

Bureau International des Poids et Mesures

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**by**

**J. Viallon, P. Moussay and R.I. Wielgosz  
BIPM**

**and**

**J. Novak and M. Vokoun  
CHMI**

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# Comparison of Ozone Reference Standards of the CHMI and the BIPM, September 2004

By J. Viallon\*, P. Moussay\*, R.I. Wielgosz\*, J. Novak\*\* and M. Vokoun\*\*

\* Bureau International des Poids et Mesures, F-92312 Sèvres Cedex

\*\* Czech Hydrometeorological Institute, Prague, Czech Republic

## 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 800 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 two 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 two instruments maintained at the BIPM, and used in this comparison, have the serial numbers SRP27 and SRP28. 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:

$$C = \frac{-1}{2\alpha L} \frac{T_{\text{mes}}}{T_{\text{std}}} \frac{P_{\text{std}}}{P_{\text{mes}}} \ln(D) \quad (1)$$

where

- $\alpha$  is the absorption cross-section of ozone at 253.7nm in standard conditions of temperature and pressure. The value used is:  $1.1476 \times 10^{-17} \text{ cm}^2/\text{molecule}$  [3].
- $L$  is the optical pathlength of one of the cells,
- $T_{\text{mes}}$  is the temperature measured in the cells,
- $T_{\text{std}}$  is the standard temperature (273.15 K),
- $P_{\text{mes}}$  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

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

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:

$$x = \frac{-1}{2\alpha L} \frac{R}{N_A} \frac{T_{\text{mes}}}{P_{\text{mes}}} \ln(D) \quad (3)$$

where

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

### 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  $1.1476 \times 10^{-17} \text{ cm}^2/\text{molecule}$ , 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. Estimates for the uncertainty of the absorption cross section vary, with a conservative estimate being 1.5 % [3] at a 95% level of confidence.

### 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  $\text{O}_2$  molecules contained in purified air using radiation at 185 nm. The amount of  $\text{O}_3$  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 0.2 nmol/mol to 1000 nmol/mol of ozone in air.

### 3.4 Comparison of SRPs at the BIPM

In this comparison, two of the BIPM SRPs have been compared against the instrument of the guest laboratory. The comparability 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 ozonized air 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  $3 \mu\text{mol}/\text{mol}$ . 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 ozonized air to the SRPs. The two columns of this manifold are vented to atmospheric pressure.

A comparison between SRPs consists of producing ozonized air 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.

### *3.5 Analysis of the measurement points by generalised least-square regression*

The comparability of 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 B\_Least, recommended by the ISO standard 6143:2001 is used [4]. 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:

$$x_{\text{SRP}n} = a_0 + a_1 x_{\text{SRP}27} \quad (4)$$

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 parameters to validate the fitting function.

Although correlations between measurements performed with the same instrument at different ozone mole fractions exist, they are not included in the calculations. For that reason, the uncertainties on the parameters may be slightly under-evaluated.

## **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 ten comparison runs between SRP27, SRP28 and SRP17 were performed. Ozone was generated using the Environics 6100 generator with an airflow of 8 L/min. The ozone mole fraction range covered during this exercise was (0 to 800) nmol/mol. The result of one of these ten runs is presented in detail in the section 4.1. The repeatability of the results over the ten runs is shown in section 4.2, and the stability of the BIPM standards in section 4.3.

#### 4.1 Results of one comparison run

The result of the fourth of the ten recorded runs is shown in Figure 1. The comparability of SRP17 and SRP27 is given by the result of the generalised least-square regression:

$$x_{\text{SRP17}} = -0.08 + 1.0035 \cdot x_{\text{SRP27}} \quad (5)$$

The uncertainties on the parameters of the regression are given in Table 1, as well as the covariance between the two parameters.

*Table 1 : Parameters of the generalised least-square regression performed on SRP17-SRP27 comparison results*

<b>Slope <math>a_1</math></b>	<b><math>u(a_1)</math></b>	<b>Intercept <math>a_0</math></b>	<b><math>u(a_0)</math></b>	<b><math>\text{cov}(a_0, a_1)</math></b>
1.0035	0.0005	-0.08 nmol/mol	0.21 nmol/mol	$-7.63 \times 10^{-5}$

Compared to the previous comparison performed in December 2002, there is an increase of +0.0024 in the value of the slope, and +0.06 nmol/mol in the value of the intercept. However, the agreement between SRP17 and SRP27 is still better than 0.5% on the concentration range (100 to 1000) nmol/mol and better than 1 nmol/mol on the range (0 to 100) nmol/mol, which are the specifications by the NIST for SRP comparisons [2].

In order to validate the regression fit, the difference between the measured and fitted value for each mole fraction should be smaller or equal to the expanded combined standard uncertainty of these values. In Figure 2, the values  $\Delta x = (x_{\text{predicted}} - x_{\text{measured}})$  for SRP27 and SRP17 are plotted, and in each case are smaller in magnitude than the expanded standard uncertainties shown in the same figure. Another way to validate the fit is to consider the goodness-of-fit  $F$  which is also calculated by the program. In this example,  $F=0.41$ . As it is less than 2, the function described in (5) can be considered as a good fit of the measurement points.

Figure 1 : Results of one comparison between SRP17 and SRP27 : linear regression fit of the measurement points.

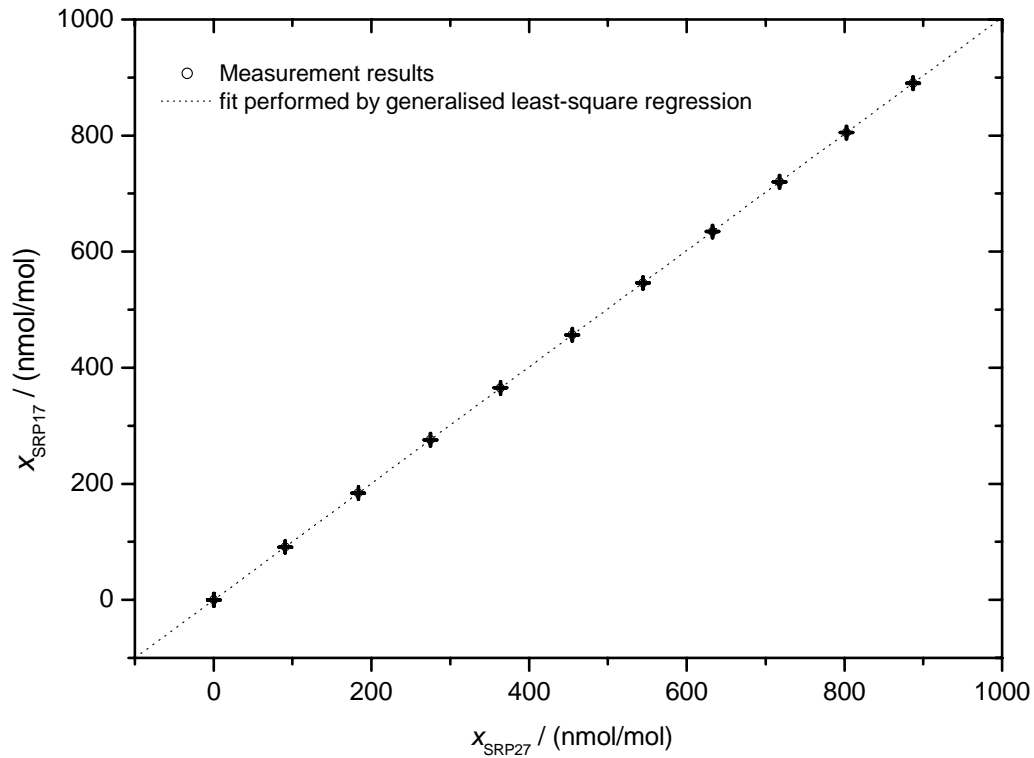
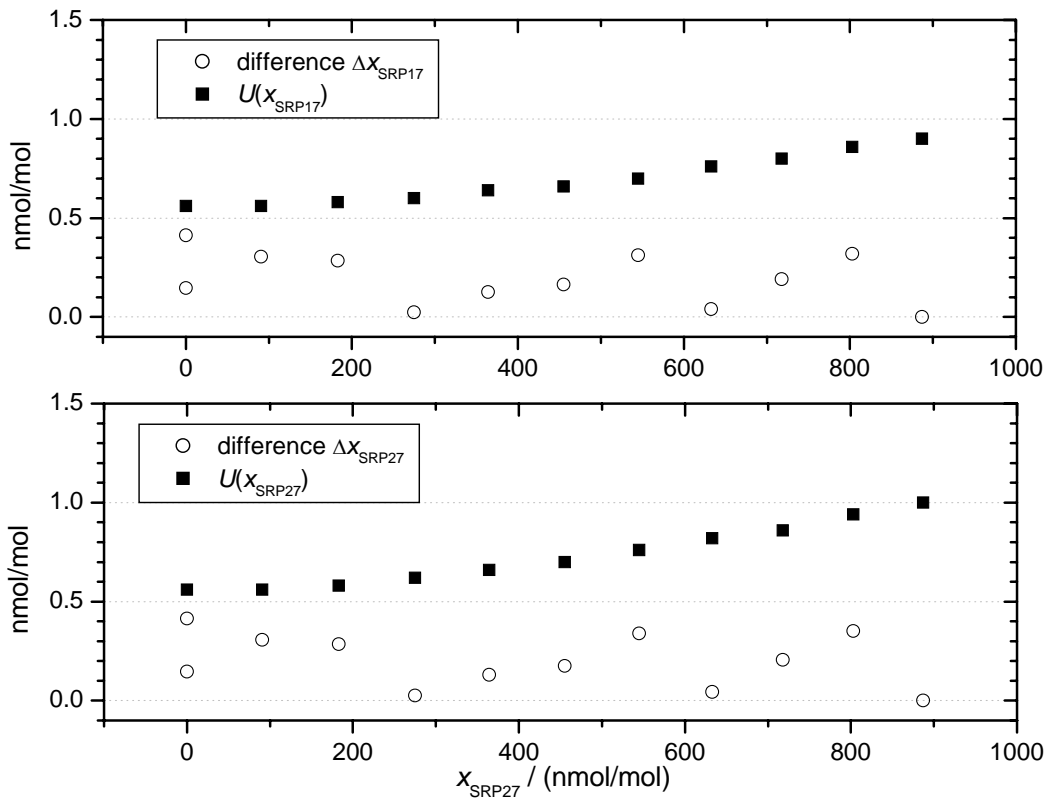


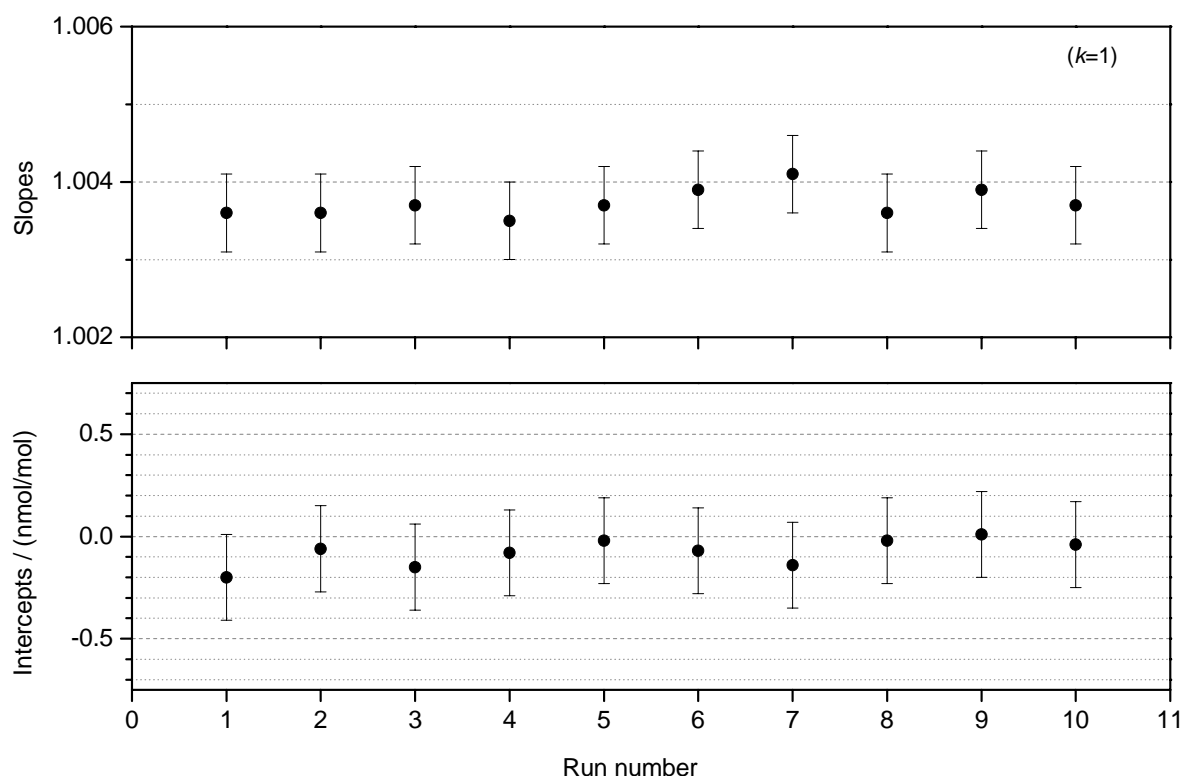
Figure 2 : Difference  $\Delta$  between the calculated and measured points, in  $x$  ( $x_{\text{SRP27}}$ ) and  $y$  ( $x_{\text{SRP17}}$ ), compared with the expanded standard uncertainties on the measured point.



## 4.2 Repeatability

Figure 3 shows the results of the ten comparison runs. The two parameters of the least-square regression fits are plotted versus the run number. The error bars represent the associated standard uncertainties ( $k=1$ ). The maximum changes observed during this period were 0.0006 in the value of the slopes and 0.21 nmol/mol in the value of the intercept.

Figure 3 : Parameters of the least-square regression performed on the ten comparison runs recorded between SRP17 and SRP27



## 4.3 Stability of SRP28 and SRP27

In order to demonstrate the stability of the two BIPM SRPs, comparisons between SRP28 and SRP27 were performed prior to and after the comparison with SRP17. Measurements were performed on 17/09/04, 22/09/04 and 05/10/04, respectively. Results of these comparisons are shown in Figure 4. All the comparisons were performed using the Environics 6100 ozone generator. During the series of runs recorded on 05/10/04, the ozone mole fraction range was (0 to 500) nmol/mol, instead of (0 to 800) nmol/mol for the two first series. This explains the higher uncertainties on the slopes calculated with the generalised least-square regression. The maximum changes observed during this period were 0.0013 in the value of the slopes and 0.34 nmol/mol in the value of the intercepts.



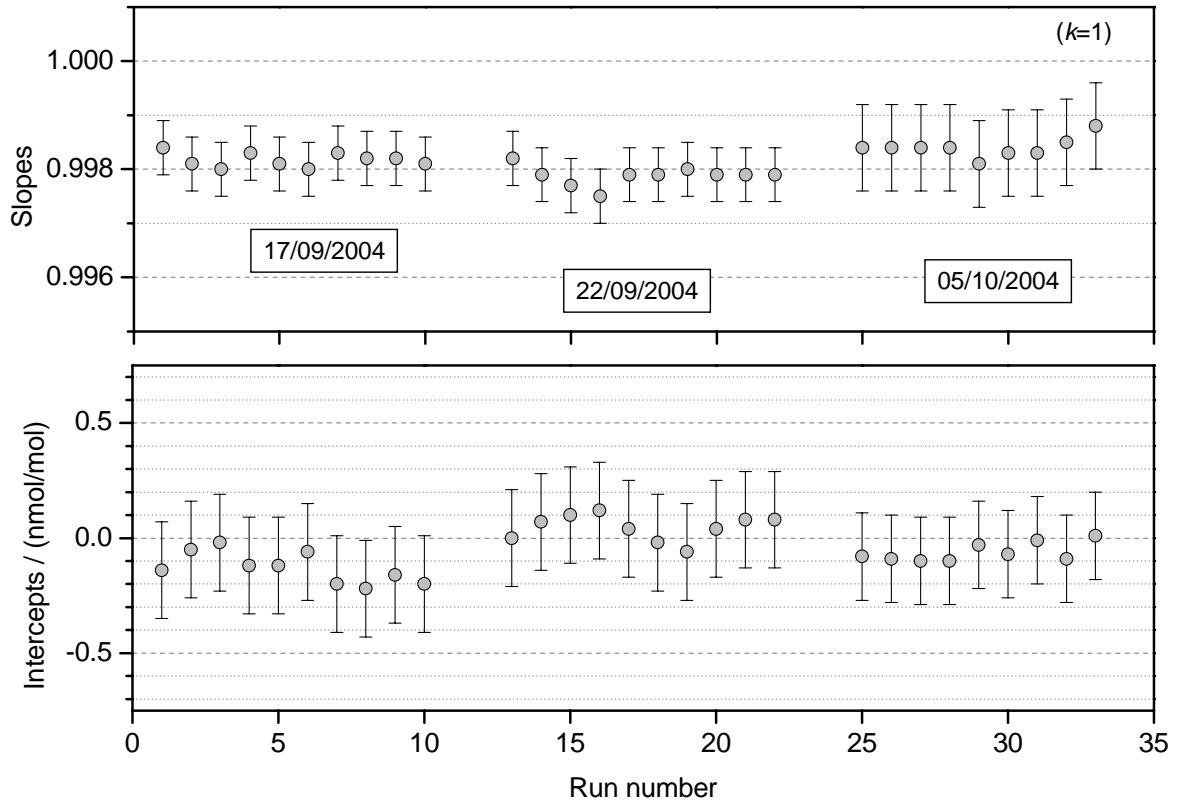


Figure 4 : Results of comparison between SRP28 and SRP27 before, during and after the CHMI-BIPM comparison.

## 5. Uncertainty budget

The uncertainty budget for an SRP has been detailed in a previous report [1]. The values of the principal components of the uncertainty are given in Table 2 for the three SRPs. SRP27 and SRP28 have the same uncertainty budget. The CHMI gave slightly different values for SRP17. The uncertainty components have been combined according to the Guide to the Expression of Uncertainty in Measurement [5].

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

$$x = \frac{-1}{2\alpha L} \frac{R}{N_A} \frac{T_{\text{mes}}}{P_{\text{mes}}} \ln(D) \quad (6)$$

can to be written :

$$x = B \ln(D) \quad (7)$$

where :

$$B = \frac{-1}{2\alpha L} \frac{R}{N_A} \frac{T_{\text{mes}}}{P_{\text{mes}}} \quad (8)$$

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:

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

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

$$D \approx 1, \quad (10)$$

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

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

Table 2 : Uncertainty budget

Component (y)	Standard uncertainty $u(y)$		Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to $u(x)$ $ c_i  \cdot u(y)$
	SRP17	SRP27 and SRP28		
Optical Path (2L)	0.02 cm	0.014 cm	$-\frac{x}{2L}$	$\frac{u(2L) \cdot x}{2L}$
Pressure (P)	0.034 kPa	0.034 kPa	$-\frac{x}{P}$	$\frac{u(P) \cdot x}{P}$
Temperature (T)	0.07 K	0.087 K	$\frac{x}{T}$	$\frac{u(T) \cdot x}{T}$
Ratio of intensities (D)	$1.43 \times 10^{-5}$	$1.4 \times 10^{-5}$	$\frac{x}{D \ln(D)}$	$\frac{u(D) \cdot x}{D \ln(D)}$
Absorption Cross section ( $\alpha$ )	-	-		-

The application for SRP17 ( $L = 89.5$  cm), with a measurement temperature equal to 295 K and a measurement pressure equal to 100 kPa gives a numerical equation (where the numerical values of  $x$  are for ozone mole fractions given in units of nmol/mol) :

$$u(x_{\text{SRP17}}) = \sqrt{(0.28)^2 + (3.97 \cdot 10^{-4} x)^2} \quad (12)$$

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

$$u(x_{\text{SRP17}}) = \sqrt{(0.28)^2 + (7.51 \cdot 10^{-3} x)^2} \quad (13)$$

The application for SRP27 and SRP28 ( $L = 89.8$  cm) with the same values of the temperature and pressure gives the numerical equation (without  $u(\alpha)$ ):

$$u(x_{\text{SRP27}}) = \sqrt{(0.28)^2 + (4.64 \cdot 10^{-4} x)^2} \quad (14)$$

These uncertainties have been used to calculate the regression parameters for the fit of measurement results from SRP27 and SRP17. In assessing the degree of equivalence of the standards (SRPs) the difference between the calculated slope 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.  $|a_0| < 2u(a_0)$ . However, the calculated value of the slope differs from unity by a value greater than twice the uncertainty in the slope; i.e.  $|1-a_1| > 2 u(a_1)$ . The difference from unity is found to be 0.35%, which equates to the relative difference between ozone mole fractions measured by SRP27 and SRP17. The expanded uncertainty in the value of the slope is 0.1%. This result indicates that either the uncertainty in the regression parameter or the uncertainty budget components are being underestimated. The former may arise since correlations between measurements have not been taken into account. Both issues are being studied as part of the CCQM-P28 comparison coordinated by the BIPM. The difference of 0.35 % between SRP17 and SRP27 is however considerably smaller than the operational specifications of the SRP, which are stated as having with an expanded combined uncertainty (at  $k = 2$ ) of 2 nmol/mol over the range (0 to 100) nmol/mol, and a combined relative expanded uncertainty of 2 % over the range (100 to 1000) nmol/mol.

## 6. Conclusions

The comparison has demonstrated the level of agreement of SRP17 with the ozone reference standards SRP27 and SRP28. Consideration of the total measurement uncertainty, including the contribution from the absorption cross section, confirms that SRP17 is operating within its specifications, with an expanded combined uncertainty (at  $k = 2$ ) of 2 nmol/mol over the range (0 to 100) nmol/mol, and a combined relative expanded uncertainty of 2 % over the range (100 to 1000) nmol/mol.

## 7. References

- [1] R. Wielgosz and J. Viallon, Comparison of Ozone Reference Standards of the CHMI and the BIPM, 2003, *BIPM Report-2003/03*, 11 pp.
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- [5] Guide to the Expression of Uncertainty in Measurement (ISO, Geneva, 1995).