Final report, On-going Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with KRISS, 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 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 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 Korea Research Institute of Standards and Science (KRISS) are reported here. The KRISS was the seventh 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
- $x_{\mathrm{A},i}$: ith measurement of the nominal value x_{nom} by the photometer A.
- $\bar{x}_{\mathrm{A}}$: the mean of N measurements of the nominal value x_{nom} measured by the photometer A : $\bar{\boldsymbol{x}}_{\mathrm{A}} = \frac{1}{\boldsymbol{N}} \sum_{\boldsymbol{i}=1}^{\boldsymbol{N}} \boldsymbol{x}_{\mathrm{A},\boldsymbol{i}}$
- s_{A} : standard deviation of N measurements of the nominal value x_{nom} measured by the photometer A : $\boldsymbol{s}_{\mathrm{A}}{}^{2} = \frac{1}{\boldsymbol{N}-1} \sum_{\boldsymbol{i}=1}^{\boldsymbol{N}} (\boldsymbol{x}_{\mathrm{A},\boldsymbol{i}} - \bar{\boldsymbol{x}}_{\mathrm{A}})^{2}$
- 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: $\boldsymbol{x}_{\mathrm{A}} = \boldsymbol{a}_{\mathrm{A,B}} \boldsymbol{x}_{\mathrm{B}} + \boldsymbol{b}_{\mathrm{A,B}}$. With this notation, the photometer A is compared versus the photometer B. $a_{\mathrm{A,B}}$ is dimensionless and $b_{\mathrm{A,B}}$ 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 08 to 11 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 direct comparison between the KRISS national standard KRISS-1 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-KRISS-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

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 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:

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

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

$$Tr = \frac{I_{\mathrm{ozone}}}{I_{\mathrm{air}}} \tag{2}$$

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:

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

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:

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

where

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

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

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):

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

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:

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

where:

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

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 KRISS-1

Compared to the original design of a NIST SRP, some new features were implemented in the KRISS instrument during its conception in 2002:

- Optical pieces encountered by the UV light (windows at both ends of the gas cells, filters, detectors) were tilted to avoid multiple reflections of the light beam. Thus, the optical design of the KRISS-1 is almost like in upgraded NIST SRPs.
- The source block is more isolated from the gas cells than in a NIST SRP. Thus, the temperature gradient revealed in [4] should be reduced. A maximum difference of 0.9 K in the gas temperature along the cell was measured by the KRISS.

12.7. Uncertainty budget of the KRISS-1

The uncertainty budget for the ozone mole fraction in dry air x measured by the KRISS standard KRISS-1 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 KRISS-1 can be expressed as a numerical equation (numerical values expressed as nmol/mol):

$$u(x) = \sqrt{(0.52)^2 + (4.8 \cdot 10^{-3} x)^2} \qquad (9)$$

No covariance term for the KRISS-1 was included in the calculations.

Table 2: Uncertainty budget for the KRISS-1

Input Component	Uncertainty				Sensitivity coefficient
	Source	Distribu-tion	Standard uncertainty	Combinded standard uncertainty	
Ratio of intensity (F)	Repeatability	Normal	2.5x10-5	2.7x10-5	$\frac{c}{F\ln(F)}$
	Resolution	Triang.	1.0x10-5		
Optical Path length (L)	Resolution	Triang.	0.058 cm	0.27 cm	$-\frac{c}{L}$
	Optical Path Bias	Rect.	0.26 cm		
Temperature (t)	Repeatability	Normal	0.000 K	0.52 K	$-\frac{c}{t}$
	Difference	Rect.	0.52 K		
Pressure (P)	Repeatability	Normal	0.023 hPa	0.034 hPa	$-\frac{c}{P}$
	Difference	Rect.	0.025 hPa		
Absorption coefficient (α)	Conventional value	-	-	-	-

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-KRISS-07 given in appendix.

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:

$$D_i = x_i - x_{\text{SRP27}} \qquad (10)$$

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-KRISS-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 KRISS 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	82.13	0.65	80.23	0.37	1.89	0.75	1.50
420	422.03	2.09	419.54	1.26	2.49	2.44	4.88

The degrees of equivalence between the KRISS standard and the common reference standard BIPM SRP27 indicate agreement between the standards at 420 nmol/mol only. 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 SRPn 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.

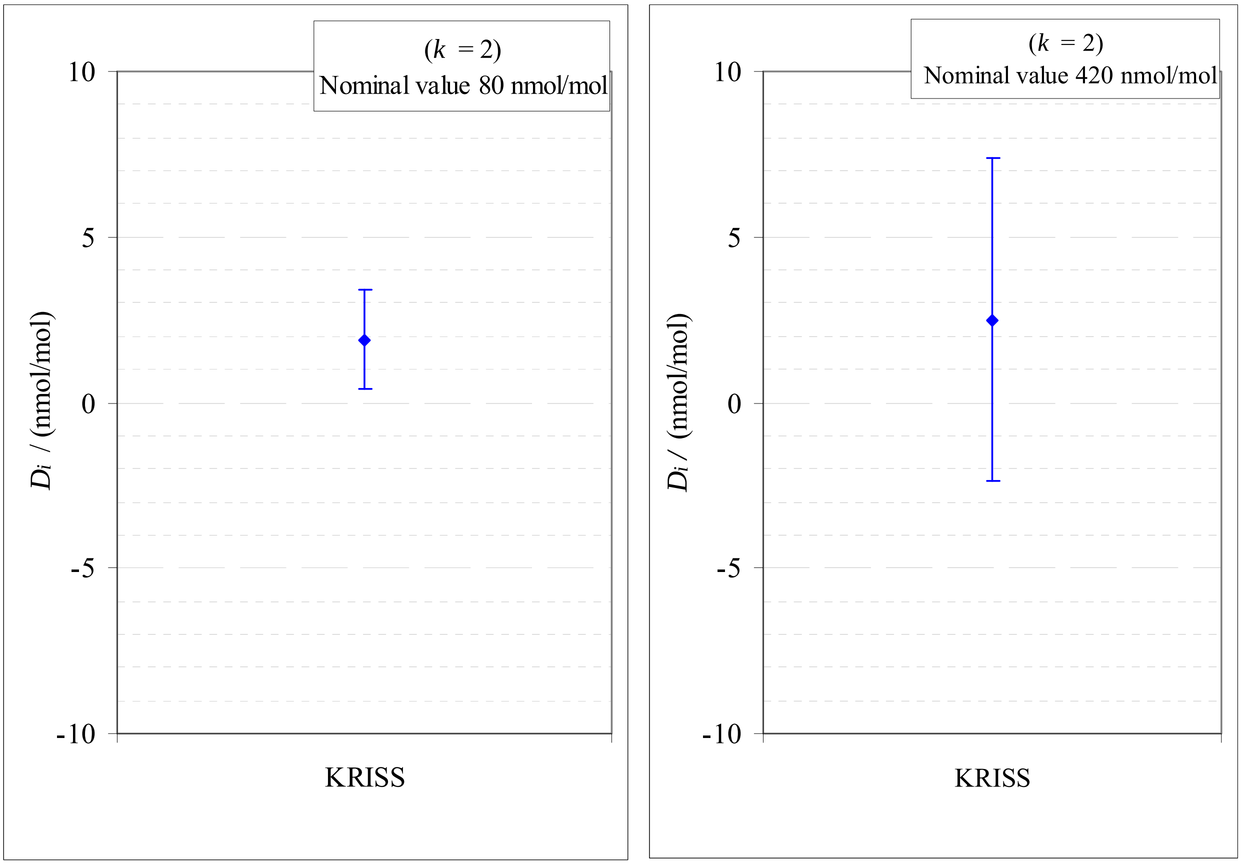


Figure 1: graphs of equivalence of the KRISS at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol

15.1. Least-square regression results

The relationship between KRISS-1 and SRP27 is:

$$x_{\text{KRISS-1}} = 0.25 + 1.0030 \cdot x_{\text{SRP27}} \tag{13}$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0037$ for the slope and $u(a_0) = 0.33$ nmol/mol for the intercept. The covariance between the two parameters is $\text{cov}(a_0, a_1) = -4.65 \times 10^{-4}$ 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 5.13 and a goodness of fit (GoF) equals to 1.63.

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. $|1 - a_1| < 2\,u(\text{a}_1)$.

16. History of comparisons between the BIPM and the KRISS

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.

The KRISS participated in the pilot study CCQM-P28 with the instrument KRISS-2, and with the instrument KRISS-1 during this key comparison. Both instruments are based on the same design. The sole difference lies in a piece called "beam parallelizers", which was present in the KRISS-2 and not in the KRISS-1. This piece has the shape of a 6-shots gun cylinder with the rotation axis aligned with the light beam. Its purpose is to block all light rays that are not parallel to the cells axe. After some investigation in the KRISS-2 instrument, the KRISS decided to remove this piece because it showed no effect on the ozone concentration measurements.

Figure 2 demonstrates that the agreement between the KRISS and the BIPM standards has been improved between September 2003 and October 2007. As explained in [4], the upgrade of SRPs comes with an enlargement of the uncertainties and should allow a better agreement among all SRPs in this key comparison exercise, compared to the pilot study CCQM-P28.

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

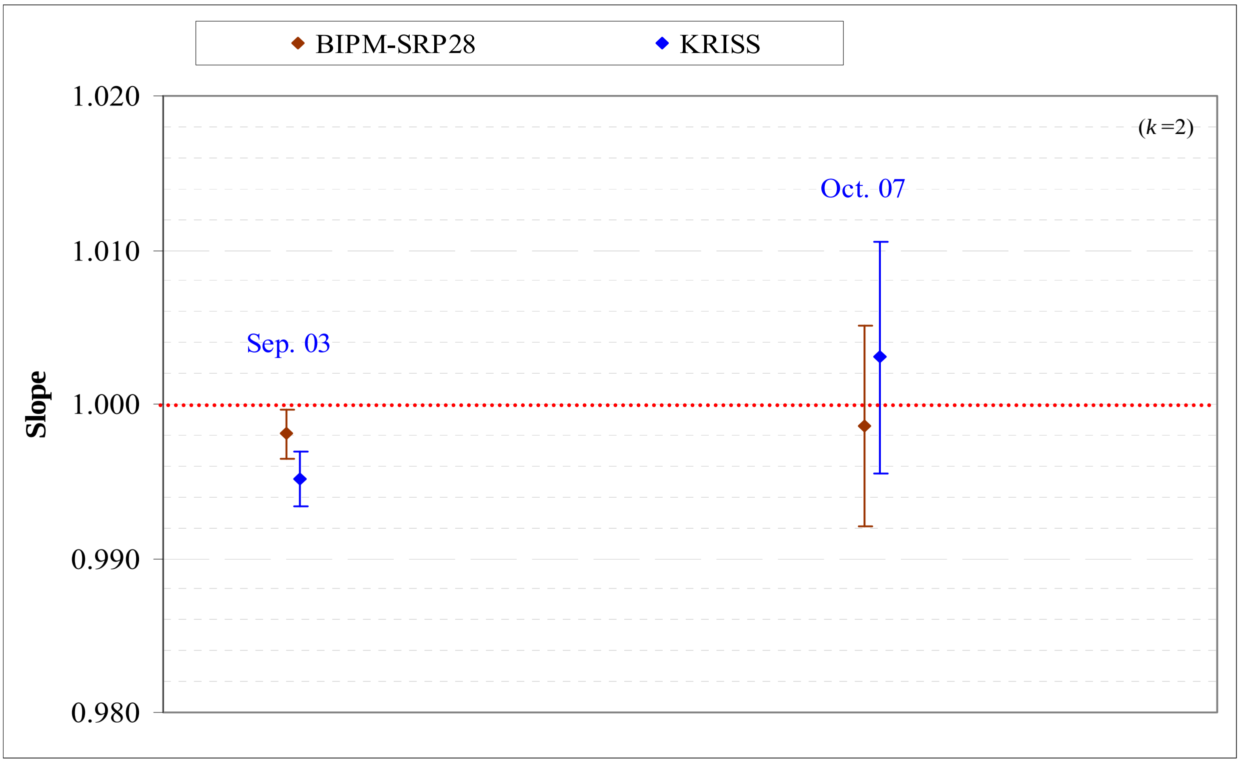
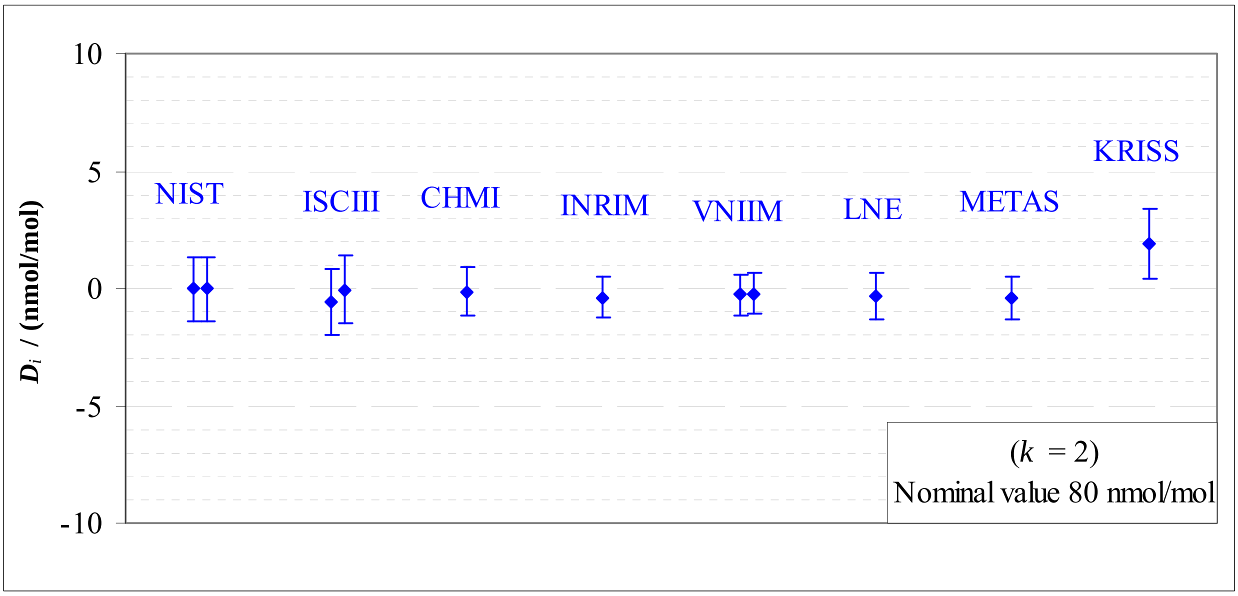


Figure 2 : Results of the comparisons between SRP27, SRP28 and the KRISS national standard performed at the BIPM during the pilot study CCQM-P28 and the key comparison BIPM.QM-K1. Uncertainties are calculated at k=2, with the uncertainty budget in use at the time of each comparison.

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

Graphs of equivalence including previous participants with published results [7] are displayed in Figure 3.



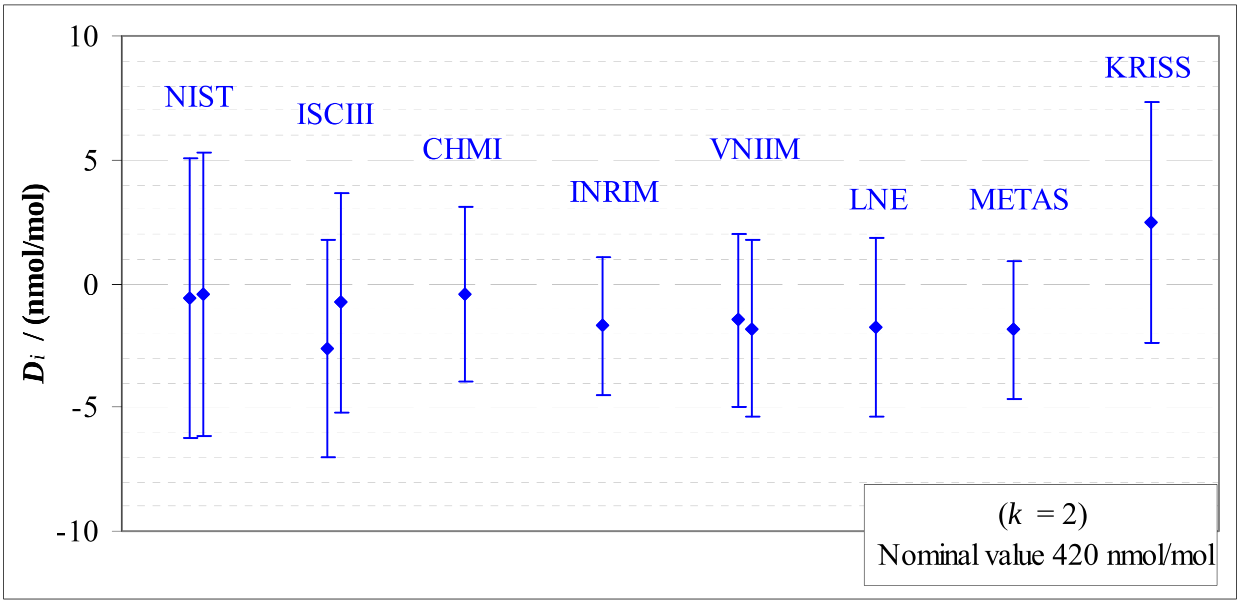


Figure 3: graphs of equivalence at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol, for all participants in BIPM.QM-K1 in the present cycle.

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 KRISS 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 was upgraded before this comparison, and the KRISS was already designed to avoid the biases. Degrees of equivalence of this comparison indicated a better agreement between both standards at 420 nmol/mol than at 80 nmol/mol.

19. References

1. Viallon, J., et al., *PILOT STUDY: International Comparison CCQM-P28: Ozone at ambient level,* Metrologia, 2006, **43, *Tech. Suppl.***: 08010.
2. Paur, R.J., et al., *Standard reference photometer for the assay of ozone in calibration atmospheres*, **NISTIR 6369**, 25 p
3. ISO, 13964 : 1996, *Ambient air - Determination of ozone - Ultraviolet photometric method*, International Organization for Standardization
4. Viallon, J., et al., *A study of systematic biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard Reference Photometer,* Metrologia, 2006, **43**: 441-450.
5. Bremser, W., J. Viallon, and R.I. Wielgosz, *Influence of correlation on the assessment of measurement result compatibility over a dynamic range,* Metrologia, 2007, **44**: 495-504.
6. ISO, 6143.2 : 2001, *Gas analysis - Determination of the composition of calibration gas mixtures - Comparison methods*, International Organization for Standardization
7. Viallon, J., et al., *Final report of the on-going key comparison BIPM.QM-K1: Ozone at ambient level, comparison with CHMI, 2007,* Metrologia, 2008, **45, *Tech. Supl.*** : 08005.

Appendix 1 - Form BIPM.QM-K1-R1-KRISS-077

See next 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	**Dr. jin-Chun Woo**
Email	jcwoo@kriss.re.kr
Telephone	**+82 42 868 5364**

Instruments information

	Reference Standard	**National Standard**
Manufacturer	NIST	KRISS
Type	SRP	O3-SRP (KRISS made)
Serial number	SRP27	KRISS-1

Content of the report

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

Operator	J. Viallon/P. Moussay J.C. Woo/B>M> Kim	**Location**	ROOM CHEM 9
Comparison begin date / time	08/10/2007 00:00	**Comparison end date / time**	11/10/2007 08:30

Comparison results

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

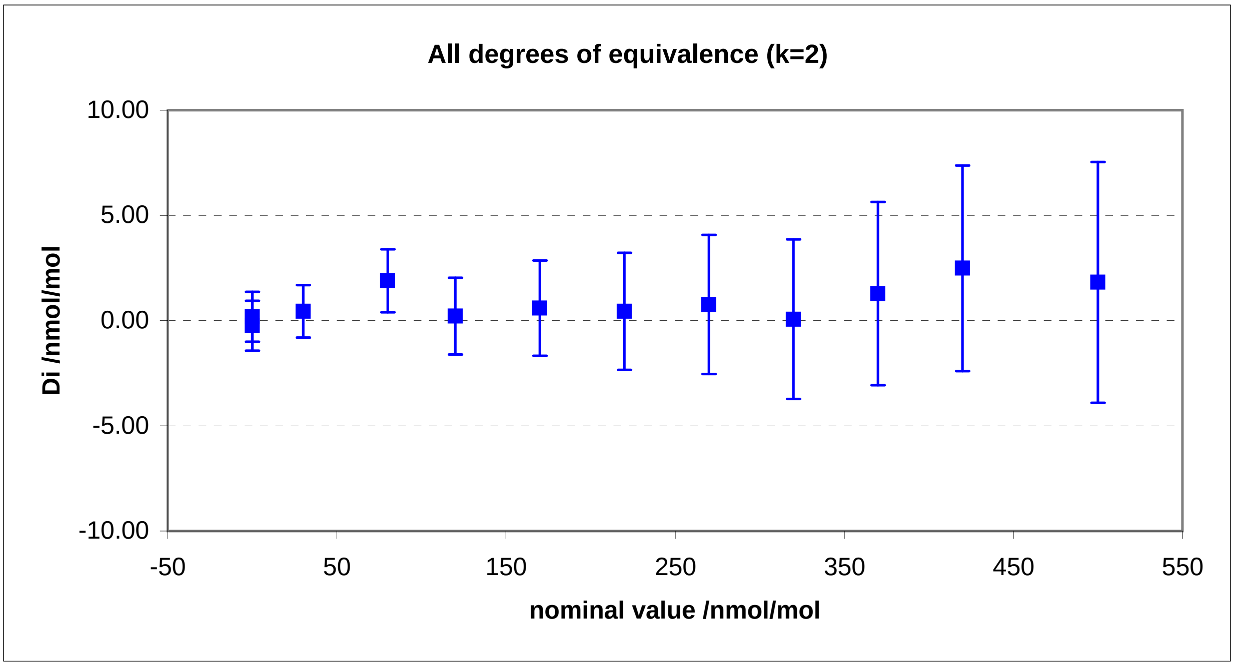
Least-square regression parameters

$a_{TS,RS}$	$u(a_{TS,RS})$	$b_{TS,RS}$ (nmol/mol)	$u(b_{TS,RS})$ (nmol/mol)	$u(a,b)$
1.0030	**0.0037**	**0.25**	**0.33**	**-4.65E-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	**1.89**	**0.75**	**1.50**
420	**2.49**	**2.44**	**4.88**



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	0.07	0.20	0.28	-0.16	0.32	0.52
220	223.60	0.22	0.71	224.05	0.30	1.20
80	80.23	0.18	0.37	82.13	0.46	0.65
420	419.54	0.26	1.26	422.03	0.38	2.09
120	123.12	0.22	0.46	123.34	0.39	0.79
320	320.07	0.21	0.98	320.13	0.51	1.62
30	33.66	0.29	0.30	34.10	0.19	0.55
370	371.92	0.43	1.12	373.20	0.38	1.87
170	171.17	0.21	0.57	171.75	0.58	0.98
500	496.70	0.23	1.48	498.52	0.33	2.45
270	273.26	0.17	0.85	274.02	0.48	1.42
0	0.08	0.20	0.28	0.27	0.31	0.52

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**	-0.24	0.59	1.19
2	**220**	0.44	1.39	2.78
3	**80**	1.89	0.75	1.50
4	**420**	2.49	2.44	4.88
5	**120**	0.21	0.91	1.82
6	**320**	0.07	1.89	3.79
7	**30**	0.43	0.62	1.25
8	**370**	1.28	2.18	4.36
9	**170**	0.59	1.13	2.26
10	**500**	1.82	2.86	5.72
11	**270**	0.77	1.65	3.30
12	**0**	0.19	0.59	1.19

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	22.5-22.6 °C
Room pressure (min-max) / hpa	1018
Zero air source	oil free compressor + dryer+ aadco 737-R
Reference air flow rate (L/min)	20
Sample flow rate (L/min)	10
Instruments stabilisation time	> 8 hours
Instruments acquisition time /s (one measurement)	5 both
Instruments averaging time /s	5
Total time for ozone conditioning	> 2 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	8
Data files names and location	\\chem5\Program Files\NIST\SRPControl\Data\2007
C071010003.xls to C071010010.xls	

Instruments checks and adjustments

Reference Standard

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

National Standard

KRISS procedure
temperature sensor calibrated
pressure sensor calibrated - small change
flow rate increased from 1.2 to 2 L/Min
flush time increased from 10s to 20s

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

The uncertainty budget is given as the same method applied for BIPM-SRP27 uncertainty budget. But, the following equation of ozone concetration with nmol/mol unit is used for the evaluation.

$$c=\frac{-\ln F}{2\alpha L}\cdot\frac{t}{273.15}\cdot\frac{101.325}{P}\times 10^9=B\cdot\ln F$$

Input Component	Uncertainty				Sensitivity coefficient
	Source	Distribu-tion	Standard uncertainty	Combinded standard uncertainty	
Ratio of intensity (F)	Repeatability	Normal	2.5x10-5	2.7x10-5	$\frac{c}{F\text{In}(F)}$
	Resolution	Triang.	1.0x10-5		
Optical Path length (L)	Resolution	Triang.	0.058 cm	0.27 cm	$-\frac{c}{L}$
	Optical Path Bias	Rect.	0.26 cm		
Temperature (t)	Repeatability	Normal	0.000 K	0.52 K	$-\frac{c}{t}$
	Difference	Rect.	0.52 K		
Pressure (P)	Repeatability	Normal	0.023 hPa	0.034 hPa	$-\frac{c}{P}$
	Difference	Rect.	0.025 hPa		
Absorption coefficient (α)	Conventional value	-	-	-	-

$$\left(\frac{u_c(c)}{c}\right)^2=\left(\frac{u(F)}{F\cdot\ln F}\right)^2+\left(\frac{u(L)}{L}\right)^2+\left(\frac{u(P)}{P}\right)^2+\left(\frac{u(t)}{t}\right)^2$$

$$u_c(c)=\sqrt{\left(\frac{u(F)}{F\cdot\ln F}\right)^2\cdot c^2+\left[\left(\frac{u(L)}{L}\right)^2+\left(\frac{u(P)}{P}\right)^2+\left(\frac{u(t)}{t}\right)^2\right]\cdot c^2}$$

$$u_c(c)=\sqrt{u^2(F)\cdot B^2+\left[\left(\frac{u(L)}{L}\right)^2+\left(\frac{u(P)}{P}\right)^2+\left(\frac{u(t)}{t}\right)^2\right]\cdot c^2}$$

where, $F\approx 1$ for the measurement range(0 to 500) nmol/mol.

$$\boxed{u_c(c)=\sqrt{0.52^2+\left(4.8\times 10^{-3}\cdot c\right)^2}}$$

where L =90.18 cm, with t = 295 K and P =101.3 hPa at the ordinary measurement condition.