Protocol for the key comparison CCQM-K137, Nitrogen Monoxide in nitrogen, at 30 µmol mol^{-1} and 70 µmol mol^{-1}

Coordinating laboratory: Bureau International des Poids et Mesures

Contact person: Joële Viallon, BIPM, Pavillon de Breteuil, F-92312 France
email: jviallon@bipm.org , Tel: +33 1 45 07 62 70, Fax: +33 1 45 07 20 21.

Summary

The key comparison CCQM-K137 is aimed at evaluating the level of comparability of laboratories' preparative capabilities for gravimetric nitrogen monoxide/nitrogen primary reference mixtures at mole fractions of 30 µmol mol^{-1} and 70 µmol mol^{-1}.

The comparison will be organised by 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 at the nominal values of 30 µmol mol^{-1} and 70 µmol mol^{-1}. Two independent analytical methods will be used by the BIPM to analyse the amount fraction of NO in nitrogen, UV spectrophotometry and chemiluminescence. Additionally the purity of all standards will be analysed by Fourier Transform Infrared Spectroscopy, in order to investigate any potential outliers.

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 gravimetric 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 line 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-K137 is a Track A comparison at the nominal mole fraction of 70 µmol mol^{-1}. Results of this comparison at this mole fraction can be used to assess the basic capabilities of NMIs active in gas analysis.

The Comparison will underpin CMC claims for nitrogen monoxide in nitrogen: Lowest mole fraction boundary (LB) equal to the smallest participant's reported expanded uncertainty (8 nmol/mol expected based on CCQM-P73 results) to the upper boundary (UB) of 500 mmol/mol.

At the nominal mole fraction of 30 µmol mol^{-1}, the key comparison CCQM-K137 is considered to present an analytical challenge and therefore considered as a Track B comparison.

Contents

1 Purpose

The CCQM-K137 comparison is a Track A comparisons designed to evaluate the level of comparability of National Metrology Institutes (NMI) or Designated Institutes (DI) preparative capabilities for nitrogen monoxide in nitrogen primary reference mixtures at two nominal mole fractions values 30 µmol mol^{-1} to 70 µmol mol^{-1}, and provide measurement results that can underpin claims over a much wider range.

2 Measurand, quantities and Units

The measurand is the mole fraction of nitrogen monoxide in nitrogen, 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

Each participant is required to provide two standards: one at the nominal mole fraction of 30 µmol mol^{-1}, the other at 70 µmol mol^{-1}. The final mole fraction of NO in each cylinder shall be within ± 1 µmol mol^{-1} of the nominal value.

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.

The mixtures are to be prepared and analysed by participants using their usual procedure.

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-K137 envisages that the mixtures may be prepared as early as July 2016 but not shipped to the BIPM until June 2017. 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 2018 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 01 July 2017. 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 31 January 2018 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 material inert to NO (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 a 30-inlet automatic gas sampler.

The sampler is connected to two analysers, a Thermo 42C chemiluminescence NO analyser and an ABB LIMAS UV11 ultraviolet spectrophotometry NO analyser. 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.

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 will be analysed sequentially, together with a zero control cylinder (pure nitrogen of quality 5.0 or

higher) and a span control cylinder (working standard with a nominal mole fraction of 50 µmol mol^{-1}).

The measurement sequence starts and finishes by zero and span control measurements and these two control measurements are performed every five analysis of standards. The duration of the measurement sequence will be defined after times series analysis of the two analysers' responses to the zero and span control cylinders, in order to minimise the measurement uncertainties while keeping each individual measurement time below 300 s. Each standard will be analysed a minimum of three 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 Purity analysis

The BIPM may subject certain mixtures to purity analysis by FTIR spectroscopy, to confirm participants' estimates of impurity levels of infrared active species.

6.4 Regression analysis

For each analyser a regression will be constructed where the *x*-axis data will be the NO mole fractions reported by participants and their respective standard uncertainties. The *y*-axis data will be the analyser response data (y_{CLD} for the Chemiluminescence analyser and y_{UV} for the UV absorption analyser) and their standard uncertainties. The regression analyses will be performed using the Generalised Least Squares approach described by ISO 6143:2001 *Gas analysis – Comparison methods for determining and checking the composition of gas mixtures*.

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
01 Oct. 2016	Registration
01 Jul. 2017	Shipment of standards to BIPM
30 Oct. 2017	Comparison measurements
31 Jan. 2018	Collection of standards by participants

30 Apr. 2018	Second analysis (optional) and submission of result forms
30 Jun. 2018	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 01 July 2017, 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 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-K137 is a Track A comparison at the nominal mole fraction of 70 µmol mol^{-1}. Results of this comparison at this mole fraction can be used to assess the basic capabilities of NMIs active in gas analysis. Participants successful in this comparison may use their result in the flexible scheme and underpin claims for all core mixtures listed in Table 1:

COMPONENTS AND MATRIX	AMOUNT-OF-SUBSTANCE FRACTION RANGE
CO, CO_2, O_2, CH_4, C_2H_6 or C_3H_8 in N_2 or air	10 µmol/mol – 500 mmol/mol
CO, CO_2, C_3H_8 and O_2 in N_2	10 µmol/mol – 500 mmol/mol
NO in N_2	50 µmol/mol – 500 mmol/mol
SO_2 in N_2 or air	50 µmol/mol – 500 mmol/mol

Table 1: Components and amount-of-substance fraction ranges to assess core competences

The Comparison will underpin CMC claims for nitrogen monoxide in nitrogen: Lowest mole fraction boundary (LB) equal to the smallest participant's reported expanded uncertainty (8 nmol/mol expected based on CCQM-P73 results) to the upper boundary (UB) of 500 mmol/mol.

At the nominal mole fraction of 30 µmol mol^{-1}, the key comparison CCQM-K137 is considered to present an analytical challenge and therefore considered as a Track B comparison.

Participant Submission Form
CCQM-K137, NO in N_2, (30 and 70) µmol mol^{-1}

- This form should be completed by participants in the key comparison CCQM-K137 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			
Institute			
Address			
Contact person			
Telephone		**Fax**	
Email			

Information on Standards sent to the BIPM		
	30 µmol mol^{-1}	**70 µmol mol^{-1}**
Date of preparation		
Serial number		
Pressure		
Volume		
Connection type		

Results of measurements

Please indicate below the value and associated expanded uncertainty of the NO mole fraction in each of the two standards.

Nominal mole fraction / µmol mol^{-1}	**NO mole fraction *x*(NO) / µmol mol^{-1}**	**Expanded uncertainty *U*(x(NO)) / µmol mol^{-1}**	**Coverage factor**
30			
70			

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.

Additional information

Please include in this section the following information:

- a purity table with uncertainties for the nominally pure NO parent gas;
- a purity table with uncertainties for the nominally pure N_2 gas;
- a brief outline of the dilution series undertaken to produce the final mixtures;
- a purity table for each of the final mixtures, including gravimetric 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**