Final report, Ongoing Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with NPL, (June 2022)

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Abstract

As part of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of United Kingdom maintained by the National Physical Laboratory (NPL) and the common reference standard of the key comparison, maintained by the Bureau International des Poids et Mesures (BIPM). The instruments have been compared over a nominal ozone amount fraction range of 0 nmol mol^{-1} to 500 nmol mol^{-1}.

Contents:

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1. Field

Amount of substance.

2. Subject

Comparison of reference measurement standards for ozone at ambient level.

3. Participants

BIPM.QM-K1 is an ongoing key comparison, which is structured as an ongoing series of bilateral comparisons. The results of the comparison with the National Physical Laboratory (NPL) are reported here.

4. Organizing body

BIPM.

5. Rationale

The ongoing key comparison BIPM.QM-K1 has been running since January 2007. It follows the pilot study CCQM-P28 that included 23 participants and was performed between July 2003 and February 2005 [1]. It is aimed at evaluating the degree of equivalence of ozone photometers that are maintained as national standards, or as primary standards within international networks for ambient ozone measurements. The reference value is determined using the NIST Standard Reference Photometer (BIPM-SRP27) maintained by the BIPM as a common reference.

6. Terms and definitions

- x_{nom}: nominal ozone amount 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.
- $\bar{x}_A$: 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: $x_A = a_{\mathrm{A,B}} x_B + b_{\mathrm{A,B}}$. 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^{-1}.

7. Measurements schedule

This is the fourth participation of NPL since 2007. Measurements reported in this report were performed on 22 June 2022 at the BIPM.

8. Measurement protocol

The comparison protocol is summarised in this section. The complete version can be downloaded from the BIPM website (BIPM.QM-K1 protocol).

This comparison was performed following protocol A, corresponding to a comparison between the NPL national standard SRP20 and the common reference standard BIPM-SRP27 maintained at the BIPM. A comparison between two (or more) ozone photometers consists of producing ozone-air mixtures at different amount 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. Starting from compressed ambient air, the purification system consisted of a first refrigeration dryer, a catalytic converter to burn residual oil, a second refrigeration dryer, a particulate filter to remove particles larger than 0.1 µm, an active coal filter, and a final zero air generator (AADCO 737R-12), which ensured that the amount fraction of ozone, hydrocarbons, and nitrogen oxides remaining in the air was below detectable limits. This final system also ensured a constant amount fraction of oxygen in air, which is important to generate constant ozone amount fractions in the ozone generator. The relative humidity of the reference air was monitored and the amount fraction of water in air was typically found to be less than 3 µmol mol^{-1}.

Ozone in air mixtures were produced from the purified air inside the ozone generator (Environics) equipped with a UV lamp to enable the photolysis of oxygen at a wavelength of 185 nm. To obtain a range of ozone amount fractions, the UV lamp intensity was tuned at appropriate levels. These actions were all controlled by the SRP operating software.

A common dual external Pyrex manifold was used to furnish the necessary flows of reference air and ozone-air mixtures to the ozone photometers. The two columns of this manifold were vented to atmospheric pressure. The same length of Teflon tubing was used to deliver both gas flows to all photometers under comparison, ensuring that they all received homogenized samples and reference air.

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 on BIPM SRPs and NPL SRP20.

One comparison run includes ten different amount fractions of ozone distributed to cover the range, together with the measurement of reference air at the beginning and end of each run. The nominal amount 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^{-1}. Each of these points is an average of ten single measurements.

For each nominal value of the ozone amount 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^{-1}, 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 ongoing key comparison.

9. Reporting measurement results

The participant and the BIPM staff reported the measurement results in the result form BIPM.QM-K1-R1 provided by the BIPM and available on the BIPM website. It includes details on the comparison conditions, measurement results and associated uncertainties, as well as the standard deviation for each series of 10 ozone amount fractions measured by the participant' standard and the common reference standard. The completed form BIPM.QM-K1-R1-NPL-22 is given in appendix 1.

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). Additionally, the degrees of equivalence at all nominal ozone amount 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 and NPL are Standard Reference Photometers (SRP) built by the NIST. More details on the instrument's principle and its capabilities can be found in [2]. The following section describes the SRP operating principle and uncertainty budget.

12.1. Measurement equation of a NIST SRP

The measurement of the ozone amount 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 density ($C_{\mathrm{O_3}}$) of ozone is calculated from:

$$C_{\mathrm{O_3}} = \frac{-1}{2\sigma L_{\mathrm{opt}}} \frac{T}{T_{\mathrm{std}}} \frac{P_{\mathrm{std}}}{P} ln(D) \qquad (1)$$

where

- σ is the absorption cross-section per molecule of ozone at 253.7 nm under standard conditions of temperature and pressure, 1.1476×10^{-17} cm^2 [3].
- L_{opt} is the mean optical path length of the two cells;
- T is the measured temperature of the cells;
- T_{std} is the standard temperature (273.15 K);
- P is the measured pressure of the cells;
- P_{std} is the standard pressure (101.325 kPa);
- D is the product of transmittances of two cells, with the transmittance (T_{r}) of one cell defined as

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

where

I_{ozone} is the UV radiation intensity measured from the cell when containing ozonized air, and

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

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

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

where

N_{A} is the Avogadro constant, 6.022 140 76 x 10^{23} mol^{-1}

R is the gas constant, 8.314 462 618 J mol^{-1} K^{-1}

The formulation implemented in the SRP software, although equivalent in terms of the measurement results, differs from the above in the choice of a unit system based on the "atm" (atmosphere) as unit for the pressure, rather than the SI. The conversion between the two systems is further detailed in a BIPM report[4], in which the units and values for the ozone absorption cross section at 253.65 nm (air) are discussed as well.

12.2. Absorption cross-section for ozone

The absorption coefficient under standard conditions α_0 used within the SRP software algorithm is 308.32 atm^{-1} cm^{-1}. This corresponds to a value for the absorption cross section σ of 1.1476 $\times 10^{-17}$ cm^2, rather than the more often quoted 1.147×10^{-17} cm^2 reported by Hearn in 1961 [5]. The CCQM recommended in 2020 [6] that a new value for the ozone absorption cross section be used in the on-going key comparison BIPM.QM-K1 and in all ozone photometers acting as ozone standards. A CCQM Task Group was created in 2020 to manage the synchronous change of ozone cross-section worldwide, with the aim to implement the new, consensus value, named CCQM.O3.2019 proposed by Hodges *et al.* [7], within the next 1 to 3 years.

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.

12.3. Condition of the BIPM SRPs

SRP27 and SRP28 were built in 2002. Compared to the original design described in [2], both instruments have been modified to deal with two biases revealed by the study conducted by the BIPM and the NIST in 2006 [8]. In 2009, an "SRP upgrade kit" was installed in the instruments [9]. In 2021, their electronic modules were upgraded. Negligible impact on their measurement results was demonstrated [10].

12.4. Uncertainty budget of the common reference BIPM-SRP27

The uncertainty budget for the ozone amount fraction in dry air (x) measured by the instruments BIPM-SRP27 and BIPM-SRP28 in the nominal range 0 nmol mol^{-1} to 500 nmol mol^{-1} 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^{-1}
	Source	**Distribution**	**Standard Uncertainty**	**Combined standard uncertainty $u(y)$**		
Optical Path L_{opt}	Measurement scale	Rectangular	0.0006 cm	0.52 cm	$-\frac{x}{L_{\mathrm{opt}}}$	$2.89 \times 10^{-3}x$
	Repeatability	Normal	0.01 cm			
	Correction factor	Rectangular	0.52 cm			
Pressure P	Pressure gauge	Rectangular	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37 \times 10^{-4}x$
	Difference between cells	Rectangular	0.017 kPa			
Temperature T	Temperature probe	Rectangular	0.03 K	0.07 K	$\frac{x}{T}$	$2.29 \times 10^{-4}x$
	Temperature gradient	Rectangular	0.058 K			
Ratio of intensities D	Scaler resolution	Rectangular	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D\,ln(D)}$	0.28
	Repeatability	Triangular	1.1×10^{-5}			
Absorption Cross section per molecule σ	Hearn value		1.22×10^{-19} cm²	1.22×10^{-19} cm²	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$

Following this budget, as explained in the protocol of the comparison, the standard uncertainty associated with the ozone amount fraction measurement with the BIPM SRPs can be expressed as a numerical equation (numerical values expressed as nmol mol^{-1}):

$$u(x) = \sqrt{(0.28)^2 + (2.92 \cdot 10^{-3}x)^2} \tag{4}$$

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 amount 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:

$$u(x_i, x_j) = x_i \cdot x_j \cdot u_b^2 \tag{5}$$

where:

$$u_b^2 = \frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} + \frac{u^2(L_{\mathrm{opt}})}{{L_{\mathrm{opt}}}^2} \tag{6}$$

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

12.6. Condition of the NPL SRP20

SRP20 maintained by the NPL has been constructed by NIST in 1997 and modified in 2008 to include the "SRP upgrade kit" in order to deal with the two biases revealed in [4]. Prior to the comparison reported here, its electronic module was exchanged as well for the new model proposed since 2020, as was done on BIPM SRPs [10]. Further details of measurements performed before and after the modification are provided in an annex to this report.

12.7. Uncertainty budget of the NPL SRP20

NPL SRP20 is based on the same measurement principle as described above, but the measurement equation (3) is written with different symbols as displayed in equation (7). It is recognised that equation (7) represents a simplification of the true SRP measurement, which has two parallel measurement cells, designed to reduce uncertainties due to instability of the light source. In effect this results in two measured values for I/I_0 that are averaged to give the value of I/I_0 in the below equation. It is the value of I/I_0 which is given by the instrument software, which does not distinguish between the two cells.

$$x = -\frac{1}{al}\ln\left(\frac{I}{I_0}\right)\frac{T}{T_0}\frac{P_0}{P} \qquad (7)$$

Where:

x Ozone amount fraction
a Absorption coefficient at standard conditions
l Average optical path length of cells
I Light intensity (254 nm) with ozone in the cell
I_0 Light intensity (254 nm) with no ozone in the cell
T Temperature in cells
T_0 Temperature at standard conditions (273.15 K)
P_0 Pressure at standard conditions (101.325 kPa)
P Pressure in cells

The uncertainty budget for the ozone amount fraction in dry air *x* measured by the NPL standard SRP20 in the nominal range 0 nmol mol^{-1}to to 500 nmol mol^{-1} to is given in Table 2.

Table 2. Uncertainty budget of SRP 20 after the upgrade. The values and uncertainty shown correspond to an ozone amount fraction of approximately 300 nmol mol^{-1} using typical temperature and pressure.

Component (y)	**Value**	**Standard uncertainty**	**Distribution**	**Contribution to uncertainty $u(x) = \|c_i\| \cdot u(y)$ [nmol mol^{-1}]**
a	308.32 atm^{-1} cm^{-1}	Exact	Gaussian	-
l	89.663 cm	0.004 cm	Gaussian	$4.46\times10^{-5}x$
		0.26 cm	Gaussian	$2.90\times10^{-3}x$
I	80546 a.u.	1.0 a.u.	Rectangular	~0.28[b]
I_0	81166 a.u.	1.0 a.u.	Rectangular	0.28
T	295 K	0.1 K	Gaussian	$3.39\times10^{-4}x$
T_0	273.15 K	Exact	Gaussian	-
P_0	101.325 kPa	Exact	Gaussian	-
P	101.1 kPa	0.05 kPa	Gaussian	$4.95\times10^{-4}x$

Following this budget, the standard uncertainty associated with the ozone amount fraction measurement with the NPL SRP20 can be expressed as equation (8) (numerical values expressed as nmol mol^{-1}):

[b] In the ozone fraction range between 0 and 500 nmol mol^{-1}

$$u(x) = \sqrt{(0.4)^2 + (2.96 \cdot 10^{-3} x)^2} \quad (8)$$

In equation (8), the term in the first bracket is the absolute uncertainty component and the term in the second bracket is the relative uncertainty component. No covariance term for the NPL SRP20 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 amount fraction can be found in the form BIPM.QM-K1-R1-NPL-22 given in appendix 1.

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, using the software OzonE. This software, which is documented in a publication [11], is an extension of the previously used software B_Least recommended by the ISO standard 6143:2001 [12]. It includes the possibility to take into account correlations between measurements performed with the same instrument at different ozone amount fractions.

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

$$x_i = a_0 + a_1 x_{\mathrm{SRP27}} \quad (9)$$

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 SRP20 and SRP27 is:

$$x_{\mathrm{SRP20}} = -0.02 + 1.0008 x_{\mathrm{SRP27}} \quad (10)$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0032$ for the slope and $u(a_0) = 0.25$ nmol mol^{-1} for the intercept. The covariance between the two parameters is $\mathrm{cov}(a_0, a_1) = -2.27 \times 10^{-4}$.

The least-squares regression results confirm that a linear fit is appropriate, with a sum of the squared deviations (SSD) of 0.39 and a goodness of fit (GoF) equals to 0.26.

To assess the agreement of the standards using equations 11 and 12, the difference between the calculated slope value and unity, and the intercept value and zero, together with their measurement uncertainties need to be considered. In this comparison, the value of the intercept is consistent with an intercept of zero, considering the uncertainty in the value of this parameter; i.e $|a_0| < 2u(a_0)$, and the value of the slope is consistent with a slope of 1; i.e. $|1 - a_1| < 2u(a_1)$.

15. Degrees of equivalence

Degrees of equivalence are calculated at two nominal ozone amount fractions among the twelve measured in each comparison, in the nominal range 0 nmol mol^{-1} to 500 nmol mol^{-1}: 80 nmol mol^{-1} and 420 nmol mol^{-1}. These values correspond to points number 3 and 4 recorded in each comparison. As an ozone generator has limited reproducibility, the ozone amount 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^{-1} 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

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

$$D_i = x_i - x_{\text{SRP27}} \tag{11}$$

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:

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

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

15.2. Values of the degrees of equivalence

The degrees of equivalence and their uncertainties calculated in the form BIPM.QM-K1-R1-NPL-22 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 NPL at the ozone nominal amount fractions 80 nmol mol^{-1}and 420 nmol mol^{-1}

Nominal value	x_i / (nmol mol^{-1})	u_i / (nmol mol^{-1})	x_{SRP27} / (nmol mol^{-1})	u_{SRP27} / (nmol mol^{-1})	D_i / (nmol mol^{-1})	$u(D_i)$ / (nmol mol^{-1})	$U(D_i)$ / (nmol mol^{-1})
80	83.20	0.47	83.35	0.37	-0.15	0.60	1.20
420	420.27	1.31	419.78	1.26	0.49	1.81	3.63

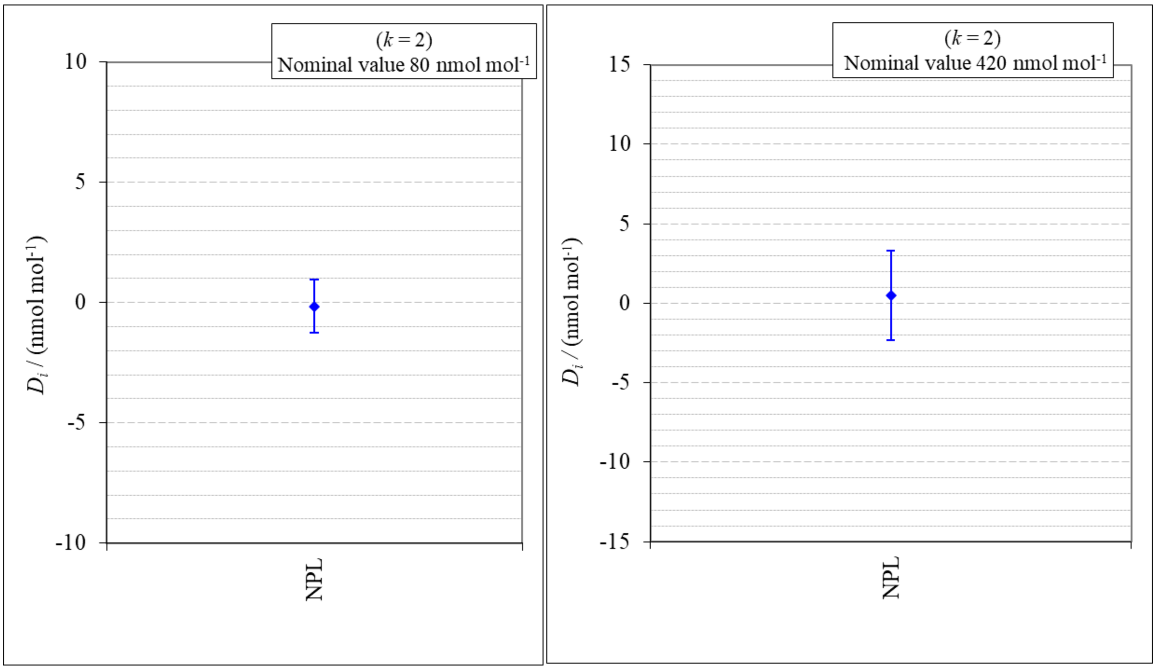

Figure 1: degrees of equivalence of the NPL at the two nominal ozone amount fractions 80 nmol mol^{-1}and 420 nmol mol^{-1}

The degrees of equivalence between the NPL 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. History of comparisons between BIPM SRP27, SRP28 and NPL SRP20

Results of the previous comparison performed with NPL are displayed in

Figure 2 together with the results of this comparison. The slopes a_1 of the linear relation $x_{SRPn} = a_0 + a_1\, x_{\mathrm{SRP27}}$ are represented together with their associated uncertainties calculated at the time of each comparison.

Figure 2 shows that all standards included in these comparisons stayed in close agreement.

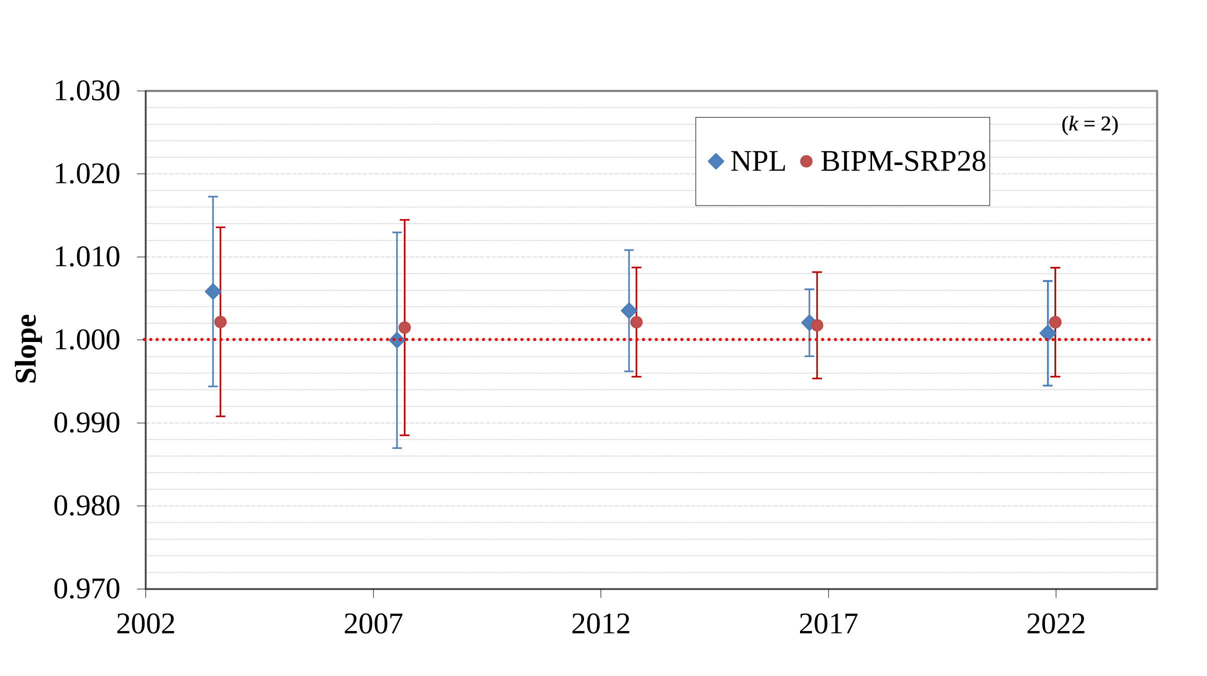

Figure 2: Results of previous comparisons between SRP27, SRP28 and NPL-SRP20 realised at the BIPM. Uncertainties are calculated at k = 2, with the uncertainty budget in use at the time of each comparison.

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

The comparison with NPL is the fourth one since the start of BIPM.QM-K1 in 2007. An updated summary of BIPM.QM-K1 results can be found in the key comparison database: http://kcdb.bipm.org/appendixB/.

18. Conclusion

For the fourth time since the launch of the ongoing key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of United Kingdom, maintained by the NPL, and the common reference standard of the key comparison, maintained by the BIPM. The instruments have been compared over a nominal ozone amount fraction range of 0 nmol mol^{-1} to 500 nmol mol^{-1}. Degrees of equivalence of this comparison indicated very good agreement between both standards.

19. References

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Appendix 1 - Form BIPM.QM-K1-R1-NPL-22

See the following pages.

Appendix 2 - Upgrade of the electronics modules of the NPL SRP20 prior to the comparison

NIST and the BIPM have jointly developed a new electronics module based on National Instrument cDAQ (compact Data Acquisition) components in response to concerns about aging electronic components within the NIST SRPs, which are increasingly difficult to maintain. Two similar prototypes of the electronics module have been validated by the two institutes. SRP20 maintained by the NPL was upgraded at the BIPM prior to its comparison with SRP27. To demonstrate negligible impact on the agreement between both standards, the comparison protocol was followed to compare their results before and after the upgrade. Results recorded after are displayed in the main body of the report, and results recorded before as displayed in the appendix.

1.1. Upgrade actions

The upgrade reported here consisted of:

1. Initial comparison between SRP20 and SRP27 following BIPM.QM-K1 protocol.
2. Exchange of the electronics box with the new one. This is expected to have no impact on the measurements as it does not modify its principle.
3. Replacement of the single temperature probe by a total of four probes located on the gas cells and connection to the electronic box. The two gas cells were thus equipped with two probes each, attached to each end of the cells. This allows the monitoring of any residual temperature gradient along each gas cell.

4. Calibration of all temperature probes against reference probes, which were themselves calibrated by the LNE. This was done by comparison of all probes when located close to each other in a temperature-controlled room. The reference temperature was entered in the O3Conductor software, which calculates the corrections to apply to each of the four probes.
5. Second comparison following BIPM.QM-K1 protocol.

1.2. Results

The results of the initial comparison are reported in a copy of the result form displayed in appendix of this document (PDF version only), showing as well the uncertainty budget for SRP20. As a summary, the linear relationships between SRP20 and SRP27 before and after the upgrade are compared in the table below. They demonstrate a negligible impact of the upgrade.

Table 4: parameters of the linear regression performed between SRP20 and SRP27 before and after the upgrade (slope a_1 and its standard uncertainty, intercept a_0 and its standard uncertainty, and the covariance between both)

	a_1	$u(a_1)$	a_0 / (nmol mol^{-1})	$u(a_0)$ / (nmol mol^{-1})	$u(a_0, a_1)$ / (nmol mol^{-2})
Before	1.0020	0.0045	0.13	0.38	-7.19×10^{-04}
After	1.0008	0.0032	−0.02	0.25	-2.27×10^{-04}

Appendix 3 - Uncertainty budget for SRP20

For the BIPM intercomparison, only the uncertainty sources related to the Beer-Lambert equation were taken into consideration. Furthermore, the ozone cross-section uncertainty was not considered as both institutions are using the same cross-section value for calculating ozone fractions.

The ozone fraction of the sample is determined by the application of the Beer-Lambert Law, shown in Eq. 1. It is recognised that the below equation represents a simplification of the true SRP measurement, which has two parallel measurement cells, designed to reduce uncertainties due to instability of the light source. In effect this results in two measured values for I/I_0 that are averaged to give the value of I/I_0 in the below equation.

$$x = -\frac{1}{al}\ln\left(\frac{I}{I_0}\right)\frac{T}{T_0}\frac{P_0}{P} \qquad \textit{Eq. 1}$$

Where:

x Ozone fraction
a Absorption coefficient at standard conditions
l Average optical path length of cells
I Light intensity (254 nm) with ozone in the cell
I_0 Light intensity (254 nm) with no ozone in the cell
T Temperature in cells
T_0 Temperature at standard conditions (273.15 K)
P_0 Pressure at standard conditions (101.325 kPa)
P Pressure in cells

After taking the partial derivative of Eq. 1, the sensitivity coefficient for each variable is given by:

Variable	**Sensitivity coefficient $c_i = \partial x/\partial y$**	
a	$\frac{1}{a^2 l} ln\left(\frac{I}{I_0}\right)\frac{T}{T_0}\frac{P_0}{P} = -\frac{x}{a}$	*Eq. 2*
l	$\frac{1}{al^2} ln\left(\frac{I}{I_0}\right)\frac{T}{T_0}\frac{P_0}{P} = -\frac{x}{l}$	*Eq. 3*
I	$-\frac{1}{I}\frac{1}{al}\frac{T}{T_0}\frac{P_0}{P} = \frac{x}{I \ln\left(\frac{I}{I_0}\right)}$	*Eq. 4*
I_0	$\frac{1}{I_0}\frac{1}{al}\frac{T}{T_0}\frac{P_0}{P} = -\frac{x}{I_0 \ln\left(\frac{I}{I_0}\right)}$	*Eq. 5*
T	$-\frac{1}{al} ln\left(\frac{I}{I_0}\right)\frac{1}{T_0}\frac{P_0}{P} = \frac{x}{T}$	*Eq. 6*
T_0	Not relevant	
P_0	Not relevant	
P	$\frac{1}{al} ln\left(\frac{I}{I_0}\right)\frac{1}{T_0}\frac{P_0}{P^2} = -\frac{x}{P}$	*Eq. 7*

1. Before SRP upgrade

Table 5 shows the typical values of variables in Eq. 1 for an ozone fraction of approximately 300 nmol/mol.

Table 5. Uncertainty budget of SRP 20 before the upgrade. The values and uncertainty shown correspond to an ozone fraction of approximately 300 nmol/mol using typical temperature and pressure.

Component (y)	**Value**	**Standard uncertainty**	**Distribution**	**Contribution to uncertainty $u(x) = \|c_i\| \cdot u(y)$ [nmol mol^{-1}]**
a	308.32 atm^{-1} cm^{-1}	Exact	Gaussian	-
l	90 cm	0.01 cm	Gaussian	$1.11\times10^{-4}x$
		0.26 cm	Gaussian	$2.89\times10^{-3}x$
I	107375 a.u.	1 a.u.	Rectangular	~0.22[c]
I_0	108181 a.u.	1 a.u.	Rectangular	0.21
T	303 K	1 K	Gaussian	$3.30\times10^{-3}x$
T_0	273.15 K	Exact	Gaussian	-
P_0	101.325 kPa	Exact	Gaussian	-
P	101.1 kPa	0.2 kPa	Gaussian	$1.98\times10^{-3}x$

Combined standard uncertainty (k = 1): 0.3 nmol/mol + 0.481% (to be added in quadrature)

[c] In the ozone fraction range between 0 and 500 nmol mol^{-1}

$$u(x) = \sqrt{(0.3)^2 + (4.81 \times 10^{-3} x)^2}\ [nmol\ mol^{-1}]$$

2. After SRP upgrade

Table 2 shows the typical values of variables in Eq. 1 for an ozone fraction of approximately 300 nmol/mol.

Table 6. Uncertainty budget of SRP 20 after the upgrade. The values and uncertainty shown correspond to an ozone fraction of approximately 300 nmol/mol using typical temperature and pressure.

Component (y)	**Value**	**Standard uncertainty**	**Distribution**	**Contribution to uncertainty $u(x) = \lvert c_i \rvert \cdot u(y)$ [nmol mol^{-1}]**
a	308.32 atm^{-1} cm^{-1}	Exact	Gaussian	-
l	89.663 cm	0.004 cm	Gaussian	$4.46\times10^{-5}x$
		0.26 cm	Gaussian	$2.90\times10^{-3}x$
I	80546 a.u.	1.0 a.u.	Rectangular	~0.28[d]
I_0	81166 a.u.	1.0 a.u.	Rectangular	0.28
T	295 K	0.1 K	Gaussian	$3.39\times10^{-4}x$
T_0	273.15 K	Exact	Gaussian	-
P_0	101.325 kPa	Exact	Gaussian	-
P	101.1 kPa	0.05 kPa	Gaussian	$4.95\times10^{-4}x$

Combined standard uncertainty (k = 1): 0.4 nmol/mol + 0.296% (to be added in quadrature)

$$u(x) = \sqrt{(0.4)^2 + (2.96 \times 10^{-3} x)^2}\ [nmol\ mol^{-1}]$$

[d] In the ozone fraction range between 0 and 500 nmol mol^{-1}

OZONE COMPARISON RESULT - PROTOCOL A - DIRECT COMPARISON

Participating institute information	
Institute	**National Physical Laboratory**
Address	Hampton Road Teddington Middlesex TW11 0LW United Kingdom
Contact	**Jesus Marval**
Email	jesus.marval@npl.co.uk
Telephone	**+44 (0)20 8943 6037**

Instruments information		
	Reference Standard	**National Standard**
Manufacturer	NIST	NIST
Type	SRP	SRP
Serial number	SRP27	SRP20

Content of the report

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

Operator	F. IDREES	**Location**	BIPM/CHEM09
Comparison begin date / time	2022-06-21 04:02	**Comparison end date / time**	2022-06-21 06:33

Comparison results

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

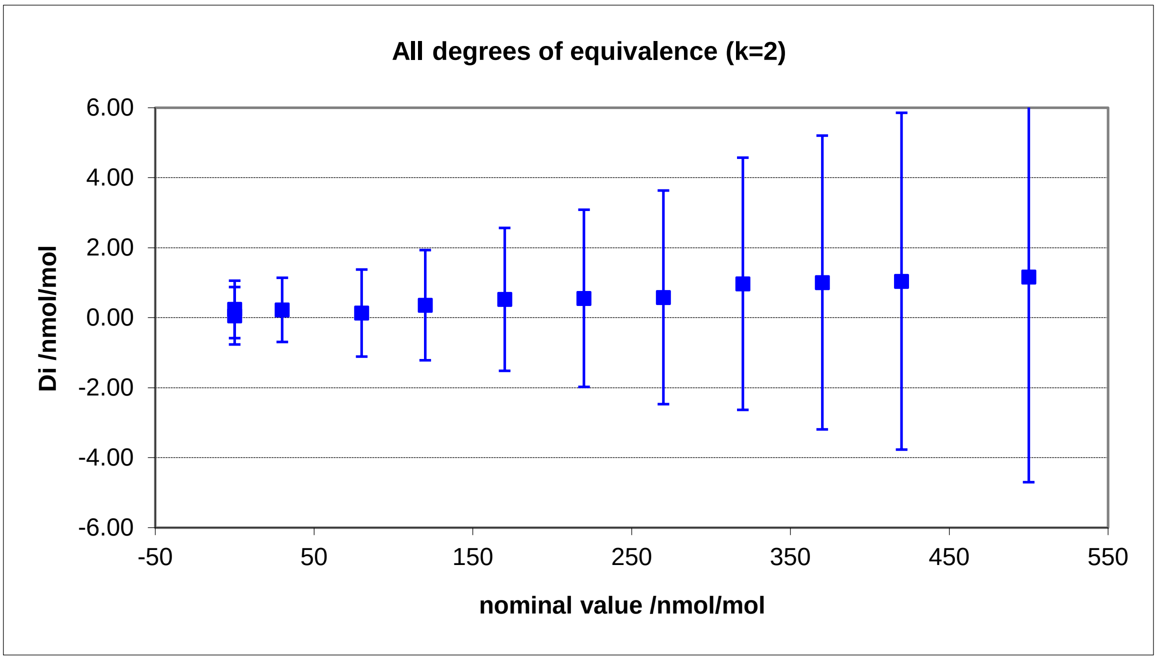
Least-square regression parameters

$a_{TS,RS}$	$u(a_{TS,RS})$	$b_{TS,RS}$ (nmol/mol)	$u(b_{TS,RS})$ (nmol/mol)	$u(a,b)$
1.0020	**0.0045**	**0.13**	**0.38**	**-7.19E-04**

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

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

Nom value (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
80	**0.133326**	**0.62193919**	**1.24387838**
420	**1.044161**	**2.4060505**	**4.81210099**



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	-0.17	0.29	0.28	0.07	0.16	0.30
220	212.39	0.13	0.68	212.95	0.19	1.07
80	82.96	0.27	0.37	83.09	0.18	0.50
420	420.57	0.29	1.26	421.61	0.35	2.05
120	119.13	0.17	0.45	119.49	0.27	0.65
320	311.09	0.31	0.95	312.06	0.27	1.53
30	36.17	0.25	0.30	36.40	0.12	0.35
370	365.10	0.27	1.10	366.11	0.21	1.79
170	165.74	0.23	0.56	166.27	0.19	0.85
500	515.15	0.24	1.53	516.31	0.30	2.50
270	260.83	0.21	0.81	261.41	0.28	1.29
0	0.06	0.20	0.28	0.12	0.27	0.30

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	0.41	0.82
2	**220**	0.55	1.27	2.53
3	**80**	0.13	0.62	1.24
4	**420**	1.04	2.41	4.81
5	**120**	0.36	0.79	1.57
6	**320**	0.97	1.80	3.60
7	**30**	0.22	0.46	0.92
8	**370**	1.01	2.10	4.20
9	**170**	0.52	1.02	2.04
10	**500**	1.17	2.93	5.86
11	**270**	0.58	1.53	3.05
12	**0**	0.06	0.41	0.82

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	25.6 - 25.7
Room pressure (min-max) / hpa	1000.9 - 1001.4
Zero air source	compressor + BekoKAT + dryer+ aadco 737-R
Reference air flow rate (L/min)	14
Sample flow rate (L/min)	10
Instruments stabilisation time	> 8 hours
Instruments acquisition time /s (one measurement)	5
Instruments averaging time /s	5
Total time for ozone conditioning	> 24 hours
Ozone mole fraction during conditioning	1000 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	G:\Gas\Ozone\BIPM.QM-K1\Participants results\2206 NPL
Cal22062003.xls to Cal22062102.xls	

Instruments checks and adjustments

Reference Standard

National Standard

Uncertainty budgets (description or reference)

Reference Standard

National Standard

The standard uncertainty in the measurements made by SRP 20 can be summarised by the equation:

$u(c)=[(0.3)^2 + (0.00481c)^2]^{0.5}$

There is no contribution due to the uncertainty in the absorption cross section in this uncertainty estimate.

OZONE COMPARISON RESULT - PROTOCOL A - DIRECT COMPARISON

Participating institute information	
Institute	**National Physical Laboratory**
Address	Hampton Road Teddington Middlesex TW11 0LW United Kingdom
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Instruments information		
	Reference Standard	**National Standard**
Manufacturer	NIST	NIST
Type	SRP	SRP
Serial number	SRP27	SRP20

Content of the report

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

Operator	F. IDREES	**Location**	BIPM/CHEM09
Comparison begin date / time	2022-06-22 01:54	**Comparison end date / time**	2022-06-22 04:14

Comparison results

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

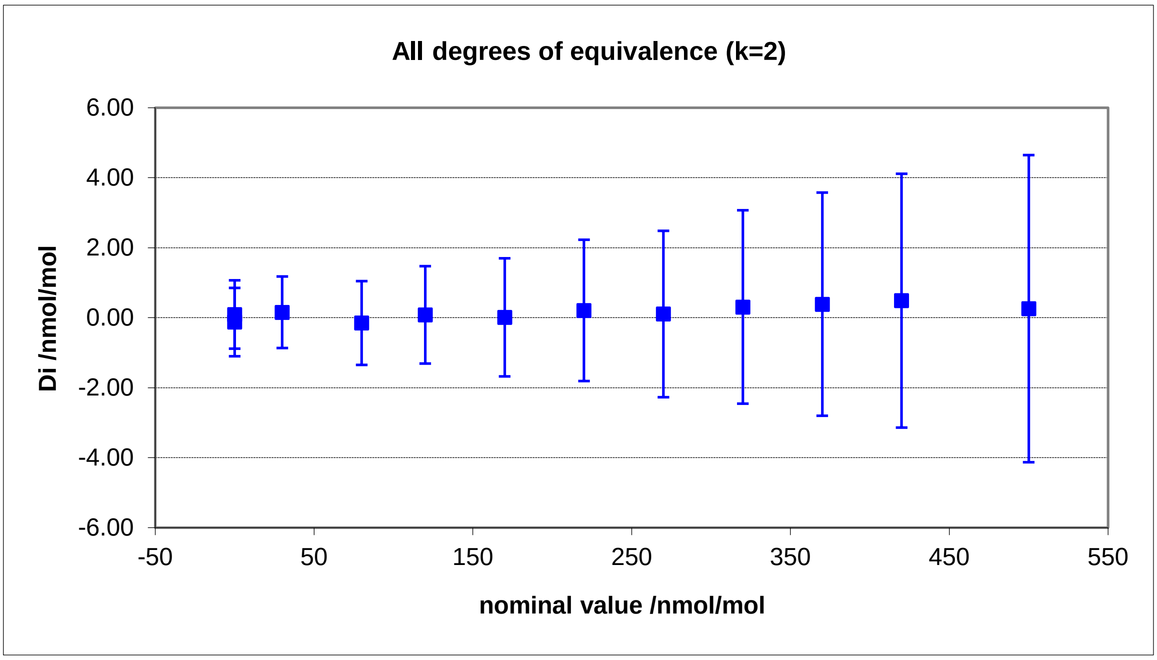
Least-square regression parameters

$a_{TS,RS}$	$u(a_{TS,RS})$	$b_{TS,RS}$ (nmol/mol)	$u(b_{TS,RS})$ (nmol/mol)	$u(a,b)$
1.0008	**0.0032**	**-0.02**	**0.25**	**-2.27E-04**

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

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

Nom value (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (nmol/mol)
80	**-0.151162**	**0.5985738**	**1.19714759**
420	**0.487212**	**1.81338789**	**3.62677579**



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	0.11	0.18	0.28	-0.02	0.17	0.40
220	212.37	0.25	0.68	212.58	0.24	0.75
80	83.35	0.57	0.37	83.20	0.22	0.47
420	419.78	0.19	1.26	420.27	0.17	1.31
120	119.17	0.25	0.45	119.25	0.30	0.53
320	310.69	0.34	0.95	311.00	0.31	1.00
30	36.17	0.23	0.30	36.33	0.21	0.41
370	364.85	0.13	1.10	365.24	0.25	1.15
170	165.48	0.19	0.56	165.49	0.22	0.63
500	514.36	0.31	1.53	514.62	0.27	1.57
270	260.59	0.20	0.81	260.69	0.18	0.87
0	0.03	0.29	0.28	0.12	0.32	0.40

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**	-0.12	0.49	0.98
2	**220**	0.21	1.01	2.02
3	**80**	-0.15	0.60	1.20
4	**420**	0.49	1.81	3.63
5	**120**	0.08	0.70	1.39
6	**320**	0.31	1.38	2.76
7	**30**	0.16	0.51	1.02
8	**370**	0.39	1.59	3.19
9	**170**	0.01	0.84	1.69
10	**500**	0.26	2.19	4.39
11	**270**	0.11	1.19	2.38
12	**0**	0.09	0.49	0.98

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	24.9 - 25.0
Room pressure (min-max) / hpa	1000.8 - 1001.9
Zero air source	compressor + BekoKAT + dryer+ aadco 737-R
Reference air flow rate (L/min)	14
Sample flow rate (L/min)	10
Instruments stabilisation time	> 8 hours
Instruments acquisition time /s (one measurement)	5
Instruments averaging time /s	5
Total time for ozone conditioning	> 24 hours
Ozone mole fraction during conditioning	1000 nmol/mol
Comparison repeated continously (Yes/No)	yes
If no, ozone mole fraction in between the comparison repeats	
Total number of comparison repeats realised	6
Data files names and location	G:\Gas\Ozone\BIPM.QM-K1\Participants results\2206 NPL
Cal22062103.xls to Cal22062201.xls	

Instruments checks and adjustments

Reference Standard

National Standard

Uncertainty budgets (description or reference)

Reference Standard

National Standard

The standard uncertainty in the measurements made by SRP 20 can be summarised by the equation:

$u(c)=[(0.4)^2 + (0.00296c)^2]^{0.5}$

There is no contribution due to the uncertainty in the absorption cross section in this uncertainty estimate.