Final report, On-going Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with UBA, 2007

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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 the Umweltbundesamt (UBA) 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 mole fraction range of 0 nmol/mol to 500 nmol/mol.

Contents:

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1. Field

Amount of substance.

2. Subject

Comparison of ozone (at ambient level) reference measurement standards.

3. Participants

BIPM.QM-K1 is an on-going key comparison, which is structured as an on-going series of bilateral comparisons. The results of the comparison with the Umweltbundesamt (UBA) are reported here. The list of all participants in BIPM.QM-K1 can be found on the BIPM website[2].

4. Organizing body

BIPM.

5. Rationale

The on-going key comparison BIPM.QM-K1 follows the pilot study CCQM-P28 which included 23 participants and was preformed 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_{nom}: nominal ozone mole fraction in dry air furnished by the ozone generator
- $x_{A,i}$: ith measurement of the nominal value x_{nom} by the photometer A.
- $\bar{x}_A$: the mean of N measurements of the nominal value x_{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_{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 versus the photometer B. $a_{A,B}$ is dimensionless and $b_{A,B}$ is expressed in units of nmol/mol.

[2] http://www.bipm.org/en/scientific/chem/gas_metrology/ozone_comparisons.html

7. Measurements schedule

The key comparison BIPM.QM-K1 is organised in rounds of 2 years. The 2007-2008 round started in January 2007 with a comparison with the NIST. Measurements reported in this report were performed in January 2007 at the BIPM and in March 2007 at UBA.

8. Measurement protocol

The comparison protocol is summarised 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 UBA national standard SRP29 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 January 2007. Then SRP0 was compared with the national standard SRP29 at UBA in October 2007.

A comparison between two (or more) ozone photometers consists of producing ozone-air mixtures at different mole fractions over the required range, and measuring these with the photometers.

8.1. Comparisons at UBA

a). Ozone generation

The air is purified by a commercial purifier system made by MCZ. The compressed air is dried by a heatless dryer and watertrap. The dry compressed air is scrubbed with activated charcoal , molecular sieve and heated catalytic gas purifier (Palladium 350°C). This air is used to provide reference air as well as the ozone-air mixture to each ozone photometer. Ozone is produced using the ozone generator included in SRP29. 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 three days. Characteristics of the instruments were checked at this time following a procedure recommended by NIST. Only temperature and dark count adjustments were made at SRP 0.

One comparison run includes 10 different mole fractions distributed to cover the range, together with the measurement of reference air at the beginning and end of each run. The nominal mole 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 mole fraction x_{nom} furnished by the ozone generator, the standard deviation s_{SRP29} on the set of 10 consecutive measurements $x_{\mathrm{SRP29},i}$ recorded by

SRP29 was calculated. The measurement results were considered as valid if s_{SRP29} was less than 1.5 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 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 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 mole fractions distributed to cover the range, together with the measurement of reference air at the beginning and end of each run. The nominal mole 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 mole fraction x_{nom} furnished by the ozone generator, the standard deviation s_{SRP27} on the set of 10 consecutive measurements $x_{SRP27,i}$ recorded by BIPM-SRP27 was calculated. The measurement results were considered as valid if s_{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 on-going 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 mole fractions measured by the participant standard and the common reference standard. The completed form BIPM.QM-K1-R3-UBA-07 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). For information, the degrees of equivalence at all nominal ozone mole fractions are reported in the same form, as well as the linear relationship between the participant standard and the common reference standard.

11. Deviations from the comparison protocol

The original protocol for comparisons performed via a linking laboratory requested two comparisons to be performed between the participant and the linking laboratory within a reasonable period, in order to asses the transfer standard stability. For practical reasons, a second comparison between UBA and NIST could not be achieved. Instead, comparison between the transfer standard SRP0 and the NIST national standard SRP2 were used.

12. Measurement standards

All instruments included in this comparison were Standard Reference Photometers built by the NIST. More details on the instrument's principle and its capabilities can be found in [2]. The following section describes their measurement principle and their uncertainty budgets.

12.1. Measurement equation of a NIST 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:

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

where

- σ is the absorption cross-section of ozone at 253.7nm in standard conditions of temperature and pressure. The value used is: 1.1476×10^{-17} cm^2/molecule [3].
- L_{opt} is the optical path length of one of the cells,
- T is the measured temperature of the cells,
- T_{std} is the standard temperature (273.15 K),
- P is the measured pressure of the cells,
- P_{std} is the standard pressure (101.325 kPa),
- D is the product of transmittances of two cells, with the transmittance (Tr) of one cell defined as

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

where

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

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

where

- N_{A} is the Avogadro constant, 6.022142×10^{23} mol^{-1}, and
- R is the gas constant, 8.314472 J mol^{-1} K^{-1}

The formulation implemented in the SRP software is:

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

where

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

$$\alpha_{\text{x}} = \sigma \frac{N_{\text{A}}}{R} \frac{P_{\text{std}}}{T_{\text{std}}} \quad (5)$$

12.2. Absorption cross section for ozone

The linear absorption coefficient at standard conditions α_{x} used within the SRP software algorithm is 308.32 cm^{-1}. This corresponds to a value for the absorption cross section σ of 1.1476×10^{-17} cm^2/molecule, rather than the more often quoted 1.147×10^{-17} cm^2/molecule. In the comparison of two SRP instruments, the absorption cross section can be considered to have a conventional value and its uncertainty can be set to zero. However, in the comparison of different methods or when considering the complete uncertainty budget of the method the uncertainty of the absorption cross section should be taken into account. A consensus value of 2.12% at a 95% level of confidence for the uncertainty of the absorption cross section has been proposed by the BIPM and the NIST in a recent publication [4].

12.3. Actual state 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]:

- The SRPs are equipped with a thermo-electric cooling device to remove excess heat from the lamp housing and prevent heating of the cells. Together with a regular calibration of their temperature probe, this ensures the removal of the bias on 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.

12.4. Uncertainty budget of the common reference BIPM-SRP27

The uncertainty budget for the ozone mole 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

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	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89\times10^{-3}x$
	Repeatability	Normal	0.01 cm			
	Correction factor	Rect	0.52 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	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D\ln(D)}$	0.28
	Repeatability	Triangular	1.1×10^{-5}			
Absorption Cross section σ	Hearn value		1.22×10^{-19} cm²/molecule	1.22×10^{-19} cm²/molecule	$-\frac{x}{\sigma}$	$1.06\times10^{-2}x$

Following this budget, as explained in the protocol of the comparison, the standard uncertainty associated with the ozone mole fraction measurement with the BIPM SRPs can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u(x) = \sqrt{(0.28)^2 + (2.92 \cdot 10^{-3} x)^2} \tag{6}$$

12.5. Covariance terms for the common reference BIPM-SRP27

As explained in section 14, correlations in between the results of two measurements performed at two different ozone mole fractions with BIPM-SRP27 were taken into account in the software OzonE. More details on the covariance expression can be found in the protocol. The following expression was applied:

$$\boldsymbol{u}(\boldsymbol{x}_i, \boldsymbol{x}_j) = \boldsymbol{x}_i \cdot \boldsymbol{x}_j \cdot \boldsymbol{u}_\mathrm{b}^2 \tag{7}$$

where:

$$\boldsymbol{u}_\mathrm{b}^2 = \frac{\boldsymbol{u}^2(\boldsymbol{T})}{\boldsymbol{T}^2} + \frac{\boldsymbol{u}^2(\boldsymbol{P})}{\boldsymbol{P}^2} + \frac{\boldsymbol{u}^2(\boldsymbol{L}_\mathrm{opt})}{\boldsymbol{L}_\mathrm{opt}^{\ 2}} \tag{8}$$

The value of u_b is given by the expression of the measurement uncertainty: $u_\mathrm{b} = 2.92 \times 10^{-3}$ or $u_\mathrm{b}^2 = 8.5 \times 10^{-6}$.

12.6. Actual state of the UBA SRP29

Compared to the original design, the UBA SRP29 has been modified to deal with the two biases revealed in [4]. In March 2007, just before this comparison, an "SRP upgrade kit" was installed by NIST at the UBA laboratories. It consists in 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.
- A new set of absorption cells were 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 plane to avoid multiple reflections along the light path. However, to take into account a residual bias due to the beam divergence, the uncertainty is increased by the same amount as in SRP27 and SRP28.

12.7. Uncertainty budget of the UBA SRP29

The uncertainty budget for the ozone mole fraction in dry air x measured by the UBA standard SRP29 in the nominal range 0 nmol/mol to 500 nmol/mol will follow the BIPM/NIST paper [4] (see Table 1) with an additional component based on the temperature probe heating effect. The initial uncertainty can be summarised by the formula:

$$u(x)=\sqrt{(0.28)^2+(2.92\times10^{-3}x)^2} \quad (9)$$

After correcting for the temperature probe heating bias, the final uncertainty is calculated by:

$$u(x)^+=u(x);u(x)^-=u(x)+\left(-0.001\times x\right) \quad (10)$$

Because the BIPM.QM-K1-R3 spreadsheet does not allow the uncertainty to be expressed by different positive and negative amounts, it has been expressed as:

$$u(x)=u(x)+\left(0.001\times x\right) \quad (11)$$

No covariance term for the UBA SRP29 was included in the calculations.

12.8. Transfer standard SRP0

SRP0 uncertainty budget is the same as SRP29.

13. Measurement results and uncertainties

Details of the measurement results, the measurement uncertainties and the standard deviations at each nominal ozone mole fraction can be found in the form BIPM.QM-K1-R3-UBA-07 given in appendix.

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 [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. 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 UBA 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 mole fractions measured by SRP*n* and SRP27 is obtained:

$$x_{\mathrm{SRP}n}=a_0+a_1x_{\mathrm{SRP27}} \quad (12)$$

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-square regression results

The relationship between SRP29 and SRP27 is:

$$x_{\mathrm{SRP29}} = 0.00 + 0.9979 \cdot x_{\mathrm{SRP27}} \qquad (13)$$

with the uncertainties $u(a_0)$ = 0.32 nmol/mol, $u(a_1)$ = 0.0041, cov(a_0, a_1) = -5.01×10^{-4} nmol/mol.

To assess the agreement of the standards from equations 11, 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 both comparisons, 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 mole 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 mole 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_{nom} is defined as:

$$D = x_i - \hat{x}_{\mathrm{SRP27}} \qquad (14)$$

Where x_i is the measurement results of the national standard at the nominal value x_{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:

$$u(D) = \sqrt{u^2(x_i) + u^2(\hat{x}_{\mathrm{SRP27}})} \qquad (15)$$

where $u(x_i)$ is the measurement uncertainty 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 $\overline{x}_{\mathrm{RS}}$ and $\overline{x}_{\mathrm{TS}}$ are fitted using the generalised least square program OzonE, taking into account the associated uncertainties $u(\overline{x}_{\mathrm{RS}})$ and $u(\overline{x}_{\mathrm{TS}})$, as well as covariance terms between the reference standard measurement results.

The parameters $a_{\mathrm{RS,TS}}$ and $b_{\mathrm{RS,TS}}$ of the linear relationship between x_{RS} and x_{TS} ($x_{\mathrm{RS}} = a_{\mathrm{RS,TS}}\, x_{\mathrm{TS}} + b_{\mathrm{RS,T}}$) are calculated as well as their uncertainties.

Then, for each value $\overline{x}_{\mathrm{TS}}$ measured with the transfer standard during its comparison with the national standard, a predicted value $\hat{x}_{\mathrm{RS}}$ for the reference standard is evaluated using the linear relationships between the two instruments calculated above.

The standard uncertainties associated with the predicted values $\hat{x}_{\mathrm{RS}}$ are evaluated according to the equation:

$$u(\hat{x}_{\mathrm{RS}}) = \sqrt{u^2(b_{\mathrm{RS,TS}}) + x_{\mathrm{TS}}^2 \cdot u^2(a_{\mathrm{RS,TS}}) + a_{\mathrm{RS,TS}}^2 \cdot u^2(x_{\mathrm{TS}}) + 2 \cdot x_{\mathrm{TS}} \cdot u(a_{\mathrm{RS,TS}}, b_{\mathrm{RS,TS}})} \quad (16)$$

Where the uncertainty components $u(a_{\mathrm{RS,TS}})$, $u(b_{\mathrm{RS,TS}})$ and $u(a_{\mathrm{RS,TS}}, b_{\mathrm{RS,TS}})$ 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-UBA-07 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 2 : degrees of equivalence of UBA at the ozone nominal mole fractions 80 nmol/mol and 420 nmol/mol

Nominal value	x_i / (nmol/mol)	u_i / (nmol/mol)	x_{SRP27} / (nmol/mol)	u_{SRP27} / (nmol/mol)	D_i / (nmol/mol)	$u(D_i)$ / (nmol/mol)	$U(D_i)$ / (nmol/mol)
80	78.31	0.44	78.58	0.53	-0.28	0.69	1.38
420	419.70	1.68	420.62	2.18	-0.92	2.75	5.50

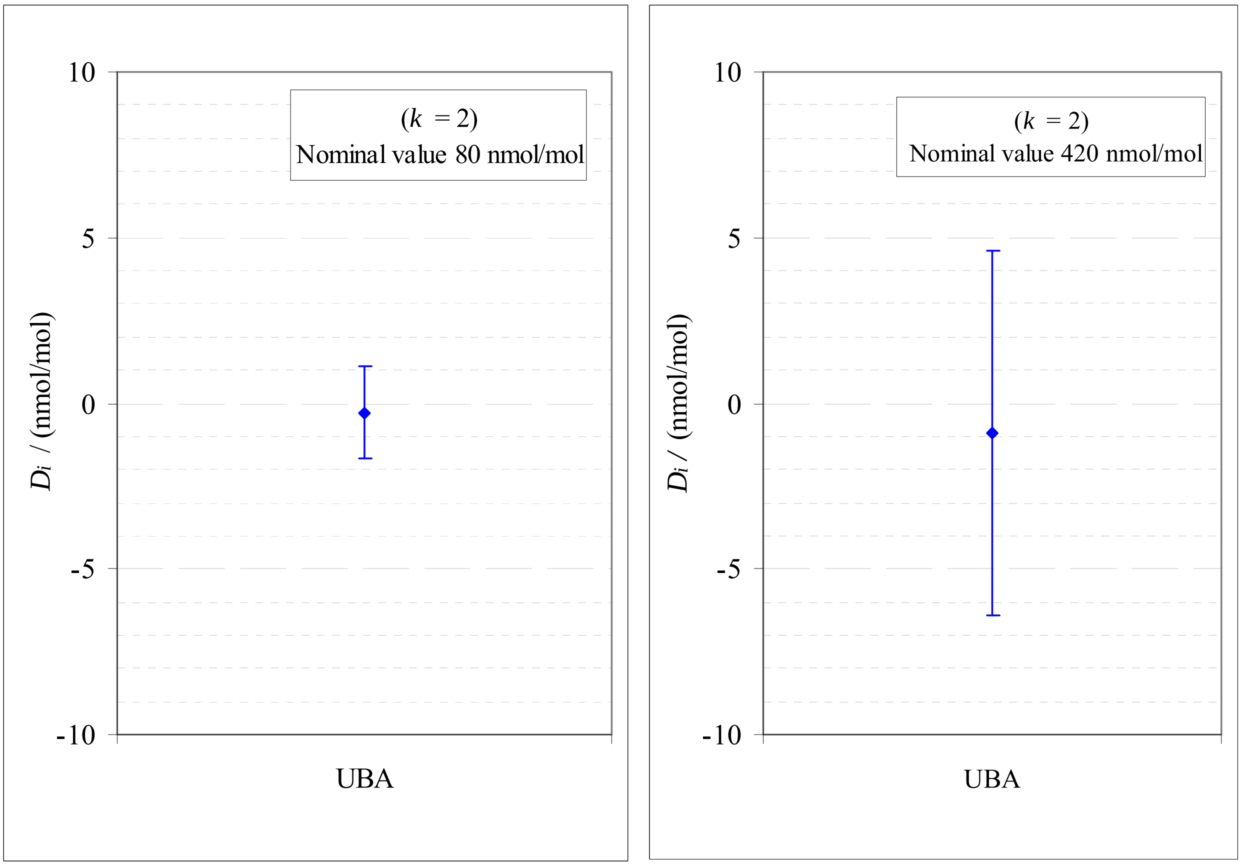


Figure 1: degrees of equivalence of UBA at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol

The degrees of equivalence between the UBA 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

As stated in section 11, the stability of the transfer standard SRP0 could not be assessed using a second comparison with UBA SRP29. Instead, comparisons performed at NIST between SRP0 and SRP2 were analysed. On the period January 2007 to October 2007, a maximum variation of 0.07% on the slope of the relationship between the two instruments has been observed. This is negligible compared to the uncertainties declared in this comparison .

17. History of comparisons between BIPM SRP27, SRP28 and UBA SRP29

Results of the previous comparison performed in 2003 during the pilot study CCQM-P28 are displayed in Figure 2 together with the results of this comparison. 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.

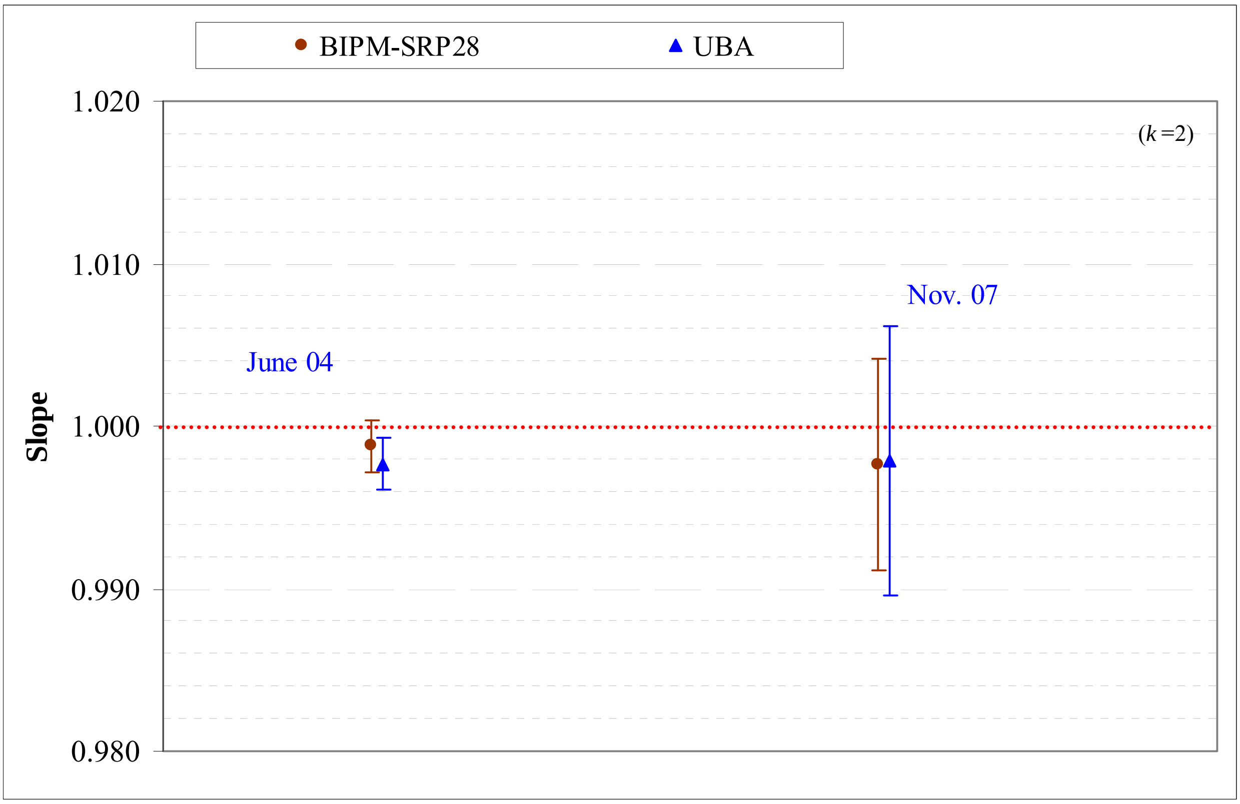


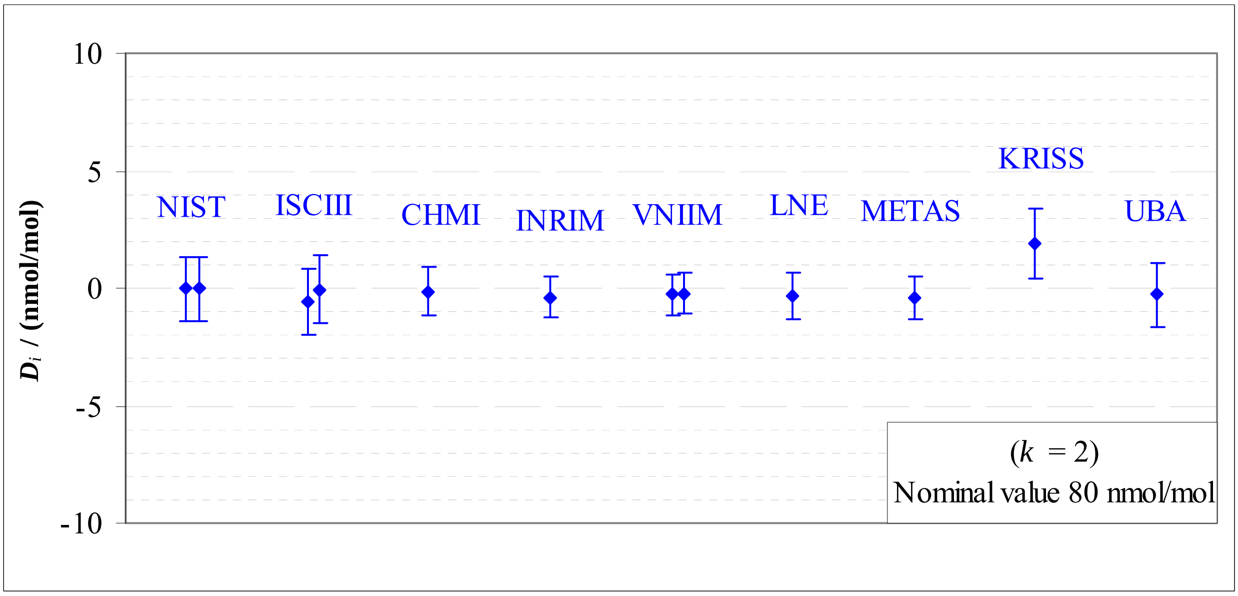
Figure 2: Results of the comparisons between SRP27, SRP28 and UBA-SRP29 realised at the BIPM during the pilot study CCQM-P28 and the key comparison BIPM.QM-K1. Uncertainties are calculated at k=2, with the uncertainty budget in use at the time of each comparison.

Figure 2 shows that the agreement between UBA and BIPM standards has been improved in between June 2004 and March 2007, thanks to an enlargement of their uncertainties. As explained in [4], this larger uncertainty comes from a remaining bias in SRPs. A better agreement among all SRPs in this key comparison exercise was indeed foreseen, compared to the pilot study CCQM-P28.

One noticeable output of this comparison is that the upgrade of both UBA-SRP29 and BIPM-SRP27 did not change the slope of the linear relationship between them. This finding was different for some other SRPs already compared in BIPM.QM-K1, for example in CHMI SRP17 where a decrease of 0.5% has been observed [7]. Forthcoming results of upgrades performed in other SRPs will be interesting to analyse, for a better understanding of the remaining bias.

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

Graphs of equivalence including previous participants with published results [8] are displayed in Figure 3.



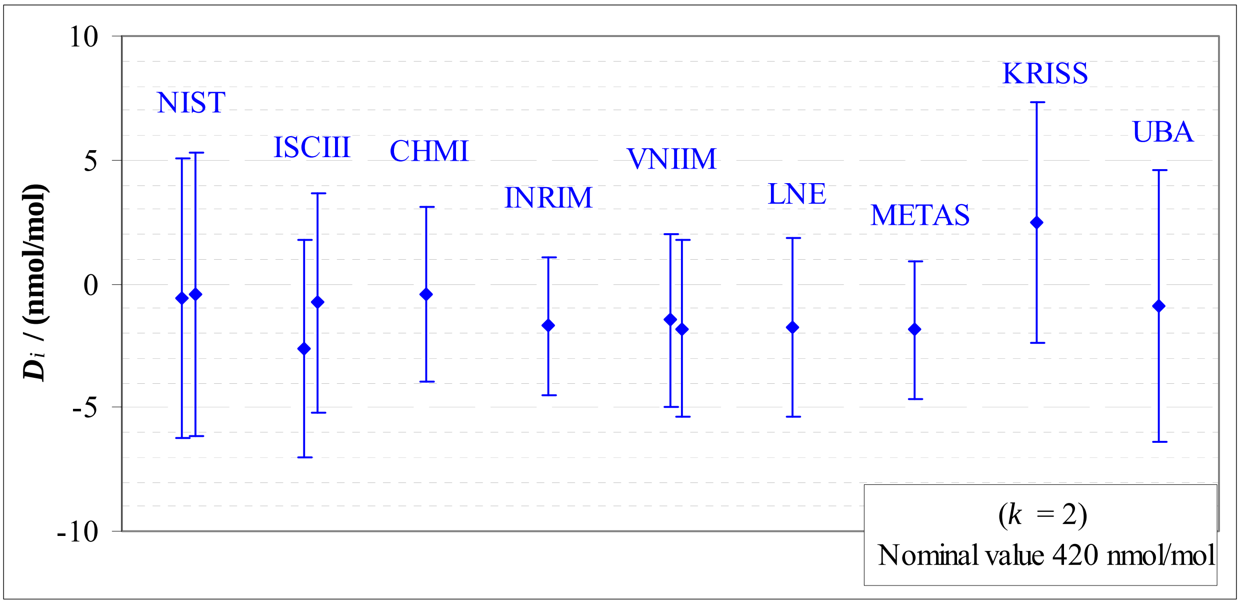


Figure 3: graphs of equivalence at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol, for all participants in BIPM.QM-K1 in the present cycle.

19. Conclusion

As part of the on-going key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of the UBA and the common reference standard of the key comparison, maintained by the BIPM. The instruments have been compared over a nominal ozone mole fraction range of 0 nmol/mol to 500 nmol/mol. This comparison is one of the first comparisons performed via a linking laboratory (NIST). Degrees of equivalence of this comparison indicated good agreement between both standards.

20. References

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Appendix 1 - Form BIPM.QM-K1-R3-UBA-07

See next pages.

OZONE COMPARISON BIPM.QM-K1
RESULTS FORM TO LINK AN RMO COMPARISON

Linking institute information	
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Instruments information

	Reference Standard Photometer	**Participating Institute National Standard**	**Linking institute National Standard**
Manufacturer	NIST	NIST	NIST
Type	SRP	SRP	SRP
Serial number	SRP27	SRP29	SRP0[1]
ozone cross-section value	308.32 atm^{-1} cm^{-1}	308.32 atm-1 cm-1	308.32 atm-1 cm-1

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

[1] *See explanations next page*

Note : In this comparison, the standard SRP0 maintained by NIST as a transfer standard has been used instead of the National Standard SRP2. SRP0 has the same metrological performances as SRP2, and was indeed compared directly to both the reference standard SRP27 and the participating institute national standard SRP29.

Content of the report

Please complete the cells containing blue stars only.
After completion of the appropriate section of this report, please send to Joële Viallon
by email (jviallon@bipm.org), fax (+33 1 45342021), or mail (BIPM, Pavillon de Breteuil, F-92312 Sèvres)

comparison national standard (NS) vs reference standard (RS)

Summary of comparison results

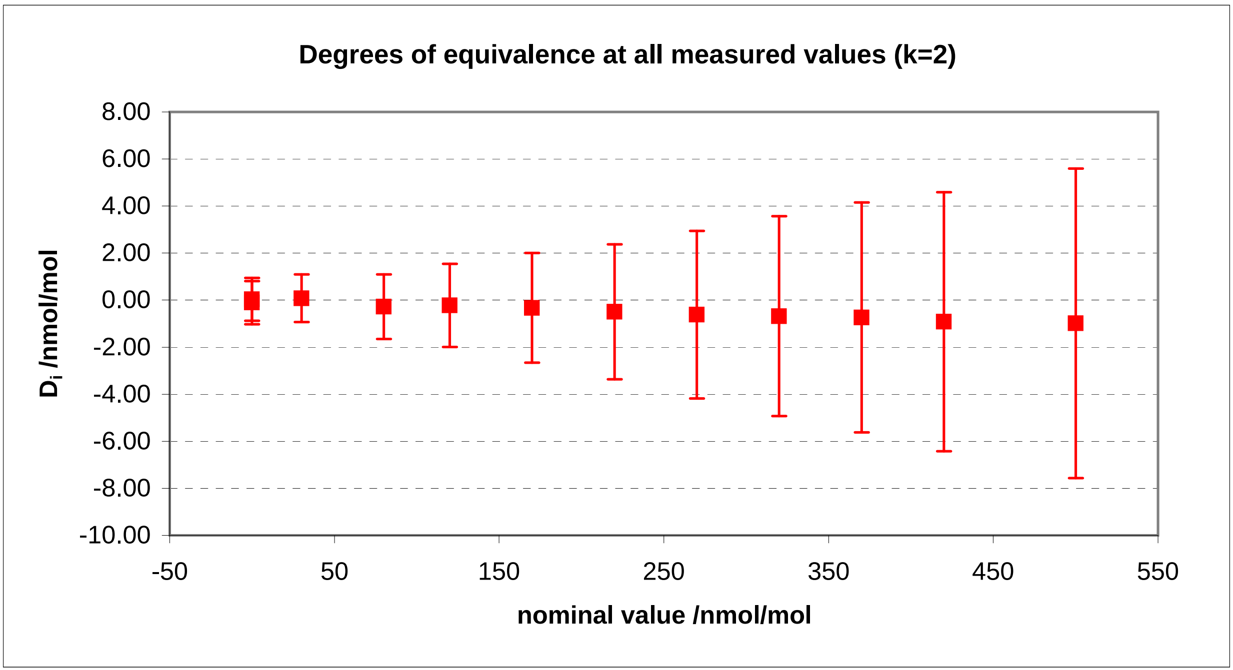
Equation $x_{NS} = a_{NS,RS}\, x_{RS} + b_{NS,RS}$

Least-square regression parameters

	$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
first comparison	**0.9979**	**0.0041**	**0.00**	**0.32**	**-5.01E-04**
second comparison	*no second comparison*				

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

	Nom value (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
first comparison	**80**	-0.28	0.69	1.38
	420	-0.92	2.75	5.50
second comparison	**80**			
	420			



Calculation of the National Standard vs Reference Standard comparison results through the first National Standard vs Transfer Standard comparison

First comparison results

	National standard measurement results		Transfer standard measurement results		Reference Standard prediced values	
Nominal value	x_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_{TS} nmol/mol	$u(x_{TS})$ nmol/mol	x'_{RS} nmol/mol	$u(x'_{RS})$ nmol/mol
0	-0.09	0.28	0.02	0.28	0.02	0.36
220	211.35	0.89	211.46	0.89	211.85	1.13
80	78.31	0.44	78.44	0.44	78.58	0.53
420	419.70	1.68	419.84	1.68	420.62	2.18
120	116.52	0.56	116.53	0.56	116.74	0.68
320	321.67	1.30	321.75	1.30	322.36	1.68
30	29.40	0.32	29.27	0.32	29.32	0.39
370	371.57	1.49	371.61	1.49	372.30	1.93
170	166.38	0.73	166.40	0.73	166.71	0.91
500	503.52	2.00	503.56	2.00	504.51	2.61
270	267.02	1.10	267.14	1.10	267.64	1.41
0	-0.10	0.28	-0.13	0.28	-0.14	0.36

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)

$$x'_{RS} = a_{RS,TS}x_{TS} + b_{RS,TS} \qquad u(x'_{RS}) = \sqrt{a^2_{RS,TS}\cdot u(x_{TS})^2 + x^2_{TS}\cdot u(a_{RS,TS})^2 + u(b_{RS,TS})^2 + 2\cdot x_{TS}\cdot u(a_{RS,TS},b_{RS,TS})}$$

$a_{RS,TS}$	1.0019	$b_{NRS,TS}$ (nmol/mol)	-0.01	$u(a,b)$	-2.35E-04
$u(a_{RS,TS})$	0.0034	$u(b_{RS,TS})$ (nmol/mol)	0.23		

Degrees of Equivalence $D_i = x_{NS} - x'_{RS}$

Point Number	Nom value (nmol/mol)	D_i *(nmol/mol)*	$u(D_i)$ *(nmol/mol)*	$U(D_i)$ *(nmol/mol)*
1	**0**	-0.11	0.46	0.91
2	**220**	-0.50	1.44	2.87
3	**80**	-0.28	0.69	1.38
4	**420**	-0.92	2.75	5.50
5	**120**	-0.22	0.88	1.77
6	**320**	-0.68	2.13	4.25
7	**30**	0.08	0.51	1.01
8	**370**	-0.74	2.44	4.89
9	**170**	-0.33	1.17	2.33
10	**500**	-0.98	3.29	6.58
11	**270**	-0.62	1.78	3.56
12	**0**	0.04	0.46	0.91

Least-square regression parameters

$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
0.9979	**0.0041**	**0.00**	**0.32**	**-0.000501**

Calculation of the National Standard vs Reference Standard comparison results through the second National Standard vs Transfer Standard comparison

Second comparison results						
	National standard measurement results		Transfer standard measurement results		Reference Standard prediced values	
Nominal value	x_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_{TS} nmol/mol	$u(x_{TS})$ nmol/mol	x'_{RS} nmol/mol	$u(x'_{RS})$ nmol/mol
0	0.00	0.00	0.00	0.00	0.00	0.00
220	0.00	0.00	0.00	0.00	0.00	0.00
80	0.00	0.00	0.00	0.00	0.00	0.00
420	0.00	0.00	0.00	0.00	0.00	0.00
120	0.00	0.00	0.00	0.00	0.00	0.00
320	0.00	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00
370	0.00	0.00	0.00	0.00	0.00	0.00
170	0.00	0.00	0.00	0.00	0.00	0.00
500	0.00	0.00	0.00	0.00	0.00	0.00
270	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00

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)

$$x'_{RS} = a_{RS,TS}x_{TS} + b_{RS,TS} \qquad u(x'_{RS}) = \sqrt{a^2_{RS,TS}\cdot u(x_{TS})^2 + x^2_{TS}\cdot u(a_{RS,TS})^2 + u(b_{RS,TS})^2 + 2\cdot x_{TS}\cdot u(a_{RS,TS}, b_{RS,TS})}$$

$a_{RS,TS}$ $b_{NRS,TS}$ (nmol/mol) $u(a,b)$

$u(a_{RS,TS})$ $u(b_{RS,TS})$ (nmol/mol)

Degrees of Equivalence $D_i = x_{NS} - x'_{RS}$				
Point Number	Nom value (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
1	0	0.00	0.00	0.00
2	220	0.00	0.00	0.00
3	80	0.00	0.00	0.00
4	420	0.00	0.00	0.00
5	120	0.00	0.00	0.00
6	320	0.00	0.00	0.00
7	30	0.00	0.00	0.00
8	370	0.00	0.00	0.00
9	170	0.00	0.00	0.00
10	500	0.00	0.00	0.00
11	270	0.00	0.00	0.00
12	0	0.00	0.00	0.00

Least-square regression parameters				
$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
0.9860	0.4391	-0.02	0.36	0.0071356

Data reporting sheet
First comparison of transfer standard (TS) vs national standard (NS)

Operator	**V. Stummer/J. Norris**	**Location**	**UBA**
Comparison begin date / time	**3/11/07 4:37**	**Comparison end date / time**	**03/11/2007 06:36**

measurement results						
	Transfer standard (TS)			National Standard (NS)		
Nominal value	x_{TS} nmol/mol	s_{TS} nmol/mol	$u(x_{TS})$ nmol/mol	x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol
0	0.0	0.2	0.280	-0.09	0.19	0.280
220	211.5	0.2	0.889	211.35	0.17	0.889
80	78.4	0.2	0.440	78.31	0.16	0.440
420	419.8	1.1	1.677	419.70	1.07	1.677
120	116.5	0.2	0.557	116.52	0.33	0.557
320	321.8	0.7	1.302	321.67	0.61	1.302
30	29.3	0.1	0.322	29.40	0.22	0.322
370	371.6	1.0	1.492	371.57	1.03	1.492
170	166.4	0.5	0.727	166.38	0.44	0.727
500	503.6	1.7	2.000	503.52	1.52	2.000
270	267.1	0.8	1.096	267.02	0.72	1.095
0	-0.1	0.1	0.280	-0.10	0.15	0.280

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 $u(x_i, x_j) = \alpha \cdot x_i \cdot x_j$ Value of α 0.00E+00

Comparison conditions

Ozone generator manufacturer	NIST
Ozone generator type	NIST SRP
Ozone generator serial number	29
Room temperature(min-max) / °C	21,78/22,32
Room pressure (average) / hpa	1013
Zero air source	MCZ purifier
Reference air flow rate (L/min)	5
Sample flow rate (L/min)	5
Instruments stabilisation time	>1 month
Instruments acquisition time /s (one measurement)	25
Instruments averaging time /s	25
Total time for ozone conditioning	120 min.
Ozone mole fraction during conditioning	640 nmol/mol
Comparison repeated continously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	8

Instruments checks and adjustments

National Standard

Performed SRP Operating Characteristics Checkout.

Transfer Standard

Performed SRP Operating Characteristics Checkout.

calibration of the transfer standard (TS) by the reference standard (RS)

Operator	J.Norris/P.Moussay	**Location**	BIPM
Comparison begin date / time	26/1/07 14:19	**Comparison end date / time**	26/1/07 16:24

Calibration results

Equation $$x_{RS} = a_{RS,TS} x_{TS} + b_{RS,TS}$$

Least-square regression parameters				
$a_{RS,TS}$	$u(a_{RS,TS})$	$b_{RS,TS}$ (nmol/mol)	$u(b_{RS,TS})$ (nmol/mol)	$u(a,b)$
1.0019	**0.0034**	**-0.01**	**0.23**	**-0.00023**

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

Measurement results

	Transfer standard (TS)			Reference Standard (RS)		
Nominal value	x_{TS} nmol/mol	s_{TS} nmol/mol	$u(x_{TS})$ nmol/mol	x_{RS} nmol/mol	s_{RS} nmol/mol	$u(x_{RS})$ nmol/mol
0	0.00	0.20	0.28	0.05	0.21	0.28
220	225.00	0.30	0.94	225.37	0.25	0.72
80	80.90	0.20	0.45	81.11	0.41	0.37
420	422.10	0.20	1.69	422.83	0.20	1.27
120	124.30	0.30	0.58	124.64	0.24	0.46
320	321.60	0.20	1.30	322.25	0.24	0.98
30	33.80	0.20	0.33	33.86	0.16	0.30
370	374.00	0.30	1.50	374.61	0.40	1.13
170	172.60	0.10	0.75	172.86	0.15	0.58
500	499.00	0.20	1.98	499.68	0.21	1.49
270	274.80	0.20	1.13	275.38	0.24	0.85
0	0.10	0.20	0.28	-0.01	0.18	0.28

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 α 8.53E-06

Comparison conditions

Ozone generator manufacturer	Environics
Ozone generator type	Model 6100
Ozone generator serial number	***
Room temperature(min-max) / °C	22.47/22.74
Room pressure (average) / hpa	***
Zero air source	Addco 737
Reference air flow rate (L/min)	17 or 18
Sample flow rate (L/min)	10
Instruments stabilisation time	1.5 weeks
Instruments acquisition time /s (one measurement)	25
Instruments averaging time /s	25
Total time for ozone conditioning	120 min.
Ozone mole fraction during conditioning	1000
Comparison repeated continously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	44
Data files names and location	c070124016 at BIPM
	***

***

Instruments checks and adjustments

Reference Standard

Performed SRP Operating Characteristics Checkout.

Transfer Standard

Performed SRP Operating Characteristics Checkout.

Data reporting sheet
Second comparison of transfer standard (TS) vs national standard (NS)

Operator	***	**Location**	***
Comparison begin date / time	***	**Comparison end date / time**	***

measurement results

	Transfer standard (TS)			National Standard (NS)		
Nominal value	x_{TS} nmol/mol	s_{TS} nmol/mol	$u(x_{TS})$ nmol/mol	x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol
0	***	***	***	***	***	***
220	***	***	***	***	***	***
80	***	***	***	***	***	***
420	***	***	***	***	***	***
120	***	***	***	***	***	***
320	***	***	***	***	***	***
30	***	***	***	***	***	***
370	***	***	***	***	***	***
170	***	***	***	***	***	***
500	***	***	***	***	***	***
270	***	***	***	***	***	***
0	***	***	***	***	***	***

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 $u(x_i, x_j) = \alpha \cdot x_i \cdot x_j$ Value of α ***

Comparison conditions

Ozone generator manufacturer	***
Ozone generator type	***
Ozone generator serial number	***
Room temperature(min-max) / °C	***
Room pressure (average) / hpa	***
Zero air source	***
Reference air flow rate (L/min)	***
Sample flow rate (L/min)	***
Instruments stabilisation time	***
Instruments acquisition time /s (one measurement)	***
Instruments averaging time /s	***
Total time for ozone conditioning	***
Ozone mole fraction during conditioning	***
Comparison repeated continously (Yes/No)	***
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	***

Instruments checks and adjustments

National 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 Januray 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 uncertainty budget for NIST SRP 0 will follow the BIPM/NIST bias paper with the addition of an additional component based on the temperature probe heating affect. The initial uncertainty can be summarised by the formula:

$$u(x) = \sqrt{(0.28)^2 + \left(2.92 \times 10^{-3} x\right)^2}\, nmol/mol$$

After correcting for the temperature probe heating bias, the final uncertainty is calculated by:

$$u(x)^+ = u(x);\ u(x)^- = u(x) + (-0.001 \times x) nmol/mol$$

Because the BIPM.QM-K1-R2 spreadsheet does not allow the uncertainty to be expressed with different positive and negitive amounts, it has been expressed as:

$$u(x) = u(x) + (0.001 \times x) nmol/mol$$

Because NIST SRP 0 has the new 3 degree angled cell windows, there is no path-length correction.

National Standard

Uncertainty Budget Summary – SRP 29

Component (y)	Source	Distribution	Standard Uncertainty	Combined Standard Uncertainty μ(y)	Sensistivity Coefficient $c_i = \partial x/\partial y$	Contribution to μ(x), c_i • μ(y)/nmol mol^{-1}
Optical Path-length, L	Measurement scale Variability Divergence	Rectangular Rectangular Rectangular	0.0005 cm 0.003 cm. 0.52 cm	0.52 cm.	$-x/L_{opt}$	$2.89\times10^{-3}\,x$
Pressure, P	P Gauge P difference between cells	Rectangular Rectangular	0.029 kPa 0.017 kPa	0.034 kPa	$-x/P$	$3.37\times10^{-4}\,x$
Temperature, T	T probe T gradient **T heating bias**	Rectangular Rectangular **Rectangular**	0.029 K 0.058 K **$-1.0\times10^{-3}\,x$**	0.07K	x/T	$2.29\times10^{-4}x$ **Bias**
Ratio of intensities, D	Scaler resolution Repeatability	Rectangular Triangular	8.0×10^{-6} 1.1×10^{-5}	1.4×10^{-5}	$x/D\ln(D)$	0.28
Absorption cross-section, σ	Conventional value		1.22×10^{-19} cm^2/molecule	1.22×10^{-19} cm^2/molecule	$-x/\sigma$	$1.06\times10^{-2}\,x$

The effective number of degrees of freedom for all components is large therefore, the conventional 95% coverage factor of 2 is appropriate.

As in the BIPM-NIST Bias paper [3], the uncertainty budget above is summarised in one equation describing the uncertainty as a function of ozone mole fraction:

$$u(x) = \sqrt{(0.28)^2 + \left(1.1\times10^{-2}\,x\right)^2}\ nmol/mol$$

Removing the absorption cross-section uncertainty, the equation becomes:

$$u(x) = \sqrt{(0.28)^2 + \left(2.92\times10^{-3}\,x\right)^2}\ nmol/mol$$

This summarizes the above uncertainty budget for SRP 29 without the absorption cross-section uncertainty or the temperature probe heating bias included. Without the temperature probe bias, the 95% level of confidence expanded uncertainty is:

$$U_{95} = \pm\, 2 \times u(x)\ \text{nmol/mol}$$

With the temperature probe bias, the 95% level of confidence expanded uncertainty is:

$$U^{+}_{95} = 2 \times u(x)\ \text{nmol/mol},\ U^{-}_{95} = (-2 \times u(x) - 0.001 \times x)\ \text{nmol/mol}$$