

Protocol for the Key Comparison BIPM.QM-K1, Ozone at ambient level

Coordinating laboratory: Bureau International des Poids et Mesures

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Forms distributed with this protocol:

- BIPM.QM-K1-R1: comparison results form, protocol A
- BIPM.QM-K1-R2: comparison results form, protocol B
- BIPM.QM-K1-R3: comparison results form to link a RMO comparison
- BIPM.QM-K1-R4: registration form
- ADM-DOU-P03: information for laboratories shipping equipment to the BIPM for comparisons
- ADM-DOU-F12: Shipping instructions for comparisons

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 BIPM.

The level of comparability will be determined using the NIST Standard Reference Photometer (BIPM-SRP27) maintained by the BIPM 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 mole fraction range covered by the comparisons starts at the limit of quantification of the common reference, 2 nmol/mol, and ends by convention at 500 nmol/mol.

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

Any institute fulfilling the formal requirements for participation in a key comparison and holding appropriate standards may participate in BIPM.QM-K1. The rules on eligibility for participation in key comparisons are stated in paragraph 6 of the CIPM-MRA, and are given in an appendix in the document "Guidelines for Key Comparisons" on the BIPM web page (<http://www.bipm.org/utis/en/pdf/guidelines.pdf>).

3. Measurement schedule

A call for participation in the comparison will be sent out every two years, and a schedule with available weeks within two years will be published on the BIPM webpage. 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.

4. Terms and definitions

- x_{nom} : nominal ozone mole fraction in dry air furnished by the ozone generator
- $x_{A,i}$: i th 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 : $\bar{x}_A = \frac{1}{N} \sum_{i=1}^N x_{A,i}$
- 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.

5. 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 instruments to and from the BIPM, and to ensure that proper arrangements are made for local customs formalities. The laboratory shall inform the BIPM of its transport and customs arrangements prior to equipment leaving their laboratory. All information can be found in the form BIPM/ADM-DOU-P-03 provided with this protocol.

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 mole fractions of ozone in dry air in the range (0 to 500) nmol/mol. 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, attached to this protocol, 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. Quantities and Units

A number of quantities can be used to express the composition of mixtures, and this is true within the field of ambient ozone measurements. In this protocol the measurand is the mole fraction of ozone in air, with measurement results being expressed in units of nmol/mol. The numerical value of a mole 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.

Laboratories are to use $1.1476 \times 10^{-21} \text{ m}^2$ (equivalent to $308.32 \text{ atm}^{-1} \text{ cm}^{-1}$) as the conventional value of the ozone absorption cross section at 253.7 nm, in order to calculate their ozone mole fractions.

5. 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.

Recording of SRP operating characteristics (for laboratories that operate SRPs)

‘SRP operating characteristics data sheets’ (BIPM/CHEM-R-01) shall be completed for all SRPs after their initial warm up period. The data sheets to be completed will be provided by the BIPM. Copies of the participating institute’s data sheet shall be kept by the BIPM. The participating institutes are free to make adjustments to their instrument’s operating parameters following their usual operating procedures. Any adjustments made will be noted within the data sheets.

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 mole fraction of ozone and nitrogen oxides remaining in the air is below detectable limits. The relative humidity of the reference air is monitored and the mole fraction of water in air typically found to be less than $3 \mu\text{mol/mol}$. The mole fraction of volatile organic hydrocarbons in the reference air has been measured (November 2002), with no mole fraction of any detected component exceeding 1 nmol/mol . The maximum available flow rate is 25 L/min .

Ozone generator

One common ozone generator will be used to generate the ozone 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 mole fractions over the range (0 to 500) nmol/mol , 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. 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 mole fraction greater than 500 nmol/mol for at least 2 hours. This can eventually be done during the instrument stabilisation period.

Ozone mole fraction nominal values

12 nominal values will be measured by the photometers. These values include the measurement of 0 nmol/mol (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. Due to the operational characteristics of ozone generators, it is expected that the actual delivered values will be within ± 15 nmol/mol of those nominal values.

Ozone generator stability

For each nominal value of the ozone mole 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. If s_{SRP27} is found greater than 1 nmol/mol, 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}_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 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.

7. Uncertainty budgets

National standard

The standard uncertainties associated with the twelve values \bar{x}_{NS} 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}_{SRP27} (and eventually \bar{x}_{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.

Absorption cross section value and uncertainty

Ozone photometers measure ozone mole fractions by the absorption of radiation by ozone at 253.7 nm. As a consequence, 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. This should appear clearly in the uncertainty budget. Furthermore, all laboratories shall calculate their ozone mole fractions using the conventional value for the absorption cross section of $308.32 \text{ atm}^{-1}\text{cm}^{-1}$ (equivalent to $1.1476 \times 10^{-17} \text{ cm}^2/\text{molecule}$). If the laboratory ordinarily uses a different value for the absorption cross section, this should be stated in the form BIPM.QM-K1-R1, but not used in the calculation.

8. Linear regression fits

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

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

$$u(x_{\text{NS},i}, x_{\text{NS},j}) = \alpha \cdot x_{\text{NS},i} \cdot x_{\text{NS},j} \quad [1]$$

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.

9. Degrees of equivalence

Two degrees of equivalence will be evaluated at two ozone nominal values: 80 nmol/mol and 420 nmol/mol.

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

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

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:

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

10. 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.

11. 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 and the uncertainty budgets. It is sent in confidence to the participant for discussion and approbation. A section or an appendix will then be added to the report containing the proposals for degrees of equivalence with the key comparison reference value, following the agreed format for inclusion in the BIPM key comparison database. The report is then termed a Draft B and is circulated to all participants and the Consultative Committee or designated Working Group. The Draft B is amended according to comments received. Once the report has been approved by the Consultative Committee 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.

- The Draft B report is sent to all the participants for comment, with a reasonable deadline for replies. If any controversial or contradictory comments are received by the BIPM, they are circulated to all participants and discussion continues until a consensus is reached.

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 instruments to and from the BIPM, and to ensure that proper arrangements are made for local customs formalities. The laboratory shall inform the BIPM of its transport and customs arrangements prior to equipment leaving their laboratory. All information can be found in the form BIPM/ADM-DOU-P-03 provided with this protocol.

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 7 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 mole fractions of ozone in dry air in the range (0 to 500) nmol/mol. 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. Quantities and Units

A number of quantities can be used to express the composition of mixtures, and this is true within the field of ambient ozone measurements. In this protocol the measurand is the mole fraction of ozone in air, with measurement results being expressed in units of nmol/mol. The numerical value of a mole 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.

Laboratories are to use $1.1476 \times 10^{-21} \text{ m}^2$ (equivalent to $308.32 \text{ atm}^{-1} \text{ cm}^{-1}$) as the conventional value of the ozone absorption cross section at 253.7 nm, in order to calculate their ozone mole fractions.

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

6.1 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 of ozone mole 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.

6.2 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 mole fraction greater than 500 nmol/mol for at least 2 hours. This can eventually be done during the instruments stabilisation period.

Ozone mole fraction nominal values

12 nominal values will be measured by the photometers. These values include the measurement of 0 nmol/mol 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. Due to the operational characteristics of ozone generators, it is expected that the actual delivered values will be within ± 15 nmol/mol of those nominal values.

Ozone generator stability

For each nominal value of the ozone mole 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 or 1.5 % of the average value (which ever 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 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.

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

7.1 Comparison description

A direct comparison will be made at the BIPM between BIPM-SRP27 and the transfer standard of the visiting laboratory over 12 mole fractions of ozone in dry air in the range (0 to 500) nmol/mol. 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 version 4.05 (2001) 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.

7.2 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.

Recording of SRP operating characteristics (for laboratories that operate SRPs)

'SRP operating characteristics data sheets' (BIPM/CHEM-R-01) shall be completed for all SRPs after their initial warm up period. The data sheets to be completed will be provided by the BIPM. Copies of the participating institute's data sheet shall be kept by the BIPM. The participating institutes are free to make adjustments to their instrument's operating parameters following their usual operating procedures. Any adjustments made will be noted within the data sheets.

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 mole fraction of ozone and nitrogen oxides remaining in the air is below detectable limits. The relative humidity of the reference air is monitored and the mole fraction of water in air typically found to be less than 3 $\mu\text{mol/mol}$. The mole fraction of volatile organic hydrocarbons in the reference air has been measured (November 2002), with no mole fraction of any detected component exceeding 1 nmol/mol . The maximum available flow rate is 25 L/min.

Ozone generator

One common ozone generator will be used to generate the ozone 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 mole fractions over the range (0 to 500) nmol/mol , 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.

7.3 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 mole fraction greater than 500 nmol/mol for at least 2 hours. This can eventually be done during the instrument stabilisation period.

Ozone mole fraction nominal values

12 nominal values will be measured by the photometers. These values include the measurement of 0 nmol/mol (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. Due to the operational characteristics of ozone generators, it is expected that the actual delivered values will be within ± 15 nmol/mol of those nominal values.

Ozone generator stability

For each nominal value of the ozone mole 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. If s_{SRP27} is found greater than 1 nmol/mol, 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}_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 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.

7.4 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.

8. 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.

8.1 Pre-comparison requirements

The requirements are the same as those described for the first comparison in the paragraph 6.1 of this protocol.

8.2 Comparison procedure

The comparison procedure is the same as the one described in the paragraph 6.2 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.

9. Uncertainty budgets

National standard

The standard uncertainties associated with the twelve values \bar{x}_{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 \bar{x}_{SRP27} (and eventually \bar{x}_{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 mole 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

Ozone photometers measure ozone mole fractions by the absorption of radiation by ozone at 253.7 nm. As a consequence, 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. This should appear clearly in the uncertainty budget. Furthermore, all laboratories should calculate their ozone mole fractions using the conventional value for the absorption cross section of 308.32 atm⁻¹ cm⁻¹ (equivalent to 1.1476×10⁻¹⁷ cm²/molecule). If the laboratory ordinarily uses a different value for the absorption cross section, this should be stated in form BIPM.QM-K1-R2, but the value given here should be used in the calculation.

10. 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 mole fractions:

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

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.

11. Degrees of equivalence

11.1 Definition

Two degrees of equivalence will be evaluated at two ozone nominal values: 80 nmol/mol and 420 nmol/mol.

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:

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

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:

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

11.2 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 \bar{x}_{RS} and \bar{x}_{TS} will be fitted using the generalised least square program OzonE, taking into account the associated uncertainties $u(\bar{x}_{RS})$ and $u(\bar{x}_{TS})$, 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} ($x_{RS} = a_{RS,TS} x_{TS} + b_{RS,TS}$) will be calculated as well as their uncertainties.

Then, for each value \bar{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:

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

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.

12. 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 ($k=2$).

13. 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 and the uncertainty budgets. It is sent in confidence to the participant for discussion and approbation. A section or an appendix will then be added to the report containing the proposals for degrees of equivalence with the key comparison reference value, following the agreed format for inclusion in the BIPM key comparison database. The report is then termed a Draft B and is circulated to all participants and the Consultative Committee or designated Working Group. The Draft B is amended according to comments received. Once the report has been approved by the Consultative Committee 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.
- The Draft B report is sent to all the participants for comment, with a reasonable deadline for replies. If any controversial or contradictory comments are received by

the BIPM, they are circulated to all participants and discussion continues until a consensus is reached.

APPENDIX 1 - BIPM-SRP27 uncertainty budget

1. Uncertainty budget

The uncertainty budget associated with the ozone mole fraction in dry air x measured by BIPM-SRP27 and BIPM-SRP28 in the range (0 to 500) nmol/mol is given in the following table. More details on the uncertainty components can be found in a published paper¹. 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 mole 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 mole fraction measurements. This bias is numerically corrected, and its uncertainty represents the main contribution to the standard uncertainty on ozone mole fractions measurements ($2.89 \times 10^{-3} x$).

Component (y)	Uncertainty $u(y)$				Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to $u(x)$ $ c_i \cdot u(y)$ nmol/mol
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$		
Optical Path L_{opt}	Measurement Scale	Rect.	0.0006 cm	0.052 cm	$-\frac{x}{L_{opt}}$	$2.89 \times 10^{-3} x$
	Repeatability	Normal	0.01 cm			
	Bias	Rect	0.052 cm			
Pressure P	Pressure gauge	Rect.	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37 \times 10^{-4} x$
	Difference between cells	Rect.	0.017 kPa			
Temperature T	Temperature probe	Rect.	0.03 K	0.07 K	$\frac{x}{T}$	$2.29 \times 10^{-4} x$
	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		-	-	-	-

2. Simple expression of the uncertainty

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

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

¹ 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.

can to be written :

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

where

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

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:

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

Since for the measurement range (0 to 500) nmol/mol:

$$D \approx 1 \quad [12]$$

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

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

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 mole fractions given in units of nmol/mol) :

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

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

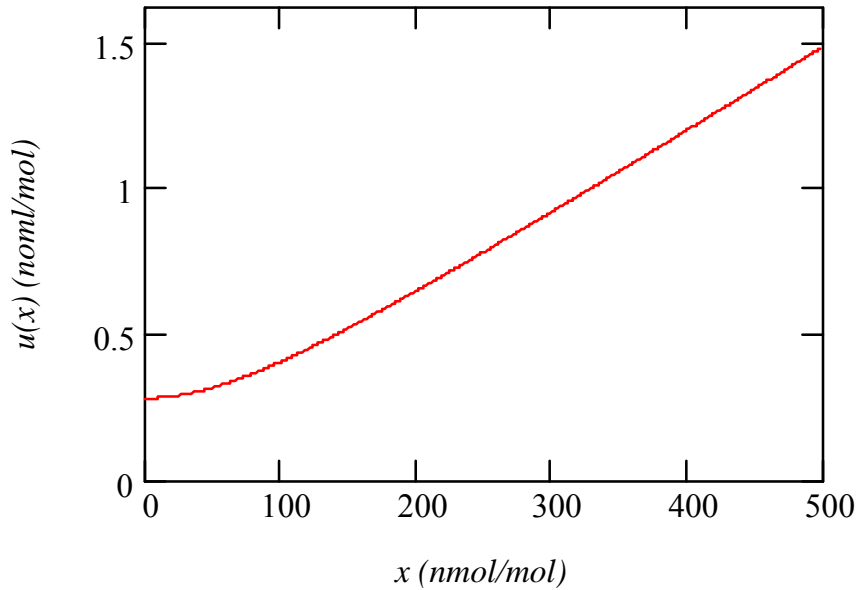


Figure 1 : Combined standard uncertainty associated with the measured mole fraction of ozone in dry air for BIPM-SRP27.

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 mole 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:

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

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:

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

So that:

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

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

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: $u_b = 2.92 \times 10^{-3}$.