Final report, Ongoing Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with KRISS, (March 2012)

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Abstract

As part of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of Korea maintained by the Korea Research Institute of Standards and Science (KRISS) 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 amount-of-substance fraction range of 0 nmol/mol to 500 nmol/mol.

Contents:

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1. Field

Amount of substance.

2. Subject

Comparison of reference measurement standards for ozone at ambient level.

3. Participants

BIPM.QM-K1 is an ongoing key comparison, which is structured as an ongoing series of bilateral comparisons. The results of the comparison with the Korea Research Institute of Standards and Science (KRISS) are reported here.

4. Organizing body

BIPM.

5. Rationale

The ongoing key comparison BIPM.QM-K1 has been running since January 2007. It follows the pilot study CCQM-P28 that included 23 participants and that was performed 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 amount-of-substance 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.
- $\overline{x}_{\text{A}}$: the mean of N measurements of the nominal value x_{nom} measured by the photometer A : $\overline{\boldsymbol{x}}_{\text{A}} = \frac{1}{\boldsymbol{N}}\sum_{\boldsymbol{i}=1}^{\boldsymbol{N}} \boldsymbol{x}_{\text{A},\boldsymbol{i}}$
- s_{A} : standard deviation of N measurements of the nominal value x_{nom} measured by the photometer A : $\boldsymbol{s}_{\text{A}}{}^{2} = \frac{1}{\boldsymbol{N}-1}\sum_{\boldsymbol{i}=1}^{\boldsymbol{N}} (\boldsymbol{x}_{\text{A},\boldsymbol{i}} - \overline{\boldsymbol{x}}_{\text{A}})^{2}$
- 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: $\boldsymbol{x}_{\text{A}} = \boldsymbol{a}_{\text{A,B}}\boldsymbol{x}_{\text{B}} + \boldsymbol{b}_{\text{A,B}}$. With this notation, the photometer A is compared against the photometer B. $a_{\text{A,B}}$ is dimensionless and $b_{\text{A,B}}$ is expressed in units of nmol/mol.

7. Measurement schedule

The key comparison BIPM.QM-K1 was initially organised as 2 years cycles. The 2007 to 2008 round, the results of which are published in the Key Comparison Database of the BIPM, included 16 participants. The second round of BIPM.QM-K1 started in March 2009 for a period of 4 years, following the decision of the CCQM/GAWG to reduce the repeat frequency of bilateral comparisons. Measurements reported in this report were performed on 5 March 2012 at the BIPM.

8. Measurement protocol

The comparison protocol is summarized 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 direct comparison between the KRISS national standard KRISS-O_3-SRP3 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 amount-of-substance 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 is 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 amount-of-substance fractions distributed to cover the range, together with the measurement of zero reference air at the beginning and end of each run. The nominal amount-of-substance 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 amount-of-substance 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 during 28 hours 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 ongoing 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 amount-of-substance fractions measured by the participant's standard and the common reference standard. The completed form BIPM.QM-K1-R1-KRISS-12 is given in Appendix 1. 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). Additionally, the degrees of equivalence at all nominal ozone amount-of-substance fractions are reported in the same form, as well as the linear relationship between the participant standard and the common reference standard.

10. Deviations from the comparison protocol

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

11. Measurement standards

The instruments maintained by the BIPM are Standard Reference Photometers (SRP) built by the NIST, and the instrument maintained by the KRISS was built at the KRISS on the same pattern. More details on the NIST SRP principle and its capabilities can be found in [2]. The following section describes briefly the instruments' measurement principle and their uncertainty budgets.

11.1. Measurement equation of a NIST SRP

The measurement of the ozone amount-of-substance 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:

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

where

- σ is the absorption cross-section of ozone at 253.7 nm under standard conditions of temperature and pressure, 1.1476×10^{-17} cm^2/molecule [3].
- L_{opt} is the mean optical path length of the two 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 (T_{r}) of one cell defined as

$$T_{\text{r}} = \frac{I_{\text{ozone}}}{I_{\text{air}}} \tag{2}$$

where

- I_{ozone} is the UV radiation intensity measured from the cell when containing ozonized air, and
- I_{air} is the UV radiation intensity measured from 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 amount-of-substance fraction (x) of ozone in air:

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

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:

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

where

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

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

11.2. Absorption cross-section for ozone

The linear absorption coefficient under 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].

11.3. Condition 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]. In 2009, an “SRP upgrade kit” was installed in the instruments, as described in the report [5].

11.4. Uncertainty budget of the common reference BIPM-SRP27

The uncertainty budget for the ozone amount-of-substance 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	$-\frac{x}{L_{opt}}$	$2.89 \times 10^{-3}x$
	Repeatability	Normal	0.01 cm			
	Correction factor	Rectangular	0.52 cm			
Pressure P	Pressure gauge	Rectangular	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37 \times 10^{-4}x$
	Difference between cells	Rectangular	0.017 kPa			
Temperature T	Temperature probe	Rectangular	0.03 K	0.07 K	$\frac{x}{T}$	$2.29 \times 10^{-4}x$
	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	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$

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

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

11.5. Covariance terms for the common reference BIPM-SRP27

As explained in section 13, correlations in between the results of two measurements performed at two different ozone amount-of-substance fractions with BIPM-SRP27 were taken into account using the software OzonE. Details about the analysis of the covariance 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: $u_{\mathrm{b}} = 2.92 \times 10^{-3}$.

11.6. Condition of the KRISS-O_3-SRP3

KRISS-O_3-SRP3 has been newly built by KRISS. Although the principle of the KRISS-O_3-SRP3 is the same as those of NIST SRPs and previous KRISS SRPs, there are differences such as the position of a band-path filter and the number of sample temperature and pressure sensors. The band-path filter, which is tilted 3°, is located right behind a plano-convex lens instead of one end of the two gas cells. Sample temperature and pressure are measured at both gas cells for better uncertainty estimation. The windows at both ends of the gas cells are tilted 3° in order to minimize the light reflections. The resolution of transmittance measurement is improved by a factor of 7 compared with the previous KRISS SRPs.

11.7. Uncertainty budget of the KRISS-O3-SRP3

The uncertainty budget for the ozone mole fraction in dry air x measured by the KRISS-O3-SRP3 in the nominal range 0 nmol/mol to 500 nmol/mol is given in Table 2.

Following this budget, the standard uncertainty associated with the ozone mole fraction measurement with the KRISS SRP3 can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u(x)=\sqrt{\left(0.24\right)^2+\left(2.92\cdot 10^{-3}x\right)^2} \tag{9}$$

A covariance term of $u_{\mathrm{b}} = 2.92 \times 10^{-3}$ was included for the KRISS-O3-SRP3 in the calculations.

Table 2: Uncertainty budget for the standard KRISS-O3-SRP3 maintained by the KRISS

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	0.003 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89 \times 10^{-3}x$
	Variability	Rectangular	0.03 cm			
	Divergence	Rectangular	0.52 cm			
Pressure P	Pressure gauge	Rectangular	0.029 kPa	0.032 kPa	$-\frac{x}{P}$	$3.23 \times 10^{-4}x$
	Difference between cells	Rectangular	0.014 kPa			
Temperature T	Temperature probe	Rectangular	0.029 K	0.065 K	$\frac{x}{T}$	$2.15 \times 10^{-4}x$
	Temperature bias	Rectangular	0.058 K			
Ratio of intensities D	Scaler resolution	Rectangular	1.38×10^{-6}	1.21×10^{-5}	$\frac{x}{D \ln(D)}$	0.24
	Repeatability	Triangular	1.20×10^{-5}			
Absorption Cross section σ	Conventional value		1.22×10^{-19} cm²/molecule	1.22×10^{-19} cm²/molecule	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$

12. Measurement results and uncertainties

Details of the measurement results, the measurement uncertainties and the standard deviations at each nominal ozone amount-of-substance fraction are provided in appendix (form BIPM.QM-K1-R1-KRISS-12).

13. 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, using the software OzonE. This software, which is documented in a publication [7], is an extension of the previously used software B_Least recommended by the ISO standard 6143:2001 [8]. It includes the possibility to take into account correlations between measurements performed with the same instrument at different ozone amount-of-substance fractions. It also facilitates the use of a transfer standard, by handling of unavoidable correlations, which arise since this instrument needs to be calibrated by the reference standard.

In a direct comparison, a linear relationship between the ozone amount-of-substance fractions measured by the instrument i and SRP27 is obtained:

$$x_i = a_0 + a_1 x_{\mathrm{SRP27}} \tag{10}$$

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.

13.1. Least-squares regression results

The relationship between standard KRISS SRP3 and SRP27 is:

$$x_{\text{KRISS-3}} = 0.09 + 0.9991 \cdot x_{\text{SRP27}} \tag{11}$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0042$ for the slope and $u(a_0) = 0.20$ nmol/mol for the intercept. The covariance between the two parameters is $\text{cov}(a_0, a_1) = -1.56 \times 10^{-4}$.

The least-squares regression results confirm that a linear fit is appropriate, with a sum of the squared deviations (SSD) of 0.74 and a goodness of fit (GoF) equals to 0.35.

To assess the agreement of the standards using equations 11 and 12, 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 this 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. $|1 - a_1| < 2u(a_1)$.

14. Degrees of equivalence

Degrees of equivalence are calculated at two nominal ozone amount-of-substance 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 amount-of-substance 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:

$$D_i = x_i - x_{\text{SRP27}} \tag{12}$$

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:

$$u(D_i) = \sqrt{u_i^2 + u_{\mathrm{SRP27}}^2} \tag{13}$$

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-KRISS-12 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 KRISS at the ozone nominal amount-of-substance fractions 80 nmol/mol and 420 nmol/mol

Nominal value / (nmol/mol)	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	81.56	0.34	81.59	0.37	-0.03	0.50	1.00
420	423.82	1.26	423.73	1.27	0.09	1.79	3.58

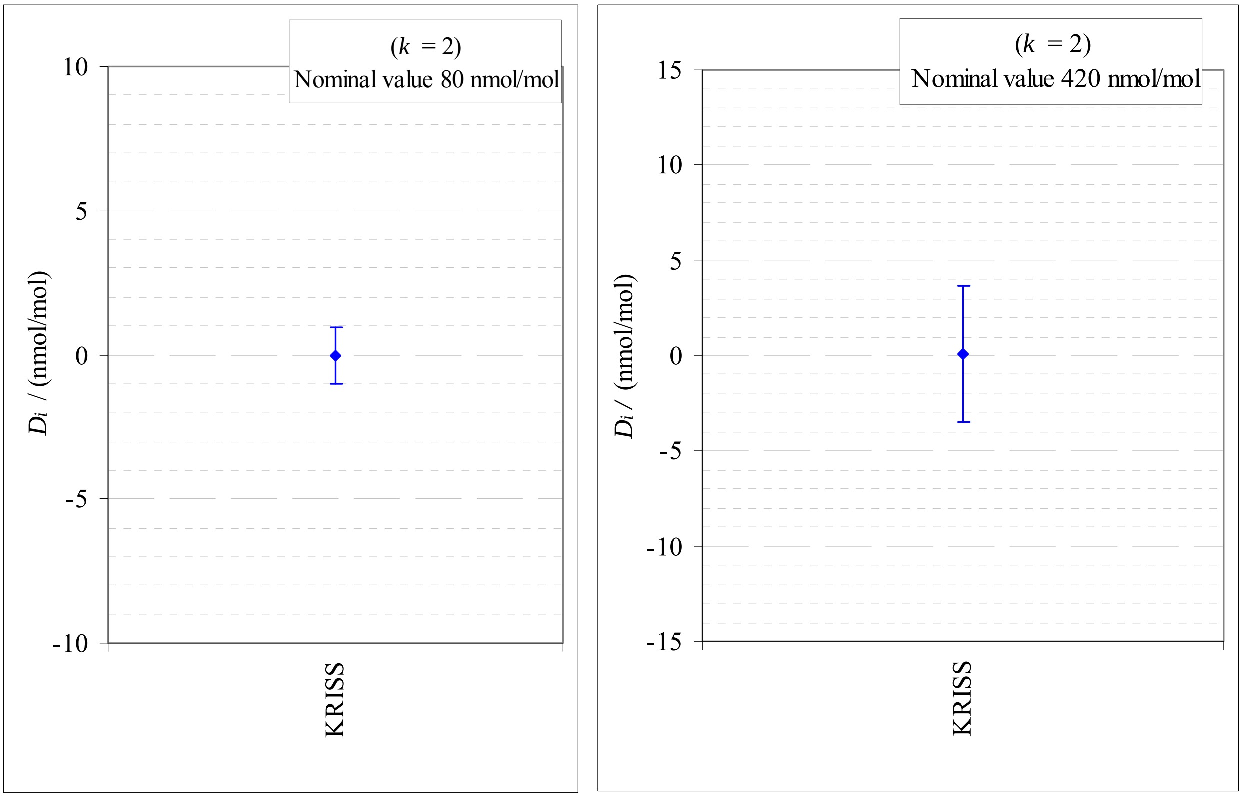

Figure 1: degrees of equivalence of the KRISS at the two nominal ozone amount-of-substance fractions 80 nmol/mol and 420 nmol/mol

The degrees of equivalence between the KRISS 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. History of comparisons between BIPM SRP27, SRP28 and KRISS SRP3

Results of the previous comparison performed in 2003 during the pilot study CCQM-P28 and in 2007 during the first participation of the KRISS in the key comparison BIPM.QM-K1 are displayed in Figure 2 together with the results of this comparison. To show the stability of the reference standard BIPM-SRP27, results of comparisons between BIPM-SRP27 and BIPM-SRP28 are also displayed. The slopes a_1 of the linear relation $x_{SRPn} = a_0 + a_1\, x_{\mathrm{SRP27}}$ are represented together with their associated uncertainties calculated at the time of each comparison. Results of previous comparisons have been corrected to take into account the changes in the reference BIPM-SRP27 described in [5] which explains the larger uncertainties associated with the corresponding slopes.

Figure 2 shows that although the KRISS changed its national standard instrument between each comparison (KRISS SRP2 in December 2003, KRISS SRP1 in October 2007 and KRISS-O_3-SRP3 in March 2012), the agreement with BIPM-SRP27 has been maintained. The figure also shows that SRP27 and SRP28 stability was maintained as well, with no more than 0.1% of variation

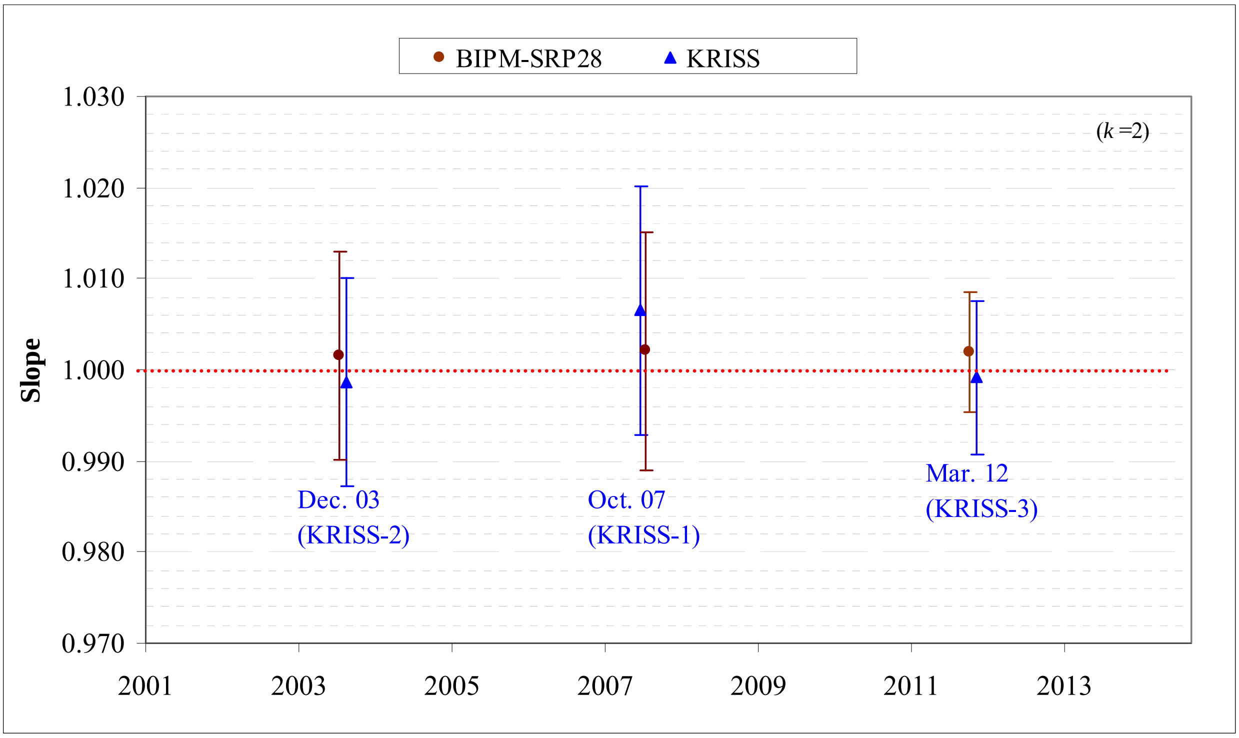

Figure 2 : Results of previous comparisons between SRP27, SRP28 and KRISS standards realised at the BIPM. Uncertainties are calculated at *k* = 2, with the uncertainty budget in use at the time of each comparison.

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

The comparison with KRISS is the tenth one in the 2009-2012 round of BIPM.QM-K1. An updated summary of BIPM.QM-K1 results can be found in the BIPM key comparison database: http://kcdb.bipm.org/appendixB/.

17. Conclusion

For the second time since the launch of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of Korea maintained by the KRISS and the common reference standard of the key comparison maintained by the BIPM. The instruments have been compared over a nominal ozone amount-of-substance fraction range of 0 nmol/mol to 500 nmol/mol. Degrees of equivalence of this comparison indicated very good agreement between the two standards.

18. References

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Appendix 1 - Form BIPM.QM-K1-R1-KRISS-12

See the following pages.

OZONE COMPARISON RESULT - PROTOCOL A - DIRECT COMPARISON

Participating institute information	
Institute	**KRISS**
Address	Dev. Of Metrology for Quality Life Korea Research Institute of Standards and Science P.O. Box 102, Yuseong Daejeon 305-606, Rep of KOREA
Contact	**Sangil Lee**
Email	slee@kriss.re.kr
Telephone	**82-42-868-5864**

Instruments information

	Reference Standard	National Standard
Manufacturer	NIST	KRISS
Type	SRP	O3-SRP (KRISS made)
Serial number	SRP27	KRISS-3

Content of the report

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

Operator	Faraz Idrees / Lee Sangil	**Location**	ROOM CHEM 9
Comparison begin date / time	06/03/2012 11:00	**Comparison end date / time**	07/03/2012 16:00

Comparison results

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

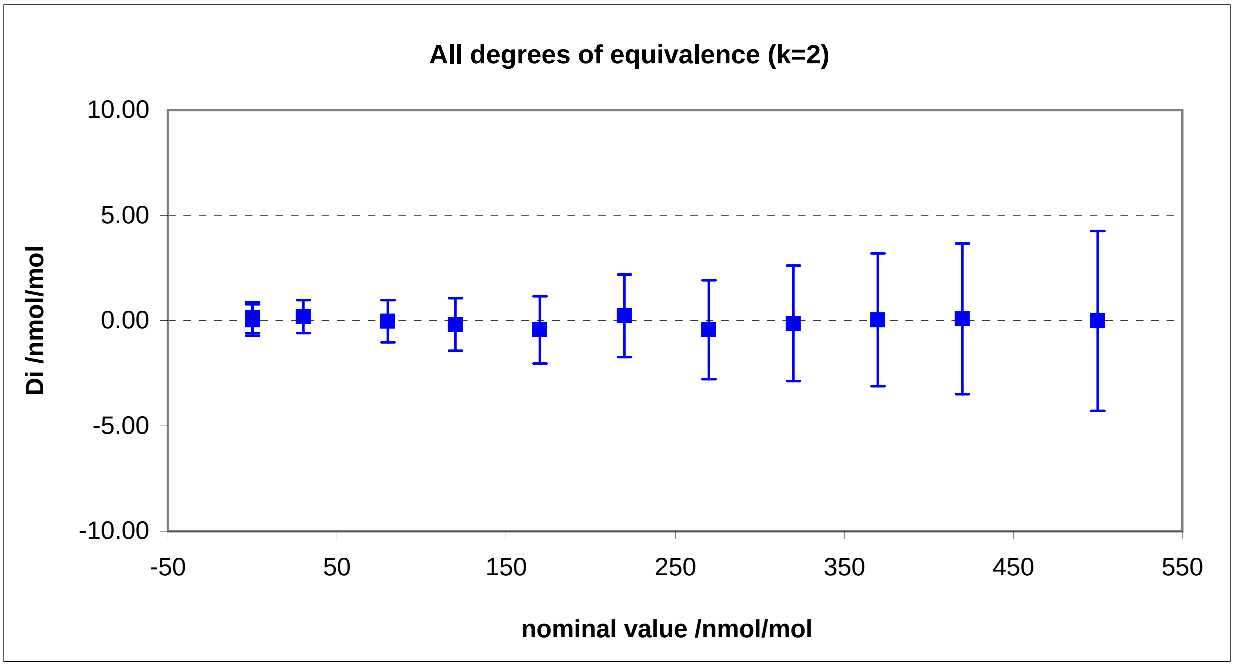
Least-square regression parameters

$a_{TS,RS}$	$u(a_{TS,RS})$	$b_{TS,RS}$ (nmol/mol)	$u(b_{TS,RS})$ (nmol/mol)	$u(a,b)$
0.9991	**0.0042**	**0.09**	**0.20**	**-1.56E-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	**-0.03**	**0.50**	**1.00**
420	**0.09**	**1.79**	**3.58**



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	-0.09	0.15	0.28	0.06	0.14	0.24
220	219.69	0.24	0.70	219.92	0.32	0.69
80	81.59	0.13	0.37	81.56	0.14	0.34
420	423.73	0.17	1.27	423.82	0.20	1.26
120	121.59	0.28	0.45	121.40	0.16	0.43
320	319.78	0.19	0.97	319.65	0.27	0.96
30	32.26	0.27	0.30	32.45	0.15	0.26
370	370.92	0.19	1.12	370.96	0.23	1.11
170	171.34	0.16	0.57	170.90	0.13	0.55
500	509.75	0.22	1.51	509.73	0.23	1.51
270	269.93	0.21	0.84	269.50	0.15	0.82
0	0.00	0.30	0.28	0.04	0.17	0.24

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**	0.15	0.37	0.74
2	**220**	0.22	0.98	1.96
3	**80**	-0.03	0.50	1.00
4	**420**	0.09	1.79	3.58
5	**120**	-0.19	0.62	1.25
6	**320**	-0.13	1.37	2.74
7	**30**	0.19	0.39	0.78
8	**370**	0.04	1.58	3.15
9	**170**	-0.44	0.80	1.59
10	**500**	-0.02	2.14	4.27
11	**270**	-0.43	1.17	2.35
12	**0**	0.03	0.37	0.74

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 8.52E-06

Value of α for the national standard 8.52E-06

Comparison conditions

Ozone generator manufacturer	Environics
Ozone generator type	Model 6100
Ozone generator serial number	3128
Room temperature(min-max) / °C	22.9
Room pressure (min-max) / hpa	1012.9
Zero air source	oil free compressor + dryer+ aadco 737-R
Reference air flow rate (L/min)	14
Sample flow rate (L/min)	10
Instruments stabilisation time	> 8 hours
Instruments acquisition time /s (one measurement)	5
Instruments averaging time /s	5
Total time for ozone conditioning	24 hours
Ozone mole fraction during conditioning (nmol/mol)	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	14
Data files names and location	\\chem5\Program Files\NIST\SRPControl\Data\2012
C120306001.xls to C120306014.xls	

Instruments checks and adjustments

Reference Standard

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

National 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:

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

National Standard

uncertainty budget for KRISS O3 SRP3 is desribed in the table below. It can be summarized by the formula:

$$\boxed{u(x) = \sqrt{(0.24)^2 + (2.92 \times 10^{-3} x)^2}}$$

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	0.003 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89 \times 10^{-3}x$
	Variability	Rectangular	0.03 cm			
	Divergence	Rectangular	0.52 cm			
Pressure P	Pressure gauge	Rectangular	0.029 kPa	0.032 kPa	$-\frac{x}{P}$	$3.23 \times 10^{-4}x$
	Difference between cells	Rectangular	0.014 kPa			
Temperature T	Temperature probe	Rectangular	0.029 K	0.065 K	$\frac{x}{T}$	$2.15 \times 10^{-4}x$
	Temperature bias	Rectangular	0.058 K			
Ratio of intensities D	Scaler resolution	Rectangular	1.38×10^{-6}	1.21×10^{-5}	$\frac{x}{D \ln(D)}$	0.24
	Repeatability	Triangular	1.20×10^{-5}			
Absorption Cross section σ	Conventional value		1.22×10^{-19} cm²/molecule	1.22×10^{-19} cm²/molecule	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$