Final report, On-going Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with LNE, 2008

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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 Laboratoire National de métrologie et d'Essais (LNE) 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:

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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 Laboratoire National de métrologie et d'Essais (LNE) are reported here. The LNE was the tenth 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 performed 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.

6. 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 versus the photometer B. $a_{\mathrm{A,B}}$ is dimensionless and $b_{\mathrm{A,B}}$ 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 14^{th} to the 17^{th} of April 2008 at 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 A, corresponding to a direct comparison between the LNE national standard SRP40 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.

8.1. 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.

8.2. 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.

8.3. 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.

8.4. 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 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-LNE-08 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

During the comparison with SRP40, a small shift in the value of the slope of the common reference standard BIPM-SRP27 with respect to the second BIPM standard BIPM-SRP28 was observed. This shift was not observed during the previous comparison performed with VNIIM in November 2007. The change in the value of the slope was small and covered by the component of uncertainty attributed to the optical path length value in the cells, and therefore SRP27 was deemed to be operating within its specifications. Following the completion of the comparison with SRP40, the UV filters within SRP27 were replaced with new ones and a comparison with SRP28 was performed. The results are shown in Figure 1, with a recovery of the agreement observed in November 2007. The shift in value in SRP27 was attributed to a visible degradation of the UV filters, notably on the gas cell subjected to the higher UV light intensity, which in turn affected the reflectivity of the filters and the optical pathlength. This effect was corrected by the introduction of new UV filters within SRP27.

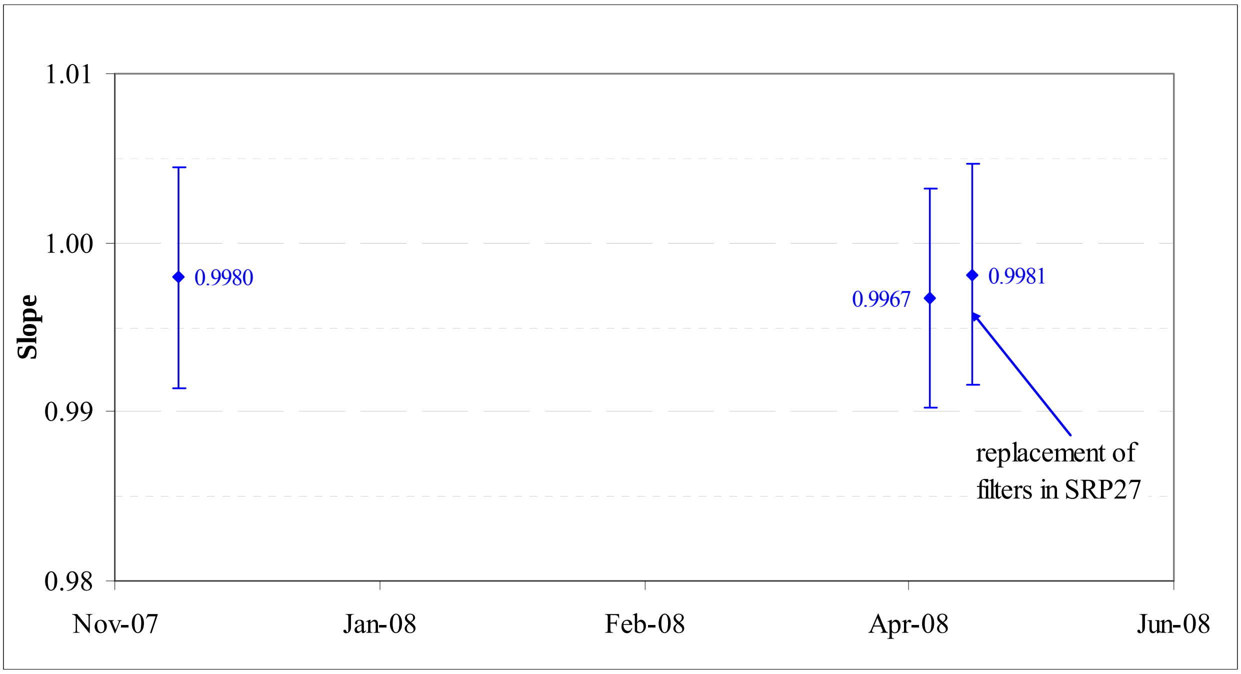


Figure 1: slope of SRP28 with respect to SRP27, first in November 2007 during the comparison with VNIIM, then in April 2008 during the comparison with LNE and finally after replacement of the filters in SRP27.

The LNE and the BIPM agreed to calculate the degrees of equivalence of the LNE standard with BIPM-SRP27 after replacement of its filters using BIPM-SRP28 as a transfer standard. To this end, the predicted values of the reference standard BIPM-SRP27 obtained after maintenance are compared to LNE SRP40.

All measurement results originally reported in the form BIPM.QM-K1-R1-LNE-08.xls were reproduced in the form BIPM.QM-K1-R2-LNE-08.xls to make clear how BIPM-SRP28 was used as a transfer standard.

12. Measurement standards

All instruments 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:

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

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

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

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:

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

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}.

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

- 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):

$$u(x) = \sqrt{(0.28)^2 + (2.92 \cdot 10^{-3} x)^2} \qquad (4)$$

12.5. Covariance terms for the common reference BIPM-SRP27

As explained in section 15, 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:

$$\boldsymbol{u}(\boldsymbol{x}_i, \boldsymbol{x}_j) = \boldsymbol{x}_i \cdot \boldsymbol{x}_j \cdot \boldsymbol{u}_\mathrm{b}^2 \tag{5}$$

where:

$$\boldsymbol{u}_\mathrm{b}^2 = \frac{\boldsymbol{u}^2(\boldsymbol{T})}{\boldsymbol{T}^2} + \frac{\boldsymbol{u}^2(\boldsymbol{P})}{\boldsymbol{P}^2} + \frac{\boldsymbol{u}^2(\boldsymbol{L}_\mathrm{opt})}{\boldsymbol{L}_\mathrm{opt}^{\ 2}} \tag{6}$$

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

12.6. Actual state of the LNE SRP40

The LNE SRP40 was constructed by the NIST in 2007 with the new design, which includes the "SRP upgrade kit" in order to deal with the two biases revealed in [4]. This kit includes two components:

- a new source block, which was designed to minimise 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.
- and, a new set of absorption cells. 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. However, to take into account a residual bias due to the beam divergence, the uncertainty is increased by the same amount as in SRP27 and SRP28.

12.7. Uncertainty budget of the LNE SRP40

The uncertainty budget for the ozone mole fraction in dry air x measured by the LNE standard SRP40 in the nominal range 0 nmol/mol to 500 nmol/mol is given in Table 2.

Following this budget, as explained in the protocol of the comparison, the standard uncertainty associated with the ozone mole fraction measurement with the LNE SRP40 can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u(x) = \sqrt{(0.28)^2 + (2.92\cdot10^{-3}x)^2} \tag{7}$$

No covariance term for the LNE SRP40 was included in the calculations.

Table 2: Uncertainty budget for the LNE SRP40

Component (y)	Source	Standard uncertainty	Distribution	Combined standard uncertainty $u(y)$	Sensitivity coefficient c_i	Contribution $\lvert c_i \rvert .u(y)$ in nmol.mol^{-1}
Optical path L	BIPM [4]	0.90 cm	Rectangular	0.52 cm	$-x/L$	2.9 x 10^{-3} x
Pressure P	Calibration	15 Pa	Rectangular	23 Pa	$-x/P$	2.3 x 10^{-4} x
	Drift	15 Pa	Rectangular			
	Difference between the cells	25 Pa	Rectangular			
Temperature T	Gradient [4]	0.1K	Rectangular	0,10 K	x/T	3.4 x 10^{-4} x
	Calibration	0.1K	Rectangular			
	Drift	0.1K	Rectangular			
Ratio of intensities D	Scaler resolution	1.2 x 10^{-5}	Rectangular	1.4 x 10^{-5}	$x/D\ln(D)$	0.28
	Repeatability	1.2 x 10^{-5}	-			
Absorption cross-section α	Hearn value [4] [5]	0.0106 x α	-	1.22 x 10^{-19} cm^2.molécule^{-1}	$-x/\alpha$	1.06 x 10^{-2} x

12.8. Transfer standard BIPM SRP28

BIPM-SRP28 is identical to BIPM-SRP27 described in section 12.3. As it is used here as a transfer standard, the sole uncertainty component taken into account is the experimental standard deviation *s* associated with each of the twelve measurement points. An analysis of repeats of comparisons performed between BIPM-SRP28 and BIPM-SRP31 (another SRP maintained by the BIPM) before and after the comparison with LNE showed that the standard deviation on the slope and intercepts of those comparisons are negligible compared to their standard uncertainties.

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-LNE-08 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 [6], is an extension of the previously used software B_Least recommended by the ISO standard 6143:2001 [7]. 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.

14.1. Least-square regression calculations

The comparison results are calculated in two steps:

- A linear regression on the twelve data points from the comparison between the BIPM-SRP27 (x_{RS}) and the BIPM-SRP28 (x_{TS}) performed after BIPM-SRP27 maintenance to evaluate the following relationship:

$$x_{\mathrm{RS}} = b_{\mathrm{RS,TS}} + x_{\mathrm{TS}} \cdot a_{\mathrm{RS,TS}} \qquad (8)$$

- A second linear regression of the twelve data points from the comparison between the LNE-SRP40 (x_{NS}) and the BIPM-SRP27 ($\hat{x}_{\mathrm{RS}}$), $\hat{x}_{\mathrm{RS}}$ being the predicted values of the reference standard, deduced from the BIPM-SRP28 measurement results, thanks to equation 8 (associated uncertainties are deduced from equation 13), to evaluate the following relationship:

$$x_{\mathrm{NS}} = a_0 + a_1 \cdot \hat{x}_{\mathrm{RS}} \qquad (9)$$

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.

14.2. Least-square regression results

The above calculations lead to the following relationship between SRP28 and SRP27 after its maintenance:

$$x_{\mathrm{SRP27}} = -0.06 + 1.0018 \cdot x_{\mathrm{SRP28}} \qquad (10)$$

With the uncertainties $u(a_0)$ = 0.18 nmol/mol, $u(a_1)$ = 0.0031, cov(a_0, a_1) = -1.2×10^{-4} nmol/mol.

and to the following relationship between SRP40 and SRP27:

$$x_{\mathrm{SRP40}} = -0.05 + 0.9957 \cdot \hat{x}_{\mathrm{SRP27}} \qquad (11)$$

With the uncertainties $u(a_0)$ = 0.26 nmol/mol, $u(a_1)$ = 0.0033, cov(a_0, a_1) = -2.76×10^{-4} nmol/mol.

To assess the agreement of the standards from equation 10, the difference between the calculated slope value and unity, and the intercept value and zero, together with their measurement uncertainties need to be considered. In the comparison, the value of the intercept is consistent with an intercept of zero, considering the uncertainty in the value of this parameter; i.e $|a_0| < 2u(a_0)$, and the value of the slope is consistent with a slope of 1; i.e. $|1 - a_1| < 2\,u(a_1)$.

15. Degrees of equivalence

Degrees of equivalence are calculated at two nominal ozone mole fractions among the twelve measured in each comparison, in the 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

When using a transfer standard, the degree of equivalence of the participant i, at a nominal value x_{nom} is defined as:

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

Where x_{i} is the measurement results of the national standard at the nominal value x_{nom}, and $\hat{x}_{\text{SRP27}}$ 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:

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

where $u(x_i)$ is the measurement uncertainties of the participant i and $u(\hat{x}_{\text{SRP27}})$ 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 $\overline{x}_{\text{RS}}$ and $\overline{x}_{\text{TS}}$ are fitted using the generalised least square program OzonE, taking into account the associated uncertainties $u(\overline{x}_{\text{RS}})$ and $u(\overline{x}_{\text{TS}})$, as well as covariance terms between the reference standard measurement results.

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

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

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

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

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

15.3. Values of the degrees of equivalence

The degrees of equivalence and their uncertainties calculated in the form BIPM.QM-K1-R2-LNE-08 are reported in the table below. Corresponding graphs of equivalence are displayed in Figure 2. The expanded uncertainties are calculated with a coverage factor $k = 2$.

Table 3 : degrees of equivalence of the LNE at the ozone nominal 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	80.79	0.37	81.14	0.35	-0.35	0.51	1.01
420	420.51	1.26	422.31	1.29	-1.80	1.80	3.61

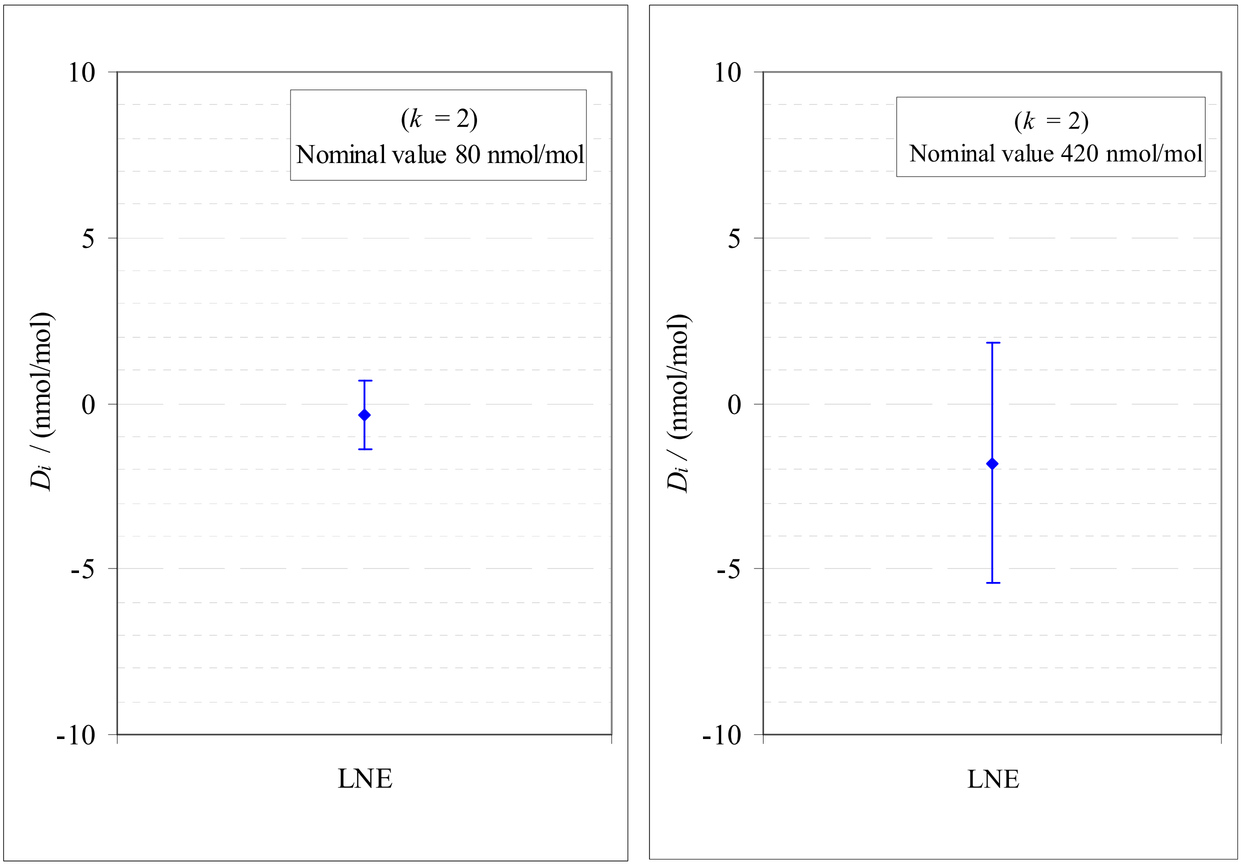


Figure 2: graphs of equivalence of the LNE at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol

The degrees of equivalence between the LNE 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. History of comparisons between BIPM and LNE

The LNE changed its national standard in 2008 and the results of the previous comparison performed in 2004 during the pilot study CCQM-P28 are displayed in Figure 3 together with the results of this comparison. 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 3 shows a good agreement between BIPM-SRP27, BIPM-SRP28, LNE-SRP24 and LNE-SRP40. The replacement of LNE national standard from a first generation SRP (SRP24) to a newly designed SRP (SRP40) was done without a major change in their comparability with the BIPM SRPs.

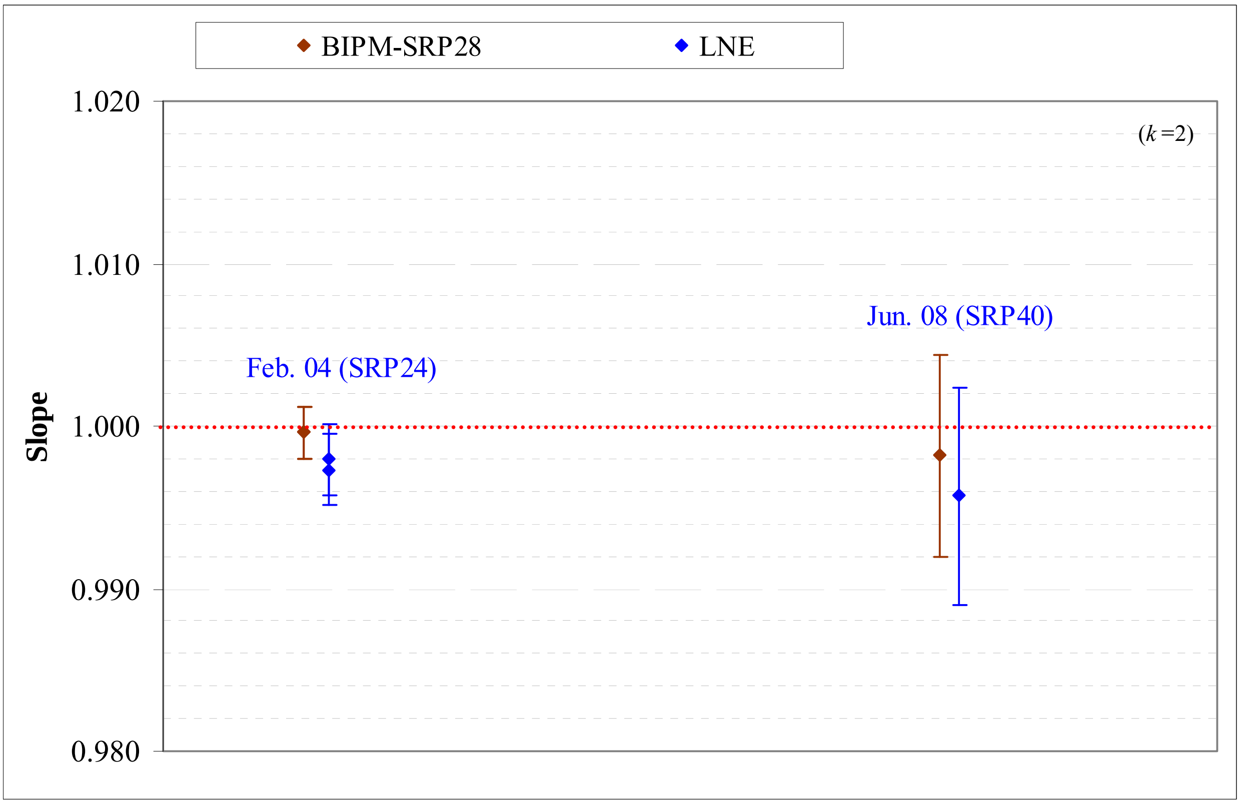
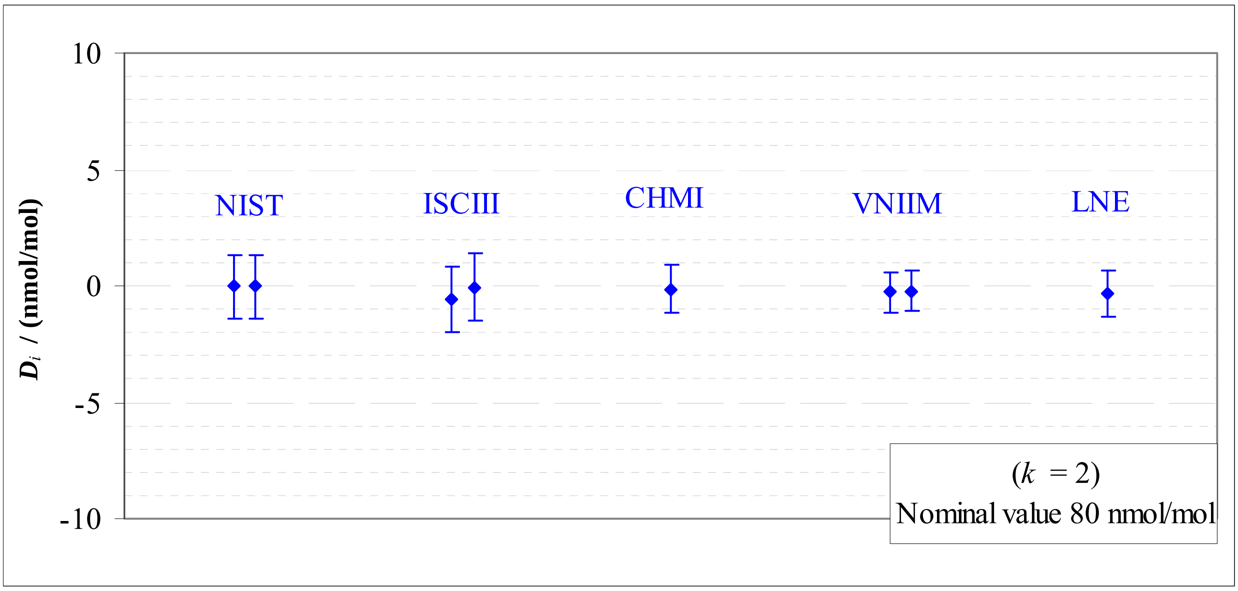


Figure 3 : Results of the comparisons between SRP27, SRP28 and the LNE standards performed at the BIPM during the pilot study CCQM-P28 and the key comparison BIPM.QM-K1. Uncertainties are calculated at k=2, with the uncertainty budget in use at the time of each comparison. Note that the LNE national standard is not the same instrument in the two comparisons.

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

Graphs of equivalence including previous participants with published results [8] are displayed in Figure 4.



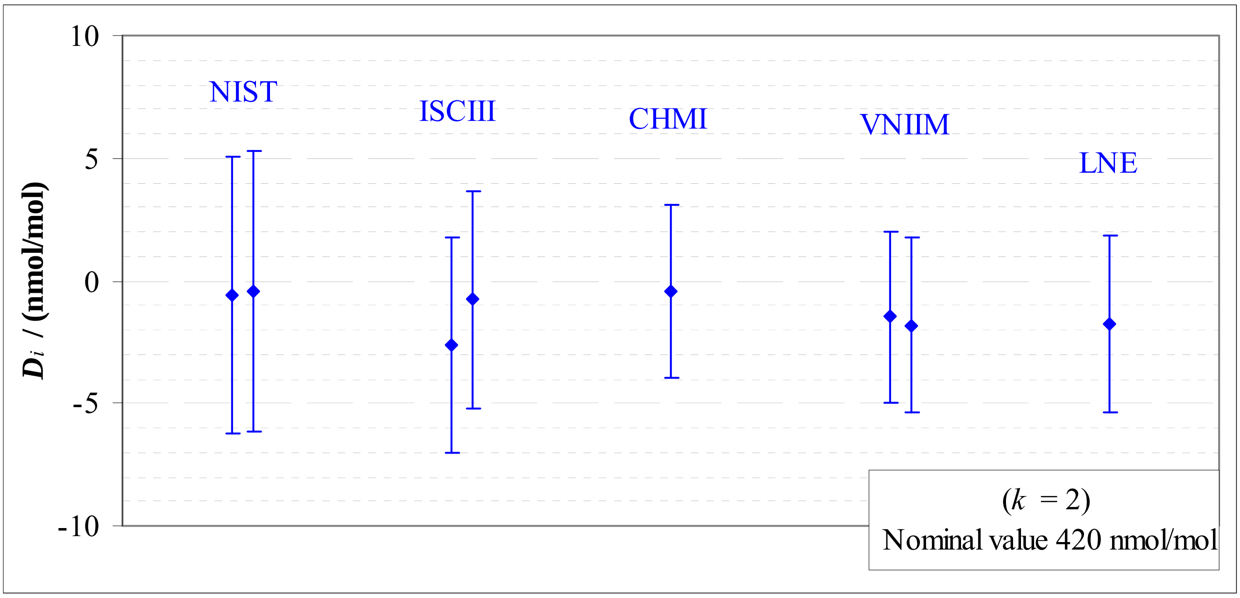


Figure 4: graphs of equivalence at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol, for all participants in BIPM.QM-K1 in the present cycle.

18. Conclusion

As part of the on-going key comparison BIPM.QM-K1, a comparison was performed between the ozone national standard of the LNE 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 LNE now maintains a new upgraded NIST-SRP as a standard. Degrees of equivalence of this comparison indicated a good agreement between both standards.

19. References

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Appendix 1 - Form BIPM.QM-K1-R2-LNE-08

See next pages.

OZONE COMPARISON RESULT - PROTOCOL B - WITH A TRANSFER STANDARD

Participating institute information	
Institute	**Laboratoire National de métrologie et d'Essais (LNE)**
Address	**1, rue Gaston Boissier** **75724 Paris Cedex 15**
Contact	**Tatiana Macé**
Email	tatiana.mace@lne.fr
Telephone	**33 1 40 43 38 53**

Instruments information			
	Reference Standard	**National Standard**	**Transfer Standard**
Manufacturer	NIST	NIST	NIST
Type	SRP	SRP	SRP
Serial number	SRP27	SRP40	SRP28
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

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

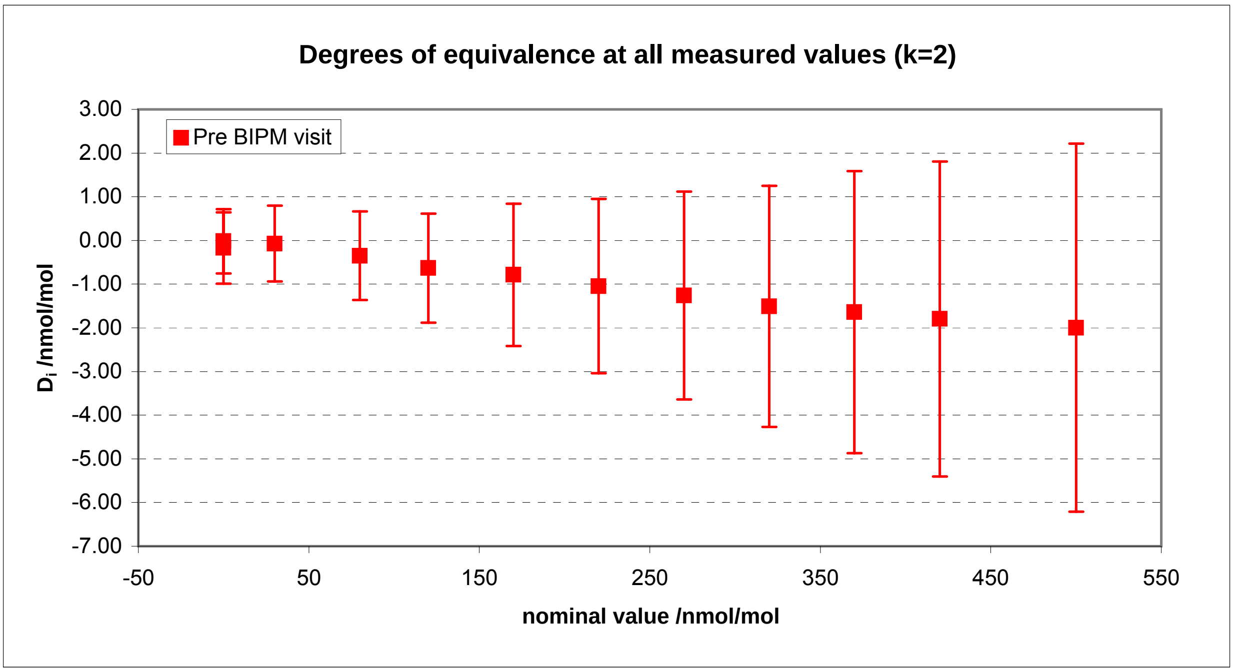
Equation $$x_{\mathrm{NS}} = a_{NS,RS}\, x_{\mathrm{RS}} + b_{NS,RS}$$

Least-square regression parameters

	$a_{NS,RS}$	$u(a_{\mathrm{NS,RS}})$	$b_{\mathrm{NS,RS}}$ (nmol/mol)	$u(b_{\mathrm{NS,RS}})$ (nmol/mol)	$u(a,b)$
first comparison	0.9957	0.0033	-0.05	0.26	-2.76E-04
second comparison	*no second comparison*				

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	-0.35	0.51	1.01
	420	-1.80	1.80	3.61
second comparison	80			
	420			



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	-0.05	0.28	0.02	0.16	-0.03	0.24
220	223.61	0.71	224.30	0.21	224.66	0.70
80	80.79	0.37	81.04	0.22	81.14	0.35
420	420.51	1.26	421.59	0.28	422.31	1.29
120	123.50	0.46	123.97	0.19	124.14	0.43
320	319.98	0.98	320.95	0.19	321.49	0.98
30	34.45	0.30	34.52	0.26	34.53	0.32
370	371.97	1.12	372.98	0.34	373.61	1.16
170	171.38	0.57	171.90	0.26	172.16	0.58
500	496.98	1.48	498.12	0.15	498.98	1.50
270	273.41	0.85	274.23	0.18	274.67	0.84
0	-0.16	0.28	0.07	0.24	0.02	0.30

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)

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

$a_{\mathrm{RS,TS}}$	1.0018	$b_{\mathrm{NRS,TS}}$ (nmol/mol)	-0.06	$u(a,b)$	-1.19E-04
$u(a_{\mathrm{RS,TS}})$	0.0031	$u(b_{\mathrm{RS,TS}})$ (nmol/mol)	0.18		

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**	-0.02	0.37	0.74
2	**220**	-1.05	1.00	1.99
3	**80**	-0.35	0.51	1.01
4	**420**	-1.80	1.80	3.61
5	**120**	-0.63	0.62	1.25
6	**320**	-1.51	1.38	2.76
7	**30**	-0.07	0.43	0.87
8	**370**	-1.64	1.62	3.23
9	**170**	-0.79	0.81	1.63
10	**500**	-2.00	2.11	4.21
11	**270**	-1.26	1.19	2.38
12	**0**	-0.17	0.41	0.81

Least-square regression parameters

$a_{NS,RS}$	$u(a_{\mathrm{NS,RS}})$	$b_{\mathrm{NS,RS}}$ (nmol/mol)	$u(b_{\mathrm{NS,RS}})$ (nmol/mol)	$u(a,b)$
0.9957	**0.0033**	**-0.05**	**0.26**	**-0.0002759**

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	0.00	0.00	0.00	0.00	-0.06	0.18
220	0.00	0.00	0.00	0.00	-0.06	0.18
80	0.00	0.00	0.00	0.00	-0.06	0.18
420	0.00	0.00	0.00	0.00	-0.06	0.18
120	0.00	0.00	0.00	0.00	-0.06	0.18
320	0.00	0.00	0.00	0.00	-0.06	0.18
30	0.00	0.00	0.00	0.00	-0.06	0.18
370	0.00	0.00	0.00	0.00	-0.06	0.18
170	0.00	0.00	0.00	0.00	-0.06	0.18
500	0.00	0.00	0.00	0.00	-0.06	0.18
270	0.00	0.00	0.00	0.00	-0.06	0.18
0	0.00	0.00	0.00	0.00	-0.06	0.18

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)

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

$a_{RS,TS}$	1.0018	$b_{NRS,TS}$ (nmol/mol)	-0.06	$u(a,b)$	-1.19E-04
$u(a_{RS,TS})$	0.0031	$u(b_{RS,TS})$ (nmol/mol)	0.18		

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	0.18	0.35
2	**220**	0.06	0.18	0.35
3	**80**	0.06	0.18	0.35
4	**420**	0.06	0.18	0.35
5	**120**	0.06	0.18	0.35
6	**320**	0.06	0.18	0.35
7	**30**	0.06	0.18	0.35
8	**370**	0.06	0.18	0.35
9	**170**	0.06	0.18	0.35
10	**500**	0.06	0.18	0.35
11	**270**	0.06	0.18	0.35
12	**0**	0.06	0.18	0.35

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

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

Operator	**Philippe Moussay**	**Location**	**BIPM**
Comparison begin date / time	**14/04/2008 14:00**	**Comparison end date / time**	**17/04/2008 15:00**

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	0.02	0.16	0.16	-0.05	0.20	0.28
220	224.30	0.21	0.21	223.61	0.15	0.71
80	81.04	0.22	0.22	80.79	0.20	0.37
420	421.59	0.28	0.28	420.51	0.20	1.26
120	123.97	0.19	0.19	123.50	0.17	0.46
320	320.95	0.19	0.19	319.98	0.15	0.98
30	34.52	0.26	0.26	34.45	0.15	0.30
370	372.98	0.34	0.34	371.97	0.32	1.12
170	171.90	0.26	0.26	171.38	0.18	0.57
500	498.12	0.15	0.15	496.98	0.22	1.48
270	274.23	0.18	0.18	273.41	0.18	0.85
0	0.07	0.24	0.24	-0.16	0.21	0.28

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	Environics
Ozone generator type	Model 6100
Ozone generator serial number	3128
Room temperature(min-max) / °C	22.4 / 23.1
Room pressure (average) / hpa	993 / 995
Zero air source	oil free compressor + dryer+ aadco 737-R
Reference air flow rate (L/min)	14
Sample flow rate (L/min)	10
Instruments stabilisation time	2 days
Instruments acquisition time /s (one measurement)	5s
Instruments averaging time /s	5s
Total time for ozone conditioning	17 h
Ozone mole fraction during conditioning	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	11

Instruments checks and adjustments

National Standard

Transfer Standard

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

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

Operator	P. Moussay	**Location**	BIPM
Comparison begin date / time	24/04/2008	**Comparison end date / time**	25/04/2008

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)	$u(a,b)$
1.0018	**0.0031**	**-0.06**	**0.18**	**-0.00012**

(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	-0.05	0.16	0.16	0.04	0.32	0.28
220	223.78	0.21	0.21	224.11	0.28	0.71
80	80.55	0.14	0.14	80.61	0.27	0.37
420	419.98	0.39	0.39	420.56	0.47	1.26
120	123.36	0.25	0.25	123.62	0.38	0.46
320	319.59	0.33	0.33	320.25	0.24	0.98
30	34.07	0.17	0.17	34.01	0.24	0.30
370	372.25	0.25	0.25	372.78	0.32	1.12
170	171.02	0.26	0.26	171.34	0.28	0.57
500	496.76	0.28	0.28	497.71	0.36	1.48
270	273.55	0.25	0.25	273.95	0.24	0.85
0	0.21	0.24	0.24	0.02	0.22	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 8.56E-06

Comparison conditions

Ozone generator manufacturer	Environics
Ozone generator type	Model 6100
Ozone generator serial number	3128
Room temperature(min-max) / °C	22.4 / 23.1
Room pressure (average) / hpa	993 / 995
Zero air source	oil free compressor + dryer+ aadco 737-R
Reference air flow rate (L/min)	14
Sample flow rate (L/min)	10
Instruments stabilisation time	
Instruments acquisition time /s (one measurement)	5s
Instruments averaging time /s	5s
Total time for ozone conditioning	17 h
Ozone mole fraction during conditioning	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	12
Data files names and location	\\chem5\Program Files\NIST\SRPControl\Data\2008
C080424001.XLS to C080424012.XLS	

Instruments checks and adjustments

Reference Standard

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

Transfer Standard

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

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

Operator	***	**Location**	***
Comparison begin date / time	***	**Comparison end date / time**	***

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	***	***	***	***	***	***
220	***	***	***	***	***	***
80	***	***	***	***	***	***
420	***	***	***	***	***	***
120	***	***	***	***	***	***
320	***	***	***	***	***	***
30	***	***	***	***	***	***
370	***	***	***	***	***	***
170	***	***	***	***	***	***
500	***	***	***	***	***	***
270	***	***	***	***	***	***
0	***	***	***	***	***	***

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 ***

Comparison conditions

Ozone generator manufacturer	***
Ozone generator type	***
Ozone generator serial number	***
Room temperature(min-max) / °C	***
Room pressure (average) / hpa	***
Zero air source	***
Reference air flow rate (L/min)	***
Sample flow rate (L/min)	***
Instruments stabilisation time	***
Instruments acquisition time /s (one measurement)	***
Instruments averaging time /s	***
Total time for ozone conditioning	***
Ozone mole fraction during conditioning	***
Comparison repeated continously (Yes/No)	***
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	***

Instruments checks and adjustments

National Standard

****

Transfer 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:

$$\boxed{u(x)=\sqrt{(0.28)^2+(2,92\cdot 10^{-3}x)^2}}$$

Transfer Standard

repeatability term : experimental standard deviation s.

National Standard

The uncertainty budget is calculated as explained in the following table.

Component (y)	Source	Standard uncertainty	Distribution	Combined standard uncertainty u(y)	Sensitivity coefficient C_i	Contribution $\lvert C_i\rvert.u(y)$ in $nmol.mol^{-1}$
Optical path L	BIPM *[1]*	0.90 cm	Rectangular	0.52 cm	-C/L	2.9×10^{-3} C
Pressure P	Calibration Drift Difference between the cells	15 Pa 15 Pa 25 Pa	Rectangular Rectangular Rectangular	23 Pa	-C/P	2.3×10^{-4} C
Temperature T	Gradient [1] Calibration Drift	0.1K 0.1K 0.1K	Rectangular Rectangular Rectangular	0,10 K	C/T	3.4×10^{-4} C
Ratio of intensities D	Scaler resolution Repeatability	1.2×10^{-5} 1.2×10^{-5}	Rectangular -	1.4×10^{-5}	C/Dln(D)	0.28
Absorption cross-section α	Hearn value *[1] [2]*	0.0106 x α	-	1.22×10^{-19} cm^2.molécule^{-1}	-C/α	1.06×10^{-2} C

The expanded uncertainty on the ozone concentration is estimated by combining all the

$$U(C_i) = 2 * \sqrt{\left(1.1x10^{-2} \times C\right)^2 + (0.28)^2}$$

But, for this comparison, the uncertainty on the absorption cross-section is not taken into

$$\boxed{U(C_i) = 2 * \sqrt{\left(2.92x10^{-3} \times C\right)^2 + (0.28)^2}}$$

[1] : A study of systematic biases and measurrment uncertainties in ozone mole fraction measurements with the
[2] The absorption of Ozone in the Ultra violet and visible Region of the Spectrum by A.G.Hearn (1961)