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Comparison of Ozone Reference Standards of the DECC NSW and the BIPM

by

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Comparison of Ozone Reference Standards of the DECC NSW and the BIPM, October 2008

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Abstract

A comparison of the ozone reference standards of the Department of Environment and Climate Change NSW (DECC NSW) 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 mole fraction range of 0 nmol/mol to 500 nmol/mol and the results showed good agreement.

Contents:

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1. Introduction

A comparison of the ozone reference standards of the Department of Environment and Climate Change NSW (DECC NSW) 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. This comparison was performed following the protocol established for the key comparison BIPM.QM-K1, described briefly in section 4. A description of the standards is given in section 7 of this report, together with their uncertainty budgets. The results of the comparison are given in sections 8, 9 and 10.

2. Terms and definitions

- x_{nom}: nominal ozone mole fraction in dry air furnished by the ozone generator
- $x_{\mathrm{A},i}$: ith measurement of the nominal value x_{nom} by the photometer A
- $\bar{x}_{\mathrm{A}}$: the mean of N measurements of the nominal value x_{nom} measured by the photometer A : $\bar{x}_{\mathrm{A}} = \frac{1}{N}\sum_{i=1}^{N} x_{\mathrm{A},i}$
- s_{A} : standard deviation of N measurements of the nominal value x_{nom} measured by the photometer A : $s_{\mathrm{A}}{}^{2} = \frac{1}{N-1}\sum_{i=1}^{N} (x_{\mathrm{A},i} - \bar{x}_{\mathrm{A}})^{2}$
- 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: $x_{\mathrm{A}} = a_{\mathrm{A,B}} x_{\mathrm{B}} + b_{\mathrm{A,B}}$. With this notation, the photometer A is compared against the photometer B. $a_{\mathrm{A,B}}$ is dimensionless and $b_{\mathrm{A,B}}$ is expressed in units of nmol/mol.

3. Measurement schedule

Measurements reported in this report were performed from 20 to 22 October 2008 at the BIPM.

4. Measurement protocol

This comparison was performed following the protocol established for the key comparison BIPM.QM-K1. As DECC 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 DECC NSW 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 mole 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 mole 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 mole fraction of water in air typically found to be less than 3 µmol/mol. The mole fraction of volatile organic hydrocarbons in the reference air was measured (November 2002), with no mole fraction of any detected component exceeding 1 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.

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 mole fractions distributed over 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. Each of these points is an average of 10 single measurements.

For each nominal value of the ozone mole fraction x_{nom} furnished by the ozone generator, the standard deviation s_{SRP27} of the set of 10 consecutive measurements $x_{\mathrm{SRP27},i}$ recorded by BIPM-SRP27 was calculated. The measurement results were considered valid if s_{SRP27} was less than 1 nmol/mol, 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 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 mole fractions measured by the participant standard and the common reference standard. The completed form BIPM.QM-K1-R1-DECC-08 is given in the annex.

6. Post-comparison calculation

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

7. Measurement standards

The instruments maintained by the BIPM and the DECC NSW 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 ozone mole 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 concentration (C) of ozone is calculated from:

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

where

- α is the absorption cross-section of ozone at 253.7 nm under standard conditions of temperature and pressure. The value used is: 1.1476×10^{-17} $\mathrm{cm^2/molecule}$ [2].
- L_{opt} is the optical path length of one of the 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) of one cell defined as

$$T = \frac{I_{\mathrm{ozone}}}{I_{\mathrm{air}}} \qquad (2)$$

where

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

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 a mole fraction (x) of ozone in air:

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

where

N_{A} is the Avogadro constant, 6.022142×10^{23} mol^{-1}, and

R is the gas constant, 8.314472 J mol^{-1} K^{-1}.

7.2. Absorption cross section for ozone

The absorption cross section used within the SRP software algorithm is 308.32 atm^{-1}cm^{-1}. This corresponds to a value of 1.1476×10^{-17} cm^2/molecule, rather than the more often quoted 1.147×10^{-17} cm^2/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. In a recent publication [3] 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.

7.3. Current state of the BIPM SRPs

Compared to the original design described in , SRP27 and SRP28 have been modified to deal with two biases revealed by the study conducted by the BIPM and the NIST [3]:

- The SRPs are equipped with a thermo-electric cooling device to remove excess heat from the lamp housing and prevent heating of the cells. Together with a regular calibration of their temperature probe, this ensures the removal of the bias on the temperature measurement of the gas cell.
- In SRP27 and SRP28 the optical path length is now calculated as being 1.005 times the total length of the two cells within each instrument. Together with an increased uncertainty, this takes into account the bias on the optical path length.

7.4. Uncertainty budget of the common reference BIPM-SRP27

The uncertainty budget for the ozone mole fraction in dry air x measured by the instruments BIPM-SRP27 and BIPM-SRP28 in the nominal range 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 $u(x)$ $\lvert c_i \rvert \cdot u(y)$ nmol/mol
	Source	Distribution	Standard uncertainty	Combined standard uncertainty $u(y)$		
Optical Path L_{opt}	Measurement Scale	Rectangular	0.0006 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89\times10^{-3}x$
	Repeatability	Normal	0.01 cm			
	Correction factor	Rect	0.52 cm			
Pressure P	Pressure gauge	Rectangular	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37\times10^{-4}x$
	Difference between cells	Rectangular	0.017 kPa			
Temperature T	Temperature probe	Rectangular	0.03 K	0.07 K	$\frac{x}{T}$	$2.29\times10^{-4}x$
	Temperature gradient	Rectangular	0.058 K			
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 α	Hearn value		1.22×10^{-19} cm²/molecule	1.22×10^{-19} cm²/molecule	$-\frac{x}{\alpha}$	$1.06\times10^{-2}x$

Following this budget, as explained in the protocol of the comparison, the standard uncertainty associated with the ozone mole fraction measurement with the BIPM SRPs can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u(x) = \sqrt{(0.28)^2 + (2.92\cdot10^{-3}x)^2} \tag{4}$$

7.5. Covariance terms for the common reference BIPM-SRP27

As explained in section 10, correlations between the results of two measurements performed at two different ozone mole 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:

$$u(x_i, x_j) = x_i \times x_j \times u_{\mathrm{b}}^2 \tag{5}$$

where:

$$u_{\mathrm{b}}^2 = \frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} + \frac{u^2(L_{\mathrm{opt}})}{L_{\mathrm{opt}}^2} \tag{6}$$

The value of u_b is given by the expression of the measurement uncertainty: $u_b = 2.92\times10^{-3}$ or $u_b^2 = 8.5\times10^{-6}$.

7.6. Current state of the SRP21

Compared to the original design, the DECC NSW 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 DECC NSW laboratories. The kit consists of two parts:

- A new source block was designed to minimize the gas temperature evaluation bias by better thermally insulating the UV source lamp (heated at a temperature of about 60 °C) from the rest of the optical bench, thus avoiding the temperature gradient observed in the SRP when the original source block is used.
- A new set of absorption cells was installed. The new cells are quartz tubes closed at both ends by optically sealed quartz windows. These windows are tilted by 3° with respect to the vertical plane to avoid multiple reflections along the light path.

7.7. Uncertainty budget of the SRP21

The uncertainty budget for the ozone mole fraction in dry air x measured by the DECC NSW standard SRP21 in the nominal range 0 nmol/mol to 500 nmol/mol is given in Table 2.

Following this budget, the standard uncertainty associated with the ozone mole fraction measurement with the SRP21 can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u(x) = \sqrt{(0.51)^2 + 9.31\cdot10^{-6}x^2} \tag{7}$$

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	Sensibility Coefficient	Contribution to u(x)
Optical Path (*L*)	89.92 cm	Measurement	Rect	0.520 cm	0.520 cm	$-\frac{x}{L}$	0.289 %
Pressure (*P*)	101.325 kPa	Gauge	Rect	0.077 kPa	0.086 kPa	$\frac{-x}{P}$	0.085 %
		Difference	Rect	0.038 kPa			
Temperature (*T*)	273.15 °K	Probe	Rect	0.115 K	0.129 K	$\frac{x}{T}$	0.047 %
		Gradient	Rect	0.058 K			
Repeatability		Repeat Measurements	Rect	0.095 ppb	0.095 ppb	1	0.095 ppb
Resolution			Rect	0.500 ppb	0.500 ppb	1	0.500 ppb
Absorption Cross Section (*α*)	308.32 cm^{-1}	Conventional Value	Rect	1.732 cm^{-1}	1.732 cm^{-1}	$\frac{x}{\alpha}$	0.562 %

8. Measurement results and uncertainties

Details of the measurement results, the measurement uncertainties and the standard deviations at each nominal ozone mole fraction can be found in the form BIPM.QM-K1-R1-DECC-08 given in the appendix.

9. Differences from the reference values

As for the key comparison BIPM.QM-K1, differences from the reference values were calculated at the twelve nominal ozone mole fractions measured, but are only displayed in this report at two particular values: 80 nmol/mol and 420 nmol/mol. These values correspond to points 3 and 4 recorded in each comparison. As an ozone generator has limited reproducibility, the ozone mole 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 ±15 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.

9.1. Definition

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

$$D_i = x_i - x_{\text{SRP27}} \qquad (8)$$

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:

$$u(D_i) = \sqrt{u_i^2 + u_{SRP27}^2} \quad (9)$$

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-08 are reported in table Table 3 below. Corresponding graphs of equivalence are displayed in Figure 1. The expanded uncertainties are calculated with a coverage factor $k = 2$.

Table 3 : Differences from the reference values of the DECC NSW at the nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol

Nom value	x_i / (nmol/mol)	u_i / (nmol/mol)	x_{SRP27} / (nmol/mol)	u_{SRP27} / (nmol/mol)	D_i / (nmol/mol)	$u(D_i)$ / (nmol/mol)	$U(D_i)$ / (nmol/mol)
80	79.38	0.56	79.74	0.36	-0.36	0.67	1.34
420	417.66	1.37	419.25	1.26	-1.60	1.86	3.72

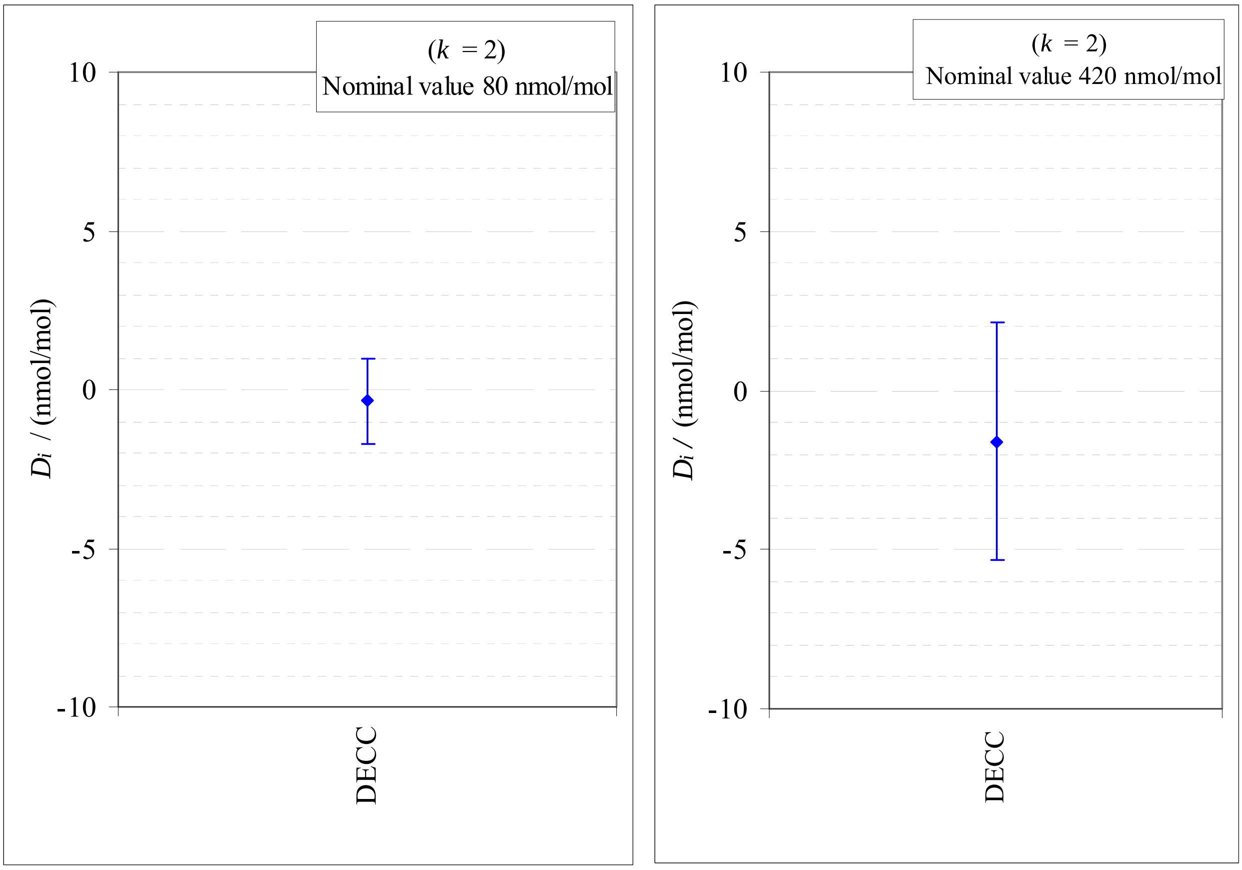

Figure 1: Graphs of equivalence of the DECC NSW at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol

The differences between the DECC NSW 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 also evaluated with a generalized least-square regression fit performed on the two sets of measured ozone mole fractions, taking into account standard measurement uncertainties. To this end, a software called OzonE was used. This software, which is documented in a publication [4], is an extension of the previously used software B_Least recommended by the ISO standard 6143:2001 [5]. It includes the possibility to take into account correlations between measurements performed with the same instrument at different ozone mole fractions.

In a direct comparison, a linear relationship between the ozone mole fractions measured by SRP*n* and SRP27 is obtained:

$$x_{\mathrm{SRP}n} = a_0 + a_1 x_{\mathrm{SRP27}} \qquad (10)$$

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.

10.1. Least-square regression results

The relationship between SRP21 and SRP27 is:

$$x_{\mathrm{SRP21}} = 0.03 + 0.9960 \cdot x_{\mathrm{SRP27}} \tag{11}$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0034$ for the slope and $u(a_0) = 0.30$ nmol/mol for the intercept. The covariance between the two parameters is $\mathrm{cov}(a_0, a_1) = -3.65 \times 10^{-4}$ nmol/mol.

The least-square regression statistical parameters confirm the appropriate choice of a linear relation, with a sum of the squared deviations (SSD) of 0.27 and a goodness of fit (GoF) equals to 0.33.

To asses 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. $|1 - a_1| < 2\,u(\mathrm{a}_1)$.

11. Stability of the reference standard BIPM-SRP27

Results of previous comparison performed between BIPM-SRP27 and BIPM-SRP28 during the course of the key comparison BIPM.QM-K1 are displayed in Figure 2. The slopes a_1 of the linear relation $x_{SRPn} = a_0 + a_1\, x_{SRP27}$ are represented together with their associated uncertainties calculated at the time of each comparison. Figure 2 demonstrates that the stability of both instruments was maintained during the entire comparison exercise, with no more than 0.1% of variation

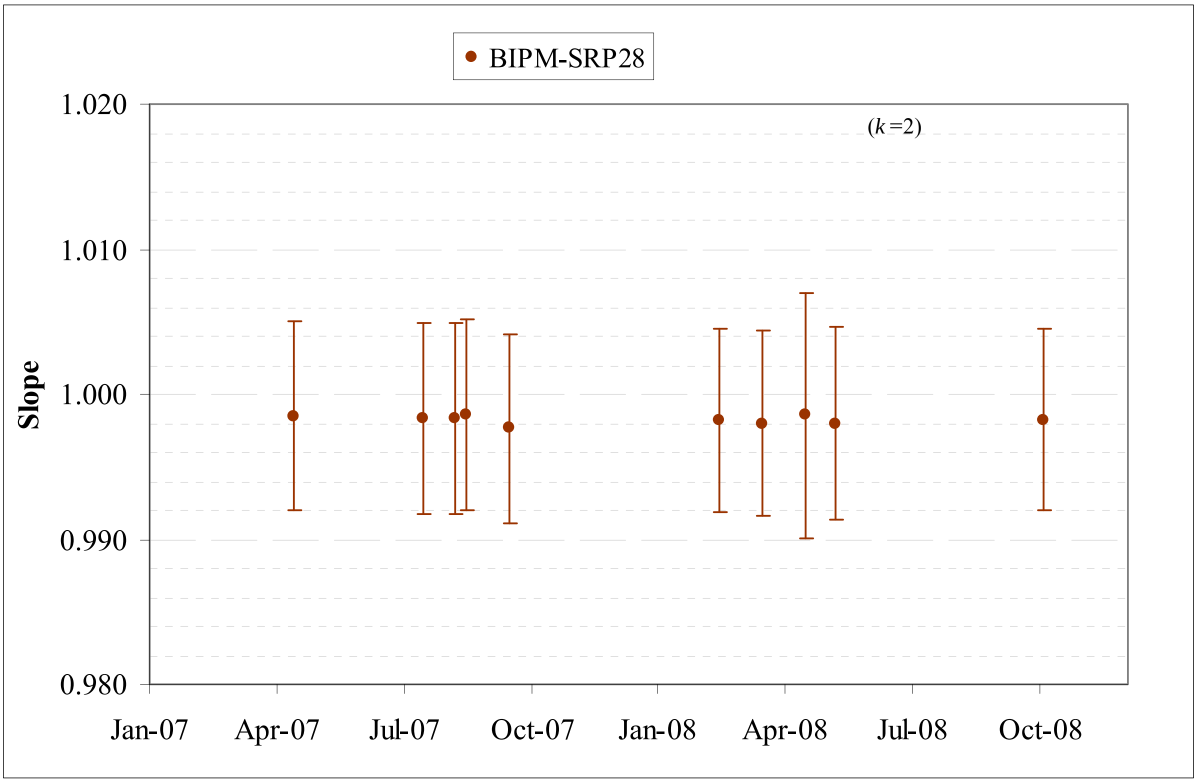

Figure 2 : Results of the comparisons between SRP27 and SRP28 performed at the BIPM during the course of the key comparison BIPM.QM-K1. Uncertainties are calculated at k=2, with the uncertainty budget in use at the time of each comparison.

12. Conclusion

A comparison has been performed between the ozone reference standards of the DECC NSW and of the BIPM. The instruments have been compared over a nominal ozone mole fraction range of 0 nmol/mol to 500 nmol/mol. Following the study of biases in SRP measurement results conducted by NIST and BIPM in 2006, both instruments were upgraded before this comparison. Results of this comparison indicated good agreement between both standards.

13. 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** (NIST)

[2] 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] 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

[5] ISO 6143.2 : 2001 Gas analysis - Determination of the composition of calibration gas mixtures - Comparison methods (International Organization for Standardization)

Appendix 1 - Form BIPM.QM-K1-R1-DECC-08

See next pages.

OZONE COMPARISON RESULT - PROTOCOL A - DIRECT COMPARISON

Participating institute information	
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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

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

Operator	P. MOUSSAY	**Location**	CHEM-9
Comparison begin date / time	20/10/2008 13:00	**Comparison end date / time**	22/10/2008 08:00

Comparison results

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

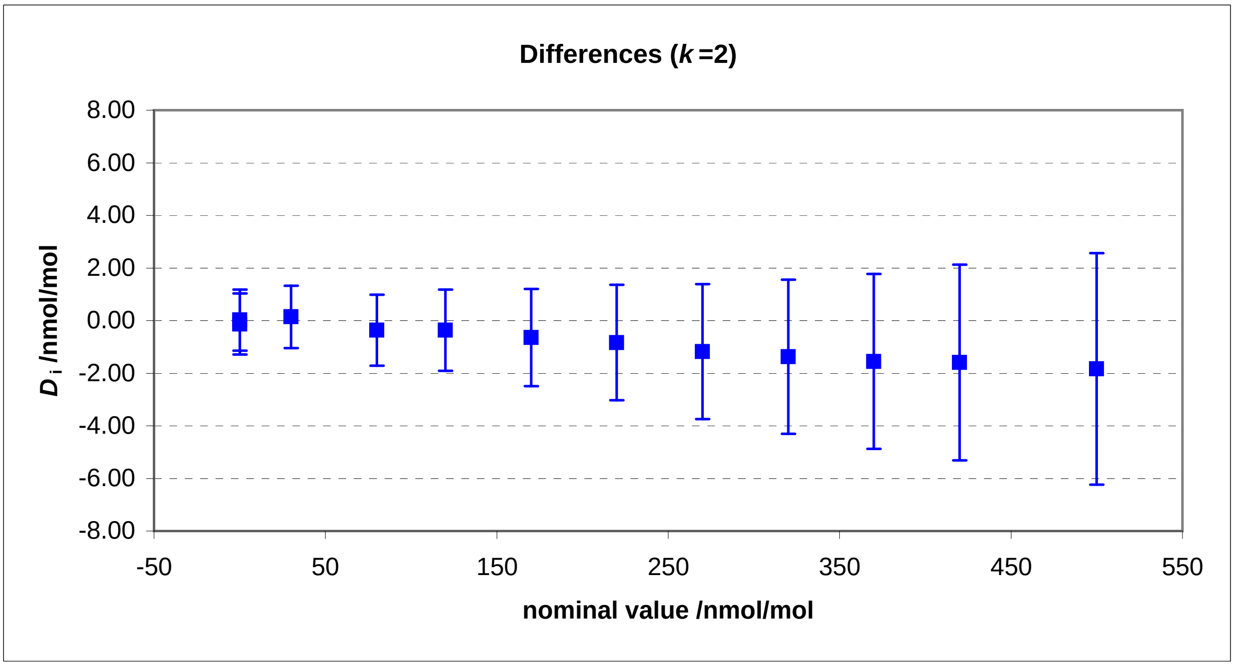
Least-square regression parameters

$a_{TS,RS}$	$u(a_{TS,RS})$	$b_{TS,RS}$ (nmol/mol)	$u(b_{TS,RS})$ (nmol/mol)	$u(a,b)$
0.9960	**0.0034**	**0.03**	**0.30**	**-3.65E-04**

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

Difference from the reference value 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)
80	**-0.36**	**0.67**	**1.34**
420	**-1.60**	**1.86**	**3.72**



Measurement results						
	Reference Standard (RS)			National standard (NS)		
Nominal value	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
0	0.04	0.28	0.28	-0.09	0.23	0.51
220	220.92	0.13	0.70	220.08	0.16	0.84
80	79.74	0.19	0.36	79.38	0.16	0.56
420	419.25	0.36	1.26	417.66	0.38	1.37
120	119.79	0.27	0.45	119.43	0.21	0.63
320	319.73	0.20	0.97	318.36	0.21	1.10
30	29.34	0.32	0.29	29.48	0.18	0.52
370	369.19	0.39	1.11	367.64	0.19	1.23
170	169.87	0.34	0.57	169.23	0.16	0.73
500	503.18	0.23	1.50	501.34	0.24	1.61
270	271.45	0.26	0.84	270.28	0.15	0.97
0	0.01	0.26	0.28	0.03	0.17	0.51

Differences				
Point Number	Nom value (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
1	**0**	-0.13	0.58	1.16
2	**220**	-0.84	1.10	2.20
3	**80**	-0.36	0.67	1.34
4	**420**	-1.60	1.86	3.72
5	**120**	-0.36	0.77	1.54
6	**320**	-1.37	1.47	2.94
7	**30**	0.14	0.59	1.19
8	**370**	-1.55	1.66	3.32
9	**170**	-0.64	0.92	1.85
10	**500**	-1.84	2.20	4.40
11	**270**	-1.18	1.28	2.57
12	**0**	0.02	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

Comparison conditions

Ozone generator manufacturer	Environics
Ozone generator type	Model 6100
Ozone generator serial number	3128
Room temperature(min-max) / °C	22.3 - 22.9
Room pressure (min-max) / hpa	1013 - 1015
Zero air source	oil free compressor + dryer+ aadco 737-R
Reference air flow rate (L/min)	18
Sample flow rate (L/min)	10
Instruments stabilisation time	3 days
Instruments acquisition time /s (one measurement)	5s
Instruments averaging time /s	5s
Total time for ozone conditioning	72 hours
Ozone mole fraction during conditioning (nmol/mol)	870 nmol/mol
Comparison repeated continously (Yes/No)	yes
If no, ozone mole fraction in between the comparison repeats	
Total number of comparison repeats realised	17
Data files names and location	\\chem5\Program Files\NIST\SRPControl\Data\2008
c081020001.xls to c081020006.xls and c081021001.xls to c081021011.xls	

Instruments checks and adjustments

Reference Standard

National Standard

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

SRP Uncertainty Statement - Department of Environment and Climate Change NSW

Component	Value	Source	Distributio	Standard Uncertainty	Combined Standard Uncertainty	Sensibility Coefficien	Contribution to u(x)
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	Rect	0.077 kPa	0.086 kPa	$-\frac{x}{P}$	0.085 %
		Difference	Rect	0.038 kPa			
Temperat ure (T)	273.15 °K	Probe	Rect	0.115 °K	0.129 °K	$\frac{x}{T}$	0.047 %
		Gradient	Rect	0.058 °K			
Repeatabi lity		Repeat Measureme	Rect	0.095 nmol/mol	0.095 nmol/mol	1	0.095 nmol/mol
Resolution			Rect	0.500 nmol/mol	0.500 nmol/mol	1	0.500 nmol/mol
Absorptio n Cross	308.32 cm^{-1}	Conventio nal 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

$$u_{SRP} = \sqrt{(0.51)^2 + 9.31 \times 10^{-6} x^2} \quad (1)$$

Combined standard uncertainty including absorption coefficient uncertainty

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