

Protocol for the Key Comparison BIPM.QM-K6, Nitrogen dioxide in nitrogen, 10 $\mu\text{mol/mol}$

Coordinating laboratory: Bureau International des Poids et Mesures

Contact: Edgar Flores, BIPM, Pavillon de Breteuil, F-92312 France

edgar.flores@bipm.org

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1 Purpose and scope

The Key Comparison BIPM.QM-K6 is aimed at underpinning the capabilities of the participants to value assign the amount fraction of nitrogen dioxide (NO₂) in nitrogen standards at a nominal amount fraction of 10 µmol/mol with a method ensuring traceability of the measurements to the SI and taking into account the stability of the gas standards submitted for the comparison. The standards to be sent by the participants are reference gas mixtures in high pressure cylinders, further described in section 5 of this protocol.

The comparison is run as a series of bilateral comparisons between each participant and the BIPM. The facility maintained by the BIPM provides the Key Comparison Reference Value (KCRV) in each case and quantifies NO₂ amount fractions in nitrogen samples via the dynamic nitrogen dioxide primary gas mixtures obtained from the BIPM Nitrogen Dioxide (NO₂) Primary Facility.

The BIPM facility's performance has been validated during the [CCQM-K74](#) and [CCQM-K74.2018](#) Key Comparisons. At the same time, these comparisons have demonstrated that reference gas mixtures in high pressure cylinders of NO₂ in nitrogen at nominal amount fractions of 10 µmol/mol can demonstrate decay in NO₂ values and increase in HNO₃ amount fractions as a function of time, with the rates of change dependant on cylinder treatments and preparation methods. It is the responsibility of the participant to account for any instability in the standards submitted for the comparison, with the requirement that the participant provides a value and uncertainty for the standard(s) that they submit that is valid at the time of measurement by the BIPM.

Participants may send one or two NO₂ in N₂ standards at the nominal amount fraction of 10 µmol mol⁻¹ for the bilateral comparison with the BIPM.

The participant must provide values and uncertainties that they consider to be valid at the time of measurement by the BIPM. Participants can choose to provide values and uncertainties derived from measurements at their institute before and after the measurement performed at the BIPM.

2 Participants

BIPM.QM-K6 is open to laboratories listed in Appendix A of the CIPM MRA, available on the BIPM website (<https://www.bipm.org/en/cipm-mra/participation>).

3 Measurement schedule and registration

Laboratories wishing to participate should register their interest using the registration form provided (BIPM.QM-K6-R1) and return this to the coordinator at least three months before the requested comparison date, and indicate if their submitted results will be derived from measurements before and after those undertaken by the BIPM. A date will then be agreed between the laboratory and the coordinator, which may differ from the proposal depending on the workload of the BIPM.

The minimum period for completion of measurements at the BIPM, after delivery of standards, is one month and not expected to be longer than three months. In the event of technical issues which would extend this duration, the coordinator will contact the

participant to agree on the way forward. The laboratory should take into account the time for the transport of cylinders to and from the BIPM based on its knowledge of dangerous goods' shipments between its country and France. More details regarding transport of cylinders are provided in section 6.

4 Measurand, quantities and units

The measurand is the amount fraction of nitrogen dioxide in nitrogen, with measurement results being expressed in mol/mol (or one of its multiples mmol/mol, $\mu\text{mol/mol}$ or nmol/mol).

5 Standards submitted by the participant

The mixtures are to be prepared and/or analysed by participants using their usual procedure, with the constraints detailed below:

5.1 Cylinder characteristics and volume of gas used

The nitrogen dioxide standards submitted for the BIPM.QM-K6 comparison shall be cylinders with a volume equal or greater than 5 L, with total pressure in the range 10 MPa to 15 MPa (100 bar to 150 bar) on arrival at the BIPM. Participants will be asked to provide this information to the BIPM upon registration. The BIPM measurements will use a maximum of 30 L of gas (at room temperature and pressure) and exceptionally 60 L of gas in case of a problem with one of the measurements runs on the standard.

Participants will also be requested to provide detailed information on the cylinder material and any passivation treatment applied, as these factors can significantly affect the stability, integrity, and long-term reliability of the nitrogen dioxide gas mixtures.

5.2 Nominal NO₂ amount fractions

The nominal NO₂ amount fraction shall be 10 $\mu\text{mol mol}^{-1}$, within an acceptable range of 9 $\mu\text{mol mol}^{-1}$ to 11 $\mu\text{mol mol}^{-1}$. Prior to the start of the comparison, the participant shall declare whether they intend to derive their reported value and uncertainty for their standard(s), at the time of measurement at the BIPM, from their measurements prior to and after measurement at the BIPM, or submit a value and uncertainty they consider to be valid during the duration of the comparison and at the time of measurement at the BIPM.

5.3 Analysis of mixtures by the participant

The participant shall make sure that its value assignment procedures and stability testing allow determination of the NO₂ amount fraction in the mixtures at the date of the analysis by the BIPM. Participants can choose to derive their value and uncertainty from two periods of analysis, one before shipment to the BIPM, and one upon return of the mixtures in the participant's laboratory. This case is described in the subsequent clauses.

5.3.1 Before shipment to the BIPM

The participant should measure the NO₂ amount fraction in their submitted standard(s) with a method that permits the decay profile of the NO₂ amount fraction over time to be

determined. The participant should record the dates of analysis and measured values and uncertainties and prepare them for inclusion in information sheet.

5.3.2 Upon return from the BIPM

The BIPM shall have measured the value of the participant's standard(s) using its reference method and record the date and time of measurements and transmit the dates and time to the participant.

The participant should measure the NO₂ amount fraction in their submitted standard(s) with a method that permits the decay profile of the NO₂ amount fraction over time to be followed. The participant should record the dates of analysis and measured values and uncertainties and report them in the information sheet.

The participant should determine the value and uncertainty of its standard(s) at the time of measurements at the BIPM based on its measurements prior to shipment, and where applicable, after return from the BIPM. The participant shall record the calculated value(s) and uncertainties in the result form, as well as details of calculations in the accompanying information sheet.

6 Transport of cylinders to and from the BIPM

Cylinders shall be shipped to the BIPM no later than one week before the comparison date. The participating laboratory shall cover the cost and organise transport of their cylinders to the BIPM (door to door delivery), and to ensure that proper arrangements are made for local customs formalities. There are three likely scenarios depending on the location of the participating laboratory:

- countries within the E.U.;
- countries outside the E.U. and where the ATA carnet system is recognised;
- countries outside the E.U. but where the ATA is not recognised.

Laboratories are invited to consult the BIPM administrative document ADM-DOU-T-02 – *Information for laboratories shipping equipment to the BIPM for comparisons* - for additional information regarding the steps to be taken in each of the three cases above.

Laboratories are invited to inform the BIPM of its transport and customs arrangements prior to the cylinders leaving their laboratory by completing and returning the BIPM administrative document ADM-DOU-F-02 – *Shipping instructions for comparisons*. Any additional cost associated with custom clearance process which may be applied in case no form has been received will be charged to the participant.

At the conclusion of the BIPM value assignment the participants are responsible for the arrangements and costs of shipping the cylinders from the BIPM back to their laboratories. Any cylinders still remaining at the BIPM three months after the conclusion of the measurements will be shipped by the BIPM back to the participants at the participants' expense. This will also be noted as deviation from the protocol, with potential impact on the comparisons results.

7 Comparison measurement procedure

7.1 Preparation of the BIPM comparison facility

The BIPM comparison facility is permanently monitored and will be prepared for a series of analyses before starting the measurement procedure, meaning that all necessary calibrations of the measuring instruments will have been performed within the appropriate period and that all quality controls will have been realised within one month prior to the measurements.

The BIPM makes use of quality control mixtures of NO₂ in nitrogen which are analysed with every new permeation device in its facility. In addition, these mixtures will be analysed in the weeks before and at the time of the comparison measurement to demonstrate the stability of the BIPM facility.

7.2 Preparation and connection of the cylinders

After receipt by the BIPM, the participant's cylinder(s) will be allowed to equilibrate at laboratory temperature for at least 24 hours. The cylinder(s) will then be rolled for at least 1 hour to ensure homogeneity of the mixture before being transferred to the permeation laboratory. The cylinder connector appropriate to the cylinder valve will be provided by the BIPM. A pressure reducer will be connected between the cylinder connector and the input tubing of the facility.

7.3 Analysis of mixtures

The facility samples 25 L of gas for each analysis.

The amount fraction of NO₂ in the mixtures will be measured using a Fourier Transformed InfraRed (FTIR) spectrometer and verified with a UV absorption (LIMAS) analyser, both calibrated during the analysis sequence with NO₂ in nitrogen mixtures generated by the BIPM facility, based on permeation of NO₂ in a known flow of nitrogen and continuous measurements of the mass loss of the permeation tube with a Magnetic Suspension Balance (MSB). A typical calibration sequence includes four dynamic mixtures, obtained by changing the flow rate of the nitrogen matrix.

It is known that small levels of HNO₃ can be present in mixtures of NO₂ in nitrogen, regardless of their production method. Therefore, the amount fraction of HNO₃ in the mixtures of the participant and in the dynamic mixtures generated by the BIPM facility will be measured using the FTIR calibrated first with synthetic spectra generated from the HITRAN database and corrected to ensure SI traceable values and uncertainties for these as determined and validated in the [CCQM-P172](#) comparison¹. The HNO₃ amount fractions will finally be used to correct the NO₂ amount fraction in dynamic mixtures generated for this comparison. The BIPM measured value will be verified with a second measurement in the course of one week.

The BIPM analysis date will be communicated to the participant.

¹ During the comparison CCQM-P172, to better characterize the bias between nitric acid amount fractions anchored to HITRAN and dynamic standards, thirty-two HNO₃ spectra measured on mixtures from the permeation facility were reprocessed. The amount fraction of HNO₃ determined by the FTIR-HITRAN method is then corrected to the Permeation Method Reference values by multiplying by the factor $b = 0.81$. The uncertainty on this value is the statistical uncertainty of the linear fit, $u(b) = 0.004$. For more details see the report of CCQM-K74.2018 (Flores et al.²).

7.4 BIPM calculation of NO₂ amount fractions

Calculations described in the report of CCQM-K74.2018 comparison have been automated using custom-developed software that post-processes the data acquired by the BIPM measurement system, which controls the dynamic standards generation system.

The BIPM software calculates the NO₂ amount fraction and its uncertainty from the permeation tube mass loss and nitrogen flow rate, assuming no impurities. Then it calculates the HNO₃ amount fractions in the calibration mixtures based on the value measured by FTIR, to correct the NO₂ amount fractions. This process is done for the four dynamic mixtures generated during a measurement sequence. The four values and their uncertainties are used to calibrate the FTIR responses, using a Generalized Least Squares (GLS) algorithm. Correlations are accounted for by inclusion a constant uncertainty component, previously estimated during tests performed with and without correlations.

7.5 Analysis of other compounds

Compounds other than NO₂ measured by FTIR in the participant's mixtures, including HNO₃, may be reported to the participant in the comparison report, if this information is found valuable for the understanding of the comparisons results.

8 Uncertainty budgets

8.1 Uncertainty budgets for the participants standards

Participants shall complete the information sheet for BIPM.QM-K6-R3 after return of their standard(s) to them and any subsequent measurements they perform. A full uncertainty budget shall be submitted to justify the uncertainty submitted, explaining how the uncertainties associated with the measurement results were obtained. It shall describe clearly the sources of uncertainty identified, their values, and how they were combined.

8.2 Uncertainty budget of the BIPM

The uncertainty associated with the value assignment by the BIPM facility was detailed in the CCQM-K74.2018 report by Flores et al. (2021), and has been incorporated into a BIPM post-processing software, which has been validated. The software is specifically designed for the evaluation of nitrogen dioxide (NO₂) standards in nitrogen, within an amount fraction range of 7 $\mu\text{mol mol}^{-1}$ to 13 $\mu\text{mol mol}^{-1}$. Each step described in section 7.4 includes an uncertainty determination to account for all sources, resulting in typical standard uncertainties between 0.03 $\mu\text{mol mol}^{-1}$ and 0.07 $\mu\text{mol mol}^{-1}$.

9 Key Comparison Reference Values (KCRVs)

For each standard of the participant, the KCRV is the NO₂ amount fraction measured by the BIPM, calculated as explained in 7.4, with its measurement uncertainty obtained in 8.2. The KCRVs will be calculated by the coordinator and reported in the result form of the comparison.

10 Degrees of equivalence

Each comparison will result in a degree of equivalence, for each standard, defined as:

$$D_i = x_{i,\text{lab}} - x_{i,\text{KCRV}} \quad (1)$$

Where $x_{i,\text{lab}}$ ($i = 1$ or 2) is the measurement results of the participants for the standard i (at the date of BIPM value assignment), and $x_{i,\text{KCRV}}$ is the KCRV for the same standard as defined in section 9. Its associated standard uncertainty is:

$$u(D_i) = \sqrt{u_{i,\text{lab}}^2 + u_{i,\text{KCRV}}^2} \quad (2)$$

where $u_{i,\text{lab}}$ and $u_{i,\text{KCRV}}$ are the measurement uncertainties of the participant and of the BIPM respectively for the standard i .

11 Support of calibration and measurement capabilities

BIPM.QM-K6 is a specialised comparison (Track C). 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 µmol mol⁻¹ to 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.

12 Reporting and publication of Results

Upon completion of the measurements with the BIPM facility, the coordinator informs the participant of the date at which measurements were performed at the BIPM.

Following this, and any subsequent measurements by the participant, the participant reports the values and uncertainties of their standards at the time of measurement at the BIPM using the result form BIPM.QM-K6-R2 (Excel workbook) and submits it to the coordinator, as well as the information sheet describing how the values and uncertainties were determined.

When the result form is complete, the coordinator analysis the data and verify the absence of anomalies. In case of suspicious results, the coordinator can contact the participant and suggest a verification of its results.

The coordinator is responsible for the preparation of the reports of the comparisons. The first draft, Draft A, can be completed once the results form has been submitted by the participant. The draft A report includes the calculation of the KCRVs and the degrees of equivalence. The participant can make editorial changes to the report and suggest more important changes to the description of its standards and measurements techniques if relevant.

The second draft, Draft B, is prepared by the coordinator and reviewed by the CCQM/GAWG following their agreed process.

After consideration of comments received from the CCQM/GAWG by the coordinator, the final report is prepared and the coordinator also communicates the results of the comparison to the BIPM KCDB.

In agreeing to participate in the comparison, the participant agrees for their result to be identified in the comparison's report. The participants are co-authors of the final report publication.

13 Bibliography

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