# Final report, On-going Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with CMS-ITRI, June 2016

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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 ITRI Center for Measurement Standards (CMS-ITRI) and the common reference standard of the key comparison, maintained by the Bureau International des Poids et Mesures (BIPM), via a transfer standard maintained by the National Institute of Standards and Technology (NIST). The instruments have been compared over a nominal ozone amount-of-substance fraction range of 0 nmol/mol to 500 nmol/mol.

Contents:



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## 1. Field

Amount of substance.

## 2. Subject

Comparison of reference measurement standards for ozone at ambient level.

## 3. Participants

BIPM.QM-K1 is an ongoing key comparison, which is structured as an ongoing series of bilateral comparisons. The results of the comparison with the ITRI Center for Measurement Standards (CMS-ITRI) are reported here.

## 4. Organizing body

BIPM.

## 5. Rationale

The ongoing key comparison BIPM.QM-K1 has been running since January 2007. It follows the pilot study CCQM-P28 that included 23 participants and that 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 amount-of-substance fraction in dry air furnished by the ozone generator
- $x_{A,i}$: $i$th measurement of the nominal value $x_{nom}$ by the photometer A.
- $\bar{x}_A$ : the mean of $N$ measurements of the nominal value $x_{nom}$ 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 $x_{nom}$ 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 against the photometer B. $a_{A,B}$ is dimensionless and $b_{A,B}$ is expressed in units of nmol/mol.

## 7. Measurement schedule

The key comparison BIPM.QM-K1 has been organised as 4 year cycles since 2009. The 2009 to 2012 round, the results of which are published in the Key Comparison Database of the BIPM, included 15 participants. The third round of BIPM.QM-K1 started in January 2013. Measurements reported in this report were performed on 7 July 2015 at the BIPM and on 09 June 2016 at the ITRI.

## 8. Measurement protocol

The comparison protocol is summarized in this section. The complete version can be downloaded from the BIPM website (http://www.bipm.org/utils/en/pdf/BIPM.QM-K1_protocol.pdf).

This comparison was performed following protocol B, corresponding to a comparison between the CMS-ITRI national standard SRP57 and the common reference standard BIPM-SRP27 maintained at the BIPM via the transfer standard SRP0 maintained by the NIST. The common reference standard SRP27 and the transfer standard SRP0 were first compared at the BIPM in July 2015. Then SRP0 was compared with the national standard SRP57 at the CMS-ITRI one year later.

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

### 8.1. Comparisons at the CMS-ITRI

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. 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 content of NMHCs is expected to be lower than 1 nmol/mol. The relative humidity of the reference was measured after the comparison and the mole fraction of water was found less than 3 µmol/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. Characteristics of the instruments were checked at this time following a procedure recommended by NIST. Adjustments were made as necessary to match all SRPs to a common pressure standard and temperature standard.

One comparison run includes 10 different amount-of-substance fractions distributed to cover the range, together with the measurement of reference air at the beginning and end of each run. The nominal amount-of-substance 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 amount-of-substance fraction $x_{\mathrm{nom}}$ furnished by the ozone generator, the standard deviation $s_{\mathrm{SRP57}}$ on the set of 10 consecutive measurements $x_{\mathrm{SRP57},i}$ recorded by SRP57 was calculated. The measurement results were considered as valid if $s_{\mathrm{SRP57}}$ 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.

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 amount-of-substance 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 amount-of-substance fraction of water in air typically is less than 3 μmol/mol. The amount-of-substance fraction of volatile organic hydrocarbons in the reference air was measured (November 2002), with no amount-of-substance 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 amount-of-substance fractions distributed to cover the range, together with the measurement of zero air at the beginning and end of each run. The nominal amount-of-substance 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 amount-of-substance 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 ongoing key comparison.

## 9. Reporting measurement results

The participant and the NIST staff reported the measurement results in the result form BIPM.QM-K1-R3 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 amount-of-substance fractions measured by the participant standard and the common reference standard. The completed form BIPM.QM-K1-R3-CMS-16 is given in the annex.

## 10. Post comparison calculation

All calculations were performed by the BIPM using the form BIPM.QM-K1-R3. It includes the two degrees of equivalence that are reported as comparison results in the Appendix B of the BIPM KCDB (key comparison database). Additionally, the degrees of equivalence at all nominal ozone amount-of-substance 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

The instruments maintained by the BIPM, by the NIST and by the CMS-ITRI are Standard Reference Photometers (SRP) built by the NIST. More details on the NIST SRP principle and its capabilities can be found in [2]. The following section describes briefly the instruments' measurement principle and their uncertainty budgets.

### 12.1. Measurement equation of a NIST SRP

The measurement of the ozone amount-of-substance fraction by an SRP is based on the absorption of radiation at 253.7 nm by ozonized air in the gas cells of the instrument. One particularity of the instrument design is the use of two gas cells to overcome the instability of the light source. The measurement equation is derived from the Beer-Lambert and ideal gas laws. The number concentration ($C$) of ozone is calculated from:

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

where

- $\sigma$ is the absorption cross-section of ozone at 253.7 nm under standard conditions of temperature and pressure, $1.1476 \times 10^{-17}$ cm$^2$/molecule [3].
- $L_{\mathrm{opt}}$ is the mean optical path length of the two cells;
- $T$ is the measured temperature of the cells;
- $T_{\mathrm{std}}$ is the standard temperature (273.15 K);
- $P$ is the measured pressure of the cells;
- $P_{\mathrm{std}}$ is the standard pressure (101.325 kPa);
- $D$ is the product of transmittances of two cells, with the transmittance ($T_{\mathrm{r}}$) of one cell defined as

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

where

- $I_{\mathrm{ozone}}$ is the UV radiation intensity measured from the cell when containing ozonized air, and
- $I_{\mathrm{air}}$ is the UV radiation intensity measured from the cell when containing pure air (also called reference or zero air).

Using the ideal gas law equation (1) can be recast in order to express the measurement results as a amount-of-substance fraction ($x$) of ozone in air:

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

where

$N_A$ is the Avogadro constant, $6.022142 \times 10^{23}$ mol$^{-1}$, and

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

The formulation implemented in the SRP software is:

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

where

$\alpha_x$ is the linear absorption coefficient at standard conditions, expressed in cm$^{-1}$, linked to the absorption cross-section with the relation:

$$\alpha_x = \sigma \frac{N_A}{R} \frac{P_{\text{std}}}{T_{\text{std}}} \qquad (5)$$

12.2. Absorption cross-section for ozone

The linear absorption coefficient under standard conditions $\alpha_x$ used within the SRP software algorithm is 308.32 cm$^{-1}$. This corresponds to a value for the absorption cross section $\sigma$ of $1.1476 \times 10^{-17}$ cm$^2$/molecule, rather than the more often quoted $1.147\times10^{-17}$ 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. Condition 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]. In 2009, an “SRP upgrade kit” was installed in the instruments, as described in the report [5].

12.4. Uncertainty budget of the common reference BIPM-SRP27

The uncertainty budget for the ozone amount-of-substance 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 | $8\times10^{-6}$ | $1.4\times10^{-5}$ | $\frac{x}{D\ln(D)}$ | 0.28 |
| | Repeatability | Triangular | $1.1\times10^{-5}$ | | | |
| **Absorption Cross section $\alpha$** | Hearn value | | $1.22\times10^{-19}$ cm²/molecule | $1.22\times10^{-19}$ cm²/molecule | $-\frac{x}{\alpha}$ | $1.06\times10^{-2}x$ |

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

$$u(x) = \sqrt{(0.28)^2 + (2.92\cdot10^{-3}x)^2} \qquad (6)$$

12.5. <u>Covariance terms for the common reference BIPM-SRP27</u>

Correlations between the results of two measurements performed at two different ozone amount-of-substance fractions with BIPM-SRP27 were taken into account using the software OzonE. Details about the analysis of the covariance can be found in the protocol. The following expression was applied:

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

where:

$$\boldsymbol{u}_{\mathrm{b}}^2 = \frac{\boldsymbol{u}^2(\boldsymbol{T})}{\boldsymbol{T}^2} + \frac{\boldsymbol{u}^2(\boldsymbol{P})}{\boldsymbol{P}^2} + \frac{\boldsymbol{u}^2(\boldsymbol{L}_{\mathrm{opt}})}{\boldsymbol{L}_{\mathrm{opt}}^2} \qquad (8)$$

The value of $u_{\mathrm{b}}$ is given by the expression of the measurement uncertainty: $u_{\mathrm{b}} = 2.92 \times 10^{-3}$.

12.6. <u>Condition of the CMS-ITRI SRP57</u>

The SRP57 maintained by the CMS-ITRI has been constructed by NIST in 2014 with the new design, which includes the “SRP upgrade kit” in order to deal with the two biases revealed in [4].

12.7. Uncertainty budget of the CMS-ITRI SRP57

The uncertainty budget for the ozone amount-of-substance fraction in dry air *x* measured by the CMS-ITRI standard SRP57 in the range 0 nmol/mol to 500 nmol/mol is given in Table 2.

*Table 2: Uncertainty budget for the SRP maintained by the CMS-ITRI*

| Component (y) | Uncertainty *u(y)* Source | Distribution | Standard uncertainty | Combined Standard 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 |
|---|---|---|---|---|---|---|
| Optical Path $L_{opt}$ | Measurement | Rectangular | 0.004 cm | 0.52 cm | $-\frac{x}{L_{opt}}$ | $2.90 \cdot 10^{-3} \cdot x$ |
| | Divergence | Rectangular | 0.52 cm | | | |
| Pressure *P* | Pressure Gauge | Rectangular | 0.029 kPa | 0.034 kPa | $-\frac{x}{P}$ | $3.37 \cdot 10^{-4} \cdot x$ |
| | Difference between cells | Rectangular | 0.017 kPa | | | |
| Temperature *T* | Temperature Probe | Rectangular | 0.03 K | 0.07 K | $\frac{x}{T}$ | $2.29 \cdot 10^{-4} \cdot x$ |
| | Gradient over cells | Rectangular | 0.058 k | | | |
| Ratio of Intensities *D* | Scaler resolution | Rectangular | $8.0 \cdot 10^{-6}$ | $1.4 \cdot 10^{-5}$ | $\frac{x}{D \cdot \ln(D)}$ | 0.28 |
| | Repeatability | Triangular | $1.1 \cdot 10^{-5}$ | | | |
| Absorption Cross section $\alpha$ | Hearn value | | $1.22 \cdot 10^{-19}$ cm$^2$/molecule | $1.22 \cdot 10^{-19}$ cm$^2$/molecule | $-\frac{x}{\alpha}$ | $1.06 \cdot 10^{-2} \cdot x$ |

Following this budget the standard uncertainty associated with the ozone amount-of-substance fraction measurement with SRP57 can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u(x) = \sqrt{0.28^2 + (2.93 \times 10^{-3} x)^2} \quad (9)$$

No covariance term for the SRP57 was included in the calculations.

12.8. Transfer standard SRP0

The uncertainty budget for the ozone amount-of-substance fraction in dry air *x* measured by the NIST standard SRP0 in the range 0 nmol/mol to 500 nmol/mol will follow the BIPM/NIST paper [4] (see Table 1). This uncertainty budget includes the removal of the former temperature heating bias, which has been eliminated by using a lower current temperature circuit card in SRP 0.

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

No covariance term for the NIST SRP0 was 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 amount-of-substance fraction are provided in appendix (form BIPM.QM-K1-R3-CMS-16).

## 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 amount-of-substance 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 comparison results are calculated by performing a linear regression on the twelve data points from the comparison at BIPM ($x_{RS}$, $x_{TS}$) (calibration of the transfer standard) followed by a second linear regression of the twelve data points from the comparison at CMS-ITRI ($x_{NS}$, $x'_{TS}$), $x'_{TS}$ being the corrected values of the transfer standard calibrated by the reference standard.

A linear relationship between the ozone amount-of-substance fractions measured by SRP*n* and SRP27 is obtained:

$$x_{\mathrm{SRP}n} = a_0 + a_1 x_{\mathrm{SRP27}} \qquad (11)$$

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-squares regression results

The relationship between SRP57 and SRP27 is:

$$x_{SRP57} = 1.0007 x_{SRP27} - 0.11 \qquad (12)$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0038$ for the slope and $u(a_0) = 0.31$ nmol/mol for the intercept. The covariance between the two parameters is $\mathrm{cov}(a_0, a_1) = -4.36 \times 10^{-4}$.

The least-squares regression results confirm that a linear fit is appropriate, with a sum of the squared deviations (SSD) of 0.28 and a goodness of fit (GoF) equals to 0.29.

To assess the agreement of the standards using 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 this comparison, the value of the intercept is consistent with an intercept of zero, considering the uncertainty in the value of this parameter; i.e $|a_0| < 2u(a_0)$, and the value of the slope is consistent with a slope of 1; i.e. $|1 - a_1| < 2u(\mathrm{a}_1)$.

## 15. Degrees of equivalence

Degrees of equivalence are calculated at two nominal ozone amount-of-substance 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 amount-of-substance 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 $x_{\mathrm{nom}}$ is defined as:

$$D = x_i - \hat{x}_{\mathrm{SRP27}} \tag{13}$$

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

$$u(D) = \sqrt{u^2(x_i) + u^2(\hat{x}_{\mathrm{SRP27}})} \tag{14}$$

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

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

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

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

$$u(\hat{x}_{\mathrm{RS}}) = \sqrt{u^2(b_{\mathrm{RS,TS}}) + x_{\mathrm{TS}}^2 \cdot u^2(a_{\mathrm{RS,TS}}) + a_{\mathrm{RS,TS}}^2 \cdot u^2(x_{\mathrm{TS}}) + 2 \cdot x_{\mathrm{TS}} \cdot u(a_{\mathrm{RS,TS}}, b_{\mathrm{RS,TS}})} \tag{15}$$

Where the uncertainty components $u(a_{\mathrm{RS,TS}})$, $u(b_{\mathrm{RS,TS}})$ and $u(a_{\mathrm{RS,TS}}, b_{\mathrm{RS,TS}})$ 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-R3-CMS-16 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 3 : degrees of equivalence of the CMS-ITRI at the ozone nominal amount-of-substance fractions 80 nmol/mol and 420 nmol/mol**

| Nominal value / (nmol/mol) | $x_i$ / (nmol/mol) | $u_i$ / (nmol/mol) | $x_{SRP27}$ / (nmol/mol) | $u_{SRP27}$ / (nmol/mol) | $D_i$ / (nmol/mol) | $u(D_i)$ / (nmol/mol) | $U(D_i)$ / (nmol/mol) |
|---|---|---|---|---|---|---|---|
| **80** | 86.33 | 0.38 | 86.36 | 0.48 | -0.03 | 0.61 | 1.23 |
| **420** | 419.59 | 1.26 | 419.40 | 1.83 | 0.19 | 2.22 | 4.44 |

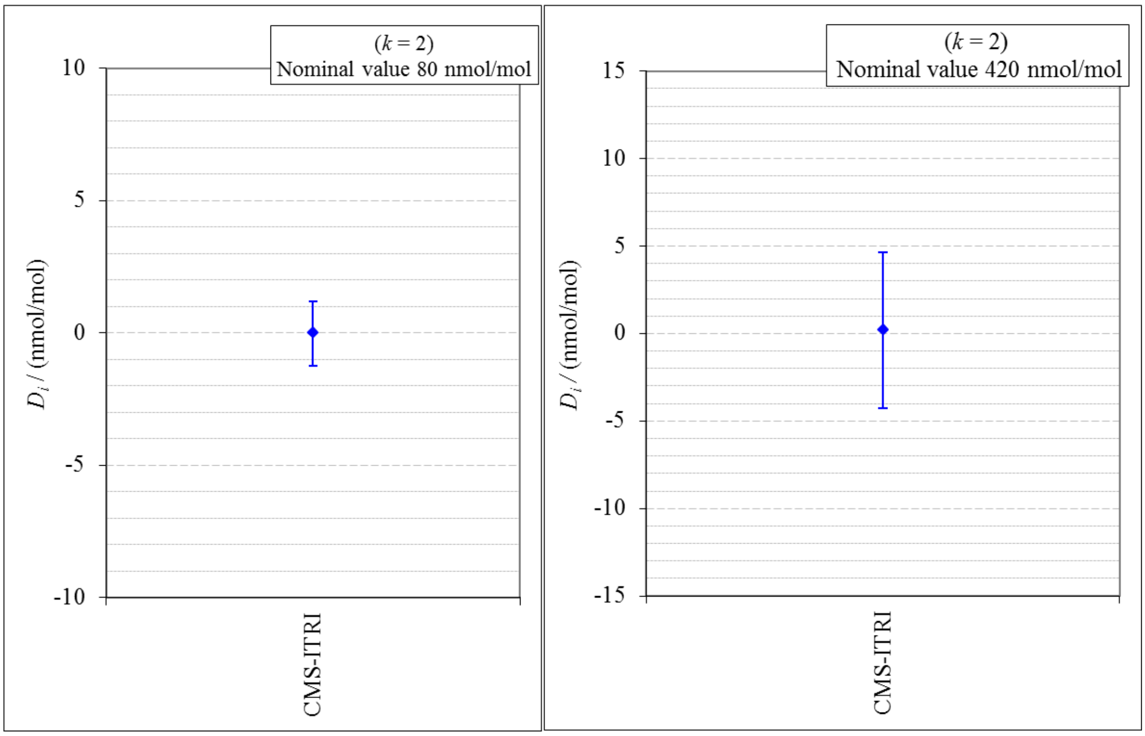



*Figure 1: degrees of equivalence of the CMS-ITRI at the two nominal ozone amount-of-substance fractions 80 nmol/mol and 420 nmol/mol*

The degrees of equivalence between the CMS-ITRI 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

In between December 2014 and July 2015, comparisons performed at NIST between the transfer standard SRP0 and NIST national standard SRP2 have shown a maximum variation of 0.1% on the slope of the relationship between the two instruments. This is negligible compared to the uncertainties declared in this comparison.

## 17. History of comparisons between BIPM SRP27, SRP28 and CMS-ITRI SRP57

This comparison was the first participation of the CMS-ITRI in the key comparison BIPM.QM-K1. To show the stability of the reference standard BIPM-SRP27, results of comparisons between BIPM-SRP27 and BIPM-SRP28 performed during this cycle are displayed in Figure 2 together with the result of this comparison. This figure demonstrates that both instruments have been stable throughout the entire comparison exercise, with no more than 0.05 % of variation.

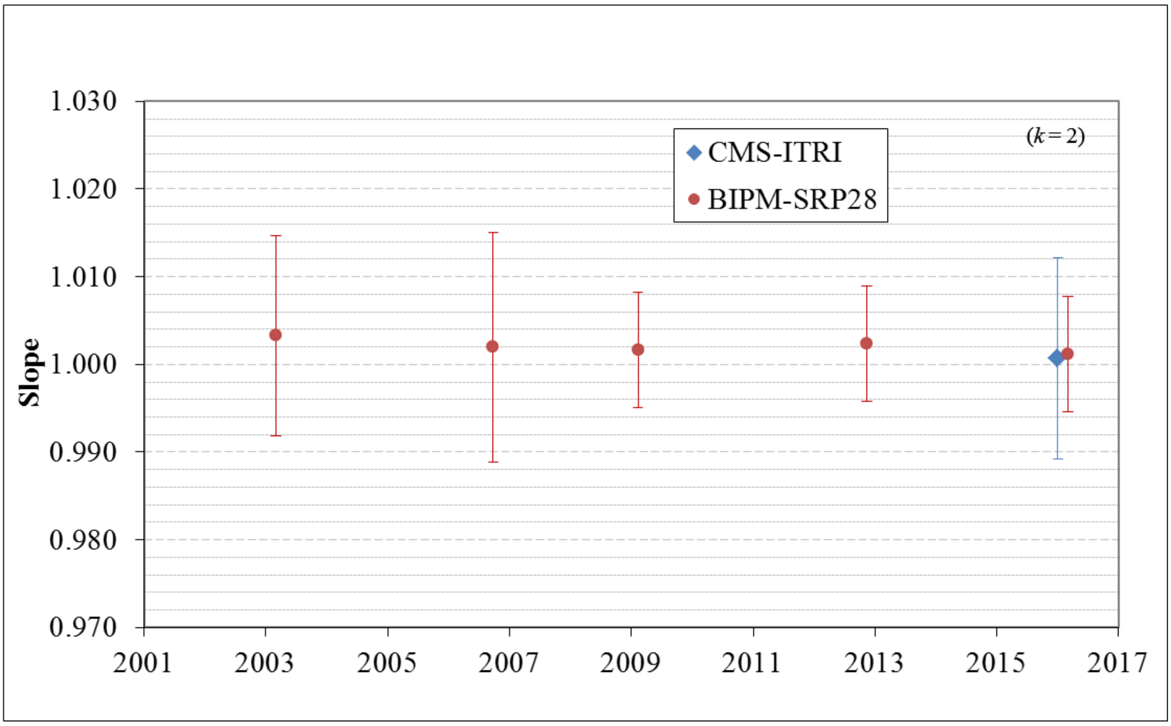



**Figure 2 : Results of previous comparisons between SRP27 and SRP28 realised at the BIPM, and result of the comparison with SRP57. Uncertainties are calculated at $k$ = 2.**

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

The comparison with CMS-ITRI is the 14th one in the 2013-2016 round of BIPM.QM-K1. An updated summary of BIPM.QM-K1 results can be found in the BIPM key comparison database: [http://kcdb.bipm.org/appendixB/](http://kcdb.bipm.org/appendixB/).

## 19. Conclusion

For the first time since the launch of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of Chinese Taipei maintained by the CMS-ITRI and the common reference standard of the key comparison maintained by the BIPM. The instruments have been compared over a nominal ozone amount-of-substance fraction range of 0 nmol/mol to 500 nmol/mol. Degrees of equivalence of this comparison indicated very good agreement between the two standards.

## 20. References


[1] Viallon J., Moussay P., Esler M., Wielgosz R., Bremser W., Novák J., Vokoun M., Botha A., Janse Van Rensburg M., Zellweger C., Goldthorp S., Borowiak A., Lagler F., Walden J., Malgeri E., Sassi M.P., Morillo Gomez P., Fernandez Patier R., Galan

Madruga D., Woo J.-C., Doo Kim Y., Macé T., Sutour C., Surget A., Niederhauser B., Schwaller D., Frigy B., Györgyné Váraljai I., Hashimoto S., Mukai H., Tanimoto H., Ahleson H.P., Egeløv A., Ladegard N., Marsteen L., Tørnkvist K., Guenther F.R., Norris J.E., Hafkenscheid T.L., Van Rijn M.M., Quincey P., Sweeney B., Langer S., Magnusson B., Bastian J., Stummer V., Fröhlich M., Wolf A., Konopelko L.A., Kustikov Y.A. and Rumyanstev D.V., 2006,PILOT STUDY: International Comparison CCQM-P28: Ozone at ambient level, *Metrologia*, ***43, Tech. Suppl.***, 08010

[2] Paur R.J., Bass A.M., Norris J.E. and Buckley T.J. 2003 Standard reference photometer for the assay of ozone in calibration atmospheres *Env. Sci. Technol.* **NISTIR 6369**, 25 pp

[3] ISO 13964 : 1996 Ambient air - Determination of ozone - Ultraviolet photometric method (International Organization for Standardization)

[4] Viallon J., Moussay P., Norris J.E., Guenther F.R. and Wielgosz R.I., 2006,A study of systematic biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard Reference Photometer, *Metrologia*, **43**, 441-450

[5] Viallon J., Moussay P., Idrees F. and Wielgosz R.I. 2010 Upgrade of the BIPM Standard Reference Photometers for Ozone and the effect on the on-going key comparison BIPM.QM-K1 **Rapport BIPM-2010/07**, 16 pp

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

[7] ISO 6143.2 : 2001 Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures - Comparison methods (International Organization for Standardization)

## Appendix 1 - Form BIPM.QM-K1-R3-CMS-16

See next pages.

# OZONE COMPARISON BIPM.QM-K1
# RESULTS FORM TO LINK AN RMO COMPARISON

| Linking institute information | |
|---|---|
| **Institute** | **NIST** |
| **RMO** | **SIM/APMP** |
| **Address** | **100 Bureau Drive, Gaithersburg, MD, 20899 USA** |
| **Contact** | **James Norris** |
| **Email** | james.norris@nist.gov |
| **Telephone** | **001 301 975 3936** |

| Participating institute information | |
|---|---|
| **Institute** | **CMS-ITRI** |
| **RMO** | **APMP** |
| **Address** | **321 Sec 2 Kung Fu Rd, Hsinchu, Taiwan** |
| **Contact** | **LIN, Tsai-Yin** |
| **Email** | tsaiyin@itri.org.tw |
| **Telephone** | **886 3 5732204** |

| Instruments information | | | |
|---|---|---|---|
| | **Reference Standard Photometer** | **Participating Institute National Standard** | **Linking institute National Standard** |
| **Manufacturer** | NIST | NIST | NIST |
| **Type** | SRP | SRP | SRP |
| **Serial number** | SRP27 | SRP57 | SRP0 |
| **ozone cross-section value** | 308.32 $atm^{-1}$ $cm^{-1}$ | 308.32 $atm^{-1}$ $cm^{-1}$ | 308.32 $atm^{-1}$ $cm^{-1}$ |

*Note: in this form, the term "transfer standard (TS)" is used to designate the linking laboratory's standard, and the term "national standard (NS)" designates the participating institute's standard*

## Content of the report



*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 (NS) vs reference standard (RS)

### Summary of comparison results

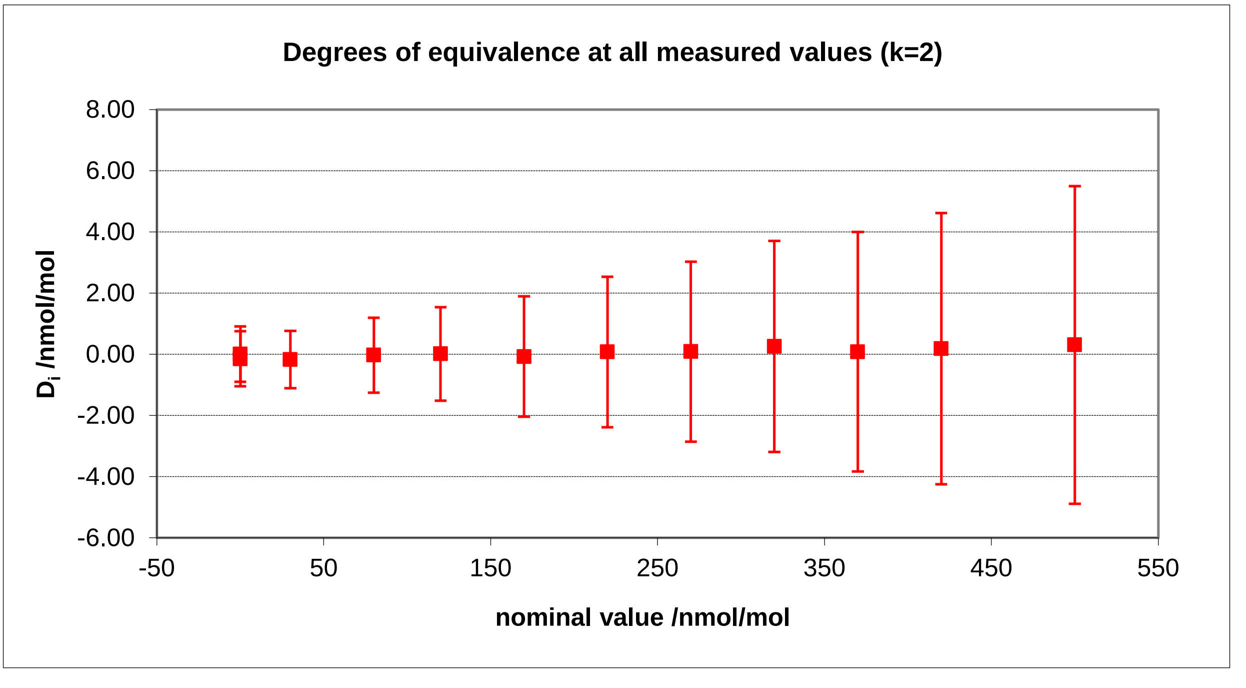
**Equation** $x_{NS} = a_{NS,RS}\, x_{RS} + b_{NS,RS}$

### 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 | 1.0007 | 0.0038 | -0.11 | 0.31 | -4.36E-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) |
|---|---|---|---|
| **80** | -0.03 | 0.61 | 1.23 |
| **420** | 0.19 | 2.22 | 4.44 |



# Calculation of the National Standard vs Reference Standard comparison results through theNational 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 | 0.01 | 0.28 | 0.10 | 0.35 |
| **220** | 225.06 | 0.71 | 225.29 | 0.71 | 224.99 | 1.00 |
| **80** | 86.33 | 0.38 | 86.42 | 0.38 | 86.36 | 0.48 |
| **420** | 419.59 | 1.26 | 420.04 | 1.26 | 419.40 | 1.83 |
| **120** | 124.68 | 0.46 | 124.80 | 0.46 | 124.67 | 0.61 |
| **320** | 323.43 | 0.99 | 323.65 | 0.99 | 323.18 | 1.42 |
| **30** | 32.43 | 0.30 | 32.57 | 0.30 | 32.60 | 0.36 |
| **370** | 368.82 | 1.11 | 369.29 | 1.11 | 368.74 | 1.61 |
| **170** | 173.34 | 0.58 | 173.63 | 0.58 | 173.42 | 0.80 |
| **500** | 492.51 | 1.47 | 492.97 | 1.47 | 492.21 | 2.14 |
| **270** | 272.83 | 0.84 | 273.13 | 0.85 | 272.74 | 1.20 |
| **0** | 0.01 | 0.28 | -0.09 | 0.28 | 0.00 | 0.35 |

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)

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

| | | | | | |
|---|---|---|---|---|---|
| $a_{RS,TS}$ | 0.9983 | $b_{NRS,TS}$ (nmol/mol) | 0.09 | $u(a,b)$ | -2.01E-04 |
| $u(a_{RS,TS})$ | 0.0033 | $u(b_{RS,TS})$ (nmol/mol) | 0.22 | | |

| 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** | -0.15 | 0.45 | 0.90 |
| **2** | **220** | 0.08 | 1.23 | 2.46 |
| **3** | **80** | -0.03 | 0.61 | 1.23 |
| **4** | **420** | 0.19 | 2.22 | 4.44 |
| **5** | **120** | 0.01 | 0.76 | 1.53 |
| **6** | **320** | 0.25 | 1.72 | 3.45 |
| **7** | **30** | -0.17 | 0.47 | 0.94 |
| **8** | **370** | 0.08 | 1.96 | 3.91 |
| **9** | **170** | -0.08 | 0.98 | 1.97 |
| **10** | **500** | 0.31 | 2.60 | 5.19 |
| **11** | **270** | 0.09 | 1.47 | 2.94 |
| **12** | **0** | 0.01 | 0.45 | 0.90 |

| Least-square regression parameters | | | | |
|---|---|---|---|---|
| $a_{NS,RS}$ | $u(a_{NS,RS})$ | $b_{NS,RS}$ (nmol/mol) | $u(b_{NS,RS})$ (nmol/mol) | $u(a,b)$ |
| **1.0006800** | **0.0037550** | **-0.1052575** | **0.3121865** | **-0.0004356** |

## Data reporting sheet
## Comparison of transfer standard (TS) vs national standard (NS)

| | | | |
|---|---|---|---|
| **Operator** | **Jim Norris** | **Location** | **CMS-ITRI** |
| **Comparison begin date / time** | **25/06/2016** | **Comparison end date / time** | **25/06/2016** |

**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 | 0.14 | 0.28 | -0.05 | 0.34 | 0.28 |
| 220 | 225.29 | 0.51 | 0.71 | 225.06 | 0.66 | 0.71 |
| 80 | 86.42 | 0.16 | 0.38 | 86.33 | 0.42 | 0.38 |
| 420 | 420.04 | 0.32 | 1.26 | 419.59 | 0.46 | 1.26 |
| 120 | 124.80 | 0.24 | 0.46 | 124.68 | 0.34 | 0.46 |
| 320 | 323.65 | 0.22 | 0.99 | 323.43 | 0.46 | 0.99 |
| 30 | 32.57 | 0.24 | 0.30 | 32.43 | 0.37 | 0.30 |
| 370 | 369.29 | 0.23 | 1.11 | 368.82 | 0.44 | 1.11 |
| 170 | 173.63 | 0.19 | 0.58 | 173.34 | 0.30 | 0.58 |
| 500 | 492.97 | 0.30 | 1.47 | 492.51 | 0.45 | 1.47 |
| 270 | 273.13 | 0.25 | 0.85 | 272.83 | 0.29 | 0.84 |
| 0 | -0.09 | 0.15 | 0.28 | 0.01 | 0.39 | 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 $\alpha$ 0.00E+00

**Comparison conditions**

| | |
|---|---|
| Ozone generator manufacturer | SRP 57 |
| Ozone generator type | Customised |
| Ozone generator serial number | 1299979 |
| Room temperature(min-max) / °C | 23.4 - 24.8 |
| Room pressure (average) / hpa | 1007 |
| Zero air source | UZAG-50/1 |
| Reference air flow rate (L/min) | 7 |
| Sample flow rate (L/min) | 7 |
| Instruments stabilisation time | more than 24 hours |
| Instruments acquisition time /s (one measurement) | 25 s |
| Instruments averaging time /s | 25 s |
| Total time for ozone conditioning | 30 min |
| Ozone mole fraction during conditioning | 800 nmol/mol |
| Comparison repeated continously (Yes/No) | Yes |
| If no, ozone mole fraction in between the comparison repeats | *** |
| Total number of comparison repeats realised | 20 comparisons repeats, the last one data file |

# Instruments checks and adjustments

## National Standard

## Transfer Standard

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

| | | | |
|---|---|---|---|
| **Operator** | Jim Norris | **Location** | BIPM |
| **Comparison begin date / time** | 09.7.2015 | **Comparison end date / time** | 09.07.2015 |

## 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) | $u(a,b)$ |
| **0.9982705** | **0.0032687** | **0.0890264** | **0.2159966** | **-0.0002013** |

*(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** | 0.01 | 0.10 | 0.28 | -0.17 | 0.38 | 0.28 |
| **220** | 217.75 | 0.12 | 0.69 | 217.56 | 0.21 | 0.69 |
| **80** | 80.31 | 0.10 | 0.37 | 80.28 | 0.34 | 0.37 |
| **420** | 421.36 | 0.32 | 1.26 | 420.77 | 0.46 | 1.26 |
| **120** | 120.26 | 0.16 | 0.45 | 120.27 | 0.38 | 0.45 |
| **320** | 317.59 | 0.16 | 0.97 | 316.96 | 0.30 | 0.97 |
| **30** | 31.74 | 0.21 | 0.29 | 31.75 | 0.35 | 0.29 |
| **370** | 368.98 | 0.14 | 1.11 | 368.58 | 0.13 | 1.11 |
| **170** | 169.54 | 0.14 | 0.57 | 169.30 | 0.31 | 0.57 |
| **500** | 508.02 | 0.21 | 1.51 | 507.06 | 0.32 | 1.51 |
| **270** | 267.75 | 0.14 | 0.83 | 267.20 | 0.30 | 0.83 |
| **0** | -0.07 | 0.21 | 0.28 | 0.27 | 0.26 | 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

## Comparison conditions

| | |
|---|---|
| Ozone generator manufacturer | environics |
| Ozone generator type | Model 6100 |
| Ozone generator serial number | 3128 |
| Room temperature(min-max) / °C | 20.1 - 21.2 |
| Room pressure (average) / hpa | 1009 |
| Zero air source | oil free compressor + dryer + Aadco 737 -R |
| Reference air flow rate (L/min) | 15 |
| Sample flow rate (L/min) | 10 |
| Instruments stabilisation time | more than 48 hours |
| Instruments acquisition time /s (one measurement) | 5 |
| Instruments averaging time /s | 5 |
| Total time for ozone conditioning | more than 48 hours |
| Ozone mole fraction during conditioning | 830 nmol/mol |
| Comparison repeated continously (Yes/No) | Yes |
| If no, ozone mole fraction in between the comparison repeats | *** |
| Total number of comparison repeats realised | 37 |
| Data files names and location | \\chem5\program files\NIST\SRPControl\Data\2015 |
| | c150706001.xls to c150706001.xls |

***

## Instruments checks and adjustments

### Reference 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:

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

### Transfer Standard

$$u(x) = \sqrt{(0.28)^2 + \left(2.92 \times 10^{-3} x\right)^2} \; nmol/mol$$

# National Standard

| Component (y) | Uncertainty $u(y)$ Source | Distribution | Standard uncertainty | Combined Standard 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 |
|---|---|---|---|---|---|---|
| Optical Path $L_{opt}$ | Measurement | Rectangular | 0.004 cm | 0.52 cm | $-\frac{x}{L_{opt}}$ | $2.90 \cdot 10^{-3} \cdot x$ |
| | Divergence | Rectangular | 0.52 cm | | | |
| Pressure $P$ | Pressure Gauge | Rectangular | 0.029 kPa | 0.034 kPa | $-\frac{x}{P}$ | $3.37 \cdot 10^{-4} \cdot x$ |
| | Difference between cells | Rectangular | 0.017 kPa | | | |
| Temperature $T$ | Temperature Probe | Rectangular | 0.03 K | 0.07 K | $\frac{x}{T}$ | $2.29 \cdot 10^{-4} \cdot x$ |
| | Gradient over cells | Rectangular | 0.058 k | | | |
| Ratio of Intensities $D$ | Scaler resolution | Rectangular | $8.0 \cdot 10^{-6}$ | $1.4 \cdot 10^{-5}$ | $\frac{x}{D \cdot \ln(D)}$ | 0.28 |
| | Repeatability | Triangular | $1.1 \cdot 10^{-5}$ | | | |
| Absorption Cross section $\alpha$ | Hearn value | | $1.22 \cdot 10^{-19}$ cm²/molecule | $1.22 \cdot 10^{-19}$ cm²/molecule | $-\frac{x}{\alpha}$ | $1.06 \cdot 10^{-2} \cdot x$ |

$$u(x) = \sqrt{0.28^2 + (2.93 \cdot 10^{-3}\, x)^2}$$