

Bureau International des Poids et Mesures

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

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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 800 nmol/mol. The reference standards show agreement that is consistent with an evaluation of the uncertainty of the measurements.

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. Both institutes maintain Standard Reference Photometers (SRPs), developed by the National Institute of Standards and Technology (NIST), as their reference standards. This is the first comparison of SRPs performed at the BIPM. 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 sections 4 and 5.

2. Quantities and Units

A number of quantities can be used to express the composition of mixtures, and this is true within the field of ambient ozone measurements. In this report the measurand is the mole fraction of ozone in dry 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 three SRPs built by the National Institute of Standards and Technology (NIST). More details on the instrument principle and its capabilities can be found in [1]. 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 SRP is dedicated to the measurement of the ozone concentration in air at ambient level. The measurement 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 Lambert-Beer 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

α is the absorption cross-section of ozone at 253.7nm in standard conditions of temperature and pressure. The value used is: $1.1476 \times 10^{-21} \text{ m}^2$ [1].

L is the optical pathlength of one of the cells,

T_{mes} is the temperature measured in the cells,

T_{std} is the standard temperature (273.15 K),

P_{mes} is the pressure measured in the cells,

P_{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_{ozone} is the UV radiation intensity measured in the cell when containing ozonized air, and

I_{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 % [2] 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. Each SRP system includes an ozone generator. This generator is based on the photolysis of O_2 molecules contained in air using radiation at 185 nm. The amount of O_3 molecules produced depends on the radiation intensity and the flow rate of air. In the SRP, 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 nmol/mol to 1000 nmol/mol of ozone in air.

3.4 Comparison of SRPs at the BIPM

The BIPM has operated three SRPs since their installation in April 2002. 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 $3 \mu\text{mol/mol}$. 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 appropriately 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 (close

to 1000 nmol/mol) for a sufficient period of time to avoid ozone losses inside the SRPs during the measurement runs.

The comparability of two SRPs is evaluated with a simple linear regression fit performed on the two sets of measured 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:

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

The uncertainty budget corresponding to the measurement is discussed in section 6. A more rigorous treatment of the comparison data would utilize a generalized least-squares regression fit between the variables, taking into account the uncertainties on both variables. This kind of treatment is being implemented and will be used for the future comparisons. It had been agreed with the CHMI that for this particular comparison the data would be analysed with a simple linear regression fit, which is consistent with current practice for such comparisons. The result of a comparison run between two instruments is reported as the slope and the intercept of the linear regression fit.

4. CHMI-BIPM SRP 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 seven comparison runs between SRP27, SRP28 and SRP17 was performed. Ozone was generated using the generator of the SRP28 system, with an airflow of 7.5 L/min. The ozone mole fraction range covered during this exercise was (0 to 500) nmol/mol. The result of one of these seven runs is presented in detail in Figure 1. The repeatability of the results over the seven runs is demonstrated in Figure 2.

4.1 Results of a comparison run

The result of the fourth of the seven recorded runs is shown in Figure 1. The comparability of SRP17 and SRP27 is given by the result of the linear regression:

$$x_{\text{SRP}17} = -0.14 + 1.0011x_{\text{SRP}27} \quad (5)$$

The residuals for the fit are shown in the same figure.

4.2 Repeatability

Figure 2 shows the results of the seven comparison runs. The duration of one run is between 2 h and 3 h, with the entire measurement cycle lasting 16 h. The slopes and intercepts of the linear regression fits are plotted versus the time from the first run. The maximum changes observed during this period were 0.0015 in the value of the slopes and 0.2 nmol/mol in the value of the intercept.

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

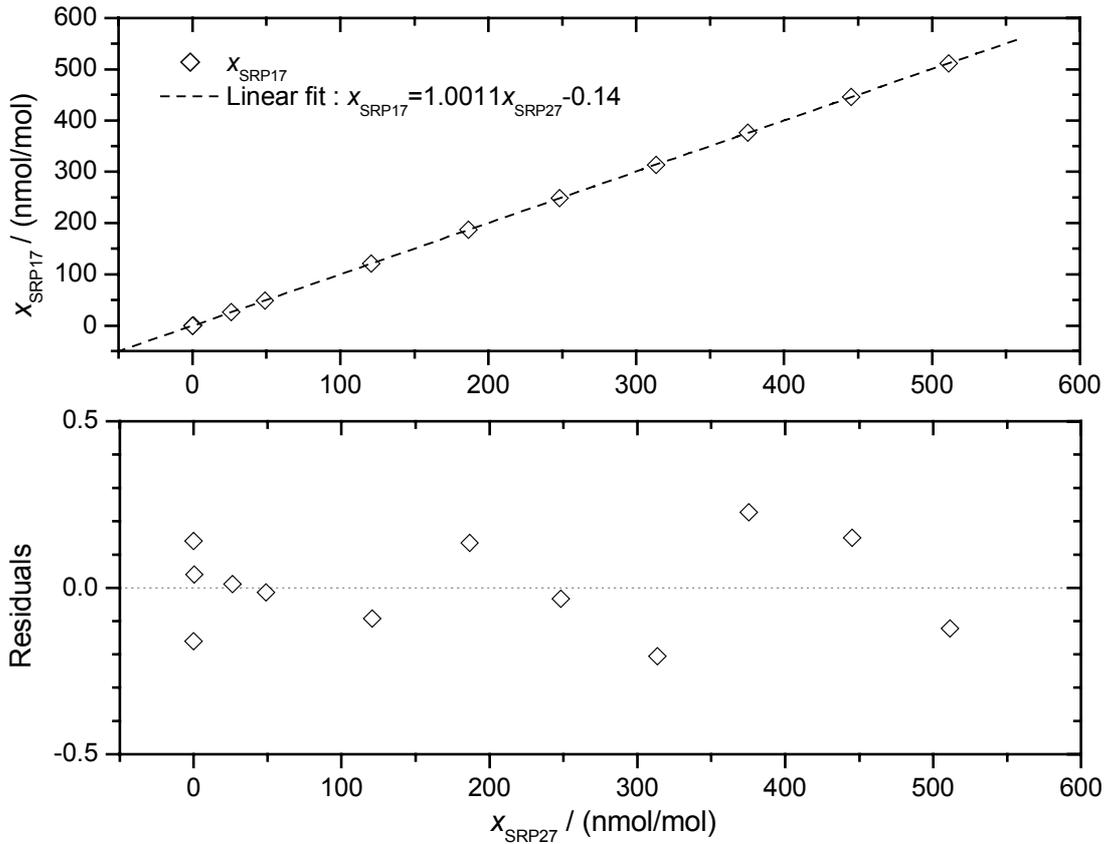
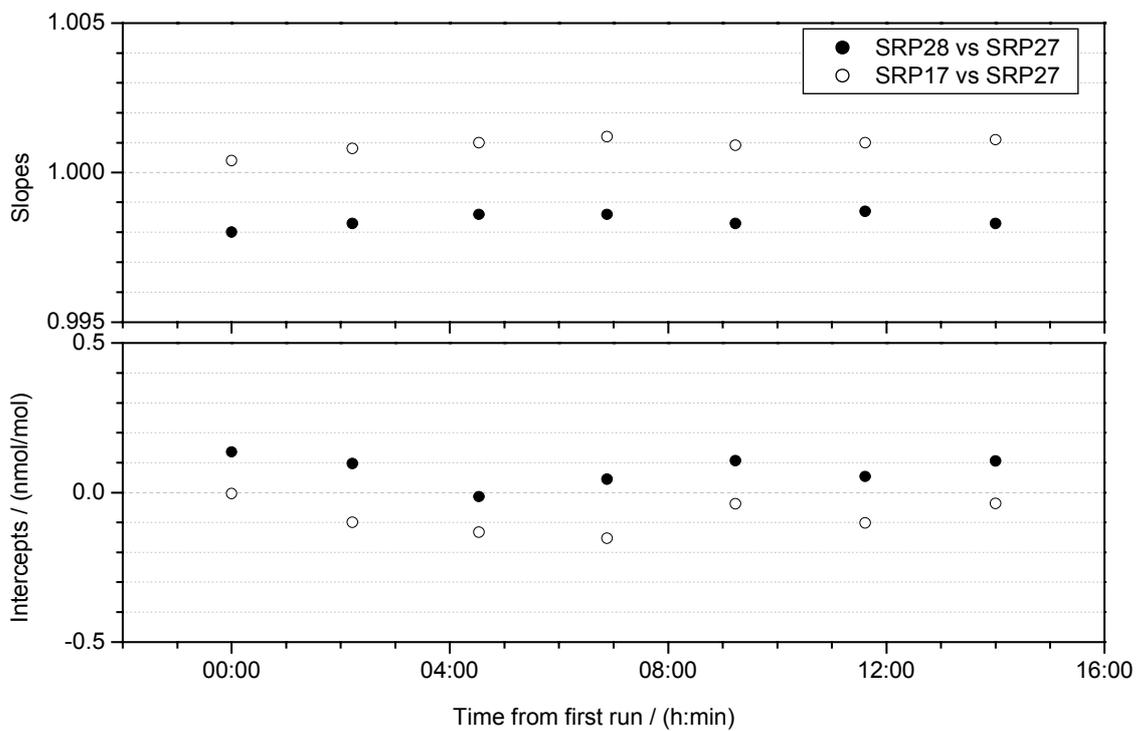


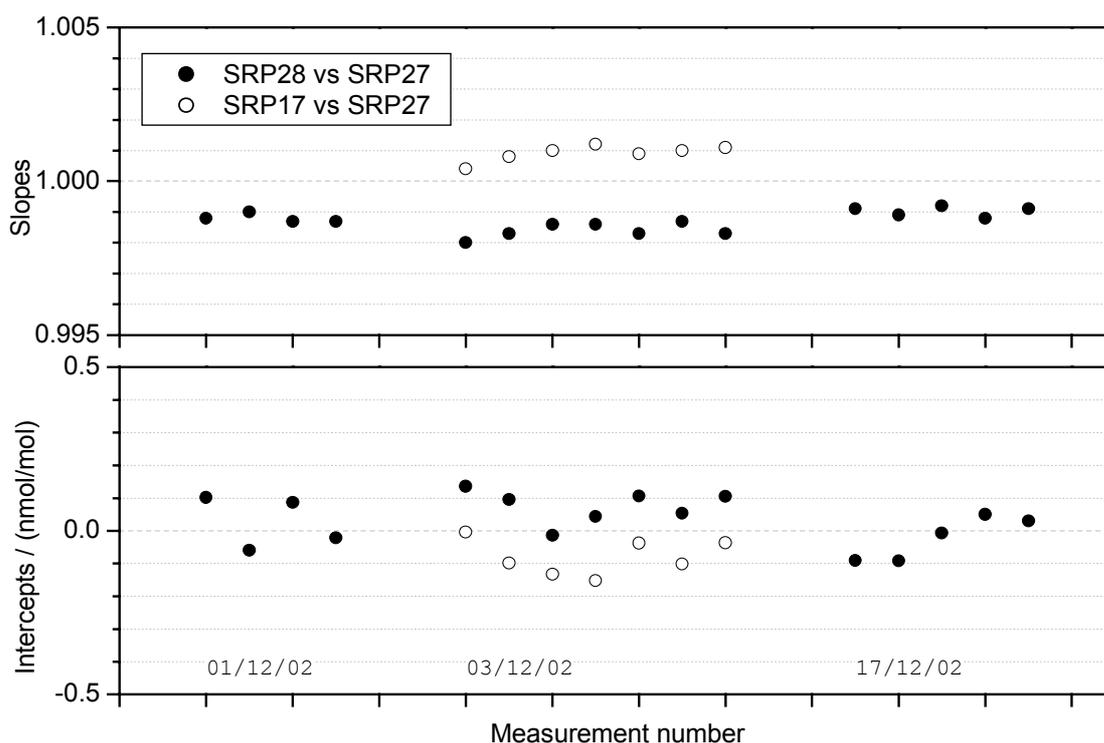
Figure 2 : Slopes and intercepts from the linear regression fits of seven comparison runs performed between SRP17 and SRP27, and SRP28 and SRP27



4.3 Stability of SRP28 and SRP27

In order to demonstrate the stability of the two BIPM SRPs, and also the equivalence of comparisons that involve either two or three instruments, comparisons between SRP28 and SRP27 were performed prior to and after the comparison with SRP17. Measurements were performed on 01/12/02, 17/12/02 and 03/12/02, respectively. Results of these comparisons are shown in Figure 3 together with the results from the CHMI-BIPM comparison. All the comparisons were performed using the SRP28 system ozone generator. The maximum changes observed during this period were 0.0015 in the value of the slopes and 0.2 nmol/mol in the value of the intercepts.

Figure 3 : Results of comparison between SRP28 and SRP27 before, during and after the CHMI-BIPM comparison.



4.4 Extension of the range of the comparison to 800 nmol/mol

A series of comparisons were performed over an extended ozone mole fraction range of (0 to 800) nmol/mol. The comparison runs were performed between two instruments (SRP27 and SRP17) using the ozone generator of SRP28 at a reduced flow rate of 5.5 L/min. Results are shown in Figure 4. The results of the comparison runs performed over the range (0-500) nmol/mol are also depicted. As can be seen on the figure, the comparability between SRP17 and SRP27 is not dependent on the range chosen for the comparison.

5. Additional comparison using the SRP17 system ozone generator

A series of comparisons were performed with the CHMI SRP17 system ozone generator, with an airflow of 7.5 L/min. The goal of this additional comparison was to test the state of the SRP17 system ozone generator, and in particular its stability. Results are shown in Figure 5 together with the results obtained using the SRP28 system ozone generator. The measurements of the three SRPs were compared over the range (0-500) nmol/mol, demonstrating the stability of the SRP17 system ozone generator.

Figure 4 : Slopes and intercepts from linear regression fits of the SRP17-SRP27 comparison results performed over the ozone mole fraction ranges (0-500) nmol/mol and (0-800) nmol/mol.

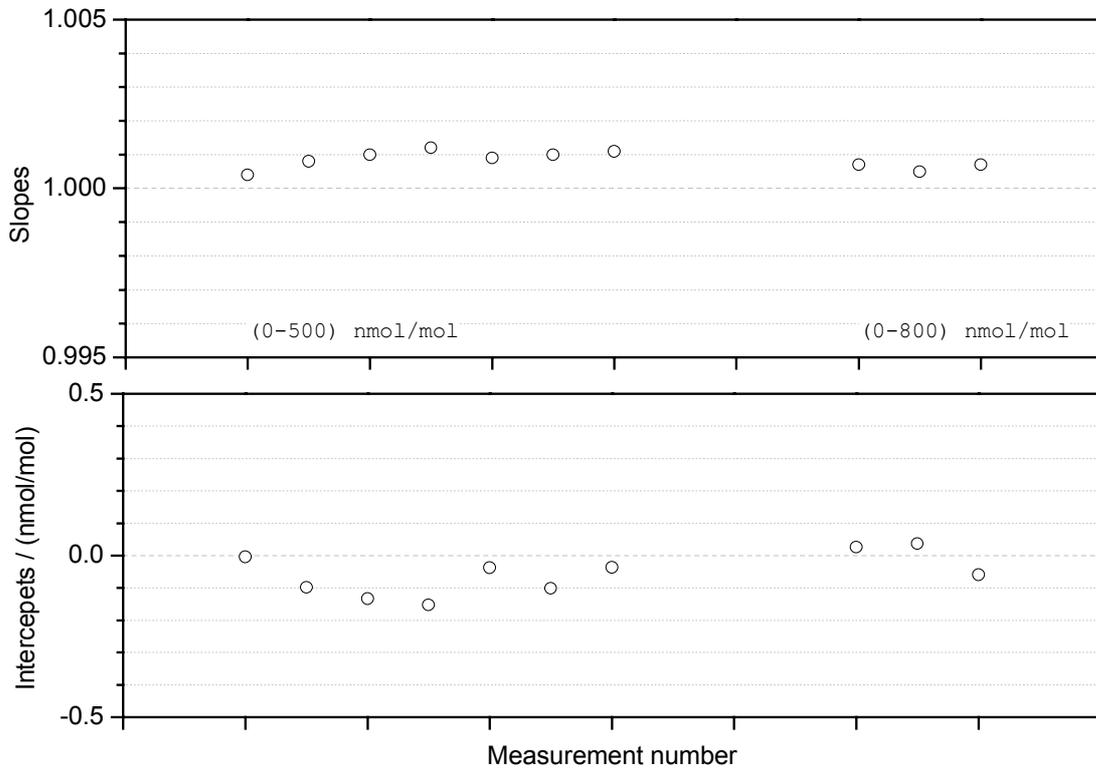
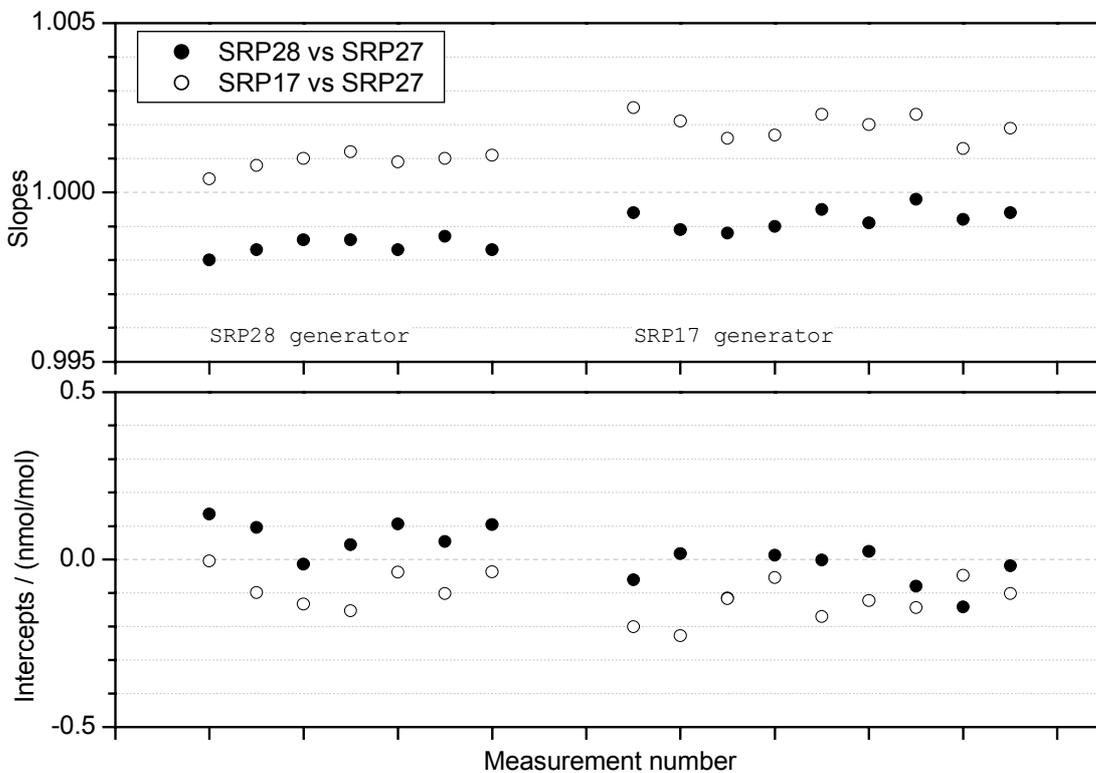


Figure 5 : Results of linear regression fits obtained using the SRP28 system ozone generator and then using the SRP17 system ozone generator.



6. Uncertainty budget

The uncertainty budget for the measurement of ozone mole fractions with an SRP is given in Table 1. The uncertainty components have been combined according to the Guide to the Expression of Uncertainty in Measurement [3]. These uncertainties are calculated at a nominal value of the ozone mole fraction of 200 nmol/mol, for SRP17. The uncertainty budget for SRP27 and SRP 28 would be calculated in a similar manner.

The principal components of the uncertainty budget are:

- Optical path length ($2L$): the optical path is assumed to be identical to the total length of the two cells, each cell length (L) being the distance between the windows enclosing the cell.
- Pressure: the pressure transducer has been calibrated with a stated relative uncertainty of $\pm 0.05\%$ of full scale. Assuming these to be the upper and lower boundaries of a rectangular probability distribution, this corresponds to a standard uncertainty of 0.029 kPa. Furthermore, recent measurements performed at the NIST and at the BIPM showed that the difference of pressure between the two cells within the SRP could have a maximum value of 0.06kPa, leading to an uncertainty of $\frac{0.03}{\sqrt{3}} = 0.017$ kPa in the pressure measurement.
- Temperature: the temperature probe has a stated uncertainty of ± 0.15 K at 295 K [1]. Assuming these to be the upper and lower boundaries of a rectangular probability distribution, this corresponds to a standard uncertainty of 0.087 K.
- Ratio of intensities: the repeatability of this quantity has been estimated from the measurement of this ratio with no flow of reference air or ozonized air within the cells. In the case of SRP17, analysis of 100 measurement points showed a maximum dispersion in these measurements of 5×10^{-5} . Assuming a triangular distribution, which is consistent with this data set, the standard uncertainty of this estimate is 1×10^{-5} . The other component of the uncertainty in D is derived from the uncertainty of the optical frequencies used to calculate D . The value of this standard uncertainty is 8×10^{-6} as explained in more detail in [1].
- Absorption cross-section: all SRPs use the same conventional value, and thus the uncertainty in the calculation below has been set to zero, in order to consider the comparability of two instruments. However, this contribution cannot be neglected when considering the overall uncertainty of the measurement. The more conservative estimate of the relative uncertainty of this quantity is 1.5 % at a 95 % level of confidence.

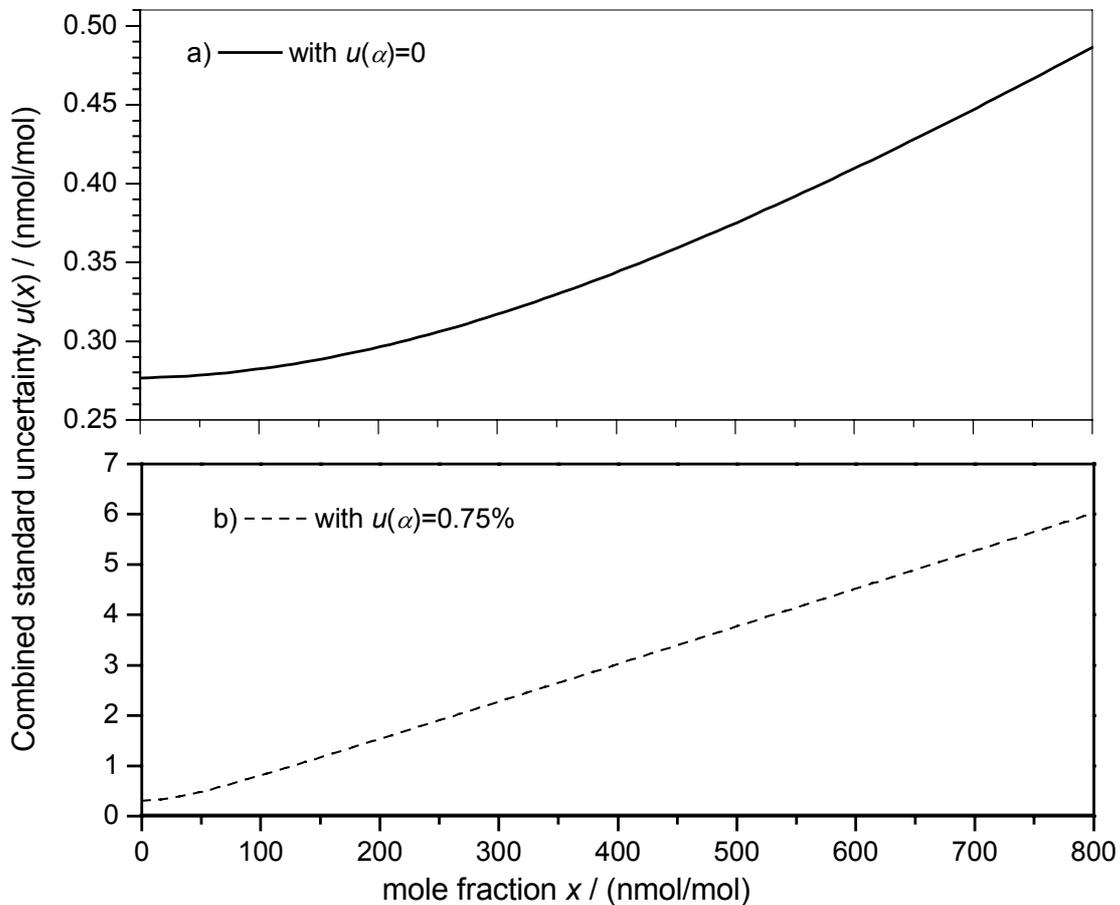
Combing these uncertainties (Table1) results in a standard uncertainty of 0.29 nmol/mol for an ozone mole fraction of 199.27 nmol/mol.

Table 1: Uncertainty budget associated with the measurement of an ozone mole fraction equal to 199.27 nmol/mol with SRP17

Component (y)	Value	Uncertainty $u(y)$				Relative contribution to $u(x)$
		Source	Distribution	Standard Uncertainty	Combined standard uncertainty	
Optical Path $2L$	179.00 cm	Measurement Scale	Rect.	0.0011 cm	0.01 cm	0.01 %
		Repeatability	Normal	0.01 cm		
Pressure P	100 kPa	Pressure gauge	Rect.	0.029 kPa	0.034 kPa	0.03 %
		Difference between cells	Rect.	0.017 kPa		
Temperature T	295 K	Temperature probe	Rect.	0.087 K	0.087 K	0.03 %
Ratio of intensities D	0.99	Scalers resolution	Rect.	8×10^{-6}	1.4×10^{-5}	0.14 %
		Repeatability	Triang.	1.1×10^{-5}		
Absorption Cross section α	1.1476×10^{-17} cm ² /molecule	Conventional value	-	-	-	-
Combined relative standard uncertainty (for the mole fraction , $x = 199.27$ nmol.mol⁻¹)						0.15% ($k=1$)

The calculation has been repeated over the mole fraction range (0-800) nmol/mol, and the results are depicted in Figure 6.

Figure 6: Combined standard uncertainty $u(x)$ of ozone mole fraction measurements with SRP17, with $u(\alpha)=0$ (a) and with $u(\alpha)=0.75\%$ (b).



7. Conclusions

The comparison has demonstrated the level of agreement of SRP17 with the ozone reference standards SRP27 and SRP28. The level of agreement of the standards as demonstrated in the comparison measurements is consistent with the uncertainty calculated for SRP17, depicted in Figure 6a. Consideration of the total measurement uncertainty, including the contribution from the absorption cross section (Figure 6b), confirms that SRP17 is operating within its specifications, with an expanded combined uncertainty (at $k = 2$) of 2 nmol/mol over the range (0-100) nmol/mol, and a combined relative expanded uncertainty (at $k = 2$) of 2 % over the range (100-1000) nmol/mol.

8. Acknowledgements

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9. References

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