Protocol for BIPM.QM-K1,
On-demand Key Comparison of
Ozone at ambient level

Coordinating laboratory: Bureau International des Poids et Mesures

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1. Introduction

The on-going key comparison BIPM.QM-K1 is aimed at evaluating the level of comparability of ozone reference standards that are maintained as national standards, or as primary standards within international networks for ambient ozone measurements.

This protocol applies to ozone standards based on the UV photometry principle. Other types of instruments can participate in the key comparison, but with a modified version of the protocol. Laboratories wishing to participate with such a standard should contact the comparison coordinator.

The level of comparability will be determined using the NIST Standard Reference Photometer (BIPM-SRP27) maintained by the BIPM Headquarter (here after simplified as BIPM only) as a common reference. Comparisons will be performed at the BIPM either directly with a visiting laboratory's national standard, or by means of the visiting laboratory's transfer standard. Instruments (national or transfer standards) participating in comparisons at the BIPM can be either sent or brought by a person from the participating laboratory.

This document contains protocols for both these situations.

Laboratories that send or bring their national ozone standard to the BIPM should follow Protocol A.

Laboratories that send or bring a transfer standard to the BIPM should follow Protocol B.

The ozone amount fraction range covered by the comparisons starts at the limit of quantification of the common reference, 2 nmol mol^{-1}, and ends by convention at 500 nmol mol^{-1}.

An expression for the degree of equivalence between each national standard and the common reference BIPM-SRP27 will be calculated by the BIPM from the comparison results and measurement uncertainties submitted by participating laboratories.

2. Participants

BIPM.QM-K1 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

Laboratories wishing to participate should register their interest using the registration form provided (BIPM.QM-K1-R4) and return this to the BIPM at least three months before the requested comparison date. 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.

4. Measurand, quantities and units

The measurand is the amount fraction of ozone in dry 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}). The numerical value of the amount fraction of ozone in air expressed in this unit, is equivalent to the numerical value of the volume fraction expressed as ppb (parts per billion, 1 billion = 10^9) or ppbv, which may be encountered but not recommended.

1.1 Absorption cross-section for ozone

Ozone standards based on the UV photometry principle make use of the ozone absorption cross section at 253.7 nm, to calculate the measured ozone amount fraction. Starting on 1st January 2025, this quantity is expected to take the consensus value named CCQM.O3.2019 recommended by the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) [1]. The value of CCQM.O3.2019 is 1.1329(35) × 10^{-17} cm^2 molecule^{-1}. This value is also recommended in the ISO Standard 13964:1998/Amd 1:2024.

Participants in BIPM.QM-K1 may still be using the previous recommended value of 1.147×10^{-17} cm^2 reported by Hearn in 1961 and included in the previous version of the ISO Standard 13964:1998. Using a different value than CCQM.O3.2019 will result in a noticeable difference in the agreement between the participant and the BIPM.

In the comparison of two UV photometers using the same value of the absorption cross-section, its uncertainty can be set to zero. However, in the comparison of different methods, or of UV photometers with different values, or when considering the complete uncertainty budget of the method, the uncertainty of the absorption cross-section should be included.

5. Terms and definitions

- x_{nom}: nominal ozone amount fraction in dry air furnished by the ozone generator
- $x_{A,i}$: ith measurement of the nominal value x_{nom} by the photometer A.
- $\bar{x}_A$: the mean of N measurements of the nominal value x_{nom} measured by the photometer A : $\bar{x}_A = \frac{1}{N}\sum_{i=1}^{N} x_{A,i}$

[1] Recommendation 1 (2020): On the recommended value of the ozone absorption cross section per molecule at 253.65 nm (air) for applications including the measurement of atmospheric ozone amount fractions.

- s_A : standard deviation of N measurements of the nominal value x_{nom} measured by the photometer A : $s_A^2 = \frac{1}{N-1}\sum_{i=1}^{N}(x_{A,i} - \bar{x}_A)^2$
- The result of the linear regression fit performed between two sets of data measured by the photometers A and B during a comparison is written: $x_A = a_{A,B}x_B + b_{A,B}$. With this notation, the photometer A is compared versus the photometer B. $a_{A,B}$ is dimensionless and $b_{A,B}$ is expressed in units of nmol mol^{-1}.

6. Linking an RMO comparison to BIPM.QM-K1

A laboratory can compare its ozone national standard to the common reference BIPM–SRP27 via a comparison with the ozone national standard of another laboratory in the same Regional Metrology Organisation. The protocol to apply is similar to the protocol B of this key comparison, the transfer standard being the national standard of the so-called "linking laboratory". The comparison between the national standards of the candidate laboratory and the linking laboratory can take place in either of the two laboratories.

As the linking laboratory's national standard plays the role of a transfer standard, its stability should be assessed. Following the protocol B, its comparison with the candidate laboratory standard should be repeated in a reasonable time interval. Furthermore, the linking laboratory should ensure that the results of its comparison relative to the reference standard performed at the BIPM are still valid when undertaking comparison with another laboratory.

The comparison information and results form BIPM.QM-K1-R3, available on the BIPM web page, shall be completed by the linking laboratory and sent to the BIPM after completion of the comparison. The excel file created should be named BIPM.QM-K1-R3-LAB-YY.xls (LAB stands for the candidate laboratory acronym, YY stands for the year on two digits). The results of the comparison between the candidate laboratory and the BIPM will be calculated by the BIPM.

BIPM.QM-K1 Protocol A

For laboratories that send or bring their national standard to the BIPM

1. Transport of instruments to and from the BIPM

It is the responsibility of the participating laboratory to organise transport of their instrument(s) to and from the BIPM, 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 comparison period the participants are responsible for the arrangements and costs of shipping the instrument(s) from the BIPM back to their laboratories. Any instrument(s) still remaining at the BIPM 4 months after the comparison will be shipped by the BIPM back to the participants' expense.

2. Handling of instruments sent to the BIPM

Instruments that are sent to the BIPM and that will be handled only by the BIPM staff during the comparison should be accompanied with a list of instructions. They should include unpacking instructions, any tests to be carried out before measurements, the conditions of use of the instruments during measurements, and any other relevant information.

3. Comparison description

A direct comparison will be performed at the BIPM between BIPM-SRP27 and the national ozone reference standard of the visiting laboratory over 12 amount fractions of ozone in dry air in the range (0 to 500) nmol mol^{-1}. Where possible, BIPM-SRP28 will also be included in the comparison to ensure the stability of BIPM-SRP27.

The BIPM will provide the source of zero air for the comparison. The BIPM will utilise its ozone generator for the comparisons, unless the visiting laboratory's instrument cannot operate in this mode, in which case the visiting laboratory's generator will be used. Data will be acquired using the SRP control programme unless the communication between this programme and the participating laboratory's standard is not possible.

A copy of the comparison information and results form BIPM.QM-K1-R1, available on the BIPM website, shall be completed and verified by the participating laboratory and the BIPM staff. The form is an excel workbook protected with a password (O3K1). The copy should be renamed BIPM.QM-K1-R1-LAB-YY.xls (LAB stands for the laboratory acronym, YY stands for the year).

4. Pre-comparison requirements

Stabilisation of instruments
Prior to the comparison, all the instruments that will be used for the comparison shall be switched on and allowed to stabilise for at least eight hours.

Test and adjustment of the instrument measurement system
The instruments measurement system can be tested after the initial warm up period, following their usual operating procedures. If any adjustments are required, they will be noted.

Source of purified air
One common source of pure air will be used to provide the flows of reference air and ozone. This air will be furnished by the BIPM. It is ambient air compressed with an oil-free compressor, dried and scrubbed with a commercial purification system so that the amount fraction of ozone, hydrocarbons, and nitrogen oxides remaining in the air is below detectable limits. The relative humidity of the reference air is monitored and the amount fraction of water in air typically found to be less than 3 µmol/mol. The maximum available flow rate is 25 L/min.

Ozone generator
One common ozone generator will be used to generate the ozone in dry air flow to be measured by all the instruments included in the comparison. The ozone generator utilised in the comparison will be capable of producing stable ozone amount fractions over the range (0 to 500) nmol mol^{-1}, at a minimum flow rate equal to 2 L/min plus the flow rate needed by the guest instrument plus an excess flow rate of 1 L/min. When possible, ozone will be generated with one of the BIPM ozone generators.

Gas manifold
When possible, the BIPM external dual manifold system will be used to redistribute the zero air and ozone/air to instruments. If the guest instrument possesses its own manifold, the participating laboratory shall decide whether or not it wishes to make use of it.

Flow rates
Gas flows shall be provided to photometers with a minimum excess of 1 L/min compared to the combined requirements of the photometers included in the comparison.

5. Comparison procedure

The following procedure will be followed for the comparison.

Conditioning of the photometers and the pneumatic lines before the comparison
At the beginning of the comparison, the photometers as well as interconnecting pneumatic lines will be conditioned with a nominal value of the ozone amount fraction greater than 500 nmol mol^{-1} for at least 2 hours. This step can be combined with the instrument stabilisation period.

Ozone amount fraction nominal values
12 nominal values will be measured by the photometers. These values include the measurement of 0 nmol mol^{-1} (no ozone produced) at the beginning and the end of the comparison. The 12 nominal values will be produced in the following sequence: (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270, and 0) nmol mol^{-1}. Due to the operational characteristics of ozone generators, it is expected that the actual delivered values will be within $\pm$ 15 nmol mol^{-1} of those nominal values.

Ozone generator stability
For each nominal value of the ozone amount fraction x_{nom} furnished by the ozone generator, it is important to ensure that the photometers are measuring a stable value. To this end, the standard deviation s_{SRP27} on the set of 10 consecutive measurements $x_{SRP27,i}$ recorded by BIPM-SRP27 will be calculated. This set is considered as valid if s_{SRP27} is less than 1 nmol mol^{-1}. If s_{SRP27} is found greater than 1 nmol mol^{-1}, another set of 10 consecutive measurements of the same nominal values is taken. Repeated instances of unacceptable values of s_{SRP27} indicate that there are instabilities in the ozone generator or in the BIPM-SRP27 measurement system. The reasons for these will be examined and documented prior to continuing the comparison.

Recorded values
For each nominal value x_{nom}, the value recorded for each photometer A is the mean ($\overline{x}_A$) of 10 consecutive single measurements $x_{A,i}$ taken in a stable regime as defined above.

Comparison repeatability
The comparison procedure may be repeated to evaluate its repeatability. The participant and the BIPM will commonly decide when both instruments are stable enough to start recording a set of measurement results to be considered as the official comparison results. These measurement results will be recorded in the form BIPM.QM-K1-R1-LAB-YY.xls. In between the comparison repeats, ozone at a nominal value greater than

500 nmol mol^{-1} should be flowed through the instruments, or the comparison procedure should be repeated continuously. Details of this choice will be reported in the same form. The all process should not take more than three days.

6. Uncertainty budgets

National standard
The standard uncertainties associated with the twelve values measured by the national standard (NS) will be evaluated by the participating laboratory. The laboratory will provide an uncertainty budget used to calculate the values in the report form BIPM.QM-K1-R1-LAB-YY.xls. This budget should preferably be presented in a table, showing the different uncertainty components with their type as described in the GUM.

Reference standard
The uncertainties associated with the twelve values $\bar{x}_{\mathrm{SRP27}}$ (and eventually $\bar{x}_{\mathrm{SRP28}}$) measured by the BIPM-SRP27 (and BIPM-SRP28 if appropriate) will be evaluated by the BIPM. Details of the uncertainty budget for the BIPM-SRPs can be found at the end of this document.

Absorption cross section value and uncertainty
As introduced in section 1.1, ozone photometers measure ozone amount fractions by the absorption of radiation by ozone at 253.7 nm. Consequently, the uncertainty on the absorption cross section of ozone at 253.7 nm can be conventionally set to zero if all the instruments use the same value for this parameter but must be included if different values are used. The value and uncertainty of the ozone absorption cross-section used by the participant shall appear clearly in the result form and the uncertainty budgets.

7. Linear regression fits

The sets of the twelve data points ($\bar{x}_{\mathrm{SRP27}}$ and $\bar{x}_{\mathrm{NS}}$) will be fitted using the generalised least square program OzonE, taking into account the associated uncertainties $u(\bar{x}_{\mathrm{SRP27}})$, $u(\bar{x}_{\mathrm{NS}})$ as well as the covariance terms $u(x_{\mathrm{SRP27,i}}, x_{\mathrm{SRP27,j}})$ in between two different ozone amount fraction measurements performed by BIPM-SRP27. This will be performed by the BIPM. The parameters $a_{\mathrm{NS,SRP27}}$ and $b_{\mathrm{NS,SRP27}}$ of the linear relationship between x_{NS} and x_{SRP27} ($x_{\mathrm{NS}} = a_{\mathrm{NS,SRP27}}\, x_{\mathrm{SRP27}} + b_{\mathrm{NS,SRP27}}$) will be calculated as well as their uncertainties.

Covariance terms for the participant standard, $u(x_{\mathrm{NS,i}}, x_{\mathrm{NS,j}})$ can be taken into account if they are written as a constant times the product of the two ozone amount fractions:

$$u\left(x_{\mathrm{NS},i}, x_{\mathrm{NS},j}\right) = \alpha x_{\mathrm{NS},i} x_{\mathrm{NS},j} \qquad [1]$$

Where α is a constant to be entered into the program OzonE. The participant is free to provide a value for this constant. If no value is given, the covariance terms will be assumed to be zero. As an example, covariance terms in between two measurement results of the BIPM SRPs are described in annex.

8. Degrees of equivalence

Two degrees of equivalence will be evaluated at two ozone nominal values: 80 nmol mol^{-1} and 420 nmol mol^{-1}.

The degree of equivalence of the national standard with the reference standard SRP27, at the nominal value x_{nom} is the following:

$$\boldsymbol{D = x_{NS} - x_{SRP27}} \quad [2]$$

Where x_{NS} and x_{SRP27} are the measurement results of the national standard ($\bar{x}_{NS}$) and of SRP27 ($\bar{x}_{SRP27}$) at the nominal value x_{nom}.

Its associated standard uncertainty is:

$$u(\boldsymbol{D}) = \sqrt{\boldsymbol{u^2(x_{NS}) + u^2(x_{SRP27})}} \quad [3]$$

9. Data acquisition and backup

The SRP control software automatically generates one excel file per comparison run. This file contains all the data recorded during the run. A copy of all recorded files can be provided on demand to the participant, but they are not considered as the results of the comparison. Names and location of the original files kept at the BIPM will be noted in the form BIPM.QM-K1-R1.

10. Reporting of results

The measurement results together with the uncertainties and any additional information required will be reported in the excel form BIPM.QM-K1-R1-LAB-YY.xls. A PDF version of this file will be created and stored at the BIPM. If, on examination of the results, one or more appear to be anomalous, the institute is invited to check their results for numerical errors but without being informed as to the magnitude or sign of the apparent anomaly. If no numerical error is found, the final results are then derived and communicated to the participant. Note that once the participant has been informed of the results, individual values and uncertainties may be changed or removed only with the agreement of the Consultative Committee, and on the basis of a failure of a standard or some other phenomenon.

The BIPM is responsible for the preparation of a report of the comparison. A report will be produced for each bilateral comparison. There are a number of stages to the publication of the results before they can be accepted for degrees of equivalence in the key comparison database. Two formal stages are referred to here as Drafts A and B.

The Draft A report of a bilateral comparison is prepared as soon as the results have been agreed by the participant. It includes the results transmitted by the participant, identified by name, full details of the comparison, the uncertainty budgets, the proposals for degrees of equivalence with the key comparison reference value. It is sent in confidence

to the participant for discussion and approbation. The report is then termed a Draft B and is sent for review to the reviewers designated by the Gas Analysis Working Group (GAWG) of the CCQM. The Draft B is amended according to comments received. Once the report has been approved by the reviewers it is considered to be the final report of the comparison and is published in *Metrologia Technical Supplement*, and the results published in the key comparison database.

In the procedure for producing Drafts A and B, the following points should be noted:

- A result from a participant is not considered complete without an associated uncertainty and will not be published in Draft A unless it is accompanied by an uncertainty supported by a complete uncertainty budget.
- An institute that considers its result unrepresentative of its standards may request a subsequent separate comparison with the BIPM. This should take place as soon as possible after the completion of the comparison. The subsequent comparison is considered as a new and distinct comparison, the results of which will supersede those of the earlier comparison.

BIPM.QM-K1 Protocol B

For laboratories that send or bring a transfer standard to the BIPM

1. Transport of instruments to and from the BIPM

It is the responsibility of the participating laboratory to organise transport of their instrument(s) to and from the BIPM, 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 comparison period the participants are responsible for the arrangements and costs of shipping the instrument(s) from the BIPM back to their laboratories. Any instrument(s) still remaining at the BIPM 4 months after the comparison will be shipped by the BIPM back to the participants at the participants' expense.

2. Handling of instruments sent to the BIPM

Instruments that are sent to the BIPM and that will be handled only by the BIPM staff during the comparison should be accompanied with a list of instructions. They should include unpacking instructions, any tests to be carried out before measurements, the conditions of use of the instruments during measurements, and any other relevant information

3. Stability and characteristics of transfer standards

Laboratories employing a transfer standard should ensure that the standard has good short-term stability and stability during transport. Ozone reference transfer standards should fulfil the requirements described in section 6 of this protocol.

4. Comparison description

A series of comparisons will be performed utilising an ozone reference transfer standard in order to determine the degree of equivalence between the participating laboratory national standard (designated with NS) and the BIPM-SRP27. Comparisons shall be performed over 12 amount fractions of ozone in dry air in the range (0 to 500) nmol mol^{-1}. The comparisons will be in three parts:

1. National standard (NS) vs. Transfer standard (TS) comparison at the laboratory of the participating institute: within the six weeks prior to sending the transfer standard to the BIPM, a direct comparison between the transfer standard and the national standard will be performed in the laboratory of the participating institute. The corresponding section of the comparison information and results form BIPM.QM-K1-R2, attached to this protocol, shall be completed by the participating laboratory. The excel file created should be named BIPM.QM-K1-R2-LAB-YY.xls (LAB stand for the laboratory acronym, YY stand for the year of the comparison date on two digits) and sent to the BIPM.

2. Transfer standard (TS) vs. BIPM-SRP27 at the BIPM: comparison between the transfer standard (TS) and BIPM-SRP27 will be performed at the BIPM. The corresponding section of the form BIPM.QM-K1-R2-LAB-YY.xls shall be completed and verified by the participating laboratory and the BIPM staff.

3. National standard (NS) vs. Transfer standard (TS) comparison at the laboratory of the participating institute: within the six weeks following the comparison at the BIPM, a second comparison between the transfer standard (TS) and the national standard (NS) will be performed in the laboratory of the participating institute. The corresponding section of the form BIPM.QM-K1-R2-LAB-YY.xls, shall be completed by the participating laboratory and sent to the BIPM.

5. Comparison between the national standard and the transfer standard before travelling with the transfer standard

5.1. Pre-comparison requirements

Stabilisation of instruments
Prior to the comparison, all the instruments that will be used for the comparison shall be switched on and allowed to stabilise for at least 8 hours.

Test and adjustment of the instrument measurement system
The instruments measurement system can be tested after the initial warm up period, following their usual operating procedures. If any adjustments are required, they will be noted.

Source of purified air
One common source of pure air shall be used to provide the flows of reference air and ozone. The source of pure air shall be free of ozone, nitrogen oxides and any other interfering substance that can cause an undesired positive or negative response in the UV photometer.

Ozone generator
One common ozone generator will be used to generate the ozone to be measured by the national standard and the transfer standard. This ozone generator should be able to produce a maximum of 500 nmol mol^{-1} of ozone amount fractions in dry air at the flow rate needed for the comparison.

Flow rates
All the gas flows provided to the instruments (reference air and/or ozonized air) should have flow rates with a minimum excess of 1 L/min compared to what is needed by the national standard plus the transfer standard.

5.2. Comparison procedure

Conditioning of the photometers and the pneumatic lines before the comparison
At the beginning of the comparison, the photometers as well as interconnecting pneumatic lines will be conditioned with a nominal value of the ozone amount fraction greater than 500 nmol mol^{-1} for at least 2 hours. This step can be combined with the instruments stabilisation period.

Ozone amount fraction nominal values
12 nominal values will be measured by the photometers. These values include the measurement of 0 nmol mol^{-1} at the beginning and the end of the comparison. The 12 nominal values will be produced in the following sequence: (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270, 0) nmol mol^{-1}. Due to the operational characteristics of ozone generators, it is expected that the actual delivered values will be within $\pm$ 15 nmol mol^{-1} of those nominal values.

Ozone generator stability

For each nominal value of the ozone amount fraction x_{nom} furnished by the ozone generator, it is important to ensure that the photometers are measuring a stable value. To this end, each of the twelve points will be sampled for at least ten minutes by the two photometers. Following this, ten consecutive output values from each instrument will be recorded. The averages $\bar{x}_{NS}$ and $\bar{x}_{T}$ as well as the standard deviations s_{NS} and s_{TS} of the recorded values will be evaluated. The two values $\bar{x}_{NS}$ and $\bar{x}_{T}$ are considered as valid if the associated standard deviation s_{NS} and s_{TS} do not exceed 2 nmol mol^{-1} or 1.5 % of the average value (whichever is the largest). If any of the two values is not valid, the point will be taken again after five minutes of sampling at the same nominal value. Repeated instances of unacceptable values of s_{NS} or s_{TS} indicate that there are instabilities in the ozone generator or in the measurement systems. The reasons for these will be examined and documented prior to the comparison continuing.

Laboratories are free to use more restrictive conditions than those described above (see for example the conditions used with an SRP in protocol A). These conditions shall be noted in the comparison information form BIPM.QM-K1-R2-LAB-YY.xls.

Comparison repeatability

The comparison procedure may be repeated to evaluate its repeatability. The participant will then decide when both instruments are stable enough to start recording a set of measurement results to be considered as the official comparison results. Those measurement results will be recorded in the form BIPM.QM-K1-R2-LAB-YY.xls. In between the comparison repeats, ozone at a nominal value greater than 500 nmol mol^{-1} should be flowed inside the instruments, or the comparison procedure should be repeated continuously. Details of this choice will be reported in the same form. The all process should not take more than three days.

6. Comparison between the transfer standard and BIPM-SRP27 at the BIPM

6.1. Comparison description

A direct comparison will be made at the BIPM between BIPM-SRP27 and the transfer standard of the visiting laboratory over 12 amount fractions of ozone in dry air in the range (0 to 500) nmol mol^{-1}. Where possible, BIPM-SRP28 will also be included in the comparison to ensure the stability of BIPM-SRP27.

The BIPM will provide the source of zero air for the comparison. The BIPM will utilise its ozone generator for the comparisons, unless the visiting laboratory's instrument cannot operate in this mode, in which case the visiting laboratory's generator will be used. Data will be acquired using the SRP control programme 03 Conductor version 03D or higher unless the communication between this programme and the participating standard is not possible.

The comparison information form BIPM.QM-K1-R2, attached to this protocol, shall be completed and verified by the participating laboratory and the BIPM staff.

6.2. Pre-comparison requirements

Stabilisation of instruments
Prior to the comparison, all the instruments that will be used for the comparison shall be switched on and allowed to stabilise for at least eight hours.

Test and adjustment of the instrument measurement system
The instruments measurement system can be tested after the initial warm up period, following their usual operating procedures. If any adjustments are required, they will be noted.

Source of purified air
One common source of pure air will be used to provide the flows of reference air and ozone. This air will be furnished by the BIPM. It is ambient air compressed with an oil-free compressor, dried and scrubbed with a commercial purification system so that the amount fraction of ozone, hydrocarbons, and nitrogen oxides remaining in the air is below detectable limits. The relative humidity of the reference air is monitored and the amount fraction of water in air typically found to be less than 3 µmol/mol. The maximum available flow rate is 25 L/min.

Ozone generator
One common ozone generator will be used to generate the ozone in dry air flow to be measured by all the instruments included in the comparison. The ozone generator utilised in the comparison will be capable of producing stable ozone amount fractions over the range (0 to 500) nmol mol^{-1}, at a minimum flow rate equal to 2 L/min plus the flow rate needed by the guest instrument plus an excess flow rate of 1 L/min. When possible, ozone will be generated with one of the BIPM ozone generators.

Gas manifold
When possible, the BIPM external dual manifold system will be used to redistribute the zero air and ozone/air to instruments. If the guest instrument possesses its own manifold, the participating laboratory shall decide whether or not it wishes to make use of it.

Flow rates
Gas flows shall be provided to photometers with a minimum excess of 1 L/min compared to the combined requirements of the photometers included in the comparison.

6.3. Comparison procedure

The following procedure will be followed for the comparison.

Conditioning of the photometers and the pneumatic lines before the comparison
At the beginning of the comparison, the photometers as well as interconnecting pneumatic lines will be conditioned with a nominal value of the ozone amount fraction greater than 500 nmol mol^{-1} for at least 2 hours. This step can be combined with the instrument stabilisation period.

Ozone amount fraction nominal values
12 nominal values will be measured by the photometers. These values include the measurement of 0 nmol mol^{-1} (no ozone produced) at the beginning and the end of the comparison. The 12 nominal values will be produced in the following sequence: (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270, and 0) nmol mol^{-1}. Due to the operational characteristics of ozone generators, it is expected that the actual delivered values will be within $\pm$ 15 nmol mol^{-1} of those nominal values.

Ozone generator stability
For each nominal value of the ozone amount fraction x_{nom} furnished by the ozone generator, it is important to ensure that the photometers are measuring a stable value. To this end, the standard deviation s_{SRP27} on the set of 10 consecutive measurements $x_{\text{SRP27},i}$ recorded by BIPM-SRP27 will be calculated. This set is considered as valid if s_{SRP27} is less than 1 nmol mol^{-1}. If s_{SRP27} is found greater than 1 nmol mol^{-1}, another set of 10 consecutive measurements of the same nominal values is taken. Repeated instances of unacceptable values of s_{SRP27} indicate that there are instabilities in the ozone generator or in the BIPM-SRP27 measurement system. The reasons for these will be examined and documented prior to continuing the comparison.

Recorded values
For each nominal value x_{nom}, the value recorded for each photometer A is the mean ($\bar{x}_{\text{A}}$) of 10 consecutive single measurements $x_{\text{A},i}$ taken in a stable regime as defined above.

Comparison repeatability
The comparison procedure may be repeated to evaluate its repeatability. The participant and the BIPM will commonly decide when both instruments are stable enough to start recording a set of measurement results to be considered as the official comparison results. These measurement results will be recorded in the form BIPM.QM-K1-R1-LAB-YY.xls. In between the comparison repeats, ozone at a nominal value greater than 500 nmol mol^{-1} should be flowed through the instruments, or the comparison procedure should be repeated continuously. Details of this choice will be reported in the same form. The all process should not take more than three days.

6.4. Data acquisition and backup

The SRP control software automatically generates one excel file per comparison run. This file contains all the data recorded during the run. A copy of all recorded files can be provided on demand to the participant, but they are not considered as the results of the comparison. Names and location of the original files kept at the BIPM will be noted in the form BIPM.QM-K1-R2.

7. Subsequent comparison between the national standard and the transfer standard at the laboratory of the participating institute

The aim of this second comparison between the national and the transfer standard is to demonstrate that no significant drift has occurred in those instruments since the time of

their first comparison at the participating institute's laboratory. In consequence, this comparison should be as close as possible of the first comparison.

7.1. Pre-comparison requirements

The requirements are the same as those described for the first comparison in the paragraph 5.1 of this protocol.

7.2. Comparison procedure

The comparison procedure is the same as the one described in the paragraph 5.2 of this protocol. The comparison information form BIPM.QM-K1-R2 attached to this protocol shall be completed by the participating laboratory. The comparison should be completed and relevant results form received by the BIPM no later than six weeks after the comparison at the BIPM.

8. Uncertainty budgets

National standard
The standard uncertainties associated with the twelve values $\overline{x}_{\mathrm{NS}}$ will be evaluated by the participating laboratory. The laboratory will provide an uncertainty budget used to calculate the values in the report form BIPM.QM-K1-R2. This budget should preferably be presented in a table, showing the different uncertainty components with their type as described in the GUM.

Reference standard
The uncertainties associated with the twelve values $\overline{x}_{\mathrm{SRP27}}$ (and eventually $\overline{x}_{\mathrm{SRP28}}$) measured by the BIPM-SRP27 (and eventually BIPM-SRP28) will be evaluated by the BIPM. Details of the uncertainty budget for the BIPM-SRPs can be found at the end of this document.

Transfer standard
Only the components of the uncertainty corresponding to the repeatability and reproducibility of a transfer standard's measurements should be considered, since it is assumed that any causes of bias in the transfer standard's measurement remains constant over the time period of the comparisons.

The repeatability time scale may be taken as the duration of the measurement of one nominal ozone amount fraction. The reproducibility time scale is at least the time between the two comparisons performed between the national standard and the transfer standard.

Absorption cross section value and uncertainty
As introduced in section 1.1, ozone photometers measure ozone amount fractions by the absorption of radiation by ozone at 253.7 nm. Consequently, the uncertainty on the absorption cross section of ozone at 253.7 nm can be conventionally set to zero if all the instruments use the same value for this parameter but must be included if different

values are used. The value and uncertainty of the ozone absorption cross-section used by the participant shall appear clearly in the result form and the uncertainty budgets..

9. Calculation of the relationship between the national standard and the reference standard

The parameters $a_{NS,SRP27}$ and $b_{NS,SRP27}$ of the linear relationship between x_{NS} and x_{SRP27} ($x_{NS} = a_{NS,SRP27}\, x_{SRP27} + b_{NS,SRP27}$) will be computed by the BIPM using the program OzonE. This will be done from the measurement results of the two comparisons performed via the transfer standard and their related uncertainties:

- The first comparison results are calculated by performing a linear regression on the twelve data points from the BIPM visit (x_{RS}, x_{TS}) (calibration of the transfer standard) followed by a second linear regression of the twelve data points from the **pre** BIPM visit (x_{NS}, x'_{TS}), x'_{TS} being the corrected values of the transfer standard calibrated by the reference standard.

- The second comparison results are calculated by performing a linear regression on the twelve data points from the BIPM visit (x_{RS}, x_{TS}) (calibration of the transfer standard) followed by a second linear regression of the twelve data points from the **post** BIPM visit (x_{NS}, x'_{TS}), x'_{TS} being the corrected values of the transfer standard calibrated by the reference standard.

Covariance terms in between two measurement results of the BIPM SRPs will be included. They are described at the end of this document.

Covariance terms for the participant national standard $u(x_{NS,i}, x_{NS,j})$ can be taken into account if they are written as a constant times the product of the two ozone amount fractions:

$$u(x_{NS,i}, x_{NS,j}) = \alpha \cdot x_{NS,i} \cdot x_{NS,j} \qquad [4]$$

Where α is a constant to be entered into the program OzonE. The participant is free to provide a value for those constants. If no value is given, the covariance terms will be assumed to be zero.

Covariance terms for the transfer standard are not taken into account in this protocol.

The two linear relationships will be noted in the form BIPM.QM-K1-R2.

10. Degrees of equivalence

10.1. Definition

Two degrees of equivalence will be evaluated at two ozone nominal values: 80 nmol mol^{-1} and 420 nmol mol^{-1}.

In order to evaluate the difference between the measurement results of the national standard and the common reference SRP27, the transfer standard is first calibrated by SRP27. Thus, the degree of equivalence of the national standard with the reference standard SRP27, at the nominal value x_{nom} is the following:

$$\boldsymbol{D = x_{NS} - \hat{x}_{SRP27}} \qquad [5]$$

Where x_{NS} is the measurement results of the national standard at the nominal value x_{nom}, and $\hat{x}_{SRP27}$ is the predicted value of SRP27 at the same nominal value, deduced from the transfer standard measurement result during its comparison with the national standard.

Its associated standard uncertainty is:

$$u(D) = \sqrt{u^2(x_{NS}) + u^2(\hat{x}_{SRP27})} \qquad [6]$$

10.2. Calculation of SRP27 predicted values and their related uncertainties

The comparison performed at the BIPM between the transfer standard and the reference standard SRP27 is used to calibrate the transfer standard. The data $\overline{x}_{RS}$ and $\overline{x}_{TS}$ will be fitted using the generalised least square program OzonE, taking into account the associated uncertainties $u(\overline{x}_{RS})$ and $u(\overline{x}_{TS})$, as well as covariance terms between the reference standard measurement results.

The parameters $a_{RS,TS}$ and $b_{RS,TS}$ of the linear relationship between x_{RS} and x_{TS} ($x_{RS} = a_{RS,TS}\, x_{TS} + b_{RS,T}$) will be calculated as well as their uncertainties.

Then, for each value $\overline{x}_{TS}$ measured with the transfer standard during its comparison with the national standard, a predicted value $\hat{x}_{RS}$ for the reference standard will be evaluated using the linear relationships between the two instruments calculated above.

The standard uncertainties associated with the predicted values $\hat{x}_{RS}$ will be evaluated according to the equation:

$$u(\hat{x}_{RS}) = \sqrt{u^2(b_{RS,TS}) + x_{TS}^2 \cdot u^2(a_{RS,TS}) + a_{RS,TS}^2 \cdot u^2(x_{TS}) + 2x_{TS} \cdot u(a_{RS,TS}, b_{RS,TS})} \qquad [7]$$

Where the uncertainty components $u(a_{RS,TS})$, $u(b_{RS,TS})$ and $u(a_{RS,TS}, b_{RS,TS})$ are calculated with the generalised least-square software OzonE.

11. Comparability of the two degrees of equivalence for each nominal value

As protocol B includes two comparison between the national standard and the transfer standard (before and after the comparison at the BIPM), two degrees of equivalence are calculated for one nominal value x_{nom}.

At each nominal value, these two degrees of equivalence will be compared with their associated enlarged uncertainties (k=2).

12. Reporting of results

The measurement results together with the uncertainties and any additional information required will be reported in the excel form BIPM.QM-K1-R2-LAB-YY.xls. A PDF version of this file will be created and stored at the BIPM. If, on examination of the results, one or more appear to be anomalous, the institute is invited to check their results for numerical errors but without being informed as to the magnitude or sign of the apparent anomaly. If no numerical error is found, the final results are then derived and communicated to the participant. Note that once the participant has been informed of the results, individual values and uncertainties may be changed or removed only with the agreement of the Consultative Committee, and on the basis of a failure of a standard or some other phenomenon.

The BIPM is responsible for the preparation of a report of the comparison. A report will be produced for each bilateral comparison. There are a number of stages to the publication of the results before they can be accepted for degrees of equivalence in the key comparison database. Two formal stages are referred to here as Drafts A and B.

The Draft A report of a bilateral comparison is prepared as soon as the results have been agreed by the participant. It includes the results transmitted by the participant, identified by name, full details of the comparison, the uncertainty budgets, the proposals for degrees of equivalence with the key comparison reference value. It is sent in confidence to the participant for discussion and approbation. The report is then termed a Draft B and is sent for review to the reviewers designated by the Gas Analysis Working Group (GAWG) of the CCQM. The Draft B is amended according to comments received. Once the report has been approved by the reviewers it is considered to be the final report of the comparison and is published in *Metrologia Technical Supplement*, and the results published in the key comparison database.

In the procedure for producing Drafts A and B, the following points should be noted:

- A result from a participant is not considered complete without an associated uncertainty and will not be published in Draft A unless it is accompanied by an uncertainty supported by a complete uncertainty budget.
- An institute that considers its result unrepresentative of its standards may request a subsequent separate comparison with the BIPM. This should take place as soon as possible after the completion of the comparison. The subsequent comparison is considered as a new and distinct comparison, the results of which will supersede those of the earlier comparison.

APPENDIX 1 - BIPM-SRP27 uncertainty budget

1. Uncertainty budget

The uncertainty budget associated with the ozone amount fraction in dry air x measured by BIPM-SRP27 and BIPM-SRP28 in the range (0 to 500) nmol mol^{-1} is given in the following table. More details on the uncertainty components can be found in a published paper[2]. As explained in this paper, this uncertainty budget applies to SRPs maintained by the BIPM, in which two biases have recently been identified. The first one is a bias in the temperature measurement leading to a 0.4 % under evaluation of ozone amount fraction measurements. This bias is removed thanks to a temperature control unit. The second one is a bias in the optical path length leading to a 0.5 % over evaluation of ozone amount fraction measurements. This bias is numerically corrected, and its uncertainty represents the main contribution to the standard uncertainty on ozone amount fractions measurements ($2.89\times10^{-3}x$).

[2] Viallon J, Moussay P, Norris J.E, Guenther F and Wielgosz R.I, "A study of systematic biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard Reference Photometer » Metrologia **43** (2006) 441-450.

Component (*y*)	Uncertainty *u*(*y*)				Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to *u*(*x*) $\lvert c_i \rvert \cdot u(y)$ nmol mol^{-1}
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty *u*(*y*)		
Optical Path L_{opt}	Measurement Scale	Rect.	0.0006 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89\times10^{-3}x$
	Repeatability	Normal	0.01 cm			
	Bias	Rect	0.52 cm			
Pressure *P*	Pressure gauge	Rect.	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37\times10^{-4}x$
	Difference between cells	Rect.	0.017 kPa			
Temperature *T*	Temperature probe	Rect.	0.03 K	0.07 K	$\frac{x}{T}$	$2.29\times10^{-4}x$
	Residual bias	Rect.	0.058 K			
Ratio of intensities *D*	Scalers resolution	Rect.	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D\ln(D)}$	0.28
	Repeatability	Triang.	1.1×10^{-5}			
Absorption Cross section σ	Conventional value CCQM.O3.2019		0.35×10^{-19} cm^{2}molecule^{-1}	0.35×10^{-19} cm^{2}molecule^{-1}	$-\frac{x}{\sigma}$	-

2. Simple expression of the uncertainty

To obtain a simple form for the combined standard uncertainty *u*(*x*), the measurement equation

$$x = \frac{-1}{2\alpha L}\frac{R}{N_A}\frac{T_{mes}}{P_{mes}}\ln(D) \qquad [8]$$

can to be written :

$$x = B\ln(D) \qquad [9]$$

where

$$B = \frac{-1}{2\alpha L}\frac{R}{N_A}\frac{T_{mes}}{P_{mes}} \qquad [10]$$

and is constant for a given temperature and pressure.

So that the uncertainty contribution from the ratio of intensities D (to the combined standard uncertainty of x) can be written:

$$\boldsymbol{u_D = \frac{u(D)x}{D\,ln(D)} = \frac{u(D)B}{D} \approx u(D)B} \quad [11]$$

Since for the measurement range (0 to 500) nmol mol^{-1}:

$$\boldsymbol{D \approx 1} \quad [12]$$

And the combined standard uncertainty $u(x)$:

$$\boldsymbol{u(x) = \sqrt{(u(D)B)^2 + \left(\left(\frac{u(L_{opt})}{L_{opt}}\right)^2 + \left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(T)}{T}\right)^2\right)x^2}} \quad [13]$$

The application for BIPM-SRP27 (L = 89.8 cm), with a measurement temperature equal to 295 K and a measurement pressure equal to 100 kPa gives a numerical equation (where the numerical values of x are for ozone amount fractions given in units of nmol mol^{-1}) :

$$\boldsymbol{u(x) = \sqrt{(0.28)^2 + (2.92 \cdot 10^{-3}x)^2}} \quad [14]$$

The Figure 1 depicts the corresponding variations of $u(x)$ with the ozone amount fraction x.

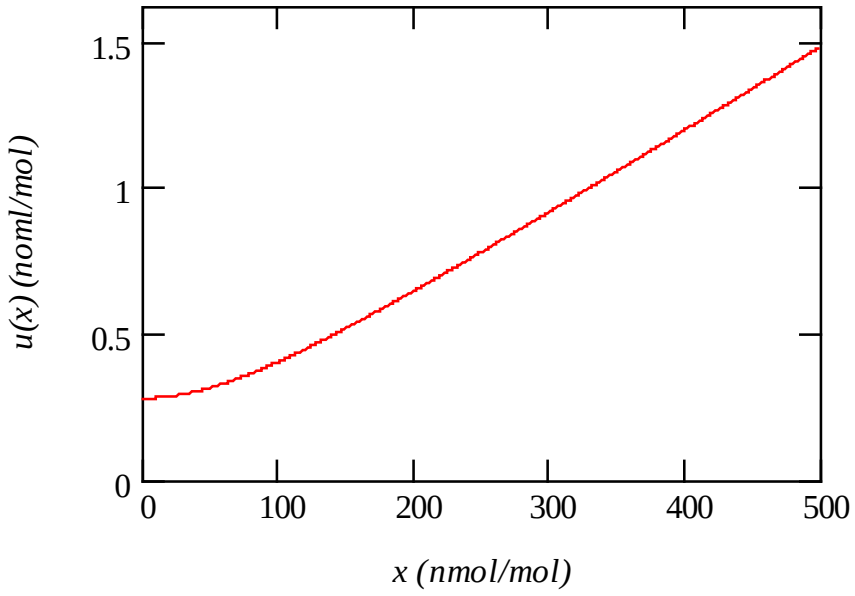

Figure 1 : Combined standard uncertainty associated with the measured amount fraction of ozone in dry air for BIPM-SRP27.

3. Covariance terms

When considering the SRP measurement equation, it appears that there are correlations in between the results of two measurements performed at two different ozone amount fractions with the same SRP. This should be taken into account when a generalized least-squares regression is performed on measurements performed with an SRP.

The general expression of the covariance terms between two measurement results x_i and x_j given by the GUM (Section F.1.2.3 equation F.2) is:

$$u(x_i, x_j) = \sum_{l=1}^{L} \left(\frac{\partial}{\partial q_l} x_i\right)\left(\frac{\partial}{\partial q_l} x_j\right) u(q_l)^2 \qquad [15]$$

Where the q_l are common variables in between x_i and x_j.

The common variables between x_i and x_j are the temperature T, the pressure P, and the optical path length L_{opt}. For those three variables, the partial derivate of x_i takes the same expression:

$$\frac{\partial x_i}{\partial q_l} = \frac{x_i}{q_l} \qquad [16]$$

So that:

$$u(x_i, x_j) = \sum_{l=1}^{L} \left(\frac{x_i}{q_l}\right)\left(\frac{x_j}{q_l}\right) u(q_l)^2 \qquad [17]$$

$$u(x_i, x_j) = x_i \cdot x_j \sum_{l=1}^{L} \left(\frac{u(q_l)^2}{q_l^2} \right) \quad [18]$$

Or, with the variables q_l expressed:

$$u(x_i, x_j) = x_i \cdot x_j \left(\frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} + \frac{u^2(L_{opt})}{{L_{opt}}^2} \right) \quad [19]$$

This can be written:

$$u(x_i, x_j) = x_i \cdot x_j \cdot u_b^2 \quad [20]$$

Where:

$$u_b^2 = \frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} + \frac{u^2(L_{opt})}{{L_{opt}}^2} \quad [21]$$

The value of u_b is given by the expression of the measurement uncertainty: $u_b = 2.92 \times 10^{-3}$.