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# BIPM.QM-K1 (NMISA 2023)

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## Ozone at ambient level

**KEY COMPARISON**

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# Ongoing Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with NMISA (June 2023)

## *Final Report*

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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 South Africa maintained by the National Metrology Institute of South Africa (NMISA) 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>.

### Contents:

1. FIELD .....	2
2. SUBJECT .....	2
3. PARTICIPANTS .....	2
4. ORGANIZING BODY.....	2
5. RATIONALE .....	2
6. TERMS AND DEFINITIONS.....	2
7. MEASUREMENTS SCHEDULE .....	2
8. MEASUREMENT PROTOCOL .....	2
9. REPORTING MEASUREMENT RESULTS .....	4
10. POST COMPARISON CALCULATION.....	5
11. DEVIATIONS FROM THE COMPARISON PROTOCOL .....	5
12. MEASUREMENT STANDARDS .....	5
13. MEASUREMENT RESULTS AND UNCERTAINTIES .....	8
14. ANALYSIS OF THE MEASUREMENT RESULTS BY GENERALISED LEAST-SQUARE REGRESSION .....	9
15. DEGREES OF EQUIVALENCE .....	9
16. HISTORY OF COMPARISONS BETWEEN BIPM SRP27, SRP28 AND NMISA SRP60 .....	11
17. SUMMARY OF PREVIOUS COMPARISONS INCLUDED IN BIPM.QM-K1 .....	12
18. CONCLUSION .....	12
19. REFERENCES .....	12

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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 National Metrology Institute of South Africa (NMISA) 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 fifth participation of NMISA since the launch of the comparison in 2007. Measurements reported in this report were performed between June 2022 and June 2023 at the BIPM and the NIST.

## 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 B, corresponding to a comparison between the NMISA national standard SRP60 and the common reference standard BIPM-SRP27

maintained at the BIPM via the NIST transfer standard SRP0. SRP0 was first compared with the common reference standard SRP27 at the BIPM in June 2022. Then the national standard SRP60 and the transfer standard SRP0 were compared at the NIST in (June 2023).

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 NIST

#### a). Ozone generation

The air is compressed with an oil-free compressor, dried and scrubbed with a commercial purification system so that the amount fraction of ozone and nitrogen oxides remaining in the air is below detectable limits. This air is used to provide reference air as well as the ozone-air mixture to each ozone photometer. Ozone is produced using an external commercial generator. 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 12 hours. Characteristics of the instruments were checked at this time following a procedure recommended by NIST. Adjustments were made as necessary to match all SRPs to a common pressure standard and temperature standard.

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

For each nominal value of the ozone amount-of-substance fraction  $x_{\text{nom}}$  furnished by the ozone generator, the standard deviation  $s_{\text{SRP60}}$  on the set of 10 consecutive measurements  $x_{\text{SRP60},i}$  recorded by SRP60 was calculated. The measurement results were considered as valid if  $s_{\text{SRP60}}$  was less than 1 nmol mol<sup>-1</sup>, which ensures that the photometers were measuring a stable ozone concentration. If not, another series of 10 consecutive measurements was performed.

#### c). Comparison repeatability

The comparison procedure was repeated continuously to evaluate its repeatability.

### 8.2. Comparisons at the BIPM

#### a). Ozone generation

The same source of purified air is used for all the ozone photometers being compared. Starting from compressed ambient air, the purification system consisted of a first refrigeration dryer, a catalytic converter to burn residual oil, a second refrigeration dryer, a particulate filter to remove particles larger than 0.1 µm, an active coal filter, and a final zero air generator (AADCO 737R-12), which ensured that the amount fraction of ozone, hydrocarbons, and nitrogen oxides remaining in the air was below detectable limits. This final system also ensured a constant amount fraction of oxygen in air, which is important to generate constant ozone amount

fractions in the ozone generator. The relative humidity of the reference air was monitored and the amount fraction of water in air was typically found to be less than  $3 \mu\text{mol mol}^{-1}$ .

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

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

#### b). Comparison procedure

Prior to the comparison, all the instruments were switched on and allowed to stabilise for at least 8 hours. The pressure and temperature measurement systems of the instruments were checked at this time. If any adjustments were required, these were noted.

For this comparison, no adjustments were necessary on BIPM SRPs and NIST SRP0.

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

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

#### c). Comparison repeatability

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

### 8.3. 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 NIST staff reported the measurement results in the result form BIPM.QM-K1-R3 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-R3-NMISA-23 is given in appendix 1.

## 10. Post comparison calculation

All calculations were performed by the BIPM using the form BIPM.QM-K1-R3. 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

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

## 12. Measurement standards

The instruments maintained by the BIPM and NMISA 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 253.65 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 253.65 nm under standard conditions of temperature and pressure,  $1.1476 \times 10^{-17} \text{ cm}^2$  [3].

$L_{opt}$  is the mean optical path length of the two cells;

$T$  is the measured temperature of the cells;

$T_{std}$  is the standard temperature (273.15 K);

$P$  is the measured pressure of the cells;

$P_{std}$  is the standard pressure (101.325 kPa);

$D$  is the product of transmittances of two cells, with the transmittance ( $T_r$ ) of one cell defined as

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

where

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

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

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

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

where

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

The formulation implemented in the SRP software, although equivalent in terms of the measurement results, differs from the above in the choice of a unit system based on the “atm” (atmosphere) as unit for the pressure, rather than the SI. 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. However this new, consensus value, named CCQM.O3.2019 and proposed by Hodges *et al.* [7], was adopted by both institutes in this comparison in 2025, after the measurements reported in this report.

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

## 12.3. Condition of the BIPM SRPs

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

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

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

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

Component ( <i>y</i> )	Uncertainty <i>u(y)</i>				Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to <i>u(x)</i> $ c_i  \cdot u(y)$ nmol mol <sup>-1</sup>
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty <i>u(y)</i>		
<b>Optical Path</b> <i>L<sub>opt</sub></i>	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 <i>P</i></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 <i>T</i></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 <i>D</i></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 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 NMISA SRP60

As reported in the report of the previous comparison [11], the NMISA SRP60 has been constructed by NIST in 2016 with the new design, which includes the “SRP upgrade kit” in order to deal with the two biases revealed in [4]. Its electronic module was changed prior to this comparison by NIST staff in NIST laboratories, to install the most recent electronic module, similar to the one included in BIPM SRPs [10].

### 12.7. Uncertainty budget of the NMISA SRP60

The uncertainty budget for the ozone amount-of-substance fraction in dry air ( $x$ ) measured by the NMISA standard SRP60 in the range  $0 \text{ nmol mol}^{-1}$  to  $500 \text{ nmol mol}^{-1}$  is given in .

**Table 2: Uncertainty budget for NMISA SRP60**

Component ( $y$ )	Uncertainty $u(y)$				Sensitivity coefficient $c_i = \partial x / \partial y$	contribution to $u(x)$ , $ c_i  \cdot u(y)$ nmol/mol
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$		
<b>Optical Path</b> $L_{opt}$	Measurement scale	Rectangular	0,0005 cm	0,52 cm	$-x/L_{opt}$	$2,89 \times 10^{-3} x$
	Variability	Normal	0,004 cm			
	Divergence	Rectangular	0,52 cm			
<b>Pressure <math>P</math></b>	P gauge	Rectangular	0,029 kPa	0,034 kPa	$-x/P$	$3,37 \times 10^{-4} x$
	P difference between cells	Rectangular	0,017 kPa			
<b>Temperature <math>T</math></b>	T probe	Rectangular	0,029 K	0,07 K	$x/T$	$2,29 \times 10^{-4} x$
	T gradient	Rectangular	0,058 K			
<b>Ratio of intensities <math>D</math></b>	Scaler resolution	Rectangular	$8,0 \times 10^{-6}$	$1,4 \times 10^{-5}$	$x/D \ln(D)$	0,28
	Repeatability	Triangular	$1,1 \times 10^{-5}$			
<b>Absorption Cross section per molecule <math>\sigma</math></b>	Hearn value		$1,22 \times 10^{-19} \text{ cm}^2/\text{molecule}$	$1,22 \times 10^{-19} \text{ cm}^2/\text{molecule}$	$-\frac{x}{\alpha}$	$1,06 \times 10^{-2} x$

Following this budget, the standard uncertainty associated with the ozone amount fraction measurement with the SRP60 can be expressed as a numerical equation (numerical values expressed as  $\text{nmol mol}^{-1}$ ):

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

No covariance term for the NMISA SRP60 was included in the calculations.

### 12.8. Transfer standard SRP0

SRP 0 was upgraded to the new cDAQ electronics system and now contains two independent pressure transducers for each cell. The SRP0 uncertainty budget remains the same until further evaluations can be made. It is reproduced in the last comparison report for NIST [12].

## 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-R3-NMISA-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 [13], is an extension of the previously used software B\_Least recommended by the ISO standard 6143:2025 [14]. It includes the possibility to take into account correlations between measurements performed with the same instrument at different ozone amount fractions.

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

- The first comparison results are calculated by performing a linear regression on the twelve data points from the BIPM visit ( $x_{RS}, x_{TS}$ ) (calibration of the transfer standard) followed by a second linear regression of the twelve data points from the pre BIPM visit ( $x_{NS}, x'_{TS}$ ),  $x'_{TS}$  being the corrected values of the transfer standard calibrated by the reference standard.

- The second comparison results are calculated by performing a linear regression on the twelve data points from the BIPM visit ( $x_{RS}, x_{TS}$ ) (calibration of the transfer standard) followed by a second linear regression of the twelve data points from the post BIPM visit ( $x_{NS}, x'_{TS}$ ),  $x'_{TS}$  being the corrected values of the transfer standard calibrated by the reference standard.

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

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

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 SRP60 and SRP27 is:

$$x_{SRP60} = -0.08 \text{ nmol mol}^{-1} + 1.0018 x_{SRP27} \quad (11)$$

and the standard uncertainties on the parameters of the regression are  $u(a_1) = 0.0038$  for the slope and  $u(a_0) = 0.31 \text{ nmol mol}^{-1}$  for the intercept. The covariance between the two parameters is  $\text{cov}(a_0, a_1) = -4.40 \times 10^{-4}$ ,

The least-squares regression results confirm that a linear fit is appropriate, with a sum of the squared deviations (SSD) of 0.39 and a goodness of fit (GoF) equals to 0.38.

To assess the agreement of the standards using equation 9, 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:

$$D_i = x_i - \hat{x}_{\text{SRP27}} \quad (12)$$

Where  $x_i$  is the measurement results of the national standard at the nominal value  $x_{\text{nom}}$ , and  $\hat{x}_{\text{SRP27}}$  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:

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

where  $u_i$  and  $\hat{u}_{\text{SRP27}}$  are the measurement uncertainties of the participant  $i$  and of SRP27 predicted value respectively.

### 15.2. Calculation of SRP27 predicted values and their related uncertainties

The comparison performed at the BIPM between the transfer standard and the reference standard SRP27 is used to calibrate the transfer standard. The data  $\bar{x}_{\text{RS}}$  and  $\bar{x}_{\text{TS}}$  are fitted using the generalised least square program OzonE, taking into account the associated uncertainties  $u(\bar{x}_{\text{RS}})$  and  $u(\bar{x}_{\text{TS}})$ , as well as covariance terms between the reference standard measurement results.

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

Then, for each value  $\bar{x}_{\text{TS}}$  measured with the transfer standard during its comparison with the national standard, a predicted value  $\hat{x}_{\text{RS}}$  for the reference standard is evaluated using the linear relationships between the two instruments calculated above.

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

$$u(\hat{x}_{\text{RS}}) = \sqrt{u^2(b_{\text{RS,TS}}) + x_{\text{TS}}^2 \cdot u^2(a_{\text{RS,TS}}) + a_{\text{RS,TS}}^2 \cdot u^2(x_{\text{TS}}) + 2 \cdot x_{\text{TS}} \cdot u(a_{\text{RS,TS}}, b_{\text{RS,TS}})} \quad (14)$$

Where the uncertainty components  $u(a_{\text{RS,TS}})$ ,  $u(b_{\text{RS,TS}})$  and  $u(a_{\text{RS,TS}}, b_{\text{RS,TS}})$  are calculated with the generalised least-square software OzonE.

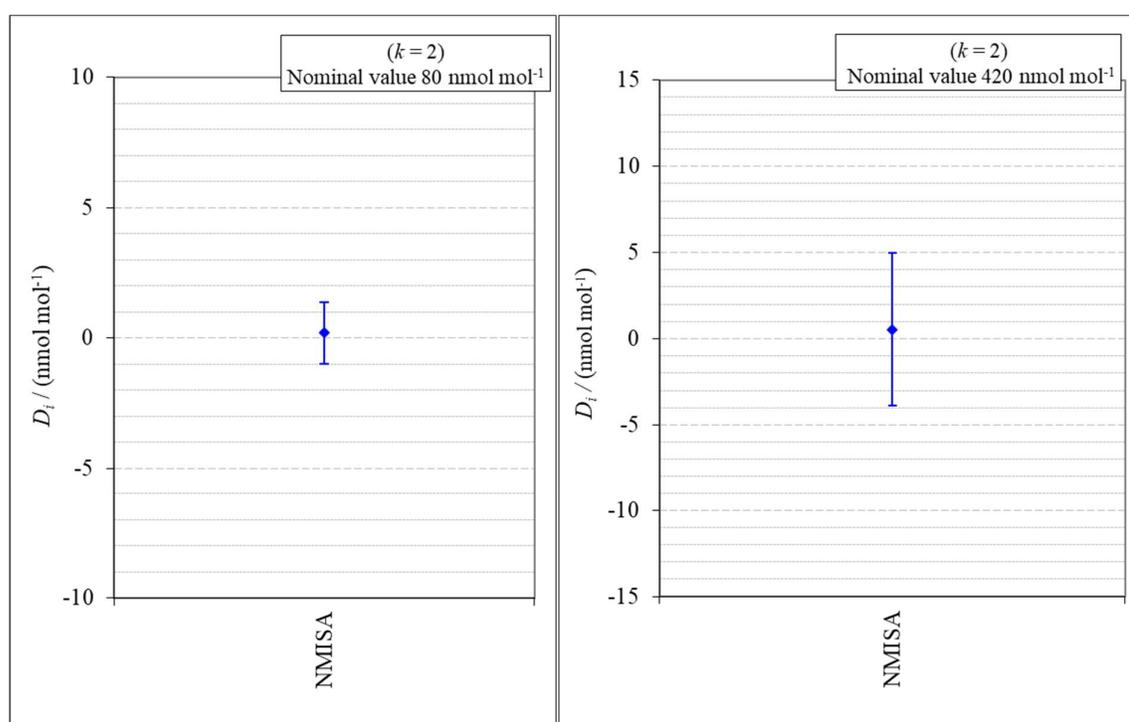
### 15.3. Values of the degrees of equivalence

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-R3-NMISA-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 the NMISA at the ozone nominal amount fractions 80 nmol mol<sup>-1</sup> and 420 nmol mol<sup>-1</sup>**

Nominal value	$x_i /$	$u_i /$	$x_{SRP27} /$	$u_{SRP27} /$	$D_i /$	$u(D_i) /$	$U(D_i) /$
	(nmol mol <sup>-1</sup> )						
80	81.75	0.37	81.55	0.47	0.19	0.60	1.19
420	419.88	1.26	419.34	1.83	0.53	2.22	4.44

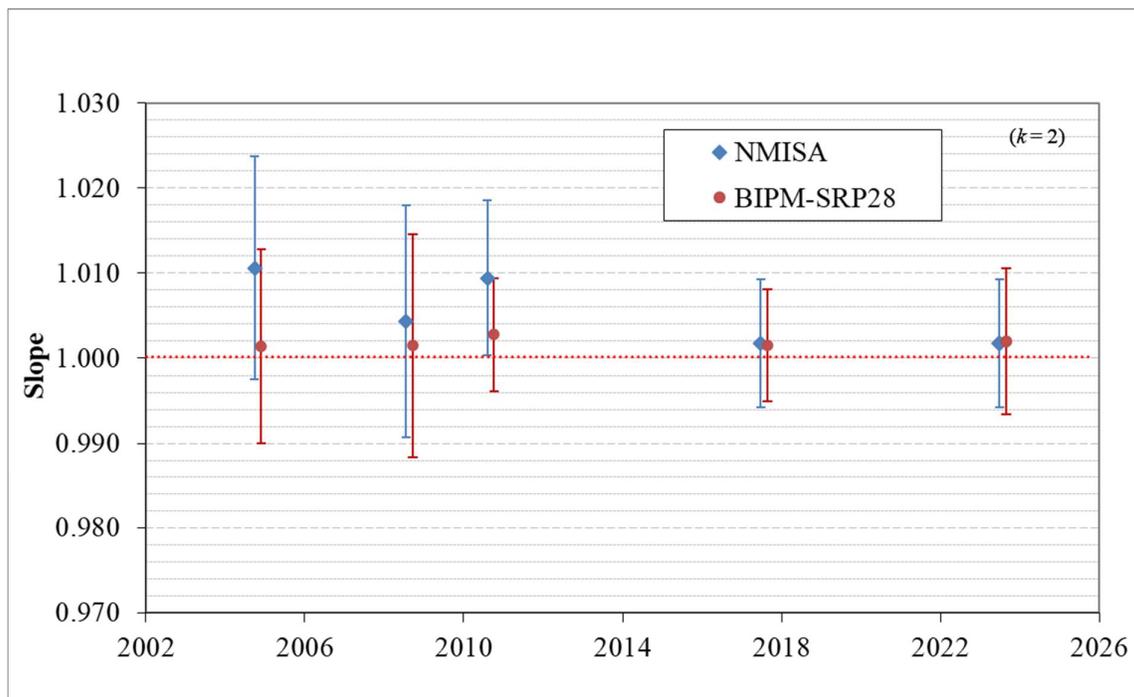


**Figure 1: Degrees of equivalence of the NMISA at the two nominal ozone amount fractions 80 nmol mol<sup>-1</sup> and 420 nmol mol<sup>-1</sup>**

The degrees of equivalence between the NMISA 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 NMISA SRP60

Results of the previous comparison performed with NMISA during 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  $x_{SRP_n} = a_0 + a_1 x_{SRP27}$  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 NMISA-SRP60 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 NMISA is the fifth 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 fifth time since the launch of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone standard of South Africa, maintained by the NMISA, 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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## Appendix 1 - Form BIPM.QM-K1-R3-NMISA-23

See the following pages.