Final report, Ongoing Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with NMISA , (July 2012)

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Abstract

As part of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone standard of the World Meteorological Organisation maintained by the National Metrology Institute of South Africa (NMISA ) 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 amount-of-substance fraction range of 0 nmol/mol to 500 nmol/mol.

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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 National Metrology Institute of South Africa (NMISA) 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
- \( x_{\text{nom}} \): nominal ozone amount-of-substance fraction in dry air furnished by the ozone generator
- \( x_{A,i} \): \( i \)th measurement of the nominal value \( x_{\text{nom}} \) 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 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 was initially organised as 2 year cycles. The 2007 to 2008 round, the results of which are published in the Key Comparison Database of the BIPM, included 16 participants. The second round of BIPM.QM-K1 started in March 2009 for a period of 4 years, following the decision of the CCQM/GAWG to reduce the repeat frequency.
of bilateral comparisons. Measurements reported in this report were performed on 6 June 2012 at the BIPM.

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 A, corresponding to a direct comparison between the NMISA standard API400-823 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 amount-of-substance 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 is less than 3 μmol/mol. The mole fraction of volatile organic hydrocarbons in the reference air was measured (November 2002), with no mole fraction of any detected component exceeding 1 nmol/mol.

The NMISA ozone generator API 401, serial number 106, was used to produce ozone in dry air.

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 amount-of-substance fractions distributed to cover the range, together with the measurement of zero 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 $x_{\text{nom}}$ 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.
8.3. **Comparison repeatability**

The comparison procedure was repeated continuously during two cycles of 22 hours each 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**

Normally, a second ozone reference standard, BIPM-SRP28, is included in the comparison to verify its agreement with BIPM-SRP27 and thus follow its stability over the period of the ongoing key comparison. This was not feasible during this comparison, as the NMISA ozone generator delivers insufficient flow of ozone in air. BIPM-SRP28 and BIPM-SRP27 were compared in the week before the measurements reported here.

9. **Reporting measurement results**

The participant and the BIPM staff reported the measurement results in the result form BIPM.QM-K1-R1 provided by the BIPM and available on the BIPM website. It includes details on the comparison conditions, measurement results and associated uncertainties, as well as the standard deviation for each series of 10 ozone amount-of-substance fractions measured by the participant’s standard and the common reference standard. The completed form BIPM.QM-K1-R1-NMISA-12 is given in Appendix 1.

10. **Post comparison calculation**

All calculations were performed by the BIPM using the form BIPM.QM-K1-R1. 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**

The standard deviation $s_{RS}$ on 10 successive measurements recorded with the BIPM-SRP27 was not always less than 1 nmol/mol, as required in the protocol of the comparison. This demonstrates that NMISA’s ozone generator was not operating in a stable regime. These instabilities have less effect on the standard deviations $s_{NS}$ on measurements recorded with the NMISA standard because this instrument performs an automatic moving average on 32 successive measurements. This feature could not be turned off.

As no stable regime could be reached when performing further measurements, it was decided to continue the comparison and to include the value $s_{RS}$ in the uncertainty associated with NMISA measurement results, as this was a characteristic of the ozone generator normally used with NMISA instrument.

12. **Measurement standards**

The instruments maintained by the BIPM 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:

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

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].
- $L_{opt}$ is the mean optical path length of the two cells;
- $T$ is the measured temperature of the cells;
- $T_{std}$ is the standard temperature (273.15 K);
- $P$ is the measured pressure of the cells;
- $P_{std}$ is the standard pressure (101.325 kPa);
- $D$ is the product of transmittances of two cells, with the transmittance ($T_r$) of one cell defined as

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

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

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

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

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:

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

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

$$\alpha_x = \frac{N_A}{R} \frac{P_{std}}{T_{std}} \quad (5)$$
12.2. Absorption cross-section for ozone

The linear absorption coefficient under standard conditions \( \alpha \) 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 \( 1.147 \times 10^{-17} \) 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. 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>
<thead>
<tr>
<th>Component (y)</th>
<th>Uncertainty u(y)</th>
<th>Sensitivity coefficient</th>
<th>Contribution to ( u(x) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>Distribution</td>
<td>Standard Uncertainty</td>
<td>Combined standard uncertainty ( u(y) )</td>
</tr>
<tr>
<td>Optical Path ( L_{opt} )</td>
<td>Measurement scale</td>
<td>Rectangular</td>
<td>0.0006 cm</td>
</tr>
<tr>
<td></td>
<td>Repeatability</td>
<td>Normal</td>
<td>0.01 cm</td>
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<tr>
<td></td>
<td>Correction factor</td>
<td>Rectangular</td>
<td>0.52 cm</td>
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<tr>
<td>Pressure ( P )</td>
<td>Pressure gauge</td>
<td>Rectangular</td>
<td>0.029 kPa</td>
</tr>
<tr>
<td></td>
<td>Difference between cells</td>
<td>Rectangular</td>
<td>0.017 kPa</td>
</tr>
<tr>
<td>Temperature ( T )</td>
<td>Temperature probe</td>
<td>Rectangular</td>
<td>0.03 K</td>
</tr>
<tr>
<td></td>
<td>Temperature gradient</td>
<td>Rectangular</td>
<td>0.058 K</td>
</tr>
<tr>
<td>Ratio of intensities ( D )</td>
<td>Scaler resolution</td>
<td>Rectangular</td>
<td>8 \times 10^{-6}</td>
</tr>
<tr>
<td></td>
<td>Repeatability</td>
<td>Triangular</td>
<td>1.1 \times 10^{-5}</td>
</tr>
<tr>
<td>Absorption Cross section ( \sigma )</td>
<td>Hearn value</td>
<td>Rectangular</td>
<td>1.22 \times 10^{-19} cm(^2)/molecule</td>
</tr>
</tbody>
</table>

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):

\[
u(x) = \sqrt{(0.28)^2 + (2.92 \cdot 10^{-3} x)^2}
\]

(6)
12.5. Covariance terms for the common reference BIPM-SRP27

As explained in section 14, 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:

\[ u(x_i, x_j) = x_i \cdot x_j \cdot u_b^2 \]  

(7)

where:

\[ u_b^2 = \frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} + \frac{u^2(L_{opt})}{L_{opt}^2} \]  

(8)

The value of \( u_b \) is given by the expression of the measurement uncertainty: \( u_b = 2.92 \times 10^{-3} \).

12.6. Condition of the NMISA standard API400-823

The NMISA API400-823 is a UV photometric analyser, which is used as a transfer standard for the calibration of customers’ ozone generators. It was calibrated at the BIPM against BIPM-SRP27 two weeks before this comparison.

12.7. Uncertainty budget of the NMISA API400-823

The ozone amount-of-substance fraction \( x_{\text{measured}} \) measured by the NMISA API400-823 during the comparison was corrected with the regression data from the calibration of the instrument, to give the value \( x_{\text{corrected}} \) that was used in the comparison form:

\[ x_{\text{corrected}} = a_0 + a_1 x_{\text{measured}} = -0.68 + 0.9686 x_{\text{measured}} \]  

(9)

In the same manner the value \( u(x_{\text{measured}}) \) was corrected using the data from the regression analysis performed during the same calibration:

\[ u_{x_{\text{corrected}}} = \sqrt{u_{a_0}^2 + a_1^2 u(x_{\text{measured}})^2 + x_{\text{measured}}^2 u_{a_1}^2 + 2 x_{\text{measured}} u_{a_0} a_1} \]  

(10)

Where the standard uncertainties on the parameters of the regression are \( u(a_1) = 0.0034 \) for the slope and \( u(a_0) = 0.41 \text{ nmol mol}^{-1} \) for the intercept. The covariance between the two parameters is \( \text{cov}(a_0, a_1) = -3 \times 10^{-4} \text{ nmol mol}^{-1} \).

The \( u(x_{\text{measured}}) \) values were obtained by linearly combining (with root sum squares), the standard deviation of SRP27 \( s_{\text{RS}} \) with the standard deviation of the API400-823 \( s_{\text{NS}} \), measured during the comparison. These values were then further combined linearly (with root sum squares) with the zero drift uncertainty for measurements at 0 nmol/mol nominal value:

\[ u_{\text{zero_drift}}(x_{\text{measured}}) = \frac{x_{\text{measured}}}{\sqrt{3}} \]  

(11)

Or with the ‘span drift’ uncertainty for all other measurements:

\[ u_{\text{span_drift}}(x_{\text{measured}}) = \frac{x_{\text{measured}}}{100\sqrt{3}} \]  

(12)

So that the uncertainty associated with measured (not corrected) values with the API400-823 is the combination of three terms:
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-R1-NMISA-12).

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

The relationship between both standards was first evaluated with a generalised least-square regression fit, using the software OzonE. This software, which is documented in a publication [7], is an extension of the previously used software B_Least recommended by the ISO standard 6143:2001 [8]. 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 since this instrument needs to be calibrated by the reference standard.

In a direct comparison, a linear relationship between the ozone amount-of-substance fractions measured by the instrument $i$ and SRP27 is obtained:

$$ x_i = a_0 + a_1 x_{SRP27} $$

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.

Because the NMISA API400-823 was calibrated by the BIPM-SRP27 instrument prior to this comparison, the values of the two instruments are correlated. Covariance terms between the values associated with each instrument at the same nominal amount-of-substance fraction should be calculated and taken into account. Unfortunately, this feature is not implemented in the software OzonE. As the least-square results are given in this report for information only, parameters were calculated without these covariances.

14.1. Least-squares regression results

The relationship between standard API400-823 and SRP27 is:

$$ x_{SRP15} = -1.15 + 1.0030 \cdot x_{SRP27} $$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0045$ for the slope and $u(a_0) = 0.46$ nmol/mol for the intercept. The covariance between the two parameters is $\text{cov}(a_0, a_1) = -9.66 \times 10^{-4}$ nmol mol$^{-1}$.

The least-squares regression results confirm that a linear fit is appropriate, with a sum of the squared deviations (SSD) of 0.64 and a goodness of fit (GoF) equals to 0.49.

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 not consistent with an intercept of zero, considering the uncertainty in the value of this parameter; i.e. $\left| a_0 \right| < 2u(a_0)$, and the value of the slope is consistent with a slope of 1; i.e. $\left| 1 - a_1 \right| < 2u(a_1)$.

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

The degree of equivalence of the participant $i$, at a nominal value $x_{\text{nom}}$ is defined as:

$$D_i = x_i - x_{\text{SRP27}}$$

(16)

where $x_i$ and $x_{\text{SRP27}}$ are the measurement result of the participant $i$ and of SRP27 at the nominal value $x_{\text{nom}}$.

Its associated standard uncertainty is:

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

(17)

where $u_i$ and $u_{\text{SRP27}}$ are the measurement uncertainties of the participant $i$ and of SRP27 respectively.

For this particular comparison, because the NMISA API400-823 was calibrated by the BIPM-SRP27 instrument prior to the comparison, the values of the two instruments are fully correlated. This is taken into account in the calculation of the uncertainty of the degrees of equivalence using the following formula:

$$u(D_i) = \sqrt{u(x_i)^2 + (1 - 2a_1)u(x_{\text{SRP27}})^2}$$

(18)

Where $a_1$ is the slope of the linear relationship between NMISA API400-823 and SRP27 (equation 9). Here, because $a_1$ is very close to 1, equation 15 can be written:

$$u(D_i) = \sqrt{u(x_i)^2 - u(x_{\text{SRP27}})^2}$$

(19)

15.2. Values of the degrees of equivalence

The degrees of equivalence and their uncertainties calculated in the form BIPM.QM-K1-R1-NMISA-12 are reported in the table below. Corresponding graphs of equivalence are displayed in Figure 1. The expanded uncertainties are calculated with a coverage factor $k = 2$.

<p>| Table 2 : degrees of equivalence of the NMISA at the ozone nominal amount-of-substance fractions 80 nmol/mol and 420 nmol/mol |  |  |</p>
<table>
<thead>
<tr>
<th>Nominal value (nmol/mol)</th>
<th>$x_i$ (nmol/mol)</th>
<th>$u_i$ (nmol/mol)</th>
<th>$x_{SRP27}$ (nmol/mol)</th>
<th>$u_{SRP27}$ (nmol/mol)</th>
<th>$D_i$ (nmol/mol)</th>
<th>$u(D_i)$ (nmol/mol)</th>
<th>$U(D_i)$ (nmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>76.77</td>
<td>1.16</td>
<td>77.07</td>
<td>0.36</td>
<td>-0.30</td>
<td>1.10</td>
<td>2.21</td>
</tr>
<tr>
<td>420</td>
<td>406.16</td>
<td>2.88</td>
<td>406.18</td>
<td>1.22</td>
<td>-0.02</td>
<td>2.61</td>
<td>5.22</td>
</tr>
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</table>

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

The degrees of equivalence between the NMISA 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 SRP27, SRP28 and API400-823

Results of previous comparisons performed since the first one in 2004 during the pilot study CCQM-P28 are displayed in Figure 2 together with the results of this comparison. To show the stability of the reference standard BIPM-SRP27, results of comparisons between BIPM-SRP27 and BIPM-SRP28 are also displayed. The slopes $a_1$ of the linear relation $x_{SRP_n} = a_0 + a_1 x_{SRP27}$ are represented together with their associated uncertainties calculated at the time of each comparison. Results of comparisons before 2010 have been corrected to take into account the changes in the reference BIPM-SRP27 described in [5] which explains the larger uncertainties associated with the corresponding slopes. Figure 2 shows that all standards included in these comparisons stayed in close agreement.
Figure 2: Results of previous comparisons between SRP27, SRP28 and NMISA standards realised at the BIPM. Uncertainties are calculated at $k=2$, with the uncertainty budget in use at the time of each comparison.

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

The comparison with NMISA is the sixteenth in the 2009-2012 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/.

18. Conclusion

For the third time since the launch of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between South Africa’s ozone national standard held by the NMISA 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 good agreement between the two standards.

19. References


Appendix 1 - Form BIPM.QM-K1-R1-NMISA-12

See the following pages.
**OZONE COMPARISON RESULT - PROTOCOL A - DIRECT COMPARISON**

**Participating institute information**

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<th>NMISA</th>
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<td>Address</td>
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</tr>
<tr>
<td></td>
<td>Lynnwood Ridge</td>
</tr>
<tr>
<td></td>
<td>0040 South Africa</td>
</tr>
<tr>
<td>Contact</td>
<td>Angelique Botha</td>
</tr>
<tr>
<td>Email</td>
<td><a href="mailto:abotha@nmisa.org">abotha@nmisa.org</a></td>
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**Instruments information**

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</tbody>
</table>

**Content of the report**

- page 1  general informations
- page 2  comparison results
- page 3  measurements results
- page 4  comparison description
- page 5  uncertainty budgets
# Ozone comparison form

**BIPM.QM-K1-R1**  
**Version 2.0**  
**Modified on 14/09/2007**

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**Comparison reference standard (RS) - national standard (NS)**

<table>
<thead>
<tr>
<th>Operator</th>
<th>F.Idrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>BIPM/Room CHEM09</td>
</tr>
</tbody>
</table>

**Comparison begin date / time**  
27/07/2012 18:00

**Comparison end date / time**  
28/07/2012 08:30

---

**Comparison results**

**Equation**

\[ x_{NS} = a_{NS,RS} x_{RS} + b_{NS,RS} \]

**Least-square regression parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a_{TS,RS}</td>
<td>1.0030</td>
</tr>
<tr>
<td>u(a_{TS,RS})</td>
<td>0.0045</td>
</tr>
<tr>
<td>b_{TS,RS}</td>
<td>-1.15</td>
</tr>
<tr>
<td>u(b_{TS,RS})</td>
<td>0.46</td>
</tr>
<tr>
<td>u(a,b)</td>
<td>-9.66E-04</td>
</tr>
</tbody>
</table>

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

---

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

<table>
<thead>
<tr>
<th>Nominal value</th>
<th>(D_i) (nmol/mol)</th>
<th>u((D_i)) (nmol/mol)</th>
<th>U((D_i)) (nmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>-0.30</td>
<td>1.10</td>
<td>2.21</td>
</tr>
<tr>
<td>420</td>
<td>-0.02</td>
<td>2.61</td>
<td>5.22</td>
</tr>
</tbody>
</table>

---

**All degrees of equivalence (k=2)**

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---
### Measurement results

<table>
<thead>
<tr>
<th>Nominal value</th>
<th>Reference Standard (RS)</th>
<th>National standard (NS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_{RS}$ (nmol/mol)</td>
<td>$s_{RS}$ (nmol/mol)</td>
</tr>
<tr>
<td>0</td>
<td>1.08</td>
<td>0.204</td>
</tr>
<tr>
<td>220</td>
<td>213.07</td>
<td>0.969</td>
</tr>
<tr>
<td>80</td>
<td>77.07</td>
<td>0.622</td>
</tr>
<tr>
<td>420</td>
<td>406.18</td>
<td>1.429</td>
</tr>
<tr>
<td>120</td>
<td>116.69</td>
<td>0.866</td>
</tr>
<tr>
<td>320</td>
<td>309.60</td>
<td>0.792</td>
</tr>
<tr>
<td>30</td>
<td>48.89</td>
<td>1.010</td>
</tr>
<tr>
<td>370</td>
<td>358.04</td>
<td>1.006</td>
</tr>
<tr>
<td>170</td>
<td>164.70</td>
<td>0.680</td>
</tr>
<tr>
<td>500</td>
<td>473.41</td>
<td>1.649</td>
</tr>
<tr>
<td>270</td>
<td>260.98</td>
<td>0.952</td>
</tr>
<tr>
<td>0</td>
<td>0.84</td>
<td>0.315</td>
</tr>
</tbody>
</table>

### Degrees of Equivalence

<table>
<thead>
<tr>
<th>Point Number</th>
<th>Nominal value (nmol/mol)</th>
<th>$D_i$ (nmol/mol)</th>
<th>$u(D_i)$ (nmol/mol)</th>
<th>$U(D_i)$ (nmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>-1.44</td>
<td>0.67</td>
<td>1.35</td>
</tr>
<tr>
<td>2</td>
<td>220</td>
<td>-0.60</td>
<td>1.82</td>
<td>3.63</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>-0.30</td>
<td>1.10</td>
<td>2.21</td>
</tr>
<tr>
<td>4</td>
<td>420</td>
<td>-0.02</td>
<td>2.61</td>
<td>5.22</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>-1.04</td>
<td>1.35</td>
<td>2.70</td>
</tr>
<tr>
<td>6</td>
<td>320</td>
<td>-0.42</td>
<td>2.09</td>
<td>4.17</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>-1.13</td>
<td>0.67</td>
<td>1.34</td>
</tr>
<tr>
<td>8</td>
<td>370</td>
<td>-0.40</td>
<td>2.48</td>
<td>4.97</td>
</tr>
<tr>
<td>9</td>
<td>170</td>
<td>-0.70</td>
<td>1.28</td>
<td>2.57</td>
</tr>
<tr>
<td>10</td>
<td>500</td>
<td>0.45</td>
<td>3.14</td>
<td>6.28</td>
</tr>
<tr>
<td>11</td>
<td>270</td>
<td>-0.03</td>
<td>1.86</td>
<td>3.72</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>-0.85</td>
<td>0.74</td>
<td>1.48</td>
</tr>
</tbody>
</table>

Covariance terms in between two measurement results of each standard

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

Value of $\alpha$ for the reference standard: 8.50E-06
Value of $\alpha$ for the national standard: 0.00E+00

Note 1: values measured by the NMISA national standard API400 have been corrected according to the calibration performed at the BIPM on 20 July 2012 as explained with the uncertainty budget.

Note 2: due to the calibration, the NMISA values are fully correlated with SRP27 values. This is taken into account in the calculation of the degrees of equivalence uncertainty:

$$u(D_i) = \sqrt{u(x_i)^2 - u(x_{ref})^2}$$
### Comparison conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone generator manufacturer</td>
<td>API</td>
</tr>
<tr>
<td>Ozone generator type</td>
<td>401</td>
</tr>
<tr>
<td>Ozone generator serial number</td>
<td>106</td>
</tr>
<tr>
<td>Room temperature (min-max) °C</td>
<td></td>
</tr>
<tr>
<td>Total number of comparison repeats realised</td>
<td>15</td>
</tr>
<tr>
<td>Data files names and location</td>
<td>D:\Data\2012\c120727015.xls</td>
</tr>
<tr>
<td>Zero air source</td>
<td>compressor + BekoKAT + dryer + aadco 737-R</td>
</tr>
<tr>
<td>Reference air flow rate (L/min)</td>
<td>10 L/min to SRP27</td>
</tr>
<tr>
<td>Sample flow rate (L/min)</td>
<td>4.6 L/min for SRP27 and API400</td>
</tr>
<tr>
<td>Instruments stabilisation time</td>
<td>more than 24 hours both</td>
</tr>
<tr>
<td>Instruments acquisition time /s (one measurement)</td>
<td>SRP27 5 s / API 400 1.064 s</td>
</tr>
<tr>
<td>Instruments averaging time /s</td>
<td>SRP27 none / API 400 34.05 s</td>
</tr>
<tr>
<td>Total time for ozone conditioning</td>
<td>more than 24 hours both</td>
</tr>
<tr>
<td>Ozone mole fraction during conditioning (nmol/mol)</td>
<td>1000 nmol/mol</td>
</tr>
<tr>
<td>Comparison repeated continuously (Yes/No)</td>
<td>Yes</td>
</tr>
<tr>
<td>If no, ozone mole fraction in between the comparison repeats</td>
<td>***</td>
</tr>
<tr>
<td>Reference Standard</td>
<td></td>
</tr>
</tbody>
</table>

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

### National Standard

| Reference Standard                              |                                      |

| National Standard                               |                                      |

| Data files names and location                   | D:\Data\2012\c120727015.xls         |
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 January 2007, available on BIPM website. It can be summarised by the formula:

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

**National Standard**

Uncertainty budget: BIPM.QM-K1

\[ u(x_{\text{corrected}}) = \sqrt{u(a_0)^2 + a_1^2 u(x_{\text{measured}})^2 + x_{\text{measured}}^2 u(a_1)^2 + 2x_{\text{measured}} u(a_0, a_1)} \]

where

\[ u(a_0) = 0.41 \text{ nmol/mol} \]
\[ a_1 = 0.9686 \]
\[ u(a_1) = 0.0034 \]
\[ u(a_0, a_1) = -0.0003 \text{ nmol/mol} \]

\[ x_{\text{corrected}} = a_0 + a_1 \cdot x_{\text{measured}} \]

where

\[ a_0 = -0.68 \text{ nmol/mol} \]
\[ a_1 = 0.9686 \]

To express the uncertainty as an equation

\[ u_x = \sqrt{0.41^2 + 0.9686^2 u(x_{\text{measured}})^2 + 0.0034^2 x_{\text{measured}}^2 + 2(-0.0003) x_{\text{measured}}} \]

Thus

\[ u_x = \sqrt{0.1681 + 0.9382 u(x_{\text{measured}})^2 + 1.156 \times 10^{-5} x_{\text{measured}}^2 - 0.0006 x_{\text{measured}}} \]