Bureau International des Poids et Mesures

Comparison of Ozone Reference Standards of the ECCC the BIPM

2020

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Foreword

A comparison of the ozone reference standards of the Environment and Climate Change Canada (ECCC) and of the Bureau International des Poids et Mesures (BIPM) has been performed. Both institutes maintain Standard Reference Photometers (SRPs), developed by the National Institute of Standards and Technology (NIST), as their reference standards. The instruments were compared over a nominal ozone amount-of-substance fraction range of $0\,\mathrm{nmol \cdot mol^{-1}}$ to $500\,\mathrm{nmol \cdot mol^{-1}}$ and the results showed good agreement.

Comparison of Ozone Reference Standards of the ECCC and the BIPM

Contents

1. Introduction

A comparison of the ozone reference standards of the Environment and Climate Change Canada (ECCC) and of the Bureau International des Poids et Mesures (BIPM) was performed. Both institutes maintain Standard Reference Photometers (SRPs), developed by the National Institute of Standards and Technology (NIST) as their reference standards. This comparison was performed following the protocol established for the key comparison BIPM.QM-K1, described briefly in Chapter 4. A description of the standards is given in Chapter 7 of this report, together with their uncertainty budgets. The results of the comparison are given in Chapter 8, Chapter 9 and Chapter 10.

2. Terms and definitions

No terms and definitions are listed in this document.

x_{nom} nominal ozone amount-of-substance fraction in dry air furnished by the ozone generator

$x_{\mathrm{A,i}}$ i th 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: $s_{\mathrm{A}}^2 = \frac{1}{N-1}\sum_{i=1}^{N}\left(x_{\mathrm{A,i}} - \bar{x}_{\mathrm{A}}\right)^2$

- 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 $\mathrm{nmol \cdot mol^{-1}}$.

3. Measurement schedule

Measurements reported in this report were performed from 3 to 6 February 2020 at the BIPM.

4. Measurement protocol

This comparison was performed following the protocol established for the key comparison BIPM.QM-K1. As ECCC is not a Designated Institute under the CIPM MRA, the results of this comparison cannot be included in BIPM.QM-K1, but are published in this BIPM report.

The protocol is summarized in this section. The complete version can be downloaded from the BIPM website (http://www.bipm.org/utils/en/pdf/BIPM.QM-K1_protocol.pdf).

This comparison was performed following protocol A, corresponding to a direct comparison between the ECCC national standard SRP12 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-of-substance fractions over the required range, and measuring these with the photometers.

4.1. Ozone generation

The same source of purified air is used for all the ozone photometers being compared. This air is used to provide reference air as well as the ozone-air mixture to each ozone photometer. Ambient air is used as the source for reference air. The air is compressed with an oil-free compressor, dried and scrubbed with a commercial purification system so that the amount-of-substance fraction of ozone and nitrogen oxides remaining in the air is below detectable limits. The relative humidity of the reference air is monitored and the amount-of-substance fraction of water in air is typically found to be less than $3 \mu\text{mol} \cdot \text{mol}^{-1}$. The amount-of-substance fraction of volatile organic hydrocarbons in the reference air was measured (November 2002), with no amount-of-substance fraction of any detected component exceeding $1 \text{nmol} \cdot \text{mol}^{-1}$.

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.

4.2. 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. For this comparison, no adjustments were necessary.

One comparison run includes ten different amount-of-substance fractions distributed over the range, together with the measurement of reference 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) $\text{nmol} \cdot \text{mol}^{-1}$. Each of these points is an average of ten single measurements.

For each nominal value of the ozone amount-of-substance fraction xnom furnished by the ozone generator, the standard deviation s_{SRP27} of the set of ten consecutive measurements x_{SRP27},i recorded by BIPM-SRP27 was calculated. The measurement results were considered valid if s_{SRP27} was less than $1 \text{nmol} \cdot \text{mol}^{-1}$, which ensures that the photometers were measuring a stable ozone concentration. If not, another series of ten consecutive measurements was performed.

4.3. Comparison repeatability

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

4.4. 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.

5. Reporting measurement results

The participant and the BIPM staff reported the measurement results on the result form BIPM.QM-K1-R1, provided by the BIPM, and which is available on the BIPM website. It includes details of the comparison conditions, measurement results and associated uncertainties, as well as the standard deviation for each series of ten ozone amount-of-substance fractions measured by the participant's standard and the common reference standard. The completed form, BIPM.QM-K1-R1-ECCC-20 is given in the Appendix 1.

6. Post-comparison calculation

All calculations were performed by the BIPM using the information on form BIPM.QM-K1-R1. It includes the difference from the reference value at two nominal ozone amount-of-substance fractions, which are considered as degrees of equivalence for the key comparison BIPM.QM-K1. For information, the difference from the reference value at all nominal ozone amount-of-substance fractions are reported in the same form, as well as the linear relationship between the participant's standard and the common reference standard.

7. Measurement standards

The instruments maintained by the BIPM and the ECCC are Standard Reference Photometers (SRP) built by the NIST. More details on the instrument's operating principle and its capabilities can be found in [1]. The following section describes the measurement principle and the uncertainty budgets.

7.1. Measurement equation of a NIST SRP

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

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

where

σ is the absorption cross-section of ozone at 253.7nm under standard conditions of temperature and pressure, 1.1476×10^{-17}cm²/molecule [2].

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 (273.15K);

P is the measured pressure of the cells;

P_{std} is the standard pressure (101.325kPa);

D is the product of transmittances of two cells, with the transmittance (T_{r}) of one cell defined as

$$T_{\mathrm{r}} = \frac{I_{\mathrm{ozone}}}{I_{\mathrm{air}}} \tag{2}$$

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).

The ideal gas law equation Equation (1) can be rewritten in order to express the measurement results as an amount-of-substance fraction (x) of ozone in air:

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

where

N_{A} is the Avogadro constant, $6.022\,142 \times 10^{23}\mathrm{mol}^{-1}$, and

R is the gas constant, $8.314\,472\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$

The formulation implemented in the SRP software is:

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

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

$$\alpha_x = \sigma \frac{N_{\mathrm{A}}}{R} \frac{P_{\mathrm{std}}}{T_{\mathrm{std}}} \tag{5}$$

7.2. Absorption cross-section for ozone

The linear absorption coefficient under standard conditions αxused within the SRP software algorithm is $308.32\mathrm{cm^{-1}}$. This corresponds to a value for the absorption cross section σ of $1.1476 \times 10^{-17}\mathrm{cm^2/molecule}$, rather than the more often quoted $1.147 \times 10^{-17}\mathrm{cm^2/molecule}$. In the comparison of two SRP instruments, the absorption cross-section can be considered to have a conventional value and its uncertainty can be set to zero. However, in the comparison of different methods or when considering the complete uncertainty budget of the method, the uncertainty of the absorption cross-section should be taken into account. A consensus value of 2.12 % at a 95 % level of confidence for the uncertainty of the absorption cross-section has been proposed by the BIPM and the NIST in a recent publication [3].

7.3. Condition of the BIPM SRPs

Compared to the original design described in [1], SRP27 and SRP28 have been modified to take into account two biases revealed by the study conducted by the BIPM and the NIST [3]. In 2009, an "SRP upgrade kit" was installed in the instruments, as described in the report [4].

7.4. Uncertainty budget of the common reference BIPM-SRP27

The uncertainty budget for the ozone amount-of-substance fraction in dry air (x) measured by the instruments BIPM-SRP27 and BIPM-SRP28 in the nominal range $0\mathrm{nmol \cdot mol^{-1}}$ to $500\mathrm{nmol \cdot mol^{-1}}$ is given in Table 1.

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

Component (y)	Uncertainty $u(y)$				Sensitivity coefficient	contribution to $u(x)$
	Source	Distribution	Standard Uncertainty	Combined standard	$c_i = \frac{\delta x}{\delta y}$	$\lvert c_i \rvert \cdot u(y)$ $\mathrm{nmol \cdot mol^{-1}}$

				uncertainty $u(y)$		
Optical Path L_{opt}	Measurement scale	Rectangular	0.0006cm	0.52cm	$-\frac{x}{L_{opt}}$	$2.89 \times 10^{-3}x$
	Repeatability	Normal	0.01cm			
	Correction factor	Rectangular	0.52cm			
Pressure P	Pressure gauge	Rectangular	0.029kPa	0.034kPa	$-\frac{x}{P}$	$3.37 \times 10^{-4}x$
	Difference between cells	Rectangular	0.017kPa			
Temperature T	Temperature probe	Rectangular	0.03K	0.07K	$\frac{x}{T}$	$2.29 \times 10^{-4}x$
	Temperature gradient	Rectangular	0.058K			
Ratio of intensities D	Scaler resolution	Rectangular	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D\ln D}$	0.28
	Repeatability	Triangular	1.1×10^{-5}			
Absorption Cross section σ	Hearn value		1.22×10^{-19}cm² /molecule	1.22×10^{-19}cm² /molecule	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$

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

$$u(x) = \sqrt{(0.28)^2 + \left(2.92 + 10^{-3}x\right)^2} \tag{6}$$

7.5. Covariance terms for the common reference BIPM-SRP27

Correlations between the results of two measurements performed at two different ozone amount-of-substance fractions with BIPM-SRP27 were taken into account using the software OzonE. Details about the analysis of the covariance can be found in the protocol. The following expression was applied:

$$u\left(x_i, x_j\right) = x_i \cdot x_j \cdot u_b^2 \tag{7}$$

where:

$$u_b^2 = \frac{u^2\,(T)}{T^2} + \frac{u^2\,(P)}{P^2} + \frac{u^2\,\left(L_{opt}\right)}{L_{opt}^2} \tag{8}$$

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

7.6. Condition of the SRP12

The ECCC SRP12 was built by the NIST in 1988. It was modified in 2013 to install the same “SRP upgrade kit” as in the two BIPM SRPs.

7.7. Uncertainty budget of the SRP12

The uncertainty budget for the ozone amount-of-substance fraction in dry air x measured by the ECCC standard SRP12 in the nominal range $0\text{nmol}\cdot\text{mol}^{-1}$ to $500\text{nmol}\cdot\text{mol}^{-1}$ is given in Table 2.

Following this budget, the standard uncertainty associated with the ozone amount-of-substance fraction measurement with the SRP12 can be expressed as a numerical equation (numerical values expressed as $\text{nmol}\cdot\text{mol}^{-1}$):

$$u(x)=\sqrt{(0.28)^2+\left(2.92\cdot 10^{-3}x\right)^2} \tag{9}$$

No covariance term for the SRP12 was included in the calculations.

Table 2. Uncertainty budget for the SRP12

Component (y)	Uncertainty $u(y)$				Sensitivity coefficient	contribution to $u(x)$
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$	$c_i=\frac{\delta x}{\delta y}$	$\lvert c_i\rvert\cdot u(y)\text{nmol}\cdot\text{mol}^{-1}$
Optical Path L_{opt}	Measurement scale	Rectangular	0.0006cm	0.52cm	$-\frac{x}{L_{\text{opt}}}$	$2.89\times 10^{-3}x$
	Repeatability	Normal	0.01cm			
	Correction factor	Rectangular	0.52cm			
Pressure P	Pressure gauge	Rectangular	0.029kPa	0.034kPa	$-\frac{x}{P}$	$3.37\times 10^{-4}x$
	Difference between cells	Rectangular	0.017kPa			
Temperature T	Temperature probe	Rectangular	0.03K	0.07K	$\frac{x}{T}$	$2.29\times 10^{-4}x$
	Temperature gradient	Rectangular	0.058K			
Ratio of intensities D	Scaler resolution	Rectangular	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D\ln(D)}$	0.28
	Repeatability	Triangular	1.1×10^{-5}			
Absorption Cross section σ	Hearn value		$1.22\times 10^{-19}\text{cm}^2$ /molecule	$1.22\times 10^{-19}\text{cm}^2$ /molecule	$-\frac{x}{\alpha}$	$1.06\times 10^{-2}x$

8. 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 given in the form BIPM.QM-K1-R1-ECCC-20 (Appendix 1, see p. 24).

9. Differences from the reference values

For the key comparison BIPM.QM-K1, differences from the reference values were calculated at the twelve nominal ozone amount-of-substance fractions measured, but are only shown in this report at two particular values: $80 \mathrm{nmol} \cdot \mathrm{mol}^{-1}$ and $420 \mathrm{nmol} \cdot \mathrm{mol}^{-1}$. These values correspond to points 3 and 4 recorded in each comparison. The ozone amount-of-substance fractions measured by the ozone standards can differ from the nominal values because an ozone generator has limited reproducibility. However, as stated in the protocol, the value measured by the common reference SRP27 was expected to be within $\pm 15 \mathrm{nmol} \cdot \mathrm{mol}^{-1}$ of the nominal value. Hence, it is meaningful to compare the degree of equivalence calculated for all the participants at the same nominal value.

9.1. Definition

The difference from the reference value of the participant i at a nominal value x_{nom} is defined as:

$$D_i = x_i - x_{\mathrm{SRP27}} \tag{10}$$

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:

$$u(D_i) = \sqrt{u_i^2 + u_{\mathrm{SRP27}}^2} \tag{11}$$

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

9.2. Values

The differences from the reference values and their uncertainties calculated in the form BIPM.QM-K1-R1-ECCC-20 are reported in Table 3 below. Corresponding graphs of equivalence are given in Figure 1. The expanded uncertainties are calculated with a coverage factor $k = 2$.

Table 3. Differences from the reference values of the ECCC at the nominal ozone amount-of-substance fractions $80 \mathrm{nmol} \cdot \mathrm{mol}^{-1}$ **and** $420 \mathrm{nmol} \cdot \mathrm{mol}^{-1}$

Nom value	x_i / (nmol/mol)	u_i / ($\mathrm{nmol} \cdot \mathrm{mol}^{-1}$)	x_{SRP27} / ($\mathrm{nmol} \cdot \mathrm{mol}^{-1}$)	u_{SRP27} / ($\mathrm{nmol} \cdot \mathrm{mol}^{-1}$)	D_i / ($\mathrm{nmol} \cdot \mathrm{mol}^{-1}$)	$u(D_i)$ / ($\mathrm{nmol} \cdot \mathrm{mol}^{-1}$)	$U(D_i)$ / ($\mathrm{nmol} \cdot \mathrm{mol}^{-1}$)
80	79.07	0.36	78.67	0.36	0.39	0.51	1.03
420	422.17	1.26	421.27	1.26	0.91	1.79	3.57

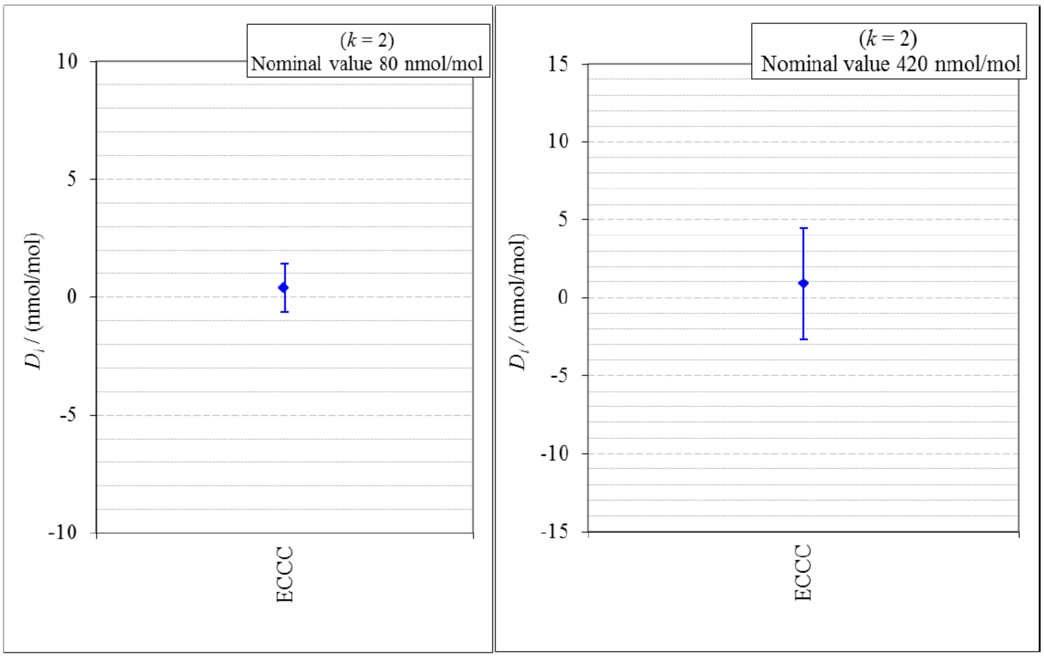


Figure 1 — Graphs of equivalence of the ECCC at the two nominal ozone amount-of-substance fractions $80\text{nmol}\cdot\text{mol}^{-1}$ **and** $420\text{nmol}\cdot\text{mol}^{-1}$

The differences between the ECCC standard and the common reference standard BIPM SRP27 indicate agreement between both standards.

10. Analysis of the measurement results by generalized least-square regression

The relationship between two ozone photometers was evaluated with a generalized least-square regression fit performed on the two sets of measured ozone amount-of-substance fractions, taking into account standard measurement uncertainties. To this end, the software package OzonE was used. This software, which is documented in a publication [5], is an extension of the previously used software B_Least, recommended by the ISO standard 6143:2001 [6]. OzonE allows users to account for correlations between measurements performed with the same instrument at different ozone amount-of-substance fractions.

In a direct comparison, a linear relationship between the ozone amount-of-substance fractions measured by SRPn and SRP27 is obtained:

$$x_{\mathrm{SRP}n} = a_0 + a_1 x_{\mathrm{SRP27}} \tag{12}$$

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

10.1. Least-square regression results

The relationship between SRP12 and SRP27 is:

$$x_{\mathrm{SRP12}} = 1.0014 x_{\mathrm{SRP27}} + 0.24 \tag{13}$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0033$ for the slope and $u(a_0) = 0.22 \mathrm{nmol} \cdot \mathrm{mol}^{-1}$ for the intercept. The covariance between the two parameters is cov $(a_0, a_1) = -2.02 \times 10^{-4} \mathrm{nmol} \cdot \mathrm{mol}^{-1}$.

The least-square regression statistical parameters confirm the appropriate choice of a linear relation, with a sum of the squared deviations (SSD) of 0.14 and a goodness of fit (GoF) equal to 0.14.

To assess the agreement of the standards from Equation (10), the difference between the calculated slope value and unity, and the intercept value and zero, together with their measurement uncertainties need to be considered. In the comparison, the value of the 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. $|1 - a_1| < 2u(a_1)$.

11. History of comparisons between BIPM SRP27, SRP28 and ECCC SRP12

Although ECCC SRP12 was one of the first SRPs built by the NIST, this is the first comparison ever performed between this instrument and the BIPM SRPs. The history of comparisons between the two BIPM SRPs can be found in previous reports of the comparison BIPM.QM-K1 (https://www.bipm.org/kcdb/comparison?id=1428).

12. Conclusion

A comparison was performed between the ozone reference standards of the ECCC and of the BIPM. The instruments were compared over a nominal ozone amount-of-substance fraction range of $0 \text{nmol} \cdot \text{mol}^{-1}$ to $500 \text{nmol} \cdot \text{mol}^{-1}$. Results of this comparison indicated good agreement between both standards.

Appendix 1. Form BIPM.QM-K1-R1-ECCC-20

See next pages.

A1.1. OZONE COMPARISON RESULT#—#PROTOCOL A#—#DIRECT COMPARISON

Participating institute information	
Institute	Environment and Climate Change Canada
Address	335 River Road, Ottawa, ON Canada
Contact	Claude Joanisse
Email	Claude.Joanisse@Canada.ca
Telephone	613-991-4052

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

Content of the report

general informations
comparison results
measurements results
comparison description
uncertainty budgets

A1.1.1. comparison reference standard (RS) — national standard (NS)

Operator	F.IDREES	Location	BIPM/CHEM09
Comparison begin date / time	2020-02-06 10:04	Comparison end date / time	2020-02-06 12:10

A1.1.2. Comparison results

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

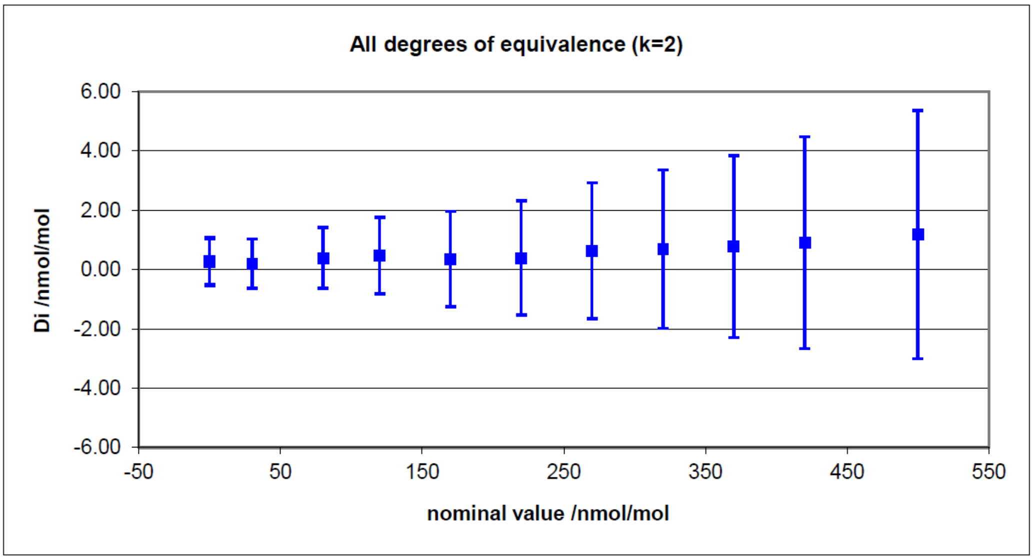
Table 1.1. Least-square regression parameters

$a_{TS,RS}$	$u(a_{TS,RS})$	$b_{TS,RS}$ $(\mathrm{nmol \cdot mol^{-1}})$	$u(b_{TS,RS})$ $(\mathrm{nmol \cdot mol^{-1}})$	$u(a, b)$
1.0014	0.0033	0.24	0.22	-2.02E-04

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

Table 1.2. **Degrees of equivalence at** $80 \mathrm{nmol \cdot mol^{-1}}$ **and** $420 \mathrm{nmol \cdot mol^{-1}}$

Nom value ($\mathrm{nmol \cdot mol^{-1}}$)	D_i ($\mathrm{nmol \cdot mol^{-1}}$)	$u(D_i)$ ($\mathrm{nmol \cdot mol^{-1}}$)	$U(D_i)$ ($\mathrm{nmol \cdot mol^{-1}}$)
80	0.39	0.51	1.03
420	0.91	1.79	3.57



A1.1.3. Measurement results

Measurement results						
	Reference Standard (RS)			National standard (NS)		
Nominal value	x_{RS} $\mathrm{nmol \cdot mol^{-1}}$	s_{RS} $\mathrm{nmol \cdot mol^{-1}}$	$u(x_{RS})$ $\mathrm{nmol \cdot mol^{-1}}$	x_{NS} $\mathrm{nmol \cdot mol^{-1}}$	s_{NS} $\mathrm{nmol \cdot mol^{-1}}$	$u(x_{NS})$ $\mathrm{nmol \cdot mol^{-1}}$
0	-0.03	0.23	0.28	0.22	0.19	0.28
220	212.80	0.43	0.68	213.19	0.18	0.68
80	78.67	0.32	0.36	79.07	0.16	0.36
420	421.27	0.55	1.26	422.17	0.35	1.26
120	122.44	0.20	0.45	122.92	0.11	0.46
320	308.57	0.31	0.94	309.26	0.20	0.95
30	30.16	0.35	0.29	30.36	0.10	0.29
370	358.17	0.31	1.08	358.95	0.23	1.08

170	169.16	0.29	0.57	169.51	0.15	0.57
500	497.11	0.22	1.48	498.29	0.32	1.48
270	259.34	0.31	0.81	259.97	0.20	0.81
0	-0.15	0.19	0.28	0.14	0.15	0.28

Degrees of Equivalence

Point Number	Nom value ($nmol \cdot mol^{-1}$)	D_i ($nmol \cdot mol^{-1}$)	$u(D_i)$ ($nmol \cdot mol^{-1}$)	$U(D_i)$ ($nmol \cdot mol^{-1}$)
1	0	0.26	0.40	0.79
2	220	0.40	0.96	1.93
3	80	0.39	0.51	1.03
4	420	0.91	1.79	3.57
5	120	0.47	0.64	1.29
6	320	0.69	1.34	2.67
7	30	0.20	0.42	0.83
8	370	0.78	1.53	3.07
9	170	0.36	0.80	1.61
10	500	1.19	2.09	4.19
11	270	0.63	1.14	2.29
12	0	0.29	0.40	0.79

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	8.53E-06
Value of α for the national standard	0.00E+00

A1.1.4. Comparison conditions

Table 1.3. Comparison conditions

Ozone generator manufacturer	Environics
Ozone generator type	Model 6100
Ozone generator serial number	3428
Room temperature(min-max) / °C	23.3 — 23.4
Room pressure (min-max) / hpa	1012.1 — 1012.7
Zero air source	oil free compressor + dryer + Aadco 737-R
Reference air flow rate ($L \cdot min^{-1}$)	15
Sample flow rate ($L \cdot min^{-1}$)	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 (nmol/mol)	$700 nmol \cdot mol^{-1}$
Comparison repeated continously (Yes/No)	Yes
If no, ozone mole fraction in between the comparison repeats	
Total number of comparison repeats realised	31
Data files names and location c200203001.xls to c200205012.xls	U:\Gas\2020\C-A1.1.1\Data\

A1.1.5. Instruments checks and adjustments

Reference Standard
Adjustments and/or checks performed as described in CHEM-GAS-T-01 technical procedure

National Standard
Adjustments and/or checks performed as described in CHEM-GAS-T-01 technical procedure

A1.1.6. Uncertainty budgets (description or reference)

Reference Standard
BIPM-SRP27 uncertainty budget is described in the protocol of this comparison: document BIPM.QM-K1 protocol, date 10 Januray 2007, available on BIPM website. It can be summarised by the formula: $u(x)=\sqrt{(0.28)^2+(2.92\cdot 10^{-3}x)^2}$

National Standard
The uncertainty budget for SRP12 is provided in the report body.

References

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