Comparison of Ozone Reference Standards of the OEH the BIPM

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Foreword

A comparison of the ozone reference standards of the Office of Environment and Heritage NSW (OEH) and of the Bureau International des Poids et Mesures (BIPM) has been performed. Both institutes maintain Standard Reference Photometers (SRPs), developed by the National Institute of Standards and Technology (NIST), as their reference standards. The instruments were compared over a nominal ozone amount-of-substance fraction range of $0\,\mathrm{nmol}\cdot\mathrm{mol}^{-1}$ to $500\,\mathrm{nmol}\cdot\mathrm{mol}^{-1}$ and the results showed good agreement.

Comparison of Ozone Reference Standards of the OEH and the BIPM   Contents

1. Introduction

A comparison of the ozone reference standards of the Office of Environment and Heritage NSW (OEH) and of the Bureau International des Poids et Mesures (BIPM) was performed. Both institutes maintain Standard Reference Photometers (SRPs), developed by the National Institute of Standards and Technology (NIST) as their reference standards. This comparison was performed following the protocol established for the key comparison BIPM.QM-K1, described briefly in Chapter 4. A description of the standards is given in Chapter 7 of this report, together with their uncertainty budgets. The results of the comparison are given in Chapter 8, Chapter 9 and Chapter 10.

2.   Terms and definitions

No terms and definitions are listed in this document.

x_{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_{nom} by the photometer A
$\bar{x}_A$	the mean of N measurements of the nominal value x_{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_{nom} measured by the photometer A : $s_A^2 = \frac{1}{N-1}\sum_{i=1}^{N}\left(x_{A,i} - \bar{x}_A\right)^2$

- 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 $nmol \cdot mol^{-1}$.

3. Measurement schedule

Measurements reported in this report were performed from 14 to 20 June 2019 at the BIPM.

4. Measurement protocol

This comparison was performed following the protocol established for the key comparison BIPM.QM-K1. As OEH NSW is not a Designated Institute under the CIPM MRA, the results of this comparison cannot be included in BIPM.QM-K1, but are published in this BIPM report.

The protocol is summarized in this section. The complete version can be downloaded from the BIPM website (http://www.bipm.org/utils/en/pdf/BIPM.QM-K1_protocol.pdf).

This comparison was performed following protocol A, corresponding to a direct comparison between the OEH national standard SRP21 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.

4.1. 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, and dried and scrubbed with a commercial purification system so that the amount-of-substance fraction of ozone and nitrogen oxides remaining in the air is below detectable limits. The relative humidity of the reference air is monitored and the amount-of-substance fraction of water in air is typically found to be less than $3\mu\text{mol}\cdot\text{mol}^{-1}$. 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 $1\text{nmol}\cdot\text{mol}^{-1}$.

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.

4.2. Comparison procedure

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

One comparison run includes 10 different amount-of-substance fractions distributed over the range, together with the measurement of 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) $\text{nmol}\cdot\text{mol}^{-1}$. Each of these points is an average of 10 single measurements.

For each nominal value of the ozone amount-of-substance fraction x_{nom} furnished by the ozone generator, the standard deviation s_{SRP27} of the set of 10 consecutive measurements x_{SRP27},i recorded by BIPM-SRP27 was calculated. The measurement results were considered valid if s_{SRP27} was less than $1\text{nmol}\cdot\text{mol}^{-1}$, which ensures that the photometers were measuring

a stable ozone concentration. If not, another series of 10 consecutive measurements was performed.

4.3. Comparison repeatability

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

4.4. 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.

5.   Reporting measurement results

The participant and the BIPM staff reported the measurement results on the results form BIPM.QM-K1-R1, provided by the BIPM, which is available on the BIPM website. It includes details of 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-OEH-19 is given in the Appendix 1.

6. Post-comparison calculation

All calculations were performed by the BIPM using the information on form BIPM.QM-K1-R1. It includes the difference from the reference value at two nominal ozone amount-of-substance fractions, which are considered as degrees of equivalence for the key comparison BIPM.QM-K1. For information, the difference from the reference value at all nominal ozone amount-of-substance fractions are reported in the same form, as well as the linear relationship between the participant's standard and the common reference standard.

7. Measurement standards

The instruments maintained by the BIPM and the OEH are Standard Reference Photometers (SRP) built by the NIST. More details on the instrument's operating principle and its capabilities can be found in [1]. The following section describes the measurement principle and the uncertainty budgets.

7.1. 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 253.7nm by ozonized air in the gas cells of the instrument. One particular feature 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:

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

where

σ	is the absorption cross-section of ozone at 253.7nm under standard conditions of temperature and pressure, $1.1476 \times 10^{-17} \mathrm{cm}^2/\mathrm{molecule}$ [2].
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 (273.15K);
P	is the measured pressure of the cells;
P_{std}	is the standard pressure (101.325kPa);
D	is the product of transmittances of two cells, with the transmittance (T_{r}) of one cell defined as

$$T_{\mathrm{r}} = \frac{I_{\mathrm{ozone}}}{I_{\mathrm{air}}} \tag{2}$$

where

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

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

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

where

N_{A} is the Avogadro constant, $6.022\ 142 \times 10^{23} \text{mol}^{-1}$, and

R is the gas constant, $8.314\ 472 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

The formulation implemented in the SRP software is:

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

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

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

7.2. Absorption cross-section for ozone

The linear absorption coefficient under standard conditions α_x used within the SRP software algorithm is 308.32cm^{-1}. This corresponds to a value for the absorption cross section σ 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 [3].

7.3. Condition of the BIPM SRPs

Compared to the original design described in [1], SRP27 and SRP28 have been modified to take into account two biases revealed by the study conducted by the BIPM and the NIST [3]. In 2009, an "SRP upgrade kit" was installed in the instruments, as described in the report [4].

7.4. Uncertainty budget of the common reference BIPM-SRP27

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

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

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

As explained in the protocol of the comparison, following this budget 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 $\cdot$ mol^{-1}):

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

7.5.   Covariance terms for the common reference BIPM-SRP27

Correlations between the results of two measurements performed at two different ozone amount-of-substance fractions with BIPM-SRP27 were taken into account using the software OzonE. Details of the analysis of the covariance can be found in the protocol. The following expression was applied:

$$u\left(x_i, x_j\right) = x_i \cdot x_j \cdot u_b^2 \tag{7}$$

where:

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

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

7.6. Condition of the SRP21

The OEH SRP21 has not been modified since the last comparison in 2015 [5] .

7.7. Uncertainty budget of the SRP21

The uncertainty budget for the ozone amount-of-substance fraction in dry air x measured by the OEH standard SRP21 in the nominal range $0\,\text{nmol}\cdot\text{mol}^{-1}$ to $500\,\text{nmol}\cdot\text{mol}^{-1}$ is given in Table 2.

Following this budget, the standard uncertainty associated with the ozone amount-of-substance fraction measurement with the SRP21 can be expressed as a numerical equation (numerical values expressed as $\text{nmol}\cdot\text{mol}^{-1}$):

$$u(x) = \sqrt{(0.51)^2 + 9.37\cdot 10^{-6}x^2} \tag{9}$$

No covariance term for the SRP21 was included in the calculations.

Table 2.   **Uncertainty budget for the SRP21**

Component	Value	Source	Distribution	Standard Uncertainty	Combined Standard Uncertainty	Sensitivity Coefficient	Contribution to $u(x)$/nmol·mol^{-1}
Optical Path (L)	89.58cm	Measurement	Rect	0.520cm	0.520cm	$-\frac{x}{L}$	$2.90 \times 10^{-3}x$
Pressure (P)	101.325kPa	Gauge Difference	Rect Rect	0.077kPa 0.038kPa	0.086kPa	$\frac{-x}{P}$	$8.5 \times 10^{-3}x$
Temperature (T)	273.15°K	Probe Gradient	Rect Rect	0.115K 0.058K	0.129K	$\frac{x}{T}$	$4.7 \times 10^{-3}x$
Repeatability		Repeat Measurements	Rect	0.095nmol·mol^{-1}	0.095nmol·mol^{-1}	1	0.095
Resolution			Rect	0.500nmol·mol^{-1}	0.500nmol·mol^{-1}	1	0.500
Absorption Cross Section (α)	308.32cm^{-1}	Conventional Value	Rect	1.732cm^{-1}	1.732cm^{-1}	$\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$

8.   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 given in the form BIPM.QM-K1-R1-OEH-19 (Appendix 1, see p. 24).

9. Differences from the reference values

For the key comparison BIPM.QM-K1, differences from the reference values were calculated at the twelve nominal ozone amount-of-substance fractions measured, but are only shown in this report at two particular values: 80nmol·mol^{-1} and 420nmol·mol^{-1}. These values correspond to points 3 and 4 recorded in each comparison. The ozone amount-of-substance fractions measured by the ozone standards can differ from the nominal values because an ozone generator has limited reproducibility. However, as stated in the protocol, the value measured by the common reference SRP27 was expected to be within ±15nmol·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.

9.1. Definition

The difference from the reference value of the participant i at a nominal value x_{nom} is defined as:

$$D_i = x_i - x_{\mathrm{SRP27}} \qquad (10)$$

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

Its associated standard uncertainty is:

$$u(D_i) = \sqrt{u_i^2 + u_{\mathrm{SRP27}}^2} \qquad (11)$$

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

9.2. Values

The differences from the reference values and their uncertainties calculated in the form BIPM.QM-K1-R1-OEH-19 are reported in Table 3 below. Corresponding graphs of equivalence are given in Figure 1. The expanded uncertainties are calculated with a coverage factor $k = 2$.

Table 3. **Differences from the reference values of the OEH at the nominal ozone amount-of-substance fractions** 80nmol·mol^{-1} **and** 420nmol·mol^{-1}

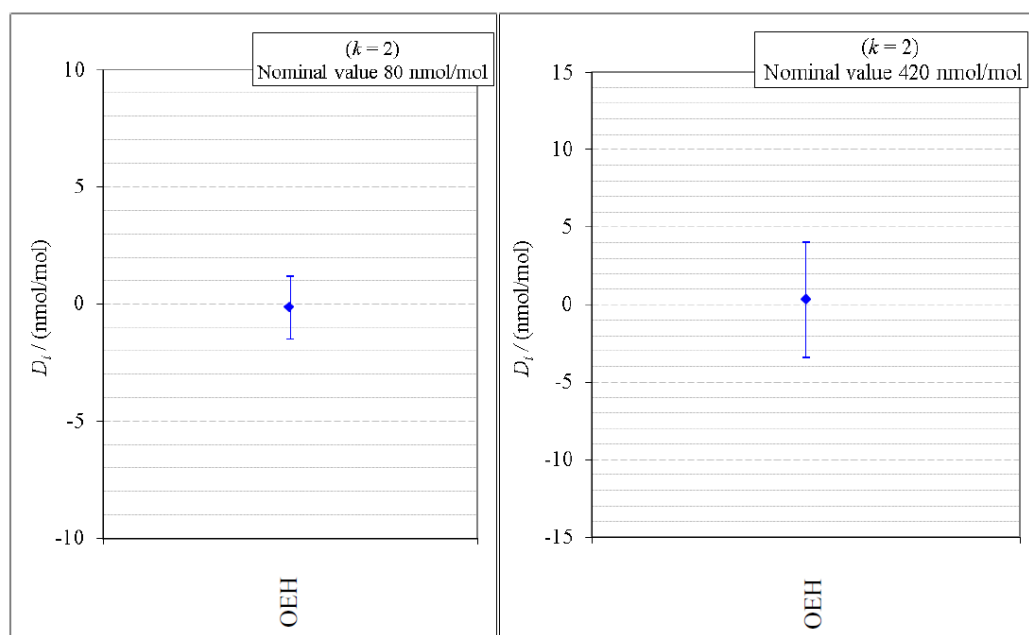| Nom value	x_i / (nmol·mol^{-1})	u_i / (nmol·mol^{-1})	x_{SRP27} / (nmol·mol^{-1})	u_{SRP27} / (nmol·mol^{-1})	D_i / (nmol·mol^{-1})	$u(D_i)$ / (nmol·mol^{-1})	$U(D_i)$ / (nmol·mol^{-1})
80	79.31	0.57	79.46	0.36	−0.15	0.68	1.35
420	419.34	1.38	419.02	1.26	0.32	1.87	3.73

Figure 1 — Graphs of equivalence of the OEH at the two nominal ozone amount-of-substance fractions $80 \mathrm{nmol} \cdot \mathrm{mol}^{-1}$ **and** $420 \mathrm{nmol} \cdot \mathrm{mol}^{-1}$

The differences between the OEH standard and the common reference standard BIPM SRP27 indicate agreement between both standards.

10. Analysis of the measurement results by generalized least-square regression

The relationship between two ozone photometers was evaluated with a generalized least-square regression fit performed on the two sets of measured ozone amount-of-substance fractions, taking into account standard measurement uncertainties. To this end, the software package OzonE was used. This software, which is documented in a publication [6], is an extension of the previously used software B_Least, recommended by the ISO standard 6143:2001 [7]. OzonE allows users to account for correlations between measurements performed with the same instrument at different ozone amount-of-substance fractions.

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

$$x_{\mathrm{SRP}n} = a_0 + a_1 x_{\mathrm{SRP27}} \tag{12}$$

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.

10.1. Least-square regression results

The relationship between SRP21 and SRP27 is:

$$x_{\mathrm{SRP21}} = 1.0018 x_{\mathrm{SRP27}} - 0.31 \tag{13}$$

The standard uncertainties on the parameters of the regression are $u(a1) = 0.0035$ for the slope and $u(a0) = 0.31 \mathrm{nmol \cdot mol^{-1}}$ for the intercept. The covariance between the two parameters is $\mathrm{cov}\,(a_0, a_1) = -3.84 \times 10^{-4} \mathrm{nmol \cdot mol^{-1}}$.

The least-square regression statistical parameters confirm the appropriate choice of a linear relation, with a sum of the squared deviations (SSD) of 0.06 and a goodness of fit (GoF) equal to 0.11.

To assess the agreement of the standards from equation 10, 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 the 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. $|1 - a_1| < 2u(a_1)$.

11. History of comparisons between BIPM SRP27, SRP28 and OEH SRP21

Results of previous comparison performed between BIPM-SRP27, BIPM-SRP28 and OEH SRP21 (named DECCW in previous reports [5], [8], [9], see p. 25) during the course of the key comparison BIPM.QM-K1 are given in Figure 2. The slopes a_1 of the linear relation $x_{\mathrm{SRP}n} = a_0 + a_1 x_{\mathrm{SRP27}}$ are represented together with their associated uncertainties calculated at the time of each comparison. Results of previous comparisons have been corrected to take into account the changes in the reference BIPM-SRP27 described in [4], which explains the larger uncertainties associated with the corresponding slopes. Results of the comparison performed in January 2015 have been reported together with results performed in April 2015 after the replacement of the instrument gas cells that broke in between the two exercises. Figure 2 shows that all standards included in these comparisons stayed in close agreement.
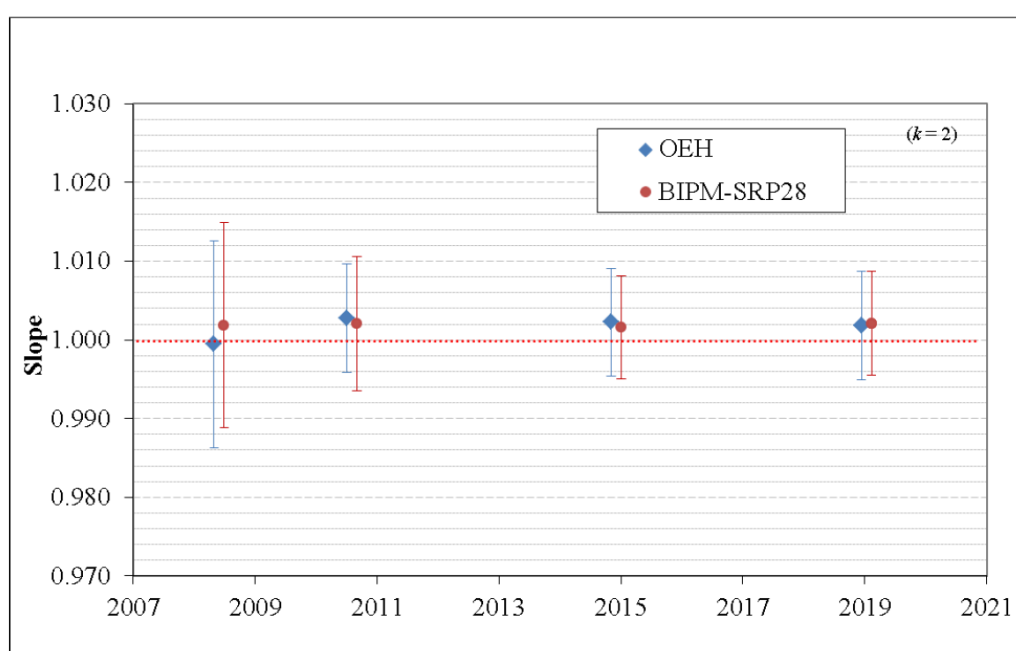

Figure 2 — Results of the comparisons between SRP27, SRP28 and OEH SRP21 performed at the BIPM during the course of the key comparison BIPM.QM-K1. Uncertainties are calculated at $k = 2$, with the uncertainty budget in use at the time of each comparison.

12. Conclusion

A comparison was performed between the ozone reference standards of the OEH and of the BIPM. The instruments were compared over a nominal ozone amount-of-substance fraction range of $0\,\mathrm{nmol\cdot mol^{-1}}$ to $500\,\mathrm{nmol\cdot mol^{-1}}$. Results of this comparison indicated good agreement between both standards.

Appendix 1. Form BIPM.QM-K1-R1-OEH-19

See next pages.

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Document Control

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