

# Final report, Ongoing Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with JRC, (July 2019)

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## Abstract

As part of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone standard of the European Commission maintained by the Joint Research Centre (JRC) 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 from 0 nmol/mol to 500 nmol/mol.

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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 Joint Research Centre (JRC) 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-of-substance 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 against the photometer B.  $a_{A,B}$  is dimensionless and  $b_{A,B}$  is expressed in units of nmol/mol.

## 7. Measurement schedule

The key comparison BIPM.QM-K1 was initially organised in 2 years cycles. The 2007-2008 round, the results of which were 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 on 04 July 2019 at the BIPM.

## 8. Measurement protocol

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

This comparison was performed following protocol A, corresponding to a direct comparison between the JRC standard SRP42 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-of-substance 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. 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 amount-of-substance fractions of ozone and nitrogen oxides remaining in the air are below detectable limits. The relative humidity of the reference air is monitored and the amount-of-substance fraction of water in air typically is below 3  $\mu\text{mol/mol}$ . The amount-of-substance fraction of volatile organic hydrocarbons in the reference air was measured (November 2002), with no amount-of-substance fraction of any detected component exceeding 1  $\text{nmol/mol}$ .

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.

### 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-SPR27. The pressure and temperature sensors of JRC SRP42 had to be adjusted following a usual procedure.

One comparison run includes 10 different amount-of-substance fractions distributed to cover the range, together with the measurement of zero reference air at the beginning and end of each run. The nominal amount-of-substance fractions were measured in a sequence imposed by the protocol (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270, and 0)  $\text{nmol/mol}$ . 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  $s_{\text{SRP27}}$  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  $\text{nmol/mol}$ , 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 during two cycles of 22 hours each 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-of-substance fractions measured by the participant's standard and the common reference standard. The completed form BIPM.QM-K1-R1-JRC-19 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-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 by the JRC are Standard Reference Photometers (SRP) built by the NIST. More details on the NIST SRP principle and its capabilities can be found in [2]. The following section describes briefly the instruments' measurement principle and their uncertainty budgets.

#### 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:

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

where

- $\sigma$  is the absorption cross-section of ozone at 253.7 nm under standard conditions of temperature and pressure,  $1.1476 \times 10^{-17}$  cm<sup>2</sup>/molecule [3].
- $L_{\text{opt}}$  is the mean optical path length of the two cells;
- $T$  is the measured temperature of the cells;
- $T_{\text{std}}$  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 an amount-of-substance fraction ( $x$ ) of ozone in air:

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

where

$N_A$  is the Avogadro constant,  $6.022142 \times 10^{23} \text{ mol}^{-1}$ , and

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

The formulation implemented in the SRP software is:

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

where

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

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

## 12.2. Absorption cross-section for ozone

The linear absorption coefficient under standard conditions  $\alpha_x$  used within the SRP software algorithm is  $308.32 \text{ cm}^{-1}$ . This corresponds to a value for the absorption cross section  $\sigma$  of  $1.1476 \times 10^{-17} \text{ cm}^2/\text{molecule}$ , rather than the more often quoted  $1.147 \times 10^{-17} \text{ cm}^2/\text{molecule}$ . 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 in a recent publication [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 range from 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 $u(x)$ $ c_i  \cdot u(y)$ nmol/mol
	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 <math>\sigma</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, 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):

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

### 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-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:

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

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 JRC SRP42

The JRC SRP42 has been constructed by NIST in 2008 with the new design, which includes the “SRP upgrade kit” in order to deal with the two biases revealed in [4].

### 12.7. Uncertainty budget of the JRC SRP42

The uncertainty budget for the ozone mole fraction in dry air  $x$  measured by the JRC SRP42 in the nominal range 0 nmol/mol to 500 nmol/mol will follow the BIPM/NIST paper [4] (see Table 1).

Following this budget, the standard uncertainty associated with the ozone amount-of-substance fraction measurement with the JRC–SRP42 can be expressed as a numerical equation (numerical values expressed as nmol/mol):

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

After correcting for the temperature probe heating bias, the final uncertainty is calculated by:

$$u(x)^+ = u(x); u(x)^- = u(x) + (-10^{-3}x) \quad (10)$$

Because the BIPM.QM-K1-R1 spreadsheet does not allow the uncertainty to be expressed by different positive and negative amounts, it has been expressed as:

$$u(x) = u(x) + (-10^{-3}x) \quad (11)$$

No covariance term was included for the JRC SRP42 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-of-substance fraction are provided in appendix (form BIPM.QM-K1-R1-JRC-19).

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

The relationship between JRC SRP42 and the 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 ISO6143:2001 [7]. 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.

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

$$x_i = a_0 + a_1 x_{SRP27} \quad (12)$$

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-squares regression results

The relationship between SRP42 and SRP27 is:

$$x_{SRP42} = -0.03 \text{ nmol/mol} + 0.9979x_{SRP27} \quad (13)$$

The standard uncertainties on the parameters of the regression are  $u(a_1) = 0.0034$  for the slope and  $u(a_0) = 0.22 \text{ nmol/mol}$  for the intercept. The covariance between the two parameters is  $\text{cov}(a_0, a_1) = -2.34 \times 10^{-4}$ .

The least-squares regression results confirm that a linear fit is appropriate, with a sum of the squared deviations (SSD) of 0.07 and a goodness of fit (GoF) equals to 0.12.

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-of-substance fractions among the twelve measured in each comparison, in the range from 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  $\pm 15 \text{ nmol/mol}$  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

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

$$D_i = x_i - x_{SRP27} \quad (14)$$

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

Its associated standard uncertainty is:

$$u(D_i) = \sqrt{u_i^2 + u_{SRP27}^2} \quad (15)$$

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

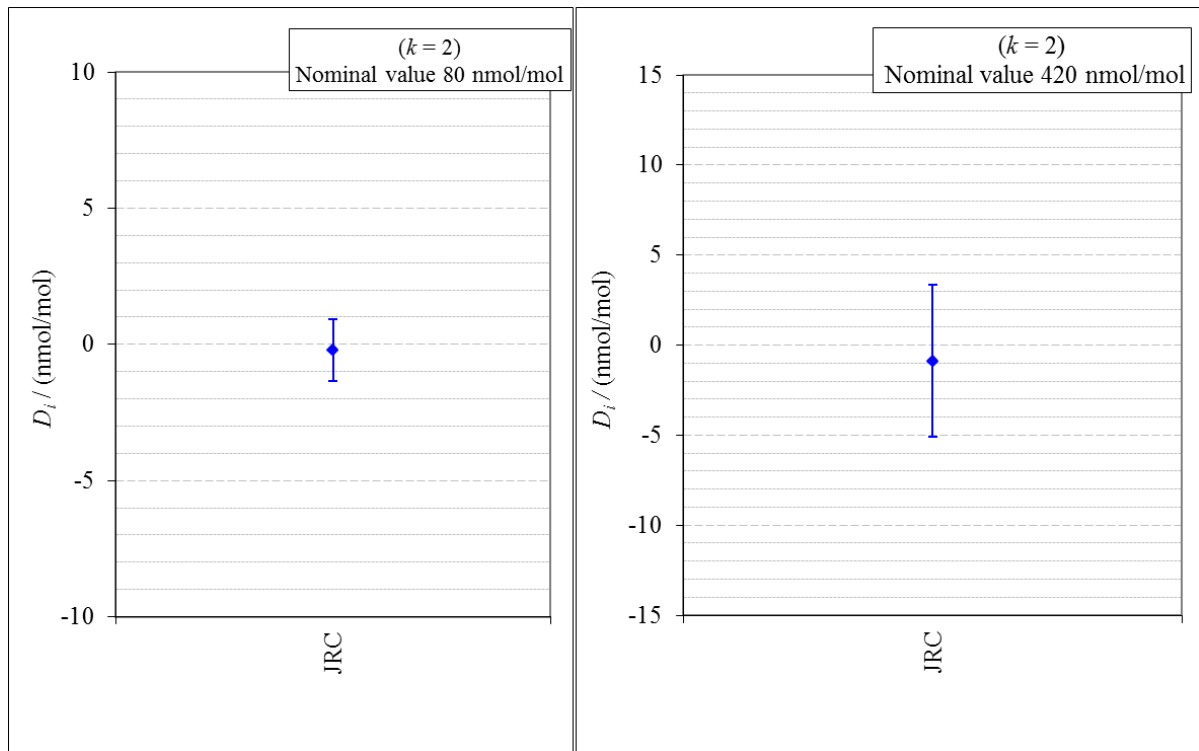


## 15.2. Values of the degrees of equivalence

The degrees of equivalence and their uncertainties calculated in the form BIPM.QM-K1-R1-JRC-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 2 : degrees of equivalence of the JRC at the ozone nominal amount-of-substance fractions 80 nmol/mol and 420 nmol/mol**

Nominal value / (nmol/mol)	$x_i /$	$u_i /$	$x_{\text{SRP27}} /$	$u_{\text{SRP27}} /$	$D_i /$	$u(D_i) /$	$U(D_i) /$
	(nmol/mol)	(nmol/mol)	(nmol/mol)	(nmol/mol)	(nmol/mol)	(nmol/mol)	(nmol/mol)
80	79.51	0.44	79.71	0.36	-0.20	0.57	1.14
420	419.69	1.68	420.56	1.26	-0.87	2.10	4.20



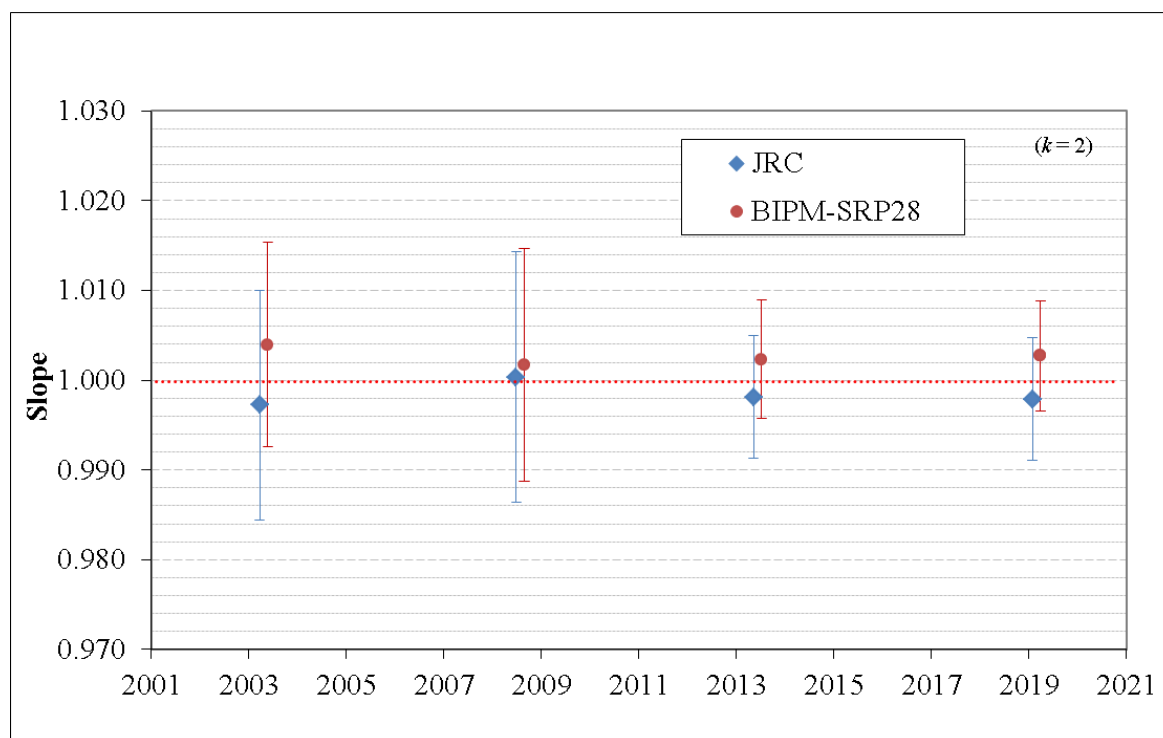
**Figure 1: degrees of equivalence of the JRC at the two nominal ozone amount-of-substance fractions 80 nmol/mol and 420 nmol/mol**

The degrees of equivalence between the JRC 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 SRP42

Results of the previous comparisons performed since 2003 are displayed in Figure 2 together with the results of this comparison. The slopes  $a_1$  of the linear relation  $x_i = a_0 + a_1 x_{\text{SRP27}}$  are represented together with their associated uncertainties calculated at the time of each comparison. Results of the 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 JRC SRP42 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 JRC is the fifteenth one in the 2017-2020 round of BIPM.QM-K1. An updated summary of BIPM.QM-K1 results can be found in the BIPM key comparison database: <http://kcdb.bipm.org/appendixB/>.

## 18. Conclusion

For the fourth time since the launch of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone standard of the European Commission maintained by the JRC and the common reference standard of the key comparison maintained by the BIPM. The instruments have been compared over an ozone amount-of-substance fraction range from 0 nmol/mol to 500 nmol/mol. Degrees of equivalence of this comparison indicated very good agreement between the two standards.

## 19. References

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- [4] 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
- [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 - comparison methods for determining and checking the composition of gas mixtures (International Organization for Standardization)

## **Appendix 1 - Form BIPM.QM-K1-R1-JRC-19**

See the following pages.

**OZONE COMPARISON RESULT - PROTOCOL A - DIRECT  
COMPARISON**

<b>Participating institute information</b>	
<b>Institute</b>	European Commission - Joint Research Center
<b>Address</b>	Via Enrico Fermi 2749 - 21027 Ispra (VA) - Italy
<b>Contact</b>	Friedrich Lagler
<b>Email</b>	<a href="mailto:friedrich.lagler@ec.europa.eu">friedrich.lagler@ec.europa.eu</a>
<b>Telephone</b>	0039-0332-789990

<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	SRP42

<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/CHEM09
<b>Comparison begin date / time</b>	04/07/2019 06:32	<b>Comparison end date / time</b>	04/07/2019 08:32

**Comparison results**

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

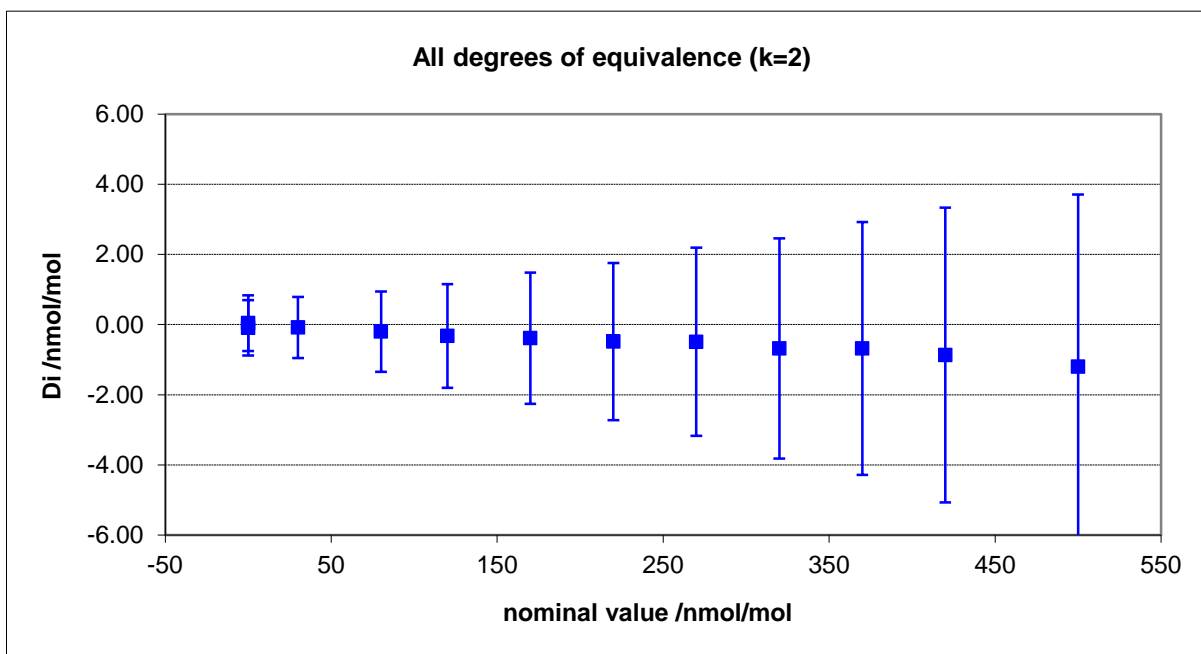
**Least-square regression parameters**

$a_{TS,RS}$	$u(a_{TS,RS})$	$b_{TS,RS}$ (nmol/mol)	$u(b_{TS,RS})$ (nmol/mol)	$u(a,b)$
<b>0.9979</b>	<b>0.0034</b>	<b>-0.03</b>	<b>0.22</b>	<b>-2.34E-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>-0.2003515</b>	<b>0.5711181</b>	<b>1.1422362</b>
<b>420</b>	<b>-0.8704292</b>	<b>2.0997232</b>	<b>4.1994465</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>	0.09	0.22	0.28	0.00	0.18	0.28
<b>220</b>	213.02	0.20	0.68	212.53	0.25	0.89
<b>80</b>	79.71	0.40	0.36	79.51	0.10	0.44
<b>420</b>	420.56	0.28	1.26	419.69	0.16	1.68
<b>120</b>	123.77	0.31	0.46	123.45	0.19	0.58
<b>320</b>	309.30	0.35	0.95	308.62	0.18	1.25
<b>30</b>	30.73	0.16	0.29	30.65	0.14	0.32
<b>370</b>	358.35	0.32	1.08	357.67	0.18	1.44
<b>170</b>	170.22	0.26	0.57	169.83	0.11	0.74
<b>500</b>	495.35	0.33	1.47	494.15	0.16	1.96
<b>270</b>	260.33	0.17	0.81	259.84	0.26	1.07
<b>0</b>	0.03	0.21	0.28	0.07	0.15	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>	-0.09	0.40	0.79
<b>2</b>	<b>220</b>	-0.49	1.12	2.24
<b>3</b>	<b>80</b>	-0.20	0.57	1.14
<b>4</b>	<b>420</b>	-0.87	2.10	4.20
<b>5</b>	<b>120</b>	-0.32	0.74	1.48
<b>6</b>	<b>320</b>	-0.68	1.57	3.13
<b>7</b>	<b>30</b>	-0.08	0.43	0.87
<b>8</b>	<b>370</b>	-0.68	1.80	3.60
<b>9</b>	<b>170</b>	-0.39	0.93	1.87
<b>10</b>	<b>500</b>	-1.20	2.45	4.90
<b>11</b>	<b>270</b>	-0.49	1.34	2.68
<b>12</b>	<b>0</b>	0.04	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 8.53E-06

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

**Comparison conditions**

Ozone generator manufacturer	Envionics
Ozone generator type	Model 6100
Ozone generator serial number	3428
Room temperature(min-max) / °C	21.4 - 21.5
Room pressure (min-max) / hpa	1010.0 - 1010.1
Zero air source	oil free compressor + dryer + Aadco 737-R
Reference air flow rate (L/min)	15
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	800 nmol/mol
Comparison repeated continuously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	
Total number of comparison repeats realised	14
Data files names and location	<a href="U:\Gas\2019\C-A1.1.1\Data\c190703001.xls">U:\Gas\2019\C-A1.1.1\Data\c190703001.xls</a> to <a href="U:\Gas\2019\C-A1.1.1\Data\c190704010.xls">c190704010.xls</a>

**Instruments checks and adjustments****Reference Standard**

Adjustments and/or checks performed as described in CHEM-GAS-T-01 technical procedure

**National Standard**

Adjustments and/or checks performed as described in SRP OPERATING CHARACTERISTICS DATA SHEET

## 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 January 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

The uncertainty budget for the ozone mole fraction in dry air  $x$  measured by the JRC standard SRP42 in the nominal range 0 nmol/mol to 500 nmol/mol will follow the BIPM/NIST paper [1] with an additional component based on the temperature probe heating effect. The initial uncertainty can be summarized by the formula:

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

After correcting for the temperature probe heating bias, the final uncertainty is calculated by:

$$u(x)^+ = u(x); \quad u(x)^- = u(x) + (-0.001 \cdot x)$$

Because the BIPM.QM-K1-R1 spreadsheet does not allow the uncertainty to be expressed by different positive and negative amounts, it has been expressed as:

$$u(x) = u(x) + (0.001 \cdot x)$$

No covariance term for the JRC SRP42 was included in the calculations.

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