

Final report, On-going Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with NPLI, 2009

Joële Viallon^{1*}, Philippe Moussay¹, Robert Wielgosz¹, B. C. Arya², Sumit K. Mishra², Arun Kumar², D. K. Shukla², James E. Norris³, Franklin R. Guenther³

¹ BIPM (Bureau International des Poids et Mesures), Pavillon de Breteuil, F-92312 Sèvres, France

² NPLI (National Physical Laboratory of India, Dr. K. S. Krishnan Marq., New Delhi-110 012, India

³ NIST (National Institute of Standards and Technology), 100 Bureau Stop 8383, Gaithersburg, MD 20899, United States

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 Physical Laboratory of India (NPLI) and the common reference standard of the key comparison, maintained by the Bureau International des Poids et Mesures (BIPM), via a transfer standard maintained by the National Institute of Standards and Technology (NIST). The instruments have been compared over a nominal ozone mole fraction range of 0 nmol/mol to 500 nmol/mol.

Contents:

FINAL REPORT, ON-GOING KEY COMPARISON BIPM.QM-K1, OZONE AT AMBIENT LEVEL, COMPARISON WITH NPLI, 2009	1
1. FIELD	2
2. SUBJECT	2
3. PARTICIPANTS	2
4. ORGANIZING BODY	2
5. RATIONALE	2
6. TERMS AND DEFINITIONS	2
7. MEASUREMENTS SCHEDULE	3
8. MEASUREMENT PROTOCOL	3
9. REPORTING MEASUREMENT RESULTS	5
10. POST COMPARISON CALCULATION	5
11. DEVIATIONS FROM THE COMPARISON PROTOCOL	5
12. MEASUREMENT STANDARDS	5
13. MEASUREMENT RESULTS AND UNCERTAINTIES	9
14. ANALYSIS OF THE MEASUREMENT RESULTS BY GENERALISED LEAST-SQUARE REGRESSION	9
15. DEGREES OF EQUIVALENCE	10
16. STABILITY OF THE TRANSFER STANDARD	12
17. HISTORY OF COMPARISONS BETWEEN BIPM SRP27, SRP28 AND NPLI SRP43	12
18. SUMMARY OF PREVIOUS COMPARISONS INCLUDED IN BIPM.QM-K1	12
19. CONCLUSION	13
20. REFERENCES	14
APPENDIX 1 - FORM BIPM.QM-K1-R3-NPLI-09.....	14

* Author for correspondence. E-mail jviallon@bipm.org, Tel: +33 1 45 07 62 70, Fax: +33 1 45 07 20 21.

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 Physical Laboratory of India (NPLI) are reported here. The list of all participants in BIPM.QM-K1 can be found on the BIPM website².

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.

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

7. Measurements schedule

The key comparison BIPM.QM-K1 is organised in rounds of 2 years. The 2007-2008 round started in January 2007 with a comparison with the NIST. Measurements reported in this report were performed in January 2007 at the BIPM and in February 2009 at the NPLI.

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 B, corresponding to a comparison between the NPLI national standard SRP43 and the common reference standard BIPM-SRP27 maintained at the BIPM via the transfer standard SRP0 maintained by the NIST. The common reference standard SRP27 and the transfer standard SRP0 were first compared at the BIPM in January 2007. Then SRP0 was compared with the national standard SRP43 at the NPLI in February 2009.

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

8.1. Comparisons at the NPLI

a). Ozone generation

A common source of zero air module model 701 Teledyne Instruments (Advanced Pollution Instrumentation) was used to provide the flows of reference air and Ozone. The source for Ozone sample and reference gas in the NPLI laboratory was SRP 43.

b). Comparison procedure

Prior to the comparison, all the instruments were switched on and allowed to stabilise for 3 days. Characteristics of the instruments were checked at this time following a procedure recommended by NIST. Adjustments were made by following the SRP Operating Characteristics Checkout procedure recommended by NIST.

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_{SRP43} on the set of 10 consecutive measurements $x_{\text{SRP43},i}$ recorded by SRP43 was calculated. The measurement results were considered as valid if s_{SRP43} was less than 1 nmol/mol, which ensures that the photometers were measuring a stable ozone concentration. If not, another series of 10 consecutive measurements was performed.

c). Comparison repeatability

The comparison procedure was repeated continuously to evaluate its repeatability.

8.2. Comparisons at the BIPM

a). Ozone generation

The same source of purified air is used for all the ozone photometers being compared. This air is used to provide reference air as well as the ozone-air mixture to each ozone photometer. Ambient air is used as the source for reference air. The air is compressed with an oil-free compressor, dried and scrubbed with a commercial purification system so that the mole fraction of ozone and nitrogen oxides remaining in the air is below detectable limits. The relative humidity of the reference air is monitored and the mole fraction of water in air typically found to be less than 3 $\mu\text{mol/mol}$. 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 .

A common dual external manifold in Pyrex is used to furnish the necessary flows of reference air and ozone-air mixtures to the ozone photometers. The two columns of this manifold are vented to atmospheric pressure.

b). Comparison procedure

Prior to the comparison, all the instruments were switched on and allowed to stabilise for at least 8 hours. The pressure and temperature measurement systems of the instruments were checked at this time. If any adjustments were required, these were noted. For this comparison, no adjustments were necessary.

One comparison run includes 10 different mole fractions distributed to cover the range, together with the measurement of reference air at the beginning and end of each run. The nominal mole fractions were measured in a sequence imposed by the protocol (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270, and 0) nmol/mol . Each of these points is an average of 10 single measurements.

For each nominal value of the ozone mole fraction x_{nom} furnished by the ozone generator, the standard deviation s_{SRP27} on the set of 10 consecutive measurements $x_{\text{SRP27},i}$ 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.

c). Comparison repeatability

The comparison procedure was repeated continuously to evaluate its repeatability. The participant and the BIPM commonly decided when both instruments were stable enough to start recording a set of measurement results to be considered as the official comparison results.

d). SRP27 stability check

A second ozone reference standard, BIPM-SRP28, was included in the comparison to verify its agreement with BIPM-SRP27 and thus follow its stability over the period of the on-going key comparison.

9. Reporting measurement results

The participant and the NIST staff reported the measurement results in the result form BIPM.QM-K1-R3 provided by the BIPM and available on the BIPM website. It includes details on the comparison conditions, measurement results and associated uncertainties, as well as the standard deviation for each series of 10 ozone mole fractions measured by the participant standard and the common reference standard. The completed form BIPM.QM-K1-R3-NPLI-09 is given in the annex.

10. Post comparison calculation

All calculations were performed by the BIPM using the form BIPM.QM-K1-R3. It includes the two degrees of equivalence that are reported as comparison results in the Appendix B of the BIPM KCDB (key comparison database). For information, the degrees of equivalence at all nominal ozone mole fractions are reported in the same form, as well as the linear relationship between the participant standard and the common reference standard.

11. Deviations from the comparison protocol

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

12. Measurement standards

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

12.1. Measurement equation of a NIST SRP

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

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

where

- σ is the absorption cross-section of ozone at 253.7nm in standard conditions of temperature and pressure. The value used is: 1.1476×10^{-17} cm²/molecule [3].
- L_{opt} is the optical path length of one of the cells,
- T is the measured temperature of the cells,
- T_{std} is the standard temperature (273.15 K),
- P is the measured pressure of the cells,
- P_{std} is the standard pressure (101.325 kPa),
- D is the product of transmittances of two cells, with the transmittance (Tr) of one cell defined as

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

where

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

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

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

where

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

The formulation implemented in the SRP software is:

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

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 1.1476×10^{-17} cm²/molecule, rather than the more often quoted 1.147×10^{-17} cm²/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 14, correlations in between the results of two measurements performed at two different ozone mole fractions with BIPM-SRP27 were taken into account in the software OzonE. More details on the covariance expression can be found in the protocol. The following expression was applied:

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

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 NPLI SRP43

The NPLI SRP43 has been constructed by NIST in 2008 with the new design, which includes the “SRP upgrade kit” in order to deal with the two biases revealed in [4]. This kit consists in two parts:

- A new source block was designed to minimise the gas temperature evaluation bias by better thermally insulating the UV source lamp (heated at a temperature of about 60°C) from the rest of the optical bench, thus avoiding the temperature gradient observed in the SRP when the original source block is used.
- A new set of absorption cells were installed. The new cells are quartz tubes closed at both ends by optically sealed quartz windows. These windows are tilted by 3° with respect to the vertical plane to avoid multiple reflections along the light path. However, to take into account a residual bias due to the beam divergence, the uncertainty is increased by the same amount as in SRP27 and SRP28.

12.7. Uncertainty budget of the NPLI SRP43

The uncertainty budget for the ozone mole fraction in dry air x measured by the NPLI standard SRP43 in the nominal range 0 nmol/mol to 500 nmol/mol will follow the BIPM/NIST paper [4] (see Table 1) with an additional component based on the temperature probe heating effect. The initial uncertainty can be summarised by the formula:

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

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

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

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

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

No covariance term for the NPLI SRP43 was included in the calculations.

12.8. Transfer standard SRP0

SRP0 uncertainty budget is the same as SRP43.

13. Measurement results and uncertainties

Details of the measurement results, the measurement uncertainties and the standard deviations at each nominal ozone mole fraction can be found in the form BIPM.QM-K1-R3-NPLI-09 given in appendix.

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

The relationship between the national and reference standards was first evaluated with a generalised least-square regression fit. To this end, the software OzonE was used. This software, which is documented in a publication [5], is an extension of the previously used software B_Least recommended by the ISO standard 6143:2001 [6]. It includes the possibility to take into account correlations between measurements performed with the same instrument at different ozone mole fractions. It also facilitates the use of a transfer standard, by handling of unavoidable correlations, which arise, as this instrument needs to be calibrated by the reference standard.

The comparison results are calculated by performing a linear regression on the twelve data points from the BIPM visit (x_{RS} , x_{TS}) (calibration of the transfer standard) followed by a second linear regression of the twelve data points from the NPLI visit (x_{NS} , x'_{TS}), x'_{TS} being the corrected values of the transfer standard calibrated by the reference standard.

A linear relationship between the ozone mole fractions measured by SRP n and SRP27 is obtained:

$$x_{SRPn} = a_0 + a_1 x_{SRP27} \quad (12)$$

The associated uncertainties on the slope $u(a_1)$ and the intercept $u(a_0)$ are given by OzonE, as well as the covariance between them and the usual statistical parameters to validate the fitting function.

14.1. Least-square regression results

The relationship between SRP43 and SRP27 is:

$$x_{\text{SRP43}} = -0.07 + 0.9964 \cdot x_{\text{SRP27}} \quad (13)$$

with the uncertainties $u(a_0) = 0.33$ nmol/mol, $u(a_1) = 0.0041$, $\text{cov}(a_0, a_1) = -5.1 \times 10^{-4}$ nmol/mol.

To assess the agreement of the standards from equations 13, the difference between the calculated slope value and unity, and the intercept value and zero, together with their measurement uncertainties need to be considered. Here the value of the intercept is consistent with an intercept of zero, considering the uncertainty in the value of this parameter; i.e. $|a_0| < 2u(a_0)$, and the value of the slope is consistent with a slope of 1; i.e. $|1 - a_1| < 2u(a_1)$.

15. Degrees of equivalence

Degrees of equivalence are calculated at two nominal ozone mole fractions among the twelve measured in each comparison, in the nominal range 0 nmol/mol to 500 nmol/mol: 80 nmol/mol and 420 nmol/mol. These values correspond to points number 3 and 4 recorded in each comparison. As an ozone generator has limited reproducibility, the ozone mole fractions measured by the ozone standards can differ from the nominal values. However, as stated in the protocol, the value measured by the common reference SRP27 was expected to be within ± 15 nmol/mol of the nominal value. Hence, it is meaningful to compare the degree of equivalence calculated for all the participants at the same nominal value.

15.1. Definition of the degrees of equivalence

Within protocol B, the degree of equivalence of the participant i , at a nominal value x_{nom} is defined as:

$$D = x_i - \hat{x}_{\text{SRP27}} \quad (14)$$

Where x_i is the measurement results of the national standard at the nominal value x_{nom} , and \hat{x}_{SRP27} is the predicted value of SRP27 at the same nominal value, deduced from the transfer standard measurement result during its comparison with the national standard.

Its associated standard uncertainty is:

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

where $u(x_i)$ is the measurement uncertainties of the participant i and $u(\hat{x}_{\text{SRP27}})$ is the uncertainty associated with the predicted value of SRP27.

15.2. Calculation of SRP27 predicted values and their related uncertainties

The comparison performed at the BIPM between the transfer standard and the reference standard SRP27 is used to calibrate the transfer standard. The data \bar{x}_{RS} and \bar{x}_{TS} are fitted using the generalised least square program OzonE, taking into account the associated

uncertainties $u(\bar{x}_{RS})$ and $u(\bar{x}_{TS})$, as well as covariance terms between the reference standard measurement results.

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

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

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

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

Where the uncertainty components $u(a_{RS,TS})$, $u(b_{RS,TS})$ and $u(a_{RS,TS}, b_{RS,TS})$ are calculated with the generalised least-square software OzonE.

15.3. Values of the degrees of equivalence

The degrees of equivalence and their uncertainties calculated in the form BIPM.QM-K1-R3-NPLI-09 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 NPLI at the ozone nominal mole fractions 80 nmol/mol and 420 nmol/mol

Nominal value	$x_i /$ (nmol/mol)	$u_i /$ (nmol/mol)	$x_{SRP27} /$ (nmol/mol)	$u_{SRP27} /$ (nmol/mol)	$D_i /$ (nmol/mol)	$u(D_i) /$ (nmol/mol)	$U(D_i) /$ (nmol/mol)
80	79.68	0.44	79.90	0.54	-0.23	0.70	1.39
420	399.50	1.60	401.12	2.08	-1.62	2.63	5.25

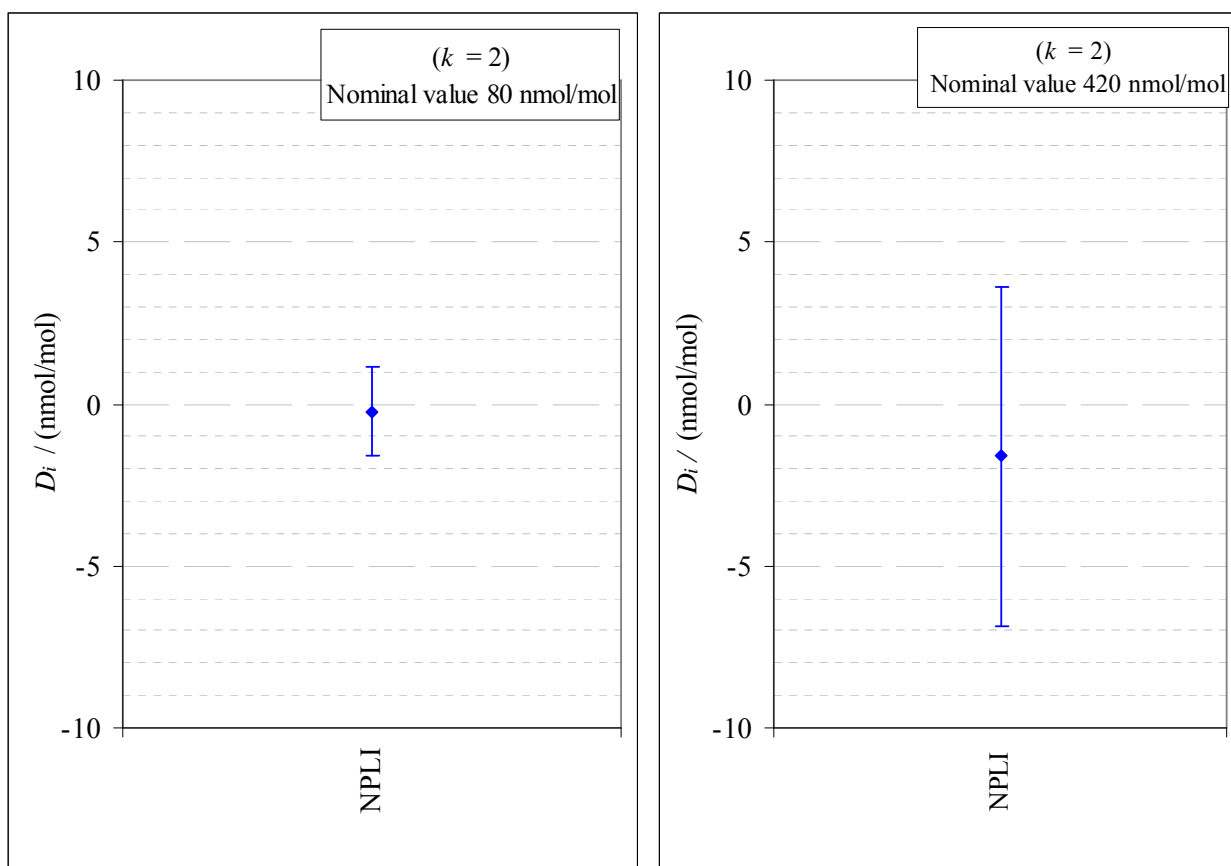


Figure 1: degrees of equivalence of the NPLI at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol

The degrees of equivalence between the NPLI standard and the common reference standard BIPM SRP27 indicate good agreement between the standards. A discussion on the relation between degrees of equivalence and CMC statements can be found in [1].

16. Stability of the transfer standard

In between January 2007 and March 2009, comparisons performed at NIST between the transfer standard SRP0 and NIST national standard SRP2 have shown a maximum variation of 0.01% on the slope of the relationship between the two instruments. This is negligible compared to the uncertainties declared in this comparison.

17. History of comparisons between BIPM SRP27, SRP28 and NPLI SRP43

This is the first time that NPLI SRP43 was compared to BIPM SRP27.

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

Graphs of equivalence including previous participants with published results are displayed in Figure 2.

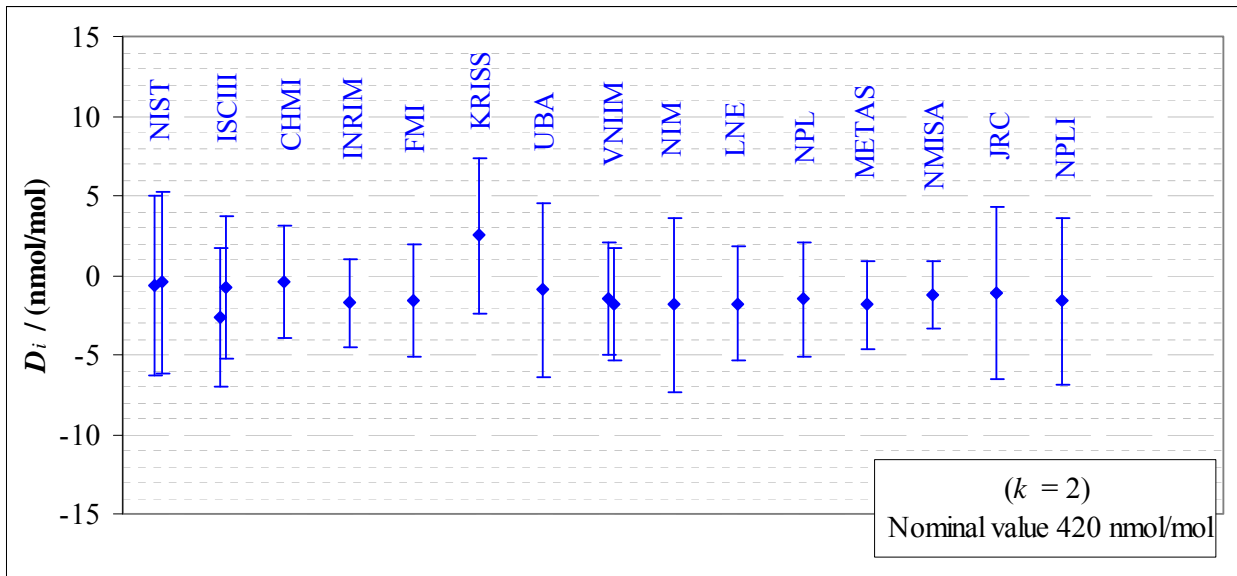
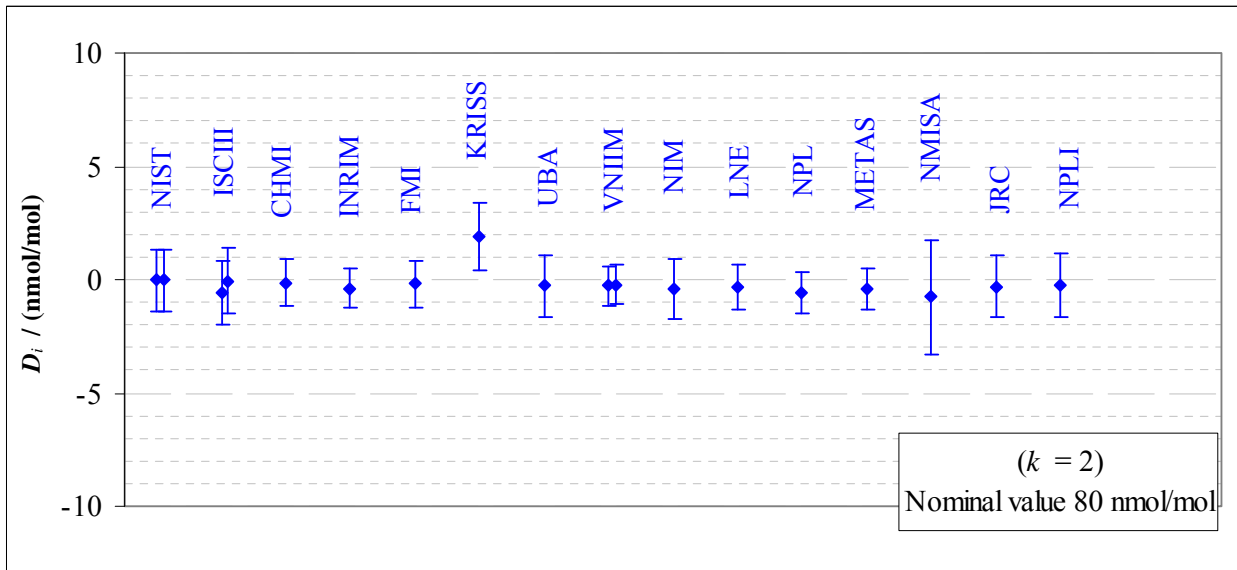


Figure 2: graphs of equivalence at the two nominal ozone mole fractions 80 nmol/mol and 420 nmol/mol, for all participants in BIPM.QM-K1 in the present cycle.

19. Conclusion

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

20. References

1. Viallon, J., P. Moussay, M. Esler, R. Wielgosz, W. Bremser, J. Novák, M. Vokoun, A. Botha, M. Janse Van Rensburg, C. Zellweger, S. Goldthorp, A. Borowiak, F. Lagler, J. Walden, E. Malgeri, M.P. Sassi, P. Morillo Gomez, R. Fernandez Patier, D. Galan Madruga, J.-C. Woo, Y. Doo Kim, T. Macé, C. Sutour, A. Surget, B. Niederhauser, D. Schwaller, B. Frigy, I. Györgyné Váraljai, S. Hashimoto, H. Mukai, H. Tanimoto, H.P. Ahleson, A. Egeløv, N. Ladegard, L. Marsteen, K. Tørnkvist, F.R. Guenther, J.E. Norris, T.L. Hafkenschied, M.M. Van Rijn, P. Quincey, B. Sweeney, S. Langer, B. Magnusson, J. Bastian, V. Stummer, M. Fröhlich, A. Wolf, L.A. Konopelko, Y.A. Kustikov, and D.V. Rumyanstev, *PILOT STUDY: International Comparison CCQM-P28: Ozone at ambient level*, Metrologia Technological Supplement, 2006, **43**: (8010).
2. Paur, R.J., A.M. Bass, J.E. Norris, and T.J. Buckley, *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., P. Moussay, J.E. Norris, F.R. Guenther, and R.I. Wielgosz, *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

Appendix 1 - Form BIPM.QM-K1-R3-NPLI-09

See next pages.

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

Linking institute information	
Institute	NIST
RMO	SIM
Address	100 Bureau Drive, Stop 8393 Gaithersburg, MD 20899
Contact	Jim Norris
Email	jnorris@nist.gov
Telephone	1-301-975-3936

Participating institute information	
Institute	NPL India
RMO	APMP
Address	Dr. K. S. Krishnan Marq., New Delhi-110 012, India
Contact	B. C. Arya/Y. Nazeer Ahammed
Email	bcarya@mail.nplindia.ernet.in / ynahammed@mail.nplindia.ernet.in
Telephone	+91-11-45608538 / +91-0-9871504264

Instruments information			
	Reference Standard Photometer	Participating Institute National Standard	Linking institute National Standard
Manufacturer	NIST	NIST	NIST
Type	SRP	SRP	SRP
Serial number	SRP27	SRP43	SRP0¹
ozone cross-section value	308.32 atm ⁻¹ cm ⁻¹	308.32 atm-1 cm-1	308.32 atm-1 cm-1

Note: in this form, the term "transfer standard (TS)" is used to designate the linking laboratory's standard, and the term "national standard (NS)" designates the participating institute's standard

¹ See explanations next page

Note : In this comparison, the standard SRP0 maintained by NIST as a transfer standard has been used instead of the National Standard SRP2. SRP0 has the same metrological performances as SRP2, and was indeed compared directly to both the reference standard SRP27 and the participating institute national standard SRP43.

Content of the report

page 1	General informations
page 3	Summary of the comparison results
page 4	calculation of the national standard vs reference standard first relationship
page 5	calculation of the national standard vs reference standard second relationship
page 6	Data reporting sheet - first comparison of the transfer standard vs the national standard
page 8	Calibration of the transfer standard by the reference standard at the BIPM
page 10	Data reporting sheet - second comparison of the transfer standard vs the national standard
page 12	Uncertainty budgets

Please complete the cells containing blue stars only.

After completion of the appropriate section of this report, please send to Joële Viallon

by email (jviallon@bipm.org), fax (+33 1 45342021), or mail (BIPM, Pavillon de Breteuil, F-92312 Sèvres)

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

Summary of comparison results

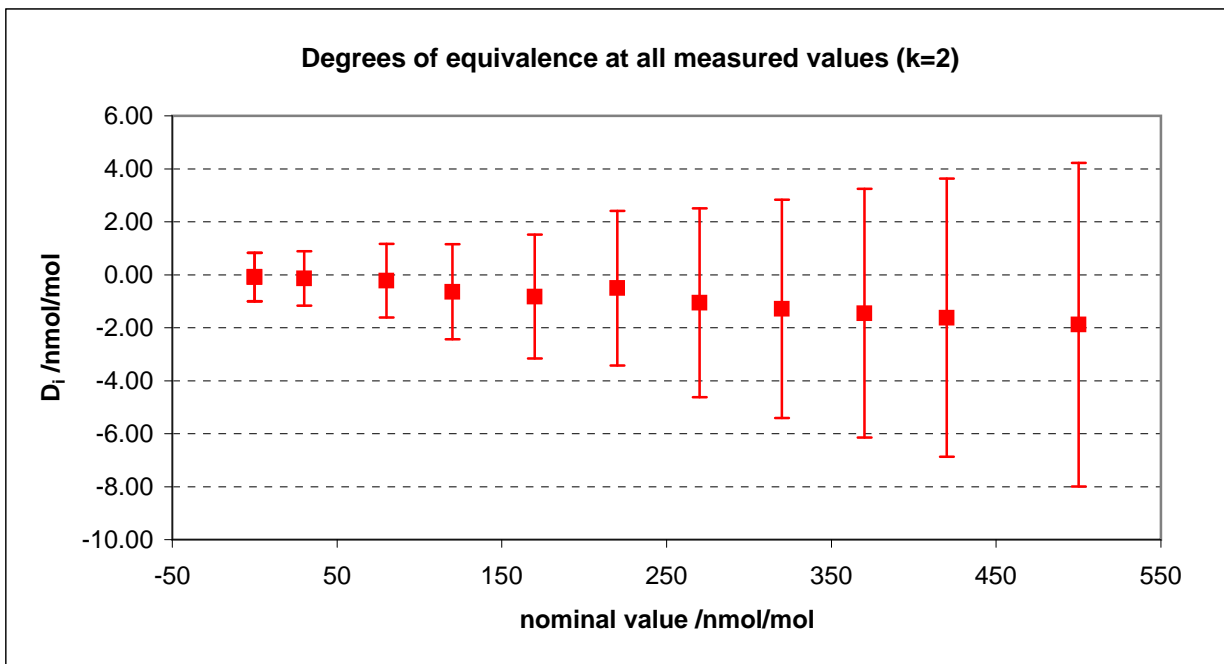
Equation
$$x_{NS} = a_{NS,RS} x_{RS} + b_{NS,RS}$$

Least-square regression parameters

	$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
first comparison	0.9964	0.0041	-0.07	0.33	-5.10E-04
second comparison	<i>no second comparison</i>				

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

	Nom value (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
first comparison	80	-0.23	0.70	1.39
	420	-1.62	2.63	5.25
second comparison	80	<i>no second comparison</i>		
	420			



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

First comparison results

Nominal value	National standard measurement results		Transfer standard measurement results		Reference Standard predicted values	
	x_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_{TS} nmol/mol	$u(x_{TS})$ nmol/mol	x'_{RS} nmol/mol	$u(x'_{RS})$ nmol/mol
0	-0.06	0.28	0.04	0.28	0.03	0.36
220	214.72	0.90	214.83	0.90	215.23	1.15
80	79.68	0.44	79.76	0.44	79.90	0.54
420	399.50	1.60	400.37	1.60	401.12	2.08
120	119.00	0.57	119.42	0.57	119.64	0.70
320	310.79	1.26	311.49	1.26	312.08	1.63
30	32.02	0.33	32.12	0.33	32.17	0.40
370	356.16	1.43	356.94	1.44	357.61	1.86
170	166.97	0.73	167.48	0.73	167.79	0.92
500	466.17	1.86	467.17	1.86	468.05	2.43
270	266.73	1.09	267.29	1.10	267.79	1.41
0	-0.06	0.28	0.03	0.28	0.02	0.36

Reference standard predicted values are deduced from the transfer standard measurement results using the calibration performed at the BIPM, with the parameters calculated in Excel Worksheet 4 (page 7)

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

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

Degrees of Equivalence		$D_i = x_{NS} - x'_{RS}$		
Point Number	Nom value (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
1	0	-0.09	0.46	0.91
2	220	-0.51	1.46	2.92
3	80	-0.23	0.70	1.39
4	420	-1.62	2.63	5.25
5	120	-0.64	0.90	1.80
6	320	-1.29	2.06	4.12
7	30	-0.14	0.51	1.03
8	370	-1.45	2.35	4.70
9	170	-0.82	1.17	2.34
10	500	-1.88	3.05	6.11
11	270	-1.06	1.78	3.56
12	0	-0.08	0.46	0.91

Least-square regression parameters				
$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
0.9964	0.0041	-0.07	0.33	-0.000510

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

Operator	B.C. Arya/Y. Nazeer Ahammed/J. Norris	Location	NPL India
Comparison begin date / time	3/3/09 13:35	Comparison end date / time	3/3/09 15:32

measurement results						
Nominal value	Transfer standard (TS)			National Standard (NS)		
	x_{TS} nmol/mol	s_{TS} nmol/mol	$u(x_{TS})$ nmol/mol	x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol
0	0.0	0.2	0.280	-0.1	0.1	0.280
220	214.8	0.2	0.902	214.7	0.3	0.901
80	79.8	0.3	0.444	79.7	0.2	0.444
420	400.4	0.2	1.603	399.5	0.1	1.599
120	119.4	0.2	0.567	119.0	0.2	0.565
320	311.5	0.3	1.263	310.8	0.2	1.260
30	32.1	0.2	0.327	32.0	0.2	0.327
370	356.9	0.5	1.436	356.2	0.5	1.433
170	167.5	0.2	0.731	167.0	0.1	0.729
500	467.2	0.2	1.860	466.2	0.1	1.856
270	267.3	0.2	1.096	266.7	0.3	1.094
0	0.0	0.2	0.280	-0.1	0.2	0.280

Note : according to the protocol, these measurement results are the last TS-NS comparison measurement results recorded

Covariance terms in between two measurement results of the national standard

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

Comparison conditions

Ozone generator manufacturer	NIST
Ozone generator type	NIST SRP
Ozone generator serial number	43
Room temperature(min-max) / °C	21.34/22.02
Room pressure (average) / hpa	978.7 mbar
Zero air source	Teledyne API-701
Reference air flow rate (L/min)	9
Sample flow rate (L/min)	5
Instruments stabilisation time	7 days
Instruments acquisition time /s (one measurement)	25
Instruments averaging time /s	25
Total time for ozone conditioning	120 min.
Ozone mole fraction during conditioning	800
Comparison repeated continuously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	4

Instruments checks and adjustments

National Standard

Performed SRP Operating Characteristics Checkout.

Transfer Standard

Performed SRP Operating Characteristics Checkout.

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

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

Calibration results

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

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

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

Measurement results

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

Note : according to the protocol, these measurement results are the last TS-RS comparison measurement results

Covariance terms in between two measurement results of the reference standard

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

Value of α 8.53E-06

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

Instruments checks and adjustments

Reference Standard

Performed SRP Operating Characteristics Checkout.

Transfer Standard

Performed SRP Operating Characteristics Checkout.

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

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

measurement results

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

Note : according to the protocol, these measurement results are the last TS-NS comparison measurement results recorded

Covariance terms in between two measurement results of the national standard

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

Comparison conditions

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

Instruments checks and adjustments

National Standard

Transfer Standard

Uncertainty budgets (description or reference)

Reference Standard

BIPM-SRP27 uncertainty budget is described in the protocol of this comparison: document BIPM.QM-K1 protocol, date 10 Januray 2007, available on BIPM website. It can be summarised by the formula:

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

Transfer Standard

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

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

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

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

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

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

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

National Standard

The uncertainty budget for NIST SRP 43 will follow the BIPM/NIST bias paper with the addition of an additional component based on the temperature probe heating affect. The initial uncertainty can be summarised by the formula:

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

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

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

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

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

Because NIST SRP 42 has the new 3 degree angled cell windows, there is no path-length correction.