**Rapport BIPM-2007/05**

Bureau International des Poids et Mesures

# Comparison of Ozone Reference Standards of the CHMI and the BIPM

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September 2007

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## Abstract

A comparison of the ozone reference standards of the Czech Hydrometeorological Institute (CHMI) and of the Bureau International des Poids et Mesures (BIPM) has been performed. Both institutes maintain Standard Reference Photometers (SRPs), developed by the National Institute of Standards and Technology (NIST), as their reference standards. The instruments have been compared over an ozone mole fraction range of 0 nmol/mol to 870 nmol/mol.

## 1. Introduction

A comparison of the ozone reference standards of the Czech Hydrometeorological Institute (CHMI) and of the Bureau International des Poids et Mesures (BIPM) has been performed. It is a repeat of the comparison performed three years ago [1]. Both institutes maintain Standard Reference Photometers (SRPs), developed by the National Institute of Standards and Technology (NIST), as their reference standards. A brief description of the SRP is given in section 3 of this report, together with details of the comparison performed at the BIPM. The results of the comparison are given in section 4. The uncertainty budget is given in section 5.

## 2. Quantities and Units

A number of quantities can be used to express the composition of mixtures within the field of ambient ozone measurements. In this report, the measurand is the mole fraction of ozone in air, with measurement results being expressed in units of nmol/mol. The numerical value of a mole fraction of ozone in air expressed in this unit, is equivalent to the numerical value of the volume fraction expressed as ppb (parts per billion, 1 billion $= 10^9$) or ppbv. Although in common usage, the use of the symbols ppb and ppbv is not recommended.

## 3. Comparison of Standard Reference Photometers at the BIPM

The BIPM currently maintains five SRPs built by the NIST. More details on the instrument's principle and its capabilities can be found in [2]. The three instruments maintained at the BIPM, and used in this comparison, have the serial numbers SRP27, SRP28 and SRP31. These have been compared with SRP17, the instrument maintained by the CHMI.

### 3.1 Ozone measurements with an SRP

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

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

where

$\alpha$ is the absorption cross-section of ozone at 253.7nm in standard conditions of temperature and pressure. The value used is: $1.1476\times10^{-17}$ $\text{cm}^2$/molecule [3].
$L_{opt}$ is the optical path length of one of the cells,
$T$ is the temperature measured in the cells,
$T_{\text{std}}$ is the standard temperature (273.15 K),
$P$ is the pressure measured in the cells,
$P_{\text{std}}$ is the standard pressure (101.325 kPa),
$D$ is the product of transmittances of two cells, with the transmittance ($T$) of one cell defined as

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

where

$I_{\text{ozone}}$ is the UV radiation intensity measured in the cell when containing ozonized air, and
$I_{\text{air}}$ is the UV radiation intensity measured in 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 mole fraction ($x$) of ozone in air:

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

where

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

### 3.2 Absorption cross section for ozone

The absorption cross section used within the SRP software algorithm is 308.32 $\text{atm}^{-1}\text{cm}^{-1}$. This corresponds to a value of $1.1476\times10^{-17}$ $\text{cm}^2$/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 relative uncertainty of the absorption cross section has been proposed by the BIPM and the NIST in a recent publication [4].

### 3.3 Ozone generation

The very reactive nature of ozone precludes its storage in cylinders. As a consequence, ozone has to be produced and measured simultaneously. During this exercise, an external ozone generator manufactured by Environics (model 6100) has been used. This generator is based on the photolysis of $O_2$ molecules contained in purified air using radiation at 185 nm. The amount of $O_3$ molecules produced depends on the radiation intensity and the flow rate of air. The airflow rate is maintained at a constant value during a comparison, and the radiation intensity is varied to obtain a range of ozone mole fractions. The typical range over which measurements are carried out is 2 nmol/mol to 1000 nmol/mol of ozone in air.

### 3.4 Current state of the BIPM SRPs

Compared to the original design described in [2], SRP27, SRP28 and SRP31 have been modified to deal with two biases revealed by the study conducted by the BIPM and the NIST [4]:

- The SRPs are equipped with a thermo-electric cooling device to maintain homogeneity of the gas temperature in their cells. Together with a regular calibration of their temperature probe, it insures the removal of the bias in the gas cell temperature measurement.
- In SRP27 and SRP28 the optical path length is now calculated as being 1.005 times the length of the two cells within each instrument respectively. Together with an increased uncertainty this ensures that the bias on the optical path length is taken into account.
- In SRP31, a new set of fittings that hold the absorption cells have been incorporated into the instrument to minimise the bias in the light path length. The cells end windows are now tilted by 3° with the vertical plan to avoid multiple reflections along the light path. In order to take into account a residual bias due to the beam divergence, the uncertainty in the pathlength was increased by the same amount as for SRP27 and SRP28.

### 3.5 Actual state of the CHMI SRP17

Compared to the original design, the CHMI SRP17 has been modified to deal with the two biases revealed in [4]. In August 2007, an “SRP upgrade kit” was installed by NIST in CHMI laboratories. It consists of two parts:

- A new source block was designed to minimise the gas temperature evaluation bias by better thermally insulating the UV source lamp (heated at a temperature of about 60°C) from the rest of the optical bench, thus avoiding the temperature gradient observed in the SRP when the original source block is used. Together with a regular calibration of SRP17 temperature probe performed in CHMI laboratories this ensures the removal of the bias on the gas cell temperature measurement.

- A new set of absorption cells was installed. The new cells are quartz tubes closed at both ends by optically sealed quartz windows. These windows are tilted by 3° with respect to the vertical plan to avoid multiple reflections along the light path. Again, to take into account a residual bias due to the beam divergence, the uncertainty was increased by the same amount as in SRP27 and SRP28.

Furthermore, prior to this comparison, CHMI requested that SRP17 detectors and voltage-to-frequency converters were replaced with new components. This request followed the comparison of SRP17 and NIST SRP0 in their laboratory, which revealed some instability in SRP17. At the BIPM, SRP17 stability was tested again after the change of detectors, using a large number (200) of measurements without air flowing inside the SRP cells. The product of transmittances $D$ showed an average value of 0.999999 with a standard deviation of $1.08\times10^{-5}$, which is consistent with the declared uncertainty budget of SRP17.

### 3.6 *Comparison of SRPs at the BIPM*

In this comparison, three of the BIPM SRPs have been compared against the instrument of the guest laboratory. The agreement of the instruments maintained at the BIPM is verified before and after any comparison.

The same source of purified air is used for all the SRPs being compared. This air is used to provide reference air as well as the ozone-air mixtures to each SRP. Ambient air is used as the source for reference air. The air is compressed with an oil-free compressor, dried and scrubbed with a commercial purification system so that the mole fraction of ozone and nitrogen oxides remaining in the air is below detectable limits. The relative humidity of the reference air is monitored and the mole fraction of water in air typically found to be less than 3 µmol/mol. The mole fraction of volatile organic hydrocarbons in the reference air was measured (November 2002), with no mole fraction of any detected component exceeding 1 nmol/mol.

A common dual external manifold in Pyrex is used to furnish the necessary flows of reference air and ozone-air mixture to the SRPs. The two columns of this manifold are vented to atmospheric pressure.

A comparison between SRPs consists of producing ozone-air mixture at different mole fractions over the required range, and measuring these with the photometers. A typical comparison run includes 10 different mole fractions correctly distributed to cover the range, together with the measurement of reference air at the beginning and end of each run. These mole fractions are measured in a random sequence. Each of these points is an average of 10 single measurements. A run can be repeated a chosen number of times. A set number of runs is referred to as a cycle. A cycle is always preceded by a period of ozone conditioning of the instruments for at least two hours. This involves passing a high ozone amount fraction (900 nmol/mol) for a sufficient period of time to avoid ozone losses inside the SRPs during the measurement runs.

### 3.7 *Analysis of the measurement results by generalised least-square regression*

The relationship between two SRPs is evaluated with a generalised least-square regression fit performed on the two sets of measured ozone mole fractions, taking into account standard uncertainties on the measurement results of the two SRPs (the uncertainty budget associated with the ozone mole fraction measurement with an SRP is discussed in section 5). To this end, a software called OzonE is used. This software, which is to be documented in a publication [5], is an extension of the previously used software B_Least recommended by the ISO standard 6143:2001 [6]. It includes the possibility to take into account correlations between measurements performed with the same instrument at different ozone mole fractions.

At the BIPM, all SRPs are compared with the so-called ‘main instrument’, which is SRP27. A linear relationship between the ozone mole fractions measured by SRP*n* and the main SRP27 is thus obtained:

$$x_{\mathrm{SRP}n} = a_0 + a_1 x_{\mathrm{SRP27}} \qquad (4)$$

The associated uncertainties on the slope $u(a_1)$ and the intercept $u(a_0)$ are given by the programme, as well as the covariance between them and the usual statistical parameters to validate the fitting function.

## 4. CHMI-BIPM SRPs comparison results

SRP17, maintained by the CHMI, was compared with the SRPs maintained by the BIPM following the general procedure outlined above. A cycle of three comparison runs between SRP27, SRP28, SRP31 and SRP17 were performed. Ozone was generated using the Environics 6100 generator with an airflow of 10 L/min. The ozone mole fraction range covered during this exercise was (0 to 870) nmol/mol. The result of the last comparison run is presented in detail in the section 4.1. The repeatability of the results over the three runs is shown in section 4.2, and the stability of the BIPM standards in section 4.3.

### *4.1 Results of the comparison*

The measurement results of the last of the three recorded runs are shown in Table 1. For each nominal ozone mole fraction, the standard deviation on the 10 successive measurements recorded is reported. The values reported here show that both instruments were in a stable regime.

*Table 1: measurement results of the comparison between the CHMI standard SRP17 and the BIPM reference standard SRP27*

| Reference standard BIPM-SRP27 (RS) | | | National standard CHMI SRP17 (NS) | | |
|---|---|---|---|---|---|
| $x_{RS}$ nmol/mol | $s_{RS}$ nmol/mol | $u(x_{RS})$ nmol/mol | $x_{NS}$ nmol/mol | $s_{NS}$ nmol/mol | $u(x_{NS})$ nmol/mol |
| -0.04 | 0.21 | 0.28 | -0.05 | 0.26 | 0.28 |
| 693.59 | 0.35 | 2.04 | 693.07 | 0.30 | 2.04 |
| 782.72 | 0.44 | 2.30 | 782.06 | 0.30 | 2.30 |
| 343.87 | 0.10 | 1.04 | 343.57 | 0.29 | 1.04 |
| 430.87 | 0.30 | 1.29 | 430.57 | 0.21 | 1.29 |
| 519.81 | 0.25 | 1.54 | 519.42 | 0.13 | 1.54 |
| 607.27 | 0.19 | 1.80 | 606.73 | 0.22 | 1.79 |
| 259.37 | 0.17 | 0.81 | 259.17 | 0.26 | 0.81 |
| 874.42 | 0.21 | 2.57 | 873.73 | 0.13 | 2.57 |
| 174.84 | 0.19 | 0.58 | 174.53 | 0.14 | 0.58 |
| 88.74 | 0.23 | 0.38 | 88.60 | 0.15 | 0.38 |
| 0.03 | 0.16 | 0.28 | 0.01 | 0.23 | 0.28 |

An interesting way to look at these results is to display the difference between the ozone mole fractions measured by SRP17 and SRP27 ($x_{17} - x_{27}$) versus the ozone mole fraction measured by SRP27. As can be seen on Figure 1, it shows that measurement results from both instruments differ little from each other over the entire concentration range of the comparison. Considering a coverage factor of $k = 2$ (95% confidence interval), the difference between both standards is much lower than their combined measurement uncertainties.

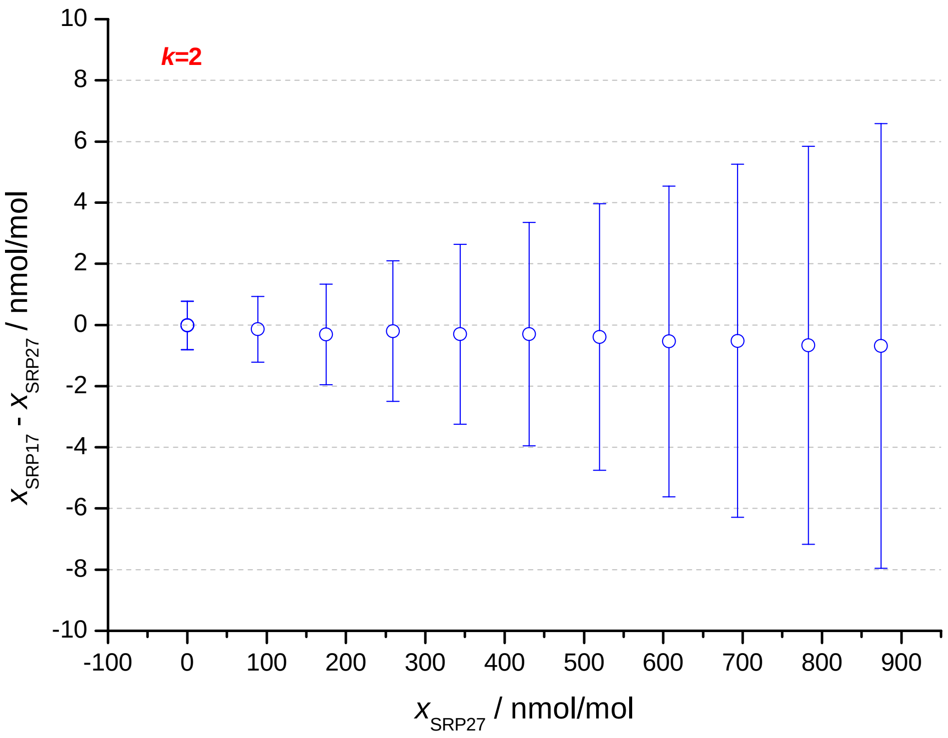

*Figure 1: difference between the ozone mole fractions measured by SRP17 and SRP27 versus the ozone mole fraction measured by SRP27.*

The relationship between SRP17 and SRP27 is given by the result of the generalised least-square regression performed following the method described in section 3.7:

$$x_{\mathrm{SRP17}} = -0.03 + 0.9992 \cdot x_{\mathrm{SRP27}} \qquad (5)$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0032$ for the slope and $u(a_0) = 0.25$ nmol/mol for the intercept. The covariance between the two parameters is $\mathrm{cov}(a_0, a_1) = -1.61\times10^{-4}$.

The least-square regression statistical parameters confirm the appropriate choice of a linear relation, with a sum of the squared deviations (SSD) of 0.04 and a goodness of fit (GoF) equals to 0.11.

To asses the agreement of the standards from equation 5, the difference between the calculated slope value and unity, and the intercept value and zero, together with their measurement uncertainties need to be considered. In the comparison, the value of the intercept is consistent with an intercept of zero, considering the uncertainty in the value of this parameter; i.e $|a_0| < 2u(a_0)$, and the value of the slope is consistent with a slope of 1; i.e. $|1-a_1| < 2\,u(\mathrm{a}_1)$.

### *4.2 Repeatability*

The results of the three comparison runs performed successively between SRP17 and SRP27 are reported in Table 2. With a standard deviation of 0.04 nmol/mol on the intercept and a relative standard deviation of 0.03% on the slope, those data show a good repeatability.

*Table 2 : results of the three comparison runs repeated successively*

| Run | Slope $a_1$ | $u(a_1)$ | Intercept $a_0$ | $u(a_0)$ | $\mathrm{cov}(a_0, a_1)$ | GoF |
|---|---|---|---|---|---|---|
| 1 | 0.9985 | 0.0032 | 0.04 | 0.24 | $-1.61\times10^{-4}$ | 0.26 |
| 2 | 0.9991 | 0.0032 | 0.02 | 0.25 | $-1.61\times10^{-4}$ | 0.24 |
| 3 | 0.9992 | 0.0032 | -0.03 | 0.23 | $-1.61\times10^{-4}$ | 0.11 |

### *4.3 History of comparisons between BIPM SRP27, SRP28 and CHMI SRP17*

Results of the three comparisons with CHMI ozone standard performed since the first one in December 2002 are displayed in Figure 2. The slopes $a_1$ of the linear relation $x_{SRPn} = a_0 + a_1\, x_{SRP27}$ are represented together with their associated uncertainties calculated at the time of each comparison.

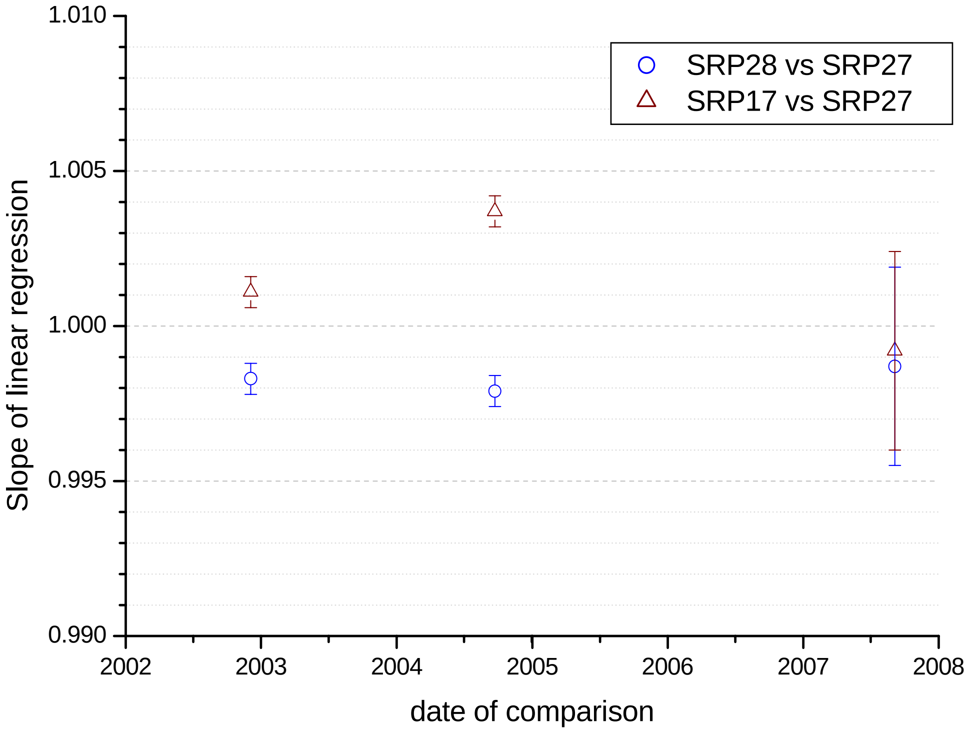

*Figure 2 : Results of the three comparisons between SRP27, SRP28 and SRP17 realised at the BIPM since December 2002. Uncertainties are calculated at k=1, with the uncertainty budget in use at the time of each comparison.*

The benefits of the studies performed in the time between the two last comparisons appear clearly. Although the SRPs were operating within their specifications during the two first comparisons, they suffered from an underestimated uncertainty budget, together with the presence of biases not corrected at that time. Correcting the biases by upgrading the instruments or by numerical correction, and considering the residual biases within the uncertainty budget lead to better agreement between the measurement results from both instruments. In particular, CHMI SRP17 measurement values are now closer to those of BIPM SRP27 than ever before.

Figure 2 also shows that SRP27 and SRP28 agreement was well maintained during the last 5 years, with no more than 0.1% of variation.

## 5. Uncertainty budgets

Since the last comparison, the uncertainty budget for a BIPM SRP has been updated following the study reported in [4]. The values of the principal components of the uncertainty are given in Table 3. SRP27, SRP28 and SRP31 have the same uncertainty budget. The CHMI provided an uncertainty budget for SRP17 reported in Table 4. The uncertainty components have been combined according to the Guide to the Expression of Uncertainty in Measurement [7] .

*Table 3 : SRP27, SRP28 and SRP31 uncertainty budget*

| **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 | 0.052 cm | $-\frac{x}{L_{opt}}$ | $2.89\times10^{-3}x$ |
| | Repeatability | Normal | 0.01 cm | | | |
| | Correction factor | Rect | 0.052 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 $\sigma$** | Hearn value | | $1.22\times10^{-19}$ cm²/molecule | $1.22\times10^{-19}$ cm²/molecule | $-\frac{x}{\sigma}$ | $1.06\times10^{-2}x$ |

*Table 4 : SRP17 uncertainty budget*

| **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 | 0.005 cm | 0.052 cm | $-\frac{x}{L_{opt}}$ | $2.89\times10^{-3}x$ |
| | Variability | Rectangular | 0.004 cm | | | |
| | Divergence | Rectangular | 0.052 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 $\sigma$** | Hearn value | | $1.22\times10^{-19}$ cm²/molecule | $1.22\times10^{-19}$ cm²/molecule | $-\frac{x}{\sigma}$ | $1.06\times10^{-2}x$ |

### *5.1 Simple expression of the uncertainty*

To obtain a simple form for the combined standard uncertainty $u(x)$, the measurement equation

$$x = \frac{-1}{2\sigma L_{opt}} \frac{T}{P} \frac{R}{N_A} \ln(D) \tag{6}$$

can to be written :

$$\boldsymbol{x} = \boldsymbol{B} \ln(\boldsymbol{D}) \tag{7}$$

where :

$$x = \frac{-1}{2\sigma L_{opt}} \frac{T}{P} \frac{R}{N_A} \tag{8}$$

and is constant for a given temperature and pressure.

So that the uncertainty contribution from the ratio of intensities $D$ (to the combined standard uncertainty of $x$) can be written:

$$u_D = \frac{u(D)x}{D\,ln(D)} = \frac{u(D)B}{D} \approx u(D)B \tag{9}$$

Since for the measurement range (0 – 800) nmol/mol:

$$D \approx 1, \tag{10}$$

and the combined standard uncertainty $u(x)$ :

$$u(x) = \sqrt{\left(u(D)B\right)^2 + \left(\left(\frac{u(2L_{opt})}{L_{opt}}\right)^2 + \left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(T)}{T}\right)^2\right)x^2} \tag{11}$$

The application of equation 11 for SRP17, SRP28 and SRP28 gives the same expression (where the numerical values of $x$ are for ozone mole fractions given in units of nmol/mol) :

$$u(x_{\mathrm{SRP}n}) = \sqrt{(0.28)^2 + \left(2.92 \cdot 10^{-3} x\right)^2} \tag{12}$$

Note that taking into account the uncertainty on the absorption cross-section, this equation becomes:

$$u(x_{\mathrm{SRP}n}) = \sqrt{(0.28)^2 + \left(1.1 \cdot 10^{-2} x\right)^2} \tag{13}$$

*5.2 Covariance terms*

When considering the SRP measurement equation, it appears that there are correlations in between the results of two measurements performed at two different ozone mole fractions with the same SRP. This should be taken into account when a generalized least-squares regression is performed on measurements carried out with an SRP.

The general expression of the covariance terms between two measurement results $x_i$ and $x_j$ given by the GUM (Section F.1.2.3 equation F.2) is:

$$\boldsymbol{u}(\boldsymbol{x}_i, \boldsymbol{x}_j) = \sum_{l=1}^{L} \left( \frac{\partial}{\partial \boldsymbol{q}_l} \boldsymbol{x}_i \right) \left( \frac{\partial}{\partial \boldsymbol{q}_l} \boldsymbol{x}_j \right) \boldsymbol{u}(\boldsymbol{q}_l)^2 \tag{14}$$

Where the $q_l$ are common variables in between $x_i$ and $x_j$.

The common variables between $x_i$ and $x_j$ are the temperature $T$, the pressure $P$, and the optical path length $L_{opt}$. For those three variables, the partial derivate of $x_i$ takes the same expression:

$$\frac{\partial \boldsymbol{x}_i}{\partial \boldsymbol{q}_l} = \frac{\boldsymbol{x}_i}{\boldsymbol{q}_l} \tag{15}$$

So that:

$$\boldsymbol{u}(\boldsymbol{x}_i, \boldsymbol{x}_j) = \sum_{l=1}^{L} \left( \frac{\boldsymbol{x}_i}{\boldsymbol{q}_l} \right) \left( \frac{\boldsymbol{x}_j}{\boldsymbol{q}_l} \right) \boldsymbol{u}(\boldsymbol{q}_l)^2 \tag{16}$$

$$\boldsymbol{u}(\boldsymbol{x}_i, \boldsymbol{x}_j) = \boldsymbol{x}_i \cdot \boldsymbol{x}_j \sum_{l=1}^{L} \left( \frac{\boldsymbol{u}(\boldsymbol{q}_l)^2}{\boldsymbol{q}_l^2} \right) \tag{17}$$

Or, with the variables $q_l$ expressed:

$$\boldsymbol{u}(\boldsymbol{x}_i, \boldsymbol{x}_j) = \boldsymbol{x}_i \cdot \boldsymbol{x}_j \left( \frac{\boldsymbol{u}^2(\boldsymbol{T})}{\boldsymbol{T}^2} + \frac{\boldsymbol{u}^2(\boldsymbol{P})}{\boldsymbol{P}^2} + \frac{\boldsymbol{u}^2(\boldsymbol{L}_{\boldsymbol{opt}})}{\boldsymbol{L}_{\boldsymbol{opt}}^2} \right) \tag{18}$$

This can be written:

$$\boldsymbol{u}(\boldsymbol{x}_i, \boldsymbol{x}_j) = \boldsymbol{x}_i \cdot \boldsymbol{x}_j \cdot \boldsymbol{u}_b^2 \tag{19}$$

Where:

$$\boldsymbol{u}_b^2 = \frac{\boldsymbol{u}^2(\boldsymbol{T})}{\boldsymbol{T}^2} + \frac{\boldsymbol{u}^2(\boldsymbol{P})}{\boldsymbol{P}^2} + \frac{\boldsymbol{u}^2(\boldsymbol{L}_{opt})}{\boldsymbol{L}_{opt}{}^2} \qquad (20)$$

The value of $u_b$ for BIPM SRPs is given by the expression of the measurement uncertainty: $u_b = 2.92\times10^{-3}$. It has been taken into account when calculating the least-square regression parameters. CHMI chose to let this covariance term to zero for SRP17.

## 6. Conclusions

For the third time in 5 years, a direct comparison between CHMI national standard SRP17 and the BIPM reference standard SRP27 has been conducted at the BIPM. Following the study of biases in SRP measurement results conducted by NIST and BIPM in 2006, both instruments were upgraded before this comparison. As expected from the results of previous studies, the agreement between them was improved. The measurement range of SRP17 at the CHMI is (10 to 870) nmol/mol. This entire range was examined during the comparison, and the relative difference between CHMI SRP17 and BIPM SRP27 measurement results was found to be 0.08% on average and much smaller than their combined measurement uncertainties.

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