Final report, On-going Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with ISCIII, 2007

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Abstract

As part of the on-going key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of the Instituto de Salud Carlos III (ISCIII) and the common reference standard of the key comparison, maintained by the Bureau International des Poids et Mesures (BIPM). The instruments have been compared over a nominal ozone mole fraction range of 0 nmol/mol to 500 nmol/mol.

Contents:

FINAL REPORT, ON-GOING KEY COMPARISON BIPM.QM-K1, OZONE AT AMBIENT LEVEL, COMPARISON WITH ISCIII, 2007 1

1. FIELD 2
2. SUBJECT 2
3. PARTICIPANTS 2
4. ORGANIZING BODY 2
5. RATIONALE 2
6. TERMS AND DEFINITIONS 2
7. MEASUREMENTS SCHEDULE 3
8. MEASUREMENT PROTOCOL 3
9. REPORTING MEASUREMENT RESULTS 5
10. POST COMPARISON CALCULATION 5
11. DEVIATIONS FROM THE COMPARISON PROTOCOL 5
12. MEASUREMENT STANDARDS 5
13. MEASUREMENT RESULTS AND UNCERTAINTIES 9
14. ANALYSIS OF THE MEASUREMENT RESULTS BY GENERALISED LEAST-SQUARE REGRESSION 9
15. DEGREES OF EQUIVALENCE 11
16. STABILITY OF THE TRANSFER STANDARD 13
17. HISTORY OF COMPARISONS BETWEEN BIPM SRP27, SRP28 AND ISCIII SRP22 13
18. SUMMARY OF PREVIOUS COMPARISONS INCLUDED IN BIPM.QM-K1 14
19. CONCLUSION 15
20. REFERENCES 16

APPENDIX 1 - FORM BIPM.QM-K1-R2-ISCIII-07 16

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1. Field

Amount of substance.

2. Subject

Comparison of ozone (at ambient level) reference measurement standards.

3. Participants

BIPM.QM-K1 is an on-going key comparison, which is structured as an on-going series of bilateral comparisons. The results of the comparison with the Instituto de Salud Carlos III (ISCIII) are reported here. The ISCIII was the third laboratory to participate in BIPM.QM-K1.

4. Organizing body

BIPM.

5. Rationale

The on-going key comparison BIPM.QM-K1 follows the pilot study CCQM-P28 which included 23 participants and was preformed between July 2003 and February 2005 [1]. It is aimed at evaluating the degree of equivalence of ozone photometers that are maintained as national standards, or as primary standards within international networks for ambient ozone measurements. The reference value is determined using the NIST Standard Reference Photometer (BIPM-SRP27) maintained by the BIPM as a common reference.

This comparison aims to support calibration and measurement capabilities (CMC) claims for ozone from 2 nmol/mol to 1000 nmol/mol.

6. 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 versus the photometer B. $a_{\text{A,B}}$ is dimensionless and $b_{\text{A,B}}$ is expressed in units of nmol/mol.

7. Measurements schedule

The key comparison BIPM.QM-K1 is organised in rounds of 2 years. The 2007-2008 round started in January 2007 with a comparison with the NIST. Measurements reported in this report were performed from the 25th of April to the 11th of July 2007 at the ISCIII and the BIPM.

8. Measurement protocol

The comparison protocol is summarised 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 B, corresponding to a comparison between the ISCIII national standard SRP22 and the common reference standard BIPM-SRP27 maintained at the BIPM via a transfer standard Thermo Environmental Instrument 49C (TEI 49C). The national standard SRP22 and the transfer standard TEI 49C were first compared at the ISCIII in April. Then the TEI 49C was compared with the common reference standard SRP27 at the BIPM in June. Finally, the national standard SRP22 and the transfer standard TEI 49C were again compared at the ISCIII in July to test the stability of the transfer standard.

A comparison between two (or more) ozone photometers consists of producing ozone-air mixtures at different mole fractions over the required range, and measuring these with the photometers.

8.1. Comparisons at the ISCIII

a). Ozone generation

The source of purified air is a compressor with scrubbers for NOx, VOCs, O_3, and humidity. This air is used to provide reference air as well as the ozone-air mixture to each ozone photometer. Ozone is produced using the generator provided with SRP22.

b). Comparison procedure

Prior to the comparison, all the instruments were switched on and allowed to stabilise for 48 hours. Characteristics of the instruments were checked at this time. No adjustments were required.

One comparison run includes 10 different mole fractions distributed to cover the range, together with the measurement of reference air at the beginning and end of each run. The nominal mole fractions were measured in a sequence imposed by the protocol (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270, and 0) nmol/mol. 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_{SRP22} on the set of 10 consecutive measurements $x_{\mathrm{SRP22},i}$ recorded by SRP22 was calculated. The measurement results were considered as valid if s_{SRP22} 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.

c). Comparison repeatability

The comparison procedure was repeated two times to evaluate its repeatability. Between two repeats, ozone at 500 nmol/mol was provided to the instruments.

8.2. Comparisons at the BIPM

a). 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.

b). Comparison procedure

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

One comparison run includes 10 different mole fractions distributed to cover the range, together with the measurement of reference air at the beginning and end of each run. The nominal mole fractions were measured in a sequence imposed by the protocol (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270, and 0) nmol/mol. 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} on the set of 10 consecutive measurements $x_{\mathrm{SRP27},i}$ recorded by BIPM-SRP27 was calculated. The measurement results were considered as 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.

c). Comparison repeatability

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

d). 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 on-going key comparison.

9. Reporting measurement results

The participant and the BIPM staff reported the measurement results in the result form BIPM.QM-K1-R2 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-R2-ISCIII-07 is given in the annex.

10. Post comparison calculation

All calculations were performed by the BIPM using the form BIPM.QM-K1-R2. It includes the two degrees of equivalence that are reported as comparison results in the Appendix B of the BIPM KCDB (key comparison database). For information, the degrees of equivalence 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.

11. Deviations from the comparison protocol

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

12. Measurement standards

All instruments except the transfer standard included in this comparison were Standard Reference Photometers built by the NIST. More details on the instrument's principle and its capabilities can be found in [2]. The following section describes their measurement principle and their uncertainty budgets.

12.1. 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:

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

where

α is the absorption cross-section of ozone at 253.7nm in standard conditions of temperature and pressure. The value used is: 1.1476×10^{-17} cm^2/molecule [3].

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

$$T = \frac{I_{\text{ozone}}}{I_{\text{air}}} \tag{2}$$

where

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

I_{air} is the UV radiation intensity measured from 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:

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

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}.

12.2. 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. 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 [4].

12.3. Actual state of the BIPM SRPs

Compared to the original design described in [2], SRP27 and SRP28 have been modified to deal with two biases revealed by the study conducted by the BIPM and the NIST [4]:

- 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 gas cell temperature measurement.

- In SRP27 and SRP28 the optical path length is now calculated as being 1.005 times the length of the two cells within each instrument respectively. Together with an increased uncertainty this ensures that the bias on the optical path length is taken into account.

12.4. 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):

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

12.5. Covariance terms for the common reference BIPM-SRP27

As explained in section 14, correlations in between the results of two measurements performed at two different ozone 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:

$$\boldsymbol{u(x_i, x_j) = x_i \cdot x_j \cdot u_b^2} \qquad (5)$$

where:

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

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

12.6. Actual state of the ISCIII SRP22

The ISCIII SRP22 is a NIST SRP with the original design described in [2].

12.7. Uncertainty budget of the ISCIII SRP22

The uncertainty budget for the ozone mole fraction in dry air x measured by the ISCIII standard SRP22 in the range (0-500) nmol/mol is given in Table 2.

Table 2 : SRP22 uncertainty budget

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	0.058 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.9\times10^{-3}x$
	Correction factor	Rectangular	0.52 cm			
Pressure P	Pressure gauge	Rectangular	0.029 kPa	0.03 kPa	$-\frac{x}{P}$	$3.3\times10^{-4}x$
	Difference between cells	Rectangular	0.017 kPa			
Temperature T	Temperature probe	Rectangular	0.087 K	0.09 K	$\frac{x}{T}$	$3.2\times10^{-4}x$
Ratio of intensities D	Scaler resolution	Rectangular	8×10^{-6}	2.4×10^{-5}	$\frac{x}{D\ln(D)}$	0.47
	Repeatability	Triangular	2.3×10^{-5}			
Temperature gradient		Rectangular	2.3×10^{-3}	2.3×10^{-3}		$2.3\times10^{-3}\,x$
Interferences		Rectangular	0.2 nmol/mol	0.2 nmol/mol		0.2 nmol/mol
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, the standard uncertainty associated with the ozone mole fraction measurement with the ISCIII SRP22 can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u(x) = \sqrt{(0.51)^2 + (3.74\cdot10^{-3}x)^2} \tag{7}$$

No covariance term for the ISCIII SRP22 was included in the calculations.

12.8. Transfer standard TEI 49C

The transfer standard used by ISCIII is a Thermo Environmental Instrument 49C. It is an ozone photometer based on a principle similar to the SRP, although many components are simplified. This model does not include any scrubber. It is normally used by ISCIII as a laboratory instrument.

The uncertainty budget for the ozone mole fraction in dry air x measured by the TEI 49C in the range (0-500) nmol/mol is given in Table 4. As recommended in the protocol, only the repeatability and the reproducibility are considered in the uncertainty budget. The following expressions were provided by ISCIII:

- **Repeatability**: maximal value of the experimental standard deviation observed at ISCII (***s*** = 0.21 nmol/mol)**.**
- **Reproducibility:** difference between the maximum and the minimum value of the slope of the regression line between the national standard and the transfer standard. Using a rectangular distribution, the standard relative uncertainty is 0.0016***x*****.**

Table 3 : TEI 49C uncertainty budget

Source	**Distribution**	**Contribution to $u(x)$** $|c_i| \cdot u(y)$ **nmol/mol**
Repeatability		0.21 nmol/mol
Reproducibility	Rectangular	0.0016 x

Following this budget, the standard uncertainty associated with the ozone mole fraction measurement with the ISCIII TEI 49C can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u_{TS}(x) = \sqrt{(0.0016x)^2 + (0.21)^2} \qquad (8)$$

For transfer standards, no covariance term are included in the calculations.

13. 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-R2-ISCIII-07 given in appendix.

14. Analysis of the measurement results by generalised least-square regression

The relationship between the national and reference standards was first evaluated with a generalised least-square regression fit. To this end, the software 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 [6]. It includes the possibility to take into account correlations between measurements performed with the same instrument at different ozone mole fractions. It also facilitates the use of a transfer standard, by handling of unavoidable correlations, which arise, as this instrument needs to be calibrated by the reference standard.

The two comparisons performed via the transfer standard are treated:

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

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

For each comparison, a linear relationship between the ozone mole fractions measured by SRPn and SRP27 is obtained:

$$x_{\mathrm{SRP}n} = a_0 + a_1 x_{\mathrm{SRP27}} \quad (9)$$

The associated uncertainties on the slope $u(a_1)$ and the intercept $u(a_0)$ are given by OzonE, as well as the covariance between them and the usual statistical parameters to validate the fitting function.

14.1. Least-square regression results

The two relationships between SRP22 and SRP27 are:

$$x_{\mathrm{SRP22}} = 0.01 + 0.9934 \cdot x_{\mathrm{SRP27}} \quad (10)$$

from the pre BIPM visit, with the uncertainties $u(a_0)$ = 1.16 nmol/mol, $u(a_1)$ = 0.0055, $\mathrm{cov}(a_0, a_1) = -4.23\times10^{-3}$,

and

$$x_{\mathrm{SRP22}} = -0.04 + 0.9985 \cdot x_{\mathrm{SRP27}} \quad (11)$$

from the post BIPM visit, with the uncertainties $u(a_0)$ = 1.16 nmol/mol, $u(a_1)$ = 0.0055, $\mathrm{cov}(a_0, a_1) = -4.18\times10^{-3}$.

To asses the agreement of the standards from equations 11 and 12, 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 both comparisons, 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. $|1-a_1| < 2\,u(a_1)$.

15. Degrees of equivalence

Degrees of equivalence are calculated at two nominal ozone mole fractions among the twelve measured in each comparison, in the nominal range 0 nmol/mol to 500 nmol/mol: 80 nmol/mol and 420 nmol/mol. These values correspond to points number 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.

15.1. Definition of the degrees of equivalence

Within protocol B, the degree of equivalence of the participant *i*, at a nominal value x_{nom} is defined as:

$$D = x_i - \hat{x}_{SRP27} \tag{12}$$

Where x_i is the measurement results of the national standard at the nominal value x_{nom}, and $\hat{x}_{SRP27}$ is the predicted value of SRP27 at the same nominal value, deduced from the transfer standard measurement result during its comparison with the national standard.

Its associated standard uncertainty is:

$$u(D) = \sqrt{u^2(x_i) + u^2(\hat{x}_{SRP27})} \tag{13}$$

where $u(x_i)$ is the measurement uncertainties of the participant *i* and $u(\hat{x}_{SRP27})$ is the uncertainty associated with the predicted value of SRP27.

15.2. Calculation of SRP27 predicted values and their related uncertainties

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

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

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

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

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

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

15.3. Values of the degrees of equivalence

When protocol B is followed, the national and reference standards are compared twice to monitor the transfer standard stability. Therefore, two degrees of equivalence are calculated at each nominal ozone mole fraction.

The degrees of equivalence and their uncertainties calculated in the form BIPM.QM-K1-R2-ISCIII-07 are reported in the table below. Corresponding graphs of equivalence are displayed in Figure 1. The expanded uncertainties are calculated with a coverage factor $k = 2$.

Table 4 : degrees of equivalence of the ISCIII at the ozone nominal 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)**
First comparison	**80**	83.95	0.60	84.56	0.38	-0.61	0.71	1.42
	420	418.06	1.64	420.70	1.45	-2.65	2.20	4.39
Second comparison	**80**	86.22	0.60	86.28	0.38	-0.06	0.71	1.43
	420	422.92	1.66	423.66	1.46	-0.75	2.22	4.43

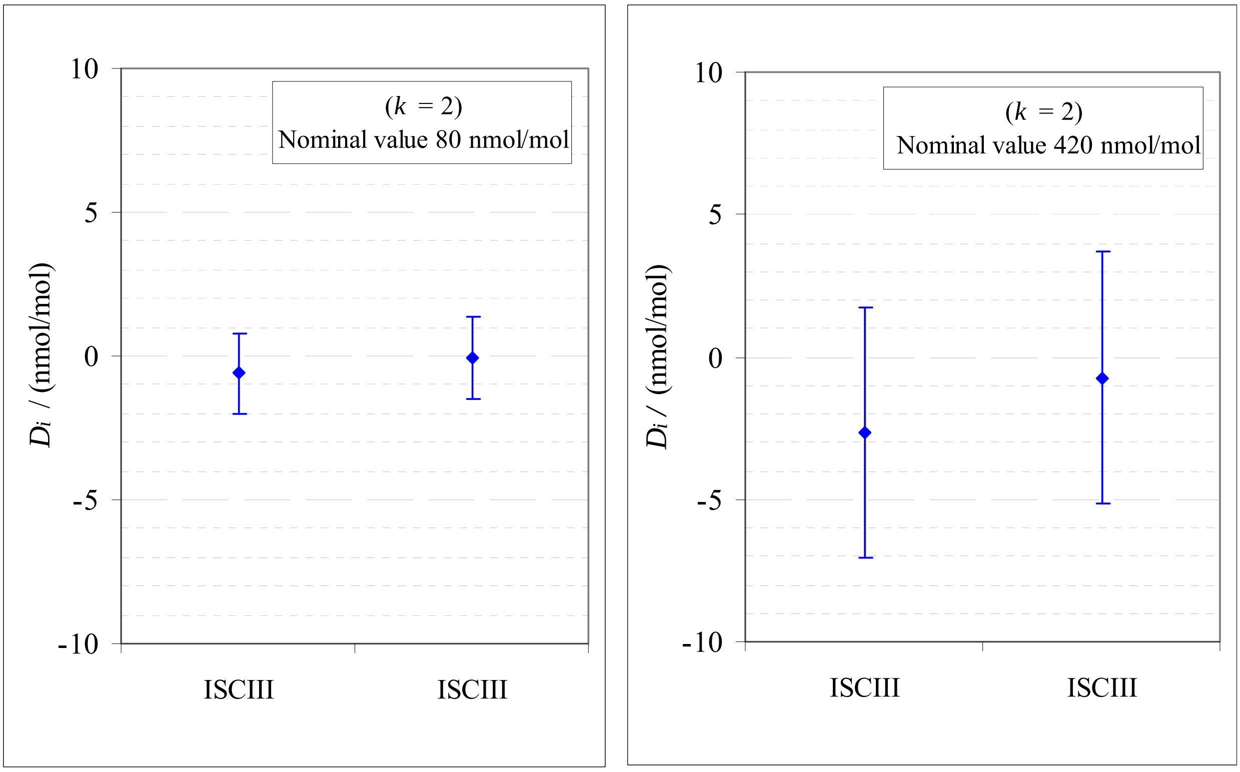


Figure 1: graphs of equivalence of the ISCIII at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol

The degrees of equivalence between the ISCIII standard and the common reference standard BIPM SRP27 indicate good agreement between the standards. A discussion on the relation between degrees of equivalence and CMC statements can be found in [1].

16. Stability of the transfer standard

The overall agreement between the national standard SRP22 and the reference standard SRP27 shows an increase of 0.5% when considering the slope of the linear relationship deduced from the two comparisons performed. Although this variation is not negligible, both comparisons are consistent according to the uncertainties.

17. History of comparisons between BIPM SRP27, SRP28 and ISCIII SRP22

Results of the previous comparison performed with ISCIII during the pilot study CCQM-P28 are displayed in Figure 2 together with the results of this comparison. 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.

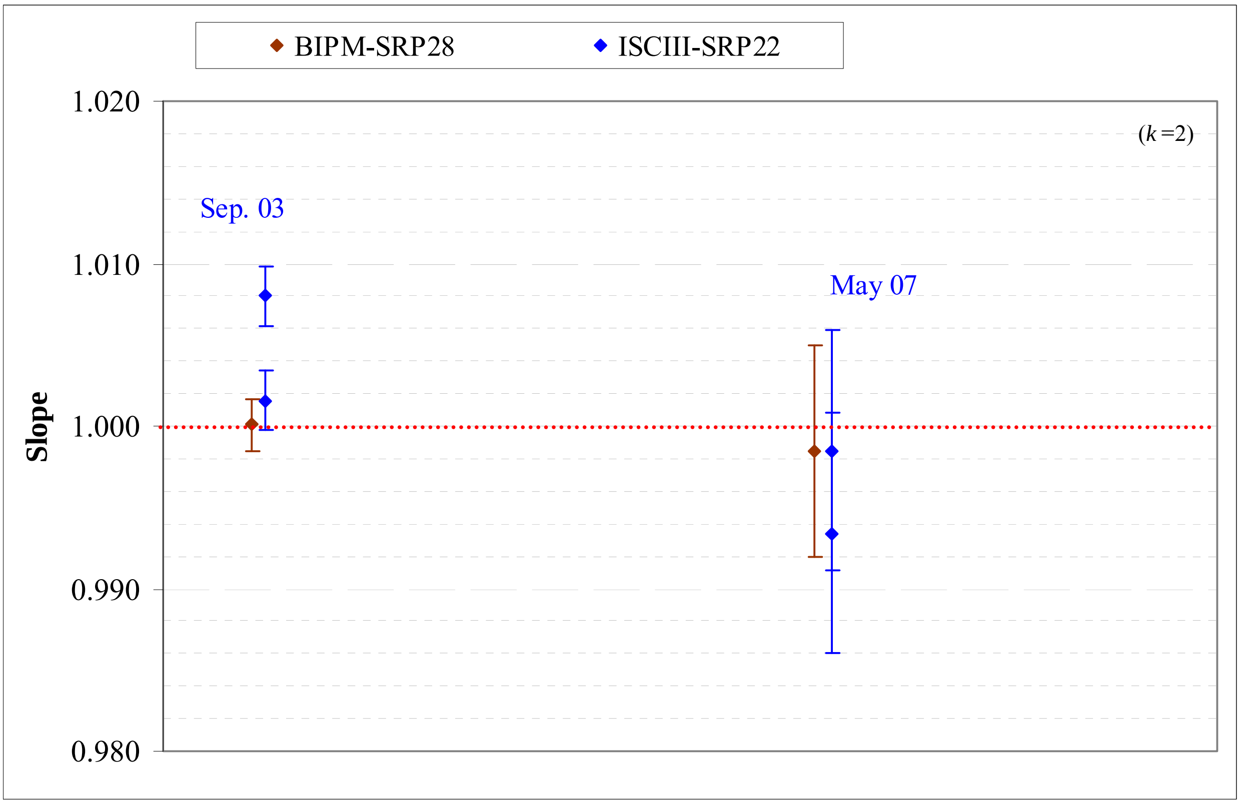


Figure 2 : Results of the two comparisons between SRP27, SRP28 and SRP22 realised at the BIPM during the pilot study CCQM-P28 and the key comparison BIPM.QM-K1. Uncertainties are calculated at k=2, with the uncertainty budget in use at the time of each comparison.

Considering the absolute value of the slope a_1, this figure reveals a possible instability in the transfer standard, with a maximal change of approximately 1% between September 2003 and July 2007. However, the revision of the uncertainty budget of all SRPs between the pilot study and the key comparison, combined with the corrections of biases in SRP27 and SRP28, lead to a better agreement between the ISCIII standard and the reference standard.

Figure 2 also shows that SRP27 and SRP28 stability was maintained between the two comparisons, with no more than 0.1% of variation.

18. Summary of previous comparisons included in BIPM.QM-K1

The comparison with ISCIII is the third one in the 2007-2008 round of BIPM.QM-K1. Degrees of equivalence including previous participants are displayed in Figure 3.

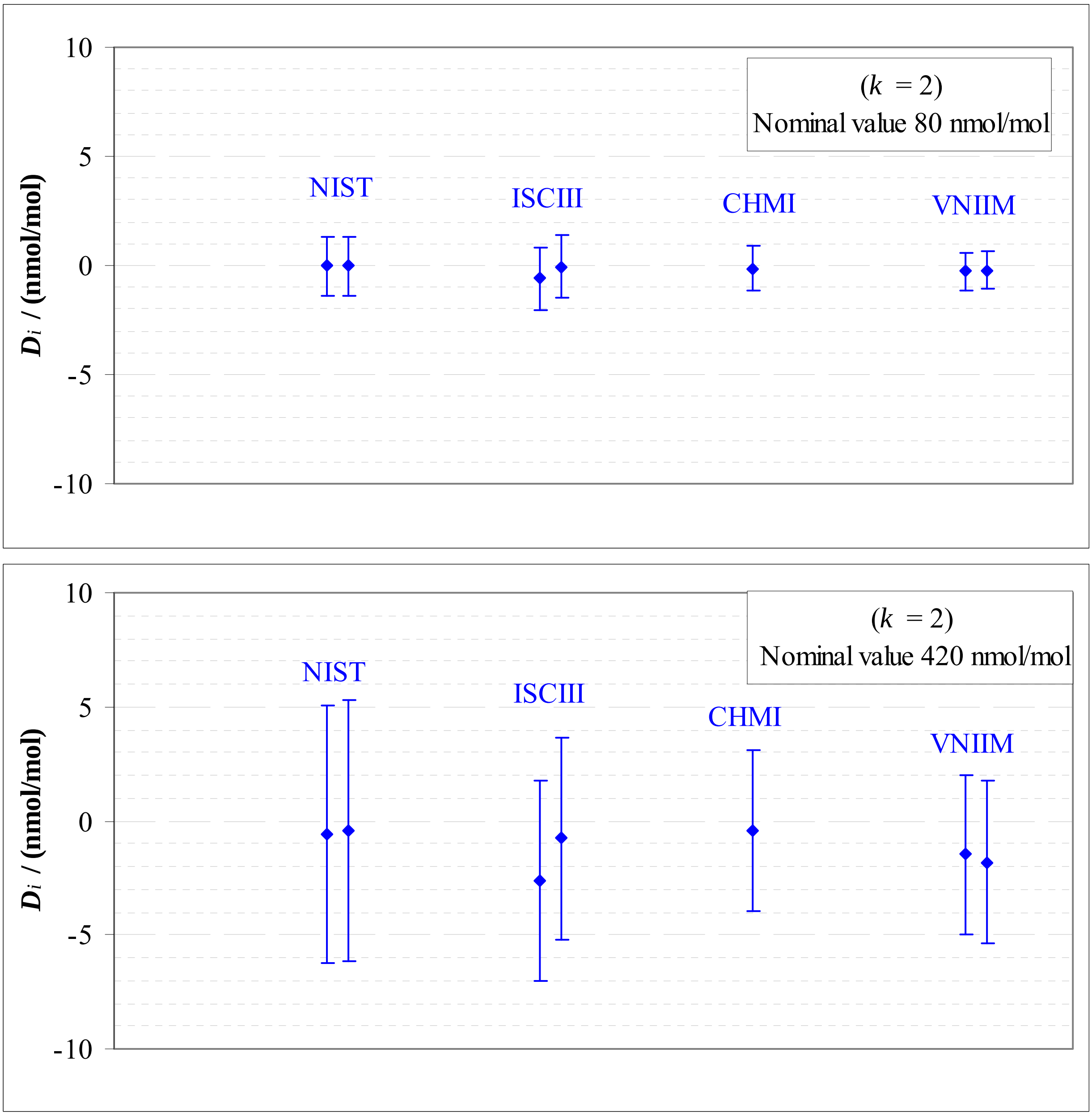


Figure 3: degrees of equivalence at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol, for all participants in BIPM.QM-K1 in the present cycle.

19. Conclusion

As part of the on-going key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of the ISCIII and the common reference standard of the key comparison, maintained by 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, the BIPM standard was upgraded before this comparison and the ISCIII standard uncertainty budget was revised. As expected in the study, the agreement between them was improved. In particular, degrees of equivalence of this comparison indicated a good agreement between both standards.

20. References

1. Viallon, J., et al., *PILOT STUDY: International Comparison CCQM-P28: Ozone at ambient level,* Metrologia Technological Supplement, 2006. 43: (8010).
2. Paur, R.J., A.M. Bass, J.E. Norris, and T.J. Buckley, *Standard reference photometer for the assay of ozone in calibration atmospheres*, 2003, NISTIR 6369: 25 p.
3. ISO, 13964 : 1996, *Ambient air - Determination of ozone - Ultraviolet photometric method*, International Organization for Standardization
4. Viallon, J., P. Moussay, J.E. Norris, F.R. Guenther, and R.I. Wielgosz, *A study of systematic biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard Reference Photometer,* Metrologia, 2006. 43: 441-450.
5. Bremser, W., J. Viallon, and R.I. Wielgosz, *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-R2-ISCIII-07

See next pages.

OZONE COMPARISON RESULT - PROTOCOL B - WITH A TRANSFER STANDARD

Participating institute information	
Institute	INSTITUTO DE SALUD CARLOS III
Address	CRTA. MAJADAHONDA-POZUELO KM 2. 28220 MAJADAHONDA
Contact	PILAR MORILLO GOMEZ
Email	pmorillo@isciii.es
Telephone	+34 91 822 35 05

Instruments information			
	Reference Standard	**National Standard**	**Transfer Standard**
Manufacturer	NIST	NIST	THERMO
Type	SRP	SRP	49C
Serial number	SRP27	SRP22	54655-300
ozone cross-section value	308.32 atm^{-1} cm^{-1}	308.32 atm^{-1}.cm^{-1}	308.32 atm-1.cm-1

Content of the report

page 1 General informations
page 2 Summaryf of the comparison results
page 3 calculation of the national standard vs reference standard first relationship
page 4 calculation of the national standard vs reference standard second relationship
page 5 Data reporting sheet - first comparison of the transfer standard vs the national standard
page 7 Calibration of the transfer standard by the reference standard at the BIPM
page 9 Data reporting sheet - second comparison of the transfer standard vs the national standard
page 11 Uncertainty budgets

This workbook contains macros. It is recommended not to use them.

Please complete the cells containing blue stars only.
After completion of the appropriate section of this report, please send to Joële Viallon
by email (jviallon@bipm.org), fax (+33 1 45342021), or mail (BIPM, Pavillon de Breteuil, F-92312 Sèvres)

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

Summary of comparison results

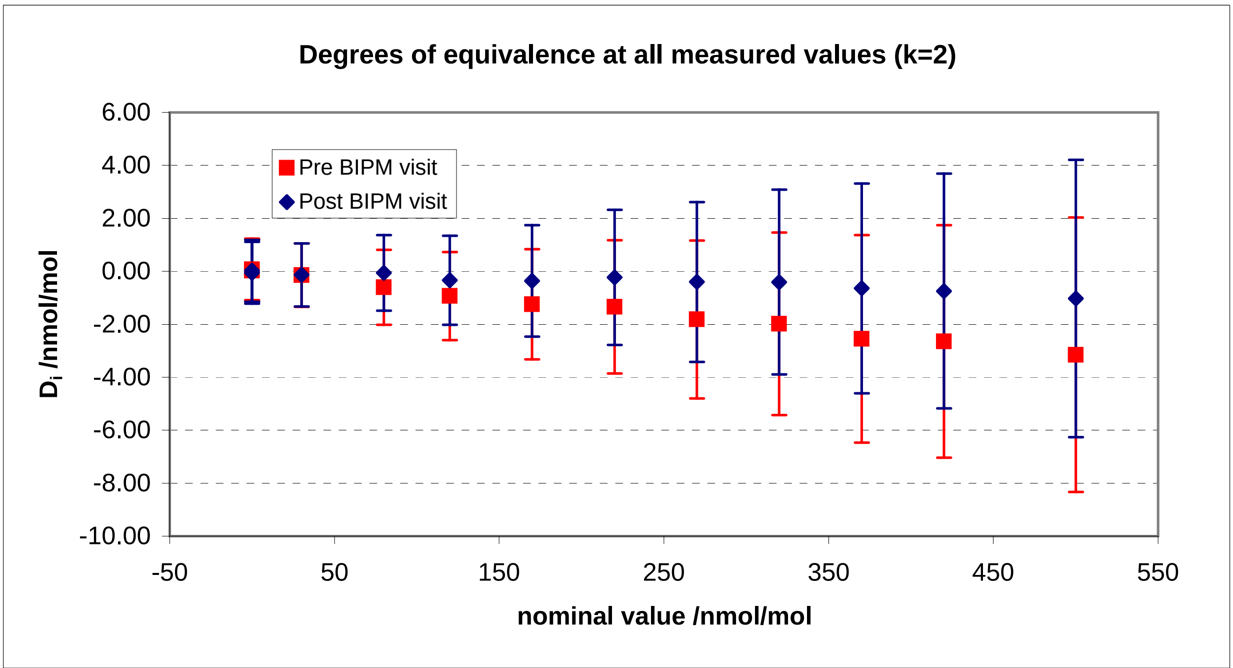
Equation $x_{NS} = a_{NS,RS}\, x_{RS} + b_{NS,RS}$

Least-square regression parameters

	$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
first comparison	0.9934	0.0037	0.01	0.35	-5.13E-04
second comparison	0.9985	0.0037	-0.04	0.35	-5.04E-04

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)
first comparison	80	-0.61	0.71	1.42
	420	-2.65	2.20	4.39
second comparison	80	-0.06	0.71	1.43
	420	-0.75	2.22	4.43



Calculation of the National Standard vs Reference Standard comparison results through the first National Standard vs Transfer Standard comparison

First comparison results						
	National standard measurement results		Transfer standard measurement results		Reference Standard prediced values	
Nominal value	x_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_{TS} nmol/mol	$u(x_{TS})$ nmol/mol	x'_{RS} nmol/mol	$u(x'_{RS})$ nmol/mol
0	-0.08	0.51	-0.01	0.21	-0.11	0.28
220	222.95	0.98	223.42	0.41	224.29	0.79
80	83.95	0.60	84.29	0.25	84.56	0.38
420	418.06	1.64	418.98	0.70	420.70	1.45
120	121.07	0.68	121.58	0.29	122.01	0.48
320	321.29	1.31	321.97	0.56	323.27	1.12
30	34.59	0.53	34.69	0.22	34.74	0.29
370	370.07	1.48	371.11	0.63	372.62	1.29
170	173.68	0.83	174.27	0.35	174.93	0.64
500	497.23	1.93	498.32	0.82	500.39	1.73
270	272.94	1.14	273.67	0.49	274.76	0.96
0	-0.11	0.51	-0.09	0.21	-0.19	0.28

Reference standard predicted values are deduced from the transfer standard measurement results using the calibration performed at the BIPM, with the parameters calculated in Excel Worksheet 4 (page 7)

$$x'_{RS} = a_{RS,TS} x_{TS} + b_{RS,TS} \qquad u(x'_{RS}) = \sqrt{a^2_{RS,TS} \cdot u(x_{TS})^2 + x^2_{TS} \cdot u(a_{RS,TS})^2 + u(b_{RS,TS})^2 + 2 \cdot x_{TS} \cdot u(a_{RS,TS}, b_{RS,TS})}$$

$a_{RS,TS}$	1.0043	$b_{NRS,TS}$ (nmol/mol)	-0.10	$u(a,b)$	-1.42E-04
$u(a_{RS,TS})$	0.0031	$u(b_{RS,TS})$ (nmol/mol)	0.19		

Degrees of Equivalence $D_i = x_{NS} - x'_{RS}$

Point Number	Nom value (nmol/mol)	D_i *(nmol/mol)*	$u(D_i)$ *(nmol/mol)*	$U(D_i)$ *(nmol/mol)*
1	**0**	0.03	0.58	1.17
2	**220**	-1.34	1.26	2.52
3	**80**	-0.61	0.71	1.42
4	**420**	-2.65	2.20	4.39
5	**120**	-0.94	0.83	1.66
6	**320**	-1.98	1.72	3.44
7	**30**	-0.14	0.60	1.20
8	**370**	-2.55	1.96	3.92
9	**170**	-1.25	1.04	2.08
10	**500**	-3.15	2.59	5.18
11	**270**	-1.82	1.49	2.98
12	**0**	0.07	0.58	1.17

Least-square regression parameters				
$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
0.9934	**0.0037**	**0.01**	**0.35**	**-0.0005134**

Calculation of the National Standard vs Reference Standard comparison results through the second National Standard vs Transfer Standard comparison

Second comparison results

	National standard measurement results		Transfer standard measurement results		Reference Standard prediced values	
Nominal value	x_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_{TS} nmol/mol	$u(x_{TS})$ nmol/mol	x'_{RS} nmol/mol	$u(x'_{RS})$ nmol/mol
0	-0.14	0.51	0.01	0.21	-0.09	0.28
220	226.93	0.99	226.28	0.42	227.16	0.80
80	86.22	0.60	86.00	0.25	86.28	0.38
420	422.92	1.66	421.93	0.71	423.66	1.46
120	123.58	0.69	123.48	0.29	123.92	0.48
320	326.60	1.32	325.69	0.56	327.01	1.14
30	28.66	0.52	28.77	0.21	28.80	0.29
370	375.16	1.49	374.28	0.63	375.81	1.30
170	176.80	0.84	176.50	0.35	177.17	0.64
500	503.74	1.95	502.68	0.83	504.76	1.74
270	277.70	1.16	277.00	0.49	278.10	0.97
0	-0.10	0.51	-0.02	0.21	-0.12	0.28

Reference standard predicted values are deduced from the transfer standard measurement results using the calibration performed at the BIPM, with the parameters calculated in Excel Worksheet 4 (page 7)

$$x'_{RS} = a_{RS,TS} x_{TS} + b_{RS,TS} \qquad u(x'_{RS}) = \sqrt{a^2_{RS,TS} \cdot u(x_{TS})^2 + x^2_{TS} \cdot u(a_{RS,TS})^2 + u(b_{RS,TS})^2 + 2 \cdot x_{TS} \cdot u(a_{RS,TS}, b_{RS,TS})}$$

$a_{RS,TS}$	1.0043	$b_{NRS,TS}$ (nmol/mol)	-0.10	$u(a,b)$	-1.42E-04
$u(a_{RS,TS})$	0.0031	$u(b_{RS,TS})$ (nmol/mol)	0.19		

Degrees of Equivalence $D_i = x_{NS} - x'_{RS}$

Point Number	Nom value (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
1	**0**	-0.06	0.58	1.17
2	**220**	-0.23	1.27	2.55
3	**80**	-0.06	0.71	1.43
4	**420**	-0.75	2.22	4.43
5	**120**	-0.33	0.84	1.68
6	**320**	-0.41	1.74	3.49
7	**30**	-0.14	0.59	1.19
8	**370**	-0.64	1.98	3.96
9	**170**	-0.36	1.05	2.11
10	**500**	-1.02	2.62	5.23
11	**270**	-0.40	1.51	3.02
12	**0**	0.02	0.58	1.17

Least-square regression parameters

$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
0.9985	**0.0037**	**-0.04**	**0.35**	**-0.0005035**

Data reporting sheet
First comparison of transfer standard (TS) vs national standard (NS)

Operator	CARMEN SANCHEZ	**Location**	LAB. 9 (ACA)
Comparison begin date / time	25/04/2007 08:30 h (one comparison)	**Comparison end date / time**	26/04/2007 14:30 h (one comparison)

measurement results						
	Transfer standard (TS)			National Standard (NS)		
Nominal value	x_{TS} nmol/mol	s_{TS} nmol/mol	$u(x_{TS})$ nmol/mol	x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol
0	-0.01	0.10	0.21	-0.08	0.39	0.51
220	223.42	0.21	0.41	222.95	0.75	0.98
80	84.29	0.11	0.25	83.95	0.72	0.60
420	418.98	0.15	0.70	418.06	0.86	1.64
120	121.58	0.11	0.29	121.07	0.36	0.68
320	321.97	0.08	0.56	321.29	0.37	1.31
30	34.69	0.10	0.22	34.59	0.19	0.53
370	371.11	0.17	0.63	370.07	0.18	1.48
170	174.27	0.11	0.35	173.68	0.17	0.83
500	498.32	0.18	0.82	497.23	0.25	1.93
270	273.67	0.15	0.49	272.94	0.27	1.14
0	-0.09	0.14	0.21	-0.11	0.56	0.51

Note : according to the protocol, these measurement results are the last TS-NS comparison measurement results recorded

Covariance terms in between two measurement results of the national standard

Equation $u(x_i, x_j) = \alpha \cdot x_i \cdot x_j$ Value of α 0.00E+00

Comparison conditions	
Ozone generator manufacturer	NIST
Ozone generator type	NIST-SRP
Ozone generator serial number	SRP22
Room temperature(min-max) / °C	18,8 ºC - 19,4 ºC
Room pressure (average) / hpa	92,9 hPa
Zero air source	Air compressor with scruberrs for NOx, VOCs, O3,
Reference air flow rate (L/min)	6 l/min
Sample flow rate (L/min)	6 l/min
Instruments stabilisation time	48 hours
Instruments acquisition time /s (one measurement)	1 min
Instruments averaging time /s	SRP22: none, TEI49C: 1 min
Total time for ozone conditioning	2 hours
Ozone mole fraction during conditioning	500 nmol/mol
Comparison repeated continously (Yes/No)	no
If no, ozone mole fraction in between the comparison repeats	500 mol/mol
Total number of comparison repeats realised	2

Instruments checks and adjustments

National Standard

INSTRUMENTS CHECKS:
Pressure
Temperature
Scaler test
Scaler test with shutter
Stability

Adjustments were not made

Transfer Standard

INSTRUMENTS CHECKS:
Pressure
Temperatures: bench and lamp
Flows
Intensities

Adjustments were not made

calibration of the transfer standard (TS) by the reference standard (RS)

Operator	P. Moussay	**Location**	BIPM room CHEM9
Comparison begin date / time	11 June 2007 10h45	**Comparison end date / time**	13 June 2007 8h00

Calibration results

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

Least-square regression parameters				
$a_{RS,TS}$	$u(a_{RS,TS})$	$b_{RS,TS}$ (nmol/mol)	$u(b_{RS,TS})$ (nmol/mol)	$u(a,b)$
1.0043	**0.0031**	**-0.10**	**0.19**	**-0.0001417**

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

Measurement results

	Transfer standard (TS)			Reference Standard (RS)		
Nominal value	x_{TS} nmol/mol	s_{TS} nmol/mol	$u(x_{TS})$ nmol/mol	x_{RS} nmol/mol	s_{RS} nmol/mol	$u(x_{RS})$ nmol/mol
0	0.06	0.40	0.21	-0.12	0.10	0.28
220	225.04	0.23	0.42	225.77	0.16	0.72
80	80.76	0.38	0.25	81.15	0.12	0.37
420	423.00	0.37	0.71	424.65	0.27	1.27
120	124.04	0.26	0.29	124.69	0.16	0.46
320	322.04	0.21	0.56	323.24	0.17	0.98
30	33.85	0.31	0.22	33.85	0.16	0.30
370	374.56	0.44	0.64	375.96	0.21	1.13
170	172.31	0.41	0.35	173.01	0.06	0.58
500	500.74	0.35	0.83	502.66	0.18	1.49
270	275.29	0.26	0.49	276.37	0.15	0.85
0	-0.04	0.27	0.21	-0.14	0.17	0.28

Note : according to the protocol, these measurement results are the last TS-RS comparison measurement results

Covariance terms in between two measurement results of the reference standard

Equation $u(x_i, x_j) = \alpha \cdot x_i \cdot x_j$

Value of α 8.50E-06

Comparison conditions

Ozone generator manufacturer	Environics
Ozone generator type	6100
Ozone generator serial number	3128
Room temperature(min-max) / °C	23.0 - 23.1
Room pressure (average) / hpa	1003
Zero air source	oil free compressor + dryer+ aadco 737-R
Reference air flow rate (L/min)	12
Sample flow rate (L/min)	10
Instruments stabilisation time	6 days
Instruments acquisition time /s (one measurement)	60 s
Instruments averaging time /s	TEI49C: 60 s, SRP27: none
Total time for ozone conditioning	2 hours
Ozone mole fraction during conditioning	880
Comparison repeated continously (Yes/No)	yes
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	20
Data files names and location	c070611001.xls to c070611020.xls
	\\chem5\srpdata\2007\c070611020.xls

***

Instruments checks and adjustments

Reference Standard

the reference SRP 27 was checked according to the procedure BIPM/CHEM-T-05 on the 8th of June.

No adjustment was necessary.

Transfer Standard

operating parameters of the transfer standard have been recorded in the file

BIPM-CHEM-R-02-54655-300-070611.doc

no adjustment made

Data reporting sheet
Second comparison of transfer standard (TS) vs national standard (NS)

Operator	CARMEN SANCHEZ	**Location**	**LAB. 9 (ACA)**
Comparison begin date / time	11/07/2007 9:15 h (one comparison)	**Comparison end date / time**	11/07/2007 14:45 h(one comparison)

measurement results

	Transfer standard (TS)			National Standard (NS)		
Nominal value	x_{TS} nmol/mol	s_{TS} nmol/mol	$u(x_{TS})$ nmol/mol	x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol
0	0.01	0.10	0.21	-0.14	0.64	0.51
220	226.28	0.11	0.42	226.93	0.34	0.99
80	86.00	0.14	0.25	86.22	0.27	0.60
420	421.93	0.21	0.71	422.92	0.46	1.66
120	123.48	0.09	0.29	123.58	0.41	0.69
320	325.69	0.11	0.56	326.60	0.33	1.32
30	28.77	0.10	0.21	28.66	0.39	0.52
370	374.28	0.14	0.63	375.16	0.28	1.49
170	176.50	0.07	0.35	176.80	0.31	0.84
500	502.68	0.15	0.83	503.74	0.40	1.95
270	277.00	0.18	0.49	277.70	0.31	1.16
0	-0.02	0.09	0.21	-0.10	0.38	0.51

Note : according to the protocol, these measurement results are the last TS-NS comparison measurement results recorded

Covariance terms in between two measurement results of the national standard

Equation $u(x_i, x_j) = \alpha \cdot x_i \cdot x_j$ Value of α 0.00E+00

Comparison conditions

Ozone generator manufacturer	NIST
Ozone generator type	NIST-SRP
Ozone generator serial number	SRP22
Room temperature(min-max) / °C	18,4 ºC - 20,0 ºC
Room pressure (average) / hpa	92,9 hPa
Zero air source	Air compressor with scruberrs for NOx, VOCs, O3,
Reference air flow rate (L/min)	6 l/min
Sample flow rate (L/min)	6 l/min
Instruments stabilisation time	48 hours
Instruments acquisition time /s (one measurement)	1 min
Instruments averaging time /s	SRP22: none, TEI49C: 1 min
Total time for ozone conditioning	2 hours
Ozone mole fraction during conditioning	500 nmol/mol
Comparison repeated continously (Yes/No)	no
If no, ozone mole fraction in between the comparison repeats	500 mol/mol
Total number of comparison repeats realised	2

Instruments checks and adjustments

National Standard

INSTRUMENTS CHECKS:
Pressure
Temperature
Scaler test
Scaler test with shutter
Stability

Adjustments were not made

Transfer Standard

INSTRUMENTS CHECKS:
Pressure
Temperatures: bench and lamp
Flows
Intensities

Adjustments were not made

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

Component (y)	Source	Distribution	Uncertainty (u/y) Standard uncertainty		Combined standard uncertainty		Sensivity coefficient $c_i = \delta x/$	Contribution to (x), $\lvert c_i \rvert \cdot u(y)$/nmol/mol	
Optical path L_{opt}	Meaurement scale	Rectangular	0.058	cm	0.52	cm	*-x/Lopt*	2.9E-03	x
	Correction factor	Rectangular	0.520	cm					
Pressure P	Pressure gauge	Rectangular	0.029	kPa	0.03	kPa	*-x/P*	3.3E-04	x
	Difference between cells	Rectangular	0.017	kPa					
Temperatura T	Temperature probe	Rectangular	0.087	K	0.09	K	*x/T*	3.2E-04	x
Ratio of intensities D	Scaler resolution	Rectangular	8.0E-06		2.4E-05		*x/Dln(D)= u(x)B*	0.47	
	Repetibility	Triangular	2.3E-05						
Ozone losses	Tª gradient bias	Rectangular	2.3E-03					2.30E-03	x
	Interferences	Rectangular	0.200	nmol/mol				0.20	nmol/mol

the national standard uncertainty can be summarised by the formula:

$$u(x) = \sqrt{(0,51)^2 + (3,74 \cdot 10^{-3} x)^2}$$

Transfer Standard

Source	Distribution	Standard uncertainty compone
Repeatability		experimental standard desviation
Reproducibility	Rectangular	reproducibility/2 $\sqrt{3}$

Repeatability: maximal value of the experimental standard deviation observed at ISCII (***s*** = 0.21 nmol/mol)

Reproducibility: difference between the maximum and the minimum value of the slope of the regression line between the national standard and the transfer standard. Using a rectangular distribution, the standard relative uncertainty is 0.0016***x***

the transfer standard uncertainty can be summarised by the formula:

$$u_{PT} = \sqrt{(0.0016\ x)^2 + (0.21)^2}$$