

Final report, On-going Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with NMISA, 2008

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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 National Metrology Institute of South Africa (NMISA) 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.

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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 National Metrology Institute of South Africa (NMISA) are reported here. The NMISA was the thirteenth 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 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 mole fraction in dry air furnished by the ozone generator
- $x_{A,i}$: i th measurement of the nominal value x_{nom} by the photometer A.
- \bar{x}_A : the mean of N measurements of the nominal value x_{nom} measured by the photometer A :
$$\bar{x}_A = \frac{1}{N} \sum_{i=1}^N x_{A,i}$$
- s_A : standard deviation of N measurements of the nominal value x_{nom} measured by the photometer A :
$$s_A^2 = \frac{1}{N-1} \sum_{i=1}^N (x_{A,i} - \bar{x}_A)^2$$
- The result of the linear regression fit performed between two sets of data measured by the photometers A and B during a comparison is written: $x_A = a_{A,B}x_B + b_{A,B}$. With this notation, the photometer A is compared versus the photometer B. $a_{A,B}$ is dimensionless and $b_{A,B}$ is expressed in units of nmol/mol.

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 22 to 25 July 2008 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/utis/en/pdf/BIPM.QM-K1_protocol.pdf).

This comparison was performed following protocol A, corresponding to a comparison between the NMISA national standard API400-823 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 $\mu\text{mol/mol}$. The mole fraction of volatile organic hydrocarbons in the reference air was measured (November 2002), with no mole fraction of any detected component exceeding 1 nmol/mol .

The NMISA ozone generator API 401, serial number 106, was used to produce ozone in dry air.

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 $x_{\text{SRP27},i}$ 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

Normally, a second ozone reference standard, BIPM-SRP28, is included in the comparison to verify its agreement with BIPM-SRP27 and thus follow its stability over the period of the ongoing key comparison. This was not feasible during this comparison, as the NMISA ozone generator delivers insufficient flow of ozone in air. BIPM-SRP28 and BIPM-SRP27 were compared in the week before the measurements reported here.

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-NMISA-08 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

The standard deviation s_{RS} on 10 successive measurements recorded with the BIPM-SRP27 was not always less than 1 nmol/mol, as required in the protocol of the comparison. This demonstrates that NMISA's ozone generator was not operating in a stable regime. These instabilities have less effect on the standard deviations s_{NS} on measurements recorded with the NMISA standard because this instrument performs an automatic moving average on 32 successive measurements. This feature could not be turned off.

As no stable regime could be reached when performing further measurements, it was decided to continue the comparison and to include the value s_{RS} in the uncertainty associated with NMISA measurement results, as this was a characteristic of the ozone generator normally used with NMISA instrument.

12. Measurement standards

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

12.1. Measurement equation of a NIST SRP

The measurement of ozone mole fraction by an SRP is based on the absorption of radiation at 253.7 nm by ozonized air in the gas cells of the instrument. One particularity of the instrument design is the use of two gas cells to overcome the instability of the light source. The measurement equation is derived from the Beer-Lambert and ideal gas laws. The number concentration (C) of ozone is calculated from:

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

where

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

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

where

- I_{ozone} is the UV radiation intensity measured from cell when containing ozonized air, and
- I_{air} is the UV radiation intensity measured from cell when containing pure air (also called reference or zero air).

Using the ideal gas law equation (1) can be recast in order to express the measurement results as a mole fraction (x) of ozone in air:

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

where

- N_A is the Avogadro constant, $6.022142 \times 10^{23} \text{ mol}^{-1}$, and
- R is the gas constant, $8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$

The formulation implemented in the SRP software is:

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

where

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

$$\alpha_x = \sigma \frac{N_A}{R} \frac{P_{\text{std}}}{T_{\text{std}}} \quad (5)$$

12.2. Absorption cross section for ozone

The linear absorption coefficient at standard conditions α_x used within the SRP software algorithm is 308.32 cm^{-1} . This corresponds to a value for the absorption cross section σ of $1.1476 \times 10^{-17} \text{ cm}^2/\text{molecule}$, rather than the more often quoted $1.147 \times 10^{-17} \text{ cm}^2/\text{molecule}$. In the comparison of two SRP instruments, the absorption cross section can be considered to have a conventional value and its uncertainty can be set to zero. However, in the comparison of different methods or when considering the complete uncertainty budget of the method the uncertainty of the absorption cross section should be taken into account. 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 $u(x)$ $ c_i \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 | Rect | 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} cm ² /molecule | 1.22×10^{-19} cm ² /molecule | $-\frac{x}{\sigma}$ | $1.06 \times 10^{-2} x$ |

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:

$$u(x_i, x_j) = x_i \cdot x_j \cdot u_b^2 \quad (7)$$

where:

$$u_b^2 = \frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} + \frac{u^2(L_{opt})}{L_{opt}^2} \quad (8)$$

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

12.6. Actual state of the NMISA API400-823

The NMISA API400-823 is a UV photometric analyser, which is used as a transfer standard for the calibration of customers' ozone generators.

12.7. Uncertainty budget of the NMISA API400-823

The national standard API400-823 was calibrated by the BIPM prior to this comparison. Following this calibration, values measured by the API400 were corrected according to the equation in nmol/mol:

$$x_{corrected} = a_0 + a_1 x_{measured} = 0.09 + 0.9992 x_{measured} \quad (9)$$

The associated uncertainties were calculated accordingly:

$$u(x_{corrected}) = \sqrt{u(a_0)^2 + a_1^2 u(x_{measured})^2 + x_{measured}^2 u(a_1)^2 + 2x_{measured} u(a_0, a_1)} \quad (10)$$

Where the standard uncertainties on the parameters of the regression are $u(a_1) = 0.0036$ for the slope and $u(a_0) = 0.29$ nmol/mol for the intercept. The covariance between the two parameters is $\text{cov}(a_0, a_1) = -2.7 \times 10^{-4}$ nmol/mol. The standard uncertainty for each measured value is the experimental standard deviation associated with this value (s_{NS}), combined with the standard deviation on measurements recorded by BIPM-SRP27 (s_{RS}). Indeed, as explained previously, the unusually high standard deviations observed with BIPM-SRP27 were attributed to the API401 ozone generator and not to BIPM-SRP27.

No covariance term for the NMISA API400-823 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-NMISA-08 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:

$$D_i = x_i - x_{\text{SRP27}} \quad (11)$$

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:

$$u(D_i) = \sqrt{u_i^2 + u_{\text{SRP27}}^2} \quad (12)$$

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

For this particular comparison, because the NMISA API400-823 was calibrated by the BIPM-SRP27 instrument prior to the comparison, the values of the two instruments are fully correlated. This is taken into account in the calculation of the uncertainty of the degrees of equivalence using the following formula:

$$u(D_i) = \sqrt{u(x_i)^2 + (1 - 2a_1)u(x_{\text{SRP27}})^2} \quad (13)$$

Where a_1 is the slope of the linear relationship between NMISA API400-823 and SRP27 (equation 9). Here, because a_1 is very close to 1, equation 13 can be written:

$$u(D_i) = \sqrt{u(x_i)^2 - u(x_{\text{SRP27}})^2} \quad (14)$$

14.2. Values of the degrees of equivalence

The degrees of equivalence and their uncertainties calculated in the form BIPM.QM-K1-R1-NMISA-08 are reported in the table below. Corresponding graphs of equivalence are displayed in Figure 1. The expanded uncertainties are calculated with a coverage factor $k = 2$.

Table 2 : degrees of equivalence of the NMISA at the ozone nominal mole fractions 80 nmol/mol and 420 nmol/mol

| Nom value | $x_i /$ (nmol/mol) | $u_i /$ (nmol/mol) | $x_{\text{SRP27}} /$ (nmol/mol) | $u_{\text{SRP27}} /$ (nmol/mol) | $D_i /$ (nmol/mol) | $u(D_i) /$ (nmol/mol) | $U(D_i) /$ (nmol/mol) |
|------------------|-----------------------|-----------------------|------------------------------------|------------------------------------|-----------------------|--------------------------|--------------------------|
| 80 | 80.00 | 1.30 | 80.76 | 0.37 | -0.77 | 1.25 | 2.50 |
| 420 | 419.61 | 1.64 | 420.86 | 1.26 | -1.24 | 1.04 | 2.09 |

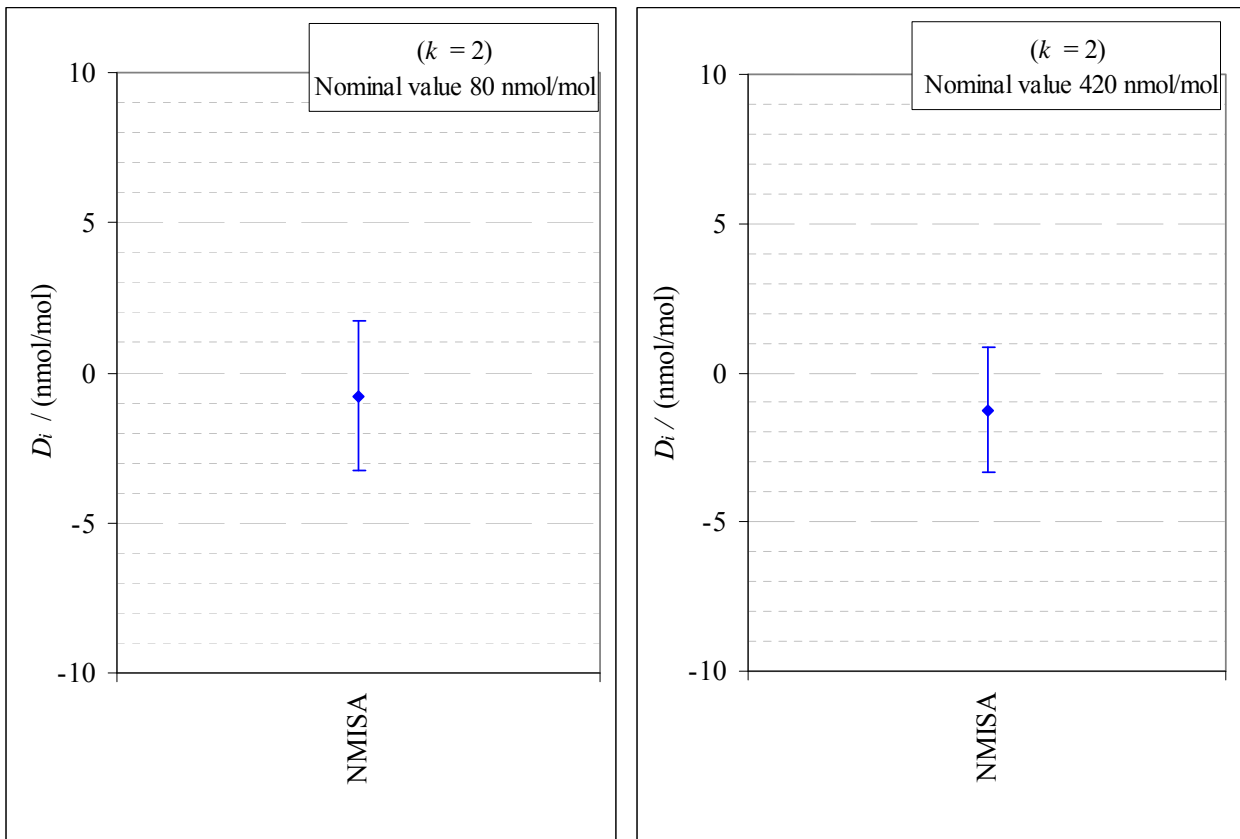


Figure 1: graphs of equivalence of the NMISA at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol

The degrees of equivalence between the NMISA 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:

$$x_{\text{SRP}_n} = a_0 + a_1 x_{\text{SRP27}} \quad (15)$$

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.

Because the NMISA API400-823 was calibrated by the BIPM-SRP27 instrument prior to this comparison, the values of the two instruments are correlated. Covariance terms between the values associated with each instrument at the same nominal mole fraction should be calculated and taken into account. Unfortunately, this feature is not implemented in the software OzonE. As the least-square results are given in this report for information only, parameters were calculated without these covariances.

15.1. Least-square regression results

The relationship between API400-823 and SRP27 is:

$$x_{\text{API400-803}} = -0.81 + 1.0009 \cdot x_{\text{SRP27}} \quad (16)$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0038$ for the slope and $u(a_0) = 0.34$ nmol/mol for the intercept. The covariance between the two parameters is $\text{cov}(a_0, a_1) = -4.67 \times 10^{-4}$ 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 1.65 and a goodness of fit (GoF) equals to 0.63.

To assess the agreement of the standards from equation 17, 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 slope is consistent with a slope of 1; i.e. $|1 - a_1| < 2 u(a_1)$, but the value of the intercept is not consistent with an intercept of zero, considering the uncertainty in the value of this parameter; i.e. $|a_0| < 2u(a_0)$. The value of the intercept is consistent with the two degrees of equivalence, which also show a negative offset of about 1 nmol/mol in the API400-823 instrument compared to SRP27. Records of the API400-823 measurement values during 72 hours show that the offset appeared during the first 30 hours and was followed by a stabilisation of the instrument. Values reported here were the last ones recorded; i.e. when the instrument was considered stable.

16. History of comparisons between the BIPM and the NMISA

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 $x_{\text{SRP}n} = a_0 + a_1 x_{\text{SRP27}}$ are represented together with their associated uncertainties calculated at the time of each comparison.

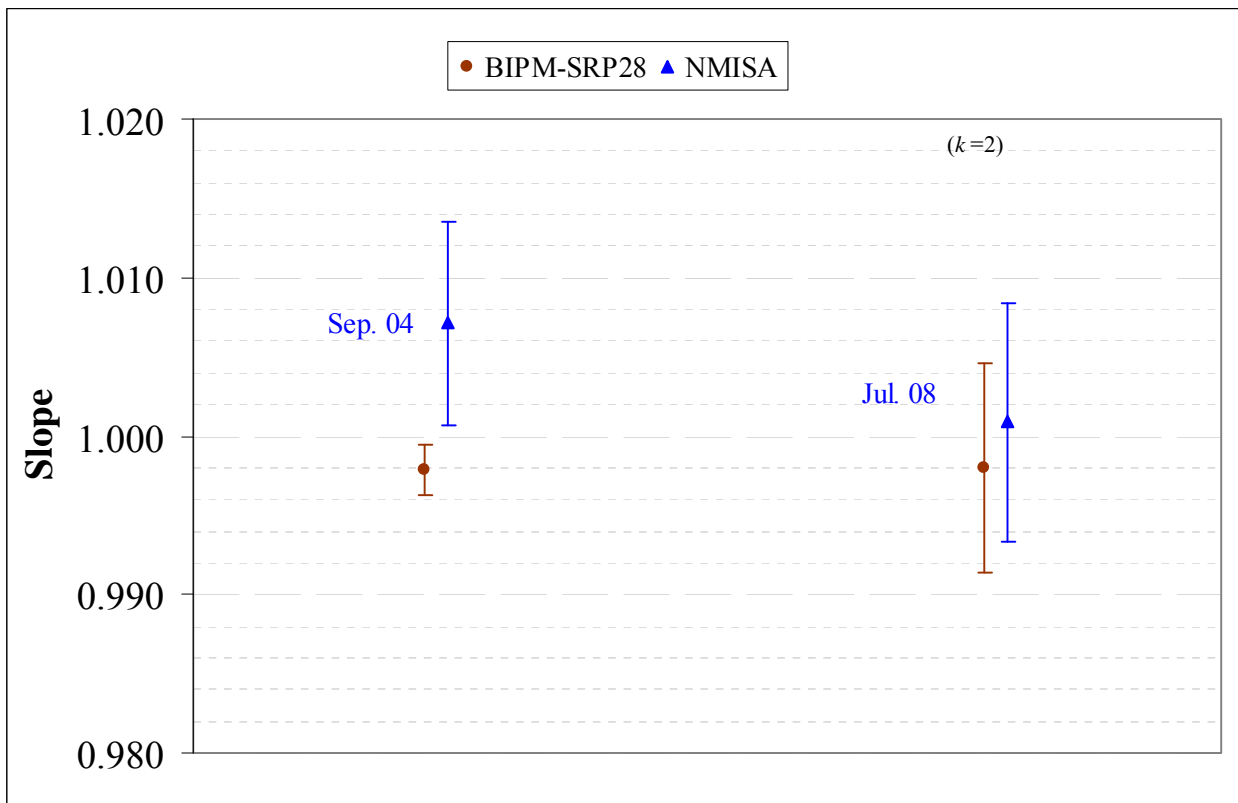


Figure 2 : Results of the comparisons between SRP27, SRP28 and NMISA-API400-823 performed at the BIPM during the pilot study CCQM-P28 and the key comparison BIPM.QM-K1. Uncertainties are calculated at $k=2$, with the uncertainty budget in use at the time of each comparison.

Figure 2 demonstrates that the agreement between the NMISA and BIPM standards has been improved between September 2004 and July 2008.

Figure 2 also shows results of comparisons between SRP27 and SRP28 recorded before the according comparisons with NMISA. It shows that stability of both instruments 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 are displayed in Figure 3.

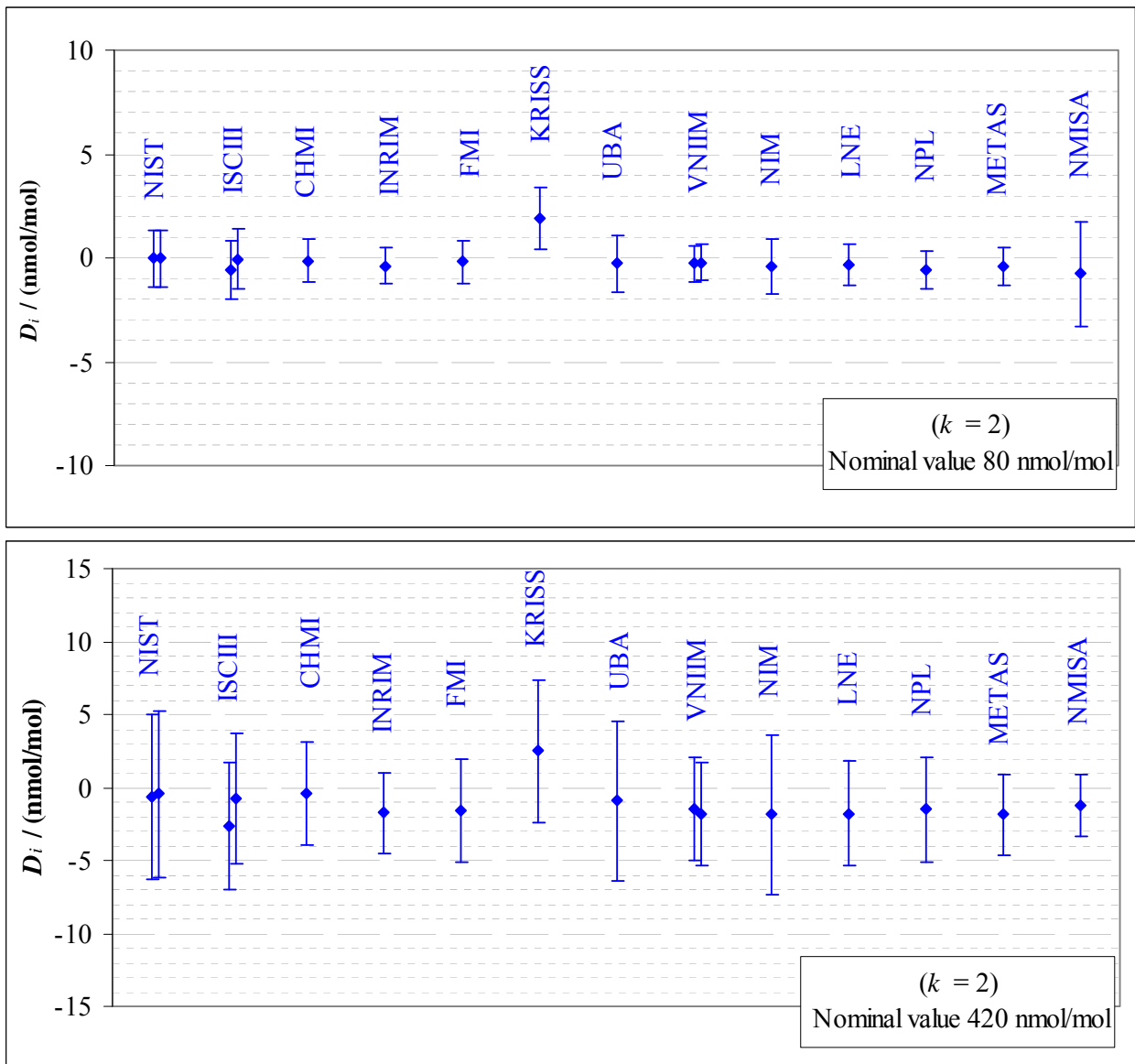


Figure 3: graphs of equivalence at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol, for all participants in BIPM.QM-K1 in the present cycle.

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 NMISA 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. Degrees of equivalence of this comparison indicated a good agreement between both standards.

19. References

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Appendix 1 - Form BIPM.QM-K1-R1-NMISA-08

See next pages.

**OZONE COMPARISON RESULT - PROTOCOL A - DIRECT
COMPARISON**

| Participating institute information | |
|--|---|
| Institute | National Metrology Institute of South Africa (NMISA) |
| Address | Private Bag X34 Lynnwood Ridge 0040 South Africa |
| Contact | Angelique Botha |
| Email | abotha@nmisa.org |
| Telephone | 27128413800 |

| Instruments information | | |
|--------------------------------|---------------------------|--------------------------|
| | Reference Standard | National Standard |
| Manufacturer | NIST | API |
| Type | SRP | 400 |
| Serial number | SRP27 | 823 |

| Content of the report | |
|------------------------------|------------------------|
| page 1 | general informations |
| page 2 | comparison results |
| page 3 | measurements results |
| page 4 | comparison description |
| page 5 | uncertainty budgets |

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

| | | | |
|-------------------------------------|------------------|-----------------------------------|------------------|
| Operator | J. Viallon | Location | CHEM09 |
| Comparison begin date / time | 22/07/2008 15:00 | Comparison end date / time | 25/07/2008 12:30 |

Comparison results

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

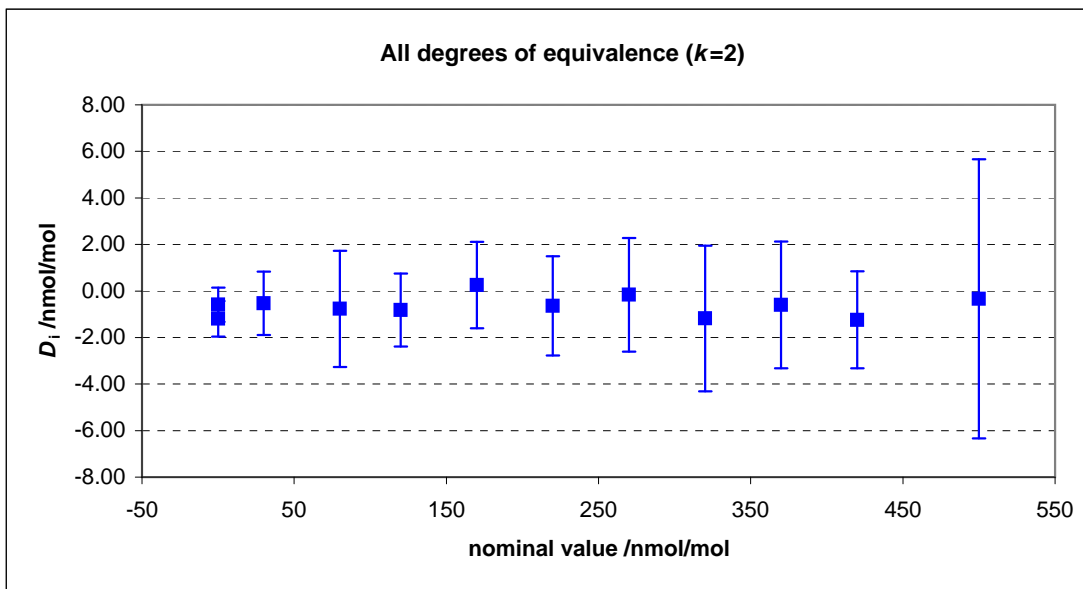
Least-square regression parameters

| $a_{TS,RS}$ | $u(a_{TS,RS})$ | $b_{TS,RS}$ (nmol/mol) | $u(b_{TS,RS})$ (nmol/mol) | $u(a,b)$ |
|---------------|----------------|---------------------------|------------------------------|------------------|
| 1.0009 | 0.0038 | -0.81 | 0.34 | -4.67E-04 |

(Least-square regression parameters will be computed by the BIPM using the software 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 | -0.77 | 1.25 | 2.50 |
| 420 | -1.24 | 1.04 | 2.09 |



| Measurement results | | | | | | | |
|---------------------|-------------------------|----------------------|-------------------------|------------------------|----------------------|-------------------------|-----------------|
| Nominal value | Reference Standard (RS) | | | National standard (NS) | | | measured values |
| | 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 | 1.20 | 0.32 | 0.28 | 0.00 | 0.20 | 0.47 | -0.09 |
| 220 | 220.50 | 1.01 | 0.70 | 219.85 | 0.14 | 1.28 | 219.94 |
| 80 | 80.76 | 1.23 | 0.37 | 80.00 | 0.25 | 1.30 | 79.97 |
| 420 | 420.86 | 0.62 | 1.26 | 419.61 | 0.39 | 1.64 | 419.86 |
| 120 | 120.83 | 0.71 | 0.45 | 120.00 | 0.33 | 0.90 | 120.01 |
| 320 | 321.08 | 1.42 | 0.98 | 319.89 | 0.38 | 1.84 | 320.06 |
| 30 | 50.66 | 0.67 | 0.32 | 50.13 | 0.16 | 0.75 | 50.08 |
| 370 | 370.35 | 1.18 | 1.12 | 369.75 | 0.25 | 1.76 | 369.96 |
| 170 | 169.68 | 0.87 | 0.57 | 169.94 | 0.25 | 1.09 | 169.99 |
| 500 | 490.22 | 2.84 | 1.46 | 489.88 | 0.41 | 3.34 | 490.18 |
| 270 | 269.90 | 1.09 | 0.84 | 269.73 | 0.35 | 1.48 | 269.86 |
| 0 | 0.74 | 0.18 | 0.28 | 0.15 | 0.31 | 0.46 | 0.06 |

| 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 | -1.20 | 0.38 | 0.77 |
| 2 | 220 | -0.64 | 1.07 | 2.13 |
| 3 | 80 | -0.77 | 1.25 | 2.50 |
| 4 | 420 | -1.24 | 1.04 | 2.09 |
| 5 | 120 | -0.82 | 0.78 | 1.57 |
| 6 | 320 | -1.18 | 1.56 | 3.13 |
| 7 | 30 | -0.53 | 0.68 | 1.36 |
| 8 | 370 | -0.59 | 1.36 | 2.73 |
| 9 | 170 | 0.26 | 0.93 | 1.86 |
| 10 | 500 | -0.34 | 3.00 | 6.00 |
| 11 | 270 | -0.16 | 1.22 | 2.45 |
| 12 | 0 | -0.59 | 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 8.50E-06

Value of α for the national standard 0.00E+00

Note 1 :values measured by the NMISA national standard API400 have been corrected according to the calibration performed at the BIPM on 17 July 2008 as explained with the uncertainty budget

Note 2: due to the calibration, the NMISA values are fully correlated with SRP27 values
This is taken into account in the calculation of the degrees of equivalence uncertainty:

$$u(D_i) = \sqrt{u(x_i)^2 - u(x_{ref})^2}$$

| |
|------------------------------|
| Comparison conditions |
|------------------------------|

| | |
|--|---|
| Ozone generator manufacturer | API |
| Ozone generator type | 401 |
| Ozone generator serial number | 106 |
| Room temperature(min-max) / °C | 22.74-22.85 °C |
| Room pressure (min-max) / hpa | 1003-1005 hPa |
| Zero air source | oil free compressor + dryer+ aadco 737-R |
| Reference air flow rate (L/min) | 5 L/min to SRP27 |
| Sample flow rate (L/min) | 4.6 L/min for SRP27 and API400 |
| Instruments stabilisation time | more than 24 hours both |
| Instruments acquisition time /s (one measurement) | SRP27 5 s / API 400 1.064 s |
| Instruments averaging time /s | SRP27 none / API 400 34.05 s |
| Total time for ozone conditioning | 2 hours |
| Ozone mole fraction during conditioning | 1000 nmol/mol |
| Comparison repeated continuously (Yes/No) | Yes |
| If no, ozone mole fraction in between the comparison repeats | |
| Total number of comparison repeats realised | 34 |
| Data files names and location | \\chem5\Program Files\NIST\SRPControl\Data\2008 files C080722001.xls to C080722020.xls and C080724001.xls to C080724014.xls |

Instruments checks and adjustments

Reference Standard

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

National Standard

Instruments parameters recorded via RS232 connection. No adjustment.

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 January 2007, available on BIPM website. It can be summarised by the formula:

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

National Standard

The national standard API400 serial number 803 was calibrated by the BIPM prior to this comparison. Following this calibration, values measured by the API400 were corrected according to the equation

$$x_{corrected} = a_0 + a_1 x_{measured} = 0.09 + 0.9992 x_{measured}, \text{ in nmol/mol}$$

associated uncertainties were calculated accordingly:

$$u(x_{corrected}) = \sqrt{u(a_0)^2 + a_1^2 u(x_{measured})^2 + x_{measured}^2 u(a_1)^2 + 2x_{measured} u(a_0, a_1)}$$

$$u(x_{corrected}) = \sqrt{0.29^2 + ((0.9992u(x_{measured}))^2 + (0.0036x_{measured})^2 - 2 \cdot 0.00027 \cdot x_{measured}}$$

where the standard uncertainty for each measured value is the experimental standard deviation associated with this value, combined with the standard deviation associated with BIPM-SRP27 measurement results..