Upgrade of the electronics modules of the BIPM Standard Reference Photometers for ozone and the effect on the on-going key comparison BIPM.QM-K1

by

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Abstract

The NIST Standard Reference Photometer #27 (BIPM-SRP27) maintained by the BIPM and used as the reference in the international key comparison BIPM.QM-K1 underwent an upgrade of its electronic module in August 2021. Negligible impact of this upgrade on the measurement results of BIPM-SRP27 was demonstrated during comparisons with BIPM-SRP28 before and after the upgrade. The same intervention had been performed in May 2021 on BIPM-SRP28 with the similar absence of impact. The on-going key comparison BIPM.QM-K1 could therefore restart on 1 September 2021 as planned.

Contents:

1. Introduction

The reference method for the measurement of ground-level ozone concentration is based on UV photometry, with the NIST SRP ozone reference standard acting as the primary standard for numerous national and international ozone monitoring networks. Several of these instruments are maintained by the BIPM, one of them being the reference standard for international comparisons of national ozone standards, which have been coordinated by the BIPM[1] since 2003.

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. The SRPs maintained by the BIPM were upgraded between March and August 2021.

This report presents the results of the upgrade of BIPM-SRP27 and BIPM-SRP28, which were compared before and after this upgrade following the protocol of BIPM.QM-K1. Section 2 summarizes the protocol, section 3 describes the instruments and the upgrade actions, section 4 presents the results of the comparison, and section 5 shows the comparison history between the two BIPM SRPs over 15 years.

2. Measurement protocol

The comparison protocol is summarized in this section. The complete version can be downloaded from the BIPM website (BIPM.QM-K1 protocol). This comparison protocol was applied for a first comparison between both SRPs before the upgrade; then again after the SRP27 upgrade; and finally after the SRP28 upgrade.

a). Ozone generation

The same source of purified air was 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

[1] https://www.bipm.org/en/gas-metrology/ozone/bipm.qm-k1

flows to all photometers under comparison, ensuring that they all received homogenized samples and reference air.

b). Comparison procedure

Prior to the comparison, all the instruments were switched on and allowed to stabilize 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.

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 ten 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 ten consecutive measurements was performed.

c). Comparison repeatability

The comparison procedure was repeated continuously for a minimum of three days to evaluate its repeatability.

3. Description of the BIPM SRPs and the upgrade actions

3.1. State of the BIPM SRPs before the upgrade

The BIPM acquired both SRP27 and SRP28 in 2003. They were modified for the first time in 2009 to account for biases on temperature measurements and on the light path length revealed by the study conducted by the BIPM and the NIST in 2006 [1]. This was reported in [2] with the impact on the comparison BIPM.QM-K1. Since 2009, no further modifications have been performed other than regular maintenance.

3.2. Upgrade actions

The upgrade reported here consisted of:

1. Exchange of control software from SRPControl to O3Conductor. This is expected to have no impact on the measurement results.

2. Exchange of the electronics box with a 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 in a temperature-controlled bath at a temperature of 23°C. The reference bath temperature was entered in the SRP control software, which calculates the corrections to apply to each of the four probes.

3.3. Uncertainty budget of the BIPM-SRPs

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. The same uncertainty budget was applied to SRPs before and after the upgrade, as the actions described above are not expected to impact the measurement uncertainty. The values of the standard uncertainties for the pressure difference between cells, the temperature probe, and the repeatability of the ratio of intensities are conservative limit values, and their compliance was checked before and during the measurements.

Table 1: Uncertainty budget for the SRPs maintained by the BIPM

Component (y)	**Uncertainty $u(y)$**				**Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$**	**Contribution to $u(x)$ $\lvert c_i \rvert \cdot u(y)$ nmol/mol**
	Source	**Distribution**	**Standard uncertainty**	**Combined standard uncertainty $u(y)$**		
Optical Path L_{opt}	Measurement Scale	Rectangular	0.0006 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89\times10^{-3}x$
	Repeatability	Normal	0.01 cm			
	Correction factor	Rect	0.52 cm			
Pressure P	Pressure gauge	Rectangular	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37\times10^{-4}x$
	Difference between cells	Rectangular	0.017 kPa			
Temperature T	Temperature probe	Rectangular	0.03 K	0.07 K	$\frac{x}{T}$	$2.29\times10^{-4}x$
	Temperature gradient	Rectangular	0.058 K			
Ratio of intensities D	Scaler resolution	Rectangular	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D\ln(D)}$	0.28
	Repeatability	Triangular	1.1×10^{-5}			
Absorption Cross section α	Hearn value		1.22×10^{-19} cm²/molecule	1.22×10^{-19} cm²/molecule	$-\frac{x}{\alpha}$	$1.06\times10^{-2}x$

Following this budget, 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^{-1}):

$$u(x) = \sqrt{(0.28)^2 + (2.92\cdot10^{-3}x)^2} \qquad \textit{(1)}$$

3.4. Covariance terms

Correlations between the results of two measurements performed at two different ozone amount fractions with the BIPM maintained SRPs were considered. More details on the covariance expression can be found in the protocol of the key comparison BIPM.QM-K1. The following expression was applied:

$$\boldsymbol{u(x_i, x_j) = x_i x_j u_b^2} \qquad (2)$$

where:

$$\boldsymbol{u_b^2 = \frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} + \frac{u^2(L_{opt})}{L_{opt}}} \qquad (3)$$

The value of u_b is given by the expression of the measurement uncertainty: $u_\mathrm{b} = 2.92\times10^{-3}$ or $u_\mathrm{b}^2 = 8.5\times10^{-6}$.

4. Analysis of the measurement results by generalized least square regression

The relationship between the SRPs was evaluated with a generalized least-square regression fit, using the software OzonE. This software, which is documented in a publication [3], is an extension of the previously used software B_Least recommended by the ISO standard 6143:2001 [4]. It includes the possibility to consider correlations between measurements performed with the same instrument at different ozone amount fractions.

For each comparison, a linear relationship between the ozone amount fractions measured by SRP28 and SRP27 is obtained:

$$\boldsymbol{x_{SRP28} = a_0 + a_1 x_{SRP27}} \qquad (4)$$

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 statistical parameters to validate the fitting function.

4.1. Least-square regression results

The relationships between SRP28 and SRP27 before any upgrade, after the SRP27 upgrade and after the SRP28 upgrade are summarized in the table below:

Table 2: parameters of the linear regression performed between SRP27 and SRP28 at the various steps of 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})
Initial comparison	1.0028	0.0043	−0.06	0.21	-1.78×10^{-04}
After software exchange	1.0019	0.0043	0.01	0.21	-1.75×10^{-04}
After upgrade of SRP28	1.0016	0.0043	0.01	0.21	-1.75×10^{-04}
After upgrade of SRP27	1.0015	0.0043	−0.05	0.21	-1.78×10^{-04}

To assess the agreement of the standards from the above parameters, 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 all three comparisons, 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. $| 1 - a_1 | < 2u(a_1)$. They also show good agreement between them, with no detectable impact attributable to the upgrades of the two SRPs.

5. History of comparisons between BIPM SRP27 and SRP28

The results of the previous comparison performed between both BIPM SRPs during the key comparison BIPM.QM-K1 are presented in Figure 1 and 2. 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. The values considered for this plot are those recorded during each comparison with a participant in BIPM.QM-K1, which always involved both SRPs. Results of comparisons performed before 2009 have been corrected to take into account the changes in the reference BIPM-SRP27 described in [2] which explains the larger uncertainties associated with the corresponding slopes. Figure 1 and 2 show that both standards stayed in close agreement for 15 years. The upgrades performed recently clearly had no impact on this agreement.

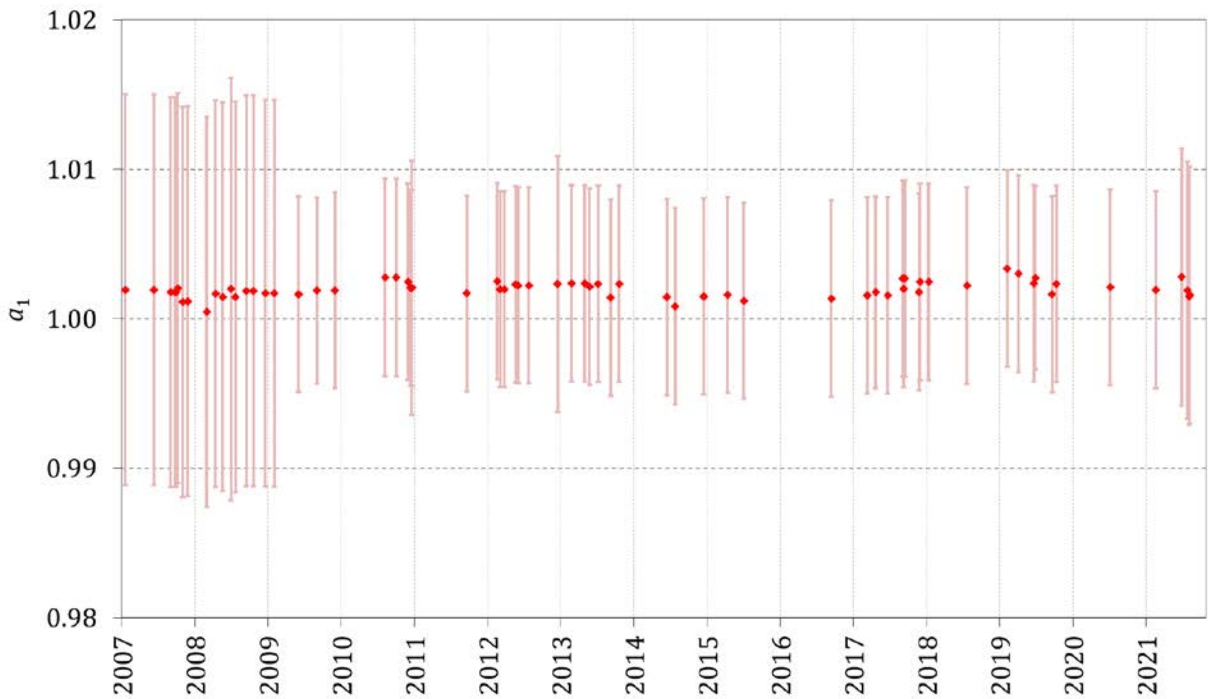

Figure 1 : Slope of the linear relationship between SRP28 and SRP27 obtained for each of the BIPM.QM-K1 comparisons realized at the BIPM. Uncertainties are calculated at *k* = 2, with the uncertainty budget in use at the time of each comparison.

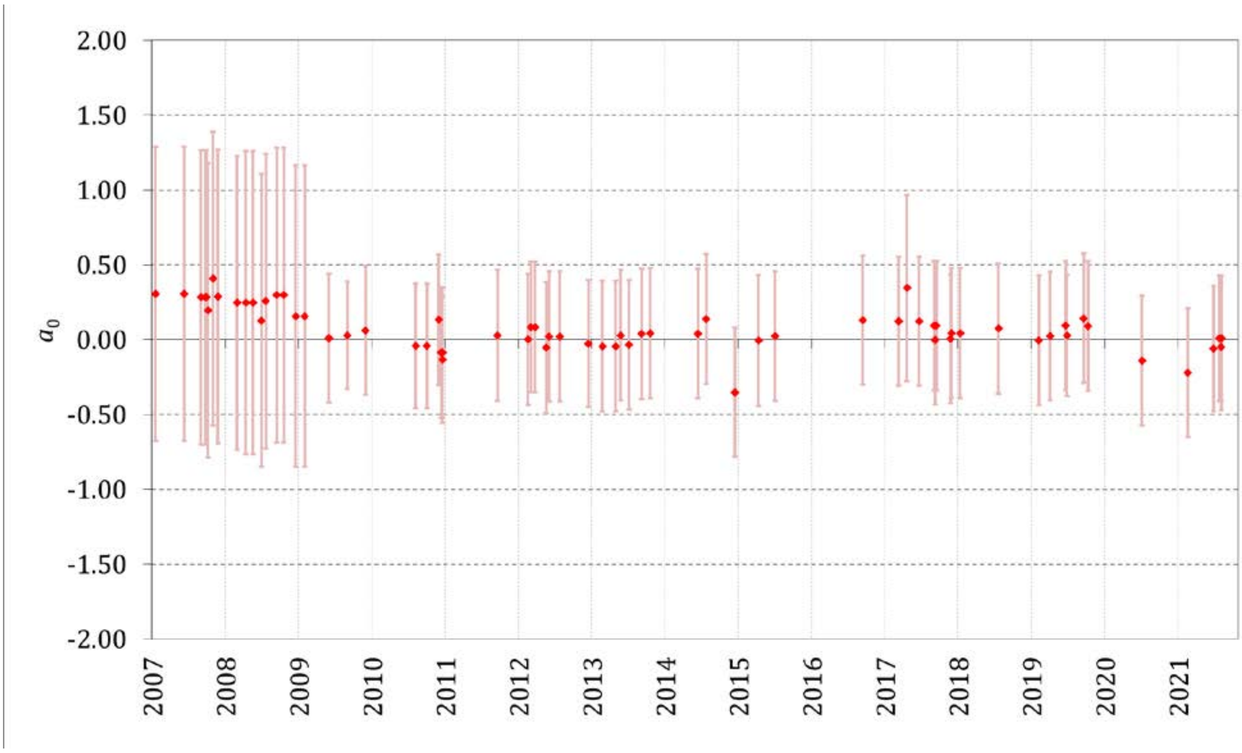

Figure 2 : Intercept of the linear relationship between SRP28 and SRP27 obtained for each of the BIPM.QM-K1 comparisons realized at the BIPM. Uncertainties are calculated at *k* = 2, with the uncertainty budget in use at the time of each comparison.

6. Conclusion

The NIST SRPs, maintained by the BIPM and used for reference in the international key comparison BIPM.QM-K1, underwent an upgrade of their electronics modules in July 2021. The protocol of the key comparison was followed to check their agreement before and after the upgrade. As expected, the effect of the upgrade on comparison results was negligible, with no detectable impact. The on-going key comparison BIPM.QM-K1 could therefore restart on 1 September 2021 as planned.

7. References

[1] Viallon J., Moussay P., Norris J.E., Guenther F.R. and Wielgosz R.I., 2006, A study of systematic biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard Reference Photometer, *Metrologia*, **43**, 441-450,

[2] Viallon J., Moussay P., Idrees F. and Wielgosz R.I. BIPM 2010 Upgrade of the BIPM Standard Reference Photometers for Ozone and the effect on the on-going key comparison BIPM.QM-K1 **Rapport BIPM-2010/07** p 16

[3] Bremser W., Viallon J. and Wielgosz R.I., 2007, Influence of correlation on the assessment of measurement result compatibility over a dynamic range, *Metrologia*, **44**, 495-504,

[4] ISO 6143: 2001 Gas analysis - Determination of the composition of calibration gas mixtures - Comparison methods (International Organization for Standardization)