

# Final report, Ongoing Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with ISCIII, (May 2023)

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## Abstract

As part of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of the Instituto de Salud Carlos III (ISCIII) and the common reference standard of the key comparison, maintained by the Bureau International des Poids et Mesures (BIPM). The instruments have been compared over a nominal ozone amount-of-substance fraction range of 0 nmol mol<sup>-1</sup> to 500 nmol mol<sup>-1</sup>.

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## 1. Field

Amount of substance.

## 2. Subject

Comparison of reference measurement standards for ozone at ambient level.

## 3. Participants

BIPM.QM-K1 is an ongoing key comparison, which is structured as an ongoing series of bilateral comparisons. The results of the comparison with the Instituto de Salud Carlos III (ISCIII) are reported here.

## 4. Organizing body

BIPM.

## 5. Rationale

The ongoing key comparison BIPM.QM-K1 has been running since January 2007. It follows the pilot study CCQM-P28 that included 23 participants and was performed between July 2003 and February 2005 [1]. It is aimed at evaluating the degree of equivalence of ozone photometers that are maintained as national standards, or as primary standards within international networks for ambient ozone measurements. The reference value is determined using the NIST Standard Reference Photometer (BIPM-SRP27) maintained by the BIPM as a common reference.

## 6. Terms and definitions

- $x_{\text{nom}}$ : nominal ozone amount fraction in dry air furnished by the ozone generator
- $x_{A,i}$ :  $i$ th measurement of the nominal value  $x_{\text{nom}}$  by the photometer A.
- $\bar{x}_A$ : the mean of  $N$  measurements of the nominal value  $x_{\text{nom}}$  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  $x_{\text{nom}}$  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  $\text{nmol mol}^{-1}$ .

## 7. Measurements schedule

The key comparison BIPM.QM-K1 was initially organised 2 years cycles. The 2007-2008 round, the results of which are published in the [Key Comparison Database](#) of the BIPM, included 16 participants. The second round of BIPM.QM-K1 started in March 2009 for a period of 4 years, following the decision of the CCQM/GAWG to reduce the repeat frequency of bilateral comparisons. Measurements reported in this report were performed from 10 April 2023 to 16 June 2023 at the ISCIII and the BIPM.

## 8. Measurement protocol

The comparison protocol is summarised in this section. The complete version can be downloaded from the BIPM website ([http://www.bipm.org/utls/en/pdf/BIPM.QM-K1\\_protocol.pdf](http://www.bipm.org/utls/en/pdf/BIPM.QM-K1_protocol.pdf)).

This comparison was performed following protocol B, corresponding to a comparison between the ISCIII national standard SRP22 and the common reference standard BIPM-SRP27 maintained at the BIPM via the transfer standard TEI49iPS-0734626227. The national standard SRP22 and the transfer standard TEI49iPS-0734626227 were first compared at the ISCIII in April 2023. Then TEI49iPS-0734626227 was compared with the common reference standard SRP27 at the BIPM two weeks later. Finally, the national standard SRP22 and the transfer standard TEI49iPS-0734626227 were again compared at the ISCIII in June 2023 to test the stability of the transfer standard.

A comparison between two (or more) ozone photometers consists of producing ozone-air mixtures at different mole fractions over the required range and measuring these with the photometers.

### 8.1. Comparisons at the ISCIII

#### a). Ozone generation

The source of purified air is a compressor with scrubbers for NO<sub>x</sub>, VOCs, O<sub>3</sub>, and humidity. This air is used to provide reference air as well as the ozone-air mixture to each ozone photometer. Ozone is produced using the generator provided with SRP22.

#### b). Comparison procedure

Prior to the comparison, all the instruments were switched on and allowed to stabilise for a week. Characteristics of the instruments were checked at this time following an internal procedure. Basic adjustments of temperature, pressure, and dark counts following the SRP operating characteristics checkout were performed.

One comparison run includes 10 different mole fractions distributed to cover the range, together with the measurement of reference air at the beginning and end of each run. The nominal mole fractions were measured in a sequence imposed by the protocol (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270, and 0) nmol mol<sup>-1</sup>. Each of these points is an average of 10 single measurements.

For each nominal value of the ozone amount-of-substance fraction  $x_{\text{nom}}$  furnished by the ozone generator, the standard deviation  $s_{\text{SRP22}}$  on the set of 10 consecutive measurements  $x_{\text{SRP22},i}$  recorded by SRP22 was calculated. The measurement results were considered as valid if  $s_{\text{SRP22}}$  was less than 1 nmol mol<sup>-1</sup>, which ensures that the photometers were measuring a stable ozone concentration. If not, another series of 10 consecutive measurements was performed.

#### c). Comparison repeatability

The comparison procedure was repeated continuously to evaluate its repeatability.

### 8.2. Comparisons at the BIPM

#### a). Ozone generation

The same source of purified air is used for all the ozone photometers being compared. Starting from compressed ambient air, the purification system consisted of a first refrigeration dryer, a

catalytic converter to burn residual oil, a second refrigeration dryer, a particulate filter to remove particles larger than 0.1  $\mu\text{m}$ , an active coal filter, and a final zero air generator (AADCO 737R-12), which ensured that the amount fraction of ozone, hydrocarbons, and nitrogen oxides remaining in the air was below detectable limits. This final system also ensured a constant amount fraction of oxygen in air, which is important to generate constant ozone amount fractions in the ozone generator. The relative humidity of the reference air was monitored and the amount fraction of water in air was typically found to be less than 3  $\mu\text{mol mol}^{-1}$ .

Ozone in air mixtures were produced from the purified air inside the ozone generator (EnviroNics) equipped with a UV lamp to enable the photolysis of oxygen at a wavelength of 185 nm. To obtain a range of ozone amount fractions, the UV lamp intensity was tuned at appropriate levels. These actions were all controlled by the SRP operating software.

A common dual external Pyrex manifold was used to furnish the necessary flows of reference air and ozone-air mixtures to the ozone photometers. The two columns of this manifold were vented to atmospheric pressure. The same length of Teflon tubing was used to deliver both gas flows to all photometers under comparison, ensuring that they all received homogenized samples and reference air.

#### b). Comparison procedure

Prior to the comparison, all the instruments were switched on and allowed to stabilise for at least 8 hours. The pressure and temperature measurement systems of the instruments were checked at this time. If any adjustments were required, these were noted. For this comparison, no adjustments were necessary.

One comparison run includes ten different amount fractions of ozone distributed to cover the range, together with the measurement of reference air at the beginning and end of each run. The nominal amount fractions were measured in a sequence imposed by the protocol (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270, and 0)  $\text{nmol mol}^{-1}$ . Each of these points is an average of ten single measurements.

For each nominal value of the ozone amount fraction  $x_{\text{nom}}$  furnished by the ozone generator, the standard deviation  $s_{\text{SRP27}}$  on the set of 10 consecutive measurements  $x_{\text{SRP27},i}$  recorded by BIPM-SRP27 was calculated. The measurement results were considered as valid if  $s_{\text{SRP27}}$  was less than 1  $\text{nmol mol}^{-1}$ , which ensures that the photometers were measuring a stable ozone concentration. If not, another series of 10 consecutive measurements was performed.

#### c). Comparison repeatability

The comparison procedure was repeated continuously to evaluate its repeatability. The participant and the BIPM commonly decided when both instruments were stable enough to start recording a set of measurement results to be considered as the official comparison results.

#### d). SRP27 stability check

A second ozone reference standard, BIPM-SRP28, was included in the comparison to verify its agreement with BIPM-SRP27 and thus follow its stability over the period of the ongoing key comparison.

## 9. Reporting measurement results

The participant and the BIPM staff reported the measurement results in the result form BIPM.QM-K1-R2 provided by the BIPM and available on the BIPM website. It includes details on the comparison conditions, measurement results and associated uncertainties, as well as the

standard deviation for each series of 10 ozone amount-of-substance fractions measured by the participant' standard and the common reference standard. The completed form BIPM.QM-K1-R2-ISCI-23 is given in appendix 1.

## 10. Post comparison calculation

All calculations were performed by the BIPM using the form BIPM.QM-K1-R2. It includes the two degrees of equivalence that are reported as comparison results in the Appendix B of the BIPM KCDB (key comparison database). Additionally, the degrees of equivalence at all nominal ozone amount-of-substance fractions are reported in the same form, as well as the linear relationship between the participant standard and the common reference standard.

## 11. Deviations from the comparison protocol

In this comparison, there was no deviation from the protocol.

## 12. Measurement standards

The instruments maintained by the BIPM and ISCI are Standard Reference Photometers (SRP) built by the NIST. More details on the instrument's principle and its capabilities can be found in [2]. The following section describes the SRP operating principle and uncertainty budget.

### 12.1. Measurement equation of a NIST SRP

The measurement of the ozone amount fraction by an SRP is based on the absorption of radiation at 253.7 nm by ozonized air in the gas cells of the instrument. One particularity of the instrument design is the use of two gas cells to overcome the instability of the light source. The measurement equation is derived from the Beer-Lambert and ideal gas laws. The number density ( $C_{O_3}$ ) of ozone is calculated from:

$$C_{O_3} = \frac{-1}{2\sigma L_{opt}} \frac{T}{T_{std}} \frac{P_{std}}{P} \ln(D) \quad (1)$$

where

- $\sigma$  is the absorption cross-section per molecule of ozone at 253.7 nm under standard conditions of temperature and pressure,  $1.1476 \times 10^{-17} \text{ cm}^2$  [3].
- $L_{opt}$  is the mean optical path length of the two cells;
- $T$  is the measured temperature of the cells;
- $T_{std}$  is the standard temperature (273.15 K);
- $P$  is the measured pressure of the cells;
- $P_{std}$  is the standard pressure (101.325 kPa);
- $D$  is the product of transmittances of two cells, with the transmittance ( $T_r$ ) of one cell defined as

$$T_r = \frac{I_{ozone}}{I_{air}} \quad (2)$$

where

- $I_{ozone}$  is the UV radiation intensity measured from the cell when containing ozonized air, and
- $I_{air}$  is the UV radiation intensity measured from the cell when containing pure air (also called reference or zero air).

Using the ideal gas law equation (1) can be recast in order to express the measurement results as an amount fraction ( $x$ ) of ozone in air:

$$x = \frac{-1}{2\sigma L_{\text{opt}}} \frac{T}{P} \frac{R}{N_A} \ln(D) \quad (3)$$

where

$N_A$  is the Avogadro constant,  $6.022\,140\,76 \times 10^{23} \text{ mol}^{-1}$   
 $R$  is the gas constant,  $8.314\,462\,618 \text{ J mol}^{-1} \text{ K}^{-1}$

The formulation implemented in the SRP software, although equivalent in terms of the measurement results, differs from the above in the choice of a unit system based on the “atm” (atmosphere) as unit for the pressure, rather than the SI. The conversion between the two systems is further detailed in a BIPM report[4], in which the units and values for the ozone absorption cross section at 253.65 nm (air) are discussed as well.

## 12.2. Absorption cross-section for ozone

The absorption coefficient under standard conditions  $\alpha_0$  used within the SRP software algorithm is  $308.32 \text{ atm}^{-1} \text{ cm}^{-1}$ . This corresponds to a value for the absorption cross section  $\sigma$  of  $1.1476 \times 10^{-17} \text{ cm}^2$ , rather than the more often quoted  $1.147 \times 10^{-17} \text{ cm}^2$  reported by Hearn in 1961 [5]. The CCQM recommended in 2020 [6] that a new value for the ozone absorption cross section be used in the on-going key comparison BIPM.QM-K1 and in all ozone photometers acting as ozone standards. A CCQM Task Group was created in 2020 to manage the synchronous change of ozone cross-section worldwide, with the aim to implement the new, consensus value, named CCQM.O3.2019 proposed by Hodges *et al.* [7], within the next 1 to 3 years.

In the comparison of two SRP instruments, the absorption cross-section can be considered to have a conventional value and its uncertainty can be set to zero. However, in the comparison of different methods or when considering the complete uncertainty budget of the method the uncertainty of the absorption cross-section should be taken into account.

## 12.3. Condition of the BIPM SRPs

SRP27 and SRP28 were built in 2002. Compared to the original design described in [2], both instruments have been modified to deal with two biases revealed by the study conducted by the BIPM and the NIST in 2006 [8]. In 2009, an “SRP upgrade kit” was installed in the instruments [9]. In 2021, their electronic modules were upgraded. Negligible impact on their measurement results was demonstrated [10].

## 12.4. Uncertainty budget of the common reference BIPM-SRP27

The uncertainty budget for the ozone amount fraction in dry air ( $x$ ) measured by the instruments BIPM-SRP27 and BIPM-SRP28 in the nominal range  $0 \text{ nmol mol}^{-1}$  to  $500 \text{ nmol mol}^{-1}$  is given in Table 1.

**Table 1: Uncertainty budget for the SRPs maintained by the BIPM**

Component (y)	Uncertainty $u(y)$				Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to $u(x)$ $ c_i  \cdot u(y)$ $\text{nmol mol}^{-1}$
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$		
<b>Optical Path</b> $L_{\text{opt}}$	Measurement scale	Rectangular	0.0006 cm	0.52 cm	$-\frac{x}{L_{\text{opt}}}$	$2.89 \times 10^{-3}x$
	Repeatability	Normal	0.01 cm			
	Correction factor	Rectangular	0.52 cm			
<b>Pressure <math>P</math></b>	Pressure gauge	Rectangular	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37 \times 10^{-4}x$
	Difference between cells	Rectangular	0.017 kPa			
<b>Temperature <math>T</math></b>	Temperature probe	Rectangular	0.03 K	0.07 K	$\frac{x}{T}$	$2.29 \times 10^{-4}x$
	Temperature gradient	Rectangular	0.058 K			
<b>Ratio of intensities <math>D</math></b>	Scaler resolution	Rectangular	$8 \times 10^{-6}$	$1.4 \times 10^{-5}$	$\frac{x}{D \ln(D)}$	0.28
	Repeatability	Triangular	$1.1 \times 10^{-5}$			
<b>Absorption Cross section per molecule <math>\sigma</math></b>	Hearn value		$1.22 \times 10^{-19} \text{ cm}^2$	$1.22 \times 10^{-19} \text{ cm}^2$	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$

Following this budget, as explained in the protocol of the comparison, the standard uncertainty associated with the ozone amount fraction measurement with the BIPM SRPs can be expressed as a numerical equation (numerical values expressed as  $\text{nmol mol}^{-1}$ ):

$$u(x) = \sqrt{(0.28)^2 + (2.92 \cdot 10^{-3}x)^2} \quad (4)$$

### 12.5. Covariance terms for the common reference BIPM-SRP27

As explained in section 14, correlations in between the results of two measurements performed at two different ozone amount fractions with BIPM-SRP27 were taken into account in the software OzoneE. More details on the covariance expression can be found in the protocol. The following expression was applied:

$$u(x_i, x_j) = x_i \cdot x_j \cdot u_b^2 \quad (5)$$

where:

$$u_b^2 = \frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} + \frac{u^2(L_{\text{opt}})}{L_{\text{opt}}^2} \quad (6)$$

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

### 12.6. Condition of the ISCIII SRP22

Compared to the original design, the ISCIII SRP22 has been modified to deal with the two biases revealed in [8]. In 2010, an ‘‘SRP upgrade kit’’ was installed by NIST.

## 12.7. Uncertainty budget of the ISCIII SRP22

The uncertainty budget for the ozone amount-of-substance fraction in dry air  $x$  measured by the ISCIII standard SRP22 in the nominal range 0 nmol mol<sup>-1</sup> to 500 nmol mol<sup>-1</sup> is given in Table 2.

Table 2 : SRP22 uncertainty budget

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 <sup>-1</sup>
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$		
<b>Optical Path</b> $L_{opt}$	Measurement Scale	Rectangular	0.0005cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89 \times 10^{-3}x$
	Repeatability	Normal	0.004 cm			
	Bias	Rectangular	0.52 cm			
<b>Pressure P</b>	Pressure gauge	Rectangular	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37 \times 10^{-4}x$
	Difference between cells	Rectangular	0.017 kPa			
<b>Temperature T</b>	Temperature probe	Rectangular	0.029 K	0.07 K	$\frac{x}{T}$	$2.29 \times 10^{-4}x$
	Residual Bias	Rectangular	0.058 K			
<b>Ratio of intensities D</b>	Scaler resolution	Rectangular	$8 \times 10^{-6}$	$1.4 \times 10^{-5}$	$\frac{x}{D \ln(D)}$	0.28
	Repeatability	Normal	$1.1 \times 10^{-5}$			
<b>Absorption Cross section <math>\alpha</math></b>	Hearn value		$1.22 \times 10^{-19}$ cm <sup>2</sup> /molecule	$1.22 \times 10^{-19}$ cm <sup>2</sup> /molecule	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$

Following this budget, the standard uncertainty associated with the ozone amount-of-substance fraction measurement with the ISCIII SRP22 can be expressed as a numerical equation (numerical values expressed as nmol mol<sup>-1</sup>):

$$u(x) = \sqrt{(0.28)^2 + (2.92 \cdot 10^{-3} x)^2} \quad (7)$$

No covariance term for the ISCIII SRP22 was included in the calculations.

## 12.8. Transfer standard TEI49iPS-0734626227

The transfer standard used by ISCIII is a TEI49iPS. It is an ozone photometer based on a principle similar to the SRP, although many components are simplified. This model does not include any scrubber. It is normally used by ISCIII as a laboratory instrument.

In 2021, the transfer standard was subjected to a corrective maintenance that included the detectors replacement and the intensity adjustments. Since then, no more corrective maintenance or adjustments have been required.

The uncertainty budget for the ozone amount-of-substance fraction in dry air  $x$  measured by the TEI49iPS-0734626227 in the nominal range 0 nmol mol<sup>-1</sup> to 500 nmol mol<sup>-1</sup> is given in Table 3. As recommended in the protocol, only the repeatability and the reproducibility are considered in the uncertainty budget. The following expressions were provided by ISCIII:

- **Repeatability:** maximal value of the experimental standard deviation observed at ISCIII (s=0.67 nmol/mol).

- **Reproducibility:** difference between the maximum and the minimum value of the slope of the regression line between the national standard and the transfer standard.

Table 3: TEI49iPS-0734626227 uncertainty budget

Source	Distribution	Contribution to $u(x)$ $ c_i  \cdot u(y)$ nmol/mol
Repeatability	Normal	0.67 nmol/mol
Reproducibility	Rectangular	0.0014x

### 13. Measurement results and uncertainties

Details of the measurement results, the measurement uncertainties and the standard deviations at each nominal ozone amount-of-substance fraction can be found in the form BIPM.QM-K1-R2-ISCI-23 given in appendix 1.

### 14. Analysis of the measurement results by generalised least-square regression

The relationship between the national and reference standards was first evaluated with a generalised least-square regression fit, using the software OzonE. This software, which is documented in a publication [11], is an extension of the previously used software B\_Least recommended by the ISO standard 6143:2001 [12]. It includes the possibility to take into account correlations between measurements performed with the same instrument at different ozone amount-of-substance fractions. It also facilitates the use of a transfer standard, by handling of unavoidable correlations, which arise since this instrument needs to be calibrated by the reference standard.

The two comparisons performed via the transfer standard were treated as follows:

- 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.

For each comparison, a linear relationship between the ozone amount-of-substance fractions measured by SRP $n$  and SRP27 is obtained:

$$x_{SRPn} = a_0 + a_1 x_{SRP27} \quad (8)$$

The associated uncertainties on the slope  $u(a_1)$  and the intercept  $u(a_0)$  are given by OzonE, as well as the covariance between them and the usual statistical parameters to validate the fitting function.

#### 14.1. Least-square regression results

The two relationships between SRP22 and SRP27 are:

$$x_{SRP22} = -0.01 + 1.0049x_{SRP27} \quad (9)$$

from the pre BIPM visit, with the uncertainties  $u(a_0) = 0.52 \text{ nmol mol}^{-1}$ ,  $u(a_1) = 0.0039$ ,  $\text{cov}(a_0, a_1) = -9.63 \times 10^{-4}$ ,

and 
$$x_{SRP22} = 0.03 + 1.0009x_{SRP27} \quad (10)$$

from the post BIPM visit, with the uncertainties  $u(a_0) = 0.52 \text{ nmol mol}^{-1}$ ,  $u(a_1) = 0.0039$ ,  $\text{cov}(a_0, a_1) = -9.56 \times 10^{-4}$ .

To assess the agreement of the standards from equations 11 and 12, the difference between the calculated slope value and unity, and the intercept value and zero, together with their measurement uncertainties need to be considered. In both comparisons, the value of the intercept is consistent with an intercept of zero, considering the uncertainty in the value of this parameter; i.e.  $|a_0| < 2u(a_0)$ , and the value of the slope is consistent with a slope of 1; i.e.  $|1 - a_1| < 2u(a_1)$ .

### 15. Degrees of equivalence

Degrees of equivalence are calculated at two nominal ozone amount-of-substance fractions among the twelve measured in each comparison, in the nominal range  $0 \text{ nmol mol}^{-1}$  to  $500 \text{ nmol mol}^{-1}$ :  $80 \text{ nmol mol}^{-1}$  and  $420 \text{ nmol mol}^{-1}$ . These values correspond to points number 3 and 4 recorded in each comparison. As an ozone generator has limited reproducibility, the ozone amount-of-substance fractions measured by the ozone standards can differ from the nominal values. However, as stated in the protocol, the value measured by the common reference SRP27 was expected to be within  $\pm 15 \text{ nmol mol}^{-1}$  of the nominal value. Hence, it is meaningful to compare the degree of equivalence calculated for all the participants at the same nominal value.

#### 15.1. Definition of the degrees of equivalence

Within protocol B, the degree of equivalence of the participant  $i$ , at a nominal value  $x_{\text{nom}}$  is defined as:

$$D = x_i - \hat{x}_{SRP27} \quad (11)$$

Where  $x_i$  is the measurement results of the national standard at the nominal value  $x_{\text{nom}}$ , 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:

$$u(D) = \sqrt{u^2(x_i) + u^2(\hat{x}_{SRP27})} \quad (12)$$

where  $u(x_i)$  is the measurement uncertainties of the participant  $i$  and  $u(\hat{x}_{SRP27})$  is the uncertainty associated with the predicted value of SRP27.

### 15.2. 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  $\bar{x}_{TS}$  are 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  $x_{TS}$  ( $x_{RS} = a_{RS,TS} x_{TS} + b_{RS,T}$ ) are 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 is evaluated using the linear relationships between the two instruments calculated above.

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

$$u(\hat{x}_{RS}) = \sqrt{u^2(b_{RS,TS}) + x_{TS}^2 \cdot u^2(a_{RS,TS}) + a_{RS,TS}^2 \cdot u^2(x_{TS}) + 2 \cdot x_{TS} \cdot u(a_{RS,TS}, b_{RS,TS})} \quad (13)$$

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.

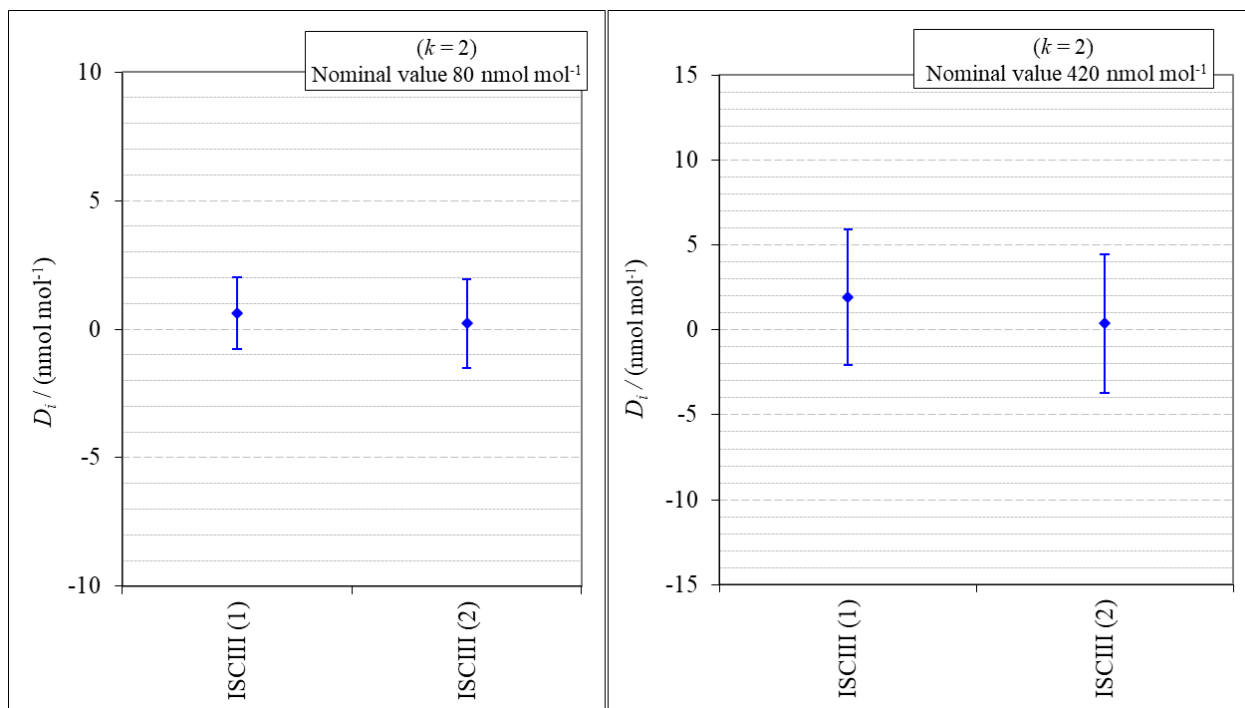
### 15.3. Values of the degrees of equivalence

When protocol B is followed, the national and reference standards are compared twice to monitor the transfer standard stability. Therefore, two degrees of equivalence are calculated at each nominal ozone amount-of-substance fraction.

The degrees of equivalence and their uncertainties calculated in the form BIPM.QM-K1-R2-ISCIII-23 are reported in the table below. Corresponding graphs of equivalence are displayed in Figure 1. The expanded uncertainties are calculated with a coverage factor  $k = 2$ .

**Table 4 : degrees of equivalence of the ISCIII at the ozone nominal amount-of-substance fractions 80 nmol mol<sup>-1</sup> and 420 nmol mol<sup>-1</sup>**

Nominal value	$x_i /$	$u_i /$	$x_{SRP27} /$	$u_{SRP27} /$	$D_i /$	$u(D_i) /$	$U(D_i) /$
	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )	(nmol mol <sup>-1</sup> )
80	81.37	0.37	80.84	0.78	0.53	0.86	1.72
420	421.30	1.26	419.42	1.59	1.88	2.03	4.05
80	80.77	0.37	80.62	0.78	0.15	0.86	1.71
420	423.13	1.27	422.68	1.60	0.45	2.04	4.08



**Figure 1: degrees of equivalence of the ISCIII at the two nominal ozone amount-of-substance fractions 80 nmol mol<sup>-1</sup> and 420 nmol mol<sup>-1</sup>**

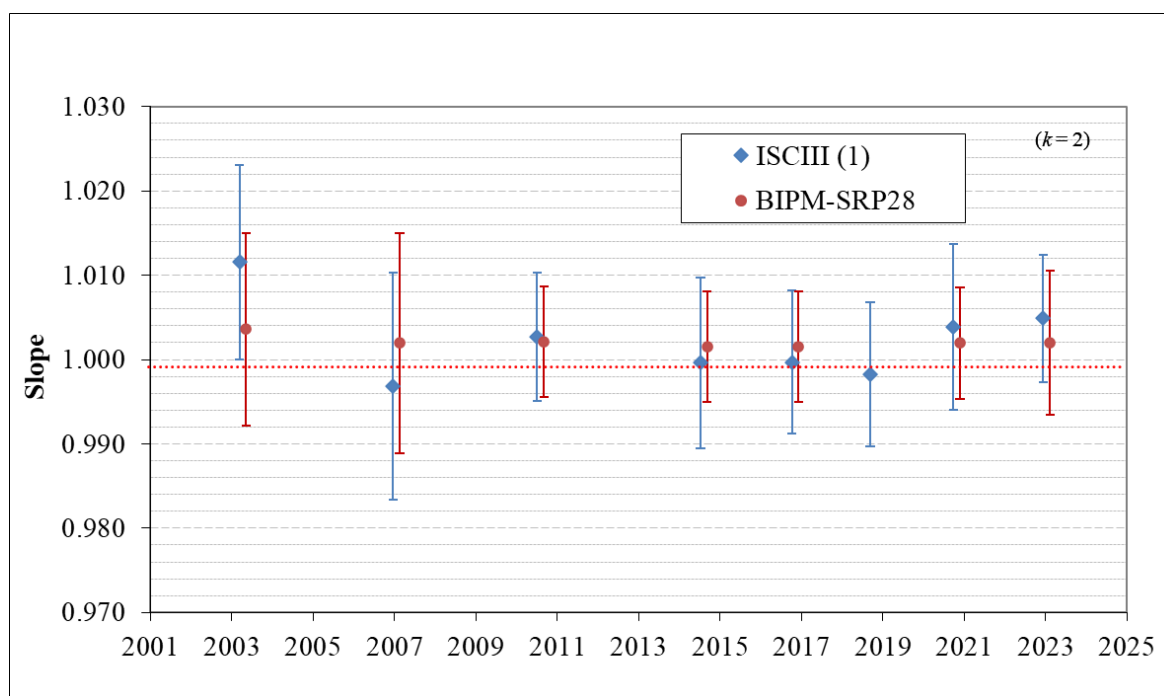
The degrees of equivalence between the ISCIII standard and the common reference standard BIPM SRP27 indicate good agreement between the standards. A discussion on the relation between degrees of equivalence and CMC statements can be found in [1].

## 16. Stability of the transfer standard

The slope of the linear relationship deduced from the two comparisons performed between the ISCIII national standard SRP22 and the common reference standard SRP27 shows a decrease of 0.4% (equations 13 and 14). This is very small compared to the uncertainties. The transfer standard TEI49iPS-0734626227 can be considered stable over the course of this comparison.

## 17. History of comparisons between BIPM SRP27, SRP28 and ISCIII SRP22

Results of the previous comparison performed with ISCIII during the pilot study CCQM-P28 and the key comparison BIPM.QM-K1 are displayed in Figure 2 together with the results of this comparison. The slopes  $a_1$  of the linear relation  $x_{SRPn} = a_0 + a_1 x_{SRP27}$  are represented together with their associated uncertainties calculated at the time of each comparison. Figure 2 shows that all standards included in these comparisons stayed in close agreement.



**Figure 2 : Results of previous comparisons between SRP27, SRP28 and ISCIII-SRP22 realised at the BIPM. Uncertainties are calculated at  $k = 2$ , with the uncertainty budget in use at the time of each comparison.**

## 18. Summary of previous comparisons included in BIPM.QM-K1

The comparison with ISCIII is the eight one since the start of BIPM.QM-K1 in 2007. An updated summary of BIPM.QM-K1 results can be found in the key comparison database: <http://kcdb.bipm.org/appendixB/>.

## 19. Conclusion

For the eighth time since the launch of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of Spain, maintained by the ISCIII, and the common reference standard of the key comparison, maintained by the BIPM. The instruments have been compared over a nominal ozone amount fraction range of 0 nmol mol<sup>-1</sup> to 500 nmol mol<sup>-1</sup>. Degrees of equivalence of this comparison indicated very good agreement between both standards.

## 20. References

- [1] Viallon J., Moussay P., Esler M., Wielgosz R., Bremser W., Novák J., Vokoun M., Botha A., Janse Van Rensburg M., Zellweger C., et al., 2006\_PILOT STUDY: International Comparison CCQM-P28: Ozone at ambient level, *Metrologia*, **43, Tech. Suppl.**, 08010, <https://doi.org/10.1088/0026-1394/43/1A/08010>
- [2] Paur R.J., Bass A.M., Norris J.E. and Buckley T.J. NIST 2003 Standard reference photometer for the assay of ozone in calibration atmospheres *Env. Sci. Technol.* **NISTIR 6369**, February 2003, p 25,
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- [4] Davis R.S., Niederhauser B., Hodges J.T., Viallon J. and Wielgosz R.I. BIPM 2022 Units and values for the ozone absorption cross section at 253.65 nm (air) with appropriate significant digits and rounding for use in documentary standards **Rapport BIPM-2022/02** p 16, <https://www.bipm.org/documents/20126/27085544/RapportBIPM-2022-02.pdf/f93def70-2544-ff13-ae63-3bc73f36688e?version=1.3&t=1646932738907&download=true>

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- [6] 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, [https://www.bipm.org/documents/20126/43885127/CCQM20-30\\_CCQM\\_recommendation\\_on\\_Ozone\\_X-Section\\_Final\\_Approved.docx.pdf/9ea02056-4a7c-b2d3-b1ea-9a9903e91fdd](https://www.bipm.org/documents/20126/43885127/CCQM20-30_CCQM_recommendation_on_Ozone_X-Section_Final_Approved.docx.pdf/9ea02056-4a7c-b2d3-b1ea-9a9903e91fdd) 2022-03-22
- [7] Hodges J.T., Viallon J., Brewer P.J., Drouin B.J., Gorshelev V., Janssen C., Lee S., Possolo A., Smith M.A.H., Walden J., et al., 2019, Recommendation of a consensus value of the ozone absorption cross-section at 253.65 nm based on a literature review, *Metrologia*, **56**, 034001, <https://doi.org/10.1088/1681-7575/ab0bdd>
- [8] Viallon J., Moussay P., Norris J.E., Guenther F.R. and Wielgosz R.I., 2006, A study of systematic biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard Reference Photometer, *Metrologia*, **43**, 441-450, <https://doi.org/10.1088/0026-1394/43/5/016>
- [9] Viallon J., Moussay P., Idrees F. and Wielgosz R.I. BIPM 2010 Upgrade of the BIPM Standard Reference Photometers for Ozone and the effect on the on-going key comparison BIPM.QM-K1 **Rapport BIPM-2010/07** p 16,
- [10] Viallon J., Moussay P., Idrees F. and Wielgosz R.I. BIPM 2022 Upgrade of the electronics modules of the BIPM Standard Reference Photometers for ozone and the effect on the on-going key comparison BIPM.QM-K1 **Rapport BIPM-2022/01** p 8, <https://www.bipm.org/documents/20126/27085544/RapportBIPM-2022-01.pdf/755a1be0-d505-3d99-0a6f-f332862de531?version=1.2&t=1646737070908&download=true>
- [11] Bremser W., Viallon J. and Wielgosz R.I., 2007, Influence of correlation on the assessment of measurement result compatibility over a dynamic range, *Metrologia*, **44**, 495-504, <https://doi.org/10.1088/0026-1394/44/6/009>
- [12] ISO 6143: 2001 Gas analysis - Determination of the composition of calibration gas mixtures - Comparison methods (International Organization for Standardization)

## Appendix 1 - Form BIPM.QM-K1-R2-ISCI-23

See the following pages.

**OZONE COMPARISON RESULT - PROTOCOL B - WITH A  
TRANSFER STANDARD**

<b>Participating institute information</b>	
<b>Institute</b>	<b>INSTITUTO DE SALUD CARLOS III</b>
<b>Address</b>	<b>Crta. Majadahonda-Pozuel Km.2 Majadahonda (Madrid)</b>
<b>Contact</b>	<b>BEATRIZ NUÑEZ, SAÚL GARCIA DOS SANTOS-ALVES</b>
<b>Email</b>	<a href="mailto:b.nunez@isciii.es">b.nunez@isciii.es</a> ; <a href="mailto:sgarcia@isciii.es">sgarcia@isciii.es</a>
<b>Telephone</b>	<b>+34 91822 35 06</b>

<b>Instruments information</b>			
	<b>Reference Standard</b>	<b>National Standard</b>	<b>Transfer Standard</b>
<b>Manufacturer</b>	NIST	NIST	THERMO
<b>Type</b>	SRP	SRP	49 iPS
<b>Serial number</b>	SRP27	SRP22	0734626227
<b>ozone cross-section value</b>	$308.32 \text{ atm}^{-1} \text{ cm}^{-1}$	$308.32 \text{ atm}^{-1} \text{ cm}^{-1}$	$308.32 \text{ atm}^{-1} \text{ cm}^{-1}$

**Content of the report**

page 1	General informations
page 2	Summary of the comparison results
page 3	calculation of the national standard vs reference standard first relationship
page 4	calculation of the national standard vs reference standard second relationship
page 5	Data reporting sheet - first comparison of the transfer standard vs the national standard
page 7	Calibration of the transfer standard by the reference standard at the BIPM
page 9	Data reporting sheet - second comparison of the transfer standard vs the national standard
page 11	Uncertainty budgets

*This workbook contains macros. It is recommended not to use them.*

*Please complete the cells containing blue stars only.*

*After completion of the appropriate section of this report, please send to Joële Viallon by email ([jviallon@bipm.org](mailto:jviallon@bipm.org)), fax (+33 1 45342021), or mail (BIPM, Pavillon de Breteuil, F-92312 Sèvres)*



**comparison national standard (RS) vs reference standard (NS)**

**Summary of comparison results**

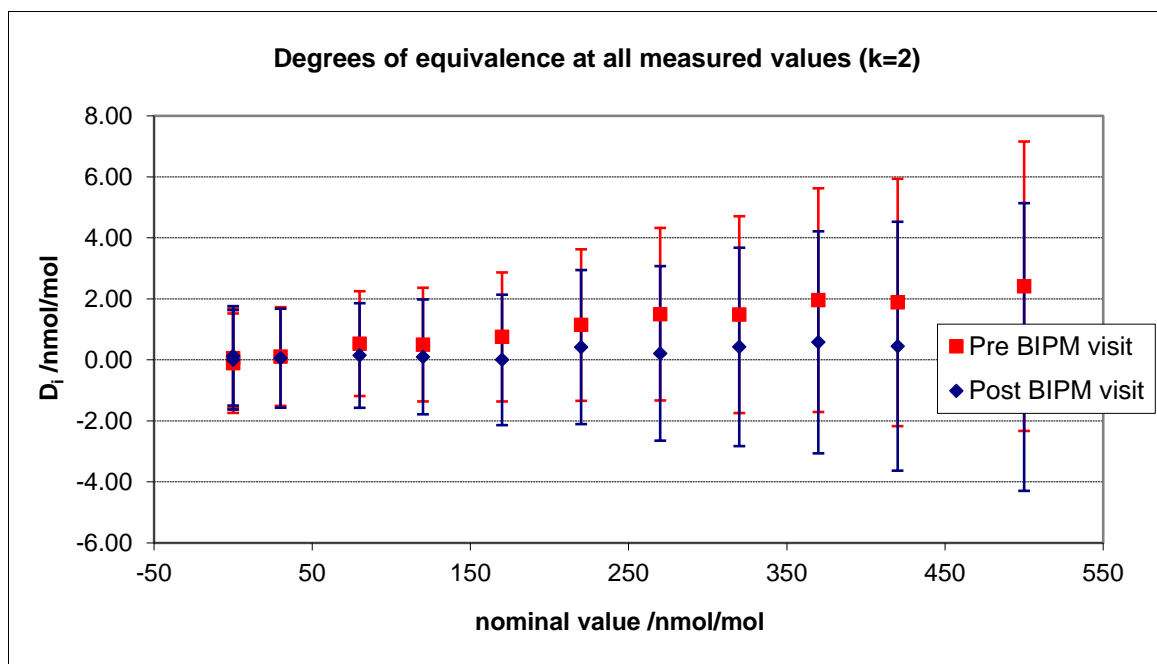
**Equation** 
$$x_{NS} = a_{NS,RS} x_{RS} + b_{NS,RS}$$

**Least-square regression parameters**

	$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
first comparison	1.0049	0.0039	-0.01	0.52	-9.63E-04
second comparison	1.0009	0.0039	0.03	0.52	-9.56E-04

**Degrees of equivalence at 80 nmol/mol and 420 nmol/mol:**

	Nom value (nmol/mol)	$D_i$ (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
first comparison	80	0.53	0.86	1.72
	420	1.88	2.03	4.05
second comparison	80	0.15	0.86	1.71
	420	0.45	2.04	4.08



**Calculation of the National Standard vs Reference Standard comparison results through the first National Standard vs Transfer Standard comparison**

**First comparison results**

Nominal value	National standard measurement results		Transfer standard measurement results		Reference Standard predicted values	
	$x_{NS}$ nmol/mol	$u(x_{NS})$ nmol/mol	$x_{TS}$ nmol/mol	$u(x_{TS})$ nmol/mol	$x'_{RS}$ nmol/mol	$u(x'_{RS})$ nmol/mol
0	-0.12	0.28	0.00	0.67	-0.01	0.77
220	223.78	0.71	221.00	0.74	222.64	1.02
80	81.37	0.37	80.25	0.68	80.84	0.78
420	421.30	1.26	416.32	0.90	419.42	1.59
120	119.26	0.45	117.89	0.69	118.76	0.82
320	321.05	0.98	317.21	0.81	319.57	1.28
30	29.98	0.29	29.66	0.67	29.87	0.75
370	374.72	1.13	370.01	0.86	372.76	1.44
170	167.98	0.56	166.00	0.71	167.23	0.90
500	501.15	1.49	495.05	0.98	498.73	1.85
270	270.42	0.84	266.94	0.77	268.92	1.14
0	0.06	0.28	0.02	0.67	0.01	0.77

Reference standard predicted values are deduced from the transfer standard measurement results using the calibration performed at the BIPM, with the parameters calculated in Excel Worksheet 4 (page 7)

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

$a_{RS,TS}$	1.0075	$b_{NRS,TS}$ (nmol/mol)	-0.01	$u(a, b)$	-4.36E-04
$u(a_{RS,TS})$	0.0033	$u(b_{RS,TS})$ (nmol/mol)	0.36		

Degrees of Equivalence		$D_i = x_{NS} - x'_{RS}$		
Point Number	Nom value (nmol/mol)	$D_i$ (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
1	0	-0.11	0.82	1.63
2	220	1.14	1.24	2.48
3	80	0.53	0.86	1.72
4	420	1.88	2.03	4.05
5	120	0.50	0.93	1.86
6	320	1.48	1.61	3.23
7	30	0.11	0.81	1.62
8	370	1.96	1.83	3.67
9	170	0.75	1.06	2.11
10	500	2.42	2.37	4.74
11	270	1.50	1.41	2.83
12	0	0.05	0.82	1.63

Least-square regression parameters				
$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a, b)$
1.0048990	0.0039117	-0.0111520	0.5215561	-0.0009625

**Calculation of the National Standard vs Reference Standard comparison results through the second National Standard vs Transfer Standard comparison**

**Second comparison results**

Nominal value	National standard measurement results		Transfer standard measurement results		Reference Standard predicted values	
	$x_{NS}$ nmol/mol	$u(x_{NS})$ nmol/mol	$x_{TS}$ nmol/mol	$u(x_{TS})$ nmol/mol	$x'_{RS}$ nmol/mol	$u(x'_{RS})$ nmol/mol
0	0.06	0.28	0.07	0.67	0.06	0.77
220	228.67	0.72	226.57	0.75	228.25	1.03
80	80.77	0.37	80.04	0.68	80.62	0.78
420	423.13	1.27	419.56	0.90	422.68	1.60
120	123.30	0.46	122.30	0.69	123.20	0.82
320	323.70	0.99	320.89	0.81	323.27	1.29
30	30.72	0.29	30.45	0.67	30.66	0.76
370	371.03	1.12	367.72	0.85	370.45	1.43
170	170.31	0.57	169.06	0.71	170.31	0.90
500	496.80	1.48	492.71	0.98	496.38	1.84
270	273.88	0.85	271.65	0.78	273.67	1.15
0	0.11	0.28	-0.01	0.67	-0.02	0.77

Reference standard predicted values are deduced from the transfer standard measurement results using the calibration performed at the BIPM, with the parameters calculated in Excel Worksheet 4 (page 7)

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

$a_{RS,TS}$	1.0075	$b_{RS,TS}$ (nmol/mol)	-0.01	$u(a, b)$	-4.36E-04
$u(a_{RS,TS})$	0.0033	$u(b_{RS,TS})$ (nmol/mol)	0.36		

Degrees of Equivalence		$D_i = x_{NS} - x'_{RS}$		
Point Number	Nom value (nmol/mol)	$D_i$ (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
1	0	0.00	0.82	1.63
2	220	0.42	1.26	2.52
3	80	0.15	0.86	1.71
4	420	0.45	2.04	4.08
5	120	0.10	0.94	1.88
6	320	0.43	1.63	3.25
7	30	0.06	0.81	1.62
8	370	0.58	1.82	3.64
9	170	0.00	1.07	2.14
10	500	0.42	2.36	4.72
11	270	0.21	1.43	2.86
12	0	0.13	0.82	1.63

Least-square regression parameters				
$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a, b)$
1.0009173	0.0038931	0.0341715	0.5207833	-0.0009562

**Data reporting sheet**  
**First comparison of transfer standard (TS) vs national standard (NS)**

<b>Operator</b>	<b>BNC</b>	<b>Location</b>	<b>51-02-23A</b>
<b>Comparison begin date / time</b>	<b>10.04.23 / 16:05h</b>	<b>Comparison end date / time</b>	<b>11.04.23 / 5:50h</b>

measurement results						
	Transfer standard (TS)			National Standard (NS)		
Nominal value	$x_{TS}$ nmol/mol	$s_{TS}$ nmol/mol	$u(x_{TS})$ nmol/mol	$x_{NS}$ nmol/mol	$s_{NS}$ nmol/mol	$u(x_{NS})$ nmol/mol
0	0.00	0.25	0.67	-0.12	0.10	0.28
220	221.00	0.23	0.74	223.78	0.39	0.71
80	80.25	0.24	0.68	81.37	0.25	0.37
420	416.32	0.37	0.90	421.30	0.26	1.26
120	117.89	0.12	0.69	119.26	0.22	0.45
320	317.21	0.33	0.81	321.05	0.50	0.98
30	29.66	0.23	0.67	29.98	0.28	0.29
370	370.01	0.48	0.86	374.72	0.22	1.13
170	166.00	0.34	0.71	167.98	0.42	0.56
500	495.05	0.42	0.98	501.15	0.37	1.49
270	266.94	0.42	0.77	270.42	0.22	0.84
0	0.02	0.11	0.67	0.06	0.15	0.28

Note : according to the protocol, these measurement results are the last TS-NS comparison measurement results recorded

Covariance terms in between two measurement results of the national standard

Equation  $u(x_i, x_j) = \alpha \cdot x_i \cdot x_j$  Value of  $\alpha$  0.00E+00

<b>Comparison conditions</b>	
Ozone generator manufacturer	NIST
Ozone generator type	NIST-SRP
Ozone generator serial number	SRP22
Room temperature(min-max) / °C	19,8 °C -20,6 °C
Room pressure (average) / hpa	934,9 hPa
Zero air source	Air compressor with scrubbers for NOx, VOCs, O3
Reference air flow rate (L/min)	5 l/min
Sample flow rate (L/min)	5 l/min
Instruments stabilisation time	48 hours
Instruments acquisition time /s (one measurement)	1 min
Instruments averaging time /s	SRP22: none ; TE 49 iPS: 1min
Total time for ozone conditioning	2 hours
Ozone mole fraction during conditioning (nmol/mol)	500 nmol/mol +- 15nmol/mol
Comparison repeated continuously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	8

**Instruments checks and adjustments**

**National Standard**

Pressure  
Temperature  
Scaler Test  
Dark counts  
Stability Test  
NO ADJUSTEMENTS WERE NECESSARY

**Transfer Standard**

INSTRUMENT CHECKS  
Pressure  
Temperature: Bench and O3 lamp  
Flow  
Intensities  
NO ADJUSTMENTS WERE NECESSARY

## calibration of the transfer standard (TS) by the reference standard (RS)

<b>Operator</b>	F.Idrees	<b>Location</b>	BIPM/MC/CHEM09
<b>Comparison begin date / time</b>	2023-05-17 15:38	<b>Comparison end date / time</b>	2023-05-17 17:48

### Calibration results

**Equation** 
$$x_{RS} = a_{RS,TS} x_{TS} + b_{RS,TS}$$

Least-square regression parameters				
$a_{RS,TS}$	$u(a_{RS,TS})$	$b_{RS,TS}$ (nmol/mol)	$u(b_{RS,TS})$ (nmol/mol)	$u(a,b)$
<b>1.0074689</b>	<b>0.0033394</b>	<b>-0.0128201</b>	<b>0.3610382</b>	<b>-0.0004364</b>

*(Least-square regression parameters will be computed by the BIPM using the software OzonE v2.0)*

### Measurement results

Nominal value	Transfer standard (TS)			Reference Standard (RS)		
	$x_{TS}$ nmol/mol	$s_{TS}$ nmol/mol	$u(x_{TS})$ nmol/mol	$x_{RS}$ nmol/mol	$s_{RS}$ nmol/mol	$u(x_{RS})$ nmol/mol
<b>0</b>	0.09	0.13	0.67	0.06	0.24	0.28
<b>220</b>	216.43	0.17	0.74	218.04	0.12	0.70
<b>80</b>	84.80	0.21	0.68	85.33	0.16	0.37
<b>420</b>	430.35	0.29	0.90	433.51	0.27	1.30
<b>120</b>	121.34	0.14	0.69	122.35	0.26	0.45
<b>320</b>	317.80	0.27	0.80	320.19	0.24	0.98
<b>30</b>	37.05	0.15	0.67	37.26	0.18	0.30
<b>370</b>	373.34	0.28	0.85	376.29	0.17	1.13
<b>170</b>	168.56	0.21	0.71	169.68	0.13	0.57
<b>500</b>	528.39	0.36	1.00	532.32	0.23	1.58
<b>270</b>	265.88	0.20	0.77	267.95	0.19	0.83
<b>0</b>	0.07	0.17	0.67	0.19	0.12	0.28

*Note : according to the protocol, these measurement results are the last TS-RS comparison measurement results*

Covariance terms in between two measurement results of the reference standard

Equation 
$$u(x_i, x_j) = \alpha \cdot x_i \cdot x_j$$

Value of  $\alpha$  8.53E-06

<b>Comparison conditions</b>	
Ozone generator manufacturer	Envionics
Ozone generator type	Model 6100
Ozone generator serial number	3128
Room temperature(min-max) / °C	22.7 - 22.72
Room pressure (average) / hpa	1015.5 - 1016.3
Zero air source	compressor + BekoKAT + dryer+ aadco 737-R
Reference air flow rate (L/min)	14
Sample flow rate (L/min)	10
Instruments stabilisation time	> 8 hours
Instruments acquisition time /s (one measurement)	5 s
Instruments averaging time /s	5 s
Total time for ozone conditioning	>12 hours
Ozone mole fraction during conditioning (nmol/mol)	600 nmol/mol
Comparison repeated continously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	
Total number of comparison repeats realised	15
Data files names and location	<a href="#">G:\Gas\Ozone\BIPM.QM-K1\Participants results\2305 ISCIII</a> Cal23051500.xls to Cal23051707.xls

**Instruments checks and adjustments**

**Reference Standard**

Pressure adjusted to lab standard

**Transfer Standard**

**Data reporting sheet**  
**Second comparison of transfer standard (TS) vs national standard (NS)**

<b>Operator</b>	BNC	<b>Location</b>	51-02-23A
<b>Comparison begin date / time</b>	15-06-23/ 16:06h	<b>Comparison end date / time</b>	16-06-2023 / 6:15h

**measurement results**

Nominal value	Transfer standard (TS)			National Standard (NS)		
	$x_{TS}$ nmol/mol	$s_{TS}$ nmol/mol	$u(x_{TS})$ nmol/mol	$x_{NS}$ nmol/mol	$s_{NS}$ nmol/mol	$u(x_{NS})$ nmol/mol
0	0.07	0.25	0.67	0.06	0.28	0.28
220	226.57	0.24	0.75	228.67	0.38	0.72
80	80.04	0.21	0.68	80.77	0.24	0.37
420	419.56	0.36	0.90	423.13	0.34	1.27
120	122.30	0.27	0.69	123.30	0.24	0.46
320	320.89	0.22	0.81	323.70	0.29	0.99
30	30.45	0.14	0.67	30.72	0.18	0.29
370	367.72	0.41	0.85	371.03	0.38	1.12
170	169.06	0.34	0.71	170.31	0.23	0.57
500	492.71	0.37	0.98	496.80	0.37	1.48
270	271.65	0.39	0.78	273.88	0.34	0.85
0	-0.01	0.17	0.67	0.11	0.17	0.28

Note : according to the protocol, these measurement results are the last TS-NS comparison measurement results recorded

Covariance terms in between two measurement results of the national standard

Equation  $u(x_i, x_j) = \alpha \cdot x_i \cdot x_j$  Value of  $\alpha$  0.00E+00

**Comparison conditions**

Ozone generator manufacturer	NIST
Ozone generator type	NIST-SRP
Ozone generator serial number	SRP22
Room temperature(min-max) / °C	20,0-21,0 °C
Room pressure (average) / hpa	933,40 hpa
Zero air source	Air compressor with scrubbers for NOx, VOCs, O3
Reference air flow rate (L/min)	5 L/min
Sample flow rate (L/min)	5 L/min
Instruments stabilisation time	48h
Instruments acquisition time /s (one measurement)	1 min
Instruments averaging time /s	SRP22: none ; TE 49 iPS: 1min
Total time for ozone conditioning	2 hours
Ozone mole fraction during conditioning (nmol/mol)	500 nmol/mol +- 15nmol/mol
Comparison repeated continuously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	8

**Instruments checks and adjustments**

**National Standard**

Pressure  
Temperature  
Scaler Test  
Dark counts  
Stability Test  
NO ADJUSTEMENTS WERE NECESSARY

**Transfer Standard**

INSTRUMENT CHECKS  
Pressure  
Temperature: Bench and O3 lamp  
Flow  
Intensities  
NO ADJUSTMENTS WERE NECESSARY

**Uncertainty budgets (description or reference )**

**Reference Standard**

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**Transfer Standard**

Component (y)	Distribution	Standard Uncertainty u(y)
<b>Repeatability</b>		Experimental standard deviation
<b>Reproducibility</b>	Rectangular	reproducibility/2√3

**Repeatability:** maximal value of the experimental standard deviation observed at ISCIII

**Reproducibility:** difference between the maximum value of the slope of the regression line between the national standard and the transfer standard.

The transfer standard uncertainty can be summarised by the equation:

$$u_{PT} = \sqrt{(0,0014 x)^2 + 0,67^2}$$

**National Standard**

Component (y)	Uncertainty u(y)				Sensitivity coefficient $c_i = \partial x / \partial y$	Contribution to u(x) $ c_i  \cdot u(y)$ nmol/mol
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty u(y)		
<b>Optical Path-length, <math>L_{opt}</math></b>	Measurement Scale	Rect.	0,0005 cm	0,52 cm	$- x/L_{opt}$	$2,89 \times 10^{-3} x$
	Repeatability	Normal	0,004 cm			
	Bias	Rect.	0,52 cm			
<b>Pressure, P</b>	P Gauge	Rect.	0,029 kPa	0,034 kPa	$- x/P$	$3,37 \times 10^{-4} x$
	Difference between cells	Rect.	0,017 kPa			
<b>Temperatura, T</b>	T probe	Rect.	0,029 K	0,07K	$x/T$	$2,29 \times 10^{-4} x$
	Residual Bias	Rect.	0,058 K			
<b>Ratio of Intensities, D</b>	Scaler resolution	Rect.	$8,0 \times 10^{-6}$	$1,4 \times 10^{-5}$	$x/D \ln(D)$	0,28
	Repeatability	Normal	$1,1 \times 10^{-5}$			
<b>Absortion Cross section, <math>\sigma</math></b>	Conventional value		-	-	-	-

$$u(x) = \sqrt{(0.28)^2 + (2.92 \cdot 10^{-3} x)^2} \text{ nmol/mol}$$

This numerical equation has been calculated without the uncertainty of absortion cross section