

Comparison of Ozone Reference Standards of the DECCW the **BIPM**

1st edition 2015



Copyright statement

This document is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

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 nmolmol⁻¹ to 500 nmolmol⁻¹ and the results showed good agreement.

Comparison of Ozone Reference Standards of the DECCW and the BIPM

Contents

1. Introduction	7
2. Terms and definitions	8
3. Measurement schedule	9
4. Measurement protocol	10
4.1. Ozone generation	10
4.2. Comparison procedure	10
4.3. Comparison repeatability	11
4.4. SRP27 stability check	11
5. Reporting measurement results	12
6. Post-comparison calculation	13
7. Measurement standards	14
7.1. Measurement equation of a NIST SRP	14
7.2. Absorption cross-section for ozone	15
7.3. Condition of the BIPM SRPs	15
7.4. Uncertainty budget of the common reference BIPM-SRP27	15
7.5. Covariance terms for the common reference BIPM-SRP27	16
7.6. Condition of the SRP21	17
7.7. Uncertainty budget of the SRP21	17
8. Measurement results and uncertainties	18
9. Differences from the reference values	19
9.1. Definition	19
9.2. Values	19
10. Analysis of the measurement results by generalized least-square regression	21
10.1. Least-square regression results	21
11. History of comparisons between BIPM SRP27, SRP28 and OEH SRP21	22
12. Conclusion	23
References	30
Annex 1. Form BIPM.QM-K1-R1-DECC-15	24

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 : $s_A^2 = \frac{1}{N-1} \sum_{i=1}^N (x_{A,i} - \bar{x}_A)^2$

- 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 nmolmol^{-1} .

3. Measurement schedule

The comparison was originally scheduled and performed in January 2015. After this first comparison, the optical cells of the instrument broke during shipment from the BIPM to the OEH. The instrument was sent back to the BIPM where new cells have been installed, and the comparison repeated. Measurements reported in this report were performed from 10 to 16 April 2015 at the BIPM. Measurements performed in January 2015 are reported for information in Chapter 11, with the aim to show that replacing the instrument's gas cells did not change its comparability with SRP27.

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/utis/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, 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 $3 \mu\text{molmol}^{-1}$. 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 nmolmol^{-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) nmolmol^{-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 $x_{\text{SRP27},i}$ recorded by BIPM-SRP27 was calculated. The measurement results were considered valid if s_{SRP27} was less than 1 nmolmol^{-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 result form BIPM.QM-K1-R1, provided by the BIPM, and 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-DECC-15 is given in the Annex 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 253.7 nm 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:

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

where

σ is the absorption cross-section of ozone at 253.7 nm under standard conditions of temperature and pressure, $1.1476 \times 10^{-17} \text{ cm}^2/\text{molecule}$ ISO 13964:1996;

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

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

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

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

7.2. Absorption cross-section for ozone

The linear absorption coefficient under standard conditions α_x used within the SRP software algorithm is 308.32 cm^{-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 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 (y)	Uncertainty $u(y)$				Sensitivity contribution coefficient to $u(x)$	
	Source	Distribution	Standard Uncertainty	Combined standard	$c_i = \frac{\partial x}{\partial y}$	$ c_i \cdot u(y)$ nmol mol^{-1}

				uncertainty $u(y)$		
Optical Path L_{opt}	Measurement Rectangular scale		0.0006 cm			
	Repeatability Normal		0.01 cm	0.52 cm	$-\frac{x}{L_{\text{opt}}}$	$2.89 \times 10^{-3}x$
	Correction Rectangular factor		0.52 cm			
Pressure P	Pressure Rectangular gauge		0.029 kPa			
	Difference Rectangular between cells		0.017 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37 \times 10^{-4}x$
Temperature T	Temperature Rectangular probe		0.03 K			
	Temperature Rectangular gradient		0.058 K	0.07 K	$\frac{x}{T}$	$2.29 \times 10^{-4}x$
Ratio of intensities D	Scaler Rectangular resolution		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	$-\frac{x}{\sigma}$	$1.06 \times 10^{-2}x$

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 nmolmol⁻¹):

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

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 about the analysis of the covariance 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:

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

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

7.6. Condition of the SRP21

Compared to the original design, the OEH SRP21 has been modified to deal with the two biases revealed in [3]. In August 2006, an “SRP upgrade kit” was installed by NIST at the NIST laboratories.

Following the replacement of the two gas cells performed in April 2015 at the BIPM, the length of the optical cell changed from 89.92 to 89.58 cm, when calculated as an average of the two cells. This new average value was provided by NIST. The new optical cell would change the input optical path length parameters whilst affecting its uncertainty evaluation.

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 nmolmol^{-1} to 500 nmolmol^{-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 nmolmol^{-1}):

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

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 Sensitivity Uncertainty	Contribution Standard Coefficient $u(x)$ / nmolmol^{-1}
Optical Path (L)	89.58 cm	Measurement	Rect	0.520 cm	0.520 cm	$-\frac{x}{L}$ $2.90 \times 10^{-3}x$
Pressure (P)	101.325 kPa	Gauge Difference	Rect Rect	0.077 kPa 0.038 kPa	0.086 kPa	$-\frac{x}{P}$ $8.5 \times 10^{-3}x$
Temperature (T)	273.15 °K	Probe Gradient	Rect Rect	0.115 K 0.058 K	0.129 K	$\frac{x}{T}$ $4.7 \times 10^{-3}x$
Repeatability		Repeat Measurements	Rect	0.095 nmolmol ⁻¹	0.095 nmolmol ⁻¹	1 0.095
Resolution			Rect	0.500 nmolmol ⁻¹	0.500 nmolmol ⁻¹	1 0.500
Absorption Cross Section (α)	0.08.32 cm ⁻¹	Conventional Value	Rect	1.732 cm ⁻¹	1.732 cm ⁻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-DECC-15 (Annex 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: 80 nmolmol⁻¹ and 420 nmolmol⁻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 ± 15 nmolmol⁻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:

$$D_i = x_i - x_{\text{SRP27}} \quad (10)$$

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:

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

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-DECC-15 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 80 nmolmol⁻¹ and 420 nmolmol⁻¹

Nom value	$x_i /$ nmolmol ⁻¹	$u_i /$ nmolmol ⁻¹	$x_{\text{SRP27}} /$ nmolmol ⁻¹	$u_{\text{SRP27}} /$ nmolmol ⁻¹	$D_i /$ nmolmol ⁻¹	$u(D_i) /$ nmolmol ⁻¹	$U(D_i) /$ nmolmol ⁻¹
80	80.75	0.57	80.72	0.37	0.03	0.67	1.35
420	423.87	1.39	423.23	1.27	0.64	1.88	3.77

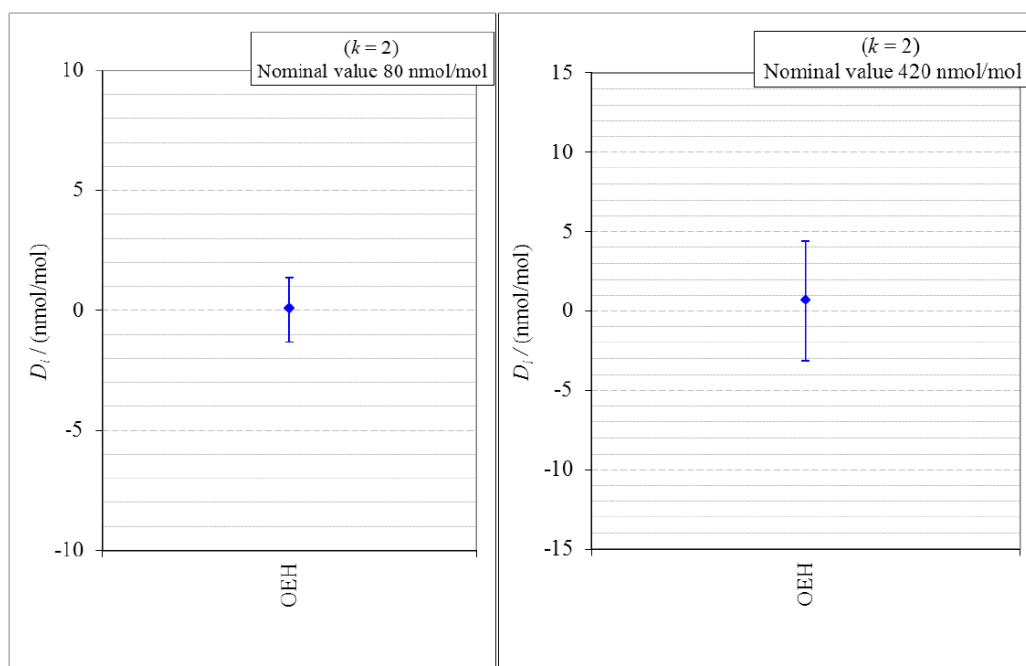


Figure 1 — Graphs of equivalence of the OEH at the two nominal ozone amount-of-substance fractions 80 nmolmol^{-1} and 420 nmolmol^{-1}

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 leastsquare 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 [5], is an extension of the previously used software B_Least, recommended by the ISO standard 6143:2001 ISO 6143.2:2001. 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 SRP n and SRP27 is obtained:

$$X_{\text{SRP}n} = a_0 + a_1 X_{\text{SRP}27} \quad (12)$$

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.

10.1. Least-square regression results

The relationship between SRP21 and SRP27 is:

$$X_{\text{SRP}21} = -0.12 + 1.0022 \cdot X_{\text{SRP}27} \quad (13)$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0034$ for the slope and $u(a_0) = 0.31 \text{ nmolmol}^{-1}$ for the intercept. The covariance between the two parameters is $\text{cov}(a_0, a_1) = -3.73 \times 10^{-4} \text{ nmolmol}^{-1}$.

The least-square regression statistical parameters confirm the appropriate choice of a linear relation, with a sum of the squared deviations (SSD) of 0.12 and a goodness of fit (GoF) equal to 0.14.

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 [7], [8], see p. 30) during the course of the key comparison BIPM.QM-K1 are given in Figure 2. The slopes a_1 of the linear relation $x_{\text{SRP}n} = a_0 + a_1 x_{\text{SRP}27}$ 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.

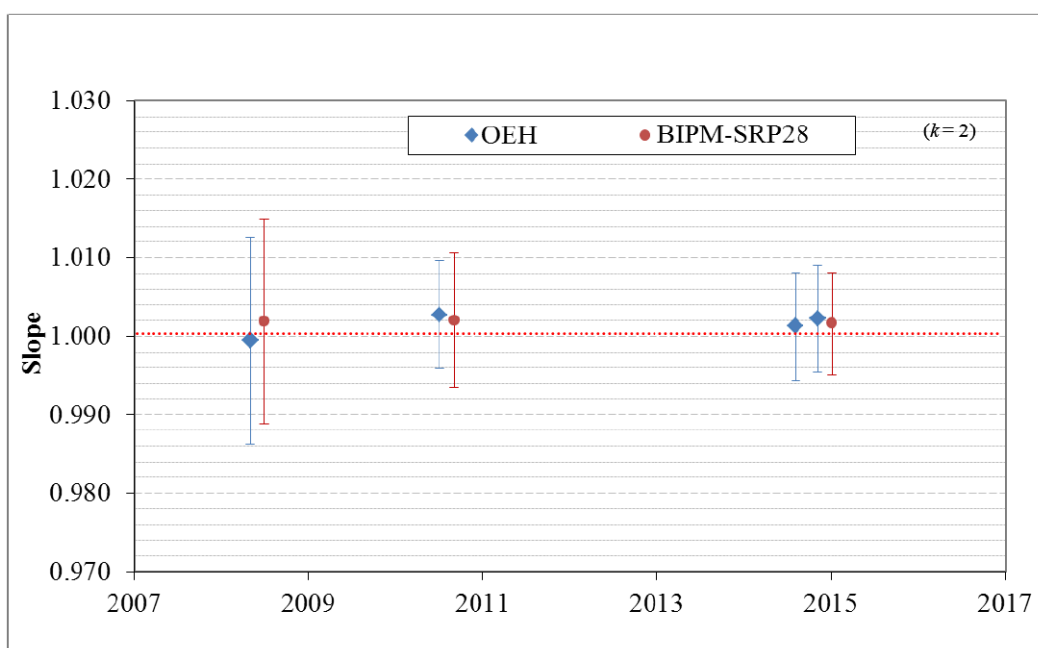


Figure 2 — Results of the comparisons between SRP27, SRP28 and OEH SRP21 performed at the BIPM during the course of the key comparison BIPM.QM-K1. Uncertainties are calculated at $k = 2$, with the uncertainty budget in use at the time of each comparison.

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 nmolmol⁻¹ to 500 nmolmol⁻¹. Results of this comparison indicated good agreement between both standards.

Annex 1. Form BIPM.QM-K1-R1-DECC-15

See next pages.

A1.1. OZONE COMPARISON RESULT#—#PROTOCOL A#—#DIRECT COMPARISON

Participating institute information		
Institute	Department of Environment and Climate Change NSW	
Address	Dock 3, Atmospheric Science Building 480 Weeroona Road Lidcombe NSW 2141 Australia	
Contact	Glenn Ross	
Email	Glenn.ross@environment.nsw.gov.au	
Telephone	61 2 9995 5166	
Instruments information		
	Reference Standard	National Standard
Manufacturer	NIST	NIST
Type	SRP	SRP
Serial number	SRP27	SRP21

Content of the report

general informations
comparison results
measurements results
comparison description
uncertainty budgets

A1.1.1. comparison reference standard (RS) — national standard (NS)

Operator	F. Idrees	Location	CHEM-9
Comparison begin date / time	10/04/2015 02:33	Comparison end date / time	16/04/ 2015 07:52

A1.1.2. Comparison results

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

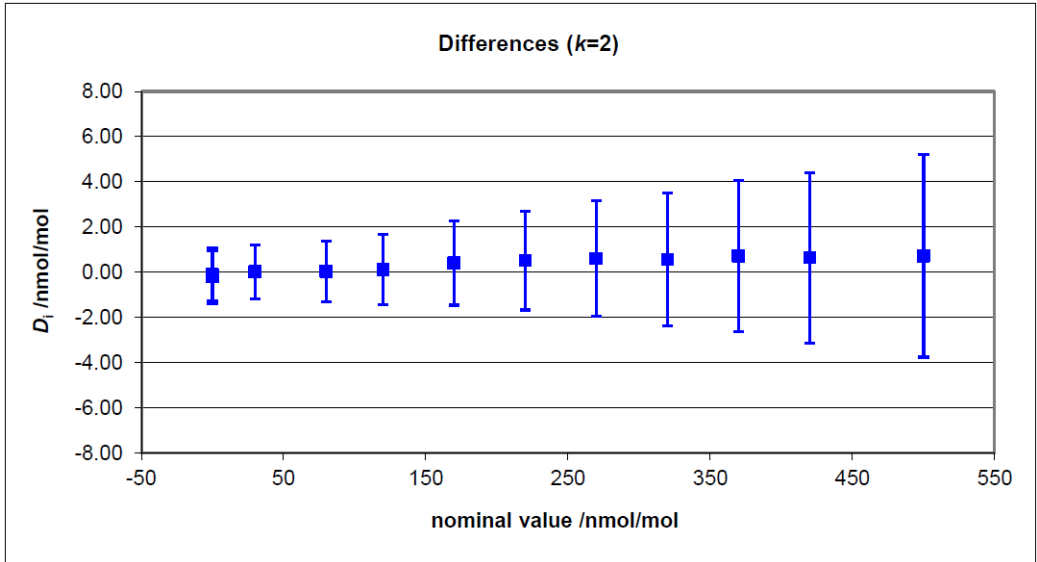
Table A1.1. Least-square regression parameters

$a_{TS,RS}$	$u(a_{TS,RS})$	$b_{TS,RS}$ nmolmol ⁻¹	$u(b_{TS,RS})$ nmolmol ⁻¹	$u(a, b)$
1.0022	0.0034	-0.12	0.31	-3.73E-04

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

Table A1.2. Difference from the reference value at 80 nmolmol⁻¹ and 420 nmolmol⁻¹:

Nom value nmolmol ⁻¹	D_i nmolmol ⁻¹	$u(D_i)$ nmolmol ⁻¹	$U(D_i)$ nmolmol ⁻¹
80	0.03	0.67	1.35
420	0.64	1.88	3.77



A1.1.3. Measurement results

Measurement results						
Nominal value	Reference Standard (RS)			National standard (NS)		
	x_{RS} nmolmol ⁻¹	s_{RS} nmolmol ⁻¹	$u(x_{RS})$ nmolmol ⁻¹	x_{NS} nmolmol ⁻¹	s_{NS} nmolmol ⁻¹	$u(x_{NS})$ nmolmol ⁻¹
0	0.10	0.33	0.28	0.00	0.19	0.51
220	218.74	0.39	0.70	219.25	0.16	0.84
80	80.72	0.29	0.37	80.75	0.19	0.57
420	423.23	0.35	1.27	423.87	0.31	1.39

120	121.33	0.42	0.45	121.45	0.17	0.63
320	319.23	0.28	0.97	319.78	0.23	1.10
30	32.00	0.18	0.30	32.02	0.20	0.52
370	370.84	0.26	1.12	371.56	0.18	1.25
170	170.26	0.22	0.57	170.66	0.18	0.73
500	510.96	0.32	1.52	511.68	0.14	1.65
270	268.88	0.28	0.83	269.48	0.13	0.97
0	0.08	0.30	0.28	-0.13	0.11	0.51

Differences

Point Number	Nom value	nmolmol ⁻¹	D_i nmolmol ⁻¹	$u(D_i)$ nmolmol ⁻¹	$U(D_i)$ nmolmol ⁻¹
1	0		-0.11	0.58	1.16
2	220		0.51	1.09	2.19
3	80		0.03	0.67	1.35
4	420		0.64	1.88	3.77
5	120		0.11	0.78	1.55
6	320		0.56	1.47	2.94
7	30		0.02	0.60	1.19
8	370		0.72	1.67	3.35
9	170		0.40	0.93	1.85
10	500		0.71	2.24	4.48
11	270		0.60	1.28	2.56
12	0		-0.21	0.58	1.16

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 α for the reference standard	8.50E-06
Value of α for the national standard	0.00E+00

A1.1.4. Comparison conditions

Table A1.3. Comparison conditions

Ozone generator manufacturer	Environics
Ozone generator type	Model 6100
Ozone generator serial number	3128
Room temperature(min-max) / °C	20.55-21.47
Room pressure (min-max) / hpa	1002.3-1002.6
Zero air source	oil free compressor + dryer+ aadco 737-R
Reference air flow rate (L min ⁻¹)	15
Sample flow rate (L min ⁻¹)	10
Instruments stabilisation time	more than 48 hours
Instruments acquisition time / s (one measurement)	5 s
Instruments averaging time / s	5 s
Total time for ozone conditioning	more than 48 hours
Ozone mole fraction during conditioning	850 nmolmol ⁻¹
Comparison repeated continuously (Yes/No)	yes
If no, ozone mole fraction in between the comparison repeats	
Total number of comparison repeats realised	31
Data files names and location	\\chem5\Program Files\NIST\SRPControl \Data\2015 c150410001.xls to c150415006.xls

A1.1.5. Instruments checks and adjustments

Reference Standard
Instrument adjusted according to BIPM internal procedures and criterions.
National Standard

A1.1.6. 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

Table A1.4. SRP Uncertainty Statement—Department of Environment and Climate Change NSW

Component	Value	Source	Distribution	Standard Uncertainty	Combined Standard Uncertainty	Sensitivity Coefficient	Contribution (%)
Optical Path (L)	89.92 cm	BIPM	Rect	0.520 cm	0.520 cm	$-\frac{x}{2L}$	0.289%
Pressure (P)	101.325 kPa	Gauge Difference	Rect	0.077 kPa 0.038 kPa	0.086 kPa	$-\frac{x}{P}$	0.085%
Temperature (T)	273.15 °K	Probe Gradient	Rect	0.115 K 0.058 °K	0.129 K	$\frac{x}{T}$	0.047%
Repeatability		Repeat Measurements	Rect	0.095 nmolmol ⁻¹	0.095 nmolmol ⁻¹		0.095 nmolmol ⁻¹
Resolution			Rect	0.500 nmolmol ⁻¹	0.500 nmolmol ⁻¹		0.500 nmolmol ⁻¹
Absorption Cross Section (α)	308.32 cm ⁻¹	Conventional Value	Rect	1.732 cm ⁻¹	1.732 cm ⁻¹	$\frac{x}{\alpha}$	0.562%

Combined Uncertainty

Combined standard uncertainty NOT including absorption coefficient uncertainty

$$u_{\text{SRP}} = \sqrt{(0.51)^2 + 9.37 \times 10^{-6} x^2} \quad (\text{A1.1})$$

Combined standard uncertainty including absorption coefficient uncertainty

$$u_{\text{SRP}} = \sqrt{(0.51)^2 + 4.09 \times 10^{-5} x^2} \quad (\text{A1.2})$$

References

- [1] Paur R.J., Bass A.M., Norris J.E. and Buckley T.J. 2003 Standard Reference Photometer for the Assay of Ozone in calibration Atmospheres *NISTIR 6963*, 65 pp
- [2] ISO 13964:1996 *ISO 13964 : 1996 Ambient air—Determination of ozone—Ultraviolet photometric method (International Organization for Standardization)*
- [3] 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
- [4] 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
- [5] 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
- [6] ISO 6143.2:2001 *ISO 6143.2 : 2001 Gas analysis—Determination of the composition of calibration gas mixtures—Comparison methods (International Organization for Standardization)*
- [7] Viallon J., Moussay P., Idrees F., Wielgosz R.I. and Ross G. 2011 Comparison of Ozone Reference Standards of the DECCW and the BIPM, December 2010 **Rapport BIPM-2011/03**, 18 pp
- [8] Viallon J., Moussay P., Wielgosz R.I. and Ross G. 2009 Comparison of Ozone Reference Standards of the DECC NSW and the BIPM, October 2008 **Rapport BIPM-2009/03**, 19 pp

Document Control

Authors: Faraz Idrees (BIPM), Philippe Moussay (BIPM), Robert Wielgosz (BIPM), and
Glenn Ross (OEH)



