Protocol for the key comparison CCQM-K68.2019, Nitrous oxide in air, ambient levels

Coordinating laboratories: Bureau International des Poids et Mesures (BIPM) and
Korea Research Institute of Standards and Science (KRISS)

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Summary

The key comparison CCQM-K68.2019 is aimed at evaluating the level of comparability of laboratories' nitrous oxide in air primary reference mixtures at ambient mole fractions, in the range 325 nmol mol^{-1} to 350 nmol mol^{-1}.

The comparison measurements will take place at the BIPM. It will consist in the simultaneous comparison of a suite of 2*n* primary gas standards, two standards to be prepared by each of the *n* participating laboratories. Two independent analytical methods will be used by the BIPM to analyse the amount fraction of N_2O in air, namely Gas Chromatography with an Electron Capture Detector (GC−ECD) and Tuneable Infrared Laser Direct Absorption Spectroscopy (TILDAS).

An expression for the degree of equivalence will be developed by the BIPM. All calculations will be performed by the BIPM based on the comparison results and the N_2O mole fraction values and uncertainties submitted by the participants.

The Key Comparison Reference Values for a given gas standard will be equal to the predicted value from a calibration function calculated from all of the standards by a Generalised Least-Square regression, or from a self-consistent subset of the standards.

The key comparison CCQM-K68.2019 is considered to present an analytical challenge and therefore classified as Track C comparison in the CCQM nomenclature.

Contents

1 Purpose and scope

The CCQM-K68.2019 comparison is designed to evaluate the level of comparability of National Metrology Institutes (NMI) or Designated Institutes (DI) nitrous oxide (N_2O) in air reference mixtures at ambient mole fractions.

The range of N_2O mole fractions covered by the comparison is from 325 nmol mol^{-1} to 350 nmol mol^{-1}. N_2O is to be prepared in a matrix of dry air, with constraints imposed on the composition of this matrix (see section 3).

Preparation of N_2O in dry air at ambient mole fractions and in the matrix imposed by this protocol is considered to represent an analytical challenge. Therefore CCQM−K68.2019 is classified as a Track C comparison in the terminology of CCQM comparisons.

2 Measurand, quantities and Units

The measurand is the mole fraction of nitrous oxide in air, with measurement results being expressed in mol mol^{-1} (or one of its multiples mmol mol^{-1}, µmol mol^{-1} or nmol mol^{-1}).

3 Preparation of mixtures by participants

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

3.1 Nominal N_2O mole fractions

Each participant is required to provide two standards containing N_2O/air at two different mole fractions. The nominal ranges of the values will be provided by the coordinating laboratory to each participant upon registration to the comparison. A total of ten participants is anticipated following recent Gas Analysis Working Group meetings. Table 1 was setup in order to span the range of the comparison with 5 sub ranges of 5 nmol mol^{-1}. A total of 4 mixtures will be prepared in each sub−range, and each participant will prepare two mixtures in sub−ranges which are separated by more than 5 nmol mol^{-1}. The goal is to obtain measurements allowing the best fit of data to be recorded with the GC−ECD analyser, which is known to present a second order polynomial response. The repartition of participants was organised such as to reach most equal weights in the regression analysis.

This scheme may be adjusted after the exact number of cylinders will be known, keeping the same constraints.

Table 1 : repartition of participants nominal values in 5 sub−ranges of N_2O mole fractions. x_{min} and x_{max} are the minimum and maximum N_2O mole fractions of the sub−ranges.

Sub-range	x_{min} / (nmol/mol)	x_{max} / (nmol/mol)	Participant #			
1	325	330	Lab 1	Lab 6	Lab 4	Lab 9
2	330	335	Lab 2	Lab 7	Lab 5	Lab 10
3	335	340	Lab 3	Lab 8	Lab 1	Lab 6
4	340	345	Lab 4	Lab 9	Lab 2	Lab 7
5	345	350	Lab 5	Lab 10	Lab 3	Lab 8

3.2 Matrix composition

N_2O shall be present in a dry air matrix, which can be either *scrubbed real air* or *synthetic air* (blended from pure gases). The matrix shall contain the major constituents of air (nitrogen, oxygen, argon) and may contain the other two major greenhouse gases (carbon dioxide and methane) at ambient mole fractions. Limits of the mole fraction of the major constituents are provided in Table 2.

Table 2: Matrix composition limits

Species	'Ambient' level mole fraction	Unit	Min mole fraction	Unit	Max mole fraction	Unit
N_2	0.780876	mol/mol	0.7804	mol/mol	0.7814	mol/mol
O_2	0.2093335	mol/mol	0.2088	mol/mol	0.2098	mol/mol
Ar	0.0093332	mol/mol	0.0089	mol/mol	0.0097	mol/mol
CO_2	380	µmol/mol	0	µmol/mol	400	µmol/mol
CH_4	1900	nmol/mol	0	nmol/mol	2000	nmol/mol

3.3 Cylinders characteristics

Mixtures are to be prepared in cylinders with a volume equal or greater than 5 L, with total pressure in the range 100 bar to 150 bar, and fitted with a suitable cylinder valve which conforms to one of the standards DIN, BS, AFNOR, CGA or JIS. Participants will inform the BIPM of the exact valve standard they used at the moment of the cylinder preparation.

4 Verification of mixtures

Participants may perform a verification of their mixture before and after shipment, according to the following principles:

4.1 Before shipment

Typically, the verification of the mixtures will be performed soon after their preparation. Further investigations of the mixtures may be undertaken over the following months to check the stability of the mixtures. The timetable for CCQM-K68.2019 envisages that the mixtures may be prepared as early as March 2019 but not shipped to the BIPM until September 2019. The mixtures will be held at the BIPM for a maximum period of 4 months.

4.2 After shipment

After measurements at the BIPM and prior to the preparation of the Draft A the laboratories will have the opportunity to perform another verification of their standards. The final results shall then be submitted to the BIPM before 30 April 2020 for inclusion in Draft A report.

5 Transport of cylinders to and from the BIPM

Cylinders are to arrive at the BIPM no later than **30 September 2019**. It is the responsibility of the participating laboratory to organise transport of their two 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.

Please see the attached 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 attached BIPM administrative document ADM-DOU-F-12 – *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 comparison period 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 after **28 February 2020** will be shipped by the BIPM back to the participants at the participants' expense.

6 Comparison measurements procedure

6.1 Preparation of the comparison facility

On receipt by the BIPM, all cylinders will be allowed to equilibrate at laboratory temperature for at least 24 hours. All cylinders will then be rolled for at least 1 hour to ensure homogeneity of the mixture. The cylinder connector appropriate to the cylinder valve will be will be provided by the BIPM. If this connector requires a gasket, it will be of an appropriately inert material inert (typically PCTFE). The same model of pressure reducer will be connected to each cylinder connector. Each cylinder will be connected from the pressure reducer to one inlet of an automatic gas sampler.

Two different automatic gas samplers will be used, each of them connected to one of the two analysers of the comparison (GC−ECD and TILDAS). The pressure reducer of each cylinder will be flushed nine times with the mixture. The cylinder valve will then be closed leaving the high pressure side of the pressure reducer at the cylinder pressure and the low pressure side of the pressure reducer at ~300 kPa (abs). The cylinders will be left stand at least 24 hours, to allow conditioning of the pressure reducers.

Analysis of mixtures by GC−ECD and TILDAS will be performed separately with different measurement sequences as described below.

6.2 Analysis of mixtures

Immediately prior to an analysis, each cylinder valve will be opened again and the pressure reducer flushed a further three times. The suite of cylinders from participants will be analysed sequentially, together with one control cylinder (mixtures of N_2O in dry air at ambient level) to correct for drifts in the analyser, respecting the scheme *Control – Sample − Control*. A minimum of two additional cylinders owned by the BIPM will be added to the set to monitor the intermediate precision.

The final measurement sequences will be decided after reception of all cylinders. The sequences will be structured such that each standard will be analysed a minimum of five times.

Once all cylinders have been sampled, the cylinder valves will be closed and the pressure reducer and connection to the gas sampler left under pressure.

6.3 Regression analysis

For each analyser a regression function will be constructed where the *x*-axis data will be the N_2O mole fractions reported by participants and their respective standard uncertainties. The *y*-axis data will be the analyser response after correction for drifts and associated standard uncertainties. The regression analyses will be performed using the Generalised Least Squares approach described in ISO 6143:2001 *Gas analysis – Comparison methods for determining and checking the composition of gas mixtures*.

Measurement results obtained with the GC−ECD analyser are expected to be best fitted with a second order polynomial function. The repartition of nominal N_2O mole fractions in participant's mixtures as described in section 3.1 provides optimised conditions for this fit. Measurement results obtained with the TILDAS analyser are expected to be best fitted with a line.

7 Key comparison reference values

The Key Comparison Reference Values will be the values predicted after regression analysis by the ensemble of standards or a self-consistent subset in case of outliers.

The Degrees of Equivalence will be calculated by difference from the values reported by participants with their associated uncertainties and the Key Comparison Reference Values. Two DoEs will be calculated for each participant, one for each standard.

8 Measurement schedule

The comparison will be organised by the BIPM following the schedule displayed in the table below.

Due Date	Event
30 April 2019	Registration
30 September 2019	Deadline for arrival of cylinders at the BIPM
31 Dec. 2019	Measurements at BIPM completed
31 Jan. 2020	Deadline for Collection of standards by participants
30 Apr. 2020	NMI Second analysis (optional) and submission of result forms
15 July 2020	Draft A report distributed to participants

9 Reporting of Results

The BIPM is responsible for the preparation of the reports of the comparisons.

The first draft, Draft A, will be prepared as soon as the analyses of the mixtures are completed. It includes the results submitted by the participants, identified by name, as well a proposal for the reference values. The results will be presented at the GAWG meeting.

In more detail, the procedure is as follows:

- A laboratory must send its two standards to the BIPM before 30 September 2019, so that they can be analysed at the same time as the other mixtures. If the gas mixtures are not received in time, they may not be reanalysed, and if so, it may not be possible to include results for this gas mixture in the comparison report;
- if, on examination of the information submitted by a participant, the BIPM finds information that appears to be anomalous, the corresponding institutes are invited to check their results but without being informed of the magnitude or sign of the apparent anomaly. If no numerical error is found the submitted information stands and the complete set of results is sent to all participants.

  Note that once all participants have been informed of the results, individual values and uncertainties may be changed or removed, or the complete comparison abandoned, only with the agreement of all participants and on the basis of a clear corruption of a mixture during its transport or some other phenomenon that renders the comparison or part of it invalid.
- Draft A of the report is sent as soon as possible after completion of the comparison to all the participants for comment, with a reasonable deadline for replies.
- Approval of the results and the KCRV by the GAWG leads to Draft B. At this stage, the results are not considered confidential and can be used to support CMCs and can be used for presentations and publications, except for the key comparison reference value and the degrees of equivalence which must be considered confidential until they are approved by the Consultative Committee and published in the KCDB. The first initiative for publication is with the BIPM. Other participants may publish the

results with the agreement of the BIPM. The Draft B report becomes the final report once it has been presented as such to the CCQM.

10 How far the light shines statement

The key comparison CCQM-K68.2019 is a Track C comparison. The Comparison will underpin CMC claims for:

a) nitrous oxide in air for standards and calibrations services, matrix matched to real air, over the mole fraction range of 200 nmol mol^{-1} to 400 nmol mol^{-1}.

b) nitrous oxide in nitrogen for standards and calibrations services, over the mole fraction range of 200 nmol mol^{-1} to 400 nmol mol^{-1}.

Registration Form
Track C Comparison CCQM-K68.2019, Nitrous oxide in dry air, ambient levels (325–350 nmol mol^{-1})

- This form should be completed by laboratories wishing to participate in the key comparison CCQM-K168.2019.

- Comparison coordinator:
Dr Joële Viallon
Chemistry Section
Bureau International des Poids et Mesures
Pavillon de Breteuil
F-92312 SEVRES CEDEX
Tel: +33 1 45 07 62 70
Email: jviallon@bipm.org

- Please complete and return the form preferably by email **before 30 April 2019.** Note that further information on the comparison will be sent by email to the contact person(s) only.

Participant information	
Institute (acronym and full name)	
Address	
Contact person(s)	
Telephone	
Email(s)	

Standards information

Each participant is required to provide two standards at nominal N_2O mole fractions which will be communicated by the coordinating laboratory upon registration.

Please give below any relevant information on the two cylinders expected to be shipped, including their volume, pressure, and the type of cylinder valve.

Participant Report Form
CCQM–K683.2019, Nitrous oxide in dry air, ambient levels (325–350 nmol mol^{-1})

- This form should be completed by participants in the key comparison CCQM-K168.2019 in two steps: the first page only is to be submitted at the same time as standards are sent to the BIPM, and the complete form after the return of the standards in participant's laboratories and evaluation of participant's final results.

- Comparison coordinator: Dr Joële Viallon
Chemistry Department
Bureau International des Poids et Mesures
Pavillon de Breteuil
F-92312 SEVRES CEDEX
Tel: +33 1 45 07 62 70
Email: jviallon@bipm.org

Return of result form:

- Please complete and return the form by email to jviallon@bipm.org

Participant information (for the comparison report)

Author(s)	
Institute	
Address	

Information on standards sent to the BIPM

	Standard 1	**Standard 2**
Nominal N_2O mole fraction		
Date of preparation		
Serial number		
Pressure (before shipment)		
Volume		
Connection type		

Results of measurements

Please indicate below the final value and associated expanded uncertainty of the N_2O mole fraction in each of the two standards.

Nominal mole fraction / µmol mol^{-1}	N_2O mole fraction $x(N_2O)$ / µmol mol^{-1}	Expanded uncertainty $U(x(N_2O))$ / µmol mol^{-1}	Coverage factor

Uncertainty budget

Please provide below the uncertainty budget used to calculate the uncertainty associated with the measurement of the nitrogen monoxide mole fraction.

Measurement procedure

Please provide below a description of the measurements performed for the validation of values obtained from the preparation, indicating which analyser(s) were used.

Additional information

Please include in this section the following information:

- a purity table with uncertainties for the nominally pure parent gases;
- a brief outline of the dilution series undertaken to produce the final mixtures;
- a purity table for each of the final mixtures, including the uncertainties;
- a brief outline of the verification procedure applied to the final mixtures;
- a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.

INSTRUCTIONS FOR METROLOGY INSTITUTES SHIPPING EQUIPMENT TO THE BIPM FOR COMPARISONS

1 General Information

- Equipment shipped to the BIPM for comparisons is subject to Customs' formalities, which vary according to the country of origin.
- Before shipping any material to the BIPM, the metrology institute shall complete the relevant parts of the form **BIPM/ADM-DOU/F-12**, and return it duly signed to the BIPM (fax: **+33 1 45 07 70 99** or e-mail at **ldelloro@bipm.org**. The form should be received by the BIPM at least 2 weeks before shipment is planned.
- Parcels from countries other than the E.U. must be labelled as follows:

BIPM - REGLEMENTATION SPECIALE - NE PAS DEDOUANER D'OFFICE

and the metrology institute from which the equipment originates should give specific instructions to their carrier to contact the BIPM
[Contact: Administration, tel.: +33 1 45 07 70 29 fax: +33 1 45 07 70 99]
prior to clearing the instrument through Customs. The BIPM will then take the appropriate action to clear the equipment through French Customs.

- No Customs' operations are carried out on Saturdays or Sundays. The metrology institute should ensure that if their equipment is subject to Customs' formalities, it should arrive in France on a working day of the week preceding that planned for the comparison.
- Customs' operations for hand carried equipment may require processing by the BIPM. In this case, relevant costs will be charged to the metrology institute.

2 Customs' formalities

2.1 Equipment arriving from a country within the E.U.:

- There are no Customs' formalities. The metrology institute does not need to take further action.

2.2 Equipment arriving from a country outside the E.U.:

- There are Customs' formalities. In order for the equipment to pass through Customs, the metrology institute is required to undertake one of the following procedures:

i. ship the equipment with an ATA carnet. This carnet is available through the Chamber of Commerce and Industry (or equivalent within your country, provided your country

recognises this system) and is issued with one year validity. It simplifies the Customs' operations and avoids duties and taxes;

ii. ship the equipment by diplomatic bag to the relevant Embassy in Paris (although this has the advantage of by-passing all Customs' formalities, it is unlikely that this process is available to all metrology institutes);

iii. if neither of these procedures can be adopted, a temporary importation will be arranged by the forwarding agent of the BIPM (all sections of the form **BIPM/ADM-DOU/F-12** must then be completed) and the relevant costs will be charged to the metrology institute. For hand carried equipment this will include an appointment on arrival at the airport with the forwarding agent of the BIPM, on a working day..

3 Transport of equipment between Paris Airports and the BIPM

3.1 Equipment arriving from a country within the E.U.:

- For equipment originating from a metrology institute within the E.U., it is expected that the metrology institute will arrange a door-to-door delivery.
- In the case of air transport, it is expected that the metrology institute will arrange for their carrier to transport the equipment to and from Paris airports and the BIPM.

3.2 Equipment arriving from a country outside the E.U.:

- For those countries employing the ATA carnet system, it is expected that the metrology institute will arrange a door-to-door delivery. In the case of air transport, it is expected that the metrology institute will arrange for their carrier to transport the equipment to and from Paris airports and the BIPM. The relevant costs will be charged to the metrology institute.
- For hand carried equipment, the metrology institute will arrange its transport between Paris airports and the BIPM.
- Where a temporary importation has to be arranged, the BIPM via its forwarding agent will arrange and meet the transport of the equipment to and from Paris airports and the BIPM.

4 Insurance of equipment

- In all cases, organisation and payment of insurance for a visiting metrology institute's instrument remain the responsibility of the visiting metrology institute.

5 Return of equipment

- It is the responsibility of the metrology institute to make prior arrangements for the return of their equipment after the comparison. The BIPM should be informed of these arrangements using form **BIPM/ADM-DOU/F-12.**
- No shipment back to the metrology institute will be arranged by the BIPM in the absence of this form duly completed and signed.
- Part "4. Instructions for return" of the form BIPM/ADM-DOU/F-12 is not applicable for BIPM equipment.

Version number	Date of Issue/Review	Author	Modifications / comments
2.1	10-12-2013	LD	Updated contact names

1. SHIPPING INSTRUCTIONS FOR COMPARISONS

- Name of the metrology institute:
- Person to be contacted:
- Address:
- Tel.: • Fax: • e-mail:

2. ATA carnet: ☐ Diplomatic bag: ☐ Other case: ☐

3. SHIPPING INFORMATION

- Description of the equipment (copy of proforma invoice required):
- Value of the equipment: • Number of packages:
- Gross weight: • Net weight:
- N° AWB (when available): • Date AWB:
- Name of the carrier:
- Hand carried by air (if necessary): • flight number*: • Date:
  * A copy of the flight ticket and passport is required for travellers coming from non European countries
- Hand carried by other means of transportation (to specify): • Date:

4. INSTRUCTIONS FOR RETURN

- Insurance: ☐ Yes ☐ No
- Name of the carrier:
- Tel.: • Fax: • e-mail:
- Your client number with the carrier:

5. I agree to pay for all the costs related to Customs' formalities and transport of equipment.

Date **Name and title** **Signature**