<td>D59 6882*</td>
<td>0.427</td>
<td>0.313</td>
<td>0.486</td>
<td>0.315</td>
<td>0.497</td>
<td>0.316</td>
</tr>
<tr>
<td>LNE</td>
<td>1191</td>
<td>0.233</td>
<td>0.335</td>
<td>0.069</td>
<td>0.268</td>
<td>0.332</td>
<td>0.228</td>
</tr>
<tr>
<td>LNE</td>
<td>1183</td>
<td>0.545</td>
<td>0.287</td>
<td>0.124</td>
<td>0.233</td>
<td>0.228</td>
<td>0.209</td>
</tr>
<tr>
<td>METAS</td>
<td>10918</td>
<td>-0.394</td>
<td>0.349</td>
<td>-0.233</td>
<td>0.278</td>
<td>-0.316</td>
<td>0.263</td>
</tr>
<tr>
<td>METAS</td>
<td>10919</td>
<td>-0.199</td>
<td>0.359</td>
<td>-0.300</td>
<td>0.285</td>
<td>-0.195</td>
<td>0.261</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804125</td>
<td>-0.008</td>
<td>0.139</td>
<td>-0.071</td>
<td>0.118</td>
<td>-0.141</td>
<td>0.112</td>
</tr>
<tr>
<td>NIM</td>
<td>L62804135</td>
<td>-0.040</td>
<td>0.123</td>
<td>-0.191</td>
<td>0.110</td>
<td>0.031</td>
<td>0.105</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0806*</td>
<td>0.321</td>
<td>0.236</td>
<td>0.408</td>
<td>0.229</td>
<td>0.461</td>
<td>0.236</td>
</tr>
<tr>
<td>NMIA</td>
<td>MK0807</td>
<td>0.450</td>
<td>0.374</td>
<td>0.490</td>
<td>0.337</td>
<td>10.057</td>
<td>0.312</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6618*</td>
<td>0.234</td>
<td>0.158</td>
<td>0.268</td>
<td>0.158</td>
<td>0.026</td>
<td>0.159</td>
</tr>
<tr>
<td>NMISA</td>
<td>D62 6554*</td>
<td>0.232</td>
<td>0.154</td>
<td>0.304</td>
<td>0.155</td>
<td>0.080</td>
<td>0.155</td>
</tr>
<tr>
<td>NPL</td>
<td>2448</td>
<td>-</td>
<td>-</td>
<td>-0.042</td>
<td>0.182</td>
<td>9.844</td>
<td>0.142</td>
</tr>
<tr>
<td>NPL</td>
<td>S357</td>
<td>-</td>
<td>-</td>
<td>0.036</td>
<td>0.159</td>
<td>-0.030</td>
<td>0.155</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9742*</td>
<td>0.365</td>
<td>0.236</td>
<td>0.262</td>
<td>0.237</td>
<td>0.333</td>
<td>0.237</td>
</tr>
<tr>
<td>SMU</td>
<td>MY9728</td>
<td>0.547</td>
<td>0.350</td>
<td>0.475</td>
<td>0.314</td>
<td>9.879</td>
<td>0.288</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499791</td>
<td>0.567</td>
<td>0.167</td>
<td>0.531</td>
<td>0.159</td>
<td>0.506</td>
<td>0.157</td>
</tr>
<tr>
<td>UME</td>
<td>PSM499783</td>
<td>9.773</td>
<td>0.157</td>
<td>0.768</td>
<td>0.166</td>
<td>0.788</td>
<td>0.159</td>
</tr>
<tr>
<td>VNIIM</td>
<td>614632</td>
<td>0.113</td>
<td>0.255</td>
<td>-0.195</td>
<td>0.238</td>
<td>-0.126</td>
<td>0.230</td>
</tr>
<tr>
<td>VNIIM</td>
<td>5603778</td>
<td>0.468</td>
<td>0.266</td>
<td>0.150</td>
<td>0.237</td>
<td>0.145</td>
<td>0.226</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL.105804</td>
<td>0.076</td>
<td>0.203</td>
<td>0.011</td>
<td>0.196</td>
<td>0.001</td>
<td>0.193</td>
</tr>
<tr>
<td>VSL</td>
<td>VSL.105806</td>
<td>-0.047</td>
<td>0.212</td>
<td>-0.031</td>
<td>0.199</td>
<td>-0.018</td>
<td>0.194</td>
</tr>
</tbody>
</table>

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol⁻¹
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 NO₂ 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 NO₂ amount fraction was quantified to be 9.710 ± 0.038 µmol mol⁻¹ (see Table 4). The spectrum also shows a clear signal for HNO₃ that according Table 5 corresponds to an amount fraction of 100 ± 21 nmol mol⁻¹. Finally H₂O can also be observed in the regions 1200 cm⁻¹ to 1950 cm⁻¹ and 3500 cm⁻¹ to 4000 cm⁻¹. The H₂O 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 NO₂ amount fraction corresponding to this spectrum is 10.450 ± 0.038 µmol mol⁻¹ containing also 176 ± 21 nmol mol⁻¹ of HNO₃ and 658 ± 107 nmol mol⁻¹ of H₂O.

Figure 32 plots the absorbance spectrum of the VNIIM 614632 mixture. The NO₂ amount fraction correspondent to this spectrum is 9.324 ± 0.038 µmol mol⁻¹. In this occasion the HNO₃ impurity amount fraction is 368 ± 21 nmol mol⁻¹ and around 12080 ± 0.646 nmol mol⁻¹ of H₂O.

Figure 30. Infrared absorbance spectrum of VSL 105804 mixture with a NO₂ 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 NO₂ amount fraction of 10.450 μmol mol⁻¹.

Figure 32. Infrared absorbance spectrum of VNIIM 614632 mixture with a NO₂ amount fraction of 9.324 μmol mol⁻¹.

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol⁻¹
Bibliography


3. Flores, E.; Viallon, J.; Moussay, P.; Wielgosz, R. I., Accurate measurements of nitrogen dioxide (NO2) and nitric acid (HNO3) mole fraction by FT-IR spectroscopy calibrated by gas standards and synthetic spectra. Appl. Spectrosc. 2012, 67 (10), 1178.


6. BIPM; IEC; IFCC; ISO; IUPAC; IUPAP; OIML. Guide to the expression of uncertainty in measurement; 2008, p. 120. http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf.


ANNEX VII - Measurement reports of participants

(see next pages – PDF version only)
# Table of Contents

ANNEX VII - Measurement reports of participants

<table>
<thead>
<tr>
<th>Entity</th>
<th>Before shipping to the BIPM</th>
<th>Post BIPM measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERI</td>
<td>..................................</td>
<td>..................................</td>
</tr>
<tr>
<td>GUM</td>
<td>..................................</td>
<td>..................................</td>
</tr>
<tr>
<td>INRIM</td>
<td>..................................</td>
<td>..................................</td>
</tr>
<tr>
<td>KRISS</td>
<td>..................................</td>
<td>..................................</td>
</tr>
<tr>
<td>LNE</td>
<td>..................................</td>
<td>..................................</td>
</tr>
<tr>
<td>METAS</td>
<td>..................................</td>
<td>..................................</td>
</tr>
<tr>
<td>NIM</td>
<td>..................................</td>
<td>..................................</td>
</tr>
<tr>
<td>NMIA</td>
<td>..................................</td>
<td>..................................</td>
</tr>
<tr>
<td>NMISA</td>
<td>..................................</td>
<td>..................................</td>
</tr>
</tbody>
</table>

---

<table>
<thead>
<tr>
<th>Name</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPL</td>
<td>100</td>
</tr>
<tr>
<td>Before shipping to the BIPM</td>
<td>100</td>
</tr>
<tr>
<td>Post BIPM measurements</td>
<td>104</td>
</tr>
<tr>
<td>SMU</td>
<td>110</td>
</tr>
<tr>
<td>Before shipping to the BIPM</td>
<td>110</td>
</tr>
<tr>
<td>Post BIPM measurements</td>
<td>113</td>
</tr>
<tr>
<td>UME</td>
<td>119</td>
</tr>
<tr>
<td>Before shipping to the BIPM</td>
<td>119</td>
</tr>
<tr>
<td>Post BIPM measurements</td>
<td>125</td>
</tr>
<tr>
<td>VNIIM</td>
<td>131</td>
</tr>
<tr>
<td>Before shipping to the BIPM</td>
<td>131</td>
</tr>
<tr>
<td>Post BIPM measurements</td>
<td>140</td>
</tr>
<tr>
<td>VSL</td>
<td>152</td>
</tr>
<tr>
<td>Before shipping to the BIPM</td>
<td>152</td>
</tr>
<tr>
<td>Post BIPM measurements</td>
<td>156</td>
</tr>
</tbody>
</table>
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**

<table>
<thead>
<tr>
<th>Institute</th>
<th>Chemicals Evaluation and Research Institute, Japan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>1600 Shimotakano, Sugito-machi, Kitakatsushika-gun, Saitama 345-0043, Japan</td>
</tr>
<tr>
<td>Contact person</td>
<td>Shinji UEHARA</td>
</tr>
</tbody>
</table>
### A2. Results

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>15/12/2017</td>
<td>10.215</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>15/1/2018</td>
<td>10.098</td>
<td>0.081</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>16/2/2018</td>
<td>10.052</td>
<td>0.080</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>12/3/2018</td>
<td>10.022</td>
<td>0.080</td>
<td>$k=2$</td>
</tr>
</tbody>
</table>

#### Cylinder 2 (CPB 18969) – Before shipping to the BIPM
<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$x_{\text{NO}_2}$ / $\mu$mol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / $\mu$mol/mol</th>
<th>Coverage factor $k$=2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>15/12/2017</td>
<td>10.194</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>15/1/2018</td>
<td>10.088</td>
<td>0.081</td>
<td>$k$=2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>16/2/2018</td>
<td>10.074</td>
<td>0.081</td>
<td>$k$=2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>12/3/2018</td>
<td>10.044</td>
<td>0.080</td>
<td>$k$=2</td>
</tr>
</tbody>
</table>

**Cylinder 1- Post BIPM measurements**

**Cylinder 2- Post BIPM measurements**
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.

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 NO₂, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

<table>
<thead>
<tr>
<th>Cylinder 1</th>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>23/3/2018</td>
<td>NO</td>
<td>20</td>
<td>3 nmol/mol</td>
<td>$k=2$</td>
<td></td>
<td>Chemiluminescence analyzer (NO mode)</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>23/3/2018</td>
<td>NO</td>
<td>20</td>
<td>3 nmol/mol</td>
<td>k=2</td>
<td>Chemiluminescence analyzer (NO mode)</td>
</tr>
</tbody>
</table>

Post BIPM measurements

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

Result form CCQM-K74.2018-R

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

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

<table>
<thead>
<tr>
<th>Institute</th>
<th>Chemicals Evaluation and Research Institute, Japan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>1600 Shimotakano, Sugito-machi, Kitakatsushika-gun, Saitama 345-0043, Japan</td>
</tr>
<tr>
<td>Contact person</td>
<td>Shinji UEHARA</td>
</tr>
<tr>
<td>Telephone</td>
<td>+81-480-37-2601</td>
</tr>
<tr>
<td>Fax</td>
<td>+81-480-37-2521</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:uehara-shinji@ceri.jp">uehara-shinji@ceri.jp</a></td>
</tr>
<tr>
<td>Serial number of cylinder received</td>
<td>CPB 25961, CPB 18969</td>
</tr>
<tr>
<td>Cylinder pressure as received</td>
<td>10 MPa</td>
</tr>
</tbody>
</table>

A2. Results

<table>
<thead>
<tr>
<th></th>
<th>Nitrogen dioxide mole fraction</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_{NO_2}$ / μmol/mol</td>
<td>$U(x_{NO_2})$ / μmol/mol</td>
<td>$k=2$</td>
</tr>
<tr>
<td>Cylinder 1</td>
<td>9.90</td>
<td>0.16</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(CPB 25961)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cylinder 2</td>
<td>9.90</td>
<td>0.18</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(CPB 18969)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

“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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$\chi_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(\chi_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>15/12/2017</td>
<td>10.215</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>15/1/2018</td>
<td>10.098</td>
<td>0.081</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>16/2/2018</td>
<td>10.052</td>
<td>0.080</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>12/3/2018</td>
<td>10.022</td>
<td>0.080</td>
<td>$k=2$</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$\chi_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(\chi_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>15/12/2017</td>
<td>10.194</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>15/1/2018</td>
<td>10.088</td>
<td>0.081</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>16/2/2018</td>
<td>10.074</td>
<td>0.081</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>12/3/2018</td>
<td>10.044</td>
<td>0.080</td>
<td>$k=2$</td>
</tr>
</tbody>
</table>
### Cylinder 1 (CPB 25961) - Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$\chi_{\text{NO}_2}/\mu\text{mol/mol}$</th>
<th>Expanded uncertainty $U(\chi_{\text{NO}_2})/\mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>10/4/2019</td>
<td>9.798</td>
<td>0.078</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>23/5/2019</td>
<td>9.742</td>
<td>0.078</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>12/7/2019</td>
<td>9.792</td>
<td>0.078</td>
<td>$k=2$</td>
</tr>
</tbody>
</table>

### Cylinder 2 (CPB 18969) - Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$\chi_{\text{NO}_2}/\mu\text{mol/mol}$</th>
<th>Expanded uncertainty $U(\chi_{\text{NO}_2})/\mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>10/4/2019</td>
<td>9.770</td>
<td>0.078</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>23/5/2019</td>
<td>9.748</td>
<td>0.078</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>12/7/2019</td>
<td>9.772</td>
<td>0.078</td>
<td>$k=2$</td>
</tr>
</tbody>
</table>
### A3. Uncertainty Budget

Please provide a complete uncertainty budget.

#### Cylinder 1 (CPB 25961)

<table>
<thead>
<tr>
<th>Uncertainty source</th>
<th>Estimate</th>
<th>Assumed distribution</th>
<th>Standard uncertainty</th>
<th>Contribution to standard uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas standards for measurements</td>
<td>0.001386</td>
<td>Normal</td>
<td>0.001386</td>
<td>0.001386</td>
</tr>
<tr>
<td>Stability*</td>
<td>0.1225 (\mu)mol/mol</td>
<td>Rectangle</td>
<td>0.07073 (\mu)mol/mol</td>
<td>0.007144</td>
</tr>
<tr>
<td>Measurement</td>
<td>0.0038</td>
<td>Normal</td>
<td>0.0038</td>
<td>0.0038</td>
</tr>
</tbody>
</table>

Combined uncertainty (Relative): 0.008210
Expanded uncertainty (Relative) \((k=2)\): 0.01642
Expanded uncertainty: 0.16 \(\mu\)mol/mol

*Uncertainty of stability was estimated as half of 0.245 \(\mu\)mol/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)

<table>
<thead>
<tr>
<th>Uncertainty source</th>
<th>Estimate</th>
<th>Assumed distribution</th>
<th>Standard uncertainty</th>
<th>Contribution to standard uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas standards for measurements</td>
<td>0.001386</td>
<td>Normal</td>
<td>0.001386</td>
<td>0.001386</td>
</tr>
<tr>
<td>Stability*</td>
<td>0.1405 (\mu)mol/mol</td>
<td>Rectangle</td>
<td>0.08112 (\mu)mol/mol</td>
<td>0.008194</td>
</tr>
<tr>
<td>Measurement</td>
<td>0.0038</td>
<td>Normal</td>
<td>0.0038</td>
<td>0.0038</td>
</tr>
</tbody>
</table>

Combined uncertainty (Relative): 0.009138
Expanded uncertainty (Relative) \((k=2)\): 0.01828
Expanded uncertainty: 0.18 \(\mu\)mol/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.

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) NO₂ can’t be analyzed in “Manual NOx” mode. NOx was regarded as NO₂ in the report. NO₂ 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:

<table>
<thead>
<tr>
<th>Cylinder</th>
<th>Pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylinder 1</td>
<td>10</td>
</tr>
<tr>
<td>Cylinder 2</td>
<td>10</td>
</tr>
</tbody>
</table>

If any other component other than NO₂, 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)

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>23/3/2018</td>
<td>NO</td>
<td>20</td>
<td>3 nmol/mol</td>
<td>(k=2)</td>
<td>Chemiluminescence analyzer (NO mode)</td>
</tr>
</tbody>
</table>

### Cylinder 2 (CPB 18969)

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>23/3/2018</td>
<td>NO</td>
<td>20</td>
<td>3 nmol/mol</td>
<td>(k=2)</td>
<td>Chemiluminescence analyzer (NO mode)</td>
</tr>
</tbody>
</table>

**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


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


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

<table>
<thead>
<tr>
<th>Institute</th>
<th>Central Office of Measures (Główny Urząd Miar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>Elektorálna 2; 00-139 Warsaw; Poland</td>
</tr>
<tr>
<td>Contact person</td>
<td>Dariusz Cieciora</td>
</tr>
<tr>
<td>Telephone</td>
<td>(48) 22 581 94 39</td>
</tr>
<tr>
<td>Fax</td>
<td>(48) 22 581 93 95</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:dariusz.cieciora@gum.gov.pl">dariusz.cieciora@gum.gov.pl</a>, <a href="mailto:gas@gum.gov.pl">gas@gum.gov.pl</a></td>
</tr>
<tr>
<td>Serial number of cylinder received</td>
<td>Cylinder 1: D298386</td>
</tr>
<tr>
<td></td>
<td>Cylinder 2: D298387</td>
</tr>
<tr>
<td>Cylinder pressure as received</td>
<td></td>
</tr>
</tbody>
</table>
A2. Results

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

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

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

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

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**

<table>
<thead>
<tr>
<th>Institute</th>
<th>Central Office of Measures (Główny Urząd Miar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>Elektoralna 2; 00-139 Warsaw; Poland</td>
</tr>
<tr>
<td>Contact person</td>
<td>Dariusz Cieciora</td>
</tr>
<tr>
<td>Telephone</td>
<td>(48) 22 581 94 39</td>
</tr>
<tr>
<td>Fax</td>
<td>(48) 22 581 93 95</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:dariusz.cieciora@gum.gov.pl">dariusz.cieciora@gum.gov.pl</a>; <a href="mailto:gas@gum.gov.pl">gas@gum.gov.pl</a></td>
</tr>
<tr>
<td>Serial number of cylinder received</td>
<td>Cylinder 1: D298386 Cylinder 2: D298387</td>
</tr>
<tr>
<td>Cylinder pressure as received</td>
<td></td>
</tr>
</tbody>
</table>

**A2. Results**
### Cylinder 1 (No D298386_1) – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2} / \mu\text{mol/mol}$</th>
<th>Expanded Uncertainty $U(x_{NO_2}) / \mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>01.02.2018</td>
<td>10,783</td>
<td>0,079</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>06.02.2018</td>
<td>10,526</td>
<td>0,234</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>07.03.2018</td>
<td>10,619</td>
<td>0,214</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>10.04.2018</td>
<td>10,906</td>
<td>0,236</td>
<td>2</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2} / \mu\text{mol/mol}$</th>
<th>Expanded Uncertainty $U(x_{NO_2}) / \mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>01.02.2018</td>
<td>10,989</td>
<td>0,092</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>06.02.2018</td>
<td>10,535</td>
<td>0,234</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>07.03.2018</td>
<td>10,604</td>
<td>0,216</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>10.04.2018</td>
<td>10,827</td>
<td>0,234</td>
<td>2</td>
</tr>
</tbody>
</table>

### Cylinder 1 (No D298386_1) – Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2} / \mu\text{mol/mol}$</th>
<th>Expanded Uncertainty $U(x_{NO_2}) / \mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>04.04.2019</td>
<td>10,446</td>
<td>0,238</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>16.05.2019</td>
<td>10,355</td>
<td>0,252</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>10.07.2019</td>
<td>10,399</td>
<td>0,286</td>
<td>2</td>
</tr>
</tbody>
</table>

### Cylinder 2 (No D298387_1) – Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2} / \mu\text{mol/mol}$</th>
<th>Expanded Uncertainty $U(x_{NO_2}) / \mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>04.04.2019</td>
<td>10,159</td>
<td>0,233</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>16.05.2019</td>
<td>10,134</td>
<td>0,248</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>10.07.2019</td>
<td>9,989</td>
<td>0,283</td>
<td>2</td>
</tr>
</tbody>
</table>
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 and 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

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

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

<table>
<thead>
<tr>
<th>Institute</th>
<th>INRIM – Istituto Nazionale di Ricerca Metrologica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>Strada delle Cacce 9, 10135 Torino, Italy</td>
</tr>
<tr>
<td>Contact person</td>
<td>Michela Sega, Francesca Rolle</td>
</tr>
<tr>
<td>Telephone</td>
<td>+39 011 3919948</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:m.sega@inrim.it">m.sega@inrim.it</a></td>
</tr>
<tr>
<td>Serial number of cylinder received</td>
<td></td>
</tr>
<tr>
<td>Cylinder pressure as received</td>
<td></td>
</tr>
</tbody>
</table>
A2. Results

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2} / \mu\text{mol/mol}$</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2}) / \mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>17/11/2017</td>
<td>9.92</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>01/12/2017</td>
<td>10.09</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>29/01/2018</td>
<td>9.90</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>26/04/2018</td>
<td>9.84</td>
<td>0.13</td>
<td>2</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2} / \mu\text{mol/mol}$</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2}) / \mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>24/11/2017</td>
<td>10.16</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>01/12/2017</td>
<td>10.36</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>29/01/2018</td>
<td>10.24</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>26/04/2018</td>
<td>10.21</td>
<td>0.13</td>
<td>2</td>
</tr>
</tbody>
</table>
Cylinder 1- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cylinder 2- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The model equation used to calculate the mole fraction of NO₂ in the final mixtures is taken from the International Standard ISO 6142-1:2015:

$$x_{\text{NO}_2, \text{prep}} = \frac{\sum_{j=1}^{c} x_{\text{NO}_2, j} \cdot m_j}{\sum_{j=1}^{c} \sum_{i=1}^{q} x_{i,j} \cdot M_i}$$

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 \(\mu\)mol/mol of NO₂, 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:

<table>
<thead>
<tr>
<th>Uncertainty component (u(x))</th>
<th>Uncertainty source</th>
<th>Standard uncertainty, (u(x))</th>
<th>(\Delta x_{\text{NO}_2, \text{prep}}/\delta x_i)</th>
<th>Contribution to (u(x_{\text{NO}_2, \text{prep}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(u(m_{\text{NO}_2}))</td>
<td>Weighed mass of the parent mixture of NO₂</td>
<td>1.2(\times)10⁻⁴ g</td>
<td>8.93(\times)10⁻⁸ mol⁻¹·g⁻¹</td>
<td>1.0(\times)10⁻¹⁰ mol⁻¹·mol⁻¹</td>
</tr>
<tr>
<td>(u(m_{\text{N}_2}))</td>
<td>Weighed mass of the balance gas N₂</td>
<td>8.2(\times)10⁻⁴ g</td>
<td>-1.58(\times)10⁻⁸ mol⁻¹·g⁻¹</td>
<td>1.3(\times)10⁻¹¹ mol⁻¹·mol⁻¹</td>
</tr>
<tr>
<td>(u(M_{\text{NO}_2}))</td>
<td>Molar mass of NO₂</td>
<td>3.0(\times)10⁻⁴ g·mol⁻¹</td>
<td>-1.99(\times)10⁻¹¹ mol²·mol⁻²·g⁻¹</td>
<td>5.9(\times)10⁻¹⁵ mol⁻¹·mol⁻¹</td>
</tr>
<tr>
<td>(u(M_{\text{N}_2}))</td>
<td>Molar mass of N₂</td>
<td>2.0(\times)10⁻⁴ g·mol⁻¹</td>
<td>2.35(\times)10⁻⁹ mol²·mol⁻²·g⁻¹</td>
<td>4.7(\times)10⁻¹³ mol⁻¹·mol⁻¹</td>
</tr>
<tr>
<td>(u(M_{\text{O}_2}))</td>
<td>Molar mass of O₂</td>
<td>2.8(\times)10⁻⁴ g·mol⁻¹</td>
<td>-2.03(\times)10⁻⁹ mol²·mol⁻²·g⁻¹</td>
<td>5.7(\times)10⁻¹³ mol⁻¹·mol⁻¹</td>
</tr>
<tr>
<td>(u(x_{\text{N}_2}\text{inNO}_2))</td>
<td>Mole fraction of N₂ in the parent mixture of NO₂</td>
<td>4.1(\times)10⁻⁷ mol⁻¹·mol⁻¹</td>
<td>-8.42(\times)10⁻⁶</td>
<td>3.4(\times)10⁻¹² mol⁻¹·mol⁻¹</td>
</tr>
<tr>
<td>(u(x_{\text{N}_2}\text{inN}_2))</td>
<td>Mole fraction of N₂ in balance gas (purity)</td>
<td>8.7(\times)10⁻⁷ mol⁻¹·mol⁻¹</td>
<td>8.43(\times)10⁻⁶</td>
<td>7.3(\times)10⁻¹² mol⁻¹·mol⁻¹</td>
</tr>
<tr>
<td>(u(x_{\text{O}_2}\text{inNO}_2))</td>
<td>Mole fraction of O₂ in the parent mixture of NO₂</td>
<td>4.2(\times)10⁻⁷ mol⁻¹·mol⁻¹</td>
<td>-9.62(\times)10⁻⁶</td>
<td>4.1(\times)10⁻¹² mol⁻¹·mol⁻¹</td>
</tr>
<tr>
<td>Uncertainty component $u(x)$</td>
<td>Uncertainty source</td>
<td>Standard uncertainty, $u(x_i)$</td>
<td>$\Delta x_{\text{NO}_2,\text{prep}}$/$\Delta x_i$</td>
<td>Contribution to $u(x_{\text{NO}_2,\text{prep}})$ $</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-------------------</td>
<td>-------------------------------</td>
<td>-------------------------------------------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>$u(x_\text{O}_2in\text{N}_2)$</td>
<td>Mole fraction of $\text{O}_2$ in balance gas (impurity)</td>
<td>1.4∙10^{-7} mol∙mol(^{-1})</td>
<td>9.63∙10^{-6}</td>
<td>1.4∙10^{-12} mol∙mol(^{-1})</td>
</tr>
<tr>
<td>$u(x_{\text{NO}_2in\text{N}_2})$</td>
<td>Mole fraction of $\text{NO}_2$ in the parent mixture of $\text{NO}_2$</td>
<td>2.0∙10^{-7} mol∙mol(^{-1})</td>
<td>1.50∙10^{-1}</td>
<td>3.0∙10^{-8} mol∙mol(^{-1})</td>
</tr>
</tbody>
</table>

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 $u(x)$ | Uncertainty source | Standard uncertainty, $u(x_i)$ | $\Delta x_{\text{NO}_2,\text{prep}}$/$\Delta x_i$ | Contribution to $u(x_{\text{NO}_2,\text{prep}})$ $|\delta x_{\text{NO}_2,\text{prep}}/\delta x_i|^2u(x_i)$ |
|-------------------------------|-------------------|-------------------------------|-------------------------------------------|-------------------------------------------------|
| $u(m_{\text{NO}_2})$ | Weighed mass of the parent mixture of $\text{NO}_2$ | 1.2∙10^{-3} g | 8.90∙10^{-8} mol∙mol\(^{-1}\)a^{-1} | 1.0∙10^{-10} mol∙mol\(^{-1}\) |
| $u(m_{\text{N}_2})$ | Weighed mass of the balance gas $\text{N}_2$ | 8.2∙10^{-4} g | -1.61∙10^{-8} mol∙mol\(^{-1}\)a^{-1} | 0.0∙10^{-11} mol∙mol\(^{-1}\) |
| $u(M_{\text{NO}_2})$ | Molar mass of $\text{NO}_2$ | 3.0∙10^{-4} g/mol\(^{-1}\) | -2.03∙10^{-11} mol\(^2\)mol\(^{-1}\)a^{-1} | 6.0∙10^{-15} mol∙mol\(^{-1}\) |
| $u(M_{\text{N}_2})$ | Molar mass of $\text{N}_2$ | 2.0∙10^{-4} g/mol\(^{-1}\) | 2.39∙10^{-8} mol\(^2\)mol\(^{-1}\)a^{-1} | 4.8∙10^{-13} mol∙mol\(^{-1}\) |
| $u(M_{\text{O}_2})$ | Molar mass of $\text{O}_2$ | 2.8∙10^{-4} g/mol\(^{-1}\) | -2.06∙10^{-9} mol\(^2\)mol\(^{-1}\)a^{-1} | 5.8∙10^{-13} mol∙mol\(^{-1}\) |
| $u(x_{\text{N}_2in\text{NO}_2})$ | Mole fraction of $\text{N}_2$ in the parent mixture of $\text{NO}_2$ | 4.0∙10^{-7} mol∙mol\(^{-1}\) | -8.59∙10^{-6} | 3.5∙10^{-12} mol∙mol\(^{-1}\) |
| $u(x_{\text{N}_2in\text{N}_2})$ | Mole fraction of $\text{N}_2$ in balance gas (purity) | 8.7∙10^{-7} mol∙mol\(^{-1}\) | 8.60∙10^{-6} | 7.4∙10^{-12} mol∙mol\(^{-1}\) |
| $u(x_{\text{O}_2in\text{NO}_2})$ | Mole fraction of $\text{O}_2$ in the parent mixture of $\text{NO}_2$ | 4.2∙10^{-7} mol∙mol\(^{-1}\) | -9.81∙10^{-6} | 4.2∙10^{-12} mol∙mol\(^{-1}\) |
| $u(x_{\text{O}_2in\text{N}_2})$ | Mole fraction of $\text{O}_2$ in balance gas (impurity) | 1.4∙10^{-7} mol∙mol\(^{-1}\) | 9.82∙10^{-6} | 1.4∙10^{-12} mol∙mol\(^{-1}\) |
| $u(x_{\text{NO}_2in\text{NO}_2})$ | Mole fraction of $\text{NO}_2$ in the parent mixture of $\text{NO}_2$ | 2.0∙10^{-7} mol∙mol\(^{-1}\) | 1.53∙10^{-1} | 3.0∙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 fraction and the associated uncertainties of the mixtures were calculated according to section A3. The following table reports the characteristics of the calibration gas mixtures:

<table>
<thead>
<tr>
<th>Mixture number</th>
<th>Cylinder number</th>
<th>NO2 molar fraction χ μmol/mol</th>
<th>U(χ) (k=2) μmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>INRIM 072</td>
<td>D56 6402</td>
<td>7.99</td>
<td>0.05</td>
</tr>
<tr>
<td>INRIM 073</td>
<td>D69 6430</td>
<td>10.04</td>
<td>0.06</td>
</tr>
<tr>
<td>INRIM 075</td>
<td>D56 6405</td>
<td>11.99</td>
<td>0.07</td>
</tr>
</tbody>
</table>

The calibration curves were validated using both a mixture of NO2 at 10.05 μmol/mol (U=0.06 μmol/mol, k=2) in N2 (INRIM 074) gravimetrically prepared at INRIM and by dynamic dilution. A further independent mixture of NO2 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 setup 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.

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 NO2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

<table>
<thead>
<tr>
<th>Cylinder 1</th>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyl. 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cylinder 2</th>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyl. 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Post BIPM measurements

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

(10 μmol/mol)

Result form CCQM-K74.2018-R


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


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

<table>
<thead>
<tr>
<th>Institute</th>
<th>INRIM – Istituto Nazionale di Ricerca Metrologica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>Strada delle Cacce 9, 10135 Torino, Italy</td>
</tr>
<tr>
<td>Contact person</td>
<td>Michela Sega, Francesca Rolle</td>
</tr>
<tr>
<td>Telephone</td>
<td>+39 011 3919948</td>
</tr>
<tr>
<td>Fax</td>
<td>+39 011 3919937</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:m.sega@inrim.it">m.sega@inrim.it</a></td>
</tr>
</tbody>
</table>
### A2. Results

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>17/11/2017</td>
<td>9.92</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>01/12/2017</td>
<td>10.09</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>29/01/2918</td>
<td>9.90</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>26/04/2018</td>
<td>9.84</td>
<td>0.13</td>
<td>2</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>24/11/2017</td>
<td>10.16</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>01/12/2017</td>
<td>10.36</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>29/01/2918</td>
<td>10.24</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>26/04/2018</td>
<td>10.21</td>
<td>0.13</td>
<td>2</td>
</tr>
</tbody>
</table>
### Cylinder 1- Post BIPM measurements (Cylinder number: P27787/D247449)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>18/04/2019</td>
<td>10.10</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>13/05/2019</td>
<td>9.91</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>21/06/2019</td>
<td>10.11</td>
<td>0.15</td>
<td>2</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>18/04/2019</td>
<td>10.08</td>
<td>0.10</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>13/05/2019</td>
<td>10.15</td>
<td>0.10</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>21/06/2019</td>
<td>10.25</td>
<td>0.13</td>
<td>2</td>
</tr>
</tbody>
</table>

### A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The model equation used to calculate the mole fraction of NO₂ in the final mixtures is taken from the International Standard ISO 6142-1:2015:
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:

<table>
<thead>
<tr>
<th>Uncertainty component $u(x_i)$</th>
<th>Uncertainty source</th>
<th>Standard uncertainty, $u(x_i)$</th>
<th>$\Delta x_{NO2, prep}/\delta x_i$</th>
<th>Contribution to $u(x_{NO2, prep})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u(m_{NO2})$</td>
<td>Weighed mass of the parent mixture of NO$_2$</td>
<td>1.2 $\cdot 10^{-3}$ g</td>
<td>8.93 $\cdot 10^{-8}$ mol$^{-1}$ g$^{-1}$</td>
<td>1.0 $\cdot 10^{-10}$ mol$^{-1}$</td>
</tr>
<tr>
<td>$u(m_{N2})$</td>
<td>Weighed mass of the balance gas N$_2$</td>
<td>8.2 $\cdot 10^{-4}$ g</td>
<td>-1.58 $\cdot 10^{-8}$ mol$^{-1}$ g$^{-1}$</td>
<td>1.3 $\cdot 10^{-11}$ mol$^{-1}$</td>
</tr>
<tr>
<td>$u(M_{NO2})$</td>
<td>Molar mass of NO$_2$</td>
<td>3.0 $\cdot 10^{-4}$ g$^{-1}$ mol$^{-1}$</td>
<td>-1.99 $\cdot 10^{-11}$ mol$^{-2}$ g$^{-1}$</td>
<td>5.9 $\cdot 10^{-15}$ mol$^{-1}$</td>
</tr>
<tr>
<td>$u(M_{N2})$</td>
<td>Molar mass of N$_2$</td>
<td>2.0 $\cdot 10^{-4}$ g$^{-1}$ mol$^{-1}$</td>
<td>2.35 $\cdot 10^{-9}$ mol$^{-2}$ g$^{-1}$</td>
<td>4.7 $\cdot 10^{-13}$ mol$^{-1}$</td>
</tr>
<tr>
<td>$u(M_{O2})$</td>
<td>Molar mass of O$_2$</td>
<td>2.8 $\cdot 10^{-4}$ g$^{-1}$ mol$^{-1}$</td>
<td>-2.03 $\cdot 10^{-9}$ mol$^{-2}$ g$^{-1}$</td>
<td>5.7 $\cdot 10^{-13}$ mol$^{-1}$</td>
</tr>
</tbody>
</table>
The following table reports the uncertainty budget for the gravimetric preparation of the Cylinder n. 2 at 10.16 µmol/mol of NO₂.

<table>
<thead>
<tr>
<th>Uncertainty component</th>
<th>Uncertainty source</th>
<th>Standard uncertainty, ( u(x_i) )</th>
<th>( \Delta x_{NO₂, \text{prep}} / \delta x_i )</th>
<th>Contribution to ( u(x_{NO₂, \text{prep}}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u(m_{NO₂}) )</td>
<td>Weighed mass of the parent mixture of NO₂</td>
<td>1.2 \cdot 10^3 \text{ g}</td>
<td>8.90 \cdot 10^{-8} \text{ mol} \cdot \text{mol}^{-1} \cdot \text{g}^{-1}</td>
<td>1.0 \cdot 10^{-10} \text{ mol} \cdot \text{mol}^{-1}</td>
</tr>
<tr>
<td>$u(m_{N2})$</td>
<td>Weighed mass of the balance gas N$_2$</td>
<td>$8.2 \cdot 10^{-4}$ g</td>
<td>$-1.61 \cdot 10^{-8}$ mol$\cdot$mol$^{-1}$g$^{-1}$</td>
<td>$1.3 \cdot 10^{-11}$ mol$\cdot$mol$^{-1}$</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------</td>
<td>-----------------------</td>
<td>---------------------------------------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>$u(M_{NO2})$</td>
<td>Molar mass of NO$_2$</td>
<td>$3.0 \cdot 10^{-4}$ g$\cdot$mol$^{-1}$</td>
<td>$-2.03 \cdot 10^{-11}$ mol$^2$$\cdot$mol$^{-1}$g$^{-1}$</td>
<td>$6.0 \cdot 10^{-15}$ mol$\cdot$mol$^{-1}$</td>
</tr>
<tr>
<td>$u(M_{N2})$</td>
<td>Molar mass of N$_2$</td>
<td>$2.0 \cdot 10^{-4}$ g$\cdot$mol$^{-1}$</td>
<td>$2.39 \cdot 10^{-9}$ mol$^2$$\cdot$mol$^{-1}$g$^{-1}$</td>
<td>$4.8 \cdot 10^{-13}$ mol$\cdot$mol$^{-1}$</td>
</tr>
<tr>
<td>$u(M_{O2})$</td>
<td>Molar mass of O$_2$</td>
<td>$2.8 \cdot 10^{-4}$ g$\cdot$mol$^{-1}$</td>
<td>$-2.06 \cdot 10^{-9}$ mol$^2$$\cdot$mol$^{-1}$g$^{-1}$</td>
<td>$5.8 \cdot 10^{-13}$ mol$\cdot$mol$^{-1}$</td>
</tr>
<tr>
<td>$u(x_{N2inNO2})$</td>
<td>Mole fraction of N$_2$ in the parent mixture of NO$_2$</td>
<td>$4.0 \cdot 10^{-7}$ mol$\cdot$mol$^{-1}$</td>
<td>$-8.59 \cdot 10^{-8}$</td>
<td>$3.5 \cdot 10^{-12}$ mol$\cdot$mol$^{-1}$</td>
</tr>
<tr>
<td>$u(x_{N2inN2})$</td>
<td>Mole fraction of N$_2$ in balance gas (purity)</td>
<td>$8.7 \cdot 10^{-7}$ mol$\cdot$mol$^{-1}$</td>
<td>$8.60 \cdot 10^{-6}$</td>
<td>$7.4 \cdot 10^{-12}$ mol$\cdot$mol$^{-1}$</td>
</tr>
<tr>
<td>$u(x_{O2inNO2})$</td>
<td>Mole fraction of O$_2$ in the parent mixture of NO$_2$</td>
<td>$4.2 \cdot 10^{-7}$ mol$\cdot$mol$^{-1}$</td>
<td>$-9.81 \cdot 10^{-6}$</td>
<td>$4.2 \cdot 10^{-12}$ mol$\cdot$mol$^{-1}$</td>
</tr>
<tr>
<td>$u(x_{O2inN2})$</td>
<td>Mole fraction of O$_2$ in balance gas (impurity)</td>
<td>$1.4 \cdot 10^{-7}$ mol$\cdot$mol$^{-1}$</td>
<td>$9.82 \cdot 10^{-6}$</td>
<td>$1.4 \cdot 10^{-12}$ mol$\cdot$mol$^{-1}$</td>
</tr>
<tr>
<td>$u(x_{NO2inNO2})$</td>
<td>Mole fraction of NO$_2$ in the parent mixture of NO$_2$</td>
<td>$2.0 \cdot 10^{-7}$ mol$\cdot$mol$^{-1}$</td>
<td>$1.53 \cdot 10^{-1}$</td>
<td>$3.0 \cdot 10^{-8}$ mol$\cdot$mol$^{-1}$</td>
</tr>
</tbody>
</table>

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.

The analysis was carried out by means of a chemiluminescence analyser CLD Thermo 42i having resolution of $0.01 \, \mu\text{mol mol}^{-1}$. 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 $100.0 \, \mu\text{mol mol}^{-1}$ ($U=0.60 \, \mu\text{mol mol}^{-1}, k=2$) 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 $0.0200 \, \text{mol mol}^{-1}$ 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:

<table>
<thead>
<tr>
<th>Mixture number</th>
<th>Cylinder number</th>
<th>NO$_2$ molar fraction $\chi$</th>
<th>$U(\chi) \ (k=2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>INRIM 072</td>
<td>D56 6402</td>
<td>7.99</td>
<td>0.05</td>
</tr>
<tr>
<td>INRIM 073</td>
<td>D69 6430</td>
<td>10.04</td>
<td>0.06</td>
</tr>
<tr>
<td>INRIM 075</td>
<td>D56 6405</td>
<td>11.99</td>
<td>0.07</td>
</tr>
</tbody>
</table>

The calibration curves were validated using both a mixture of NO$_2$ at $10.05 \, \mu\text{mol mol}^{-1}$ ($U=0.06 \, \mu\text{mol mol}^{-1}, k=2$) in $N_2$ (INRIM 074) gravimetrically prepared at INRIM and by dynamic dilution. A further independent mixture of NO$_2$ at $10.01 \, \mu\text{mol mol}^{-1}$ ($U=0.20 \, \mu\text{mol mol}^{-1}, k=2$) 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 $10.07 \, \mu\text{mol mol}^{-1}$ ($U=0.15 \, \mu\text{mol mol}^{-1}, k=2$) 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 $35 \, \text{L h}^{-1}$. 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**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
</table>

**Cylinder 2**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
</table>
KRISS

Before shipping to the BIPM

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

Result form CCQM-K74.2018-R


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


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

<table>
<thead>
<tr>
<th>Institute</th>
<th>KRISS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>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</td>
</tr>
<tr>
<td>Contact person</td>
<td>Sang-Hyub Oh</td>
</tr>
<tr>
<td>Telephone</td>
<td>+82 42 868 5341</td>
</tr>
<tr>
<td>Fax</td>
<td>+82 42 868 5042</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:shoh@kriss.re.kr">shoh@kriss.re.kr</a></td>
</tr>
</tbody>
</table>

### A2. Results

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction (x_{NO_2}/\mu\text{mol/mol})</th>
<th>Expanded uncertainty (U(x_{NO_2})/\mu\text{mol/mol})</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>May 15, 2018</td>
<td>10.04</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>May 16, 2018</td>
<td>10.03</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>May 17, 2018</td>
<td>10.03</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>May 18, 2018</td>
<td>10.05</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>(Stability 4)</td>
<td>May 19, 2018</td>
<td>10.04</td>
<td>0.30</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Cylinder 2(D59 6882)-- Before shipping to the BIPM

<table>
<thead>
<tr>
<th></th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction  ( x_{\text{NO}_2} ) / ( \mu \text{mol/mol} )</th>
<th>Expanded uncertainty  ( U(x_{\text{NO}_2}) ) / ( \mu \text{mol/mol} )</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>May 15, 2018</td>
<td>10.03</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>May 16, 2018</td>
<td>10.04</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>May 17, 2018</td>
<td>10.03</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>May 18, 2018</td>
<td>10.02</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>(Stability 4)</td>
<td>May 19, 2018</td>
<td>10.03</td>
<td>0.30</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Cylinder 1- Post BIPM measurements

<table>
<thead>
<tr>
<th></th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction  ( x_{\text{NO}_2} ) / ( \mu \text{mol/mol} )</th>
<th>Expanded uncertainty  ( U(x_{\text{NO}_2}) ) / ( \mu \text{mol/mol} )</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Cylinder 2- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / $\mu$mol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / $\mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A3. **Uncertainty Budget**
Please provide a complete uncertainty budget.

Purity table for NO$_2$ source gas

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction $\mu$ mol/mol</th>
<th>Uncertainty $\mu$ mol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>645</td>
<td>64.5</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>1 130</td>
<td>150</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1.0</td>
<td>0.05</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3 340</td>
<td>167</td>
</tr>
<tr>
<td>CO</td>
<td>8.6</td>
<td>0.4</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>75.9</td>
<td>3.8</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>22.8</td>
<td>2.3</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>994 777</td>
<td>234</td>
</tr>
<tr>
<td>Analyte</td>
<td>Relative standard uncertainties / %</td>
<td>Expanded uncertainty / %</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td></td>
<td>Gravimetry</td>
<td>Analysis</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.08</td>
<td>0.48</td>
</tr>
</tbody>
</table>

- Concentration for final mixture.

Cylinder 1(D59 6920) : 10.04 μmol/mol \( (U = 0.30 \mu\text{mol/mol}) \)

Cylinder 2(D59 6882) : 10.03 μmol/mol \( (U = 0.30 \mu\text{mol/mol}) \)

**A4. Description of the procedure used during the gas analysis**

Please describe in detail the analytical method(s) used for gas analysis⁴.

- NO₂ analyser : Chemiluminescent NO/NOx analyser (Thermo 42i-HL)
- Samples : 4 PRMs \((~10 \mu\text{mol/mol})\)
- 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 NO₂, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

- ~1000 \( \mu \text{mol/mol} \) 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

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Cylinder 2

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Post BIPM measurements

### Cylinder 1- Post BIPM measurements(D59 6920)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO2} / \mu$mol/mol</th>
<th>Expanded uncertainty $U(x_{NO2}) / \mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>2019.08.20</td>
<td>10.05</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>2019.08.22</td>
<td>10.05</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>2019.09.18</td>
<td>10.06</td>
<td>0.30</td>
<td>2.0</td>
</tr>
</tbody>
</table>

### Cylinder 2- Post BIPM measurements(D59 6882)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO2} / \mu$mol/mol</th>
<th>Expanded uncertainty $U(x_{NO2}) / \mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>2019.08.20</td>
<td>10.03</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>2019.08.22</td>
<td>10.04</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>2019.09.18</td>
<td>10.05</td>
<td>0.30</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Before shipping to the BIPM

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

Result form CCQM-K74.2018-R

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

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

<table>
<thead>
<tr>
<th>Institute</th>
<th>LNE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>1, rue Gaston Boissier</td>
</tr>
<tr>
<td></td>
<td>75724 Paris Cedex 15</td>
</tr>
<tr>
<td></td>
<td>France</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}/\mu\text{mol/mol}$</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})/\mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>19/02/2018</td>
<td>10.035</td>
<td>0.046</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>28/02/2018</td>
<td>10.10</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>28/03/2018</td>
<td>10.02</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>27/04/2018</td>
<td>9.96</td>
<td>0.12</td>
<td>2</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}/\mu\text{mol/mol}$</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})/\mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>22/02/2018</td>
<td>10.015</td>
<td>0.046</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>28/02/2018</td>
<td>10.09</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>28/03/2018</td>
<td>10.01</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>27/04/2018</td>
<td>9.97</td>
<td>0.12</td>
<td>2</td>
</tr>
</tbody>
</table>
Cylinder 1- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2} / \mu\text{mol/mol}$</th>
<th>Expanded uncertainty $U(x_{NO_2}) / \mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cylinder 2- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2} / \mu\text{mol/mol}$</th>
<th>Expanded uncertainty $U(x_{NO_2}) / \mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Uncertainty budget of the NO$_2$/N$_2$ 0001

<table>
<thead>
<tr>
<th>Uncertainty source</th>
<th>Unit</th>
<th>Value $X_i$</th>
<th>$u(X_i)$</th>
<th>Contribution to the uncertainty %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass of N$_2$</td>
<td>g/mol</td>
<td>28.01348</td>
<td>$9.9 \times 10^{-5}$</td>
<td>0.00</td>
</tr>
<tr>
<td>Molar mass of O$_2$</td>
<td>g/mol</td>
<td>31.99880</td>
<td>$4.2 \times 10^{-4}$</td>
<td>0.00</td>
</tr>
<tr>
<td>Molar mass of NO</td>
<td>g/mol</td>
<td>30.00614</td>
<td>$3.1 \times 10^{-4}$</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Unit</td>
<td>Value Xi</td>
<td>u(Xi)</td>
<td>Contribution to the uncertainty %</td>
</tr>
<tr>
<td>--------------------------</td>
<td>--------</td>
<td>------------------</td>
<td>----------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>Mass of NO/N\textsubscript{2} premix</td>
<td>g</td>
<td>65.9087</td>
<td>1.60 \times 10^{-2}</td>
<td>1.05</td>
</tr>
<tr>
<td>Mole fraction of NO/N\textsubscript{2} premix</td>
<td>mol/mol</td>
<td>2.36221 \times 10^{-4}</td>
<td>6.12 \times 10^{-8}</td>
<td>1.30</td>
</tr>
<tr>
<td>Mass of O\textsubscript{2}/N\textsubscript{2} premix</td>
<td>g</td>
<td>50.84073</td>
<td>1.50 \times 10^{-2}</td>
<td>0.00</td>
</tr>
<tr>
<td>Mole fraction of O\textsubscript{2}/N\textsubscript{2} premix</td>
<td>mol/mol</td>
<td>2.92403 \times 10^{-2}</td>
<td>6.66 \times 10^{-6}</td>
<td>0.00</td>
</tr>
<tr>
<td>Mass of N\textsubscript{2}</td>
<td>g</td>
<td>1434.992</td>
<td>2.0 \times 10^{-2}</td>
<td>0.00</td>
</tr>
<tr>
<td>N\textsubscript{2} purity</td>
<td>mol/mol</td>
<td>0.999999991</td>
<td>2.37 \times 10^{-8}</td>
<td>0.00</td>
</tr>
<tr>
<td>NO\textsubscript{2} in NO/N\textsubscript{2} premix</td>
<td>µmol/mol</td>
<td>8.43 \times 10^{-4}</td>
<td>2.6 \times 10^{-5}</td>
<td>0.00</td>
</tr>
<tr>
<td>H\textsubscript{2}O reaction</td>
<td>µmol/mol</td>
<td>0.0</td>
<td>1.0 \times 10^{-2}</td>
<td>20.75</td>
</tr>
<tr>
<td>Stability</td>
<td>µmol/mol</td>
<td>0.0</td>
<td>2 \times 10^{-2}</td>
<td>76.9</td>
</tr>
</tbody>
</table>

\[C_{\text{NO2}} = 10.035 \pm 0.046 \, \mu\text{mol/mol}\]

Uncertainty budget of the NO\textsubscript{2}/N\textsubscript{2} 0002

\[C_{\text{NO2}} = 10.015 \pm 0.046 \, \mu\text{mol/mol}\]

**A4. Description of the procedure used during the gas analysis**

Please describe in detail the analytical method(s) used for gas analysis\textsuperscript{4}.
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 NO₂ 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 Nº1191, pressure 70 bars
- Cylinder Nº1183, pressure 80 bars

If any other component other than NO₂, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

<table>
<thead>
<tr>
<th>Cylinder 1191 NO₂/N₂ 0001</th>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / µmol/mol</th>
<th>Expanded uncertainty %</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>28/02/2018</td>
<td>HNO₃</td>
<td>0.009</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td></td>
<td>28/03/2018</td>
<td>HNO₃</td>
<td>0.032</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td></td>
<td>27/04/2018</td>
<td>HNO₃</td>
<td>0.041</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cylinder 1183 NO₂/N₂ 0002</th>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / µmol/mol</th>
<th>Expanded uncertainty %</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>28/02/2018</td>
<td>HNO₃</td>
<td>0.004</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td></td>
<td>28/03/2018</td>
<td>HNO₃</td>
<td>0.039</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td></td>
<td>27/04/2018</td>
<td>HNO₃</td>
<td>0.052</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
</tbody>
</table>

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


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


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

<table>
<thead>
<tr>
<th>Institute</th>
<th>LNE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>1, rue Gaston Boissier 75724 Paris Cedex 15 France</td>
</tr>
<tr>
<td>Contact person</td>
<td>Tatiana Macé</td>
</tr>
<tr>
<td>Telephone</td>
<td>01 40 43 38 53</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:tatiana.mace@lne.fr">tatiana.mace@lne.fr</a></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Serial number of cylinder received</th>
<th></th>
</tr>
</thead>
</table>

| Cylinder pressure as received | |

A2. Results

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>19/02/2018</td>
<td>10.035</td>
<td>0.046</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>28/02/2018</td>
<td>10.10</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>28/03/2018</td>
<td>10.02</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>27/04/2018</td>
<td>9.96</td>
<td>0.12</td>
<td>2</td>
</tr>
</tbody>
</table>
### Cylinder 1183-NO/N2 0002– Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2} , / , \mu \text{mol/mol}$</th>
<th>Expanded uncertainty $U(x_{NO_2}) , / , \mu \text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>22/02/2018</td>
<td>10.015</td>
<td>0.046</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>28/02/2018</td>
<td>10.09</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>28/03/2018</td>
<td>10.01</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>27/04/2018</td>
<td>9.97</td>
<td>0.12</td>
<td>2</td>
</tr>
</tbody>
</table>

### Cylinder 1- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2} , / , \mu \text{mol/mol}$</th>
<th>Expanded uncertainty $U(x_{NO_2}) , / , \mu \text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>14/05/2019</td>
<td>9.60</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>20/06/2019</td>
<td>9.57</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>12/07/2019</td>
<td>9.62</td>
<td>0.12</td>
<td>2</td>
</tr>
</tbody>
</table>
### Cylinder 2- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction ( x_{NO_2} / \mu\text{mol/mol} )</th>
<th>Expanded uncertainty ( U(x_{NO_2}) / \mu\text{mol/mol} )</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>14/05/2019</td>
<td>9.70</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>20/06/2019</td>
<td>9.69</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>12/07/2019</td>
<td>9.74</td>
<td>0.12</td>
<td>2</td>
</tr>
</tbody>
</table>

### A3. Uncertainty Budget

Please provide a complete uncertainty budget.

#### Uncertainty budget of the NO\(_2\)/N\(_2\) 0001

<table>
<thead>
<tr>
<th>Uncertainty source</th>
<th>Unit</th>
<th>Value Xi</th>
<th>( u(X_i) )</th>
<th>Contribution to the uncertainty %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass of N(_2)</td>
<td>g/mol</td>
<td>28.01348</td>
<td>( 9.9 \times 10^{-5} )</td>
<td>0.00</td>
</tr>
<tr>
<td>Molar mass of O(_2)</td>
<td>g/mol</td>
<td>31.99880</td>
<td>( 4.2 \times 10^{-4} )</td>
<td>0.00</td>
</tr>
<tr>
<td>Molar mass of NO</td>
<td>g/mol</td>
<td>30.00614</td>
<td>( 3.1 \times 10^{-4} )</td>
<td>0.00</td>
</tr>
<tr>
<td>Mass of NO/N(_2) premix</td>
<td>g</td>
<td>65.9087</td>
<td>( 1.60 \times 10^{-2} )</td>
<td>1.05</td>
</tr>
<tr>
<td>Mole fraction of NO/N(_2) premix</td>
<td>mol/mol</td>
<td>( 2.36221 \times 10^{-4} )</td>
<td>( 6.12 \times 10^{-8} )</td>
<td>1.30</td>
</tr>
<tr>
<td>Mass of O(_2)/N(_2) premix</td>
<td>g</td>
<td>50.84073</td>
<td>( 1.50 \times 10^{-2} )</td>
<td>0.00</td>
</tr>
<tr>
<td>Mole fraction of O(_2)/N(_2) premix</td>
<td>mol/mol</td>
<td>( 2.92403 \times 10^{-2} )</td>
<td>( 6.66 \times 10^{-6} )</td>
<td>0.00</td>
</tr>
<tr>
<td>Mass of N(_2)</td>
<td>g</td>
<td>1434.992</td>
<td>( 2.0 \times 10^{-2} )</td>
<td>0.00</td>
</tr>
<tr>
<td>N(_2) purity</td>
<td>mol/mol</td>
<td>( 0.999999991 )</td>
<td>( 2.37 \times 10^{-8} )</td>
<td>0.00</td>
</tr>
<tr>
<td>Uncertainty source</td>
<td>Unit</td>
<td>Value Xi</td>
<td>u(Xi)</td>
<td>Contribution to the uncertainty %</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>---------</td>
<td>------------------</td>
<td>----------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>Molar mass of $N_2$</td>
<td>g/mol</td>
<td>28.01348</td>
<td>9.9 $10^{-5}$</td>
<td>0.00</td>
</tr>
<tr>
<td>Molar mass of $O_2$</td>
<td>g/mol</td>
<td>31.99880</td>
<td>4.2 $10^{-4}$</td>
<td>0.00</td>
</tr>
<tr>
<td>Molar mass of NO</td>
<td>g/mol</td>
<td>30.00614</td>
<td>3.1 $10^{-4}$</td>
<td>0.00</td>
</tr>
<tr>
<td>Mass of NO/N$_2$ premix</td>
<td>g</td>
<td>65.10994</td>
<td>1.3 $10^{-2}$</td>
<td>0.7</td>
</tr>
<tr>
<td>Mole fraction of NO/N$_2$ premix</td>
<td>mol/mol</td>
<td>2.36221 $10^{-4}$</td>
<td>6.12 $10^{-8}$</td>
<td>1.3</td>
</tr>
<tr>
<td>Mass of $O_2$ pre mix</td>
<td>g</td>
<td>50.75351</td>
<td>1.2 $10^{-2}$</td>
<td>0.00</td>
</tr>
<tr>
<td>Mole fraction of $O_2$ pre mix</td>
<td>mol/mol</td>
<td>2.92403 $10^{-2}$</td>
<td>6.66 $10^{-6}$</td>
<td>0.00</td>
</tr>
<tr>
<td>Mass of $N_2$</td>
<td>g</td>
<td>1420.224</td>
<td>1.7 $10^{-2}$</td>
<td>0.00</td>
</tr>
<tr>
<td>$N_2$ purity</td>
<td>mol/mol</td>
<td>0.999999991</td>
<td>2.37 $10^{-8}$</td>
<td>0.00</td>
</tr>
<tr>
<td>$NO_2$ in NO/N$_2$ premix</td>
<td>μmol/mol</td>
<td>8.4164 $10^{-4}$</td>
<td>2.6 $10^{-5}$</td>
<td>0.00</td>
</tr>
<tr>
<td>$H_2O$ reaction</td>
<td>μmol/mol</td>
<td>0.0</td>
<td>1.0 $10^{-2}$</td>
<td>20.8</td>
</tr>
<tr>
<td>Stability</td>
<td>μmol/mol</td>
<td>0.0</td>
<td>2 $10^{-2}$</td>
<td>77.2</td>
</tr>
</tbody>
</table>

$C_{NO_2}$=$10.015 \pm 0.046$ μmol/mol
A4. Description of the procedure used during the gas analysis
Please describe in detail the analytical method(s) used for gas analysis5.

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 NO₂ 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 NO₂, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

**Cylinder 1191 NO₂/N₂ 0001**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / μmol/mol</th>
<th>Expanded uncertainty %</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>28/02/2018</td>
<td>HNO₃</td>
<td>0.009</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td>28/03/2018</td>
<td>HNO₃</td>
<td>0.032</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td>27/04/2018</td>
<td>HNO₃</td>
<td>0.041</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
</tbody>
</table>

**Cylinder 1183 NO₂/N₂ 0002**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / μmol/mol</th>
<th>Expanded uncertainty %</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>28/02/2018</td>
<td>HNO₃</td>
<td>0.004</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td>28/03/2018</td>
<td>HNO₃</td>
<td>0.039</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td>27/04/2018</td>
<td>HNO₃</td>
<td>0.052</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
</tbody>
</table>

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**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / µmol/mol</th>
<th>Expanded uncertainty %</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>14/05/19</td>
<td>HNO$_3$</td>
<td>0.070</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td>20/06/19</td>
<td>HNO$_3$</td>
<td>0.066</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td>12/07/19</td>
<td>HNO$_3$</td>
<td>0.043</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
</tbody>
</table>

**Cylinder 1183 NO$_2$/N$_2$ 0002**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / µmol/mol</th>
<th>Expanded uncertainty %</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>14/05/19</td>
<td>HNO$_3$</td>
<td>0.102</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td>20/06/19</td>
<td>HNO$_3$</td>
<td>0.107</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td>12/07/19</td>
<td>HNO$_3$</td>
<td>0.095</td>
<td>10</td>
<td>2</td>
<td>FTIR</td>
</tr>
</tbody>
</table>
Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 μmol/mol)

Result form CCQM-K74.2018-R

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


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: 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**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide $X_{\text{NO}_2}$ $\mu$mol/mol</th>
<th>Expanded Uncertainty $U$ $\mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation) : VSL</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>23.03.2018</td>
<td>9.93</td>
<td>0.31</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>17.04.2018</td>
<td>9.67</td>
<td>0.26</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>23.05.2018</td>
<td>9.84</td>
<td>0.09</td>
<td>2</td>
</tr>
</tbody>
</table>

**Cylinder 2– 10919 Before shipping to the BIPM**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide $X_{\text{NO}_2}$ $\mu$mol/mol</th>
<th>Expanded Uncertainty $U$ $\mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation) : VSL</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>28.03.2018</td>
<td>9.95</td>
<td>0.31</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>18.04.2018</td>
<td>9.69</td>
<td>0.26</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>18.05.2018</td>
<td>9.85</td>
<td>0.09</td>
<td>2</td>
</tr>
</tbody>
</table>

**Cylinder 1- Post BIPM measurements**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide $X_{\text{NO}_2}$ $\mu$mol/mol</th>
<th>Expanded Uncertainty $U$ $\mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation) : VSL</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Cylinder 2- Post BIPM measurements**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide $X_{\text{NO}_2}$ $\mu$mol/mol</th>
<th>Expanded Uncertainty $U$ $\mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation) : VSL</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### A3. Uncertainty Budget

**Model Equation:**

\[
\begin{align*}
X_{1NO2} &= (qMC \cdot P \cdot VMnull / MSubstanz / q1) + XNO2N; \\
X_{2NO2} &= (qMC \cdot P \cdot VMnull / MSubstanz / q2) + XNO2N; \\
X_{3NO2} &= (qMC \cdot P \cdot VMnull / MSubstanz / q3) + XNO2N; \\
MSubstanz &= M_{Atom1} + 2 \cdot M_{Atom2}; \\
VMnull &= M_{Null} / (d_{Null} \cdot 1000 / 1000000); \\
X_{mean} &= (X_{1NO2} + X_{2NO2} + X_{3NO2}) / 3; \\
Anz_{mean} &= (Anz_{1NO2} + Anz_{2NO2} + Anz_{3NO2}) / 3; \\
b &= p / q; \\
p &= (X_{1NO2} - X_{mean}) \cdot (Anz_{1NO2} - Anz_{mean}) + (X_{2NO2} - X_{mean}) \cdot (Anz_{2NO2} - Anz_{mean}) + (X_{3NO2} - X_{mean}) \cdot (Anz_{3NO2} - Anz_{mean}); \\
q &= (X_{1NO2} - X_{mean})^2 + (X_{2NO2} - X_{mean})^2 + (X_{3NO2} - X_{mean})^2; \\
a &= Anz_{mean} - b \cdot X_{mean}; \\
X_{Res10918NO2} &= (Anz_{Res10918} - a) / b; \\
X_{Res10919NO2} &= (Anz_{Res10919} - a) / b; \\
X_{Bottle10918NO2} &= X_{Res10918NO2} \cdot (q_{VFCdil} + q_{Vduse}) / q_{Vduse} + X_{NO2N}; \\
X_{Bottle10919NO2} &= X_{Res10919NO2} \cdot (q_{VFCdil} + q_{Vduse}) / q_{Vduse} + X_{NO2N}; \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Unit</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>X1NO2</td>
<td>ppb</td>
<td>amount of Fraction NO2 1st calibration point</td>
</tr>
<tr>
<td>qMC</td>
<td>ng/min</td>
<td>permeation rate</td>
</tr>
<tr>
<td>P</td>
<td>no units</td>
<td>purity of permeator</td>
</tr>
<tr>
<td>VMnull</td>
<td>ml/mol</td>
<td>molar volume</td>
</tr>
<tr>
<td>MSubstanz</td>
<td>g/mol</td>
<td>molar mass</td>
</tr>
<tr>
<td>q1</td>
<td>ml/min</td>
<td>total flow 1st calibration point</td>
</tr>
<tr>
<td>XNO2N</td>
<td>ppb</td>
<td>residual amount of fraction NO2 in matrix gas</td>
</tr>
<tr>
<td>X2NO2</td>
<td>ppb</td>
<td>amount of Fraction NO2 2nd calibration point</td>
</tr>
<tr>
<td>q2</td>
<td>ml/min</td>
<td>total flow 2nd calibration point</td>
</tr>
<tr>
<td>X3NO2</td>
<td>ppb</td>
<td>amount of Fraction NO2 3rd calibration point</td>
</tr>
<tr>
<td>q3</td>
<td>ml/min</td>
<td>total flow 3rd calibration point</td>
</tr>
<tr>
<td>MAtom1</td>
<td>g/mol</td>
<td>molar mass nitrogen atom</td>
</tr>
<tr>
<td>MAtom2</td>
<td>g/mol</td>
<td>molar mass oxygen atom</td>
</tr>
<tr>
<td>MNull</td>
<td>g/mol</td>
<td>molar mass matrix gas</td>
</tr>
<tr>
<td>dNull</td>
<td>kg/m3</td>
<td>matrix gas density</td>
</tr>
<tr>
<td>Xmean</td>
<td>ppb</td>
<td>average amount of fraction calibration points</td>
</tr>
<tr>
<td>Anzmean</td>
<td>ppb</td>
<td>average display calibration points</td>
</tr>
<tr>
<td>Anz1NO2</td>
<td>ppb</td>
<td>display 1st calibration point</td>
</tr>
<tr>
<td>Anz2NO2</td>
<td>ppb</td>
<td>display 2nd calibration point</td>
</tr>
<tr>
<td>Anz3NO2</td>
<td>ppb</td>
<td>display 3rd calibration point</td>
</tr>
<tr>
<td>b</td>
<td>no units</td>
<td>slope calibration curve</td>
</tr>
<tr>
<td>p</td>
<td>ppb2</td>
<td>nominator for slope calibration curve</td>
</tr>
<tr>
<td>q</td>
<td>ppb2</td>
<td>denominator for slope calibration curve</td>
</tr>
</tbody>
</table>
A4. Description of the procedure used during the gas analysis

A commercial chemiluminescence trace level NO₂-analyzer (Thermo 42i-TL) was used as comparator to measure the reference mixtures and both gas cylinders (10918, 10919). The comparator was calibrated with NO₂ reference mixtures in the range from 90 to 115 nmol/mol NO₂ 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 NO2 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 NO2 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 N2 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).

Dynamic dilution in N2 from a pressurised cylinder using a cascade of critical orifices

![Figure 1: Dilution scheme of NO2 cylinder](image)

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 NO2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

<table>
<thead>
<tr>
<th>Cylinder 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
</tr>
<tr>
<td>-</td>
</tr>
</tbody>
</table>
Post BIPM measurements

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

Result form CCQM-K74.2018-R

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


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: 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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide $x_{NO_2}$ μmol/mol</th>
<th>Expanded Uncertainty $U$ μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation) : VSL</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>23.03.2018</td>
<td>9.93</td>
<td>0.31</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>17.04.2018</td>
<td>9.67</td>
<td>0.26</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>23.05.2018</td>
<td>9.84</td>
<td>0.09</td>
<td>2</td>
</tr>
</tbody>
</table>

Cylinder 2– 10919 Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide $x_{NO_2}$ μmol/mol</th>
<th>Expanded Uncertainty $U$ μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation) : VSL</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>28.03.2018</td>
<td>9.95</td>
<td>0.31</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>18.04.2018</td>
<td>9.69</td>
<td>0.26</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>18.05.2018</td>
<td>9.85</td>
<td>0.09</td>
<td>2</td>
</tr>
</tbody>
</table>

Cylinder 1- 10918 Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide $x_{NO_2}$ μmol/mol</th>
<th>Expanded Uncertainty $U$ μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation) : VSL</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>04.06.2019</td>
<td>9.50</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>03.07.2019</td>
<td>9.25</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>15.08.2019</td>
<td>9.56</td>
<td>0.21</td>
<td>2</td>
</tr>
</tbody>
</table>
Cylinder 2- 10919 Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide $X_{NO2}$ μmol/mol</th>
<th>Expanded Uncertainty $U$ μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation) : VSL</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>04.06.2019</td>
<td>9.53</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>02.07.2019</td>
<td>9.30</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>16.08.2019</td>
<td>9.44</td>
<td>0.21</td>
<td>2</td>
</tr>
</tbody>
</table>

**A3. Uncertainty Budget**

**Model Equation:**

$$X_{NO2}^1 = (qmC \times P \times VM_{null} / M_{Substanz} / q1) + X_{NO2N};$$

$$X_{NO2}^2 = (qmC \times P \times VM_{null} / M_{Substanz} / q2) + X_{NO2N};$$

$$X_{NO2}^3 = (qmC \times P \times VM_{null} / M_{Substanz} / q3) + X_{NO2N};$$

$$M_{Substanz} = M_{Atom1} + 2 \times M_{Atom2};$$

$$VM_{null} = M_{Null} / (d_{Null} \times 1000 / 1000000);$$

$$X_{mean} = (X_{NO2}^1 + X_{NO2}^2 + X_{NO2}^3) / 3;$$

$$Anz_{mean} = (Anz_{1NO2} + Anz_{2NO2} + Anz_{3NO2}) / 3;$$

$$b = p / q;$$

$$p = (X_{NO2} - X_{mean}) \times (Anz_{1NO2} - Anz_{mean}) + (X_{NO2} - X_{mean}) \times (Anz_{2NO2} - Anz_{mean}) + (X_{NO2} - X_{mean}) \times (Anz_{3NO2} - Anz_{mean});$$

$$q = (X_{NO2} - X_{mean})^2 + (X_{NO2} - X_{mean})^2 + (X_{NO2} - X_{mean})^2;$$

$$a = Anz_{mean} - b \times X_{mean};$$

$$X_{Res 10918NO2} = (Anz_{Res 10918} - a) / b;$$

$$X_{Res 10919NO2} = (Anz_{Res 10919} - a) / b;$$

$$X_{Bottle 10918NO2} = X_{Res 10918NO2} \times (qv_{MFC Cali} + qv_{dual}) / qv_{dual} + X_{NO2N};$$

$$X_{Bottle 10919NO2} = X_{Res 10919NO2} \times (qv_{MFC Cali} + qv_{dual}) / qv_{dual} + X_{NO2N};$$

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Unit</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{1NO2}$</td>
<td>ppb</td>
<td>amount of Fraction NO2 1st calibration point</td>
</tr>
<tr>
<td>$qmC$</td>
<td>ng/min</td>
<td>permeation rate</td>
</tr>
<tr>
<td>P</td>
<td>no units</td>
<td>purity of permeator</td>
</tr>
<tr>
<td>$VM_{null}$</td>
<td>ml/mol</td>
<td>molar volume</td>
</tr>
<tr>
<td>$M_{Substanz}$</td>
<td>g/mol</td>
<td>molar mass</td>
</tr>
<tr>
<td>$q1$</td>
<td>ml/min</td>
<td>total flow 1st calibration point</td>
</tr>
<tr>
<td>$X_{NO2N}$</td>
<td>ppb</td>
<td>residual amount of fraction NO2 in matrix gas</td>
</tr>
<tr>
<td>$X_{2NO2}$</td>
<td>ppb</td>
<td>amount of Fraction NO2 2nd calibration point</td>
</tr>
<tr>
<td>$q2$</td>
<td>ml/min</td>
<td>total flow 2nd calibration point</td>
</tr>
<tr>
<td>$X_{3NO2}$</td>
<td>ppb</td>
<td>amount of Fraction NO2 3rd calibration point</td>
</tr>
<tr>
<td>$q3$</td>
<td>ml/min</td>
<td>total flow 3rd calibration point</td>
</tr>
<tr>
<td>$M_{Atom1}$</td>
<td>g/mol</td>
<td>molar mass nitrogen atom</td>
</tr>
<tr>
<td>$M_{Atom2}$</td>
<td>g/mol</td>
<td>molar mass oxygen atom</td>
</tr>
<tr>
<td>$M_{Null}$</td>
<td>g/mol</td>
<td>molar mass matrix gas</td>
</tr>
<tr>
<td>$d_{Null}$</td>
<td>kg/m3</td>
<td>matrix gas density</td>
</tr>
<tr>
<td>Quantity</td>
<td>Unit</td>
<td>Definition</td>
</tr>
<tr>
<td>----------------</td>
<td>--------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>Xmean</td>
<td>ppb</td>
<td>average amount of fraction calibration points</td>
</tr>
<tr>
<td>Anzmean</td>
<td>ppb</td>
<td>average display calibration points</td>
</tr>
<tr>
<td>Anz1NO2</td>
<td>ppb</td>
<td>display 1st calibration point</td>
</tr>
<tr>
<td>Anz2NO2</td>
<td>ppb</td>
<td>display 2nd calibration point</td>
</tr>
<tr>
<td>Anz3NO2</td>
<td>ppb</td>
<td>display 3rd calibration point</td>
</tr>
<tr>
<td>b</td>
<td>no units</td>
<td>slope calibration curve</td>
</tr>
<tr>
<td>p</td>
<td>ppb²</td>
<td>nominator for slope calibration curve</td>
</tr>
<tr>
<td>q</td>
<td>ppb²</td>
<td>denominator for slope calibration curve</td>
</tr>
<tr>
<td>a</td>
<td>ppb</td>
<td>y-axis calibration curve</td>
</tr>
<tr>
<td>XRes10918NO2</td>
<td>ppb</td>
<td>amount of fraction cylinder 10918 after dilution</td>
</tr>
<tr>
<td>AnzRes10918</td>
<td>ppb</td>
<td>display cylinder 10918 after dilution</td>
</tr>
<tr>
<td>XRes10919NO2</td>
<td>ppb</td>
<td>amount of fraction cylinder 10919 after dilution</td>
</tr>
<tr>
<td>AnzRes10919</td>
<td>ppb</td>
<td>display cylinder 10919 after dilution</td>
</tr>
<tr>
<td>XBottle10918NO2</td>
<td>ppb</td>
<td>amount of fraction cylinder 10918</td>
</tr>
<tr>
<td>qvMFCdil</td>
<td>ml/min</td>
<td>dilution flow for dilution NO2 cylinder</td>
</tr>
<tr>
<td>qvduse</td>
<td>ml/min</td>
<td>flow from NO2 cylinder</td>
</tr>
<tr>
<td>XBottle10919NO2</td>
<td>ppb</td>
<td>amount of fraction cylinder 10919</td>
</tr>
</tbody>
</table>

### Amount of fraction for cylinder 10918

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Standard Uncertainty</th>
<th>Distribution</th>
<th>Sensitivity Coefficient</th>
<th>Uncertainty Contribution</th>
<th>Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>qmC</td>
<td>498.00 ng/min</td>
<td>7.72 ng/min</td>
<td>normal</td>
<td>20</td>
<td>150 ppb</td>
<td>95.6 %</td>
</tr>
<tr>
<td>P</td>
<td>0.99500 no units</td>
<td>0.00204 no units</td>
<td>triangular</td>
<td>10000</td>
<td>20 ppb</td>
<td>1.7 %</td>
</tr>
<tr>
<td>MSubstanz</td>
<td>46.005500 g/mol</td>
<td>0.000316 g/mol</td>
<td>normal</td>
<td>-4.3</td>
<td>-14 ppb</td>
<td>0.8 %</td>
</tr>
<tr>
<td>q1</td>
<td>2136.56 ml/min</td>
<td>3.20 ml/min</td>
<td>normal</td>
<td>-4.3</td>
<td>-14 ppb</td>
<td>0.8 %</td>
</tr>
<tr>
<td>XNO2N</td>
<td>0.2000 ppb</td>
<td>0.0816 ppb</td>
<td>triangular</td>
<td>88</td>
<td>7.2 ppb</td>
<td>0.2 %</td>
</tr>
<tr>
<td>q2</td>
<td>2536.85 ml/min</td>
<td>3.81 ml/min</td>
<td>normal</td>
<td>-0.75</td>
<td>-2.9 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>q3</td>
<td>2837.18 ml/min</td>
<td>4.26 ml/min</td>
<td>normal</td>
<td>0.44</td>
<td>1.9 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>MAtom1</td>
<td>14.006700 g/mol</td>
<td>0.000100 g/mol</td>
<td>normal</td>
<td>-220</td>
<td>-0.022 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>MAtom2</td>
<td>15.999400 g/mol</td>
<td>0.000150 g/mol</td>
<td>normal</td>
<td>-430</td>
<td>-0.065 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>MNull</td>
<td>28.013400 g/mol</td>
<td>0.000577 g/mol</td>
<td>rectangular</td>
<td>350</td>
<td>0.20 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>dNull</td>
<td>1.2504000 kg/m³</td>
<td>0.0000577 kg/m³</td>
<td>rectangular</td>
<td>-7900</td>
<td>-0.46 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>Xmean</td>
<td>97.90 ppb</td>
<td>1.53 ppb</td>
<td>normal</td>
<td>-79</td>
<td>-8.9 ppb</td>
<td>0.3 %</td>
</tr>
<tr>
<td>Anzmean</td>
<td>100.7600 ppb</td>
<td>0.0502 ppb</td>
<td>normal</td>
<td>-19</td>
<td>-1.4 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>Anz1NO2</td>
<td>116.630 ppb</td>
<td>0.113 ppb</td>
<td>normal</td>
<td>14</td>
<td>0.98 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>Anz2NO2</td>
<td>98.0800 ppb</td>
<td>0.0712 ppb</td>
<td>normal</td>
<td>14</td>
<td>0.98 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>Anz3NO2</td>
<td>87.5700 ppb</td>
<td>0.0694 ppb</td>
<td>normal</td>
<td>14</td>
<td>0.98 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>p</td>
<td>415.62 ppb²</td>
<td>7.50 ppb²</td>
<td>normal</td>
<td>84</td>
<td>3.2 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>q</td>
<td>398.9 ppb²</td>
<td>13.9 ppb²</td>
<td>normal</td>
<td>84</td>
<td>3.2 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>XRes10918NO2</td>
<td>113.73 ppb</td>
<td>1.79 ppb</td>
<td>normal</td>
<td>84</td>
<td>3.2 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>AnzRes10918</td>
<td>117.2500 ppb</td>
<td>0.0387 ppb</td>
<td>normal</td>
<td>84</td>
<td>3.2 ppb</td>
<td>0.0 %</td>
</tr>
<tr>
<td>qvMFCdil</td>
<td>1800.40 ml/min</td>
<td>1.80 ml/min</td>
<td>normal</td>
<td>5.5</td>
<td>9.8 ppb</td>
<td>0.4 %</td>
</tr>
<tr>
<td>qvduse</td>
<td>20.8600 ml/min</td>
<td>0.0313 ml/min</td>
<td>normal</td>
<td>-470</td>
<td>-15 ppb</td>
<td>0.9 %</td>
</tr>
<tr>
<td>XBottle10918N</td>
<td>9930 ppb</td>
<td>157 ppb</td>
<td>normal</td>
<td>-470</td>
<td>-15 ppb</td>
<td>0.9 %</td>
</tr>
</tbody>
</table>
A4. Description of the procedure used during the gas analysis

A commercial chemiluminescence trace level NO2-analyzer (Thermo 42i-TL) was used as comparator to measure the reference mixtures and both gas cylinders (10918, 10919). The comparator was calibrated with NO2 reference mixtures in the range from 58 to 121 nmol/mol NO2 in nitrogen 6.0 (purity 99.99990%). The nitrogen used as matrix gas was purified with a combination of Microturr/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 NO2 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 A4.1: Permeation units and conditions used for the calibration of the NO2-analyzer

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

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 N2 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.
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 NO₂, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

<table>
<thead>
<tr>
<th>Cylinder 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
</tr>
<tr>
<td>-</td>
</tr>
</tbody>
</table>
NIM

Before shipping to the BIPM

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

Result form CCQM-K74.2018-R

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

<table>
<thead>
<tr>
<th>Institute</th>
<th>National Institute of Metrology, China(NIM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>NO. 18 Bei san huan Dong Lu, Chao yang Dist., Beijing, P.R. China (100029)</td>
</tr>
<tr>
<td>Contact person</td>
<td>Tiqiang Zhang, Defa Wang, Hushu Guo, Qian Han</td>
</tr>
<tr>
<td>Telephone</td>
<td>+86-10-64525337</td>
</tr>
<tr>
<td>Fax</td>
<td>+86-10-64204601</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:zhangtq@nim.ac.cn">zhangtq@nim.ac.cn</a></td>
</tr>
<tr>
<td>Serial number of cylinder received</td>
<td>L62804135</td>
</tr>
<tr>
<td>Cylinder pressure as received</td>
<td>10MPa</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
# A2. Results

## Cylinder 1 (L62804135) – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $(U_{x_{NO_2}})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>25/12/2017</td>
<td>10.001</td>
<td>0.010</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>26/1/2018</td>
<td>9.936</td>
<td>0.034</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>2/3/2018</td>
<td>9.904</td>
<td>0.034</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>26/3/2018</td>
<td>9.890</td>
<td>0.034</td>
<td>2</td>
</tr>
</tbody>
</table>

## Cylinder 2 (L62804125) – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $(U_{x_{NO_2}})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>25/12/2017</td>
<td>9.998</td>
<td>0.010</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>26/1/2018</td>
<td>9.947</td>
<td>0.034</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>2/3/2018</td>
<td>9.909</td>
<td>0.034</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>26/3/2018</td>
<td>9.896</td>
<td>0.034</td>
<td>2</td>
</tr>
</tbody>
</table>

## Cylinder 1 (L62804135) - Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $(U_{x_{NO_2}})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Cylinder 2 (L62804125) - Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $(U_{x_{NO_2}})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A3. Uncertainty Budget

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

\[ u_r(x_{NO2}) = \sqrt{u_{r,\text{prep}}^2 + u_{r,\text{ver}}^2} \]

Here, \( x_{NO2} \) represents the mole fraction of NO\(_2\) in the cylinder, \( u_r \) is the relative standard uncertainty, \( u_{r,\text{prep}} \) and \( u_{r,\text{ver}} \) represent uncertainty from gravimetric preparation method and from verification method, respectively.

<table>
<thead>
<tr>
<th>Source of uncertainty</th>
<th>( u_{r,\text{prep}} )</th>
<th>( u_{r,\text{ver}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative standard uncertainty</td>
<td>0.05%</td>
<td>0.16%</td>
</tr>
<tr>
<td>Relative expanded uncertainty*</td>
<td></td>
<td>0.34%</td>
</tr>
</tbody>
</table>

*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

1\(^{st}\): Pure NO was diluted by nitrogen to reach to the mole fraction of 300 \( \mu \text{mol/mol} \) via 2 steps.

2\(^{ed}\): The 2\% mole fraction oxygen mixture was prepared by mixing oxygen and nitrogen.

3\(^{rd}\): The final standard gas (and calibration gas used for each month measurement) was prepared by adding a certain amount of 300 \( \mu \text{mol/mol} \) NO/N\(_2\) and 2\% mol/mol O\(_2\)/N\(_2\) into pure nitrogen, this gas mixture aimed to contain 10 \( \mu \text{mol/mol} \) NO\(_2\) and 980 \( \mu \text{mol/mol} \) O\(_2\).

![Diagram of gas mixture preparation](image)

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:

\[
\frac{\sum_{j=1}^{p} x_{j,A} \cdot m_{j}}{\sum_{j=1}^{p} (x_{j,A} \cdot M_{j})} \]

Components uncertainties are calculated with below equation:

\[
u^2(x_i) = \sum_{A=1}^{p} \left( \frac{\partial x_i}{\partial m_A} \right)^2 u^2(m_A) + \sum_{i=1}^{n} \left( \frac{\partial x_i}{\partial M_j} \right)^2 u^2(M_j) + \sum_{A=1}^{p} \sum_{i=1}^{n} \left( \frac{\partial x_i}{\partial x_{i,A}} \right)^2 u^2(x_{i,A})
\]

(2) Pre-treatment of the cylinder

The cylinders were found having an adsorption of NO₂, which leads to the negative effects for the long-term stability of NO₂ mixture. To decrease this effect, some treatments to the cylinders were carried out. First, the cylinders were heated to 50°C and were kept for at least 15 hours when pumping to vacuum. Second, 100 μmol/mol NO₂/N₂ 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

<table>
<thead>
<tr>
<th>Component</th>
<th>Method</th>
<th>Mole fraction (μmol/mol)</th>
<th>Distribution</th>
<th>Uncertainty (μmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>Oxygen Analyzer</td>
<td>0.05</td>
<td>Rectangular</td>
<td>0.03</td>
</tr>
<tr>
<td>Ar</td>
<td>GC-PDHID</td>
<td>45.0</td>
<td>Normal</td>
<td>0.9</td>
</tr>
<tr>
<td>H₂</td>
<td>GC-PDHID</td>
<td>0.05</td>
<td>Rectangular</td>
<td>0.03</td>
</tr>
<tr>
<td>H₂O</td>
<td>CRDs</td>
<td>0.2</td>
<td>Rectangular</td>
<td>0.12</td>
</tr>
<tr>
<td>CO</td>
<td>GC-PDHID</td>
<td>0.05</td>
<td>Rectangular</td>
<td>0.03</td>
</tr>
</tbody>
</table>
### Purity table for NO

<table>
<thead>
<tr>
<th>Component</th>
<th>Method</th>
<th>Mole fraction (μmol/mol)</th>
<th>Distribution</th>
<th>Uncertainty (μmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>FTIR</td>
<td>430.0</td>
<td>Normal</td>
<td>43.0</td>
</tr>
<tr>
<td>NO₂</td>
<td>FTIR</td>
<td>880.0</td>
<td>Normal</td>
<td>88.0</td>
</tr>
<tr>
<td>HNO₃</td>
<td>FTIR</td>
<td>200.0</td>
<td>Normal</td>
<td>100</td>
</tr>
<tr>
<td>N₂</td>
<td>GC-PDHID</td>
<td>100.0</td>
<td>Normal</td>
<td>20.0</td>
</tr>
<tr>
<td>NO</td>
<td></td>
<td>998390.0</td>
<td>-</td>
<td>141.4</td>
</tr>
</tbody>
</table>

### Purity table for O₂

<table>
<thead>
<tr>
<th>Component</th>
<th>Method</th>
<th>Mole fraction (μmol/mol)</th>
<th>Distribution</th>
<th>Uncertainty (μmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>GC-PDHID</td>
<td>2.5</td>
<td>Rectangular</td>
<td>1.4</td>
</tr>
<tr>
<td>Ar</td>
<td>GC-PED</td>
<td>1.0</td>
<td>Rectangular</td>
<td>0.6</td>
</tr>
<tr>
<td>H₂</td>
<td>GC-PDHID</td>
<td>0.25</td>
<td>Rectangular</td>
<td>0.14</td>
</tr>
<tr>
<td>H₂O</td>
<td>CRDs</td>
<td>1.0</td>
<td>Rectangular</td>
<td>0.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>GC-PDHID</td>
<td>0.47</td>
<td>Normal</td>
<td>0.03</td>
</tr>
<tr>
<td>CH₄</td>
<td>GC-PDHID</td>
<td>0.25</td>
<td>Rectangular</td>
<td>0.14</td>
</tr>
<tr>
<td>O₂</td>
<td></td>
<td>999994.4</td>
<td>-</td>
<td>1.7</td>
</tr>
</tbody>
</table>

(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 three-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 NO₂, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

<table>
<thead>
<tr>
<th>Cylinder 1</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>Component</td>
<td>Mole fraction nmol/mol</td>
<td>Expanded uncertainty</td>
<td>Coverage factor</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cylinder 2</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>Component</td>
<td>Mole fraction nmol/mol</td>
<td>Expanded uncertainty</td>
<td>Coverage factor</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Measurement technique
Post BIPM measurements

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

Result form CCQM-K74.2018-R

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

<table>
<thead>
<tr>
<th>Institute</th>
<th>National Institute of Metrology, China(NIM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>NO. 18 Bei san huan Dong lu, Chao yang Dist., Beijing, P.R. China (100029)</td>
</tr>
<tr>
<td>Contact person</td>
<td>Tiqiang Zhang, Defa Wang, Shuguo Hu, Qiao Han</td>
</tr>
<tr>
<td>Telephone</td>
<td>+86-10-64525337</td>
</tr>
<tr>
<td>Fax</td>
<td>+86-10-64204601</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:zhangtq@nim.ac.cn">zhangtq@nim.ac.cn</a></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Serial number of cylinder received</th>
<th>L62804135</th>
<th>L62804125</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylinder pressure as received</td>
<td>10MPa</td>
<td>10MPa</td>
</tr>
</tbody>
</table>
A2. Results

Cylinder 1 (L62804135) – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction (x_{\text{NO}_2}/\mu\text{mol/mol})</th>
<th>Expanded uncertainty ((U_{x_{\text{NO}_2}})/\mu\text{mol/mol})</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>25/12/2017</td>
<td>10.001</td>
<td>0.010</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>26/1/2018</td>
<td>9.936</td>
<td>0.034</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>2/3/2018</td>
<td>9.904</td>
<td>0.034</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>26/3/2018</td>
<td>9.890</td>
<td>0.034</td>
<td>2</td>
</tr>
</tbody>
</table>

Cylinder 2 (L62804125) – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction (x_{\text{NO}_2}/\mu\text{mol/mol})</th>
<th>Expanded uncertainty ((U_{x_{\text{NO}_2}})/\mu\text{mol/mol})</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>25/12/2017</td>
<td>9.998</td>
<td>0.010</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>26/1/2018</td>
<td>9.947</td>
<td>0.034</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>2/3/2018</td>
<td>9.909</td>
<td>0.034</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>26/3/2018</td>
<td>9.896</td>
<td>0.034</td>
<td>2</td>
</tr>
</tbody>
</table>

Cylinder 1 (L62804135) - Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction (x_{\text{NO}_2}/\mu\text{mol/mol})</th>
<th>Expanded uncertainty ((U_{x_{\text{NO}_2}})/\mu\text{mol/mol})</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>24/5/2019</td>
<td>9.769</td>
<td>0.033</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>28/6/2019</td>
<td>9.806</td>
<td>0.033</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>24/7/2019</td>
<td>9.785</td>
<td>0.033</td>
<td>2</td>
</tr>
</tbody>
</table>

Cylinder 2 (L62804125) - Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction (x_{\text{NO}_2}/\mu\text{mol/mol})</th>
<th>Expanded uncertainty ((U_{x_{\text{NO}_2}})/\mu\text{mol/mol})</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>29/5/2019</td>
<td>9.737</td>
<td>0.033</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>28/6/2019</td>
<td>9.759</td>
<td>0.033</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>24/7/2019</td>
<td>9.748</td>
<td>0.033</td>
<td>2</td>
</tr>
</tbody>
</table>
A3. Uncertainty Budget
The contributions of standard uncertainty were from preparation of gravimetric method and verification method.

\[ u_r(x_{NO_2}) = \sqrt{u_{r,\text{prep}}^2 + u_{r,\text{ver}}^2} \]

Here, \( x_{NO_2} \) represents the mole fraction of NO\(_2\) in the cylinder, \( u_r \) is the relative standard uncertainty, \( u_{r,\text{prep}} \) and \( u_{r,\text{ver}} \) represent uncertainty from gravimetric preparation method and from verification method, respectively.

<table>
<thead>
<tr>
<th>Source of uncertainty</th>
<th>( u_{r,\text{prep}} )</th>
<th>( u_{r,\text{ver}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative standard uncertainty</td>
<td>0.05%</td>
<td>0.16%</td>
</tr>
<tr>
<td>Relative expanded uncertainty*</td>
<td>0.34%</td>
<td></td>
</tr>
</tbody>
</table>

*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

1\(^{st}\): Pure NO was diluted by nitrogen to reach to the mole fraction of 300 μmol/mol via 2 steps.

2\(^{ed}\): The 2% mole fraction oxygen mixture was prepared by mixing oxygen and nitrogen.

3\(^{rd}\): The final standard gas (and calibration gas used for each month measurement) 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\(_2\).

![Diagram of gas preparation process]

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:

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

(2) Pre-treatment of the cylinder

The cylinders were found having an adsorption of NO₂, which leads to the negative effects for the long-term stability of NO₂ mixture. To decrease this effect, some treatments to the cylinders were carried out. First, the cylinders were heated to 50°C and were kept for at least 15 hours when pumping to vacuum. Second, 100 μmol/mol NO₂/N₂ 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

<table>
<thead>
<tr>
<th>Component</th>
<th>Method</th>
<th>Mole fraction (μmol/mol)</th>
<th>Distribution</th>
<th>Uncertainty (μmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>Oxygen Analyzer</td>
<td>0.05</td>
<td>Rectangular</td>
<td>0.03</td>
</tr>
<tr>
<td>Ar</td>
<td>GC-PDHID</td>
<td>45.0</td>
<td>Normal</td>
<td>0.9</td>
</tr>
<tr>
<td>H₂</td>
<td>GC-PDHID</td>
<td>0.05</td>
<td>Rectangular</td>
<td>0.03</td>
</tr>
<tr>
<td>H₂O</td>
<td>CRDs</td>
<td>0.2</td>
<td>Rectangular</td>
<td>0.12</td>
</tr>
</tbody>
</table>
CO | GC-PDHID | 0.05 | Rectangular | 0.03
---|---------|------|-------------|------
CO₂ | GC-PDHID | 0.05 | Rectangular | 0.03
CH₄ | GC-PDHID | 0.05 | Rectangular | 0.03
NO | APIMS   | 2.7×10⁻³ | Normal     | 1.3×10⁻³
N₂  |         | 999954.40 | -          | 0.92

Purity table for NO

<table>
<thead>
<tr>
<th>Component</th>
<th>Method</th>
<th>Mole fraction (μmol/mol)</th>
<th>Distribution</th>
<th>Uncertainty (μmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>FTIR</td>
<td>430.0</td>
<td>Normal</td>
<td>43.0</td>
</tr>
<tr>
<td>NO₂</td>
<td>FTIR</td>
<td>880.0</td>
<td>Normal</td>
<td>88.0</td>
</tr>
<tr>
<td>HNO₃</td>
<td>FTIR</td>
<td>200.0</td>
<td>Normal</td>
<td>100</td>
</tr>
<tr>
<td>N₂</td>
<td>GC-PDHID</td>
<td>100.0</td>
<td>Normal</td>
<td>20.0</td>
</tr>
<tr>
<td>NO</td>
<td></td>
<td>998390.0</td>
<td>-</td>
<td>141.4</td>
</tr>
</tbody>
</table>

Purity table for O₂

<table>
<thead>
<tr>
<th>Component</th>
<th>Method</th>
<th>Mole fraction (μmol/mol)</th>
<th>Distribution</th>
<th>Uncertainty (μmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>GC-PDHID</td>
<td>2.5</td>
<td>Rectangular</td>
<td>1.4</td>
</tr>
<tr>
<td>Ar</td>
<td>GC-PED</td>
<td>1.0</td>
<td>Rectangular</td>
<td>0.6</td>
</tr>
<tr>
<td>H₂</td>
<td>GC-PDHID</td>
<td>0.25</td>
<td>Rectangular</td>
<td>0.14</td>
</tr>
<tr>
<td>H₂O</td>
<td>CRDs</td>
<td>1.0</td>
<td>Rectangular</td>
<td>0.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>GC-PDHID</td>
<td>0.47</td>
<td>Normal</td>
<td>0.03</td>
</tr>
<tr>
<td>CH₄</td>
<td>GC-PDHID</td>
<td>0.25</td>
<td>Rectangular</td>
<td>0.14</td>
</tr>
<tr>
<td>O₂</td>
<td></td>
<td>999994.4</td>
<td>-</td>
<td>1.7</td>
</tr>
</tbody>
</table>

(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 three-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.

![Diagram of the procedure]

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 NO2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

<table>
<thead>
<tr>
<th>Cylinder 1</th>
<th>Cylinder 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>Component</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction (nmol/mol)</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
NMIA

Before shipping to the BIPM

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

Result form CCQM-K74.2018-R

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

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

<table>
<thead>
<tr>
<th>Institute</th>
<th>National Measurement Institute, Australia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>36 BRADFIELD RD. LINDFIELD NSW 2070 Australia</td>
</tr>
<tr>
<td>Contact person</td>
<td>DAMIAN SMEULDERS</td>
</tr>
<tr>
<td>Telephone</td>
<td>+61 2 84673534</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:gas@measurement.gov.au">gas@measurement.gov.au</a></td>
</tr>
<tr>
<td>Serial number of cylinder received</td>
<td>MK0806 and MK0807</td>
</tr>
<tr>
<td>Cylinder pressure as received</td>
<td>125 bar</td>
</tr>
</tbody>
</table>
A2. Results

Cylinder 1 – Before shipping to the BIPM

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

Cylinder 2 – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>16/03/2018 MK0807</td>
<td>10.140</td>
<td>0.025</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>5/4/18</td>
<td>10.27</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>5/4/18</td>
<td>10.22</td>
<td>0.09</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>6/4/18</td>
<td>10.22</td>
<td>0.15</td>
<td>2</td>
</tr>
</tbody>
</table>
Cylinder 1 - Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / $\mu$mol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / $\mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cylinder 2 - Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / $\mu$mol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / $\mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.\footnote{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.}

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**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Cylinder 2**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 μmol/mol)

Result form CCQM-K74.2018-R

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

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
e-mail: 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

<table>
<thead>
<tr>
<th>Institute</th>
<th>National Measurement Institute, Australia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>36 BRADFIELD RD. LINDFIELD NSW 2070 Australia</td>
</tr>
<tr>
<td>Contact person</td>
<td>DAMIAN SMEULDERS</td>
</tr>
<tr>
<td>Telephone</td>
<td>+61 2 84673534</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:gas@measurement.gov.au">gas@measurement.gov.au</a></td>
</tr>
<tr>
<td>Serial number of cylinder received</td>
<td>MK0806 and MK0807</td>
</tr>
<tr>
<td>Cylinder pressure as received</td>
<td>125 bar</td>
</tr>
</tbody>
</table>
A2. Results

Cylinder 1 – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>16/03/2018 MK0806</td>
<td>10.015</td>
<td>0.028</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>5/4/18 (wet regulator)</td>
<td>9.74</td>
<td>0.32</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>5/4/18</td>
<td>9.97</td>
<td>0.09</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>6/4/18</td>
<td>9.95</td>
<td>0.17</td>
<td>2</td>
</tr>
</tbody>
</table>

Cylinder 2 – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>16/03/2018 MK0807</td>
<td>10.140</td>
<td>0.025</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>5/4/18</td>
<td>10.27</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>5/4/18</td>
<td>10.22</td>
<td>0.09</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>6/4/18</td>
<td>10.22</td>
<td>0.15</td>
<td>2</td>
</tr>
</tbody>
</table>
Cylinder 1- Post BIPM measurements (MK0806)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>5/08/2019</td>
<td>9.85</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>6/08/2019</td>
<td>10.01</td>
<td>0.22</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>6/08/2019</td>
<td>10.00</td>
<td>0.22</td>
<td>2</td>
</tr>
</tbody>
</table>

Cylinder 2- Post BIPM measurements (MK0807)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>5/08/2019</td>
<td>10.02</td>
<td>0.24</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>6/08/2019</td>
<td>10.02</td>
<td>0.24</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>6/08/2019</td>
<td>10.01</td>
<td>0.24</td>
<td>2</td>
</tr>
</tbody>
</table>

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 analysis1.

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 NO₂, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Cylinder 1 MK0806 (NMIA 1)

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
</table>

Cylinder 2

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Institute</th>
<th>National Metrology Institute of South Africa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>CSIR Campus Building 5</td>
</tr>
<tr>
<td></td>
<td>Meiring Naude Road</td>
</tr>
<tr>
<td></td>
<td>Brummeria</td>
</tr>
<tr>
<td></td>
<td>Pretoria</td>
</tr>
<tr>
<td></td>
<td>0182</td>
</tr>
<tr>
<td>Contact person</td>
<td>Dr. James Tshilongo</td>
</tr>
<tr>
<td>Telephone</td>
<td>+27 12 841 2589</td>
</tr>
<tr>
<td>Fax</td>
<td>+27 12 841 2131/4458</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:jtshilongo@nmisa.org">jtshilongo@nmisa.org</a></td>
</tr>
<tr>
<td>Serial number of cylinder</td>
<td>D62 6554</td>
</tr>
<tr>
<td>received</td>
<td></td>
</tr>
<tr>
<td>Cylinder pressure as received</td>
<td>8.5 MPa</td>
</tr>
<tr>
<td>Serial number of cylinder</td>
<td>D62 6618</td>
</tr>
<tr>
<td>received</td>
<td></td>
</tr>
<tr>
<td>Cylinder pressure as received</td>
<td>10 MPa</td>
</tr>
</tbody>
</table>

A2. Results

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$x_{NO_2}$ / μmol/mol</th>
<th>$U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>07 March 2018</td>
<td>9,988</td>
<td>0,00096</td>
<td>k=2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>08 March 2018</td>
<td>9,938</td>
<td>0,136</td>
<td>k=2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>15 April 2018</td>
<td>9,943</td>
<td>0,168</td>
<td>k=2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>07 May 2018</td>
<td>9,856</td>
<td>0,137</td>
<td>k=2</td>
</tr>
</tbody>
</table>
### Result (Cylinder 1: D62 6554)

<table>
<thead>
<tr>
<th>Nitrogen dioxide mole fraction</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{\text{NO}_2} / \mu\text{mol/mol}$</td>
<td>$U(x_{\text{NO}_2}) / \mu\text{mol/mol}$</td>
<td>$k=2$</td>
</tr>
<tr>
<td>9.99</td>
<td>0.16</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>04 March 2018</td>
<td>10.0423</td>
<td>0.00096</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>12 March 2018</td>
<td>9.958</td>
<td>0.143</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>15 April 2018</td>
<td>10.029</td>
<td>0.144</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>07 May 2018</td>
<td>9.948</td>
<td>0.163</td>
<td>$k=2$</td>
</tr>
</tbody>
</table>

### Result (Cylinder 2: D62 6618)

<table>
<thead>
<tr>
<th>Nitrogen dioxide mole fraction</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{\text{NO}_2} / \mu\text{mol/mol}$</td>
<td>$U(x_{\text{NO}_2}) / \mu\text{mol/mol}$</td>
<td></td>
</tr>
<tr>
<td>10.04</td>
<td>0.16</td>
<td>2</td>
</tr>
</tbody>
</table>
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:

\[ u_c^2 = \frac{u_{\text{day1}}^2 + u_{\text{day2}}^2 + u_{\text{day3}}^2}{3} + (u_{\text{ESDM}})^2 + x_{GRV}^2 \]  

Equation 1

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

\[ U = k \times u_c, \text{ where } k = 2 \]  

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

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol/mol</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.9989086237999</td>
<td>0.00000024210390</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0010224997119</td>
<td>0.0000000201507</td>
</tr>
<tr>
<td>Ar</td>
<td>0.0000538465723</td>
<td>0.00000024232565</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.0000099888095</td>
<td>0.000000004777</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.0000000099956</td>
<td>0.0000000051606</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0000000089996</td>
<td>0.0000000046670</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0000000071098</td>
<td>0.0000000035543</td>
</tr>
<tr>
<td>CO</td>
<td>0.0000000062996</td>
<td>0.0000000032669</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.0000000099994</td>
<td>0.0000000046392</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.0000000070174</td>
<td>0.0000000035330</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.0000000062998</td>
<td>0.0000000032474</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>0.0000000051506</td>
<td>0.000000000874</td>
</tr>
<tr>
<td>C₅H₇</td>
<td>0.0000000099956</td>
<td>0.0000000051606</td>
</tr>
</tbody>
</table>

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

Table 2: purity table of D62 6618

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol/mol</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.9993231260143</td>
<td>0.00000024475825</td>
</tr>
<tr>
<td>O₂</td>
<td>0.00006078954837</td>
<td>0.0000003988938</td>
</tr>
<tr>
<td>Ar</td>
<td>0.0000538679551</td>
<td>0.0000002432565</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.0000100425992</td>
<td>0.000000004811</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.0000000099994</td>
<td>0.0000000051299</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0000000089994</td>
<td>0.0000000046392</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0000000070174</td>
<td>0.0000000035330</td>
</tr>
<tr>
<td>CO</td>
<td>0.0000000062998</td>
<td>0.0000000032474</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.0000000099994</td>
<td>0.0000000046392</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.0000000070174</td>
<td>0.0000000035330</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.0000000062998</td>
<td>0.0000000032474</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>0.0000000051506</td>
<td>0.000000000874</td>
</tr>
<tr>
<td>C₅H₇</td>
<td>0.0000000099956</td>
<td>0.0000000051606</td>
</tr>
</tbody>
</table>
A6. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis1.

The measurements were performed on the ABB Limas UV analyser using NO2 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 NO2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

**Cylinder 1: D62 6554**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty nmol/mol</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>08 May 2018</td>
<td>HNO3</td>
<td>170</td>
<td>12.5</td>
<td>k=2</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
</tbody>
</table>

**Cylinder 1: D62 6618**

No measurements of other components were measured in the cylinder; however, it is expected that HNO3 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

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

<table>
<thead>
<tr>
<th>Institute</th>
<th>National Metrology Institute of South Africa</th>
</tr>
</thead>
</table>
| 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**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$x_{\text{NO}_2}$ / μmol/mol</th>
<th>$U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>07 March 2018</td>
<td>9,988</td>
<td>0,00096</td>
<td>k=2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>08 March 2018</td>
<td>9,938</td>
<td>0,136</td>
<td>k=2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>15 April 2018</td>
<td>9,943</td>
<td>0,168</td>
<td>k=2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>07 May 2018</td>
<td>9,856</td>
<td>0,137</td>
<td>k=2</td>
</tr>
</tbody>
</table>
## Result (Cylinder 1: D62 6554)

<table>
<thead>
<tr>
<th>Nitrogen dioxide mole fraction</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{\text{NO}_2}$ / μmol/mol</td>
<td>$U(x_{\text{NO}_2})$ / μmol/mol</td>
<td>$k=2$</td>
</tr>
<tr>
<td>9.99</td>
<td>0.16</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>04 March 2018</td>
<td>10.0423</td>
<td>0.00096</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>12 March 2018</td>
<td>9.958</td>
<td>0.143</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>15 April 2018</td>
<td>10.029</td>
<td>0.144</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>07 May 2018</td>
<td>9.948</td>
<td>0.163</td>
<td>$k=2$</td>
</tr>
</tbody>
</table>

## Result (Cylinder 2: D62 6618)

<table>
<thead>
<tr>
<th>Nitrogen dioxide mole fraction</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{\text{NO}_2}$ / μmol/mol</td>
<td>$U(x_{\text{NO}_2})$ / μmol/mol</td>
<td></td>
</tr>
<tr>
<td>10.04</td>
<td>0.16</td>
<td>2</td>
</tr>
</tbody>
</table>
### Cylinder (D62 6554) 1 – Post BIPM Measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>25 April 2019</td>
<td>10.007</td>
<td>0.092</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>27 May 2019</td>
<td>9.985</td>
<td>0.116</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>25 July 2019</td>
<td>9.999</td>
<td>0.111</td>
<td>$k=2$</td>
</tr>
</tbody>
</table>

### Result (Cylinder 1: D62 6554) including stability measurements

<table>
<thead>
<tr>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.99</td>
<td>0.16</td>
<td>$k=2$</td>
</tr>
</tbody>
</table>

### Cylinder (D62 6618) 2 – Post BIPM Measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>25 April 2019</td>
<td>10.02</td>
<td>0.089</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>27 May 2019</td>
<td>10.01</td>
<td>0.118</td>
<td>$k=2$</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>25 July 2019</td>
<td>10.00</td>
<td>0.101</td>
<td>$k=2$</td>
</tr>
</tbody>
</table>
Result (Cylinder 2: D62 6618) including stability measurements

<table>
<thead>
<tr>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.04</td>
<td>0.16</td>
<td>2</td>
</tr>
</tbody>
</table>

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:

$$u^2_c = \frac{u^2_{\text{day}1} + u^2_{\text{day}2} + u^2_{\text{day}3}}{3} + \left(u_{\text{Stability}}\right)^2 + x_{\text{grv}}^2$$

Equation 1

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

$$U = k \times u_c, \text{ where } k = 2$$. 

Equation 2
A4. Description of the preparation method

The NO₂ standards were gravimetrically prepared from pure nitric oxide, pure oxygen and pure nitrogen. The production diagram for the overall NO₂ standards is show in **figure 1**

![Production diagram for the nitrogen dioxide gas mixture](image)

**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

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol/mol</th>
<th>Gravimetric uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.9989086237999</td>
<td>0.000000024210390</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0010224997119</td>
<td>0.0000000201507</td>
</tr>
<tr>
<td>Ar</td>
<td>0.0000538465723</td>
<td>0.00000024232565</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.0000099888095</td>
<td>0.000000004777</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.0000000099956</td>
<td>0.0000000051606</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0000000098575</td>
<td>0.0000000010143</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0000000099956</td>
<td>0.0000000046670</td>
</tr>
<tr>
<td>CO</td>
<td>0.0000000098575</td>
<td>0.0000000035543</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.0000000062996</td>
<td>0.0000000032669</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.0000000042917</td>
<td>0.0000000022258</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.0000000001496</td>
<td>0.000000000870</td>
</tr>
<tr>
<td>CₓHᵧ</td>
<td>0.000000000050</td>
<td>0.00000000029</td>
</tr>
</tbody>
</table>

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

Table 2: Purity table of D62 6618

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol/mol</th>
<th>Gravimetric uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.9993231260143</td>
<td>0.00000024475825</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0006078954837</td>
<td>0.0000003988938</td>
</tr>
<tr>
<td>Ar</td>
<td>0.0000538679551</td>
<td>0.00000024088070</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.0000100425992</td>
<td>0.000000004811</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.0000000099994</td>
<td>0.0000000051299</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0000000099635</td>
<td>0.0000000010086</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0000000099994</td>
<td>0.0000000046392</td>
</tr>
<tr>
<td>CO</td>
<td>0.0000000042917</td>
<td>0.0000000035330</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.0000000062998</td>
<td>0.0000000032474</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.0000000042910</td>
<td>0.0000000022125</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.0000000001506</td>
<td>0.000000000874</td>
</tr>
<tr>
<td>CₓHᵧ</td>
<td>0.000000000050</td>
<td>0.00000000029</td>
</tr>
</tbody>
</table>
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 \(\mu\)mol/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**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty nmol/mol</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>08 May 2018</td>
<td>HNO(_3)</td>
<td>Below detection limit of the FTIR</td>
<td>N/A</td>
<td>N/A</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
</tbody>
</table>

**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.
Before shipping to the BIPM
Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen
(10 μmol/mol)

Result form CCQM-K74.2018-R


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


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

<table>
<thead>
<tr>
<th><strong>Institute</strong></th>
<th>National Physical Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Address</strong></td>
<td>Hampton Road</td>
</tr>
<tr>
<td></td>
<td>Teddington</td>
</tr>
<tr>
<td></td>
<td>TW11 0LW</td>
</tr>
<tr>
<td><strong>Contact person</strong></td>
<td>Dave Worton</td>
</tr>
<tr>
<td><strong>Telephone</strong></td>
<td>+44 (0) 208 943 6591</td>
</tr>
<tr>
<td><strong>Email</strong></td>
<td><a href="mailto:dave.worton@npl.co.uk">dave.worton@npl.co.uk</a></td>
</tr>
<tr>
<td><strong>Serial number of cylinder received</strong></td>
<td>2448, S357</td>
</tr>
<tr>
<td><strong>Cylinder pressure as received</strong></td>
<td>2448 – 12.0 MPa</td>
</tr>
<tr>
<td></td>
<td>S357 – 9.0 MPa</td>
</tr>
</tbody>
</table>

### A2. Results

**Cylinder 1 – Before shipping to the BIPM (2448)**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>5th April 2018</td>
<td>9.99</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>19th April 2018</td>
<td>10.02</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>3rd May 2018</td>
<td>9.99</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>16th May 2018</td>
<td>10.02</td>
<td>0.07</td>
<td>2</td>
</tr>
</tbody>
</table>
### Cylinder 2 – Before shipping to the BIPM (S357)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$x_{NO_2}$ (μmol/mol)</th>
<th>$U(x_{NO_2})$ (μmol/mol)</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>5th April 2018</td>
<td>10.00</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>19th April 2018</td>
<td>10.04</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>3rd May 2018</td>
<td>10.01</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>16th May 2018</td>
<td>10.00</td>
<td>0.07</td>
<td>2</td>
</tr>
</tbody>
</table>

### Cylinder 1 – Post BIPM measurements (2448)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$x_{NO_2}$ (μmol/mol)</th>
<th>$U(x_{NO_2})$ (μmol/mol)</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Cylinder 2 – Post BIPM measurements (S357)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$x_{NO_2}$ (μmol/mol)</th>
<th>$U(x_{NO_2})$ (μmol/mol)</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Identifier</th>
<th>Component</th>
<th>Preparation (k=1)</th>
<th>Validation (k=1)</th>
<th>Total (k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2448</td>
<td>NO\textsubscript{2}</td>
<td>0.007</td>
<td>0.350</td>
<td>0.700</td>
</tr>
<tr>
<td>S357</td>
<td>NO\textsubscript{2}</td>
<td>0.007</td>
<td>0.350</td>
<td>0.700</td>
</tr>
</tbody>
</table>

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\textsuperscript{10}.

An ABB AO2020 LIMAS 11 UV analyser was used to validate the amount fraction of NO\textsubscript{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.

\textsuperscript{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 NO₂, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below.

**Cylinder 1 (2448)**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
</table>

**Cylinder 2 (S357)**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
</table>

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

Result form CCQM-K74.2018-R


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


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

<table>
<thead>
<tr>
<th>Institute</th>
<th>National Physical Laboratory</th>
</tr>
</thead>
</table>
| 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)**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$x_{\text{NO}_2}$/ μmol/mol</th>
<th>$U(x_{\text{NO}_2})$/ μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>5th April 2018</td>
<td>9.99</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>19th April 2018</td>
<td>10.02</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>3rd May 2018</td>
<td>9.99</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>16th May 2018</td>
<td>10.02</td>
<td>0.07</td>
<td>2</td>
</tr>
</tbody>
</table>
### Cylinder 2 – Before shipping to the BIPM (S357)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO2} / \mu$mol/mol</th>
<th>Expanded uncertainty $U(x_{NO2}) / \mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>5th April 2018</td>
<td>10.00</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>19th April 2018</td>
<td>10.04</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>3rd May 2018</td>
<td>10.01</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>16th May 2018</td>
<td>10.00</td>
<td>0.07</td>
<td>2</td>
</tr>
</tbody>
</table>

### Cylinder 1 – Post BIPM measurements (2448)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO2} / \mu$mol/mol</th>
<th>Expanded uncertainty $U(x_{NO2}) / \mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>8th May 2019</td>
<td>9.82</td>
<td>0.10</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Stability 6)*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* 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)

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

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.

<table>
<thead>
<tr>
<th>Identifier</th>
<th>Component</th>
<th>Preparation (k=1)</th>
<th>Validation (k=1)</th>
<th>Total (k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2448</td>
<td>NO₂</td>
<td>0.007</td>
<td>0.350</td>
<td>0.700</td>
</tr>
<tr>
<td>S357</td>
<td>NO₂</td>
<td>0.007</td>
<td>0.350</td>
<td>0.700</td>
</tr>
</tbody>
</table>

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\(^{11}\).

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 °C 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)

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
</table>

Cylinder 2 (S357)

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
</table>

\(^{11}\) 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.
Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 μmol/mol)

Result form CCQM-K74.2018-R

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

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
e-mail: 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

<table>
<thead>
<tr>
<th>Institute</th>
<th>Slovak Institute of Metrology, SMU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>Karloveska 63 SK-842 55 Bratislava Slovak Republic</td>
</tr>
<tr>
<td>Contact person</td>
<td>Dr. Miroslava Valkova; Dr. Viliam Stovcik</td>
</tr>
<tr>
<td>Telephone</td>
<td>+421 2 602 94211 Fax</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:valkova@smu.gov.sk">valkova@smu.gov.sk</a>; <a href="mailto:stovcik@smu.gov.sk">stovcik@smu.gov.sk</a></td>
</tr>
<tr>
<td>Serial number of cylinder received</td>
<td>Nr.1 : MY9742, Nr.2 : MY9728</td>
</tr>
<tr>
<td>Cylinder pressure as received</td>
<td>13 MPa, 13MPa</td>
</tr>
</tbody>
</table>
### A2. Results

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

**MY9742**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>4.1.2018</td>
<td>10.15</td>
<td>0.22</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>29.1.2018</td>
<td>10.18</td>
<td>0.21</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>27.2.2018</td>
<td>10.13</td>
<td>0.21</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>28.3.2018</td>
<td>10.11</td>
<td>0.21</td>
<td>2</td>
</tr>
</tbody>
</table>

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

**MY9728**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>4.1.2018</td>
<td>10.04</td>
<td>0.23</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>29.1.2018</td>
<td>10.05</td>
<td>0.23</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>27.2.2018</td>
<td>10.05</td>
<td>0.22</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>28.3.2018</td>
<td>10.06</td>
<td>0.22</td>
<td>2</td>
</tr>
</tbody>
</table>

**Cylinder 1 - Post BIPM measurements**
Cylinder 2- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 components were find - higher then 50 nmol/mol concentration (detection limit of the FT-IR instrument).

Uncertainty $u_{grav}$ included weighing and purity, $u_{anal-b least}$ is analytical uncertainty calculated by B-least, $u_{stab}$ is uncertainty of the stability of NO2 and $u_{conv}$ is uncertainty of the conversion to NO2 after adding of Oxygen. Cylinders used for intercomparison have Aculife IV passivation of inner surface.
A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis1.

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 measurement 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 measurement 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. After 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 NO2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Cylinder 1

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
</table>

Cylinder 2

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
</table>

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

Result form CCQM-K74.2018-R

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

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

<table>
<thead>
<tr>
<th>Institute</th>
<th>Slovak Institute of Metrology, SMU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>Karloveska 63 SK-842 55 Bratislava</td>
</tr>
<tr>
<td></td>
<td>Slovak Republic</td>
</tr>
<tr>
<td>Contact person</td>
<td>Dr. Miroslava Valkova; Dr. Viliam Stovcik</td>
</tr>
<tr>
<td>Telephone</td>
<td>+421 2 602 94211 Fax</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:valkova@smu.gov.sk">valkova@smu.gov.sk</a>;<a href="mailto:stovcik@smu.gov.sk">stovcik@smu.gov.sk</a></td>
</tr>
<tr>
<td>Serial number of cylinder received</td>
<td>Nr.1 : MY9742, Nr.2 : MY9728</td>
</tr>
<tr>
<td>Cylinder pressure as received</td>
<td>13 MPa, 13MPa</td>
</tr>
</tbody>
</table>

A2. Results
Cylinder 1 – Before shipping to the BIPM

**MY9742**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>4.1.2018</td>
<td>10.15</td>
<td>0.22</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>29.1.2018</td>
<td>10.18</td>
<td>0.21</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>27.2.2018</td>
<td>10.13</td>
<td>0.21</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>28.3.2018</td>
<td>10.11</td>
<td>0.21</td>
<td>2</td>
</tr>
</tbody>
</table>

Cylinder 2 – Before shipping to the BIPM

**MY9728**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>4.1.2018</td>
<td>10.04</td>
<td>0.23</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>29.1.2018</td>
<td>10.05</td>
<td>0.23</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>27.2.2018</td>
<td>10.05</td>
<td>0.22</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>28.3.2018</td>
<td>10.06</td>
<td>0.22</td>
<td>2</td>
</tr>
</tbody>
</table>
Cylinder 1- Post BIPM measurements

MY 9742

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction ( x_{\text{NO}_2} ) / ( \mu \text{mol/mol} )</th>
<th>Expanded uncertainty ( U( x_{\text{NO}_2} ) ) / ( \mu \text{mol/mol} )</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>9.4.2019</td>
<td>10.13</td>
<td>0.26</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>2.5.2019</td>
<td>10.14</td>
<td>0.23</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>5.6.2019</td>
<td>10.13</td>
<td>0.24</td>
<td>2</td>
</tr>
</tbody>
</table>

Cylinder 2- Post BIPM measurements

MY 9728

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction ( x_{\text{NO}_2} ) / ( \mu \text{mol/mol} )</th>
<th>Expanded uncertainty ( U( x_{\text{NO}_2} ) ) / ( \mu \text{mol/mol} )</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>9.4.2019</td>
<td>9.87</td>
<td>0.23</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>2.5.2019</td>
<td>9.88</td>
<td>0.23</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>5.6.2019</td>
<td>9.83</td>
<td>0.30</td>
<td>2</td>
</tr>
</tbody>
</table>
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 components were found - higher than 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

<table>
<thead>
<tr>
<th>Uncertainty source</th>
<th>Standard uncertainty/µmol/mol</th>
<th>Distribution</th>
<th>Sensitivity coefficient</th>
<th>Contribution to standard uncertainty/µmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>ugrav</td>
<td>0.011</td>
<td>Normal</td>
<td>1</td>
<td>0.011</td>
</tr>
<tr>
<td>uanal-b least</td>
<td>-</td>
<td>Standard</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>ustab</td>
<td>0.075</td>
<td>Normal</td>
<td>1</td>
<td>0.075</td>
</tr>
<tr>
<td>uconv</td>
<td>0.070</td>
<td>Rectangular</td>
<td>1</td>
<td>0.070</td>
</tr>
<tr>
<td>u</td>
<td></td>
<td></td>
<td></td>
<td>0.110</td>
</tr>
</tbody>
</table>

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 analysis1.

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 measuring cycles for calibration and measured gas samples. Goodness -of -fit for each measurement 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 measurement 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. After validation and stability measurements, pressure decrease to the 10 MPa in MY9742 and 11 MPa in MY9728 cylinder. Both cylinders contain Oxygen in less than 1000 µmol/mol concentration.

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**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Cylinder 2**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Before shipping to the BIPM

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

(10 $\mu$mol/mol)

Result form CCQM-K74.2018-R

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

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


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 $\mu$mol/mol.

Participation in this protocol is primarily intended to underpin laboratories’ CMC claims.
A1. General information

<table>
<thead>
<tr>
<th>Institute</th>
<th>UME</th>
</tr>
</thead>
</table>
| 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

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction (x_{NO2} / \mu\text{mol/mol})</th>
<th>Expanded uncertainty (U(x_{NO2}) / \mu\text{mol/mol})</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>25.12.2017</td>
<td>9.851</td>
<td>0.007</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>17.01.2018</td>
<td>9.913</td>
<td>0.100</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>21.02.2018</td>
<td>9.790</td>
<td>0.098</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>21.03.2018</td>
<td>9.819</td>
<td>0.099</td>
<td>2</td>
</tr>
</tbody>
</table>
### Cylinder 2: PSM499791 – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2} / \mu \text{mol/mol}$</th>
<th>Expanded uncertainty $U(x_{NO_2}) / \mu \text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>25.12.2017</td>
<td>10.025</td>
<td>0.007</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>17.01.2018</td>
<td>10.028</td>
<td>0.101</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>21.02.2018</td>
<td>10.123</td>
<td>0.102</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>21.03.2018</td>
<td>10.109</td>
<td>0.101</td>
<td>2</td>
</tr>
</tbody>
</table>

### Cylinder 1- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2} / \mu \text{mol/mol}$</th>
<th>Expanded uncertainty $U(x_{NO_2}) / \mu \text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Cylinder 2- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2} / \mu\text{mol/mol}$</th>
<th>Expanded uncertainty $U(x_{NO_2}) / \mu\text{mol/mol}$</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stability 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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\textsuperscript{12}.

The nitrogen dioxide (NO\textsubscript{2}) in nitrogen mixtures were analyzed with an analyzer, i.e., Thermo Fisher Scientific 42i Chemiluminescence NO-NO\textsubscript{2}-NO\textsubscript{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\textsubscript{2}-NO\textsubscript{x} analyzer at a constant flow using mass flow controller. Zero flushing was performed between each measurement. Measurement results are displayed in Figure 1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Measurements before sending the cylinders}
\end{figure}

\textbf{A5. Complementary information on the cylinder}
Mixtures were produced based on the reaction of NO with O\textsubscript{2} to NO\textsubscript{2}. They were prepared from the pure components of NO, N\textsubscript{2}, and O\textsubscript{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 \textmu mol/mol) NO in N\textsubscript{2} and 4 % O\textsubscript{2} in N\textsubscript{2}. Final NO in N\textsubscript{2} pre-mixture and 4 % O\textsubscript{2} in N\textsubscript{2} pre-mixture

\textsuperscript{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\textsubscript{2} for the final mixtures. By the reaction occurred between NO and O\textsubscript{2}, desired final mixtures (nitrogen dioxide in nitrogen) were obtained.

Cylinder pressures before shipment to the BIPM are given below.

<table>
<thead>
<tr>
<th>Cylinder Code</th>
<th>Pressure, bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSM499783</td>
<td>116</td>
</tr>
<tr>
<td>PSM499791</td>
<td>105</td>
</tr>
</tbody>
</table>

References:


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


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


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
A2. Results
Cylinder 1: PSM499783 – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction ( \frac{x_{NO_2}}{\mu \text{mol/mol}} )</th>
<th>Expanded uncertainty ( U(x_{NO_2}) / \mu \text{mol/mol} )</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>25.12.2017</td>
<td>9.851</td>
<td>0.007</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>17.01.2018</td>
<td>9.913</td>
<td>0.100</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>21.02.2018</td>
<td>9.790</td>
<td>0.098</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>21.03.2018</td>
<td>9.819</td>
<td>0.099</td>
<td>2</td>
</tr>
</tbody>
</table>
Cylinder 2: PSM499791 – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>25.12.2017</td>
<td>10.025</td>
<td>0.007</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>17.01.2018</td>
<td>10.028</td>
<td>0.101</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>21.02.2018</td>
<td>10.123</td>
<td>0.102</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>21.03.2018</td>
<td>10.109</td>
<td>0.101</td>
<td>2</td>
</tr>
</tbody>
</table>

Cylinder 1- PSM499783 – Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>28.05.2019</td>
<td>9.717</td>
<td>0.099</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>27.06.2019</td>
<td>9.748</td>
<td>0.098</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>25.07.2019</td>
<td>9.745</td>
<td>0.098</td>
<td>2</td>
</tr>
</tbody>
</table>
### Cylinder 2- PSM499791– Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO2} / \mu$mol/mol</th>
<th>Expanded uncertainty $U(x_{NO2}) / \mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>28.05.2019</td>
<td>10.003</td>
<td>0.102</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>27.06.2019</td>
<td>10.033</td>
<td>0.100</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>25.07.2019</td>
<td>10.024</td>
<td>0.100</td>
<td>2</td>
</tr>
</tbody>
</table>

### 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\(^{13}\).

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 of the cylinders](image)

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 N₂ and 4 % O₂ in N₂. Final NO in N₂ pre-mixture and 4 % O₂ in N₂ pre-mixture were used together with pure N₂ for the final mixtures. By the reaction occurred between NO and O₂, desired final mixtures (nitrogen dioxide in nitrogen) were obtained.

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

<table>
<thead>
<tr>
<th>Cylinder Code</th>
<th>Sending Pressure (bar)</th>
<th>Return Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSM499783</td>
<td>116</td>
<td>99</td>
</tr>
<tr>
<td>PSM499791</td>
<td>105</td>
<td>90</td>
</tr>
</tbody>
</table>

References:

Co-authors:
Tanıl TARHAN
Aylin BOZTEPE
Zeynep GÜLSOY

Figure 2. Preparation scheme for the mixtures
Before shipping to the BIPM

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

Result form CCQM-K74.2018-R


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


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

<table>
<thead>
<tr>
<th>Institute</th>
<th>D.I. Mendeleyev Institute for Metrology (VNIIM )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>19 Moskovsky pr., St. Petersburg, 190005, Russia</td>
</tr>
<tr>
<td>Contact person</td>
<td>Leonid Konopelko</td>
</tr>
<tr>
<td>Telephone</td>
<td>+7 812 315 11 45</td>
</tr>
<tr>
<td>Fax</td>
<td>+7 812 315 15 17</td>
</tr>
<tr>
<td>Email*</td>
<td><a href="mailto:fhi@b10.vniim.ru">fhi@b10.vniim.ru</a></td>
</tr>
<tr>
<td>Serial number of cylinder</td>
<td>APEX 614632 (V=10 L)</td>
</tr>
<tr>
<td></td>
<td>5603778 (V=5L)</td>
</tr>
<tr>
<td>Cylinder pressure as received</td>
<td></td>
</tr>
</tbody>
</table>
### Cylinder 1 (№ APEX 614632) – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation</td>
<td>15.03.18</td>
<td>9.979</td>
<td>0.007</td>
<td>2</td>
</tr>
<tr>
<td>Stability1 (Verification1)</td>
<td>20.03.18</td>
<td>9.89</td>
<td>0.14</td>
<td>2</td>
</tr>
<tr>
<td>Stability2 (Verification2)</td>
<td>04.04.18</td>
<td>9.95</td>
<td>0.14</td>
<td>2</td>
</tr>
<tr>
<td>Stability3 (Verification3)</td>
<td>18.04.18</td>
<td>9.89</td>
<td>0.14</td>
<td>2</td>
</tr>
<tr>
<td><strong>Assigned (best) value</strong></td>
<td>20.04.18</td>
<td><strong>9.87</strong></td>
<td>0.14</td>
<td>2</td>
</tr>
</tbody>
</table>

*Assigned (best) value – Gravimetric value taking into account the measured content of HNO₃*

### Cylinder 2 (№ 5603778) – Before shipping to the BIPM

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation</td>
<td>16.03.18</td>
<td>10.017</td>
<td>0.007</td>
<td>2</td>
</tr>
<tr>
<td>Stability1 (Verification1)</td>
<td>21.03.18</td>
<td>9.92</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>Stability2 (Verification2)</td>
<td>05.04.18</td>
<td>9.98</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>Stability3 (Verification3)</td>
<td>19.04.18</td>
<td>9.93</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td><strong>Assigned (best) value</strong></td>
<td>20.04.18</td>
<td><strong>9.97</strong></td>
<td>0.13</td>
<td>2</td>
</tr>
</tbody>
</table>
### Cylinder 1- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Cylinder 2- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Uncertainty Budget

Please provide a complete uncertainty budget.

**Uncertainty budget for NO\textsubscript{2} mole fraction for the cylinder № APEX 614632**

<table>
<thead>
<tr>
<th>Uncertainty source ( X_i )</th>
<th>Estimate ( x_i )</th>
<th>Evaluation type (A or B)</th>
<th>Distribution</th>
<th>Standard uncertainty ( u(x_i) )</th>
<th>Sensitivity coefficient ( c_i )</th>
<th>Contribution ( u(y) ) ( \mu \text{mol/mol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity of N\textsubscript{2}</td>
<td>999998.67 ( \mu \text{mol/mol} )</td>
<td>B</td>
<td>Rectangular</td>
<td>0.20 ( \mu \text{mol/mol} )</td>
<td>0.0000035</td>
<td>0.000007</td>
</tr>
<tr>
<td>Purity of O\textsubscript{2}</td>
<td>999997.72 ( \mu \text{mol/mol} )</td>
<td>B</td>
<td>Rectangular</td>
<td>0.05 ( \mu \text{mol/mol} )</td>
<td>2.2*10^{-9}</td>
<td>1.1*10^{-10}</td>
</tr>
<tr>
<td>Purity of NO\textsubscript{2}</td>
<td>997100 ( \mu \text{mol/mol} )</td>
<td>B</td>
<td>Rectangular</td>
<td>128 ( \mu \text{mol/mol} )</td>
<td>0.0000128</td>
<td>0.00164</td>
</tr>
<tr>
<td>Weighing 1 stage premixture (( \approx 1 % ))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>7.91559621 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.002001 g</td>
<td>-1.240222</td>
<td>-0.002481</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>478.1069511 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.009264 g</td>
<td>0.020533</td>
<td>0.000190</td>
</tr>
<tr>
<td>Weighing 2 stage premixture (240 ( \mu \text{mol/mol}^{-1} ))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>17.1116594 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.00225268 g</td>
<td>-0.568934</td>
<td>-0.001282</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>663.7317226 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.0121975 g</td>
<td>0.014272</td>
<td>0.000174</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>18.48796242 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.00230866 g</td>
<td>0.0141988</td>
<td>0.000033</td>
</tr>
<tr>
<td>Weighing final mixture</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>60.8340012 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.00224231 g</td>
<td>-0.157300</td>
<td>-0.000353</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>1413.545029 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.02466512 g</td>
<td>0.006770</td>
<td>0.000167</td>
</tr>
<tr>
<td>Measurement of nitric acid</td>
<td>0.108 ( \mu \text{mol/mol} )</td>
<td>A</td>
<td>Rectangular</td>
<td>0.021 ( \mu \text{mol/mol} )</td>
<td>1</td>
<td>0.021</td>
</tr>
<tr>
<td>Verification</td>
<td>9.871 ( \mu \text{mol/mol} )</td>
<td>A</td>
<td>Normal</td>
<td>0.031 ( \mu \text{mol/mol} )</td>
<td>1</td>
<td>0.031</td>
</tr>
<tr>
<td>Stability</td>
<td>9.871 ( \mu \text{mol/mol} )</td>
<td>A</td>
<td>Normal</td>
<td>0.058 ( \mu \text{mol/mol} )</td>
<td>1</td>
<td>0.058</td>
</tr>
<tr>
<td>Combined standard uncertainty</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.069</td>
</tr>
<tr>
<td>Expanded uncertainty k=2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.14</td>
</tr>
</tbody>
</table>
## Uncertainty budget for NO₂ mole fraction for the cylinder № 5603778

<table>
<thead>
<tr>
<th>Uncertainty source</th>
<th>Estimate $x_i$</th>
<th>Evaluation type (A or B)</th>
<th>Distribution</th>
<th>Standard uncertainty $u(x_i)$</th>
<th>Sensitivity coefficient $c_i$</th>
<th>Contribution $u_i(y)$ μmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity of N₂</td>
<td>999998.67 μmol/mol</td>
<td>B</td>
<td>Rectangular</td>
<td>0.20 μmol/mol</td>
<td>0.0000035</td>
<td>0.0000007</td>
</tr>
<tr>
<td>Purity of O₂</td>
<td>999997.72 μmol/mol</td>
<td>B</td>
<td>Rectangular</td>
<td>0.05 μmol/mol</td>
<td>2.2*10^-9</td>
<td>1.1*10^-10</td>
</tr>
<tr>
<td>Purity of NO₂</td>
<td>997100 μmol/mol</td>
<td>B</td>
<td>Rectangular</td>
<td>128 μmol/mol</td>
<td>0.0000128</td>
<td>0.00164</td>
</tr>
<tr>
<td>Weighing 1 stage premixture (≈1 %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>7.91559621 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.002001 g</td>
<td>-1.244906</td>
<td>-0.002491</td>
</tr>
<tr>
<td>N₂</td>
<td>478.1069511 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.009263 g</td>
<td>0.020612</td>
<td>0.000191</td>
</tr>
<tr>
<td>Weighing 2 stage premixture (240 μmol/mol⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 premixture</td>
<td>17.8380632 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.00225550 g</td>
<td>-0.547781</td>
<td>-0.001236</td>
</tr>
<tr>
<td>N₂</td>
<td>689.7729231 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.01320346 g</td>
<td>0.013788</td>
<td>0.000182</td>
</tr>
<tr>
<td>O₂</td>
<td>18.97975707 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.00232722 g</td>
<td>0.013718</td>
<td>0.000032</td>
</tr>
<tr>
<td>Weighing final mixture</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 premixture</td>
<td>31.4364260 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.00268348 g</td>
<td>-0.305541</td>
<td>-0.000820</td>
</tr>
<tr>
<td>N₂</td>
<td>730.1283266 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.01378776 g</td>
<td>0.013155</td>
<td>0.000181</td>
</tr>
<tr>
<td>Measurement of nitric acid</td>
<td>0.050 μmol/mol</td>
<td>A</td>
<td>Rectangular</td>
<td>0.010 μmol/mol</td>
<td>1</td>
<td>0.010</td>
</tr>
<tr>
<td>Verification</td>
<td>9.967 μmol/mol</td>
<td>A</td>
<td>Normal</td>
<td>0.031</td>
<td>1</td>
<td>0.031</td>
</tr>
<tr>
<td>Stability</td>
<td>9.967 μmol/mol</td>
<td>A</td>
<td>Normal</td>
<td>0.058</td>
<td>1</td>
<td>0.058</td>
</tr>
<tr>
<td>Combined standard uncertainty</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expanded uncertainty k=2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 \(\sim 0.8\) 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

\[
a = \frac{A}{C_{grav} \times K}
\]

(1)

where \(A\) – response of spectrometer, a.u;

\(C_{grav}\) – NO\(_2\) mole fraction in the gas mixture in accordance with gravimetric data, \(\mu\text{mol/mol}\);

\(K\) – coefficient correcting for the difference between the measurement and standard conditions

\[
K = \frac{P_m \times 293.15}{T_m \times 101.325}
\]

(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 $C'$

$$C' = C_{\text{grav}} - C_{\text{HNO3}}$$  

(3)

The response per unit of amount of substance fraction $a'$ taking into account detected nitric acid

$$a' = \frac{A}{C' \times K}$$  

(4)

For the stability measurement series value of nitrogen dioxide mole fraction $C_i$

$$C_{i(12)} = \frac{\overline{A}_{i,2(2)}}{a'_{2(1)}} / K_i$$  

(5)

where $\overline{A}_{i,2(2)}$ – 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;
\( \overline{d}_{21}^{(1)} \) – mean specific response for all measurement series for cylinder 2 or 1, respectively, taking into account correction for HNO₃ 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 NO₂/N₂ – level 1 %;

2-nd stage – 3 mixtures NO₂/(N₂+O₂) – level 240 μmol/mol;

3-nd stage – 5 target mixtures NO/(N₂+O₂) - 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:**

<table>
<thead>
<tr>
<th>Serial number of cylinder</th>
<th>APEX 614632 (V=10 L)</th>
<th>5603778 (V=5L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylinder pressure as sent to BIPM</td>
<td>80 bar</td>
<td>100 bar</td>
</tr>
</tbody>
</table>

**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)**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded Uncertainty/ nmol/mol</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
</table>
139
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 HNO3 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 abs₁₀.

Date: 16/07/2018

Authors: L.A. Konopelko, Y.A. Kustikov, A.V. Kolobova, V.S. Ballandovich, O.V. Efremova

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction /nmol/mol</th>
<th>Expanded Uncertainty nmol/mol</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.03 - 18.04.2018</td>
<td>HNO₃</td>
<td>108</td>
<td>36</td>
<td>2</td>
<td>FTIR</td>
</tr>
<tr>
<td>16.03 - 19.04.2018</td>
<td>HNO₃</td>
<td>50</td>
<td>17</td>
<td>2</td>
<td>FTIR</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Institute</th>
<th>D.I. Mendeleyev Institute for Metrology (VNIIM )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>19 Moskovsky pr., St. Petersburg, 190005, Russia</td>
</tr>
</tbody>
</table>

Contact person: Leonid Konopelko

<table>
<thead>
<tr>
<th>Telephone</th>
<th>+7 812 315 11 45</th>
<th>Fax</th>
<th>+7 812 315 15 17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Email*</td>
<td><a href="mailto:fhi@b10.vniim.ru">fhi@b10.vniim.ru</a></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation</td>
<td>15.03.18</td>
<td>9.979</td>
<td>0.007</td>
<td>2</td>
</tr>
<tr>
<td>Stability1 (Verification1)</td>
<td>20.03.18</td>
<td>9.89</td>
<td>0.14</td>
<td>2</td>
</tr>
<tr>
<td>Stability2 (Verification2)</td>
<td>04.04.18</td>
<td>9.95</td>
<td>0.14</td>
<td>2</td>
</tr>
<tr>
<td>Stability3 (Verification3)</td>
<td>18.04.18</td>
<td>9.89</td>
<td>0.14</td>
<td>2</td>
</tr>
<tr>
<td><strong>Assigned (best) value</strong>*</td>
<td>20.04.18</td>
<td><strong>9.87</strong></td>
<td>0.14</td>
<td>2</td>
</tr>
</tbody>
</table>

**Cylinder 2 (№ 5603778) – Before shipping to the BIPM**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation</td>
<td>16.03.18</td>
<td>10.017</td>
<td>0.007</td>
<td>2</td>
</tr>
<tr>
<td>Stability1 (Verification1)</td>
<td>21.03.18</td>
<td>9.92</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>Stability2 (Verification2)</td>
<td>05.04.18</td>
<td>9.98</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td>Stability3 (Verification3)</td>
<td>19.04.18</td>
<td>9.93</td>
<td>0.13</td>
<td>2</td>
</tr>
<tr>
<td><strong>Assigned (best) value</strong>*</td>
<td>20.04.18</td>
<td><strong>9.97</strong></td>
<td>0.13</td>
<td>2</td>
</tr>
</tbody>
</table>

*Assigned (best) value – Gravimetric value taking into account the measured content of HNO$_3$
<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$\chi_{NO_2}$ / $\mu$mol/mol</th>
<th>Expanded uncertainty $U(\chi_{NO_2})$ / $\mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>16.07.2019</td>
<td>9.81</td>
<td>0.15</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>28.08.2019</td>
<td>9.75</td>
<td>0.15</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>17.09.2019</td>
<td>9.74</td>
<td>0.15</td>
<td>2</td>
</tr>
</tbody>
</table>

Cylinder 2- Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>$\chi_{NO_2}$ / $\mu$mol/mol</th>
<th>Expanded uncertainty $U(\chi_{NO_2})$ / $\mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>16.07.2019</td>
<td>9.77</td>
<td>0.15</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>28.08.2019</td>
<td>9.76</td>
<td>0.15</td>
<td>2</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>17.09.2019</td>
<td>9.75</td>
<td>0.15</td>
<td>2</td>
</tr>
</tbody>
</table>
The procedure for stability 4, 5, 6 measurements was similar to that described in A4. Nitrogen dioxide mole fraction \( C_i \) (\( \mu \text{mol/mol} \)) for i measurement series was calculated in accordance with formula: \( C_i = \frac{\bar{A}_i}{\bar{a}'} / K_i \), where \( \bar{A}_i \) – 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; \( \bar{a}' \) – mean specific response for all measurement series before shipment to BIPM with correction for HNO3 content, a.u. / (\( \mu \text{mol/mol} \)).

<table>
<thead>
<tr>
<th>№</th>
<th>Uncertainty source</th>
<th>Type of evaluation</th>
<th>Standard uncertainty, ( \mu \text{mol/mol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Measurements of ( \bar{A}_i )</td>
<td>A</td>
<td>0,030</td>
</tr>
<tr>
<td>2</td>
<td>Estimate of ( K )</td>
<td>B</td>
<td>0,017</td>
</tr>
<tr>
<td>3</td>
<td>Measurements of ( \bar{a}' )</td>
<td>A</td>
<td>0,068</td>
</tr>
<tr>
<td></td>
<td>Combined standard uncertainty</td>
<td></td>
<td>0,076</td>
</tr>
<tr>
<td></td>
<td>Expanded uncertainty (k=2)</td>
<td></td>
<td>0,15</td>
</tr>
</tbody>
</table>
A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Uncertainty budget for NO₂ mole fraction for the cylinder № APEX 614632

<table>
<thead>
<tr>
<th>Uncertainty source</th>
<th>Estimate $x_i$</th>
<th>Evaluation type (A or B)</th>
<th>Distribution</th>
<th>Standard uncertainty $u(x_i)$</th>
<th>Sensitivity coefficient $c_i$</th>
<th>Contribution $u(y)$ μmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity of N₂</td>
<td>999998.67 μmol/mol</td>
<td>B</td>
<td>Rectangular</td>
<td>0.20 μmol/mol</td>
<td>0.0000035</td>
<td>0.0000007</td>
</tr>
<tr>
<td>Purity of O₂</td>
<td>999997.72 μmol/mol</td>
<td>B</td>
<td>Rectangular</td>
<td>0.05 μmol/mol</td>
<td>2.2*10^{-9}</td>
<td>1.1*10^{-10}</td>
</tr>
<tr>
<td>Purity of NO₂</td>
<td>997100 μmol/mol</td>
<td>B</td>
<td>Rectangular</td>
<td>128 μmol/mol</td>
<td>0.0000128</td>
<td>0.00164</td>
</tr>
<tr>
<td>Weighing 1 stage premixture (≈1 %)</td>
<td>NO₂  7.91559621 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.002001 g</td>
<td>-1.240222</td>
<td>-0.002481</td>
</tr>
<tr>
<td></td>
<td>N₂   478.1069511 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.009264 g</td>
<td>0.020533</td>
<td>0.000190</td>
</tr>
<tr>
<td>Weighing 2 stage premixture (240 μmol/mol⁻¹)</td>
<td>1 premixture</td>
<td>NO₂  17.1116594 g</td>
<td>A,B</td>
<td>0.00225268 g</td>
<td>-0.568934</td>
<td>-0.001282</td>
</tr>
<tr>
<td></td>
<td>N₂   663.7317226 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.0121975 g</td>
<td>0.014272</td>
<td>0.000174</td>
</tr>
<tr>
<td></td>
<td>O₂   18.48796242 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.00230866 g</td>
<td>0.0141988</td>
<td>0.000033</td>
</tr>
<tr>
<td>Weighing final mixture</td>
<td>2 premixture</td>
<td>NO₂  60.8340012 g</td>
<td>A,B</td>
<td>0.00224231 g</td>
<td>-0.157300</td>
<td>-0.000353</td>
</tr>
<tr>
<td></td>
<td>N₂   1413.545029 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.02466512 g</td>
<td>0.006770</td>
<td>0.000167</td>
</tr>
<tr>
<td>Measurement of nitric acid</td>
<td>0.108 μmol/mol</td>
<td>A</td>
<td>Rectangular</td>
<td>0.021 μmol/mol</td>
<td>1</td>
<td>0.021</td>
</tr>
<tr>
<td>Verification</td>
<td>9.871 μmol/mol</td>
<td>A</td>
<td>Normal</td>
<td>0.031 μmol/mol</td>
<td>1</td>
<td>0.031</td>
</tr>
<tr>
<td>Stability</td>
<td>9.871 μmol/mol</td>
<td>A</td>
<td>Normal</td>
<td>0.058 μmol/mol</td>
<td>1</td>
<td>0.058</td>
</tr>
<tr>
<td>Combined standard uncertainty</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.069</td>
</tr>
<tr>
<td>Expanded uncertainty k=2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.14</td>
</tr>
</tbody>
</table>
### Uncertainty budget for NO₂ mole fraction for the cylinder № 5603778

<table>
<thead>
<tr>
<th>Uncertainty source</th>
<th>Estimate $x_i$</th>
<th>Evaluation type (A or B)</th>
<th>Distribution</th>
<th>Standard uncertainty $u(x_i)$</th>
<th>Sensitivity coefficient $c_i$</th>
<th>Contribution $u(y)$ μmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity of N₂</td>
<td>999998.67 μmol/mol</td>
<td>B</td>
<td>Rectangular</td>
<td>0.20 μmol/mol</td>
<td>0.0000035</td>
<td>0.0000007</td>
</tr>
<tr>
<td>Purity of O₂</td>
<td>999997.2 μmol/mol</td>
<td>B</td>
<td>Rectangular</td>
<td>0.05 μmol/mol</td>
<td>2.2*10⁻⁹</td>
<td>1.1*10⁻¹⁰</td>
</tr>
<tr>
<td>Purity of NO₂</td>
<td>997100 μmol/mol</td>
<td>B</td>
<td>Rectangular</td>
<td>128 μmol/mol</td>
<td>0.0000128</td>
<td>0.00164</td>
</tr>
<tr>
<td>Weighing 1 stage premixture ($\sim 1%$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>7.91559621 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.002001 g</td>
<td>-1.244906</td>
<td>-0.002491</td>
</tr>
<tr>
<td>N₂</td>
<td>478.1069511 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.009263 g</td>
<td>0.020612</td>
<td>0.000191</td>
</tr>
<tr>
<td>Weighing 2 stage premixture (240 μmol/mol⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 premixture</td>
<td>17.8380632 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.00225550 g</td>
<td>-0.547781</td>
<td>-0.001236</td>
</tr>
<tr>
<td>N₂</td>
<td>689.7729231 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.01320346 g</td>
<td>0.013788</td>
<td>0.000182</td>
</tr>
<tr>
<td>O₂</td>
<td>18.97975707 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.00232722 g</td>
<td>0.013718</td>
<td>0.000032</td>
</tr>
<tr>
<td>Weighing final mixture</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 premixture</td>
<td>31.4364260 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.00268348 g</td>
<td>-0.305541</td>
<td>-0.000820</td>
</tr>
<tr>
<td>N₂</td>
<td>730.1283266 g</td>
<td>A,B</td>
<td>Normal</td>
<td>0.01378776 g</td>
<td>0.013155</td>
<td>0.000181</td>
</tr>
<tr>
<td>Measurement of nitric acid</td>
<td>0.050 μmol/mol</td>
<td>A</td>
<td>Rectangular</td>
<td>0.010 μmol/mol</td>
<td>1</td>
<td>0.010</td>
</tr>
<tr>
<td>Verification</td>
<td>9.967 μmol/mol</td>
<td>A</td>
<td>Normal</td>
<td>0.031</td>
<td>1</td>
<td>0.031</td>
</tr>
<tr>
<td>Stability</td>
<td>9.967 μmol/mol</td>
<td>A</td>
<td>Normal</td>
<td>0.058</td>
<td>1</td>
<td>0.058</td>
</tr>
</tbody>
</table>

**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

\[
a = \frac{A}{C_{grav} \times K}
\]

(1)

where \(A\) – response of spectrometer, a.u;

\(C_{grav}\) – NO\(_2\) mole fraction in the gas mixture in accordance with gravimetric data, \(\mu\text{mol/mol}\);

\(K\) – coefficient correcting for the difference between the measurement and standard conditions

\[
K = \frac{P_m \times 293.15}{T_m \times 101.325}
\]

(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 $s_a$ were calculated. The values of $s_a$, 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 months) on 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 $C'$

$$C' = C_{\text{grav}} - C_{\text{HNO}_3}$$

(3)

The response per unit of amount of substance fraction $a'$ taking into account detected nitric acid

$$a' = \frac{A}{C' \times K}$$

(4)

For the stability measurement series value of nitrogen dioxide mole fraction $C_i$

$$C_{i,1(2)} = \frac{\bar{A}_{i,1(2)} / K_i}{a'_i}$$

(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;

\[ \overline{a}_{2(i)}' \] – mean specific response for all measurement series for cylinder 2 or 1, respectively, taking into account correction for HNO₃ 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 NO₂/N₂ – level 1%;

2-nd stage – 3 mixtures NO₂/(N₂+O₂) – level 240 µmol/mol;

3-nd stage – 5 target mixtures NO/(N₂+O₂) – 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:

<table>
<thead>
<tr>
<th>Serial number of cylinder</th>
<th>Cylinder pressure as sent to BIPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>APEX 614632 (V=10 L)</td>
<td>80 bar</td>
</tr>
<tr>
<td>5603778 (V=5L)</td>
<td>100 bar</td>
</tr>
</tbody>
</table>

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)
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 HNO3 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 \(1.5 \times 10^{-4}\) 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


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


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

<table>
<thead>
<tr>
<th>Institute</th>
<th>VSL</th>
</tr>
</thead>
</table>
| Address   | Thijsseweg 11  
3029 JA Delft  
The Netherlands |
| Contact person | Iris de Krom |
| Telephone  | 0031 15 269 1754 |
| 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)**

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor $k = 2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>12-12-2017</td>
<td>10.005</td>
<td>0.0023</td>
<td></td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>5-1-2018</td>
<td>9.883</td>
<td>0.1</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>1-3-2018</td>
<td>9.851</td>
<td>0.1</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>28-3-2018</td>
<td>9.906</td>
<td>0.1</td>
<td>$k = 2$</td>
</tr>
</tbody>
</table>
### Cylinder 2 – Before shipping to the BIPM (VSL105806)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor $k = 2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>12-12-2017</td>
<td>10.001</td>
<td>0.0023</td>
<td></td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>5-1-2018</td>
<td>9.883</td>
<td>0.1</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>1-3-2018</td>
<td>9.851</td>
<td>0.1</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>28-3-2018</td>
<td>9.847</td>
<td>0.1</td>
<td>$k = 2$</td>
</tr>
</tbody>
</table>

### Cylinder 1 – Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Cylinder 2 – Post BIPM measurements

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 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.

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 NO₂, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Cylinder 1 (VSL105804)

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty / nmol/mol</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>17-1-2018</td>
<td>HNO₃</td>
<td>70</td>
<td>6</td>
<td>( k = 2 )</td>
<td>CRDS</td>
</tr>
<tr>
<td>28-2-2018</td>
<td>HNO₃</td>
<td>78</td>
<td>7</td>
<td>( k = 2 )</td>
<td>CRDS</td>
</tr>
<tr>
<td>29-3-2018</td>
<td>HNO₃</td>
<td>113</td>
<td>10</td>
<td>( k = 2 )</td>
<td>CRDS</td>
</tr>
</tbody>
</table>

Cylinder 2 (VSL105806)

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>17-1-2018</td>
<td>HNO₃</td>
<td>80</td>
<td>7</td>
<td>( k = 2 )</td>
<td>CRDS</td>
</tr>
<tr>
<td>28-2-2018</td>
<td>HNO₃</td>
<td>81</td>
<td>7</td>
<td>( k = 2 )</td>
<td>CRDS</td>
</tr>
<tr>
<td>29-3-2018</td>
<td>HNO₃</td>
<td>113</td>
<td>10</td>
<td>( k = 2 )</td>
<td>CRDS</td>
</tr>
</tbody>
</table>

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 (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

<table>
<thead>
<tr>
<th>Institute</th>
<th>VSL</th>
</tr>
</thead>
</table>
| Address   | Thijsseweg 11  
|           | 2629 JA Delft  
|           | The Netherlands |
| Contact person | Iris de Krom |
| Telephone  | 0031 15 269 1754  
| Fax       | 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)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction</th>
<th>Expanded uncertainty</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>12-12-2017</td>
<td>$x_{NOx} (grav)$ 10.005 $x_{NO2}$ 9.903</td>
<td>0.004 0.018</td>
<td>$k = 2$  $k = 2$</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>5-1-2018</td>
<td>9.875</td>
<td>0.14</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>1-3-2018</td>
<td>9.856</td>
<td>0.14</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>28-3-2018</td>
<td>9.903</td>
<td>0.14</td>
<td>$k = 2$</td>
</tr>
</tbody>
</table>
### Cylinder 2– Before shipping to the BIPM (VSL105806)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Preparation)</td>
<td>12-12-2017</td>
<td>$x_{NOx}(grav) 10.001$ $x_{NO2} 9.899$</td>
<td>0.004</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 1)</td>
<td>5-1-2018</td>
<td>9.875</td>
<td>0.14</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 2)</td>
<td>1-3-2018</td>
<td>9.846</td>
<td>0.14</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 3)</td>
<td>28-3-2018</td>
<td>9.844</td>
<td>0.14</td>
<td>$k = 2$</td>
</tr>
</tbody>
</table>

### Cylinder 1- Post BIPM measurements (VSL105804)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{NO2}$ / μmol/mol</th>
<th>Expanded uncertainty $U(x_{NO2})$ / μmol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>21-5-2019</td>
<td>9.785</td>
<td>0.14</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>25-6-2019</td>
<td>9.850</td>
<td>0.14</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>25-7-2019</td>
<td>9.834</td>
<td>0.14</td>
<td>$k = 2$</td>
</tr>
</tbody>
</table>
Cylinder 2- Post BIPM measurements (VSL105806)

<table>
<thead>
<tr>
<th>Description of measurement</th>
<th>Date of measurement</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / $\mu$mol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / $\mu$mol/mol</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Stability 4)</td>
<td>21-5-2019</td>
<td>9.775</td>
<td>0.14</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 5)</td>
<td>25-6-2019</td>
<td>9.800</td>
<td>0.14</td>
<td>$k = 2$</td>
</tr>
<tr>
<td>(Stability 6)</td>
<td>25-7-2019</td>
<td>9.754</td>
<td>0.14</td>
<td>$k = 2$</td>
</tr>
</tbody>
</table>

Proposal reference value

<table>
<thead>
<tr>
<th>Cylinder</th>
<th>Nitrogen dioxide mole fraction $x_{\text{NO}_2}$ / $\mu$mol/mol</th>
<th>Expanded uncertainty $U(x_{\text{NO}_2})$ / $\mu$mol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylinder 1 (VSL105804)</td>
<td>9.851</td>
<td>0.14</td>
</tr>
<tr>
<td>Cylinder 1 (VSL105806)</td>
<td>9.816</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The proposed reference value is determined from the average of the 6 stability measurements.

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

$x(\text{NO}_2) = x(\text{NO}_x) - x(\text{HNO}_3) - 2x(\text{N}_2\text{O}_4)$

<table>
<thead>
<tr>
<th>Measurand</th>
<th>Value</th>
<th>Distribution</th>
<th>Relative standard uncertainty (%)</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x(\text{NO}_x)$</td>
<td>10 $\mu$mol mol$^{-1}$</td>
<td>Normal</td>
<td>0.023</td>
<td>1</td>
</tr>
<tr>
<td>$x(\text{HNO}_3)$</td>
<td>0.14 $\mu$mol mol$^{-1}$</td>
<td>Normal</td>
<td>8.7</td>
<td>-1</td>
</tr>
<tr>
<td>$x(\text{N}_2\text{O}_4)$</td>
<td>0.001 $\mu$mol mol$^{-1}$</td>
<td>Normal</td>
<td>2.5</td>
<td>-2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Stability</td>
<td>Normal</td>
<td>0.4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Between cylinder</td>
<td>Normal</td>
<td>0.5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>effects</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Verification</td>
<td>Normal</td>
<td>0.25</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>x(NO₂)</td>
<td>10 µmol mol⁻¹</td>
<td>Normal</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

x(NO₄) represents the gravimetric amount fraction calculated according to ISO 6142-1:2015. The gravimetric amount fraction has been corrected for the HNO₃ amount fraction (x(HNO₃)), according to analysis, and the N₂O₄ amount fraction (x(N₂O₄)), 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 NOₓ (and the amount fraction NO₂). Between cylinder effects have been determined based on results of four gas mixtures containing approximately 10 µmol mol⁻¹ NO₂ in N₂.


A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis15.

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 NO₂ in N₂. 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 NO₂, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

**Cylinder 1 (VSL105804)**

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Mole fraction / nmol/mol</th>
<th>Expanded uncertainty / nmol/mol</th>
<th>Coverage factor</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>17-1-2018</td>
<td>HNO₃</td>
<td>70</td>
<td>12</td>
<td>$k = 2$</td>
<td>CRDS</td>
</tr>
<tr>
<td>28-2-2018</td>
<td>HNO₃</td>
<td>78</td>
<td>14</td>
<td>$k = 2$</td>
<td>CRDS</td>
</tr>
<tr>
<td>29-3-2018</td>
<td>HNO₃</td>
<td>113</td>
<td>20</td>
<td>$k = 2$</td>
<td>CRDS</td>
</tr>
<tr>
<td>31-5-2019</td>
<td>HNO₃</td>
<td>138</td>
<td>24</td>
<td>$k = 2$</td>
<td>CRDS</td>
</tr>
<tr>
<td>23-8-2019</td>
<td>HNO₃</td>
<td>141</td>
<td>25</td>
<td>$k = 2$</td>
<td>CRDS</td>
</tr>
<tr>
<td>28-8-2019</td>
<td>HNO₃</td>
<td>143</td>
<td>25</td>
<td>$k = 2$</td>
<td>CRDS</td>
</tr>
<tr>
<td>Date</td>
<td>Component</td>
<td>Mole fraction / nmol/mol</td>
<td>Expanded uncertainty</td>
<td>Coverage factor</td>
<td>Measurement technique</td>
</tr>
<tr>
<td>------------</td>
<td>-----------</td>
<td>--------------------------</td>
<td>----------------------</td>
<td>----------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>17-1-2018</td>
<td>HNO₃</td>
<td>80</td>
<td>14</td>
<td>$k = 2$</td>
<td>CRDS</td>
</tr>
<tr>
<td>28-2-2018</td>
<td>HNO₃</td>
<td>81</td>
<td>14</td>
<td>$k = 2$</td>
<td>CRDS</td>
</tr>
<tr>
<td>29-3-2018</td>
<td>HNO₃</td>
<td>113</td>
<td>20</td>
<td>$k = 2$</td>
<td>CRDS</td>
</tr>
<tr>
<td>31-5-2019</td>
<td>HNO₃</td>
<td>141</td>
<td>25</td>
<td>$k = 2$</td>
<td>CRDS</td>
</tr>
<tr>
<td>23-8-2019</td>
<td>HNO₃</td>
<td>151</td>
<td>26</td>
<td>$k = 2$</td>
<td>CRDS</td>
</tr>
<tr>
<td>28-8-2019</td>
<td>HNO₃</td>
<td>144</td>
<td>25</td>
<td>$k = 2$</td>
<td>CRDS</td>
</tr>
</tbody>
</table>