Final report, Ongoing Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with ISCIII, (February 2021)

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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 to 500 nmol/mol.

Contents:

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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 preformed 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_{nom}: nominal ozone amount-of-substance fraction in dry air furnished by the ozone generator
- $x_{\mathrm{A},i}$: ith measurement of the nominal value x_{nom} by the photometer A.
- $\bar{x}_{\mathrm{A}}$: the mean of N measurements of the nominal value x_{nom} measured by the photometer A: $\bar{x}_{\mathrm{A}} = \frac{1}{N}\sum_{i=1}^{N} x_{\mathrm{A},i}$
- s_{A}: standard deviation of N measurements of the nominal value x_{nom} measured by the photometer A: $s_{\mathrm{A}}^{2} = \frac{1}{N-1}\sum_{i=1}^{N}(x_{\mathrm{A},i} - \bar{x}_{\mathrm{A}})^{2}$
- 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: $x_{\mathrm{A}} = a_{\mathrm{A,B}} x_{\mathrm{B}} + b_{\mathrm{A,B}}$. With this notation, the photometer A is compared versus the photometer B. $a_{\mathrm{A,B}}$ is dimensionless and $b_{\mathrm{A,B}}$ is expressed in units of nmol/mol.

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 25 January 2021 to 5 March 2021 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/utils/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 January 2021. 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 March 2021 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 NOx, VOCs, O_3, 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. Each of these points is an average of 10 single measurements.

For each nominal value of the ozone amount-of-substance fraction x_{nom} furnished by the ozone generator, the standard deviation s_{SRP22} on the set of 10 consecutive measurements $x_{\mathrm{SRP22},i}$ recorded by SRP22 was calculated. The measurement results were considered as valid if s_{SRP22} was less than 1 nmol/mol, 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. This air is used to provide reference air as well as the ozone-air mixture to each ozone photometer.

Ambient air is used as the source for reference air. The air is 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 μmol/mol. The mole fraction of volatile organic hydrocarbons in the reference air was measured (November 2002), with no mole fraction of any detected component exceeding 1 nmol/mol.

A common dual external manifold in Pyrex is used to furnish the necessary flows of reference air and ozone-air mixtures to the ozone photometers. The two columns of this manifold are vented to atmospheric pressure.

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 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. Each of these points is an average of 10 single measurements.

For each nominal value of the ozone amount-of-substance fraction x_{nom} furnished by the ozone generator, the standard deviation s_{SRP27} on the set of 10 consecutive measurements $x_{\mathrm{SRP27},i}$ recorded by BIPM-SRP27 was calculated. The measurement results were considered as valid if s_{SRP27} was less than 1 nmol/mol, 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 compare with BIPM-SRP27 to verify that they are in agreement and also to follow the stability of BIPM-SPR27 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-ISCIII-21 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

All instruments included in this comparison were Standard Reference Photometers 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-of-substance 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 concentration (C) of ozone is calculated from:

$$C = \frac{-1}{2\sigma L_{\text{opt}}} \frac{T}{T_{\text{std}}} \frac{P_{\text{std}}}{P} \ln(D) \qquad (1)$$

where

- σ is the absorption cross-section of ozone at 253.7 nm under standard conditions of temperature and pressure, 1.1476×10^{-17} cm^2 molecule^{-1} [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

$$T_{\text{r}} = \frac{I_{\text{ozone}}}{I_{\text{air}}} \qquad (2)$$

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 a amount-of-substance fraction (x) of ozone in air:

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

where

N_A is the Avogadro constant, 6.022142×10^{23} mol^{-1}, and

R is the gas constant, 8.314472 J mol^{-1} K^{-1}

The formulation implemented in the SRP software is:

$$x = \frac{-1}{2\alpha_x L_{\text{opt}}} \frac{T}{T_{\text{std}}} \frac{P_{\text{std}}}{P} \ln(D) \qquad (4)$$

where

α_x is the linear absorption coefficient at standard conditions, expressed in cm^{-1}, linked to the absorption cross-section with the relation:

$$\alpha_x = \sigma \frac{N_A}{R} \frac{P_{\text{std}}}{T_{\text{std}}} \qquad (5)$$

12.2. Absorption cross-section for ozone

The linear absorption coefficient under standard conditions α_x used within the SRP software algorithm is 308.32 cm^{-1}. This corresponds to a value for the absorption cross section σ of 1.1476×10^{-17} cm^2 molecule^{-1}, rather than the more often quoted 1.147×10^{-17} cm^2 molecule^{-1}. 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. A consensus value of 2.12 % at a 95 % level of confidence for the uncertainty of the absorption cross-section has been proposed by the BIPM and the NIST [4].

12.3. Condition of the BIPM SRPs

Compared to the original design described in [2], SRP27 and SRP28 have been modified to deal with two biases revealed by the study conducted by the BIPM and the NIST [4]. In 2009, an “SRP upgrade kit” was installed in the instruments, as described in the report [5].

12.4. Uncertainty budget of the common reference BIPM-SRP27

The uncertainty budget for the ozone amount-of-substance fraction in dry air (x) measured by the instruments BIPM-SRP27 and BIPM-SRP28 in the nominal range 0 nmol/mol to 500 nmol/mol 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 $u(x)$ $\lvert c_i \rvert \cdot u(y)$ nmol/mol
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$		
Optical Path L_{opt}	Measurement scale	Rectangular	0.0006 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89 \times 10^{-3}x$
	Repeatability	Normal	0.01 cm			
	Correction factor	Rectangular	0.52 cm			
Pressure P	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			
Temperature T	Temperature probe	Rectangular	0.03 K	0.07 K	$\frac{x}{T}$	$2.29 \times 10^{-4}x$
	Temperature gradient	Rectangular	0.058 K			
Ratio of intensities D	Scaler resolution	Rectangular	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D\ln(D)}$	0.28
	Repeatability	Triangular	1.1×10^{-5}			
Absorption Cross section σ	Hearn value		1.22×10^{-19} cm² molecule^{-1}	1.22×10^{-19} cm² molecule^{-1}	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$

Following this budget, as explained in the protocol of the comparison, the standard uncertainty associated with the ozone amount-of-substance fraction measurement with the BIPM SRPs can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u(x) = \sqrt{(0.28)^2 + (2.92 \cdot 10^{-3} x)^2} \tag{6}$$

12.5. Covariance terms for the common reference BIPM-SRP27

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

$$\boldsymbol{u}(\boldsymbol{x}_i, \boldsymbol{x}_j) = \boldsymbol{x}_i \cdot \boldsymbol{x}_j \cdot \boldsymbol{u}_\mathrm{b}^2 \tag{7}$$

where:

$$\boldsymbol{u}_\mathrm{b}^2 = \frac{\boldsymbol{u}^2(\boldsymbol{T})}{\boldsymbol{T}^2} + \frac{\boldsymbol{u}^2(\boldsymbol{P})}{\boldsymbol{P}^2} + \frac{\boldsymbol{u}^2(\boldsymbol{L}_\mathrm{opt})}{\boldsymbol{L}_\mathrm{opt}^{\ 2}} \tag{8}$$

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

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 [4]. 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 to 500 nmol/mol 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*)** $\lvert c_i \rvert \cdot u(y)$ **nmol/mol**
	Source	Distribution	**Standard Uncertainty**	**Combined standard uncertainty *u*(*y*)**		
Optical Path L_{opt}	Measurement Scale	Rectangular	0.0005cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89\times10^{-3}x$
	Repeatability	Normal	0.004 cm			
	Bias	Rectangular	0.52 cm			
Pressure *P*	Pressure gauge	Rectangular	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37\times10^{-4}x$
	Difference between cells	Rectangular	0.017 kPa			
Temperature *T*	Temperature probe	Rectangular	0.029 K	0.07 K	$\frac{x}{T}$	$2.29\times10^{-4}x$
	Residual Bias	Rectangular	0.058 K			
Ratio of intensities *D*	Scaler resolution	Rectangular	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D\ln(D)}$	0.28
	Repeatability	Normal	1.1×10^{-5}			
Absorption Cross section α	Hearn value		1.22×10^{-19} cm²/molecule	1.22×10^{-19} cm²/molecule	$-\frac{x}{\alpha}$	$1.06\times10^{-2}x$

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):

$$u(x) = \sqrt{(0.28)^2 + (2.92 \cdot 10^{-3} x)^2} \quad (9)$$

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.

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 to 500 nmol/mol 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*** = 1.35 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. Using a rectangular distribution, the standard relative uncertainty is 0.00028***x*.**

Table 3: TEI49iPS-0734626227 uncertainty budget

Source	**Distribution**	**Contribution to $u(x)$** $\lvert c_i \rvert \cdot u(y)$ **nmol/mol**
Repeatability	Normal	1.35 nmol/mol
Reproducibility	Rectangular	0.00028 x

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-ISCIII-21 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 [6], is an extension of the previously used software B_Least recommended by the ISO standard 6143:2001 [7]. It includes the possibility to consider 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 SRPn and SRP27 is obtained:

$$x_{\mathrm{SRP}n} = a_0 + a_1 x_{\mathrm{SRP27}} \qquad (10)$$

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. <u>Least-square regression results</u>

The two relationships between SRP22 and SRP27 are:

$$x_{SRP22} = -0.97 + 1.0039 x_{SRP27} \quad (11)$$

from the pre BIPM visit, with the uncertainties $u(a_0)$ = 0.93 nmol/mol, $u(a_1)$ = 0.0049, $\mathrm{cov}(a_0, a_1) = -2.8 \times 10^{-3}$,

and $$x_{SRP22} = 0.63 + 1.0026 x_{SRP27} \quad (12)$$

from the post BIPM visit, with the uncertainties $u(a_0)$ = 0.93 nmol/mol, $u(a_1)$ = 0.0049, $\mathrm{cov}(a_0, a_1) = -2.78 \times 10^{-3}$.

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 nmol/mol to 500 nmol/mol: 80 nmol/mol and 420 nmol/mol. 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 ±15 nmol/mol 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_{nom} is defined as:

$$D = x_i - \hat{x}_{\mathrm{SRP27}} \quad (13)$$

Where x_{i} 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:

$$u(D) = \sqrt{u^2(x_i) + u^2(\hat{x}_{\mathrm{SRP27}})} \quad (14)$$

where $u(x_{\mathrm{i}})$ 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 $\overline{x}_{\mathrm{RS}}$ and $\overline{x}_{\mathrm{TS}}$ are fitted using the generalised least square program OzonE, taking into account the associated uncertainties

$u(\overline{x}_{RS})$ and $u(\overline{x}_{TS})$, as well as covariance terms between the reference standard measurement results.

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

Then, for each value $\overline{x}_{TS}$ measured with the transfer standard during its comparison with the national standard, a predicted value $\hat{x}_{RS}$ for the reference standard 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:

$$u(\hat{x}_{RS}) = \sqrt{u^2(b_{RS,TS}) + x_{TS}^2 \cdot u^2(a_{RS,TS}) + a_{RS,TS}^2 \cdot u^2(x_{TS}) + 2 \cdot x_{TS} \cdot u(a_{RS,TS}, b_{RS,TS})} \quad (15)$$

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-19 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 and 420 nmol/mol

Nominal value	x_i / (nmol/mol)	u_i / (nmol/mol)	x_{SRP27} / (nmol/mol)	u_{SRP27} / (nmol/mol)	D_i / (nmol/mol)	$u(D_i)$ / (nmol/mol)	$U(D_i)$ / (nmol/mol)
80	80.93	0.37	81.55	1.44	-0.62	1.49	2.98
420	428.89	1.28	428.31	1.97	0.58	2.35	4.70
80	79.00	0.36	78.12	1.44	0.88	1.49	2.98
420	421.60	1.26	420.03	1.95	1.57	2.32	4.65

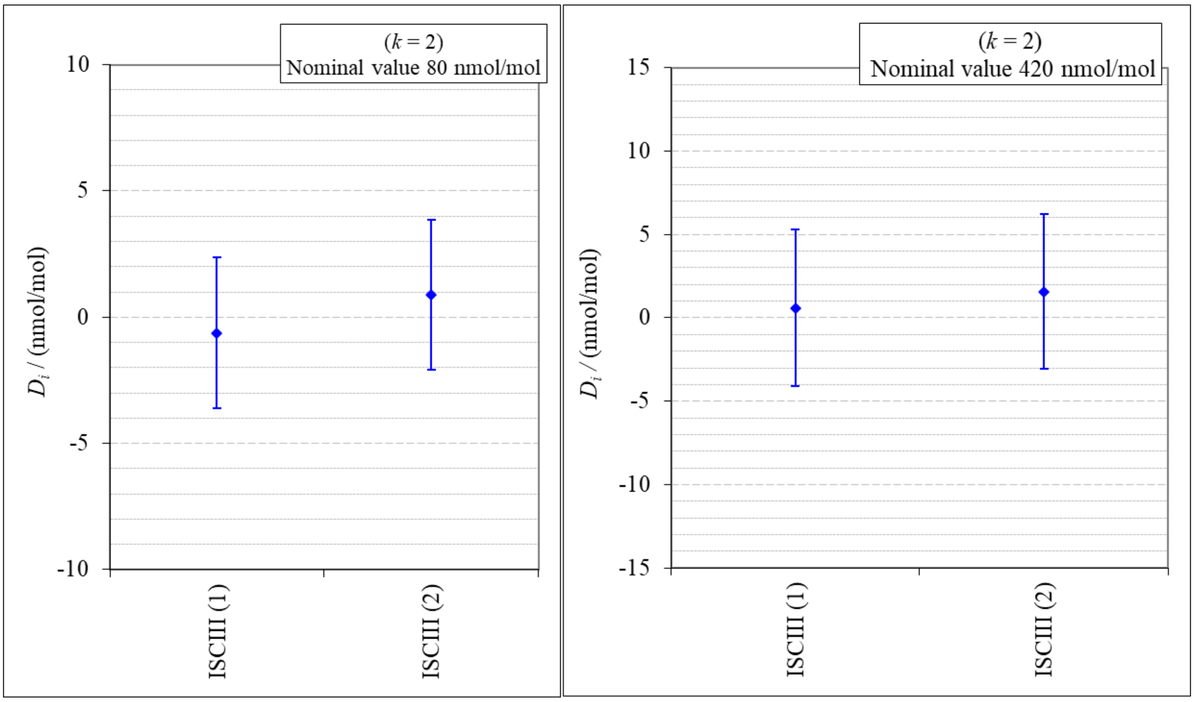

Figure 1: degrees of equivalence of the ISCIII at the two nominal ozone amount-of-substance fractions 80 nmol/mol and 420 nmol/mol

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 0.12% (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 $x_{SRPn} = a_0 + a_1\, x_{\mathrm{SRP27}}$ are represented together with their associated uncertainties calculated at the time of each comparison. Results of comparisons performed before 2009 have been corrected to take into account the changes in the reference BIPM-SRP27 described in [5] which explains the larger uncertainties associated with the corresponding slopes. Figure 2 shows that all standards included in these comparisons stayed in close agreement.

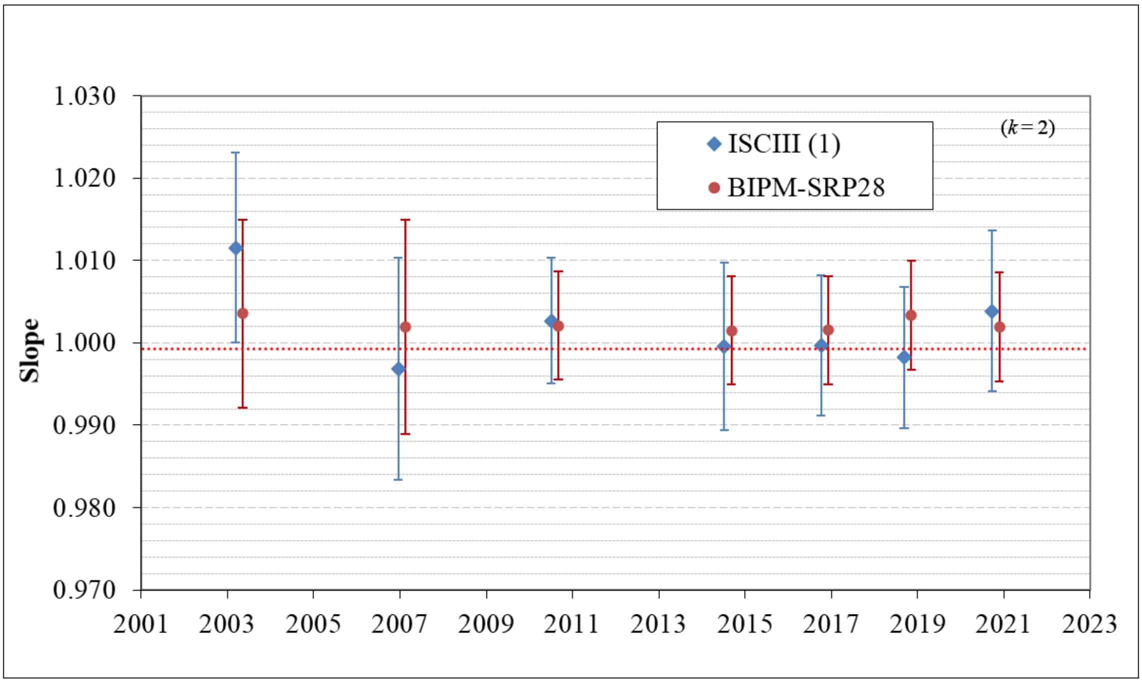

Figure 2 : Results of previous comparisons between SRP27, SRP28 and ISCIII-SRP22 realised at the BIPM. Uncertainties are calculated at *k* = 2, with the uncertainty budget in use at the time of each comparison.

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

The comparison with ISCIII is the third one in the 2017-2021 round of BIPM.QM-K1. 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 seventh 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-of-substance fraction range of 0 nmol/mol to 500 nmol/mol. Degrees of equivalence of this comparison indicated very good agreement between both standards.

20. References

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[2] Paur R.J., Bass A.M., Norris J.E. and Buckley T.J. 2003 Standard reference photometer for the assay of ozone in calibration atmospheres *Env. Sci. Technol.* **NISTIR 6369**, 25 pp
[3] ISO 13964 : 1996 Ambient air - Determination of ozone - Ultraviolet photometric method (International Organization for Standardization)
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[5] Viallon J., Moussay P., Idrees F. and Wielgosz R.I. 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**, 16 pp
[6] 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
[7] 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-ISCIII-21

See the following pages.

OZONE COMPARISON RESULT - PROTOCOL B - WITH A TRANSFER STANDARD

Participating institute information	
Institute	**INSTITUTO DE SALUD CARLOS III**
Address	**Ctra. Majadahonda-Pozuelo Km.2 Majadahonda (Madrid)**
Contact	**BEATRIZ NUÑEZ , JOSE MIGUEL DE MIGUEL, PILAR MORILLO**
Email	b.nunez@isciii.es ; jmmiguel@isciii.es ;pmorillo@isciii.es
Telephone	**+34 91 822 35 06**

Instruments information

	Reference Standard	National Standard	Transfer Standard
Manufacturer	NIST	NIST	THERMO
Type	SRP	SRP	49 iPS
Serial number	SRP27	SRP22	0734626227
ozone cross-section value	308.32 atm^{-1} cm^{-1}	308.32 atm-1 cm-1	308.32 atm-1 cm-1

Content of the report

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), 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

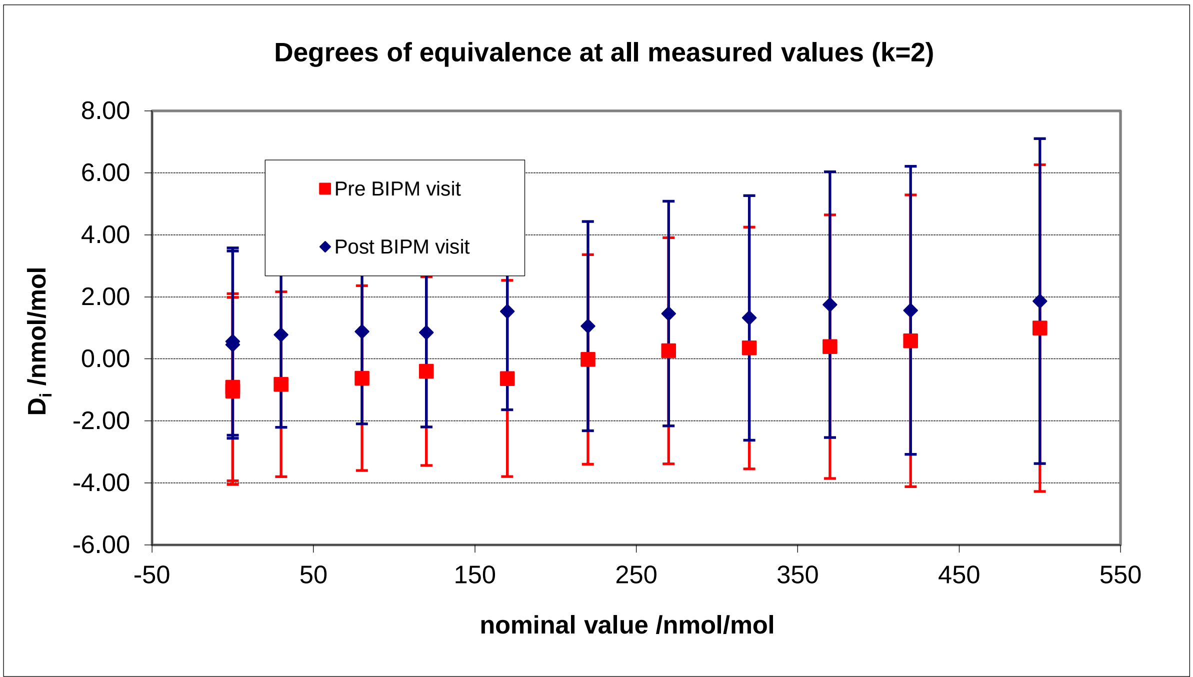
Equation $x_{NS} = a_{NS,RS} \, x_{RS} + b_{NS,RS}$

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	**1.0039**	**0.0049**	**-0.97**	**0.93**	**-2.80E-03**
second comparison	**1.0026**	**0.0049**	**0.63**	**0.93**	**-2.78E-03**

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**	-0.62	1.49	2.98
	420	0.58	2.35	4.70
second comparison	**80**	0.88	1.49	2.98
	420	1.57	2.32	4.65



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

First comparison results						
	National standard measurement results		Transfer standard measurement results		Reference Standard prediced values	
Nominal value	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	0.01	1.35	1.03	1.48
220	220.16	0.70	221.45	1.35	220.18	1.54
80	80.93	0.37	81.37	1.35	81.55	1.44
420	428.89	1.28	431.76	1.36	428.31	1.97
120	122.66	0.45	123.31	1.35	123.05	1.45
320	313.94	0.96	315.84	1.35	313.59	1.70
30	27.50	0.29	27.58	1.35	28.32	1.46
370	366.68	1.11	369.09	1.35	366.29	1.81
170	166.68	0.56	168.03	1.35	167.31	1.48
500	501.09	1.49	504.30	1.36	500.09	2.17
270	272.08	0.84	273.63	1.35	271.82	1.62
0	0.02	0.28	0.03	1.35	1.05	1.48

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)

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

$a_{RS,TS}$	0.9896	$b_{NRS,TS}$ (nmol/mol)	1.02	$u(a,b)$	-1.30E-03
$u(a_{RS,TS})$	0.0039	$u(b_{RS,TS})$ (nmol/mol)	0.64		

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**	-0.91	1.51	3.02
2	**220**	-0.02	1.69	3.38
3	**80**	-0.62	1.49	2.98
4	**420**	0.58	2.35	4.70
5	**120**	-0.39	1.52	3.04
6	**320**	0.35	1.95	3.90
7	**30**	-0.82	1.49	2.98
8	**370**	0.39	2.13	4.25
9	**170**	-0.63	1.58	3.16
10	**500**	0.99	2.63	5.27
11	**270**	0.26	1.82	3.65
12	**0**	-1.03	1.51	3.02

Least-square regression parameters				
$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
1.0038848	**0.0048947**	**-0.9653482**	**0.9294097**	**-0.0027954**

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

Second comparison results						
	National standard measurement results		Transfer standard measurement results		Reference Standard prediced values	
Nominal value	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	-0.10	0.28	-1.60	1.35	-0.56	1.48
220	219.70	0.70	219.90	1.35	218.64	1.54
80	79.00	0.36	77.90	1.35	78.12	1.44
420	421.60	1.26	423.40	1.36	420.03	1.95
120	123.20	0.46	122.60	1.35	122.35	1.45
320	321.60	0.98	322.60	1.35	320.28	1.71
30	30.30	0.29	28.80	1.35	29.52	1.46
370	372.40	1.12	373.50	1.35	370.65	1.83
170	170.10	0.57	169.30	1.35	168.57	1.48
500	498.00	1.48	500.30	1.36	496.14	2.16
270	268.40	0.83	268.70	1.35	266.94	1.61
0	0.00	0.28	-1.60	1.35	-0.56	1.48

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)

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

$a_{RS,TS}$	0.9896	$b_{NRS,TS}$ (nmol/mol)	1.02	$u(a,b)$	-1.30E-03
$u(a_{RS,TS})$	0.0039	$u(b_{RS,TS})$ (nmol/mol)	0.64		

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**	0.46	1.51	3.02
2	**220**	1.06	1.69	3.37
3	**80**	0.88	1.49	2.98
4	**420**	1.57	2.32	4.65
5	**120**	0.85	1.52	3.04
6	**320**	1.32	1.97	3.94
7	**30**	0.78	1.49	2.98
8	**370**	1.75	2.14	4.29
9	**170**	1.53	1.59	3.17
10	**500**	1.86	2.62	5.24
11	**270**	1.46	1.81	3.62
12	**0**	0.56	1.51	3.02

Least-square regression parameters				
$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
1.0026497	**0.0048889**	**0.6261660**	**0.9270619**	**-0.0027818**

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

Operator	**BNC**	**Location**	**51-02-23A**
Comparison begin date / time	**25.01.21/15:04**	**Comparison end date / time**	**26.01.21/ 4:07**

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	0.01	0.11	1.35	0.12	0.24	0.28
220	221.45	0.28	1.35	220.16	0.24	0.70
80	81.37	0.16	1.35	80.93	0.21	0.37
420	431.76	0.53	1.36	428.89	0.41	1.28
120	123.31	0.17	1.35	122.66	0.33	0.45
320	315.84	0.33	1.35	313.94	0.13	0.96
30	27.58	0.15	1.35	27.50	0.40	0.29
370	369.09	0.41	1.35	366.68	0.26	1.11
170	168.03	0.29	1.35	166.68	0.37	0.56
500	504.30	0.53	1.36	501.09	0.73	1.49
270	273.63	0.38	1.35	272.08	0.25	0.84
0	0.03	0.11	1.35	0.02	0.26	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 α 0.00E+00

Comparison conditions

Ozone generator manufacturer	NIST
Ozone generator type	NIST-SRP
Ozone generator serial number	SRP22
Room temperature(min-max) / °C	19,4 ºC - 20,3 ºC
Room pressure (average) / hpa	926,8 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	48hours
Instruments acquisition time /s (one measurement)	1 min
Instruments averaging time /s	SRP22: none ; TE 49iPS: 1min
Total time for ozone conditioning	2 hours
Ozone mole fraction during conditioning	500 nmol/mol +- 15 nmol/mol
Comparison repeated continously (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
Scaler Test with shutter
Stability
NO ADJUSTMENTS WERE NECESSARY

Transfer Standard

INSTRUMENT CHECKS
Pressure
Temperature : Bench and Lamp UV
Flow
Intensities
NO ADJUSTMENTS WERE NECESSARY

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

Operator	F. Idrees	**Location**	CHEM09
Comparison begin date / time	2021-02-18 06:12	**Comparison end date / time**	2021-02-18 08:23

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)	$u(a,b)$
0.9896303	**0.0038717**	**1.0232703**	**0.6430911**	**-0.0012969**

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

Measurement results

	Transfer standard (TS)			Reference Standard (RS)		
Nominal value	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
0	-1.07	0.15	1.35	0.07	0.20	0.28
220	207.60	0.27	1.35	206.51	0.33	0.67
80	75.82	0.16	1.35	76.10	0.15	0.36
420	412.57	0.50	1.35	408.97	0.22	1.24
120	119.10	0.16	1.35	118.91	0.27	0.45
320	301.62	0.30	1.35	299.26	0.23	0.92
30	28.38	0.11	1.35	29.18	0.19	0.29
370	350.38	0.32	1.35	347.69	0.35	1.06
170	164.78	0.19	1.35	164.09	0.32	0.56
500	486.85	0.63	1.36	482.97	0.52	1.45
270	253.24	0.29	1.35	252.17	0.60	0.79
0	-0.95	0.10	1.35	-0.24	0.31	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 α 8.53E-06

Comparison conditions

Ozone generator manufacturer	Environics
Ozone generator type	Model 6100
Ozone generator serial number	3428
Room temperature(min-max) / °C	22.9 - 23
Room pressure (average) / hpa	998.8 - 1000.1
Zero air source	oil free compressor + 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
Instruments averaging time /s	5
Total time for ozone conditioning	> 24 hours
Ozone mole fraction during conditioning	650 nmol mol
Comparison repeated continously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	91
Data files names and location	G:\Gas\Ozone\BIPM.QM-K1\Participants
	c210209001.xls to c210216019.xls

***

Instruments checks and adjustments

Reference Standard

Transfer Standard

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

Operator	BNC	Location	51-02-23A
Comparison begin date / time	04/03/2021 / 21:19	Comparison end date / time	2021-03-05 00:47

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	-1.60	0.10	1.35	-0.10	0.20	0.28
220	219.90	0.30	1.35	219.70	0.20	0.70
80	77.90	0.20	1.35	79.00	0.30	0.36
420	423.40	0.50	1.36	421.60	0.30	1.26
120	122.60	0.20	1.35	123.20	0.30	0.46
320	322.60	0.90	1.35	321.60	0.90	0.98
30	28.80	0.10	1.35	30.30	0.20	0.29
370	373.50	0.40	1.35	372.40	0.40	1.12
170	169.30	0.40	1.35	170.10	0.20	0.57
500	500.30	0.80	1.36	498.00	0.70	1.48
270	268.70	0.40	1.35	268.40	0.20	0.83
0	-1.60	0.10	1.35	0.00	0.20	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 α 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 C-20,4 C
Room pressure (average) / hpa	941,54 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 49iPS: 1min
Total time for ozone conditioning	2 hours
Ozone mole fraction during conditioning	500 nmol/mol +- 15 nmol/mol
Comparison repeated continously (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
Scaler Test with shutter
Stability
NO ADJUSTMENTS WERE NECESSARY

Transfer Standard

INSTRUMENT CHECKS
Pressure
Temperature : Bench and Lamp UV
Flow
Intensities
NO ADJUSTMENTS WERE NECESSARY

Uncertainty budgets (description or reference)

Reference Standard

Transfer Standard

Component (y)	Distribution	Standard Uncertainty u(y)
Repeatibility		Experimental standard desviation
Reproducibility	Rectangular	reproducibility/2√3

Repeatibility: maximal value of the experimental standard desviation observed at ISCIII

Reproducibility: difference between the maximun value of the slope of the regression line between the national standard and the transfer standard.
Using a rectangular distribution, the standard

The transfer standard uncertainty can be summarised by the equation:

$$u_{PT} = \sqrt{(0,00028x)^2 + 1,35^2}$$

National Standard

Component (y)	Uncertainty u(y)				Sensitivity coefficient $c_i = \partial x/\partial y$	Contribution to u(x) $\|c_i\|$. u(y) nmol/mol
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty u(y)		
Opthical Path-length, L_{opt}	Measurement Scale Repeteability Bias	Rect. Normal Rect.	0,0005 cm 0,004 cm 0,52 cm	0,52 cm	**- x/L_{opt}**	$2{,}89x10^{-3}$ x
Pressure, P	P Gauge Difference between cells	Rect. Rect.	0,029 kPa 0,017 kPa	0,034 kPa	**- x/P**	$3{,}37x10^{-4}$ x
Temperatura, T	T probe Residual Bias	Rect. Rect.	0,029 K 0,058 K	0,07K	**x/T**	$2{,}29x10^{-4}$ x
Ratio of Intensities, D	Scaler resolution Repeatibility	Rect. Normal	$8{,}0x10^{-6}$ $1{,}1x10^{-5}$	$1{,}4x10^{-5}$	**x/Dln(D)**	0,28
Absorption Cross section, σ	Conventional value		-	-	-	-

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

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