

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

Joële Viallon<sup>1\*</sup>, Philippe Moussay<sup>1</sup>, Robert Wielgosz<sup>1</sup>, Dr. L.A. Konopelko<sup>2</sup>, Y.A. Kustikov<sup>2</sup>,  
D. Selyukov<sup>2</sup>

<sup>1</sup> BIPM (Bureau International des Poids et Mesures), Pavillon de Breteuil, F-92312 Sèvres, France

<sup>2</sup> VNIIM (D.I. Mendeleev Institute for Metrology), 19 Moskovsky pr., 190005 St. Petersburg, Russia

## Abstract

As part of the on-going key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of the D.I. Mendeleev Institute for Metrology (VNIIM) 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.

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

## 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 D.I. Mendeleev Institute for Metrology (VNIIM) are reported here. The VNIIM was the seventh laboratory to participate in the 2007-2008 round of 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

- $x_{\text{nom}}$ : nominal ozone mole fraction in dry air furnished by the ozone generator
- $x_{A,i}$ :  $i$ th measurement of the nominal value  $x_{\text{nom}}$  by the photometer A.
- $\bar{x}_A$ : the mean of  $N$  measurements of the nominal value  $x_{\text{nom}}$  measured by the photometer A : 
$$\bar{x}_A = \frac{1}{N} \sum_{i=1}^N x_{A,i}$$
- $s_A$  : standard deviation of  $N$  measurements of the nominal value  $x_{\text{nom}}$  measured by the photometer A : 
$$s_A^2 = \frac{1}{N-1} \sum_{i=1}^N (x_{A,i} - \bar{x}_A)^2$$
- The result of the linear regression fit performed between two sets of data measured by the photometers A and B during a comparison is written:  $x_A = a_{A,B}x_B + b_{A,B}$ . With this notation, the photometer A is compared versus the photometer B.  $a_{A,B}$  is dimensionless and  $b_{A,B}$  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 9 November to 27 December 2007 at the VNIIM 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/utis/en/pdf/BIPM.QM-K1\\_protocol.pdf](http://www.bipm.org/utis/en/pdf/BIPM.QM-K1_protocol.pdf)).

This comparison was performed following protocol B, corresponding to a comparison between the VNIIM national standard SRP38 and the common reference standard BIPM-SRP27 maintained at the BIPM via a transfer standard Thermo Environmental Instrument 49i (TEI 49i). The national standard SRP38 and the transfer standard TEI 49i were first compared at the VNIIM in November. Then the transfer standard TEI 49i was compared with the common reference standard SRP27 at the BIPM two weeks later. Finally, the national standard SRP38 and the transfer standard TEI 49i were again compared at the VNIIM in December 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 VNIIM

#### a). Ozone generation

Purified air is produced in five steps. Ambient air is first compressed by an oil-free compressor. It is then proceed through a dryer to absorb humidity from air. In a third step, the dry air enters an oven with platinum catalyst operating at a temperature of about 200°C. Organic impurities are destroyed and oxidized in the oven. After the oven, the air goes through a commercial filter containing porous pellets impregnated with sodium permanganate, where inorganic impurities are fully oxidized and absorbed. Finally, the air goes through a cell filled with activated charcoal.

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 SRP38.

#### b). Comparison procedure

Prior to the comparison, all the instruments were switched on and allowed to stabilise for 8 hours. Characteristics of the instruments were checked at this time. No adjustments were required on the transfer standard TEI 49i. The national standard SRP38 was adjusted according to the SRP operation manual provided by NIST.

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  $x_{\text{nom}}$  furnished by the ozone generator, the standard deviation  $s_{\text{SRP38}}$  on the set of 10 consecutive measurements  $x_{\text{SRP38},i}$  recorded by SRP38 was calculated. The measurement results were considered as valid if  $s_{\text{SRP38}}$  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 four times successively to evaluate its repeatability.

## 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  $\mu\text{mol/mol}$ . 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  $x_{\text{nom}}$  furnished by the ozone generator, the standard deviation  $s_{\text{SRP27}}$  on the set of 10 consecutive measurements  $x_{\text{SRP27},i}$  recorded by BIPM-SRP27 was calculated. The measurement results were considered as valid if  $s_{\text{SRP27}}$  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-VNIIM-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:

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

where

- $\alpha$  is the absorption cross-section of ozone at 253.7nm in standard conditions of temperature and pressure. The value used is:  $1.1476 \times 10^{-17}$  cm<sup>2</sup>/molecule [3].
- $L_{\text{opt}}$  is the optical path length of one of the cells,

$T$  is the measured temperature of the cells,  
 $T_{\text{std}}$  is the standard temperature (273.15 K),  
 $P$  is the measured pressure of the cells,  
 $P_{\text{std}}$  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

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

where

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

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

where

$N_A$  is the Avogadro constant,  $6.022142 \times 10^{23} \text{ mol}^{-1}$ , and  
 $R$  is the gas constant,  $8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$ .

## 12.2. Absorption cross section for ozone

The absorption cross section used within the SRP software algorithm is  $308.32 \text{ atm}^{-1} \text{ cm}^{-1}$ . This corresponds to a value of  $1.1476 \times 10^{-17} \text{ cm}^2/\text{molecule}$ , rather than the more often quoted  $1.147 \times 10^{-17} \text{ cm}^2/\text{molecule}$ . In the comparison of two SRP instruments, the absorption cross section can be considered to have a conventional value and its uncertainty can be set to zero. However, in the comparison of different methods or when considering the complete uncertainty budget of the method the uncertainty of the absorption cross section should be taken into account. A consensus value of 2.12% at a 95% level of confidence for the uncertainty of the absorption cross section has been proposed by the BIPM and the NIST in a recent publication [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 $u(x)$ $ c_i  \cdot u(y)$ nmol/mol
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$		
<b>Optical Path</b> $L_{opt}$	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	Rect	0.52 cm			
<b>Pressure <math>P</math></b>	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			
<b>Temperature <math>T</math></b>	Temperature probe	Rectangular	0.03 K	0.07 K	$\frac{x}{T}$	$2.29 \times 10^{-4} x$
	Temperature gradient	Rectangular	0.058 K			
<b>Ratio of intensities <math>D</math></b>	Scaler resolution	Rectangular	$8 \times 10^{-6}$	$1.4 \times 10^{-5}$	$\frac{x}{D \ln(D)}$	0.28
	Repeatability	Triangular	$1.1 \times 10^{-5}$			
<b>Absorption Cross section <math>\alpha</math></b>	Hearn value		$1.22 \times 10^{-19}$ cm <sup>2</sup> /molecule	$1.22 \times 10^{-19}$ cm <sup>2</sup> /molecule	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2} x$

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):

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

#### 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:

$$u(x_i, x_j) = x_i \cdot x_j \cdot u_b^2 \quad (5)$$

where:

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

The value of  $u_b$  is given by the expression of the measurement uncertainty:  $u_b = 2.92 \times 10^{-3}$  or  $u_b^2 = 8.5 \times 10^{-6}$ .

## 12.6. Actual state of the VNIIM SRP38

The VNIIM SRP38 has been constructed by 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 consists in two parts:

- A new source block 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.
- A new set of absorption cells were installed. The new cells are quartz tubes closed at both ends by optically sealed quartz windows. These windows are tilted by 3° with respect to the vertical plane to avoid multiple reflections along the light path. 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 VNIIM SRP38

The uncertainty budget for the ozone mole fraction in dry air  $x$  measured by the VNIIM standard SRP38 in the nominal range 0 nmol/mol to 500 nmol/mol is given in Table 2.

*Table 2 : SRP38 uncertainty budget*

Component (y)	Uncertainty u(y)				Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to u(x) $ c_i  \cdot u(y)$ nmol/mol
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty u(y)		
<b>Optical Path</b> $L_{opt}$	Measurement Scale	Rectangular	0.046 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89 \times 10^{-3} x$
	Correction factor	Rectangular	0.52 cm			
<b>Pressure P</b>	Pressure gauge	Rectangular	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.36 \times 10^{-4} x$
	Difference between cells	Rectangular	0.017 kPa			
<b>Temperature T</b>	Temperature probe	Rectangular	0.087 K	0.104 K	$-\frac{x}{T}$	$3.52 \times 10^{-4} x$
	Residual bias	Rectangular	0.057 K			
<b>Ratio of intensities D</b>	Repeatability	Triangular	$0.98 \times 10^{-6}$	$1.06 \times 10^{-5}$	$\frac{x}{D \ln(D)}$	0.21
	Scaler resolution	Rectangular	$0.41 \times 10^{-6}$			
<b>Absorption Cross section <math>\alpha</math></b>	Hearn value		$1.22 \times 10^{-19}$ cm <sup>2</sup> /molecule	$1.22 \times 10^{-19}$ cm <sup>2</sup> /molecule	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2} x$

Following this budget, the standard uncertainty associated with the ozone mole fraction measurement with the VNIIM SRP38 can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u(x) = \sqrt{(0.21)^2 + (2.93 \cdot 10^{-3} x)^2} \quad (7)$$

A covariance term of  $u_b = 2.93 \times 10^{-3}$  or  $u_b^2 = 8.58 \times 10^{-6}$  was included for the VNIIM SRP38 was in the calculations.

## 12.8. Transfer standard TEI 49i

The transfer standard used by VNIIM is a Thermo Environmental Instrument 49i. It is an ozone photometer based on a principle similar to the SRP, although many components are simplified. This model includes a scrubber. It is normally used by VNIIM as a secondary standard.

The uncertainty budget for the ozone mole fraction in dry air  $x$  measured by the TEI 49i in the nominal range 0 nmol/mol to 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 VNIIM:

*Table 3 : TEI 49i uncertainty budget*

Component (y)	Uncertainty $u(y)$			Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to $u(x)$ $ c_i  \cdot u(y)$ nmol/mol
	Source	Distribution	Standard Uncertainty		
<b>Reproducibility</b>	Slope	Rectangular	$5.8 \times 10^{-4}$	$x$	$5.8 \times 10^{-4} x$
	Intercept	Rectangular	0.11 nmol/mol	1	0.11
<b>Repeatability*</b>		Normal	0.047 nmol/mol	1	0.047

\*Standard deviation of the mean for 10 measurements

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

$$u_{TS}(x) = \sqrt{(5.8 \cdot 10^{-4} \cdot x)^2 + (0.12)^2} \quad (8)$$

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-VNIIM-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 SRP $n$  and SRP27 is obtained:

$$x_{SRPn} = a_0 + a_1 x_{SRP27} \quad (9)$$

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 SRP38 and SRP27 are:

$$x_{SRP38} = 0.20 + 0.9954 \cdot x_{SRP27} \quad (10)$$

from the pre BIPM visit, with the uncertainties  $u(a_0) = 0.21$  nmol/mol,  $u(a_1) = 0.0043$ ,  $\text{cov}(a_0, a_1) = -1.85 \times 10^{-4}$ ,

and 
$$x_{\text{SRP38}} = 0.18 + 0.9949 \cdot x_{\text{SRP27}} \quad (11)$$

from the post BIPM visit, with the uncertainties  $u(a_0) = 0.21$  nmol/mol,  $u(a_1) = 0.0043$ ,  $\text{cov}(a_0, a_1) = -1.84 \times 10^{-4}$ .

To assess 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.  $|1 - a_1| < 2u(a_1)$ .

## 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  $\pm 15$  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  $x_{\text{nom}}$  is defined as:

$$D = x_i - \hat{x}_{\text{SRP27}} \quad (12)$$

Where  $x_i$  is the measurement results of the national standard at the nominal value  $x_{\text{nom}}$ , 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:

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

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  $\bar{x}_{\text{RS}}$  and  $\bar{x}_{\text{TS}}$  are fitted using the generalised least square program OzonE, taking into account the associated

uncertainties  $u(\bar{x}_{RS})$  and  $u(\bar{x}_{TS})$ , 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  $\bar{x}_{TS}$  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:

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

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-VNIIM-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 VNIIM at the ozone nominal mole fractions 80 nmol/mol and 420 nmol/mol*

<b>Nominal value</b>	$x_i /$ (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)
<b>80</b>	79.76	0.31	80.04	0.29	-0.28	0.43	0.86
<b>420</b>	410.70	1.22	412.17	1.25	-1.47	1.75	3.50
<b>80</b>	81.13	0.32	81.36	0.29	-0.22	0.43	0.87
<b>420</b>	419.70	1.25	421.52	1.28	-1.82	1.79	3.58

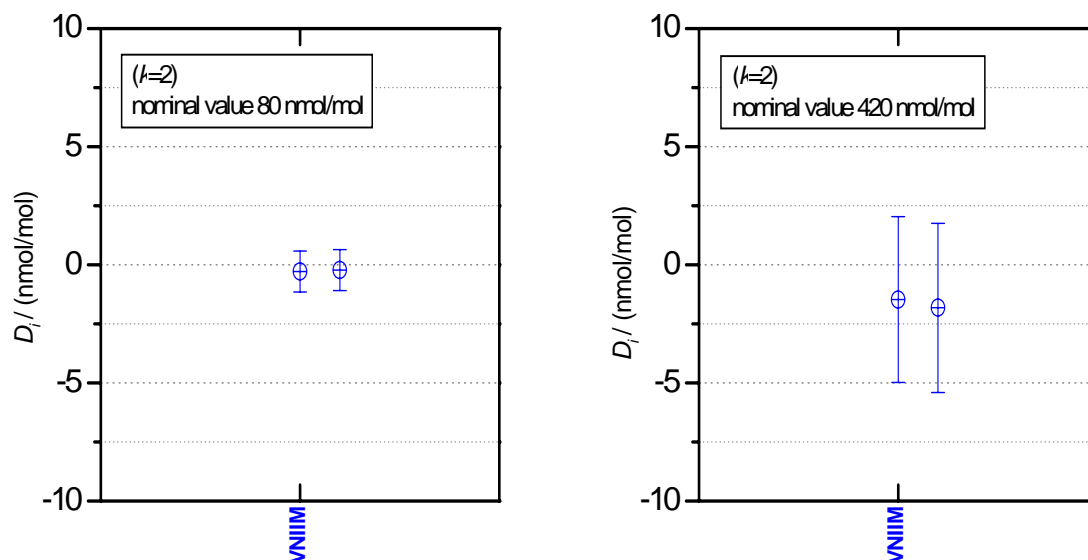


Figure 1: degrees of equivalence of the VNIIM at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol

The degrees of equivalence between the VNIIM 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 SRP38 and the reference standard SRP27 shows an increase of 0.05% when considering the slope of the linear relationship deduced from the two comparisons performed. This variation is completely negligible and both comparisons are consistent according to the uncertainties.

## 17. History of comparisons between BIPM SRP27, SRP28 and VNIIM SRP38

Although VNIIM has changed its national standard in 2007, results of the previous comparison performed in 2004 during the pilot study CCQM-P28 are displayed in Figure 2 together with the results of this comparison. The slopes  $a_1$  and the intercept  $a_0$  of the linear relation  $x_{\text{SRP}n} = a_0 + a_1 x_{\text{SRP}27}$  are represented together with their associated uncertainties calculated at the time of each comparison.

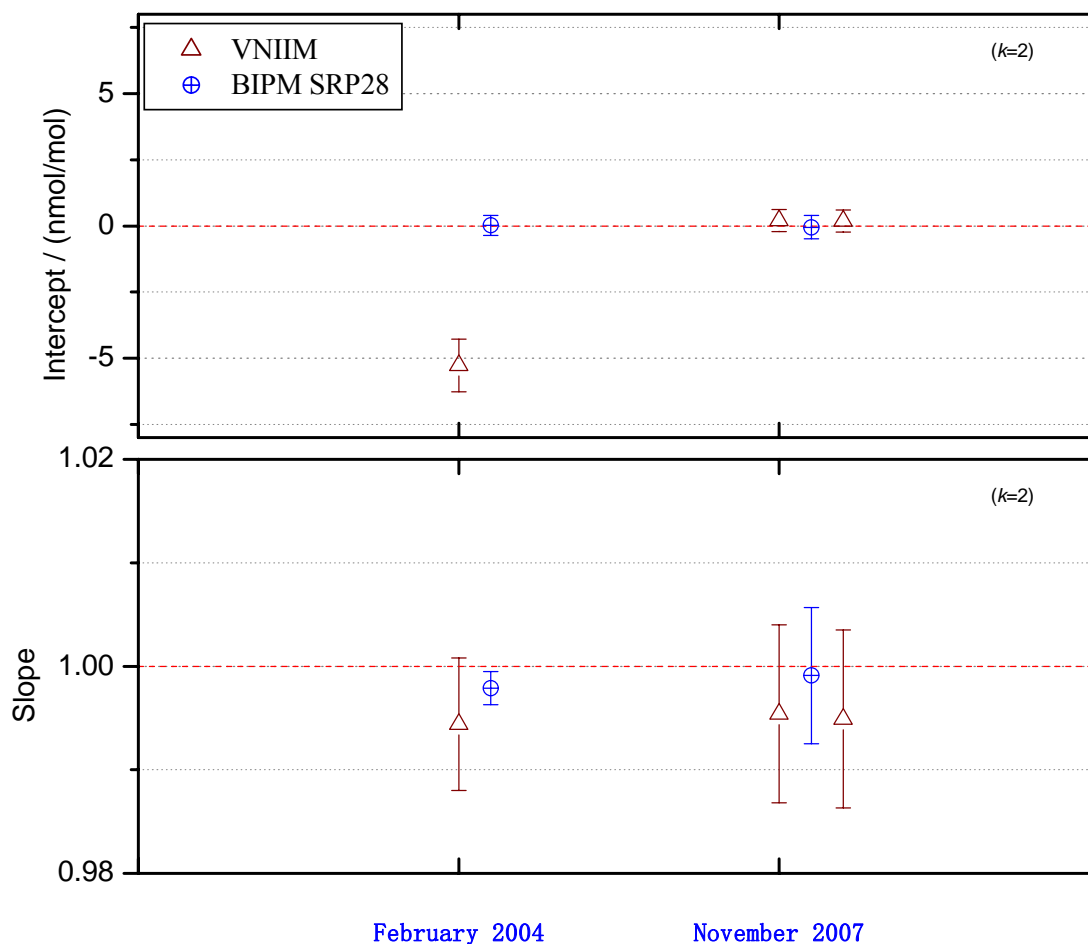


Figure 2 : Results of the two comparisons between SRP27, SRP28 and VNIIM standard realised at the BIPM during the pilot study CCQM-P28 and the key comparison BIPM.QM-K1. Uncertainties are calculated at  $k=2$ , with the uncertainty budget in use at the time of each comparison. Note that VNIIM national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

Figure 2 shows that the new VNIIM ozone national standard, SRP38, is in closer agreement with the reference standard BIPM-SRP27 than the Dasibi 1003AH maintained in 2004. In particular, the Dasibi instrument had an intercept not consistent with 0 nmol/mol.

This figure 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 VNIIM is the seventh one in the 2007-2008 round of BIPM.QM-K1. Degrees of equivalence including previous participants for which results were already published at the time of this report are displayed in Figure 3.

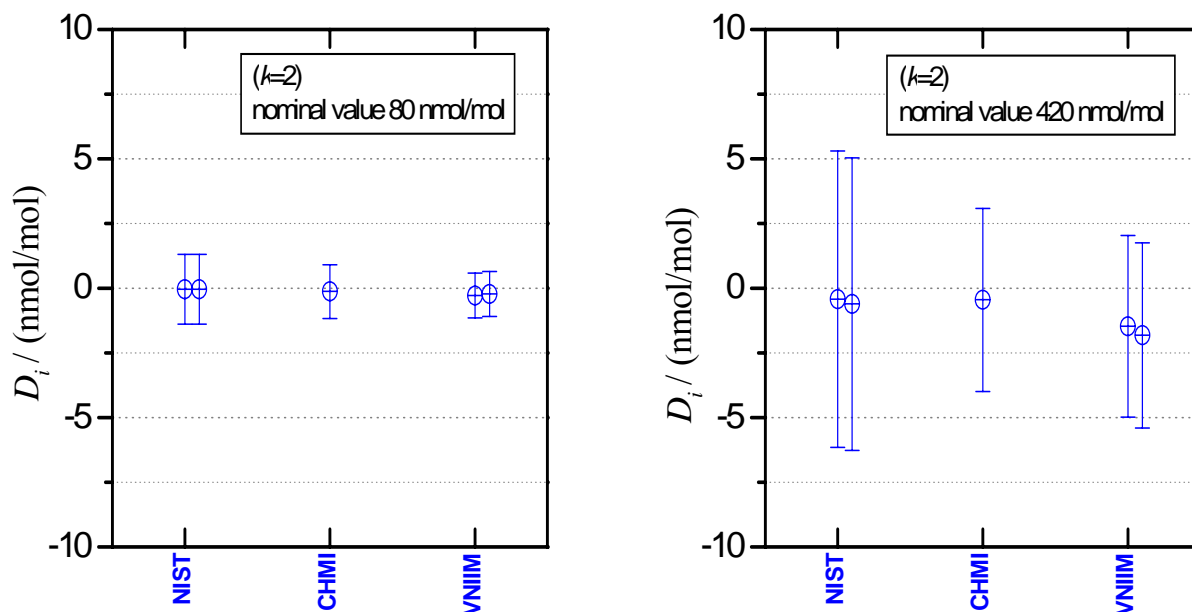


Figure 3: degrees of equivalence at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol, for all participants in BIPM.QM-K1 in the present cycle.

## 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 VNIIM 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 VNIIM is now maintaining a NIST-SRP in its new version as a standard. 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-VNIIM-07**

See next pages.

**OZONE COMPARISON RESULT - PROTOCOL B - WITH A  
TRANSFER STANDARD**

<b>Participating institute information</b>	
<b>Institute</b>	<b>D.I. Mendeleev Institute for Metrology (VNIIM)</b>
<b>Address</b>	<b>Russia, 190005, St. Petersburg, Moskovsky pr., 19</b>
<b>Contact</b>	<b>Dr. L.A. Konopelko, Y.A. Kustikov</b>
<b>Email</b>	<a href="mailto:L.A.Konopelko@vniim.ru">L.A.Konopelko@vniim.ru</a> , <a href="mailto:lkonop@b10.vniim.ru">lkonop@b10.vniim.ru</a>
<b>Telephone</b>	<b>+7-812-315-11-45</b>

<b>Instruments information</b>			
	<b>Reference Standard</b>	<b>National Standard</b>	<b>Transfer Standard</b>
<b>Manufacturer</b>	NIST	NIST	Thermo Electron
<b>Type</b>	SRP	SRP	49i
<b>Serial number</b>	SRP27	SRP38	0709421269
<b>ozone cross-section value</b>	$308.32 \text{ atm}^{-1} \text{ cm}^{-1}$	$308.32 \text{ atm}^{-1} \text{ cm}^{-1}$	***

**Content of the report**

page 1	General informations
page 2	Summary 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](mailto: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**

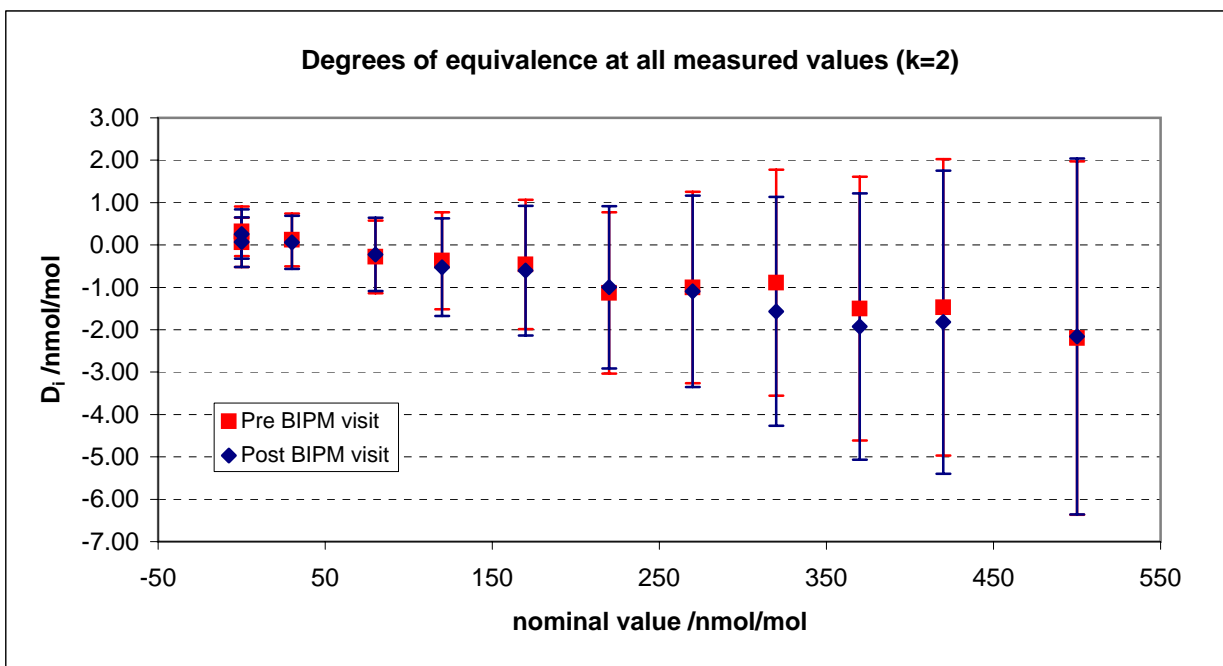
**Equation** 
$$x_{NS} = a_{NS,RS} x_{RS} + b_{NS,RS}$$

**Least-square regression parameters**

	$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
<b>first comparison</b>	<b>0.9954</b>	<b>0.0043</b>	<b>0.20</b>	<b>0.21</b>	<b>-1.85E-04</b>
<b>second comparison</b>	<b>0.9949</b>	<b>0.0043</b>	<b>0.18</b>	<b>0.21</b>	<b>-1.84E-04</b>

**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)
<b>first comparison</b>	<b>80</b>	-0.28	0.43	0.86
	<b>420</b>	-1.47	1.75	3.50
<b>second comparison</b>	<b>80</b>	-0.22	0.43	0.87
	<b>420</b>	-1.82	1.79	3.58



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

**First comparison results**

Nominal value	National standard measurement results		Transfer standard measurement results		Reference Standard predicted values	
	$x_{NS}$ 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	0.21	-0.37	0.12	-0.27	0.20
220	218.61	0.67	217.69	0.17	219.74	0.67
80	79.76	0.31	79.23	0.13	80.04	0.29
420	410.70	1.22	408.41	0.27	412.17	1.25
120	121.46	0.41	120.65	0.14	121.83	0.40
320	311.02	0.94	309.04	0.22	311.91	0.95
30	32.72	0.23	32.21	0.12	32.60	0.21
370	364.45	1.09	362.60	0.24	365.95	1.11
170	171.59	0.54	170.42	0.16	172.05	0.53
500	490.23	1.45	487.95	0.31	492.42	1.50
270	261.56	0.79	260.13	0.19	262.56	0.80
0	-0.12	0.21	-0.28	0.12	-0.18	0.20

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)

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

$a_{RS,TS}$  1.0090       $b_{NRS,TS}$  (nmol/mol) 0.10       $u(a, b)$  -1.02E-04  
 $u(a_{RS,TS})$  0.0031       $u(b_{RS,TS})$  (nmol/mol) 0.16

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	0.32	0.29	0.58
2	220	-1.13	0.95	1.91
3	80	-0.28	0.43	0.86
4	420	-1.47	1.75	3.50
5	120	-0.37	0.57	1.14
6	320	-0.89	1.33	2.66
7	30	0.12	0.31	0.62
8	370	-1.50	1.56	3.11
9	170	-0.46	0.76	1.53
10	500	-2.19	2.08	4.17
11	270	-1.00	1.13	2.26
12	0	0.06	0.29	0.58

Least-square regression parameters				
$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a, b)$
0.9954	0.0043	0.20	0.21	-1.85E-04

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

**Second comparison results**

Nominal value	National standard measurement results		Transfer standard measurement results		Reference Standard predicted values	
	$x_{NS}$ 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	0.09	0.21	-0.26	0.12	-0.16	0.20
220	219.84	0.68	218.78	0.17	220.84	0.68
80	81.13	0.32	80.54	0.13	81.36	0.29
420	419.70	1.25	417.68	0.27	421.52	1.28
120	122.10	0.41	121.43	0.14	122.62	0.40
320	315.22	0.95	313.88	0.22	316.79	0.96
30	32.98	0.23	32.53	0.12	32.92	0.21
370	367.88	1.10	366.43	0.24	369.81	1.12
170	171.94	0.55	170.91	0.16	172.54	0.54
500	494.08	1.46	491.73	0.31	496.24	1.51
270	261.87	0.80	260.53	0.19	262.96	0.80
0	-0.02	0.21	-0.19	0.12	-0.09	0.20

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)

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

$a_{RS,TS}$	1.0090	$b_{RS,TS}$ (nmol/mol)	0.10	$u(a, b)$	-1.02E-04
$u(a_{RS,TS})$	0.0031	$u(b_{RS,TS})$ (nmol/mol)	0.16		

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	0.26	0.29	0.58
2	220	-1.00	0.96	1.92
3	80	-0.22	0.43	0.87
4	420	-1.82	1.79	3.58
5	120	-0.52	0.57	1.15
6	320	-1.57	1.35	2.70
7	30	0.06	0.31	0.63
8	370	-1.93	1.57	3.14
9	170	-0.61	0.77	1.53
10	500	-2.16	2.10	4.20
11	270	-1.09	1.13	2.26
12	0	0.07	0.29	0.58

Least-square regression parameters				
$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a, b)$
0.9949	0.0043	0.18	0.21	-1.84E-04

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

<b>Operator</b>	<b>Selyukov Dmitry</b>	<b>Location</b>	<b>VNIIM</b>
<b>Comparison begin date / time</b>	<b>09-nov-07/17:00</b>	<b>Comparison end date / time</b>	<b>09-nov-2007/20:10</b>

measurement results						
Nominal value	Transfer standard (TS)			National Standard (NS)		
	$x_{TS}$ 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	-0.37	0.09	0.12	0.05	0.25	0.21
220	217.69	0.19	0.17	218.61	0.18	0.67
80	79.23	0.23	0.13	79.76	0.27	0.31
420	408.41	0.57	0.27	410.70	0.44	1.22
120	120.65	0.63	0.14	121.46	0.52	0.41
320	309.04	0.22	0.22	311.02	0.20	0.94
30	32.21	0.22	0.12	32.72	0.22	0.23
370	362.60	0.49	0.24	364.45	0.50	1.09
170	170.42	0.55	0.16	171.59	0.35	0.54
500	487.95	0.35	0.31	490.23	0.29	1.45
270	260.13	0.31	0.19	261.56	0.39	0.79
0	-0.28	0.15	0.12	-0.12	0.15	0.21

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  $\alpha$  8.58E-06

**Comparison conditions**

Ozone generator manufacturer	NIST
Ozone generator type	SRP38
Ozone generator serial number	38
Room temperature(min-max) / °C	(21.4 - 22)
Room pressure (average) / hpa	1002
Zero air source	VNIIM
Reference air flow rate (L/min)	7
Sample flow rate (L/min)	7
Instruments stabilisation time	8 h
Instruments acquisition time /s (one measurement)	20 (TE 49i)
Instruments averaging time /s	10 (TE 49i)
Total time for ozone conditioning	2 h
Ozone mole fraction during conditioning	530 ppbv
Comparison repeated continuously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	4

**Instruments checks and adjustments**

**National Standard**

According to SRP Operation Manual

**Transfer Standard**

No adjustments

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

<b>Operator</b>	P. Moussay	<b>Location</b>	CHEM09
<b>Comparison begin date / time</b>	26/11/2007 10:00	<b>Comparison end date / time</b>	27/11/2007 12:00

### 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)	$u(a,b)$
<b>1.0090</b>	<b>0.0031</b>	<b>0.10</b>	<b>0.16</b>	<b>-1.02E-04</b>

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

### Measurement results

Nominal value	Transfer standard (TS)			Reference Standard (RS)		
	$x_{TS}$ nmol/mol	$s_{TS}$ nmol/mol	$u(x_{TS})$ nmol/mol	$x_{RS}$ nmol/mol	$s_{RS}$ nmol/mol	$u(x_{RS})$ nmol/mol
<b>0</b>	-0.13	0.16	0.12	0.06	0.22	0.28
<b>220</b>	220.34	0.28	0.18	222.49	0.32	0.71
<b>80</b>	79.04	0.23	0.13	79.91	0.23	0.36
<b>420</b>	413.46	0.21	0.27	417.21	0.28	1.25
<b>120</b>	121.43	0.26	0.14	122.74	0.24	0.45
<b>320</b>	315.07	0.33	0.22	318.05	0.09	0.97
<b>30</b>	33.18	0.22	0.12	33.49	0.30	0.30
<b>370</b>	366.67	0.27	0.24	369.97	0.26	1.12
<b>170</b>	168.54	0.15	0.15	170.15	0.22	0.57
<b>500</b>	489.40	0.45	0.31	493.63	0.17	1.47
<b>270</b>	269.66	0.24	0.20	272.11	0.24	0.84
<b>0</b>	-0.08	0.15	0.12	-0.07	0.25	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  $\alpha$  8.50E-06

<b>Comparison conditions</b>
------------------------------

Ozone generator manufacturer	Enviro-nics
Ozone generator type	Model 6100
Ozone generator serial number	3128
Room temperature(min-max) / °C	22.5-22.6 °C
Room pressure (average) / hpa	1021
Zero air source	oil free compressor + dryer+ aadco 737-R
Reference air flow rate (L/min)	17
Sample flow rate (L/min)	10
Instruments stabilisation time	8 hours
Instruments acquisition time /s (one measurement)	10 s
Instruments averaging time /s	10 s
Total time for ozone conditioning	2 hours
Ozone mole fraction during conditioning	870 nmol/mol
Comparison repeated continuously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	11
Data files names and location	C071126001 to C071126011
\\chem5\Program Files\NIST\SRPControl\Data\2007	

\*\*\*

<b>Instruments checks and adjustments</b>
---

<b>Reference Standard</b>
---------------------------

As written in the procedure BIPM/CHEM-T-05  
scalars adjusted on SRP27

<b>Transfer Standard</b>
--------------------------

No check, no adjustment.

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

<b>Operator</b>	Selyukov Dmitry	<b>Location</b>	VNIIM
<b>Comparison begin date / time</b>	27-dec-07/16:20	<b>Comparison end date / time</b>	27-dec-07/18:40

**measurement results**

Nominal value	Transfer standard (TS)			National Standard (NS)		
	$x_{TS}$ 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	-0.26	0.14	0.12	0.09	0.23	0.21
220	218.78	0.32	0.17	219.84	0.26	0.68
80	80.54	0.16	0.13	81.13	0.17	0.32
420	417.68	1.15	0.27	419.70	0.98	1.25
120	121.43	0.44	0.14	122.10	0.44	0.41
320	313.88	0.79	0.22	315.22	0.57	0.95
30	32.53	0.13	0.12	32.98	0.27	0.23
370	366.43	0.48	0.24	367.88	0.38	1.10
170	170.91	0.40	0.16	171.94	0.40	0.55
500	491.73	0.39	0.31	494.08	0.34	1.46
270	260.53	0.45	0.19	261.87	0.52	0.80
0	-0.19	0.13	0.12	-0.02	0.16	0.21

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  $\alpha$  8.58E-06

**Comparison conditions**

Ozone generator manufacturer	NIST
Ozone generator type	SRP38
Ozone generator serial number	38
Room temperature(min-max) / °C	20.8-21.2
Room pressure (average) / hpa	1024
Zero air source	VNIIM
Reference air flow rate (L/min)	7
Sample flow rate (L/min)	7
Instruments stabilisation time	8
Instruments acquisition time /s (one measurement)	20 (TE 49i)
Instruments averaging time /s	10 (TE 49i)
Total time for ozone conditioning	2 h
Ozone mole fraction during conditioning	693
Comparison repeated continuously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	3

**Instruments checks and adjustments**

**National Standard**

[According to SRP Operation Manual](#)

**Transfer Standard**

[No adjustments](#)

**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:

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

**Transfer Standard**

Component (y)	Uncertainty $u(y)$			Sensitivity Coefficient $c_i = \frac{\partial x}{\partial y}$	Contribution to $u(x)$ $ c_i  \cdot u(y)$ , nmol/mol
	Source	Distribution	Standard Uncertainty		
Reproducibility	Slope	Rect.	$5.8 \cdot 10^{-4}$	$x$	$5.8 \cdot 10^{-4} \cdot x$
	Intercept	Rect.	0.11 nmol/mol	1	0.11
Repeatability*		Normal	0.047 nmol/mol	1	0.047

\* - Standard deviation of the mean for 10 measurements.

$$u(x) = \sqrt{(0.12)^2 + (5.8 \cdot 10^{-4} \cdot x)^2}$$

**National Standard**

Component (y)	Uncertainty u(y)				Sensitivity Coefficient $c_i = \frac{\partial x}{\partial y}$	Contribution to u(x) $ c_i  \cdot u(y)$ , nmol/mol
	Source	Distribution	Standard Uncertainty	Combined Standard Uncertainty u(y)		
Optical Path $L_{opt}$	Measurement	Rect.	0.0046 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89 \cdot 10^{-3} \cdot x$
	Bias	Rect.	0.52 cm			
Pressure P	Pressure Gauge	Rect.	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.36 \cdot 10^{-4} \cdot x$
	Difference between cells	Rect.	0.017 kPa			
Temperature T	Temperature Probe	Rect.	0.087 °K	0.104 °K	$-\frac{x}{T}$	$3.52 \cdot 10^{-4} \cdot x$
	Residual Bias	Rect.	0.057 °K			
Ratio of Intensities D	Repeatability	Triang.	$0.98 \cdot 10^{-6}$	$1.06 \cdot 10^{-6}$	$\frac{x}{D \cdot \ln(D)}$	0,21
	Scaler resolution	Rect.	$0.41 \cdot 10^{-6}$			
Absorption Cross section $\alpha$	Hearn value		$1,22 \cdot 10^{-19}$ cm <sup>2</sup> /molecule	$1,22 \cdot 10^{-19}$ cm <sup>2</sup> /molecule	$-\frac{x}{\alpha}$	$1.06 \cdot 10^{-2} \cdot x$

$$u(x) = \sqrt{(0.21)^2 + (2.93 \cdot 10^{-3} \cdot x)^2}$$