Final report, On-going Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with NMC, A*STAR, July 2018

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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 Singapore maintained by the National Metrology Centre, A*STAR (NMC, A*STAR) 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.

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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 Centre, A*STAR (NMC, A*STAR) 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 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 24 July 2018 at the NMC, A*STAR and on 15 September 2017 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 B, corresponding to a comparison between the NMC, A*STAR national standard SRP46 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 September 2017. Then SRP0 was compared with the national standard SRP46 at the NMC, A*STAR in July 2018.

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 NMC, A*STAR

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 is 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.

Noticing low counts (about 70k) on the scalers of SRP46, a new source lamp and a new optical filter were installed. Counts went up to 189K and 153K. The power level of the source lamp was then adjusted to obtain counts of 157K and 127K. The temperature and pressure probes were also adjusted.

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 $x_{\text{nom}}$ furnished by the ozone generator, the standard deviation $s_{\text{SRP46}}$ on the set of 10 consecutive measurements $x_{\text{SRP46,i}}$ recorded by SRP46 was calculated. The measurement results were considered as valid if $s_{\text{SRP46}}$ 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-ASTAR-18 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

After 12 hours of continuous measurements at NMC, A*STAR, unexpected results were observed in the comparison between NIST−SRP0 and NMC−SRP46. The slope of the linear relationship between the two sets of ozone mole fractions was showing values equal to 1 within 0.2% during the first 12 hours, and then decreased down to 1.3% below 1 after that. Results were also less stable, with a standard deviation of 0.2% instead of 0.1%. Staff from NIST attributed this change to the failure of a valve manifold inside the transfer standard SRP0, already observed and solved previously at NIST. The valve manifold could not be repaired in Singapore. Adjustments were made, but the valve manifold did not work properly the entire week. After return to NIST, SRP0 was compared again to SRP2 (NIST reference standard) and results showed that the valve manifold was still not working properly (standard deviation of 1%). Another valve manifold was installed in SRP0 and the results were good (standard deviation of 0.1%).

It was then decided to keep only the 12 first hours of measurements performed at NMC, A*STAR for this comparison. Results of comparisons between, SRP0 and SRP2 before and after the comparison at NMC, A*STAR are reported in Appendix 2 -, together with the results of all measurements performed at NMC, A*STAR.

12. Measurement standards

The instruments maintained by the BIPM, by the NIST and by the NMC, A*STAR 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:

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

(1)
where

- \( \sigma \) is the absorption cross-section of ozone at 253.7 nm under standard conditions of temperature and pressure, \( 1.1476 \times 10^{-17} \text{ cm}^2/\text{molecule} \) [3].
- \( L_{\text{opt}} \) is the mean optical path length of the two 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 \( (T_t) \) of one cell defined as

\[
T_t = \frac{I_{\text{ozone}}}{I_{\text{air}}} \tag{2}
\]

where

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

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

where

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

The formulation implemented in the SRP software is:

\[
x = \frac{-1}{2\alpha_x L_{\text{opt}}} \frac{T}{P_{\text{std}}} \frac{P_{\text{std}}}{P} \ln(D) \tag{4}
\]

where

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

\[
\alpha_x = \sigma \frac{N_A}{R} \frac{P_{\text{std}}}{T_{\text{std}}} \tag{5}
\]

12.2. Absorption cross-section for ozone

The linear absorption coefficient under standard conditions \( \alpha_x \) used within the SRP software algorithm is \( 308.32 \text{ cm}^{-1} \). This corresponds to a value for the absorption cross section \( \sigma \) 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. 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

<table>
<thead>
<tr>
<th>Component (y)</th>
<th>Source</th>
<th>Distribution</th>
<th>Standard Uncertainty</th>
<th>Combined standard uncertainty u(y)</th>
<th>Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$</th>
<th>contribution to $u(x)$ $[c_i] u(y)$ nmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical Path $L_{opt}$</td>
<td>Measurement Scale</td>
<td>Rectangular</td>
<td>0.0006 cm</td>
<td>0.52 cm</td>
<td>$- \frac{x}{L_{opt}}$</td>
<td>2.89×10^{-3}x</td>
</tr>
<tr>
<td></td>
<td>Repeatability</td>
<td>Normal</td>
<td>0.01 cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Correction factor</td>
<td>Rect</td>
<td>0.52 cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure $P$</td>
<td>Pressure gauge</td>
<td>Rectangular</td>
<td>0.029 kPa</td>
<td>0.034 kPa</td>
<td>$- \frac{x}{P}$</td>
<td>3.37×10^{-4}x</td>
</tr>
<tr>
<td></td>
<td>Difference between cells</td>
<td>Rectangular</td>
<td>0.017 kPa</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature $T$</td>
<td>Temperature probe</td>
<td>Rectangular</td>
<td>0.03 K</td>
<td>0.07 K</td>
<td>$\frac{x}{T}$</td>
<td>2.29×10^{-4}x</td>
</tr>
<tr>
<td></td>
<td>Temperature gradient</td>
<td>Rectangular</td>
<td>0.058 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ratio of intensities $D$</td>
<td>Scaler resolution</td>
<td>Rectangular</td>
<td>8×10^{-6}</td>
<td>1.4×10^{-5}</td>
<td>$\frac{x}{D \ln(D)}$</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>Repeatability</td>
<td>Triangular</td>
<td>1.1×10^{-5}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorption Cross section $\alpha$</td>
<td>Hearn value</td>
<td></td>
<td>1.22×10^{-9} cm²/molecule</td>
<td>1.22×10^{-9} cm²/molecule</td>
<td>$- \frac{x}{\alpha}$</td>
<td>1.06×10^{-2}x</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):

$$u(x) = \sqrt{(0.28)^2 + (2.92 \times 10^{-3} x)^2}$$  \hspace{1cm} (6)

12.5. Covariance terms for the common reference BIPM-SRP27

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:
\[ u(x_i, x_j) = x_i \cdot x_j \cdot u_b^2 \]  \hspace{1cm} (7)

where:

\[ u_b^2 = \frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} + \frac{u^2(L_{opt})}{L_{opt}^2} \]  \hspace{1cm} (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 NMC, A*STAR SRP46

The SRP46 maintained by the NMC, A*STAR has been constructed by NIST in 2010 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 NMC, A*STAR SRP46

The uncertainty budget for the ozone amount-of-substance fraction in dry air (x) measured by the instrument SRP46 in the nominal range 0 nmol/mol to 500 nmol/mol is given in Table 2.

![Table 2: Uncertainty budget for the NMC, A*STAR SRP46](image)

The ozone amount-of-substance fraction measurement with the SRP46 can be expressed as a numerical equation (numerical values expressed as nmol/mol):

\[ u(x) = \sqrt{0.28^2 + (2.93 \times 10^{-3}x)^2} \]  \hspace{1cm} (9)

No covariance term for the SRP46 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.

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

(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-ASTAR-18).

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 BIPM visit ($x_{RS}$, $x_{TS}$) (calibration of the transfer standard) followed by a second linear regression of the twelve data points from the NMC, A*STAR visit ($x_{NS}$, $x'_{TS}$), $x'_{TS}$ 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:

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

(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 SRP46 and SRP27 is:

\[ x_{SRP46} = 1.0025x_{SRP27} - 0.13 \]  

(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 \( \text{cov}(a_0, a_1) = -4.0 \times 10^{-4} \).

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. \(|1 - a_1| < 2u(a_1)\).

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 \( x_{\text{nom}} \) is defined as:

\[ D = x_i - \hat{x}_{SRP27} \]  

(13)

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

Its associated standard uncertainty is:

\[ u(D) = \sqrt{u^2(x_i) + u^2(\hat{x}_{SRP27})} \]  

(14)

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

15.2. Calculation of SRP27 predicted values and their related uncertainties

The comparison performed at the BIPM between the transfer standard and the reference standard SRP27 is used to calibrate the transfer standard. The data \( \bar{x}_{RS} \) and \( \bar{x}_{TS} \) are fitted using the generalised least square program OzonE, taking into account the associated
uncertainties \( u(x_{RS}) \) and \( u(x_{TS}) \), 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 \( x_{TS} \) (\( x_{RS} = a_{RS,TS} x_{TS} + b_{RS,TS} \)) are calculated as well as their uncertainties.

Then, for each value \( x_{TS} \) 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:

\[
\begin{align*}
\sqrt{u^2(\hat{x}_{RS})} = u^2(b_{RS,TS}) + x_{TS}^2 \cdot u^2(a_{RS,TS}) + a_{RS,TS}^2 \cdot u^2(x_{TS}) + 2 \cdot x_{TS} \cdot u(a_{RS,TS}, b_{RS,TS}) \tag{15}
\end{align*}
\]

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

The degrees of equivalence and their uncertainties calculated in the form BIPM.QM-K1-R3-ASTAR-18 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>
<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) / ) (nmol/mol)</th>
<th>( U(D) / ) (nmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>81.16</td>
<td>0.37</td>
<td>80.98</td>
<td>0.47</td>
<td>0.18</td>
<td>0.59</td>
<td>1.19</td>
</tr>
<tr>
<td>420</td>
<td>422.46</td>
<td>1.27</td>
<td>421.64</td>
<td>1.84</td>
<td>0.82</td>
<td>2.24</td>
<td>4.47</td>
</tr>
</tbody>
</table>

Table 3: degrees of equivalence of the NMC, A*STAR at the ozone nominal amount-of-substance fractions 80 nmol/mol and 420 nmol/mol
The degrees of equivalence between the NMC, A*STAR 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

Comparisons performed at NIST between the transfer standard SRP0 and NIST national standard SRP2 before and after the comparison at NMC, A*STAR (and after reparation of the valve manifold as described in section 11) have shown a maximum variation of 0.12% 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 NMC, A*STAR SRP46

Results of the previous comparison performed in 2011 during the first cycle of BIPM.QM-K1 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. Figure 2 shows that all standards included in these comparisons stayed in close agreement.
18. Summary of previous comparisons included in BIPM.QM-K1

The comparison with NMC, A*STAR is the tenth one in the 2017-2020 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 third time since the launch of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of Singapore maintained by the NMC, A*STAR 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


**Appendix 1 - Form BIPM.QM-K1-R3-ASTAR-18**

See next pages.

**Appendix 2 - Comparison between SRP0, SRP2 and SRP46**

See next pages.
## Linking institute information

<table>
<thead>
<tr>
<th>Institute</th>
<th>NIST</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMO</td>
<td>SIM</td>
</tr>
<tr>
<td><strong>Address</strong></td>
<td>100 Bureau Drive Stop 8393 Gaithersburg, MD 20899-8393</td>
</tr>
<tr>
<td><strong>Contact</strong></td>
<td>James E. Norris</td>
</tr>
<tr>
<td><strong>Email</strong></td>
<td><a href="mailto:jnorris@nist.gov">jnorris@nist.gov</a></td>
</tr>
<tr>
<td><strong>Telephone</strong></td>
<td>(301)975-3936</td>
</tr>
</tbody>
</table>

## Participating institute information

<table>
<thead>
<tr>
<th>Institute</th>
<th>NMC, A*STAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMO</td>
<td>APMP</td>
</tr>
<tr>
<td><strong>Address</strong></td>
<td>1 Science Park Drive, Singapore 118221</td>
</tr>
<tr>
<td><strong>Contact</strong></td>
<td>Kai, Fuu Ming/Wendy Liu, Hui/Fang Jie/Cui Yuxi</td>
</tr>
<tr>
<td><strong>Email</strong></td>
<td><a href="mailto:kai_fuu_ming@nmc.a-star.edu.sg">kai_fuu_ming@nmc.a-star.edu.sg</a>/lifu_hui@nmc.a-star.edu.sg/ <a href="mailto:fang_jie@nmc.a-star.edu.sg">fang_jie@nmc.a-star.edu.sg</a>/ <a href="mailto:cui_yuxi@nmc.a-star.edu.sg">cui_yuxi@nmc.a-star.edu.sg</a></td>
</tr>
<tr>
<td><strong>Telephone</strong></td>
<td>+65 6279 1942/6279 1991/6279 1910/6279 1917</td>
</tr>
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</table>

## Instruments information

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Reference Standard Photometer</th>
<th>Participating Institute National Standard</th>
<th>Linking institute National Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST</td>
<td></td>
<td>NMC</td>
<td>NIST</td>
</tr>
<tr>
<td>SRP</td>
<td>SRP</td>
<td>SRP</td>
<td>SRP0</td>
</tr>
<tr>
<td>SRP27</td>
<td>SRP46</td>
<td>SRP0</td>
<td>SRP0</td>
</tr>
<tr>
<td><strong>ozone cross-section value</strong></td>
<td><strong>308.32 atm⁻¹ cm⁻¹</strong></td>
<td><strong>308.32 atm⁻¹ cm⁻¹</strong></td>
<td><strong>308.32 atm⁻¹ cm⁻¹</strong></td>
</tr>
</tbody>
</table>

*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

<table>
<thead>
<tr>
<th>Page</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>page 1</td>
<td>General informations</td>
</tr>
<tr>
<td>page 3</td>
<td>Summary of the comparison results</td>
</tr>
<tr>
<td>page 4</td>
<td>Calculation of the national standard vs reference standard relationship</td>
</tr>
<tr>
<td>page 5</td>
<td>Data reporting sheet - first comparison of the transfer standard vs the national standard</td>
</tr>
<tr>
<td>page 7</td>
<td>Calibration of the transfer standard by the reference standard at the BIPM</td>
</tr>
<tr>
<td>page 9</td>
<td>Uncertainty budgets</td>
</tr>
</tbody>
</table>

Please complete the cells containing blue stars only.

After completion of the appropriate section of this report, please send to Joëlle Viallon by email (jviallon@bipm.org), fax (+33 1 45342021), or mail (BIPM, Pavillon de Breteuil, F-92312 Sèvres)
comparison national standard (RS) vs reference standard (NS)

Summary of comparison results

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

Least-square regression parameters

<table>
<thead>
<tr>
<th></th>
<th>( a_{NS,RS} )</th>
<th>( u(a_{NS,RS}) )</th>
<th>( b_{NS,RS} )</th>
<th>( u(b_{NS,RS}) )</th>
<th>( u(a,b) )</th>
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</thead>
<tbody>
<tr>
<td>first comparison</td>
<td>1.0025</td>
<td>0.0038</td>
<td>-0.1313</td>
<td>0.3140</td>
<td>-0.0004</td>
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</table>

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

<table>
<thead>
<tr>
<th>Nom 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>80</td>
<td>0.18</td>
<td>0.59</td>
<td>1.19</td>
</tr>
<tr>
<td>420</td>
<td>0.82</td>
<td>2.23</td>
<td>4.47</td>
</tr>
</tbody>
</table>

Degrees of equivalence at all measured values (k=2)
## Calculation of the National Standard vs Reference Standard comparison results through the National Standard vs Transfer Standard comparison

### First comparison results

<table>
<thead>
<tr>
<th>Nominal value</th>
<th>National standard measurement results</th>
<th>Transfer standard measurement results</th>
<th>Reference Standard predicted values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_{NS}$ nmol/mol</td>
<td>$u(x_{NS})$ nmol/mol</td>
<td>$x_{TS}$ nmol/mol</td>
</tr>
<tr>
<td>0</td>
<td>0.01</td>
<td>0.28</td>
<td>0.00</td>
</tr>
<tr>
<td>220</td>
<td>226.40</td>
<td>0.72</td>
<td>226.33</td>
</tr>
<tr>
<td>80</td>
<td>81.16</td>
<td>0.37</td>
<td>81.05</td>
</tr>
<tr>
<td>420</td>
<td>422.46</td>
<td>1.26</td>
<td>422.26</td>
</tr>
<tr>
<td>120</td>
<td>122.31</td>
<td>0.45</td>
<td>122.26</td>
</tr>
<tr>
<td>320</td>
<td>323.64</td>
<td>0.99</td>
<td>323.53</td>
</tr>
<tr>
<td>30</td>
<td>45.25</td>
<td>0.31</td>
<td>45.35</td>
</tr>
<tr>
<td>370</td>
<td>374.29</td>
<td>1.13</td>
<td>374.25</td>
</tr>
<tr>
<td>170</td>
<td>168.61</td>
<td>0.57</td>
<td>168.29</td>
</tr>
<tr>
<td>500</td>
<td>512.25</td>
<td>1.52</td>
<td>511.73</td>
</tr>
<tr>
<td>270</td>
<td>270.14</td>
<td>0.84</td>
<td>270.00</td>
</tr>
<tr>
<td>0</td>
<td>-0.02</td>
<td>0.28</td>
<td>0.17</td>
</tr>
</tbody>
</table>

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)

\[
x'_{RS} = a_{RS,TS} x_{TS} + b_{RS,TS}
\]

\[
\begin{align*}
    a_{RS,TS} &= 0.9984 \\
    b_{RS,TS} &= \text{Nom value (nmol/mol)} \\
    u(a_{RS,TS}) &= 0.0033 \\
    u(b_{RS,TS}) &= 0.22 \\
    u(x_{RS}) &= \sqrt{a_{RS,TS}^2 \cdot u(x_{TS})^2 + x_{TS}^2 \cdot u(a_{RS,TS})^2 + u(b_{RS,TS})^2 + 2 \cdot x_{TS} \cdot u(a_{RS,TS}, b_{RS,TS})}
\end{align*}
\]

### Degrees of Equivalence

\[D_i = x_{NS} - x'_{RS}\]

<table>
<thead>
<tr>
<th>Point Number</th>
<th>Nom 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>-0.05</td>
<td>0.45</td>
<td>0.90</td>
</tr>
<tr>
<td>2</td>
<td>220</td>
<td>0.38</td>
<td>1.24</td>
<td>2.48</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>0.18</td>
<td>0.59</td>
<td>1.19</td>
</tr>
<tr>
<td>4</td>
<td>420</td>
<td>0.82</td>
<td>2.23</td>
<td>4.47</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>0.19</td>
<td>0.75</td>
<td>1.51</td>
</tr>
<tr>
<td>6</td>
<td>320</td>
<td>0.57</td>
<td>1.73</td>
<td>3.45</td>
</tr>
<tr>
<td>7</td>
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<td>-0.09</td>
<td>0.49</td>
<td>0.98</td>
</tr>
<tr>
<td>8</td>
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<td>0.59</td>
<td>1.99</td>
<td>3.97</td>
</tr>
<tr>
<td>9</td>
<td>170</td>
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<td>0.96</td>
<td>1.92</td>
</tr>
<tr>
<td>10</td>
<td>500</td>
<td>1.28</td>
<td>2.70</td>
<td>5.39</td>
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<tr>
<td>11</td>
<td>270</td>
<td>0.52</td>
<td>1.46</td>
<td>2.91</td>
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<tr>
<td>12</td>
<td>0</td>
<td>-0.25</td>
<td>0.45</td>
<td>0.90</td>
</tr>
</tbody>
</table>

### Least-square regression parameters

\[
\begin{align*}
    a_{NS,RS} &= 1.0025332 \\
    b_{NS,RS} &= -0.037790 \\
    u(a_{NS,RS}) &= -0.1312946 \\
    u(b_{NS,RS}) &= 0.3140376 \\
    u(a,b) &= -0.0004488
\end{align*}
\]
# Data reporting sheet

Comparison of transfer standard (TS) vs national standard (NS)

## Operator
Kai, Fuu Ming/Wendy Liu, Hui/Fang Jie/Cui

## Location
NMC, A*STAR

### Measurement results

<table>
<thead>
<tr>
<th>Nominal value</th>
<th>$x_{TS}$ nmol/mol</th>
<th>$s_{TS}$ nmol/mol</th>
<th>$u(x_{TS})$ nmol/mol</th>
<th>$x_{NS}$ nmol/mol</th>
<th>$s_{NS}$ nmol/mol</th>
<th>$u(x_{NS})$ nmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
<td>0.25</td>
<td>0.28</td>
<td>0.01</td>
<td>0.11</td>
<td>0.28</td>
</tr>
<tr>
<td>220</td>
<td>226.33</td>
<td>0.19</td>
<td>0.72</td>
<td>226.40</td>
<td>0.13</td>
<td>0.72</td>
</tr>
<tr>
<td>80</td>
<td>81.05</td>
<td>0.13</td>
<td>0.37</td>
<td>81.16</td>
<td>0.19</td>
<td>0.37</td>
</tr>
<tr>
<td>420</td>
<td>422.26</td>
<td>0.23</td>
<td>1.26</td>
<td>422.46</td>
<td>0.26</td>
<td>1.26</td>
</tr>
<tr>
<td>120</td>
<td>122.26</td>
<td>0.14</td>
<td>0.45</td>
<td>122.31</td>
<td>0.19</td>
<td>0.45</td>
</tr>
<tr>
<td>320</td>
<td>323.53</td>
<td>0.21</td>
<td>0.99</td>
<td>323.64</td>
<td>0.08</td>
<td>0.99</td>
</tr>
<tr>
<td>30</td>
<td>45.35</td>
<td>0.18</td>
<td>0.31</td>
<td>45.25</td>
<td>0.28</td>
<td>0.31</td>
</tr>
<tr>
<td>370</td>
<td>374.25</td>
<td>0.16</td>
<td>1.13</td>
<td>374.29</td>
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<td>1.13</td>
</tr>
<tr>
<td>170</td>
<td>168.29</td>
<td>0.16</td>
<td>0.57</td>
<td>168.61</td>
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</tr>
<tr>
<td>500</td>
<td>511.73</td>
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<td>1.52</td>
<td>512.25</td>
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<td>1.52</td>
</tr>
<tr>
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<td>270.00</td>
<td>0.19</td>
<td>0.84</td>
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<td>0.84</td>
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<td>0.28</td>
<td>-0.02</td>
<td>0.20</td>
<td>0.28</td>
</tr>
</tbody>
</table>

**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: $u(x_i, x_j) = \alpha \cdot x_i \cdot x_j$

<table>
<thead>
<tr>
<th>Value of $\alpha$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

## Comparison conditions

- Ozone generator manufacturer: NIST
- Ozone generator type: SRP
- Ozone generator serial number: 46
- Room temperature (min-max) / °C: 22.9-23.5
- Room pressure (average) / hpa: 1005.5
- Zero air source: Aadco 737
- Reference air flow rate (L/min): 6 to 8
- Sample flow rate (L/min): 5
- Instruments stabilisation time: SRP 21 hours; SRP46 weeks
- Instruments acquisition time /s (one measurement): 25
- Instruments averaging time /s: 275
- Total time for ozone conditioning: 120 min
- Ozone mole fraction during conditioning: 600-700
- Comparison repeated continously (Yes/No): Yes
- If no, ozone mole fraction in between the comparison repeats: ***
- Total number of comparison repeats realised: 7
Instruments checks and adjustments

National Standard

Installed new source lamp in SRP 46, due to bad optical filter counts were only about 70K. Removed filter, counts were above 600K. Installed CVI F10-253.7-3-1.00 optical filter. Counts were 189K and 153K. Lowered SRP 46 source lamp power level, counts 157K, 127K. Checked and made adjustments to temperature and pressure of SRP 46.

Transfer Standard

Replaced silica gel trap in SRP 0. Lab humidity is above 60% and remained between 60%-70% during the week. Checked silica gel trap in SRP 46, seemed good. Dark counts remained a problem during entire week due to lab humidity. Dark counts were adjusted each day, but not included in measurements. Checked and made adjustments to temperature and pressure of SRP 0.
calibration of the transfer standard (TS) by the reference standard (RS)

Operator | Faraz Idrees  | Location | BIPM/CHEM9  
Comparison begin date / time | 15/09/2017 09:58 | Comparison end date / time | 15/09/2017 11:58

Calibration results

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

<table>
<thead>
<tr>
<th>Least-square regression parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_{RS,TS} )</td>
</tr>
<tr>
<td>( u(a_{RS,TS}) )</td>
</tr>
<tr>
<td>( b_{RS,TS} )</td>
</tr>
<tr>
<td>( u(b_{RS,TS}) )</td>
</tr>
<tr>
<td>( u(a,b) )</td>
</tr>
</tbody>
</table>

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 \( \alpha \) 8.56E-06
### Comparison conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone generator manufacturer</td>
<td>Environics</td>
</tr>
<tr>
<td>Ozone generator type</td>
<td>Model 6100</td>
</tr>
<tr>
<td>Ozone generator serial number</td>
<td>3128</td>
</tr>
<tr>
<td>Room temperature (min-max) / °C</td>
<td>21.1 -24.2</td>
</tr>
<tr>
<td>Room pressure (average) / hpa</td>
<td>1003.7 -1004.7</td>
</tr>
<tr>
<td>Zero air source</td>
<td>compressor + BokoKAT + dryer + Aadco 737-R</td>
</tr>
<tr>
<td>Reference air flow rate (L/min)</td>
<td>15</td>
</tr>
<tr>
<td>Sample flow rate (L/min)</td>
<td>10</td>
</tr>
<tr>
<td>Instruments stabilisation time</td>
<td>&gt; 24 hours</td>
</tr>
<tr>
<td>Instruments acquisition time /s (one measurement)</td>
<td>5</td>
</tr>
<tr>
<td>Instruments averaging time /s</td>
<td>5</td>
</tr>
<tr>
<td>Total time for ozone conditioning</td>
<td>&gt; 24 hours</td>
</tr>
<tr>
<td>Ozone mole fraction during conditioning</td>
<td>800 nmol/mol</td>
</tr>
<tr>
<td>Comparison repeated continously (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>Total number of comparison repeats realised</td>
<td>39</td>
</tr>
<tr>
<td>Data files names and location</td>
<td>c170911001.xls to c170914012.xls</td>
</tr>
</tbody>
</table>

### 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 January 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**

The transfer standard used is NIST SRP0. The uncertainty budgets can be summarised by the formula:

\[ u(x) = \sqrt{(0.28)^2 + (2,92 \cdot 10^{-3} x)^2} \]
## Optical Path \( L_{opt} \)
- Measurement Scale: Rect. 0.0005 cm
- Variability: Rect. 0.004 cm
- Divergence: Rect. 0.52 cm

## Pressure \( P \)
- Pressure gauge: Rect. 0.029 kPa
- Difference between cells: Rect. 0.017 kPa

## Temperature \( T \)
- Temperature probe: Rect. 0.086 K
- Temperature gradient: Rect. 0.058 K
- Temperature heating bias: Rect. -1.0 \( \times \) 10^{-3} K

## Ratio of intensities \( D \)
- Scaler resolution: Rect. 8.0 \( \times \) 10^{-6}
- Repeatability: Triang. 1.1 \( \times \) 10^{-5}

## Absorption Cross section \( \sigma \)
- Conventional value: 1.22 \( \times \) 10^{-19} cm^2/molecule

The uncertainty \( u(x) \) is calculated as:

\[
u(x) = \sqrt{(0.28)^2 + (2.93 \times 10^{-3} x)^2}
\]