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**Comparison of ozone reference standards
of the CHMI and the BIPM**

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Comparison of ozone reference standards of the CHMI and the BIPM (September 2009)

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Abstract

A comparison of the ozone reference standards of the Czech HydroMeteorological Institute (CHMI) 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 mole fraction range of 0 nmol/mol to 860 nmol/mol and the results showed good agreement.

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1. Introduction

A comparison of the ozone reference standards of the Czech HydroMeteorological Institute (CHMI) 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. This comparison was performed following the protocol established for the key comparison BIPM.QM-K1, adapted to the measurement range normally covered by the CHMI as part of their calibration service, which is 10 nmol/mol to 870 nmol/mol. The measurement protocol is described briefly in section 4. A description of the standards is given in section 5 of this report, together with their uncertainty budgets. The data treatment is explained in section 6, and the results of the comparison are given in section 7.

2. Terms and definitions

- x_{nom} : nominal ozone mole fraction in dry air furnished by the ozone generator
- $x_{A,i}$: i th measurement of the nominal value x_{nom} by the photometer A.
- \bar{x}_A : the mean of N measurements of the nominal value x_{nom} measured by the photometer A :
$$\bar{x}_A = \frac{1}{N} \sum_{i=1}^N x_{A,i}$$
- s_A : standard deviation of N measurements of the nominal value x_{nom} measured by the photometer A :
$$s_A^2 = \frac{1}{N-1} \sum_{i=1}^N (x_{A,i} - \bar{x}_A)^2$$
- The result of the linear regression fit performed between two sets of data measured by the photometers A and B during a comparison is written: $x_A = a_{A,B}x_B + b_{A,B}$. With this notation, the photometer A is compared versus the photometer B. $a_{A,B}$ is dimensionless and $b_{A,B}$ is expressed in units of nmol/mol.

3. Measurement schedule

Measurements reported in this report were performed on 2 September 2009 at the BIPM.

4. Measurement protocol

This comparison was performed following the protocol established for the key comparison BIPM.QM-K1, with a modified measurement range: the instruments were compared over a nominal ozone mole fraction range of 0 nmol/mol to 860 nmol/mol (instead of a nominal range of 0 nmol/mol to 500 nmol/mol).

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

This comparison was performed following protocol A, corresponding to a direct comparison between the CHMI national standard SRP17 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 mole fraction of ozone and nitrogen oxides remaining in the air is below detectable limits. The relative humidity of the reference air is monitored and the mole fraction of water in air typically is less than 3 $\mu\text{mol/mol}$. The mole fraction of volatile organic hydrocarbons in the reference air was measured (November 2002), with no mole fraction of any detected component exceeding 1 nmol/mol .

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

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 10 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) nmol/mol . Each of these points is an average of 10 single measurements.

For each nominal value of the ozone mole fraction x_{nom} furnished by the ozone generator, the standard deviation s_{SRP27} on the set of 10 consecutive measurements $x_{\text{SRP27},i}$ recorded by BIPM-SRP27 was calculated. The measurement results were considered as valid if s_{SRP27} was less than 1 nmol/mol , which ensures that the photometers were measuring a stable ozone concentration. If not, another series of 10 consecutive measurements was performed.

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. Measurement standards

All instruments included in this comparison were 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 SRP measurement principle and uncertainty budget.

5.1. Measurement equation of a NIST SRP

The measurement of ozone mole fraction by an SRP is based on the absorption of radiation at 253.7 nm by ozonized air in the gas cells of the instrument. One 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:

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

where

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

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

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 mole fraction (x) of ozone in air:

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

where

- N_A is the Avogadro constant, $6.022142 \times 10^{23} \text{ mol}^{-1}$, and
- R is the gas constant, $8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$.

The formulation implemented in the SRP software is:

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

where

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

$$\alpha_x = \sigma \frac{N_A}{R} \frac{P_{\text{std}}}{T_{\text{std}}} \quad (5)$$

5.2. Absorption cross-section for ozone

The linear absorption coefficient at standard conditions α_x used within the SRP software algorithm is 308.32 cm^{-1} . This corresponds to a value for the absorption cross-section σ of $1.1476 \times 10^{-17} \text{ cm}^2/\text{molecule}$, rather than the more often quoted $1.147 \times 10^{-17} \text{ cm}^2/\text{molecule}$. 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].

5.3. Condition of the BIPM SRPs

Compared to the original design described in [1], SRP27 and SRP28 have been modified to deal with two biases revealed by a study conducted by the BIPM and the NIST [3]. In 2009, an ‘‘SRP upgrade kit’’ was installed in the instruments, as described in [4].

5.4. Uncertainty budget of the common reference BIPM-SRP27

The uncertainty budget for the ozone mole fraction in dry air (x) measured by the instruments BIPM-SRP27 and BIPM-SRP28 in the nominal range 0 nmol/mol to 900 nmol/mol is given in Table 1.

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

Component (<i>y</i>)	Uncertainty <i>u(y)</i>				Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to <i>u(x)</i> $ c_i \cdot u(y)$ nmol/mol
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty <i>u(y)</i>		
Optical Path <i>L_{opt}</i>	Measurement scale	Rectangular	0.0006 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89 \times 10^{-3}x$
	Repeatability	Normal	0.01 cm			
	Correction factor	Rectangular	0.52 cm			
Pressure <i>P</i>	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 <i>T</i>	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 <i>D</i>	Scaler resolution	Rectangular	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D \ln(D)}$	0.28
	Repeatability	Triangular	1.1×10^{-5}			
Absorption Cross section σ	Hearn value		1.22×10^{-19} cm ² /molecule	1.22×10^{-19} cm ² /molecule	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$

As explained in the protocol of the comparison, following this budget the standard uncertainty associated with the ozone mole fraction measurement with the BIPM SRPs can be expressed as a numerical equation (numerical values expressed as nmol/mol):

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

5.5. Covariance terms for the common reference BIPM-SRP27

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

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

where:

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

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

5.6. Condition of the CHMI SRP17

Compared to the original design, the CHMI SRP17 has been modified to deal with the two biases revealed in [3]. In August 2007, an ‘‘SRP upgrade kit’’ was installed by NIST, as already described in the previous comparison report [5].

5.7. Uncertainty budget of the CHMI SRP17

The uncertainty budget for the ozone mole fraction in dry air x measured by the CHMI standard SRP17 in the nominal range 0 nmol/mol to 900 nmol/mol is given in Table 2.

Following this budget, as explained in the protocol of the comparison, the standard uncertainty associated with the ozone mole fraction measurement with the CHMI SRP17 can be expressed as a numerical equation (numerical values expressed as nmol/mol):

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

No covariance term for the CHMI standard SRP17 was included in the calculations.

Table 2 : SRP17 uncertainty budget

Component (y)	Uncertainty $u(y)$				Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to $u(x)$ $ c_i \cdot u(y)$ nmol/mol
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$		
Optical Path L_{opt}	Measurement scale	Rectangular	0.005 cm	0.52 cm	$-\frac{x}{L_{opt}}$	$2.89 \times 10^{-3}x$
	Variability	Rectangular	0.004 cm			
	Divergence	Rectangular	0.52 cm			
Pressure P	Pressure gauge	Rectangular	0.029 kPa	0.034 kPa	$-\frac{x}{P}$	$3.37 \times 10^{-4}x$
	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 α	Hearn value		1.22×10^{-19} cm ² /molecule	1.22×10^{-19} cm ² /molecule	$-\frac{x}{\alpha}$	$1.06 \times 10^{-2}x$

6. Analysis of the measurement results by generalized least-squares regression

The relationship between the national and reference standards was first evaluated with a generalized least-squares regression fit, using the software OzonE. This software, which is documented in a publication [6], is an extension of the previously used software B_Least

recommended by the ISO standard 6143:2001 [7]. It includes the possibility to take into account correlations between measurements performed with the same instrument at different ozone mole fractions. It also facilitates the use of a transfer standard, by handling of unavoidable correlations, which arise since this instrument needs to be calibrated by the reference standard.

In a direct comparison, a linear relationship between the ozone amount-of-substance fractions measured by SRP_n and SRP_{27} is obtained:

$$x_{SRP_n} = a_0 + a_1 x_{SRP_{27}} \quad (10)$$

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.

7. Results of the comparison

SRP_{17} , maintained by the CHMI, was compared with the SRPs maintained by the BIPM following the general procedure outlined above. A cycle of eight comparison runs between SRP_{27} , SRP_{28} , SRP_{31} and SRP_{17} was performed. Ozone was generated using the Environics 6100 generator with airflow of 10 L/min. The nominal ozone mole fraction range covered during this exercise was 0 nmol/mol to 860 nmol/mol. The result of the last comparison run is presented in detail in section 7.1. The repeatability of the results over the eight runs is shown in section 7.2, and the stability of the BIPM standards in section 7.3.

7.1. Measurement results

The measurement results of the last of the eight recorded runs are shown in Table 3. For each nominal ozone mole fraction, the standard deviation of the 10 successive measurements is reported. The values reported here show that both instruments were in a stable regime.

An interesting way to look at these results is to display the difference between the ozone amount-of-substance fractions measured by SRP_{17} and SRP_{27} ($x_{17} - x_{27}$) versus the ozone mole fraction measured by SRP_{27} . As can be seen in Figure 1, there is very little difference in the measurement results from both instruments over the entire concentration range of the comparison. Considering a coverage factor of $k = 2$ (95 % confidence interval), the difference between both standards is much lower than their combined measurement uncertainties.

Table 3: measurement results of the comparison between the CHMI standard SRP17 and the BIPM reference standard SRP27

Reference standard BIPM-SRP27 (RS)			National standard CHMI SRP17 (NS)		
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
-0.09	0.26	0.28	0.12	0.27	0.28
215.71	0.31	0.69	216.36	0.31	0.69
77.99	0.21	0.36	78.25	0.17	0.36
409.86	0.38	1.23	410.71	0.39	1.23
116.95	0.24	0.44	117.45	0.11	0.44
311.99	0.24	0.95	312.82	0.33	0.96
28.45	0.24	0.29	28.56	0.19	0.29
361.13	0.40	1.09	361.85	0.26	1.09
165.85	0.19	0.56	166.01	0.15	0.56
492.50	0.18	1.47	493.58	0.21	1.47
264.87	0.20	0.82	265.52	0.09	0.82
0.06	0.25	0.28	0.10	0.19	0.28
605.39	0.31	1.79	606.77	0.29	1.79
866.82	0.24	2.55	868.82	0.33	2.55
729.07	0.36	2.15	730.53	0.31	2.15
0.07	0.30	0.28	0.00	0.17	0.28

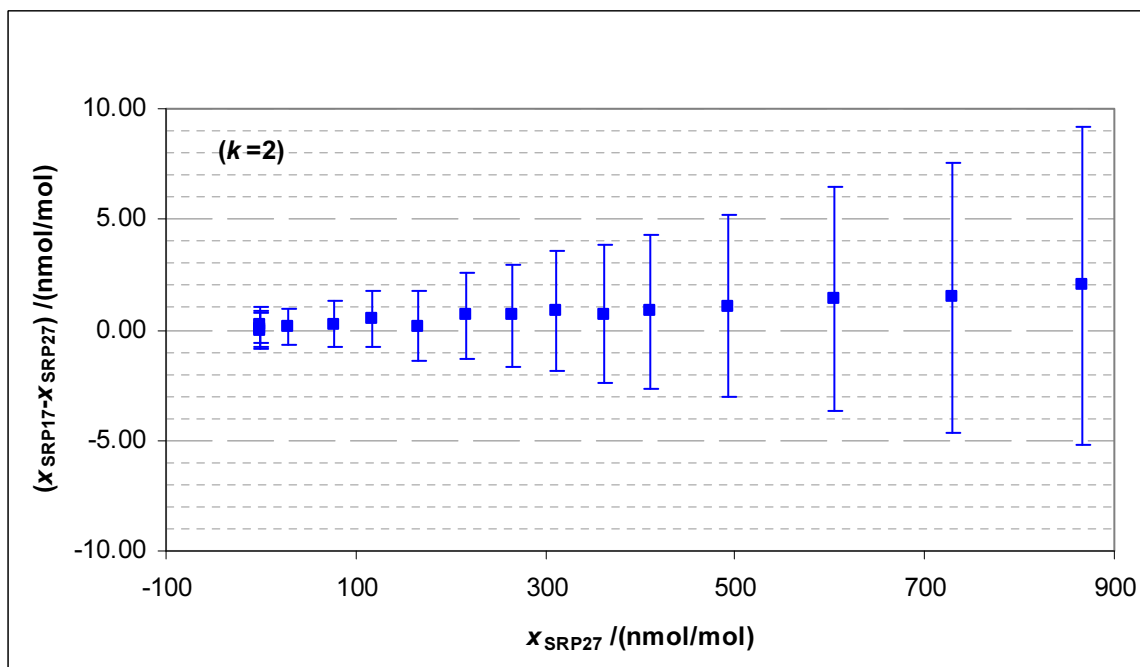


Figure 1: difference between the ozone amount-of-substance fractions measured by SRP17 and SRP27 versus the ozone mole fraction measured by SRP27.

The relationship between SRP17 and SRP27 is given by the result of the generalized least-square regression performed following the method described in section 6:

$$x_{\text{SRP17}} = 1.0021x_{\text{SRP27}} + 0.07 \quad (11)$$

The standard uncertainties on the parameters of the regression are $u(a_1) = 0.0030$ for the slope and $u(a_0) = 0.17$ nmol/mol for the intercept. The covariance between the two parameters is $\text{cov}(a_0, a_1) = -8.2 \times 10^{-5}$.

The least-squares regression results confirm that a linear fit is appropriate, with a sum of the squared deviations (SSD) of 0.38 and a goodness of fit (GoF) equal to 0.37.

To assess the agreement of the standards using 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 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. $|1 - a_1| < 2u(a_1)$.

7.2. Repeatability

The results of the eight comparison runs performed successively between SRP17 and SRP27 are reported in Table 4. With a standard deviation of 0.06 nmol/mol on the intercept and a relative standard deviation of 0.02 % on the slope, those data show a good repeatability.

Table 4 : results of the eight comparison runs repeated successively

Run	Slope a_1	$u(a_1)$	Intercept $a_0 /$ (nmol/mol)	$u(a_0) /$ (nmol/mol)	$\text{cov}(a_0, a_1)$	GoF
1	1.0023	0.0030	-0.04	0.17	-8.2×10^{-5}	0.24
2	1.0020	0.0030	0.05	0.17	-8.2×10^{-5}	0.13
3	1.0022	0.0030	-0.05	0.17	-8.2×10^{-5}	0.29
4	1.0018	0.0030	0.12	0.17	-8.2×10^{-5}	0.29
5	1.0019	0.0030	0.07	0.17	-8.2×10^{-5}	0.43
6	1.0021	0.0030	0.03	0.17	-8.2×10^{-5}	0.45
7	1.0020	0.0030	0.06	0.17	-8.2×10^{-5}	0.30
8	1.0021	0.0030	0.07	0.17	-8.2×10^{-5}	0.37

7.3. History of comparisons between BIPM SRP27, SRP28 and CHMI SRP17

Results of the previous comparison performed with CHMI on the same measurement range since the first comparison in December 2002 are displayed in Figure 2 together with the results of this comparison. The slopes a_1 of the linear relation $x_{\text{SRPn}} = a_0 + a_1 x_{\text{SRP27}}$ are represented together with their associated uncertainties calculated at the time of each comparison. Results of previous comparisons have been corrected to take into account the changes in the reference BIPM-SRP27 described in [4], which explains the larger uncertainties associated with the corresponding slopes. Figure 2 shows that all standards included in these comparisons stayed in close agreement.

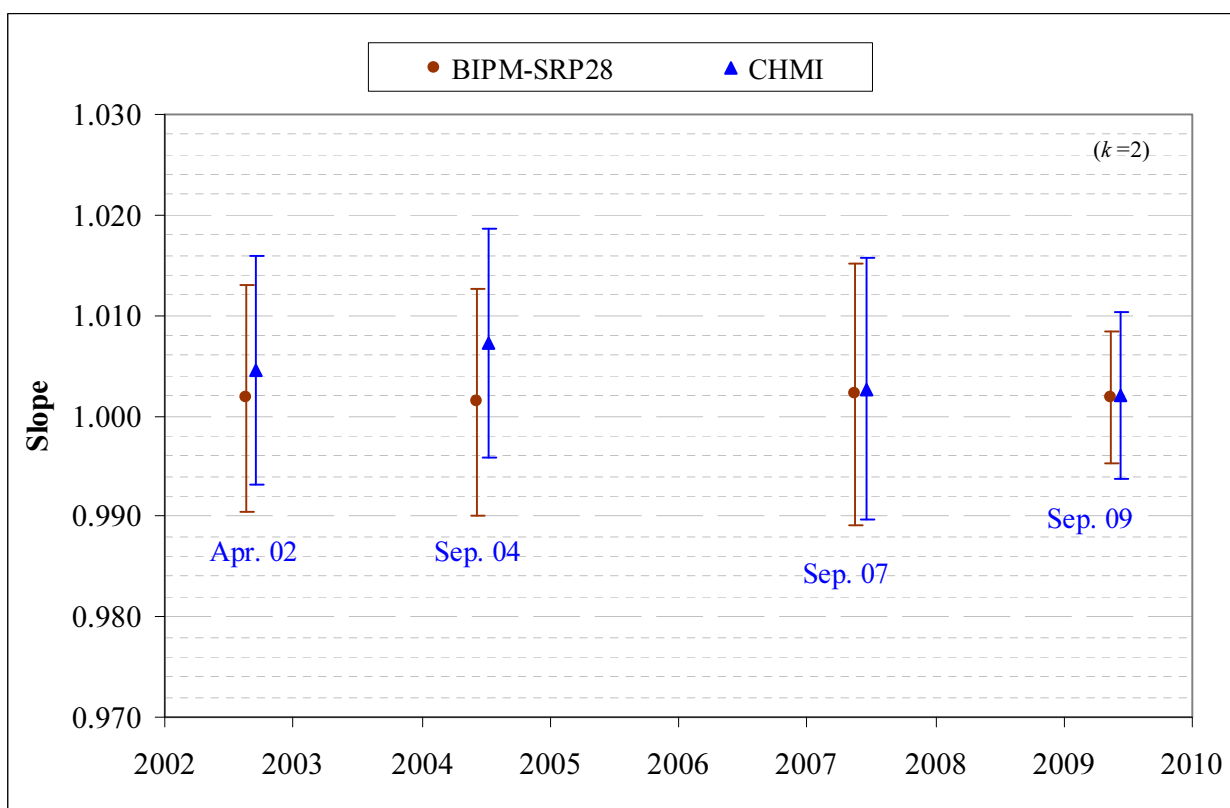


Figure 2 : Results of previous comparisons between SRP27, SRP28 and CHMI-SRP17 realised at the BIPM. Uncertainties are calculated at $k = 2$, with the uncertainty budget in use at the time of each comparison.

8. Conclusion

For the fourth time in 7 years, a direct comparison between CHMI national standard SRP17 and the BIPM reference standard SRP27 has been conducted at the BIPM. The measurement range of SRP17 at the CHMI is 10 nmol/mol to 870 nmol/mol. This entire range was examined during the comparison, and the relative difference between CHMI SRP17 and BIPM SRP27 measurement results was found to be much smaller than their combined measurement uncertainties.

9. References

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