Final report, On-going Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with FMI, 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 Finnish Meteorological Institute (FMI) and the common reference standard of the key comparison, maintained by the Bureau International des Poids et Mesures (BIPM). 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 Finnish Meteorological Institute (FMI) are reported here. The FMI was the tenth laboratory to participate in BIPM.QM-K1.

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
- $x_{\text{A},i}$: ith measurement of the nominal value x_{nom} by the photometer A.
- $\bar{x}_{\text{A}}$: the mean of N measurements of the nominal value x_{nom} measured by the photometer A : $\bar{x}_{\text{A}} = \frac{1}{N}\sum_{i=1}^{N} x_{\text{A},i}$
- s_{A} : standard deviation of N measurements of the nominal value x_{nom} measured by the photometer A : $s_{\text{A}}^{2} = \frac{1}{N-1}\sum_{i=1}^{N}(x_{\text{A},i} - \bar{x}_{\text{A}})^2$
- 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: $x_{\text{A}} = a_{\text{A,B}} x_{\text{B}} + b_{\text{A,B}}$. With this notation, the photometer A is compared versus the photometer B. $a_{\text{A,B}}$ is dimensionless and $b_{\text{A,B}}$ is expressed in units of nmol/mol.

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 from 1 to 5 October 2007 at the BIPM.

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 A, corresponding to a comparison between the FMI national standard SRP37 and the common reference standard BIPM-SRP27 maintained at the BIPM. 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. 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.

8.2. 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 $x_{\mathrm{SRP27},i}$ 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.

8.3. 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.

8.4. 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 BIPM staff reported the measurement results in the result form BIPM.QM-K1-R1 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-R1-FMI-07 is given in the annex.

10. Post comparison calculation

All calculations were performed by the BIPM using the form BIPM.QM-K1-R1. 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

In this comparison, there was no deviation from the protocol.

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:

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

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

$$Tr = \frac{I_{\mathrm{ozone}}}{I_{\mathrm{air}}} \qquad (2)$$

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:

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

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:

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

where

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

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

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):

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

12.5. Covariance terms for the common reference BIPM-SRP27

As explained in section 15, 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:

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

where:

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

The value of u_b is given by the expression of the measurement uncertainty: $u_\mathrm{b} = 2.92\times10^{-3}$ or $u_\mathrm{b}^2 = 8.5\times10^{-6}$.

12.6. Actual state of the FMI SRP37

Compared to the original design, the FMI SRP37 has been modified to deal with the two biases revealed in [4]. Prior to the key comparison exercise, an "SRP upgrade kit" manufactured by the NIST was installed by the BIPM staff in its laboratories (see the appendix 1). 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.
- 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.

12.7. Uncertainty budget of the FMI SRP37

The uncertainty budget for the ozone mole fraction in dry air x measured by the FMI standard SRP37 in the nominal range 0 nmol/mol to 500 nmol/mol is given in Table 2.

Following this budget, as explained in the protocol of the comparison, the standard uncertainty associated with the ozone mole fraction measurement with the FMI SRP37 can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u(x) = \sqrt{(0.28)^2 + (2.92 \cdot 10^{-3} x)^2} \tag{9}$$

No covariance term for the FMI SRP37 was included in the calculations.

13. Measurement results and uncertainties

Details of the measurement results, the measurement uncertainties and the standard deviations at each nominal ozone mole fraction can be found in the form BIPM.QM-K1-R1-FMI-07 given in appendix.

Table 2: Uncertainty budget for the FMI SRP37

Component (*y*)	**Value**	**Uncertainty *u(y)***			**Combined standard 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**			
Optical Path Length L_{opt} / cm	179.60	Measurement Scale	Rectangular	0.002	0.5201cm	$-\frac{x}{L_{opt}}$	$2.896 \cdot 10^{-3} \cdot x$
		Repeatability	Normal	0.01			
		Bias	Rectangular	0.52			
Pressure *p* / kPa	101.21	Pressure gauge	Rectangular	0.029	0.034 kPa	$-\frac{x}{p}$	$3.21 \cdot 10^{-4} \cdot x$
		Difference between cells	Rectangular	0.017			
Temperature *T* / K	296.55	Temperature probe	Normal	0.03	0.065 K	$\frac{x}{T}$	$2.202 \cdot 10^{-4} \cdot x$
		Residual bias	Rectangular	0.058			
Ratio of intensities *D*	0.99	Scaler resolution	Rectangular	$6 \cdot 10^{-6}$	$1.36 \cdot 10^{-5}$	$\frac{x}{D \cdot \ln(D)}$	0.28
		Repeatability	Normal	$1.1 \cdot 10^{-5}$			
Absorption cross section σ	$1.147 \cdot 10^{-17}$	Hearn value		$1.22 \cdot 10^{-19}$ cm^2/molecule	$1.22 \cdot 10^{-19}$ cm^2/molecule	$-\frac{x}{\sigma}$	$1.07 \cdot 10^{-2} \cdot x$

14. Degrees of equivalence

Degrees of equivalence are calculated at two nominal ozone mole fractions among the twelve measured in each comparison, in the 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.

14.1. Definition of the degrees of equivalence

The degree of equivalence of the participant *i*, at a nominal value x_{nom} is defined as:

$$D_i = x_i - x_{SRP27} \tag{10}$$

where x_i and x_{SRP27} are the measurement result of the participant i and of SRP27 at the nominal value x_{nom}.

Its associated standard uncertainty is:

$$u(D_i) = \sqrt{u_i^2 + u_{\mathrm{SRP27}}^2} \tag{11}$$

where u_i and u_{SRP27} are the measurement uncertainties of the participant i and of SRP27 respectively.

14.2. Values of the degrees of equivalence

The degrees of equivalence and their uncertainties calculated in the form BIPM.QM-K1-R1-FMI-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 3 : degrees of equivalence of the FMI at the ozone nominal mole fractions 80 nmol/mol and 420 nmol/mol

Nom 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	80.20	0.36	80.37	0.36	-0.17	0.52	1.03
420	418.92	1.26	420.49	1.26	-1.57	1.78	3.56

The degrees of equivalence between the FMI 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].

15. Analysis of the measurement results by generalised least-square regression

The relationship between two ozone photometers was also evaluated with a generalised least-square regression fit performed on the two sets of measured ozone mole fractions, taking into account standard measurement uncertainties. To this end, a software called 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.

In a direct comparison, a linear relationship between the ozone mole fractions measured by SRP*n* and SRP27 is obtained:

$$x_{\mathrm{SRP}n} = a_0 + a_1 x_{\mathrm{SRP27}} \tag{12}$$

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.

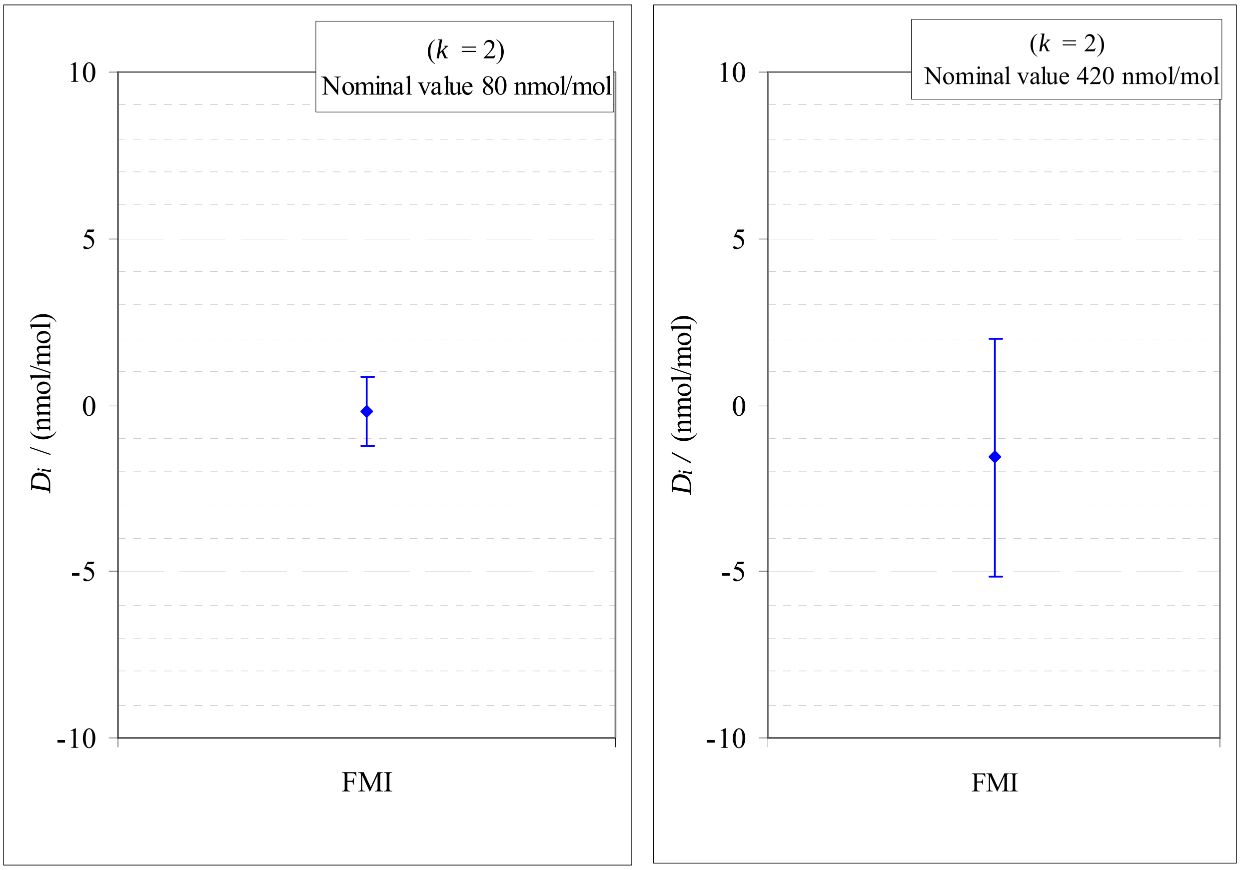


Figure 1: graphs of equivalence of the FMI at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol

15.1. <u>Least-square regression results</u>

The relationship between SRP37 and SRP27 is:

$$x_{\mathrm{SRP37}} = -0.05 + 0.9964 \cdot x_{\mathrm{SRP27}} \tag{13}$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0033$ for the slope and $u(a_0) = 0.22$ nmol/mol for the intercept. The covariance between the two parameters is $\mathrm{cov}(a_0, a_1) = -2.03 \times 10^{-4}$ nmol/mol.

The least-square regression statistical parameters confirm the appropriate choice of a linear relation, with a sum of the squared deviations (SSD) of 0.46 and a goodness of fit (GoF) equals to 0.27.

To asses the agreement of the standards from equation 10, 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. $|1 - a_1| < 2\,u(\mathrm{a}_1)$.

16. History of comparisons between BIPM and FMI

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.

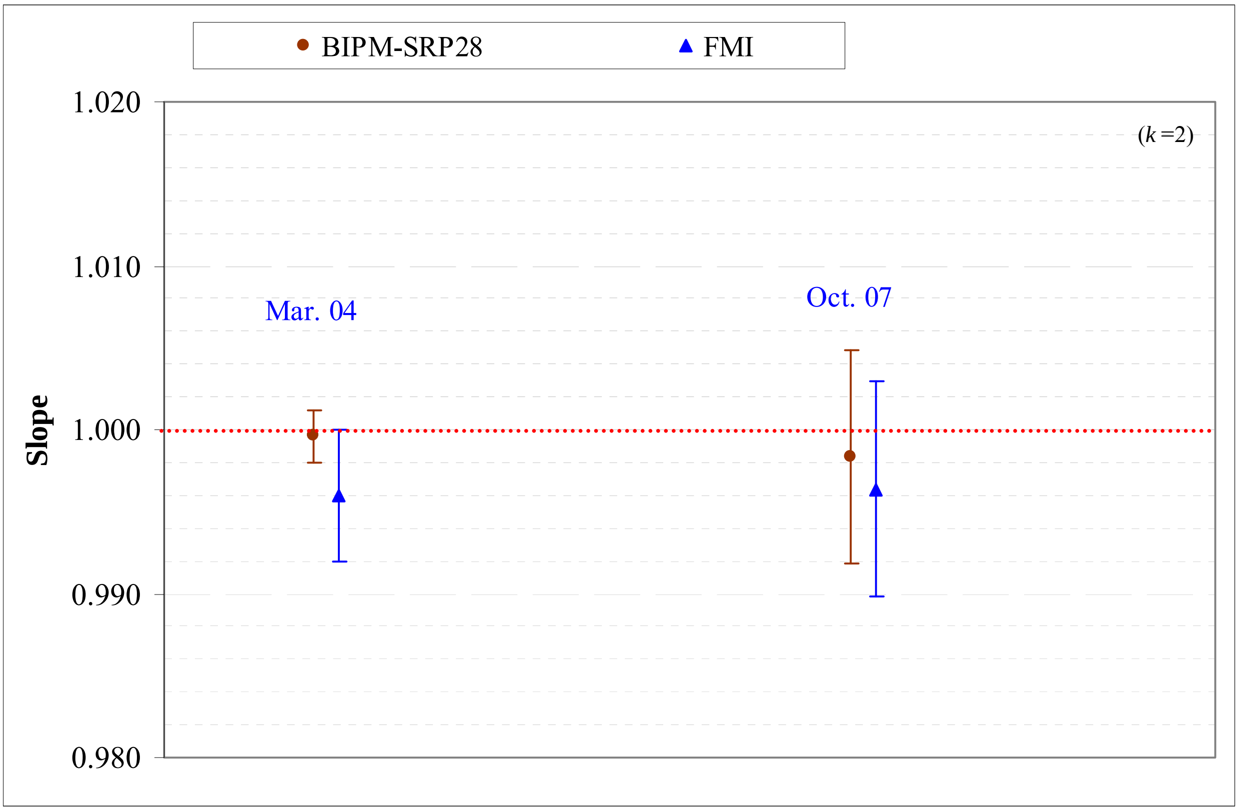


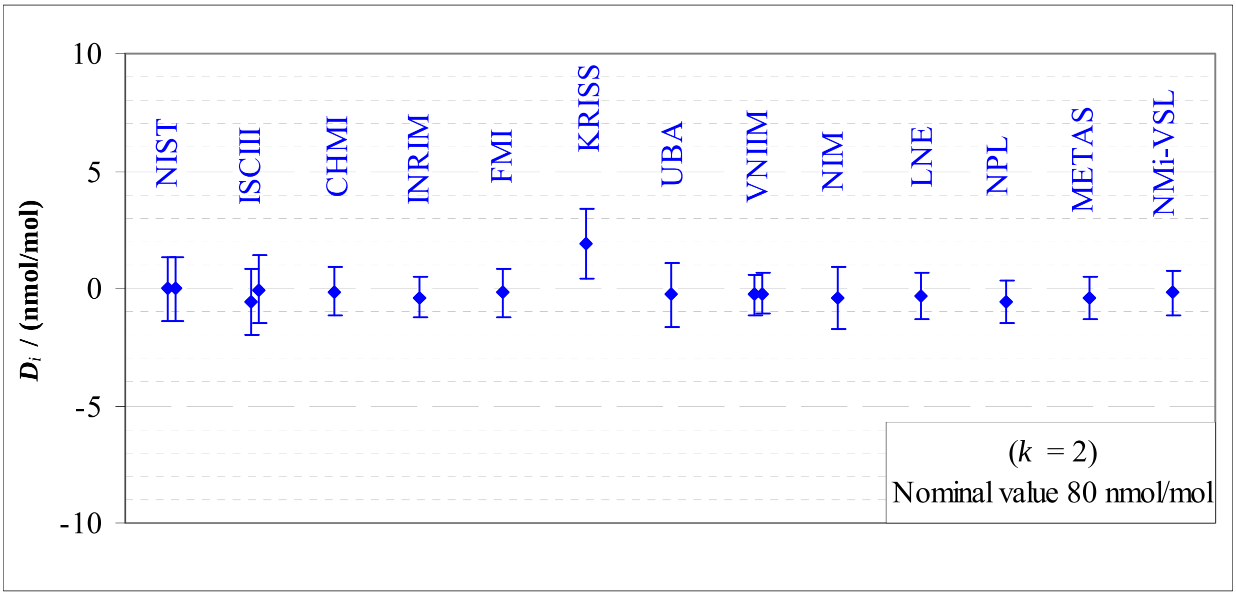
Figure 2 : Results of the comparisons between SRP27, SRP28 and FMI-SRP37 performed at the BIPM during the pilot study CCQM-P28 and the key comparison BIPM.QM-K1. Uncertainties are calculated at k=2, with the uncertainty budget in use at the time of each comparison. Note that the FMI national standard is not the same instrument in the two comparisons.

Figure 2 demonstrates that the agreement between the FMI and BIPM standards has been maintained between March 2004 and October 2007, although the FMI standard has changed between the two exercises (in March 2004, the FMI standard was a Thermo Environment 49C traceable to the LNE).

Figure 2 also shows that SRP27 and SRP28 stability was maintained between the two comparisons, with no more than 0.1% of variation.

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

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



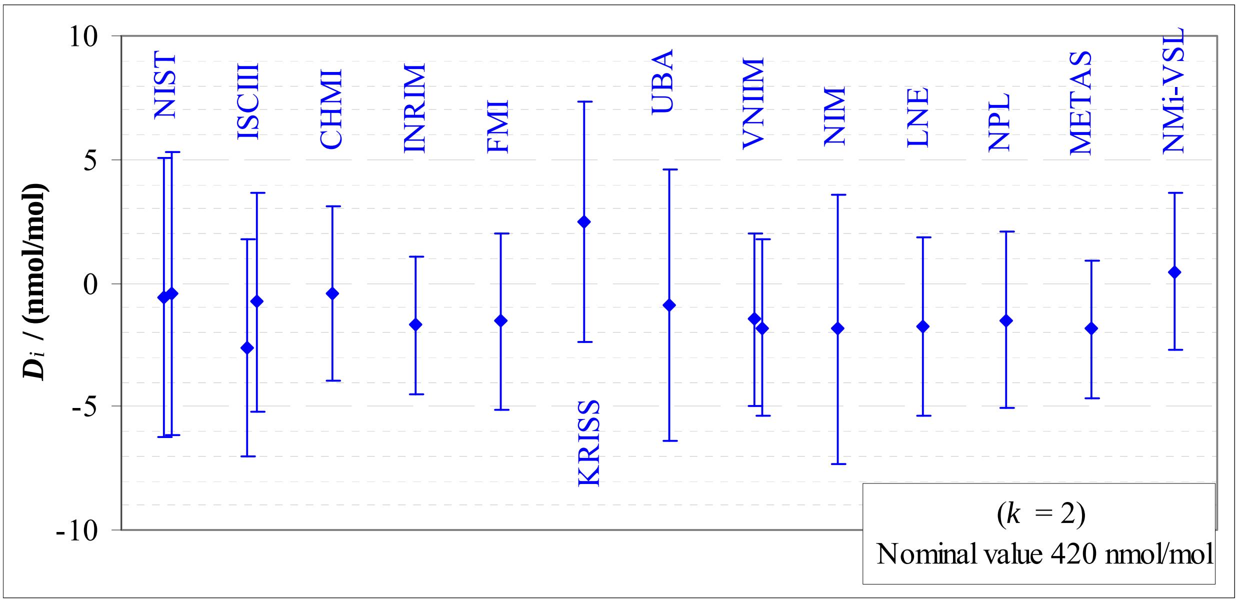


Figure 3: graphs of equivalence at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol, for all participants in BIPM.QM-K1 in the present cycle.

18. Conclusion

As part of the on-going key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of the FMI 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. Following the study of biases in SRP measurement results conducted by NIST and BIPM in 2006, the BIPM standard and the FMI standard were upgraded before this comparison. Degrees of equivalence of this comparison indicated a good agreement between both standards.

19. References

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Appendix 1 - Report of the “SRP upgrade kit” installation in FMI-SRP37

1. Introduction

The NIST Standard Reference Photometer, serial number 37 (SRP37) owned by the Finnish Meteorological Institute (FMI) was upgraded, in the BIPM laboratory, with the two components of the “SRP upgrade kit” manufactured by the NIST. The effect of the upgrade on SRP37 measurement results was assessed by comparisons with the reference standard BIPM-SRP27. All comparisons reported here were performed following the same protocol described in section 8 (“Measurement protocol”) of the main report. The comparisons are characterised by the two parameters of the linear regression performed between the measurement results of the two instruments involved, as described in section 15 of the main report.

The procedure adopted to install the components furnished by the NIST was developed in collaboration with James Norris (NIST) during the installation of the same kit on one of the BIPM SRP (SRP32) in January 2007. This procedure is referenced BIPM/CHEM-T-09 in the BIPM Quality System.

Section 2 of this report gives a description of the SRP upgrade kit. The measurement results are given in sections 3 to 7, and an analysis of the effects observed during the upgrade is presented in section 8.

1. Description of the SRP upgrade kit

The SRP upgrade kit has two components:

- Redesigned absorption cells made with approximately 3° angled windows to minimize repeated internal reflections between the cell windows and back reflections from the optical filters;
- A redesigned source/optics block to minimize transfer of heat from the source block to the gas in the absorption cells;

In addition to these redesigned components, the focal length and aperture were adjusted to provide a better-collimated light signal with less divergence, and the two optical filters originally positioned at the exit of the absorption cells were replaced with a single optical filter placed just after the collimating lens before the beam splitter, mirror, and absorption cells. Details of this SRP Upgrade will be the subject of a future publication.

1.1. <u>Gas cells length measurement</u>

The NIST glassblowing and optics shops produced a pair of quartz absorption cells made with optically sealed Suprasil # 1 quartz windows at approximate 3° angles. The 3° angled windows were made parallel to each other so the cell length is the same at any point of the cells. The cell length was measured using a Coordinate Measuring Machine with a manufacturer stated accuracy of ± 0.00866 mm. Taking this value as a uniform approximation yields a standard uncertainty of 0.0005 cm following the guide to measurement uncertainty [8]. The thickness of each quartz window was measured using a calliper with a tolerance of

0.0025 cm, which yields an uncertainty of 0.0014 cm. Nine independent measurements were made around the perimeter of each cell. This data was used to determine the average optical length and overall uncertainty of the cells. Each cell has an independent cell length, but the two cell lengths were averaged to produce one single cell length that is used in the calculation of ozone mole fractions using the SRP control software. The final average optical length and uncertainty for the new SRP37 absorption cells is 89.72 cm ± 0.003 cm.

2. Initial comparison prior to the SRP upgrade kit installation

An initial comparison between the FMI standard SRP37 and the BIPM reference standard SRP27 was performed. Nine comparison runs were recorded during 21 hours, starting on Tuesday 20 May 2008. The parameters of the linear relationship between SRP37 and SRP27 ($x_{\mathrm{SRP20}} = a_0 + a_1 \cdot x_{\mathrm{SRP27}}$) are reported below:

a_1	$u(a_1)$	a_0 / (nmol/mol)	$u(a_0)$ / (nmol/mol)	$u(a_1, a_0)$ / (nmol/mol)
1.0018	0.0033	0.01	0.22	-2.06×10^{-4}

A good stability was demonstrated during these nine runs, with standard deviations equal to 0.0004 for the slope a_1 and 0.05 nmol/mol for the intercept a_0.

Measurement uncertainties for the reference standards SRP27 and SRP37 were deduced form the uncertainty budgets presented in the main report.

3. First part of the SRP upgrade kit installation: installation of the new gas cells

The original SRP37 absorption cells were removed and the new cells were installed without powering down the instrument. The database of SRP cell lengths implemented in the SRP control program was updated with the new value for SRP37, as measured by the NIST and reported above.

4. Step 1 comparison

A second set of six comparison runs were recorded during 16 hours, starting on Tuesday 2 October 2007. The parameters of the linear relationship between SRP37 and SRP27 ($x_{\mathrm{SRP20}} = a_0 + a_1 \cdot x_{\mathrm{SRP27}}$) are reported below:

a_1	$u(a_1)$	a_0 / (nmol/mol)	$u(a_0)$ / (nmol/mol)	$u(a_1, a_0)$ / (nmol/mol)
0.9923	0.0032	-0.04	0.22	-2.03×10^{-4}

A good stability was demonstrated during these eight runs, with standard deviations equal to 0.0003 for the slope a_1 and 0.05 nmol/mol for the intercept a_0.

5. Second part of the SRP upgrade kit installation: upgrade of the source block

The new source/optics block was assembled including installation of a 2 mm aperture, source block cartridge heater, and temperature sensor. Each section is separated by a 0.125 inch (3.2 mm) cork gasket. The original SRP37 source block was removed from the system and the original collimating lens was removed and installed in the new optics block. The source/optics block was mounted to the shutter cover with another 0.125 inch (3.2 mm) cork gasket between them and the entire assembly was attached to the beam splitter/mirror block. This extra cork gasket allows for adjustment of the light beam down the cells.

The absorption cells were removed to view the alignment of the light beam onto the detectors. The entire source/optics block and shutter cover was removed and adjustments were made to change the angle of the light beam, before re-assembling and checking the light alignment. This process was repeated several times until the best alignment was obtained. Finally, the original optical filters were removed from the cell end plate and a new single optical filter was installed in the optics block before final assembly of the entire system.

6. Last comparison with the upgraded SRP

A last set of seventeen comparison runs were recorded during two days , starting on Wednesday 3 October 2007. The last run of this set was chosen as the official results if the FMI in the key comparison BIPM.QM-K1. The parameters of the linear relationship between SRP37 and SRP27 ($x_{\mathrm{SRP20}} = a_0 + a_1 \cdot x_{\mathrm{SRP27}}$), already given in the section 15.1 of the main report, are reported below:

a_1	$u(a_1)$	a_0 / (nmol/mol)	$u(a_0)$ / (nmol/mol)	$u(a_1, a_0)$ / (nmol/mol)
0.9964	0.0033	-0.05	0.22	-2.03×10^{-4}

A good stability was demonstrated during these seventeen runs, with standard deviations equal to 0.0005 for the slope a_1 and 0.05 nmol/mol for the intercept a_0.

7. Analysis of the effect of the SRP upgrade kit installation

Effects of the upgrade described above are analysed through the evolution of the slope of the linear regression. Changes in this parameter are closely related to changes in the ozone concentration measured by the SRP.

The results of the comparisons performed before the upgrade, after step 1, and after the upgrade are displayed in the Figure 4. Comparisons with BIPM-SRP28 are also displayed, to show the stability of both BIPM SRPs during the entire exercise.

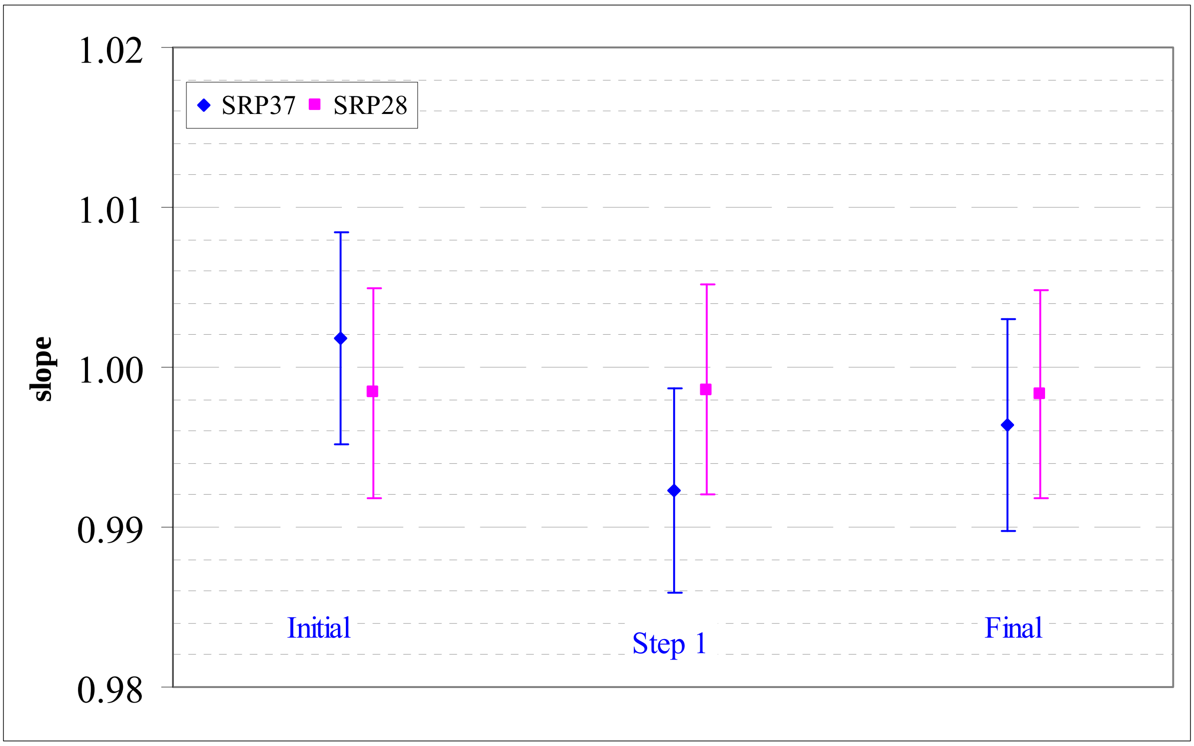


Figure 4 : results of the comparison between FMI- SRP37, BIPM-SRP28 and BIPM-SRP27 before the upgrade, after step 1, and after the upgrade. BIPM-SRP27 is the reference for the slope values.

The most important change in the SRP measurement results was observed after the replacement of the gas cells, with a decrease of 0.95%. It is a larger decrease than observed during the first study of the same effect in 2006, which was about 0.6% in BIPM-SRP33 [4]. Both situations are however not exactly comparable, due to the shape of the new cells. In BIPM-SRP33, only the windows were different, while the gas cells were identical. In the NIST upgrade kit, the windows are in quartz (compared to Pyrex), with sealed windows (compared to windows attached with Teflon pieces) and their shape is a straight tube (compared to a larger tube at both ends and a smaller tube in the middle). The shape influences the divergence of the beam in addition to the number of reflections of the light beam, which is influenced by the position of the windows only.

Nevertheless, the decrease observed here is comparable with the effect observed in other SRPs during their upgrade [9], which lies between 0.5% and 1%. It confirms the existence of a bias in the original design of SRPs.

The second effect, observed between step 1 and the final comparison, is an increase of 0.41% in the ozone concentration measured by SRP37, following the installation of the new source/optics block. It is consistent with the range of changes of 0.2% to 0.6% observed for other SRPs [9]. It should be noted that the new source/optics block removes the temperature bias, but also lowers the divergence of the light beam in using a smaller aperture.

Finally, an overall decrease of 0.54% was observed for the FMI standard SRP37 measurements results following the installation of the SRP upgrade kit. Compared to the reference standard BIPM-SRP27, FMI-SRP37 was measuring 0.18% higher before the upgrade, and is now measuring 0.36% lower. As stated in the main report, the degrees of equivalence show a good agreement between FMI-SRP37 and the reference standard, as well as the other standards included in the key comparison BIPM.QM-K1.

Appendix 2 - Form BIPM.QM-K1-R1-FMI-07

See next pages.

OZONE COMPARISON RESULT - PROTOCOL A - DIRECT COMPARISON

Participating institute information	
Institute	**FMI**
Address	Finnish Meteorological Institute Erik Palmeninaukio 1, P.O. Box 503, FI-00101 Helsinki, Finland
Contact	**Jari Walden, Pirjo Kuronen**
Email	Jari.walden@fmi.fi
Telephone	**+ 358 9 50 591 4615**

Instruments information		
	Reference Standard	**National Standard**
Manufacturer	NIST	NIST
Type	SRP	SRP
Serial number	SRP27	SRP37

Content of the report

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

Operator	P. Moussay	**Location**	BIPM/Room CHEM09
Comparison begin date / time	05/10/2007 00:00	**Comparison end date / time**	05/10/2007 00:00

Comparison results

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

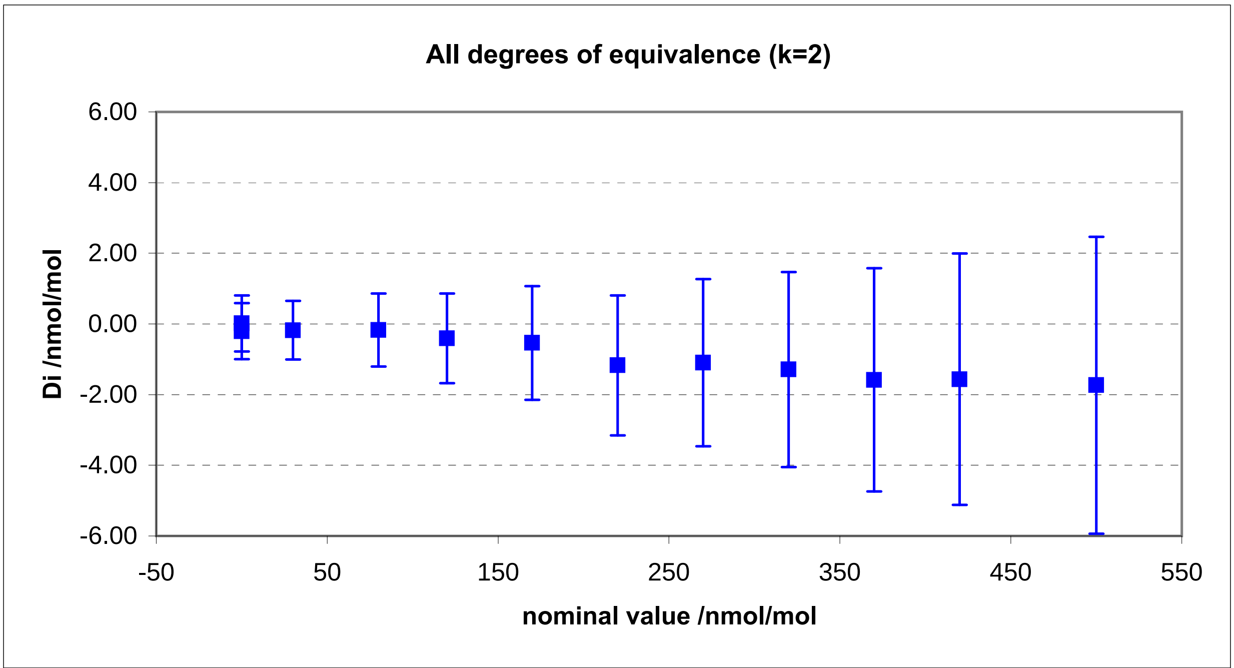
Least-square regression parameters

$a_{TS,RS}$	$u(a_{TS,RS})$	$b_{TS,RS}$ (nmol/mol)	$u(b_{TS,RS})$ (nmol/mol)	$u(a,b)$
0.9964	**0.0033**	**-0.05**	**0.22**	**-2.03E-04**

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

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)
80	-0.17	0.52	1.03
420	-1.57	1.78	3.56



Measurement results						
	Reference Standard (RS)			National standard (NS)		
Nominal value	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	0.04	0.16	0.28	-0.16	0.23	0.28
220	223.85	0.21	0.70	222.68	0.27	0.70
80	80.37	0.27	0.36	80.20	0.25	0.36
420	420.49	0.18	1.26	418.92	0.28	1.26
120	123.33	0.12	0.45	122.93	0.18	0.45
320	320.52	0.32	0.98	319.23	0.21	0.98
30	33.96	0.23	0.29	33.78	0.25	0.29
370	372.47	0.20	1.12	370.89	0.37	1.12
170	171.22	0.27	0.57	170.68	0.24	0.57
500	497.25	0.21	1.49	495.52	0.22	1.49
270	273.73	0.28	0.84	272.64	0.35	0.84
0	-0.06	0.32	0.28	-0.04	0.15	0.28

Degrees of Equivalence				
Point Number	Nom value (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
1	**0**	-0.20	0.40	0.79
2	**220**	-1.17	0.99	1.98
3	**80**	-0.17	0.52	1.03
4	**420**	-1.57	1.78	3.56
5	**120**	-0.41	0.63	1.27
6	**320**	-1.29	1.38	2.76
7	**30**	-0.18	0.41	0.83
8	**370**	-1.58	1.58	3.16
9	**170**	-0.54	0.81	1.61
10	**500**	-1.74	2.10	4.20
11	**270**	-1.09	1.18	2.37
12	**0**	0.01	0.40	0.79

Covariance terms in between two measurement results of each standard

Equation $u(x_i, x_j) = \alpha \cdot x_i \cdot x_j$

Value of α for the reference standard 8.50E-06

Value of α for the national standard 0.00E+00

Comparison conditions

Ozone generator manufacturer	Environics
Ozone generator type	Model 6100
Ozone generator serial number	3128
Room temperature(min-max) / °C	22.8-22.9 °C
Room pressure (min-max) / hpa	1014
Zero air source	oil free compressor + dryer+ aadco 737-R
Reference air flow rate (L/min)	17
Sample flow rate (L/min)	10
Instruments stabilisation time	4 days
Instruments acquisition time /s (one measurement)	5 s
Instruments averaging time /s	5 s
Total time for ozone conditioning	2 hours
Ozone mole fraction during conditioning	860 nmol/mol
Comparison repeated continously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	9
Data files names and location	\\chem5\Program Files\NIST\SRPControl\Data\2007
C0710001.xls to C0710009.xls	

Instruments checks and adjustments

Reference Standard

As written in the procedure BIPM/CHEM-T-05

National Standard

followed FMI procedure
temperature : no change.
pressure: no change.

The instument has been upgraded just before the comparison.

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:

$$\boxed{u(x)=\sqrt{(0.28)^2+(2,92\cdot 10^{-3}x)^2}}$$

National Standard

Pressure kPa **101**

Path lenght 89.8

Contribution of SRP Component y	Value	Standard uncertainty Source	Distribution	Standard uncertainty	Comb stand uncertainty	Sensitivity coefficient $c_i=\frac{\partial x}{\partial y}$	Contribution to u(x) (nmol/mol) ci u(y) or ciu(y)x
Optical path Length 2L cm	179.60	Measurement scale (cm)	Rect	0.002	0.52009999	$-\frac{x}{2L}=-\frac{x}{L_{opt}}$	
		Repeatability (cm)	Normal	0.01	0.5201		**2.896E-03**
		Bias (cm)	Rect	0.52			
Pressure kPa	101.21	Pressure gauge	Rect	0.029	0.034	$-\frac{x}{P}$	**3.321E-04**
kPa		Difference between cells	Rect	0.017			
Temperature, K	296.55	Temperature probe	Rect	0.03	0.065	$\frac{x}{T}$	**2.202E-04**
		Residual bias	Rect	0.058			
Ratio of intensities D	0.99	Scalers resolution	Rectancular	0.00	1.36E-05	$\frac{x}{D\cdot\ln(D)}$	**2.800E-01**
		Repeatability	Triang	0.000011			
Absorption Cross section α (cm^2/molecule	1.147E-17			1.227E-19		$-\frac{x}{\sigma}$	**1.07%**
uncertainty of cross	1.070E-02						

$$x=\frac{-1}{2\alpha L}\cdot\frac{R}{N_a}\cdot\frac{T_{MEAS}}{P_{MEAS}}\ln(D)=B\ln(D)_o$$

$$\boxed{u(x)=\sqrt{[(\frac{x}{L_{opt}}u(L_{opt}))^2+(\frac{x}{P}u^2(P))^2+(\frac{x}{T}u(T))^2+(\frac{B}{D}u(D))^2]}}$$

$$\boxed{u(x)=\sqrt{\{[(2{,}896\cdot 10^{-3})^2+(3{,}321\cdot 10^{-4})^2+(2{,}2\cdot 10^{-4})^2]\cdot x^2+(2{,}8^{-1})^2\}}=\sqrt{[(2{,}92\cdot 10^{-3}\cdot x)^2+(0{,}28^2]}}$$