Final report, On-going Key Comparison BIPM.QM-K1, Ozone at ambient level, comparison with NMC, A*STAR, July 2022

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Abstract

As part of the on-going key comparison BIPM.QM-K1, a comparison has been performed between the ozone national standard of Singapore maintained by the National Metrology Centre, A*STAR (NMC, A*STAR) 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 amount-of-substance fraction range of 0 nmol/mol to 500 nmol/mol.

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 Metrology Centre, A*STAR (NMC, A*STAR) 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 that 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-of-substance fraction in dry air furnished by the ozone generator
- $x_{\mathrm{A},i}$: ith measurement of the nominal value x_{nom} by the photometer A.
- $\bar{x}_{\mathrm{A}}$: the mean of N measurements of the nominal value x_{nom} measured by the photometer A : $\bar{x}_{\mathrm{A}} = \frac{1}{N}\sum_{i=1}^{N} x_{\mathrm{A},i}$
- s_{A} : standard deviation of N measurements of the nominal value x_{nom} measured by the photometer A : $s_{\mathrm{A}}^2 = \frac{1}{N-1}\sum_{i=1}^{N}(x_{\mathrm{A},i} - \bar{x}_{\mathrm{A}})^2$
- The result of the linear regression fit performed between two sets of data measured by the photometers A and B during a comparison is written: $x_{\mathrm{A}} = a_{\mathrm{A,B}} x_{\mathrm{B}} + b_{\mathrm{A,B}}$. With this notation, the photometer A is compared against the photometer B. $a_{\mathrm{A,B}}$ is dimensionless and $b_{\mathrm{A,B}}$ is expressed in units of nmol/mol.

7. Measurement schedule

This is the fourth participation of NMC, A*STAR since 2007. Measurements reported in this report were performed on 25 July 2022 at the NIST and on 3 June 2022 at the BIPM.

8. 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 was performed following protocol B, corresponding to a comparison between the NMC, A*STAR national standard SRP46 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 June 2022. Then SRP0 was compared with the national standard SRP46 at the NIST in July 2022.

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

8.1. Comparisons at the NIST

a). Ozone generation

The air is compressed with an oil-free compressor, dried and scrubbed with a commercial purification system so that the amount fraction of ozone and nitrogen oxides remaining in the air is below detectable limits. This air is used to provide reference air as well as the ozone-air mixture to each ozone photometer. Ozone is produced using an external commercial generator. 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 a week or more. Characteristics of the instruments were checked at this time following an internal procedure. Basic adjustments of temperature, pressure, and dark counts following the SRP operating characteristics checkout were performed.

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 amount-of-substance fraction x_{nom} furnished by the ozone generator, the standard deviation s_{SRP46} on the set of 10 consecutive measurements $x_{\text{SRP22},i}$ recorded by SRP46 was calculated. The measurement results were considered as valid if s_{SRP46} 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. 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.

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 amount-of-substance fractions distributed to cover the range, together with the measurement of zero air at the beginning and end of each run. The nominal amount-of-substance 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 amount-of-substance fraction x_{nom} furnished by the ozone generator, the standard deviation s_{SRP27} on the set of 10 consecutive measurements $x_{\mathrm{SRP27},i}$ recorded by BIPM-SRP27 was calculated. The measurement results were considered as valid if s_{SRP27} was less than 1 nmol/mol, which ensures that the photometers were measuring a stable ozone concentration. If not, another series of 10 consecutive measurements was performed.

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 ongoing 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 amount-of-substance fractions measured by the participant standard and the common reference standard. The completed form BIPM.QM-K1-R3-ASTAR-23 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). Additionally, the degrees of equivalence at all nominal ozone amount-of-substance 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

There was no deviation from the protocol in this comparison.

12. Measurement standards

The instruments maintained by the BIPM, the NIST, and NMC, A*STAR 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:

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

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

$$T_r = \frac{I_{\mathrm{ozone}}}{I_{\mathrm{air}}} \quad (2)$$

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 a amount fraction (x) of ozone in air:

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

where

N_A is the Avogadro constant, 6.022 140 76 x 10^{23} molecule/mol

R is the gas constant, 82.057 366 cm^3 atm 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. As explained in detail in [4], the “atm” unit system was used initially to describe the operation of ozone photometers and, though antiquated, remains in use by many practitioners. In this system, the amount fraction of ozone x is calculated from:

$$x = \frac{-1}{2\alpha_0 L_{opt}} \frac{T}{T_{std}} \frac{P_{std}}{P} ln(D) \quad (4)$$

where

α_0 is the absorption coefficient at standard temperature and pressure (0 °C and 1 atm), expressed in atm^{-1} cm^{-1}, and linked to the absorption cross-section per molecule σ via the Boltzmann constant k_B = 1.380 649 x 10^{-23} J K^{-1} with the relation:

$$\alpha_0 = \frac{\sigma}{k_B T_{std}} \quad (5)$$

12.2. Absorption cross-section for ozone

The absorption coefficient under standard conditions α_0 used within the SRP software algorithm is 308.32 cm^{-1}. This corresponds to a value for the absorption cross section σ of 1.1476×10^{-17} cm^2, 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 3 to 5 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	$-\frac{x}{L_{\text{opt}}}$	$2.89 \times 10^{-3}x$
	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} cm^2	1.22×10^{-19} cm^2	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$

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}):

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

12.5. Covariance terms for the common reference BIPM-SRP27

As explained in section 0, 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:

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

where:

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

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 NMC, A*STAR SRP46

SRP46 maintained by the NMC, A*STAR has been constructed by NIST in 2010 with the new design, which includes the "SRP upgrade kit" in order to deal with the two biases revealed in [4]. Prior to this comparison, the electronic module was upgraded to the new cDAQ design at NIST, in a similar fashion than performed on BIPM SRPs [10].

12.7. Uncertainty budget of the NMC, A*STAR SRP46

The uncertainty budget for the ozone amount fraction in dry air x measured by the NMC, A*STAR standard SRP46 in the nominal range 0 nmol mol^{-1}to to 500 nmol mol^{-1} to is given in Table 2.

Table 2 : SRP46 uncertainty budget

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	0.0005 cm	0.52 cm	$-\frac{x}{L_{opt}}$	2.89×10^{-3}x
	Variability	Rectangular	0.004 cm			
	Divergence	Rectangular	0.52 cm			
Pressure P	Pressure gauge	Rectangular	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	3.37×10^{-4}x
	Difference between cells	Rectangular	0.017 kPa			
Temperature T	Temperature probe	Rectangular	0.086 K	0.103 K	$\frac{x}{T}$	3.45×10^{-4}x
	Temperature gradient	Rectangular	0.058 K			
	Temperature heating bias	Rectangular	−1×10^{-3}x			
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	$-\frac{x}{\alpha}$	1.06×10^{-2}x

Following this budget, the standard uncertainty associated with the ozone amount fraction measurement with the NMC, A*STAR SRP46 can be expressed as a numerical equation (numerical values expressed as nmol mol^{-1}):

$$u(x) = \sqrt{(0.28)^2 + (2.93 \cdot 10^{-3} x)^2} \quad (9)$$

No covariance term for the NMC, A*STAR SRP46 was included in the calculations.

12.8. Transfer standard SRP0

The uncertainty budget for the ozone amount-of-substance fraction in dry air x measured by the NIST standard SRP0 in the range 0 nmol/mol to 500 nmol/mol will follow the BIPM/NIST paper [8] (see Table 1). This uncertainty budget includes the removal of the former temperature heating bias, which has been eliminated by using a lower current temperature circuit card in SRP 0.

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

No covariance term for the NIST SRP0 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-of-substance fraction are provided in appendix (form BIPM.QM-K1-R3-ASTAR-23).

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 [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-of-substance 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 NMC, A*STAR 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 amount-of-substance fractions measured by SRP*n* and SRP27 is obtained:

$$x_{\mathrm{SRP}n} = a_0 + a_1 x_{\mathrm{SRP27}} \tag{11}$$

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. <u>Least-squares regression results</u>

The relationship between SRP46 and SRP27 is:

$$x_{\mathrm{SRP46}} = 1.0012 x_{\mathrm{SRP27}} + 0.02 \tag{12}$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0038$ for the slope and $u(a_0) = 0.31$ nmol/mol for the intercept. The covariance between the two parameters is $\mathrm{cov}(a_0, a_1) = -4.44 \times 10^{-4}$.

The least-squares regression results confirm that a linear fit is appropriate, with a sum of the squared deviations (SSD) of 0.28 and a goodness of fit (GoF) equals to 0.29.

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-of-substance 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 amount-of-substance 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:

$$D = x_i - \hat{x}_{\mathrm{SRP27}} \tag{13}$$

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:

$$u(D) = \sqrt{u^2(x_i) + u^2(\hat{x}_{\mathrm{SRP27}})} \tag{14}$$

where $u(x_i)$ is the measurement uncertainties of the participant *i* and $u(\hat{x}_{SRP27})$ 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 $\overline{x}_{\mathrm{RS}}$ and $\overline{x}_{\mathrm{TS}}$ are fitted using the generalised least square program OzonE, taking into account the associated uncertainties $u(\overline{x}_{\mathrm{RS}})$ and $u(\overline{x}_{\mathrm{TS}})$, as well as covariance terms between the reference standard measurement results.

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

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

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

$$u(\hat{x}_{\mathrm{RS}}) = \sqrt{u^2(b_{\mathrm{RS,TS}}) + x_{\mathrm{TS}}^2 \cdot u^2(a_{\mathrm{RS,TS}}) + a_{\mathrm{RS,TS}}^2 \cdot u^2(x_{\mathrm{TS}}) + 2 \cdot x_{\mathrm{TS}} \cdot u(a_{\mathrm{RS,TS}}, b_{\mathrm{RS,TS}})} \quad (15)$$

Where the uncertainty components $u(a_{\mathrm{RS,TS}})$, $u(b_{\mathrm{RS,TS}})$ and $u(a_{\mathrm{RS,TS}}, b_{\mathrm{RS,TS}})$ 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-ASTAR-23 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 NMC, A*STAR at the ozone nominal amount-of-substance fractions 80 nmol/mol and 420 nmol/mol

Nominal value / (nmol/mol)	x_i / (nmol/mol)	u_i / (nmol/mol)	x_{SRP27} / (nmol/mol)	u_{SRP27} / (nmol/mol)	D_i / (nmol/mol)	$u(D_i)$ / (nmol/mol)	$U(D_i)$ / (nmol/mol)
80	82.35	0.37	82.26	0.47	0.09	0.60	1.20
420	416.59	1.25	416.23	1.82	0.36	2.20	4.41

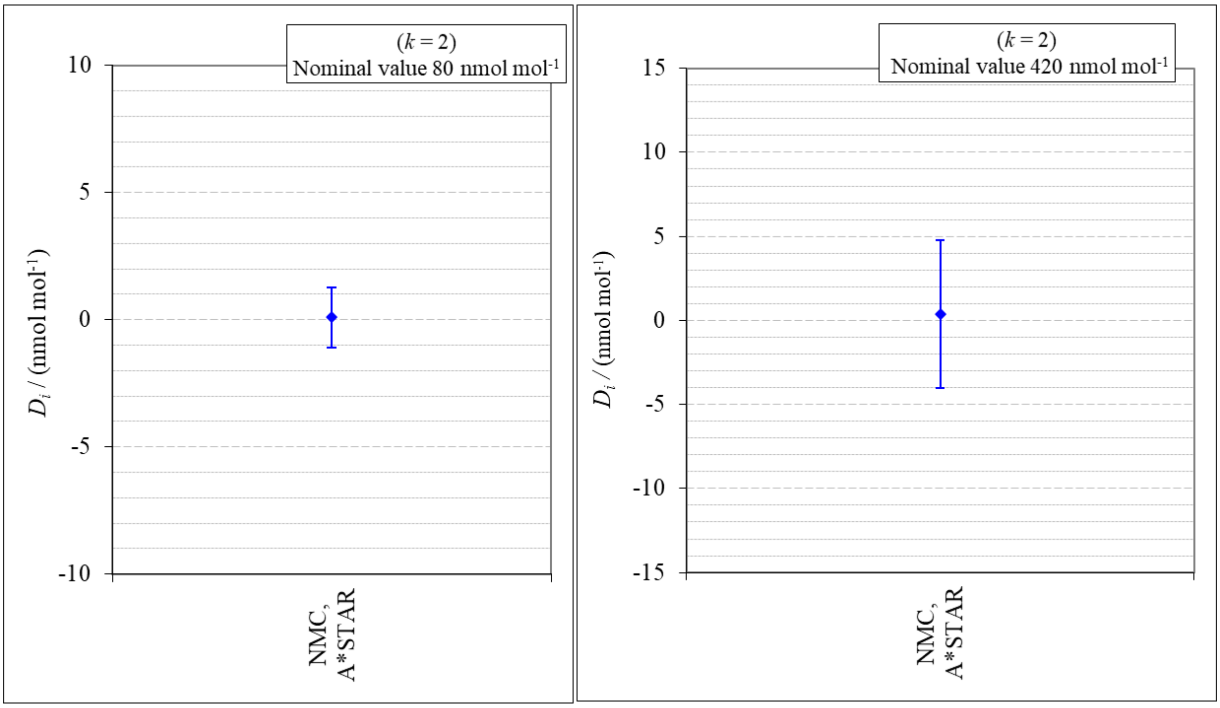

Figure 1: degrees of equivalence of the NMC, A*STAR at the two nominal ozone amount-of-substance fractions 80 nmol/mol and 420 nmol/mol

The degrees of equivalence between the NMC, A*STAR 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

Comparisons performed at NIST between the transfer standard SRP0 and NIST national standard SRP2 before and after the comparisons at BIPM and at NIST have shown a maximum variation of 0.1% 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 NMC, A*STAR SRP46

Results of the three previous comparisons are displayed in Figure 2 together with the results of this comparison. To show the stability of the reference standard BIPM-SRP27, results of comparisons between BIPM-SRP27 and BIPM-SRP28 are also displayed. The slopes a_1 of the linear relation $x_{SRPn} = a_0 + a_1 x_{SRP27}$ are represented together with their associated uncertainties calculated at the time of each comparison. Figure 2 shows that all standards included in these comparisons stayed in close agreement.

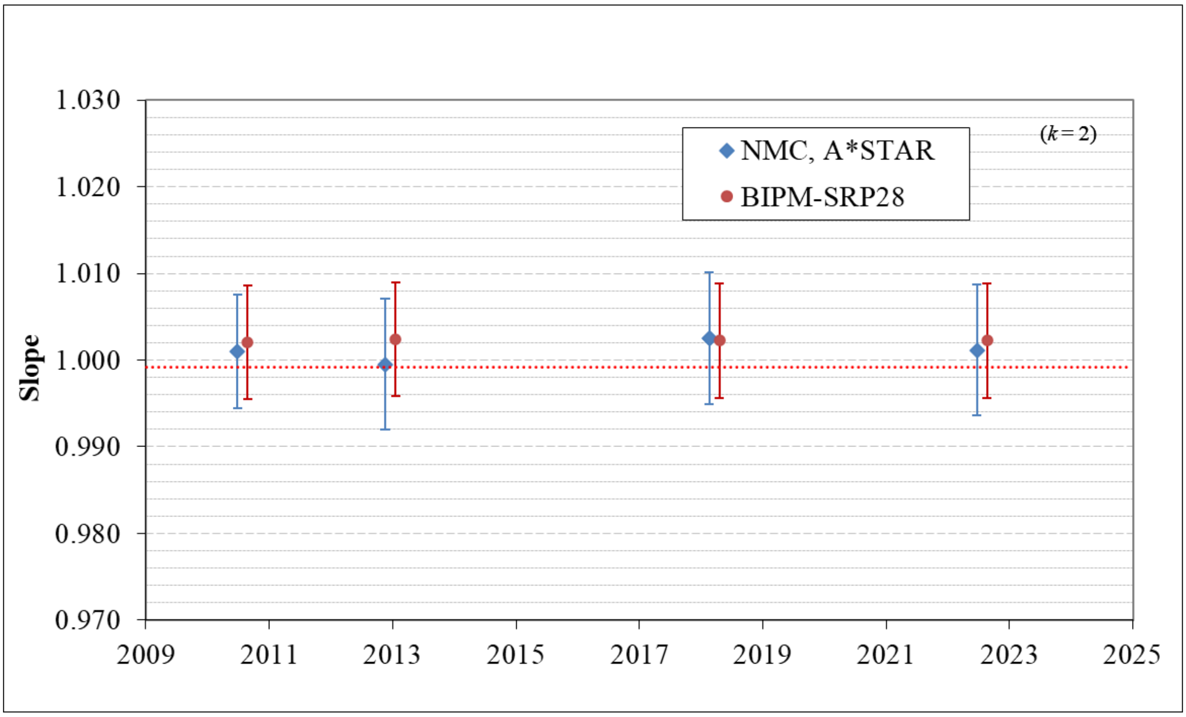

Figure 2 : Results of previous comparisons between SRP27, SRP28 and NMC, A*STAR standards. Uncertainties are calculated at *k* = 2, with the uncertainty budget in use at the time of each comparison.

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

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

19. 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 Singapore maintained by the NMC, A*STAR and the common reference standard of the key comparison maintained by the BIPM. The instruments have been compared over a nominal ozone amount-of-substance fraction range of 0 nmol/mol to 500 nmol/mol. Degrees of equivalence of this comparison indicated very good agreement between the two standards.

20. References

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Appendix 1 - Form BIPM.QM-K1-R3-ASTAR-23

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, Gaithersburg, MD 20899**
Contact	**James Norris/Peter Trask**
Email	james.norris@nist.gov/peter.trask@nist.gov
Telephone	**301-975-3936/301-975-2314**

Participating institute information	
Institute	**NMC A*STAR**
RMO	**APMP**
Address	**8 CleanTech Loop #01-20 Singapore 637145**
Contact	**Kai Fuu Ming/Cui Yuxi/ Lemuel Joel**
Email	kai_fuu_ming@nmc.a-star.edu.sg/cui_yuxi@nmc.a-star.edu.sg/Lemuel_Joel@nmc.a-star.edu.sg
Telephone	**67146232/67149290**

Instruments information

	Reference Standard Photometer	Participating Institute National Standard	Linking institute National Standard
Manufacturer	NIST	NIST	NIST
Type	SRP	SRP	SRP
Serial number	SRP27	SRP46	SRP0
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

Content of the report

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 (RS) vs reference standard (NS)

Summary of comparison results

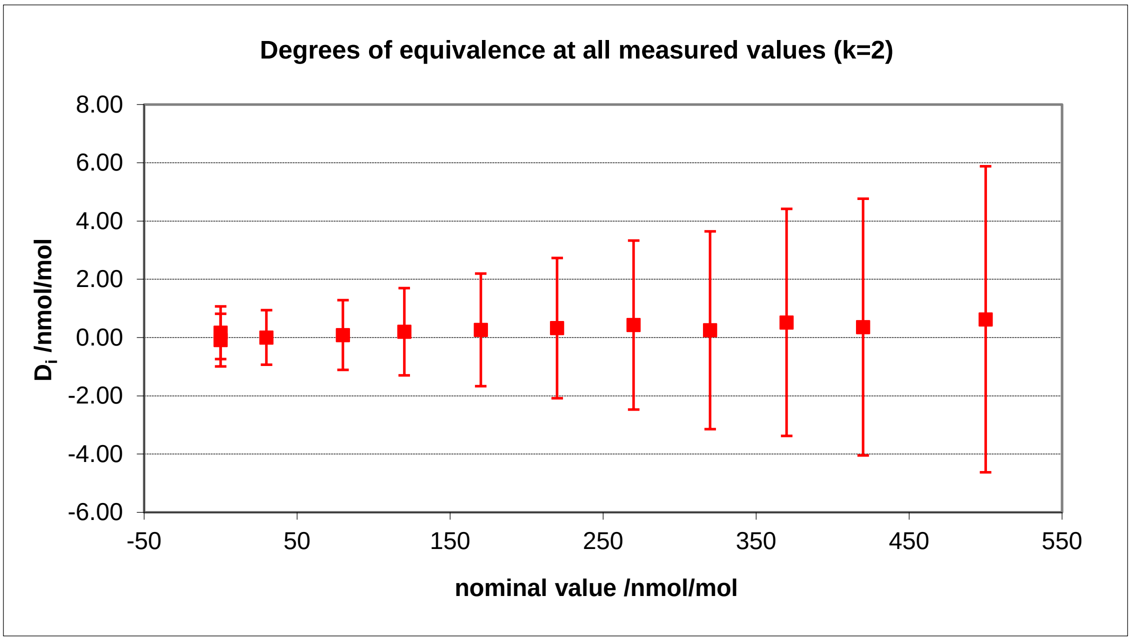
Equation $x_{NS} = a_{NS,RS}\, x_{RS} + b_{NS,RS}$

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	**1.0012**	**0.0038**	**0.02**	**0.31**	**-4.44E-04**

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	0.09	0.60	1.20
420	0.36	2.20	4.41



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

First comparison results						
	National standard measurement results		Transfer standard measurement results		Reference Standard prediced values	
Nominal value	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	0.22	0.28	-0.02	0.28	0.05	0.35
220	219.38	0.70	219.32	0.70	219.06	0.98
80	82.35	0.37	82.32	0.37	82.26	0.47
420	416.59	1.25	416.80	1.25	416.23	1.82
120	121.13	0.45	121.05	0.45	120.93	0.60
320	317.91	0.97	318.08	0.97	317.66	1.39
30	31.95	0.30	31.92	0.30	31.94	0.36
370	367.24	1.11	367.21	1.11	366.72	1.60
170	169.84	0.57	169.76	0.57	169.57	0.78
500	498.38	1.48	498.44	1.48	497.75	2.17
270	269.17	0.83	269.08	0.83	268.74	1.19
0	-0.07	0.28	-0.05	0.28	0.02	0.35

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)

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

$a_{RS,TS}$	0.9985	$b_{NRS,TS}$ (nmol/mol)	0.07	$u(a,b)$	-2.10E-04
$u(a_{RS,TS})$	0.0033	$u(b_{RS,TS})$ (nmol/mol)	0.22		

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**	0.17	0.45	0.90
2	**220**	0.32	1.20	2.41
3	**80**	0.09	0.60	1.20
4	**420**	0.36	2.20	4.41
5	**120**	0.20	0.75	1.50
6	**320**	0.25	1.70	3.40
7	**30**	0.00	0.47	0.94
8	**370**	0.52	1.95	3.90
9	**170**	0.26	0.97	1.93
10	**500**	0.63	2.63	5.25
11	**270**	0.43	1.45	2.90
12	**0**	-0.09	0.45	0.90

Least-square regression parameters				
$a_{NS,RS}$	$u(a_{NS,RS})$	$b_{NS,RS}$ (nmol/mol)	$u(b_{NS,RS})$ (nmol/mol)	$u(a,b)$
1.0011748	**0.0037706**	**0.0233881**	**0.3130639**	**-0.0004440**

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

Operator	**Jim Norris/Peter Trask**	**Location**	**NIST**
Comparison begin date / time	**25/7/2022 15:13**	**Comparison end date / time**	**25/7/2022 17:23**

measurement results

	Transfer standard (TS)			National Standard (NS)		
Nominal value	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	-0.02	0.16	0.28	0.22	0.20	0.28
220	219.32	0.17	0.70	219.38	0.28	0.70
80	82.32	0.18	0.37	82.35	0.28	0.37
420	416.80	0.14	1.25	416.59	0.29	1.25
120	121.05	0.18	0.45	121.13	0.23	0.45
320	318.08	0.10	0.97	317.91	0.23	0.97
30	31.92	0.19	0.30	31.95	0.25	0.30
370	367.21	0.21	1.11	367.24	0.17	1.11
170	169.76	0.11	0.57	169.84	0.17	0.57
500	498.44	0.37	1.48	498.38	0.32	1.48
270	269.08	0.15	0.83	269.17	0.22	0.83
0	-0.05	0.15	0.28	-0.07	0.14	0.28

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	Environics
Ozone generator type	Model 6100
Ozone generator serial number	3355
Room temperature(min-max) / °C	21.0/21.4
Room pressure (average) / hpa	1002.8
Zero air source	Aadco 737
Reference air flow rate (L/min)	2
Sample flow rate (L/min)	2
Instruments stabilisation time	weeks
Instruments acquisition time /s (one measurement)	25
Instruments averaging time /s	250
Total time for ozone conditioning	120 min.
Ozone mole fraction during conditioning (nmol/mol)	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	30

Instruments checks and adjustments

National Standard

Removed SRP 46 valves and internal sample/reference lines and cleaned them with dilute Nitric Acid, flushed with pure water, dried with Nitrogen.
Replaced plunger and cleaned inside of solenoid.
SRP 46 valve 2 solenoid was replaced.
Installed new source lamp, new optical filter, and reworked source block adding gaskets and realigned light beams.
Installed new valve manifold.
New electronics Module installed, second pressure transducer installed, auto pump installed.
Quick adjustment for pressure. Temperature offsets from the temperature sensor calibration.

Transfer Standard

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

Operator	Faraz Idrees	**Location**	BIPM/CHEM9
Comparison begin date / time	03/06/2022 12:14	**Comparison end date / time**	03/06/2022 14:19

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)	$u(a,b)$
0.9984880	**0.0032807**	**0.0668147**	**0.2185991**	**-0.0002095**

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

Measurement results

	Transfer standard (TS)			Reference Standard (RS)		
Nominal value	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	0.03	0.14	0.28	0.04	0.18	0.28
220	213.61	0.13	0.68	213.36	0.23	0.68
80	83.72	0.13	0.37	83.60	0.21	0.37
420	423.08	0.23	1.27	422.60	0.31	1.27
120	120.09	0.19	0.45	119.86	0.28	0.45
320	313.33	0.08	0.96	312.88	0.36	0.96
30	36.38	0.32	0.30	36.62	0.29	0.30
370	367.44	0.14	1.11	367.05	0.22	1.11
170	166.70	0.16	0.56	166.47	0.30	0.56
500	518.24	0.16	1.54	517.57	0.20	1.54
270	262.39	0.13	0.82	262.02	0.29	0.81
0	0.07	0.16	0.28	0.08	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	Environics
Ozone generator type	Model 6100
Ozone generator serial number	3128
Room temperature(min-max) / °C	25.3 - 25.4
Room pressure (average) / hpa	1004.9 - 1005.6
Zero air source	compressor + BokoKAT + dryer + Aadco 737-R
Reference air flow rate (L/min)	15
Sample flow rate (L/min)	10
Instruments stabilisation time	> 24 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	800 nmol/mol
Comparison repeated continously (Yes/No)	yes
If no, ozone mole fraction in between the comparison repeats	***
Total number of comparison repeats realised	42
Data files names and location	G:\Gas\Ozone\BIPM.QM-K1\Participants
	Cal22053000.xls to Cal22060305.xls

***

Instruments checks and adjustments

Reference Standard

Transfer Standard

Uncertainty budgets (description or reference)

Reference Standard

BIPM-SRP 27 uncertainty budget is desribed in the protocol of this comparison: document BIPM.QM-K1 protocol, date 10 January 2007, available on the BIPM website. It can be summarized by the formula:

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

Transfer Standard

NIST SRP 0 follows the same uncertainty budget as the BIPM SRP 27. Both BIPM and NIST have kept this uncertainty the same after the electronics upgrade.

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

National Standard

Component (y)	Uncertainty μ(y)				Sensitivity coefficient $C_i = \partial x / \partial y$	Contribution to $\mu(x)$, $\lvert C_i \rvert . \mu(y)$ nmol/mol
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty μ(y)		
Optical Path L_{opt}	Measurement Scale	Rect.	0.0005 cm	0.52 cm	$-x / L_{opt}$	$2.89 \times 10^{-3}\ x$
	Variability	Rect.	0.004 cm			
	Divergence	Rect.	0.52 cm			
Pressure P	Pressure gauge	Rect.	0.029 kPa	0.034 kPa	$-x / P$	$3.37 \times 10^{-4}\ x$
	Difference between cells	Rect.	0.017 kPa			
Temperature T	Temperature probe	Rect.	0.086 K	0.103 K	x / T	$3.45 \times 10^{-4}\ x$
	Temperature gradient	Rect.	0.058 K			
	Temperature heating bias	Rect.	$-1.0 \times 10^{-3}\ x$			Bias
Ratio of intensities D	Scaler resolution	Rect.	8.0×10^{-6}	1.4×10^{-5}	$x / D\ln(D)$	0.28
	Repeatability	Triang.	1.1×10^{-5}			
Absorption Cross section σ	Conventional value		1.22×10^{-19} cm²/molecule	1.22×10^{-19} cm²/molecule	$-x / \sigma$	$1.06 \times 10^{-2}\ x$

$$u(x) = \sqrt{(0.28)^2 + (2{,}93 \cdot 10^{-3} x)^2}$$