

# Final report, Ongoing Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with LNE, (March 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 France maintained by the Laboratoire National de métrologie et d'Essais (LNE) 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 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 Laboratoire National de métrologie et d'Essais (LNE) 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

This is the third participation of LNE since 2007. Measurements reported in this report were performed on 17 March 2023 at the BIPM.

## 8. Measurement protocol

The comparison protocol is summarised in this section. The complete version can be downloaded from the BIPM website ([BIPM.QM-K1 protocol](#)).

This comparison was performed following protocol A, corresponding to a comparison between the LNE national standard SRP40 and the common reference standard BIPM-SRP27 maintained at the BIPM. A comparison between two (or more) ozone photometers consists of

producing ozone-air mixtures at different amount fractions over the required range and measuring these with the photometers.

### 8.1. 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.

### 8.2. 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 on BIPM SRPs. Adjustment of the pressure probe were performed on the LNE standard SRP40, as reported in Appendix 1 -.

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.

### 8.3. 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.

#### 8.4. 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-R1 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 fractions measured by the participant's standard and the common reference standard. The completed form BIPM.QM-K1-R1-LNE-23 is given in appendix 1.

### 10. Post comparison calculation

All calculations were performed by the BIPM using the form BIPM.QM-K1-R1. 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 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

This comparison was preceded with an upgrade of the electronic module of SRP40. The comparison protocol was followed before and after the upgrade to monitor its impact. Additionally, the first series of measurements were observed to be sufficiently different from the previous comparison of 2012 to trigger an investigation. The pressure gauge of SRP40 had to be adjusted, and its electronic box was moved further away from its optical bench. A summary of these measurements is reported in annex of this report.

### 12. Measurement standards

The instruments maintained by the BIPM and LNE 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;  
 $P_{\text{std}}$  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

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

where

$I_{\text{ozone}}$  is the UV radiation intensity measured from the cell when containing ozonized air, and

$I_{\text{air}}$  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 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,  $6.022\,140\,76 \times 10^{23}$  molecule/mol

$R$  is the gas constant,  $82.057\,366 \text{ cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$

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. As explained in detail in [4], the “atm” unit system was used initially to describe the operation of ozone photometers and, though antiquated, remains in use by many practitioners. In this system, the amount fraction of ozone  $x$  is calculated from:

$$x = \frac{-1}{2\alpha_0 L_{\text{opt}}} \frac{T}{T_{\text{std}}} \frac{P_{\text{std}}}{P} \ln(D) \quad (4)$$

where

$\alpha_0$  is the absorption coefficient at standard temperature and pressure (0 °C and 1 atm), expressed in  $\text{atm}^{-1} \text{ cm}^{-1}$ , and linked to the absorption cross-section per molecule  $\sigma$  via the Boltzmann constant  $k_B = 1.380\,649 \times 10^{-23} \text{ J K}^{-1}$  with the relation:

$$\alpha_0 = \frac{\sigma}{k_B T_{\text{std}}} \quad (5)$$

## 12.2. Absorption cross-section for ozone

The absorption coefficient under standard conditions  $\alpha_0$  used within the SRP software algorithm is  $308.32 \text{ cm}^{-1}$ . 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 3 to 5 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 nmol mol<sup>-1</sup> to 500 nmol mol<sup>-1</sup> 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)$ nmol mol <sup>-1</sup>
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$		
<b>Optical Path</b> $L_{opt}$	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			
<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		$1.22 \times 10^{-19}$ cm <sup>2</sup>	$1.22 \times 10^{-19}$ cm <sup>2</sup>	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$

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 nmol mol<sup>-1</sup>):

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

### 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:

$$u(x_i, x_j) = x_i \cdot x_j \cdot u_b^2 \quad (7)$$

where:

$$u_b^2 = \frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} + \frac{u^2(L_{opt})}{L_{opt}^2} \quad (8)$$

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 LNE SRP40

SRP40 maintained by LNE has been constructed by NIST in 2007 with the new design, which includes the “SRP upgrade kit” in order to deal with the two biases revealed in [4]. Additionally, as the first series of measurements were observed to be sufficiently different from the previous comparison of 2012, some investigations were carried out and showed that the observed bias came from the pressure gauge of SRP40. Consequently it was decided to adjust it by BIPM. Before this comparison, the pressure gauge was adjusted by the LNE’s department in charge of pressure metrology using a pressure standard with a bias. After the comparison, a recalibration was carried out by LNE which confirmed the BIPM’s adjustment. Prior to this comparison, the electronic module was upgraded to the new cDAQ design at BIPM, in a similar fashion than performed on BIPM SRPs [10].

## 12.7. Uncertainty budget of the LNE SRP40

The uncertainty budget for the ozone amount fraction in dry air  $x$  measured by the LNE standard SRP40 in the nominal range 0 nmol mol<sup>-1</sup> to 500 nmol mol<sup>-1</sup> is given in Table 2.

Table 2 : SRP40 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 $u(y)$		
Optical Path $L_{opt}$	Divergence	Rectangular	0.52 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.90 \cdot 10^{-3} \cdot x$
	Calibration	Normal	0.015 kPa			
Pressure P	Drift	Rectangular	0.100 kPa	0.0614 kPa	$-\frac{x}{P}$	$6.1 \cdot 10^{-4} \cdot x$
	Difference between cells	Rectangular	0.025 kPa			
	Calibration	Normal	0.1 K			
Temperature T	Drift	Rectangular	0.1 K	0.13 K	$\frac{x}{T}$	$4.4 \cdot 10^{-4} \cdot x$
	Gradient over cells	Rectangular	0.1 K			
	Scaler resolution	Rectangular	$1.2 \cdot 10^{-5}$			
Ratio of Intensities D	Repeatability	-	$1.2 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$\frac{x}{D \cdot \ln(D)}$	0.28
	Absorption Cross section per molecule $\sigma$	Hearn value	$1.22 \cdot 10^{-19}$ cm <sup>2</sup>			

Following this budget, the standard uncertainty associated with the ozone amount fraction measurement with the LNE SRP40 can be expressed as a numerical equation (numerical values expressed as nmol mol<sup>-1</sup>):

$$u(x) = \sqrt{(0.28)^2 + (3.0 \cdot 10^{-3}x)^2} \quad (9)$$

No covariance term for the LNE SRP40 was included in the calculations.

### 13. Measurement results and uncertainties

Details of the measurement results, the measurement uncertainties and the standard deviations at each nominal ozone amount fraction can be found in the form BIPM.QM-K1-R1-LNE-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 fractions.

In a direct comparison, a linear relationship between the ozone amount fractions measured by the instrument  $i$  and SRP27 is obtained:

$$x_i = a_0 + a_1 x_{\text{SRP27}} \quad (10)$$

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. Least-square regression results

The relationship between SRP40 and SRP27 is:

$$x_{\text{SRP40}} = 0.11 + 1.0001 x_{\text{SRP27}} \quad (11)$$

The standard uncertainties on the parameters of the regression are  $u(a_1) = 0.0033$  for the slope and  $u(a_0) = 0.22 \text{ nmol mol}^{-1}$  for the intercept. The covariance between the two parameters is  $\text{cov}(a_0, a_1) = -2.10 \times 10^{-4}$ .

The least-squares regression results confirm that a linear fit is appropriate, with a sum of the squared deviations (SSD) of 1.13 and a goodness of fit (GoF) equals to 0.5.

To assess the agreement of the standards using 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 this comparison, 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 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 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

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

$$D_i = x_i - x_{\text{SRP27}} \quad (12)$$

where  $x_i$  and  $x_{\text{SRP27}}$  are the measurement result of the participant  $i$  and of SRP27 at the nominal value  $x_{\text{nom}}$ .

Its associated standard uncertainty is:

$$u(D_i) = \sqrt{u_i^2 + u_{\text{SRP27}}^2} \quad (13)$$

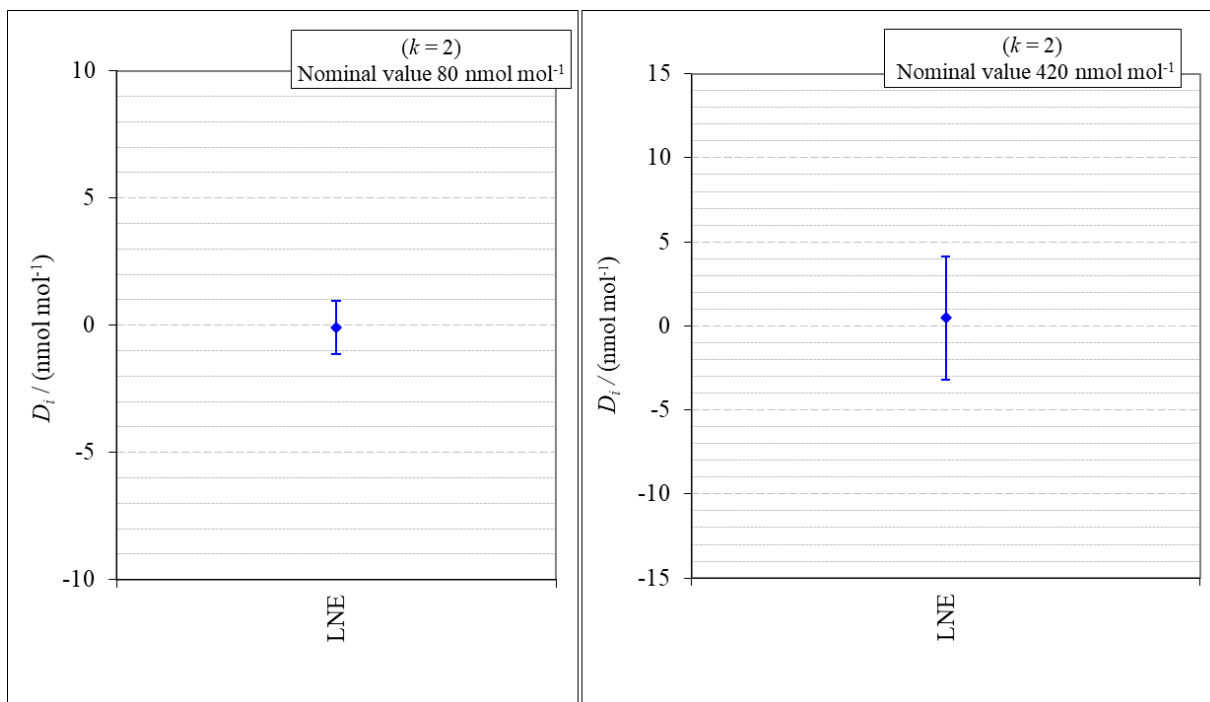
where  $u_i$  and  $u_{\text{SRP27}}$  are the measurement uncertainties of the participant  $i$  and of SRP27 respectively.

### 15.2. Values of the degrees of equivalence

The degrees of equivalence and their uncertainties calculated in the form BIPM.QM-K1-R1-LNE-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 3 : degrees of equivalence of LNE at the ozone nominal amount fractions 80 nmol mol<sup>-1</sup> and 420 nmol mol<sup>-1</sup>**

Nominal value	$x_i /$	$u_i /$	$x_{\text{SRP27}} /$	$u_{\text{SRP27}} /$	$D_i /$	$u(D_i) /$	$U(D_i) /$
	(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> )
<b>80</b>	84.02	0.38	84.10	0.37	-0.08	0.53	1.06
<b>420</b>	429.00	1.32	428.52	1.28	0.48	1.84	3.68

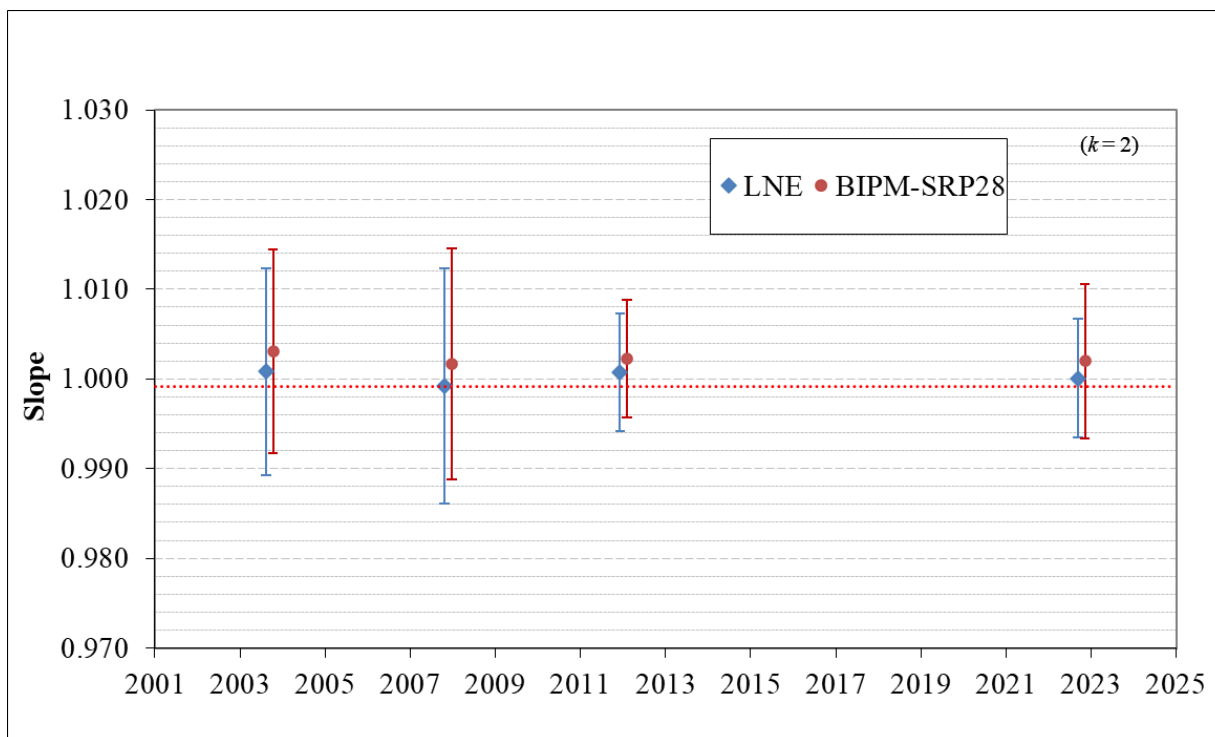


**Figure 1: degrees of equivalence of LNE at the two nominal ozone amount fractions 80 nmol mol<sup>-1</sup> and 420 nmol mol<sup>-1</sup>**

The degrees of equivalence between the LNE 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. History of comparisons between BIPM SRP27, SRP28 and LNE SRP40

Results of the previous comparison performed with LNE 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 LNE-SRP40 realised at the BIPM. Uncertainties are calculated at  $k = 2$ , with the uncertainty budget in use at the time of each comparison.**

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

The comparison with LNE is the third 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/>.

## 18. Conclusion

For the third time since the launch of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of France, maintained by LNE, 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.

## 19. References

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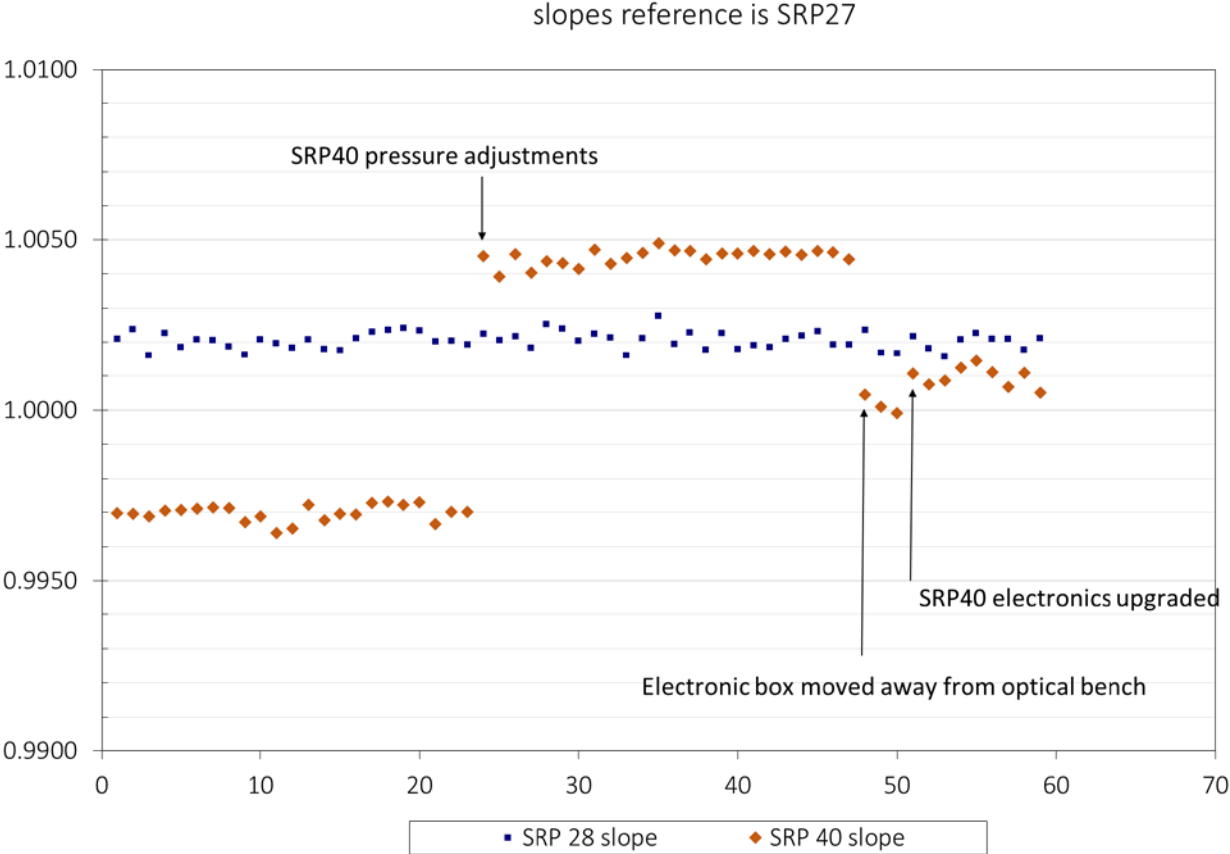
- appropriate significant digits and rounding for use in documentary standards **Rapport BIPM-2022/02** p 16,  
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## Appendix 1 - Measurements performed before the upgrade of SRP40

The measurements results are reported here in terms of the slope of the linear regression between SRP40 and SRP27. Uncertainties are not displayed as they would cover the variations of the slope, which are still considered meaningful. The results are displayed in Figure 3.

Upon arrival of SRP40, the measurements results showed a slope of 0.997, which was considered sufficiently different from the previous comparison (slope of 1.0007) to trigger an investigation. It was observed that the pressure measured by SRP40 was systematically 8 hPa lower than of SRP27. All SRPs being identical, the pressure in their gas cells during operation is normally well within 1 hPa. Therefore, the pressure gauge of SRP40 was adjusted to obtain

the same pressure. This resulted in a slope of 1.0045 compared to SRP27, which was again considered different from previous values. It was then observed that the temperature measured by SRP40 was 2.5°C higher than by SRP27. Temperatures measured by SRP would normally agree within 0.5°C. SRP40 temperature probe was checked and found consistent with local references. The electronic module was moved further away from the optical bench, as it is known to generate heat. This resulted in a decrease of the temperature measurements to values in agreement with SRP27 and SRP28, and in a slope very close to 1. It was then decided that the electronic upgrade of SRP40 could be performed. This resulted in a negligible increase of the slope, reaching the final value of 1.001 reported for this comparison.



**Figure 3 : Slope of the linear regression between SRP40, SRP28 and SRP27 obtained during all comparisons performed during the stay of SRP40 at the BIPM. Interventions on SRP40 are indicated with arrows.**

**Appendix 2 - Form BIPM.QM-K1-R1-LNE-23**

See the following pages.

<b>OZONE COMPARISON RESULT - PROTOCOL A - DIRECT COMPARISON</b>
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<b>Participating institute information</b>	
<b>Institute</b>	<b>LNE</b>
<b>Address</b>	<b>1 rue Gaston Boissier</b>
<b>Contact</b>	<b>Christophe Sutour</b>
<b>Email</b>	<a href="mailto:christophe.sutour@lne.fr">christophe.sutour@lne.fr</a>
<b>Telephone</b>	<b>+33 1 40 43 37 49</b>

<b>Instruments information</b>		
	<b>Reference Standard</b>	<b>National Standard</b>
<b>Manufacturer</b>	NIST	NIST
<b>Type</b>	SRP	SRP
<b>Serial number</b>	SRP27	SRP40

<b>Content of the report</b>	
page 1	general informations
page 2	comparison results
page 3	measurements results
page 4	comparison description
page 5	uncertainty budgets

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

<b>Operator</b>	F. Idrees	<b>Location</b>	BIPM-MC-CHEM9
<b>Comparison begin date / time</b>	2022-03-17 10:00	<b>Comparison end date / time</b>	2023-03-17 12:08

**Comparison results**

**Equation**

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

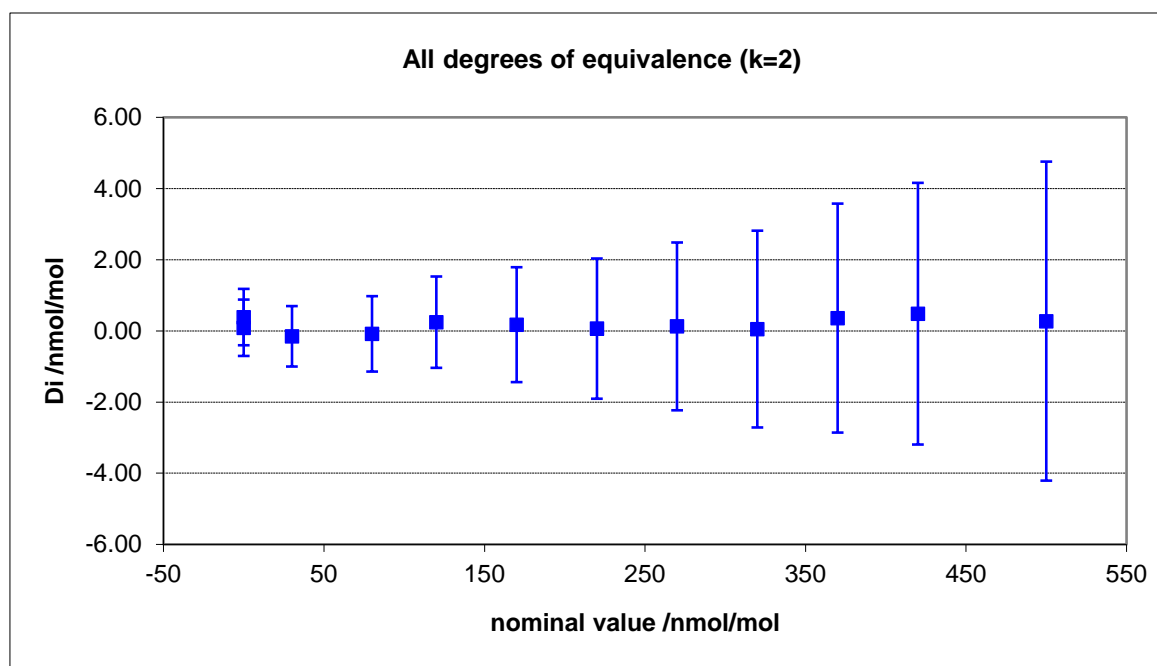
**Least-square regression parameters**

$a_{TS,RS}$	$u(a_{TS,RS})$	$b_{TS,RS}$ (nmol/mol)	$u(b_{TS,RS})$ (nmol/mol)	$u(a,b)$
<b>1.0001</b>	<b>0.0033</b>	<b>0.11</b>	<b>0.22</b>	<b>-2.10E-04</b>

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

**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)
<b>80</b>	<b>-0.083942</b>	<b>0.5297614</b>	<b>1.0595228</b>
<b>420</b>	<b>0.482879</b>	<b>1.8381809</b>	<b>3.6763618</b>



<b>Measurement results</b>						
	<b>Reference Standard (RS)</b>			<b>National standard (NS)</b>		
<b>Nominal value</b>	$x_{RS}$ nmol/mol	$s_{RS}$ nmol/mol	$u(x_{RS})$ nmol/mol	$x_{NS}$ nmol/mol	$s_{NS}$ nmol/mol	$u(x_{NS})$ nmol/mol
<b>0</b>	-0.33	0.21	0.28	0.06	0.32	0.28
<b>220</b>	215.37	0.22	0.69	215.44	0.25	0.70
<b>80</b>	84.10	0.19	0.37	84.02	0.27	0.38
<b>420</b>	428.52	0.17	1.28	429.00	0.22	1.32
<b>120</b>	120.47	0.26	0.45	120.72	0.34	0.46
<b>320</b>	316.32	0.16	0.97	316.37	0.23	0.99
<b>30</b>	36.69	0.23	0.30	36.54	0.31	0.30
<b>370</b>	372.19	0.16	1.12	372.55	0.32	1.15
<b>170</b>	167.91	0.22	0.56	168.09	0.33	0.58
<b>500</b>	526.70	0.28	1.56	526.98	0.34	1.61
<b>270</b>	265.16	0.14	0.82	265.28	0.35	0.84
<b>0</b>	0.05	0.14	0.28	0.14	0.11	0.28

<b>Degrees of Equivalence</b>				
<b>Point Number</b>	<b>Nom value (nmol/mol)</b>	$D_i$ (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
<b>1</b>	<b>0</b>	0.39	0.40	0.79
<b>2</b>	<b>220</b>	0.06	0.98	1.97
<b>3</b>	<b>80</b>	-0.08	0.53	1.06
<b>4</b>	<b>420</b>	0.48	1.84	3.68
<b>5</b>	<b>120</b>	0.24	0.64	1.28
<b>6</b>	<b>320</b>	0.05	1.38	2.76
<b>7</b>	<b>30</b>	-0.15	0.42	0.85
<b>8</b>	<b>370</b>	0.36	1.61	3.22
<b>9</b>	<b>170</b>	0.17	0.81	1.61
<b>10</b>	<b>500</b>	0.27	2.24	4.48
<b>11</b>	<b>270</b>	0.13	1.18	2.36
<b>12</b>	<b>0</b>	0.09	0.40	0.79

Covariance terms in between two measurement results of each standard

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

Value of  $\alpha$  for the reference standard 8.50E-06

Value of  $\alpha$  for the national standard 0.00E+00



<b>Comparison conditions</b>	
Ozone generator manufacturer	Envionics
Ozone generator type	Model 6100
Ozone generator serial number	3128
Room temperature(min-max) / °C	21.0 - 21.25
Room pressure (min-max) / hpa	997.3 - 997.5
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	9
Data files names and location	<a href="G:\Gas\Ozone\BIPM.QM-K1\Participants results\2303 LNE Cal23031603.xls to Cal23031604.xls">G:\Gas\Ozone\BIPM.QM-K1\Participants results\2303 LNE Cal23031603.xls to Cal23031604.xls</a>

**Instruments checks and adjustments**

**Reference Standard**

**National Standard**

Electronic box upgraded

4 temperature probes installed on Cells 1 and 2 of the optical bench

**Uncertainty budgets (description or reference )**

**Reference Standard**

BIPM-SRP27 uncertainty budget is described in the protocol of this comparison: document BIPM.QM-K1 protocol, date 10 Januray 2007, available on BIPM website. It can be summarised by the formula:

$$u(x) = \sqrt{(0.28)^2 + (2,92 \cdot 10^{-3} x)^2}$$

**National Standard**

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 $u(y)$		
Optical Path $L_{opt}$	Divergence	Rectangular	0.52 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.90 \cdot 10^{-3} \cdot x$
	Calibration	Normal	0.015 kPa			
Pressure P	Drift	Rectangular	0.100 kPa	0.0614 kPa	$-\frac{x}{P}$	$6.1 \cdot 10^{-4} \cdot x$
	Difference between cells	Rectangular	0.025 kPa			
Temperature T	Calibration	Normal	0.1 K	0.13 K	$\frac{x}{T}$	$4.4 \cdot 10^{-4} \cdot x$
	Drift	Rectangular	0.1 K			
	Gradient over cells	Rectangular	0.1 K			
Ratio of Intensities D	Scaler resolution	Rectangular	$1.2 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$\frac{x}{D \cdot \ln(D)}$	0.28
	Repeatability	-	$1.2 \cdot 10^{-5}$			
Absorption Cross section per molecule $\sigma$	Hearn value		$1.22 \cdot 10^{-19}$ cm <sup>2</sup>	$1.22 \cdot 10^{-19}$ cm <sup>2</sup>	$-\frac{x}{\sigma}$	$1.06 \cdot 10^{-2} \cdot x$