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Bureau International des Poids et Mesures

Comparison of ozone reference standards of the APA and the BIPM (December 2009)

by

J. Viallon, F. Idrees, P. Moussay and R.I. Wielgosz

BIPM

and

João Matos

APA

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Pavillon de Breteuil, F-92312 Sèvres Cedex

Comparison of ozone reference standards of the APA and the BIPM (December 2009)

Joële Viallon[1*], Philippe Moussay[1], Faraz Idrees[1], Robert Wielgosz[1], João Matos[2]

[1] BIPM (Bureau International des Poids et Mesures), Pavillon de Breteuil, F-92312 Sèvres, France
[2] APA (Agência Portuguesa do Ambiente), Rua da Murgueira, 9/9A, Zambujal, Apartado 7585, 2611-865 Amadora, Portugal

Abstract

A comparison of the ozone reference standards of the Agência Portuguesa do Ambiente (APA) 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:

* Author for correspondence. E-mail jviallon@bipm.org, Tel: +33 1 45 07 62 70, Fax: +33 1 45 07 20 21.

1. Introduction

A comparison of the ozone reference standards of the Agência Portuguesa do Ambiente (APA) 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. As APA 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. An updated summary of BIPM.QM-K1 results can be found in the BIPM key comparison database: http://kcdb.bipm.org/appendixB/.

2. Terms and definitions

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

3. Measurement schedule

Measurements reported in this report were performed on 3 December 2009 at the BIPM.

4. Measurement protocol

The comparison 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 APA national standard SRP25 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 is 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's standard and the common reference standard. The completed form BIPM.QM-K1-R1-APA-09 is given in Appendix 1.

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. In addition, the differences 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

All instruments included in this comparison were 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 SRP measurement principle and uncertainty budget.

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 number concentration (C) of ozone is calculated from:

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

where

- σ is the absorption cross-section of ozone at 253.7 nm under standard conditions of temperature and pressure, 1.1476×10^{-17} 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_r) of one cell defined as

$$T_r = \frac{I_{ozone}}{I_{air}} \tag{2}$$

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 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}.

The formulation implemented in the SRP software is:

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

where

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

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

7.2. Absorption cross–section for ozone

The linear absorption coefficient at 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 1.1476×10^{-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. 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 deal with two biases revealed by a study conducted by the BIPM and the NIST [3]. In 2009, an “SRP upgrade kit” was installed in the instruments, as described in [4].

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	$-\frac{x}{L_{opt}}$	$2.89 \times 10^{-3}x$
	Repeatability	Normal	0.01 cm			
	Correction factor	Rectangular	0.52 cm			
Pressure P	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			
Temperature T	Temperature probe	Rectangular	0.03 K	0.07 K	$\frac{x}{T}$	$2.29 \times 10^{-4}x$
	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 σ	Hearn value		1.22×10^{-19} cm²/molecule	1.22×10^{-19} cm²/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 mole fraction measurement with the BIPM SRPs can be expressed as a numerical equation (numerical values expressed as nmol/mol):

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

7.5. Covariance terms for the common reference BIPM–SRP27

Correlations in 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:

$$\boldsymbol{u}(\boldsymbol{x}_i, \boldsymbol{x}_j) = \boldsymbol{x}_i \cdot \boldsymbol{x}_j \cdot \boldsymbol{u}_{\mathrm{b}}^2 \qquad (7)$$

where:

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

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 APA SRP25

Compared to its original design, the APA SRP25 has been modified to deal with the two biases revealed in [3]: in 2007 an "SRP upgrade kit" was installed by NIST.

7.7. Uncertainty budget of the APA SRP25

The uncertainty budget for the ozone mole fraction in dry air x measured by the APA standard SRP25 in the range 0 nmol/mol to 500 nmol/mol follows the BIPM/NIST paper [3] (see Table 1) with an additional component based on the temperature probe heating effect. The complete budget is given in Table 2. The combined standard uncertainty can be summarized by the formula:

$$u(x) = \sqrt{(0.34)^2 + (2.92 \times 10^{-3} x)^2} \qquad (9)$$

No covariance term for the APA SRP25 was included in the calculations.

Table 2: Uncertainty budget for the SRP25

Component	**Source**	**Distribution**	**Standard Uncertainty**	**Combined Standard Uncertainty**	**Sensibility Coefficient**	**Contribution to u(x)**
Optical Path (*L*)	Measurement	Rect	0.520 cm	0.52 cm	$-\frac{x}{L}$	$2.89 \times 10^{-3}x$
Pressure (*P*)	Gauge	Rect	0.029 kPa	0.034 kPa	$\frac{-x}{P}$	$3.34 \times 10^{-4}x$
	Difference	Rect	0.017 kPa			
Temperature (*T*)	Probe	Rect	0.115 K	0.07 K	$\frac{x}{T}$	$2.29 \times 10^{-4}x$
	Gradient	Rect	0.058 K			
	Heating bias	Rect	$-10^{-3}x$ K			
Ratio of intensities (*D*)	Scaler resolution	Rect	8×10^{-6}	1.7×10^{-5}	$x/\ln(D)$	0.34
	Repeatability	Trian	1.5×10^{-5}			

8. Measurement results and uncertainties

Details of the measurement results, the measurement uncertainties and the standard deviations at each nominal ozone mole fraction are provided in 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:

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

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:

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

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-APA-09 are reported in 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 APA at the nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol

Nom value / (nmol/mol)	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	77.75	0.41	77.58	0.36	0.17	0.54	1.09
420	411.76	1.25	410.50	1.23	1.26	1.75	3.51

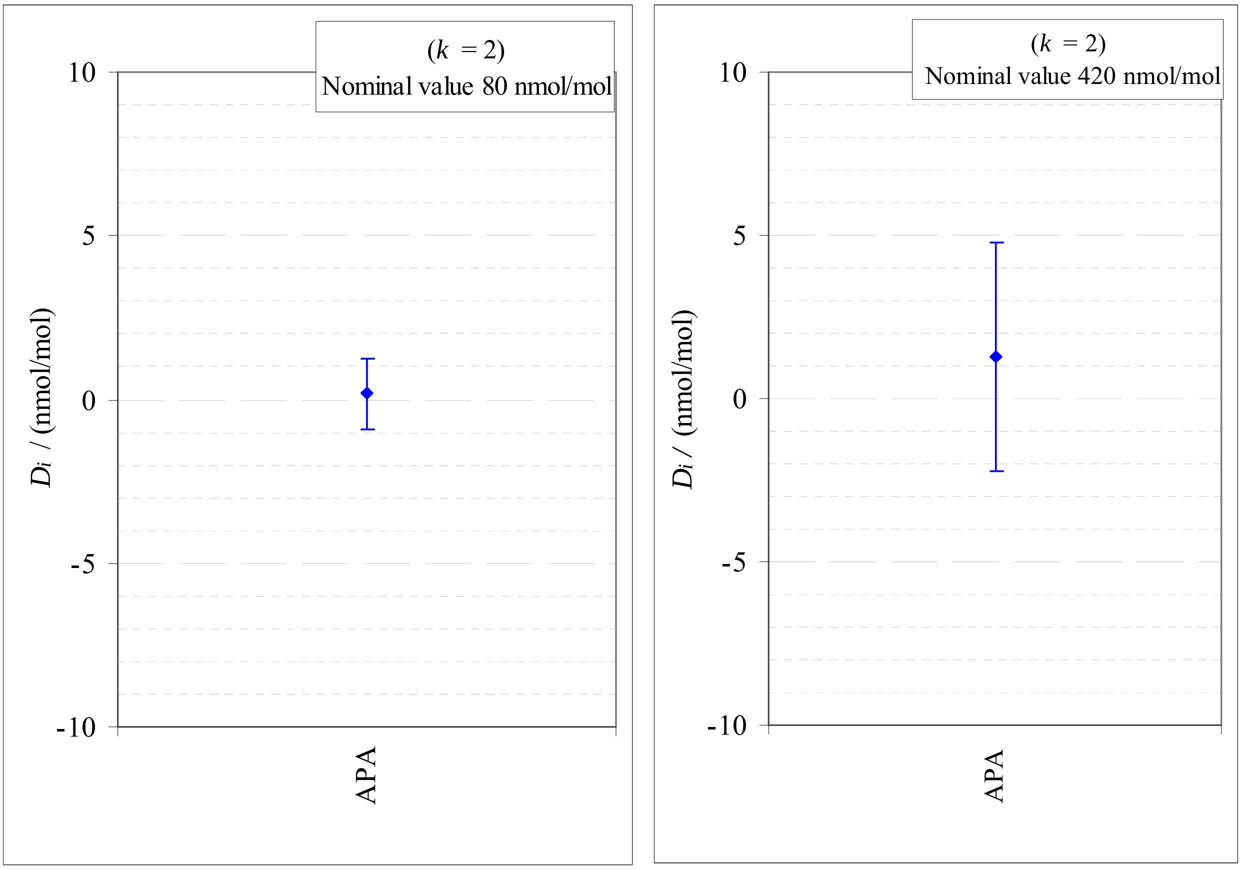


Figure 1: Graphs of equivalence of the APA at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol.

The results for the APA standard and the common reference standard BIPM SRP27 indicate agreement between the two standards.

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

The relationship between the two ozone photometers was also evaluated with a generalized least-squares regression fit performed on the two sets of measured ozone mole fractions, taking into account standard measurement uncertainties. To this end, software called OzonE [5] was used. This software is an extension of the previously used software B_Least recommended by the ISO standard 6143:2001 [6]. 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:

$$x_{\mathrm{SRP}n} = a_0 + a_1 x_{\mathrm{SRP27}} \qquad (12)$$

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-squares regression results

The relationship between SRP25 and SRP27 is:

$$x_{\mathrm{SRP25}} = 0.04 + 1.025 \cdot x_{\mathrm{SRP27}} \quad (13)$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0033$ for the slope and $u(a_0) = 0.24$ nmol/mol for the intercept. The covariance between the two parameters is $\mathrm{cov}(a_0, a_1) = -2.4 \times 10^{-4}$ nmol/mol.

The least-squares regression results confirm that a linear fit is appropriate, with a sum of the squared deviations (SSD) of 0.5 and a goodness of fit (GoF) equal to 0.29.

To assess the agreement of the standards using 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 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. $|1 - a_1| < 2\,u(\mathrm{a}_1)$.

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 $x_{\mathrm{SRPn}} = a_0 + a_1\, x_{\mathrm{SRP27}}$ are represented together with their associated uncertainties calculated at the time of each comparison. Results of comparisons performed before March 2009 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. Figure 2 demonstrates both instruments were stable throughout the entire comparison exercise, with no more than 0.1 % of variation.

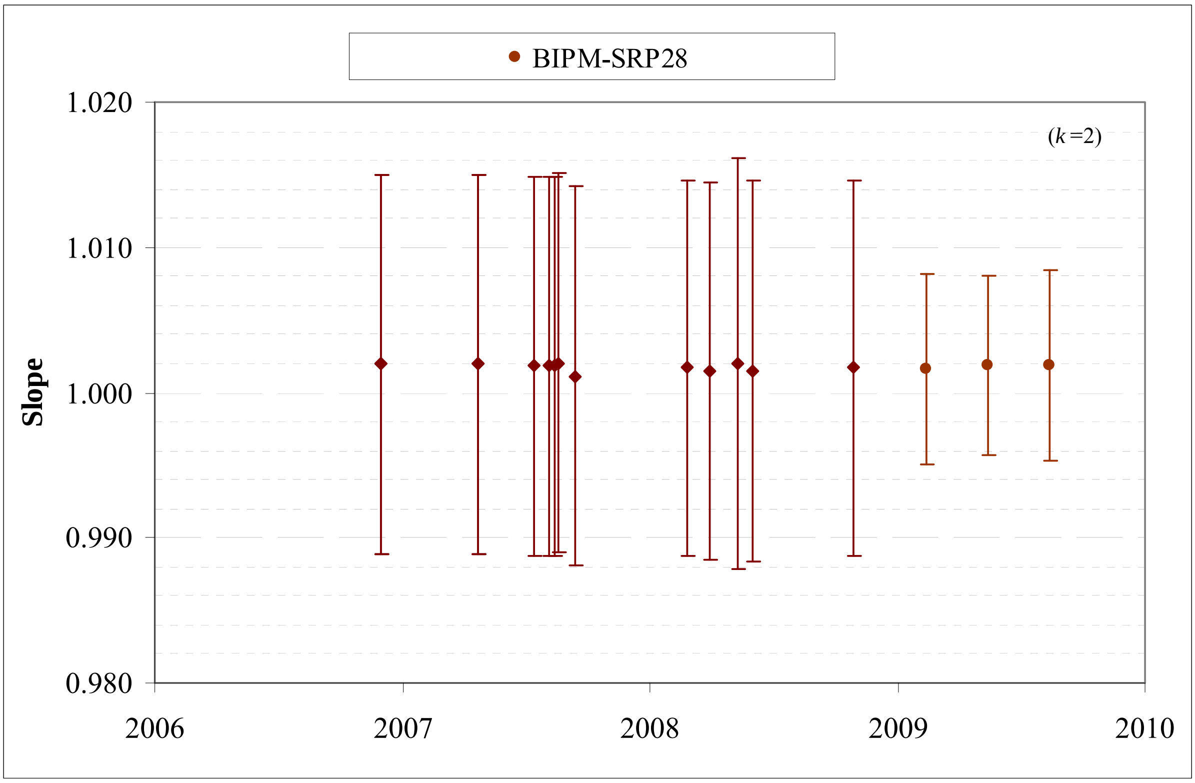


Figure 2 : Results of the comparisons between SRP27 and SRP28 performed at the BIPM during the course of the key comparison BIPM.QM-K1. Uncertainties are calculated at *k* = 2, with the uncertainty budget in use at the time of each comparison.

12. Conclusion

A comparison has been performed between the ozone reference standards of the APA and the BIPM. Following the study of biases in SRP measurement results conducted by NIST and BIPM in 2006, both instruments were upgraded before this comparison. The instruments were compared over a nominal ozone mole fraction range of 0 nmol/mol to 500 nmol/mol, and the results of the comparison indicate good agreement between the two 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 *Env. Sci. Technol.* **NISTIR 6369**, 25 pp

[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, A study of systematic biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard Reference Photometer, ***Metrologia***, **2006**, **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 ongoing key comparison BIPM.QM-K1 **Rapport BIPM-2010/07**, 16 pp

[5] Bremser W, Viallon J and Wielgosz R I, Influence of correlation on the assessment of measurement result compatibility over a dynamic range, ***Metrologia***, **2007**, **44**, 495-504

[6] 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-APA-09

See the following pages.

OZONE COMPARISON RESULT - PROTOCOL A - DIRECT COMPARISON

Participating institute information	
Institute	**APA**
Address	**Rua da Murgueira , 9/9A Bairro do Zambujal 2611-865 Amadora**
Contact	**João Matos**
Email	joao.matos@apambiente.pt
Telephone	**00351 21472 8335**

Instruments information		
	Reference Standard	**National Standard**
Manufacturer	NIST	NIST
Type	SRP	SRP
Serial number	SRP27	SRP25

Content of the report

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

Operator	P. Moussay/F.Idrees	**Location**	BIPM/Room CHEM09
Comparison begin date / time	01/12/2009 10:45	**Comparison end date / time**	03/12/2009 09:00

Comparison results

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

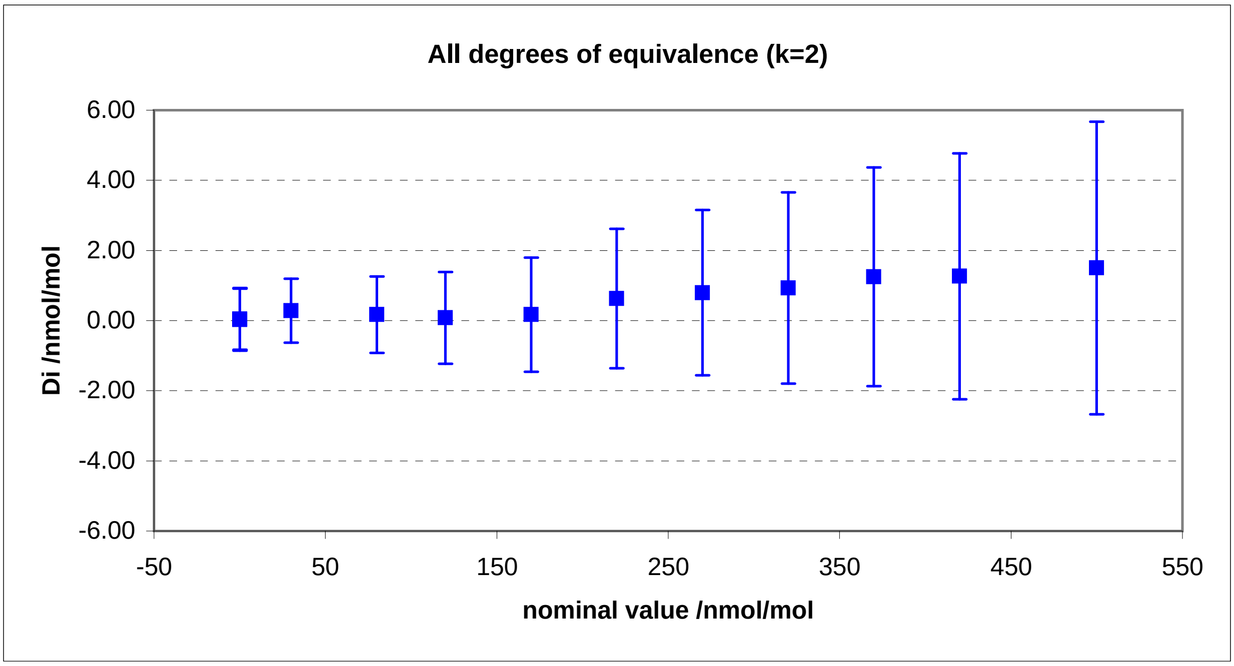
Least-square regression parameters

$a_{TS,RS}$	$u(a_{TS,RS})$	$b_{TS,RS}$ (nmol/mol)	$u(b_{TS,RS})$ (nmol/mol)	$u(a,b)$
1.0025	0.0033	0.04	0.24	-2.38E-04

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

Degrees of equivalence at 80 nmol/mol and 420 nmol/mol:

Nom value (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
80	0.17	0.54	1.09
420	1.26	1.75	3.51



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	0.13	0.25	0.28	0.16	0.28	0.34
220	215.17	0.17	0.69	215.80	0.32	0.72
80	77.58	0.32	0.36	77.75	0.30	0.41
420	410.50	0.35	1.23	411.76	0.41	1.25
120	116.79	0.31	0.44	116.87	0.20	0.48
320	312.03	0.31	0.95	312.96	0.29	0.98
30	28.36	0.17	0.29	28.64	0.24	0.35
370	361.30	0.16	1.09	362.55	0.24	1.11
170	165.53	0.28	0.56	165.70	0.35	0.59
500	493.18	0.17	1.47	494.69	0.26	1.48
270	264.63	0.33	0.82	265.43	0.32	0.85
0	-0.11	0.27	0.28	-0.06	0.43	0.34

Degrees of Equivalence				
Point Number	Nom value (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
1	**0**	0.03	0.44	0.88
2	**220**	0.63	0.99	1.99
3	**80**	0.17	0.54	1.09
4	**420**	1.26	1.75	3.51
5	**120**	0.08	0.65	1.31
6	**320**	0.93	1.36	2.73
7	**30**	0.28	0.46	0.91
8	**370**	1.25	1.56	3.12
9	**170**	0.17	0.81	1.63
10	**500**	1.50	2.09	4.17
11	**270**	0.80	1.18	2.36
12	**0**	0.05	0.44	0.88

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	23.6-23.7
Room pressure (min-max) / hpa	991.1-991.7
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	1 day
Instruments acquisition time /s (one measurement)	5 s
Instruments averaging time /s	5 s
Total time for ozone conditioning	2 hours
Ozone mole fraction during conditioning (nmol/mol)	860 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\2009\C091201002.xls to C091202011.xls

Instruments checks and adjustments

Reference Standard

As written in the procedure BIPM/CHEM-T-05

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:

National Standard

Uncertainty Budget Summary – SRP 25

Component (y)	Source	Distribution	Standard Uncertainty	Combined Standard Uncertainty μ(y)	Sensistivity Coefficient $c_i = \partial x/\partial y$	Contribution to μ(x), |c_i|• μ(y)/nmol mol^{-1}
Optical Path-length, L	Measurement scale Variability Divergence	Rectangular Rectangular Rectangular	0.0005 cm 0.003 cm. 0.052 cm	0.052 cm.	$-x/L_{opt}$	$2.89\times10^{-3}\,x$
Pressure, P	P Gauge P difference between cells	Rectangular Rectangular	0.029 kPa 0.017 kPa	0.034 kPa	$-x/P$	$3.37\times10^{-4}\,x$
Temperature, T	T probe T gradient **T heating bias**	Rectangular Rectangular **Rectangular**	0.029 K 0.058 K $\mathbf{-1.0\times10^{-3}\,x}$	0.07K	x/T	$2.29\times10^{-4}x$ **Bias**
Ratio of intensities, D	Scaler resolution Repeatability	Rectangular Triangular	8.0×10^{-6} 1.5×10^{-5}	1.7×10^{-5}	$x/D\ln(D)$	0.34

As in the BIPM-NIST Bias paper [3], the uncertainty budget above is summarised in one equation describing the uncertainty as a function of ozone mole fraction:

$$u(x) = \sqrt{(0.34)^2 + (2.92\times10^{-3}\,x)^2}\ nmol/mol$$