

International Comparison CCQM-P28, Ozone at ambient level (Pilot study)

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Abstract

We report a pilot study organized within the Consultative Committee for Amount of Substance (CCQM), in which the ozone reference standards of 23 institutes have been compared to one common reference, the BIPM ozone reference standard, in a series of bilateral comparisons carried out between July 2003 and February 2005. The BIPM, which maintains as its reference standard a standard reference photometer (SRP) developed by the National Institute of Standards and Technology (NIST, United States), served as pilot laboratory. A total of 25 instruments were compared to the common reference standard, either directly (16 comparisons) or via a transfer standard (9 comparisons). The comparisons were made over the ozone mole fraction range 0 nmol/mol to 500 nmol/mol.

Two reference methods for measuring ozone mole fractions in synthetic air were compared, thanks to the participation of two institutes maintaining a gas-phase titration system with traceability of measurements to primary gas standards of NO and NO₂, while the 23 other instruments were based on UV absorption.

In the first instance, each comparison was characterized by the two parameters of a linear equation, as well as their related uncertainties, computed with generalized least-squares regression software. Analysis of these results using the Birge ratio indicated an underestimation of the uncertainties associated with the measurement results of some of the ozone standards, particularly the NIST SRPs.

As a final result of the pilot study, the difference from the reference value (BIPM-SRP27 measurement result) and its related uncertainty were calculated for each ozone standard at the two nominal ozone mole fractions of 80 nmol/mol and 420 nmol/mol.

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1. Field

Amount of substance.

2. Subject

Comparison of ozone (at ambient level) reference measurement standards.

3. Participants

Twenty three laboratories participated in the pilot study. The full list of participants is given in Appendix 1. Acronyms of participating laboratories : BIPM (coordinating laboratory), CHMI, CSIR-NML, ERLAP, Environment Canada, FMI, INRIM (formerly IMGC), ISC III, KRISS, LNE, METAS, NDENW, NERI, NIES, NILU, NIST, NMi-VSL, NPL, SP, UBA (A), UBA (D), VNIIM, WMO/WCC-EMPA.

4. Organizing body

CCQM.

5. Rationale

Atmospheric ozone levels are of world-wide concern at ground level where increases in concentration have detrimental effects on public health and the environment, and international effort is focused on monitoring and reducing surface ozone concentrations. Global, regional, national and local networks for surface ozone are in operation, and it is important to ensure that measurements and data from these networks are comparable, so that effective decisions can be taken to ensure protection against harmful effects on human health from exposure to ozone. The comparability of measurements can be assured through their traceability to reference methods and standards with long term stability such as those based on the SI system.

The principal method of ozone concentration determination is ultraviolet photometry, for which there is an international standard (ISO 13964 [1]), and where calibration against primary UV photometers is required. Alternative methods for ozone determination, such as chemiluminescence methods, are utilised but generally require calibration by a UV ozone photometer (ISO 10313 [2]).

Since 1983, the NIST has provided Standard Reference Photometers (SRP) as a means of ensuring comparability and traceability of ground-level ozone measurements. Although these instruments were initially developed to fulfil internal US air quality measurement requirements, many of these photometers have been considered as national measurement standards in other countries. Other instruments operating on the principle of UV photometry have also been taken into account as national ozone reference standards.

An alternative reference method for ozone concentration measurements is based on gas-phase titration (GPT) with traceability of measurements to primary gas standards of NO and NO₂. The uncertainty of the gas-phase titration reference method is now approaching that of the ozone reference methods based on UV absorption. Two laboratories maintaining GPT systems have submitted results for this pilot study, allowing comparison of the UV based and GPT reference methods.

This pilot study was designed to evaluate the difference from the reference value of ozone reference measurement standards that are maintained as national standards, or as primary standards within international networks for ambient ozone measurements. The reference value has been determined using the NIST Standard Reference Photometer (BIPM-SRP27) maintained by the BIPM as a common reference.

6. Measurement standards

A full list of the measurement standards is given in Appendix 1. Almost all instruments used in this study measure ozone mole fractions in dry air based on the UV photometry principle. UV photometry based instruments compared in the study were: SRP (NIST Standard Reference Photometer), O3-SRP (KRISS Ozone Standard Reference Photometer), TEI 49C/49CPS (Thermo Environmental Instruments, model 49C and 49CPS), API M400/M401 (Advanced Pollution Instrumentation Model 401 Ozone Calibrator and Model 400E), Dasibi 1003AH, Environment SA 42, and the UMEG UV photometer. The UV photometry measurement principle is described for BIPM-SRP27 in section 12 of this report.

Two participants (BIPM and NIES) produced results based on the gas phase titration (GPT) reference method for ozone. The principle of this method is described in more detail in Section 15 of this report.

A number of national reference standards are secondary standards that have been calibrated and are thus traceable to another ozone reference standard. The table in Appendix 1 lists the ozone reference standard to which measurement results of national ozone reference standards are traceable.

7. Measurements schedule

Measurements were performed between July 2003 and February 2005. The date of each comparison performed at the BIPM is given in Appendix 1.

8. 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 instrument A.
- \bar{x}_A : the mean of N measurements of the nominal value x_{nom} measured by the instrument 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 instrument 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 instruments A and B during a comparison is written: $x_A = a_{A,B}x_B + b_{A,B}$. With this notation, instrument A is compared versus instrument B. $a_{A,B}$ is dimensionless and $b_{A,B}$ is expressed in units of nmol/mol.

9. Measurement protocol

The comparison protocol sent out to participants is included as Appendix 6. This protocol described briefly here, was developed for the comparison of ozone photometers. The protocol used for the GPT systems is briefly described in section 15.

Comparisons were performed following two protocols, either A or B, corresponding respectively to a direct or indirect (using a transfer standard) comparison between the national standard and the reference standard BIPM-SRP27.

In protocol A, a direct comparison was performed at the BIPM between the national standard and the reference standard BIPM-SRP27.

In the protocol B, a series of three comparisons were performed :

- a first comparison between the national and the transfer standard in the participating institute's laboratory. The protocol required this comparison to be performed in the six weeks before the comparison at the BIPM.
- a comparison at the BIPM between the transfer and the BIPM reference standard.
- a last comparison between the national and the transfer standard in the participating institute's laboratory. The protocol required this comparison to be performed in the six weeks after the comparison at the BIPM.

9.1 Protocol for the comparison of two instruments

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 could be checked at this time. If any adjustments were required, these were noted.

One ozone generator was used to generate the ozone to be measured by both instruments. Furthermore, a common source of pure air was used to provide the flows of reference air and ozone. The source of pure air was expected to be free of ozone, nitrogen oxides and any other interfering substance that could cause an undesired positive or negative response in the UV photometers. Gas flows were regulated to have a minimum excess of 1 l/min flow compared to the combined requirements of the photometers included in the comparison.

A comparison between two ozone measurement standards consists of producing and measuring ozone in air at different mole fractions over the range (0-500) nmol/mol. Each comparison includes 12 sampling points, consisting in 10 different ozone mole fractions distributed to cover the range, together with the measurement of reference air (reference air = reference zero air) at the beginning and end of each run. These 10 nominal values x_{nom} have been recommended by the coordinating laboratory, with the expectation that the actual delivered values will be within ± 15 nmol/mol of those. Each of the 12 sampling points is an

average (\bar{x}_A) of 10 single measurements recorded in a stable regime of the ozone generator, defined by a limit on the experimental standard deviation s_A . Each comparison was repeated at least 3 times. A set of repeated comparisons was referred to as a cycle. A cycle was always preceded by a period of ozone conditioning of the instruments for at least two hours. This involved passing a high ozone amount fraction (greater than 500 nmol/mol) through the instruments.

9.2 Post comparison calculations

In this report, the analysis of the comparisons results is performed by looking at the parameters of the linear regression performed for each comparison. To this end, the measurement results of each comparison between two standards were compared by performing a generalised least-square regression (linear) on the two sets of 12 ozone mole fractions values and their associated uncertainties. With this method, the result of a comparison is described by two parameters, the slope and intercept of the regression. The uncertainty of the parameters and the covariance between them is also given.

It was agreed during a Workshop for comparison participants (BIPM, April 2005) that the degrees of equivalence statement should be expressed as the difference between the participant and BIPM-SRP27 measurement results at two nominal ozone mole fractions. Their values as well as details on their calculation are given in section 21. However, as the term *degree of equivalence* should be used for key comparisons only, the term *difference from the reference value* is used in this report.

Furthermore, only the first of the series of three comparisons is reported as the participant's result in this exercise and subsequently used in the calculation of the difference from the reference value. For both protocols, all calculations were performed by the BIPM.

The measurement procedure at the BIPM was automated, readily allowing more than the 3 required comparisons to be performed (one comparison lasted about 2 hours). In this case, the participant was asked to choose 3 sets of data among the series of comparisons as their measurement results for the pilot study. It should be pointed out that this procedure allowed the stabilisation of the instrument and any instrument drift to be followed in detail. This was maybe not the case for the comparisons performed in the participants' laboratories.

9.3 SRP27 stability check

In the comparisons performed at the BIPM, a second ozone reference standard (BIPM-SRP28) was included when possible, to verify its comparability with BIPM-SRP27 and thus follow its stability over the period of the pilot study.

10. Reporting measurement results

Participants were asked to report results in forms provided with the protocol. For each comparison the participants were required to report the comparison conditions and their measurement results and associated uncertainties. The standard deviation for each ozone mole fraction measured was also reported. After the completion of each comparison, an excel workbook was prepared by the BIPM containing the measurement and calculation results, and sent to the participant for validation.

11. Deviations from the comparison protocol

Institute (Protocol)	Deviation from protocol
ERLAP (B)	Used 2 transfer standards (model TEI 49 CPS)
CSIR-NML (A)	After the results of the first comparison in September 2004, a second comparison was requested and performed in March 2005. During this comparison, one nominal ozone mole fraction could not be reached by the ozone generator.
NIST (B)	During the first comparison performed at NIST, the order in which ozone mole fractions were measured did not follow the protocol.
NILU (A)	The instrument remained at the BIPM longer than 1 week to achieve an optimally stable response.
SP (A)	The SP reference standard (Environment SA 42M) was calibrated by SRP11 (ITM-Stockholm university) 5 weeks after the comparison at the BIPM. A correction was applied to the measurement results obtained by SP at the BIPM. The BIPM proposed an alternative methodology for applying this correction. The two methods are described in Appendix 2.
NERI (B)	The time delay between the comparison at the BIPM and the return comparison at NERI was greater than 6 weeks (8 weeks between comparisons). During the first comparison performed at NERI, the order in which ozone mole fractions were measured did not follow the protocol.
NPL (A)	2 other NPL ozone analysers were compared with the national standard SRP20 before, during and after the comparison at the BIPM (results not included).
METAS (A/B)	In Draft A of this report, measurement protocol A was followed by METAS with the ozone standard they brought at the BIPM, SRP18. After distribution of the Draft A report to the participants, METAS asked to include their national standard SRP14 in the comparison results, following protocol B with SRP18 as a transfer standard. They provided measurement results for the SRP14-SRP18 comparison, as well as a new uncertainty budget for both SRPs measurement results (displayed in Appendix 2). The protocol of these comparisons differs slightly from the protocol of the pilot study (more sampling points, at different ozone mole fractions, in a different order).
INRIM (A)	Following the distribution of the Draft B report to the participants, it was agreed that a second corrected value for the INRIM comparison results would be included in the final report. INRIM provided the following explanation : " It takes into account the systematic effect, typically affecting O ₃ photometers, due to a temperature gradient in the gas along the two absorbing cells. The corrected value has been obtained re-calculating the ozone concentration of every data measured during the comparison for the corresponding temperature value measured at the same instant as the average

Institute (Protocol)	Deviation from protocol
	<p>temperature of the two PT100 sensors at the end of the cells. The uncertainty of the temperature is estimated as the variance of a normal distribution. This average and variance a little over-estimate the real values because an exponential distribution, not measured at the time of the comparison, is a better model for this gradient effect. The uncertainty of the corrected values takes also in count an estimated maximum value for ozone losses."</p> <p>The new measurement results are reported in Appendix 4 and the new uncertainty budget in Appendix 2.</p>

12. Measurement equation of the common reference BIPM-SRP27

The measurement of ozone mole fractions by an SRP is based on the absorption of radiation at 253.7 nm by ozone in the gas cells of the instrument. More details on the NIST SRP operation and its capabilities can be found in [3]. 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 concentration (C) of ozone is calculated from:

$$C = \frac{-1}{2\alpha L} \frac{T_{\text{mes}}}{T_{\text{std}}} \frac{P_{\text{std}}}{P_{\text{mes}}} \ln(D) \quad (1)$$

where

α is the absorption cross-section of ozone at 253.7 nm in standard conditions of temperature and pressure. The value used is: 1.1476×10^{-17} cm²/molecule [1, 4]. In (1):

L is the optical path length of one of the cells,

T_{mes} is the temperature measured in the cells,

T_{std} is the standard temperature (273.15 K),

P_{mes} is the pressure measured in the cells,

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

D is the product of transmittances of two cells :

$$D = T_1 \cdot T_2 \quad (2)$$

with the transmittance (T) of one cell defined as

$$T = \frac{I_{\text{ozone}}}{I_{\text{air}}} \quad (3)$$

where

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

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

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

$$x = \frac{-1}{2\alpha L} \frac{R}{N_A} \frac{T_{\text{mes}}}{P_{\text{mes}}} \ln(D) \quad (4)$$

where

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

13. 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 range (0-500) nmol/mol is given in Table 1.

Following this budget, as explained in the protocol of the pilot study (appendix 6), 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) :

$$u(x) = \sqrt{(0.28)^2 + (6.4 \cdot 10^{-4} x)^2} \quad (5)$$

Absorption cross section for ozone

The absorption cross section used within the SRP software algorithm is $308.32 \text{ atm}^{-1} \text{ cm}^{-1}$. This corresponds to a value 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 ozone photometers using the same value, the absorption cross section can be considered to have a conventional value and its uncertainty can be set to zero. This was the case for all the photometers encountered in this pilot study.

However, in the comparison with the gas phase titration the uncertainty of the absorption cross section has to be taken into account, in order to allow a comparison of the two reference methods. Estimates for the uncertainty of the absorption cross section vary, with a conservative estimate being 1.5 % at a 95% level of confidence. In that case, the equation (5) becomes :

$$u(x) = \sqrt{(0.28)^2 + (7.5 \cdot 10^{-3} x)^2} \quad (6)$$

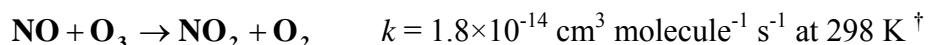
Component (y)	Uncertainty $u(y)$				Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to $u(x)$ $ c_i \cdot u(y)$
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$		
Optical Path $2L$	Measurement Scale	Rect.	0.0011 cm	0.014 cm	- $\frac{x}{2L}$	$\frac{u(2L) \cdot x}{2L}$
	Repeatability	Normal	0.01 cm			
Pressure P	Pressure gauge	Rect.	0.029 kPa	0.034 kPa	- $\frac{x}{P}$	$\frac{u(P) \cdot x}{P}$
	Difference between cells	Rect.	0.017 kPa			
Temperature T	Temperature probe	Rect.	0.087 K	0.087 K	$\frac{x}{T}$	$\frac{u(T) \cdot x}{T}$
Ratio of intensities D	Scalers resolution	Rect.	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D \ln(D)}$	$\frac{u(D) \cdot x}{D \ln(D)}$
	Repeatability	Triang.	1.1×10^{-5}			
Absorption Cross section α	Conventional value		8.6×10^{-20} cm ² /molecule	8.6×10^{-20} cm ² /molecule	- $\frac{x}{\alpha}$	$\frac{u(\alpha) \cdot x}{\alpha}$

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

14. Uncertainty budget for the participants

The following participants applied the BIPM uncertainty budget for their own SRPs : Environment Canada, METAS (first value only), NIES, NIST, UBA(A) and UBA(D). The other uncertainty budgets are described in Appendix 2. When appropriate, the equation expressing the uncertainty calculation as a function of ozone mole fraction is given.

15. Measurement of ozone by Gas Phase Titration (GPT)



The gas phase reaction of nitrogen monoxide with ozone readily lends itself to exploitation as a means of measuring ozone for the following reasons:

- the reaction proceeds very rapidly at ambient conditions to the virtual exclusion of any potentially competing gas phase chemistry involving NO, O₃, NO₂ and O₂;
- the reaction has a simple 1:1 stoichiometry giving $\Delta x_{\text{NO}} = \Delta x_{\text{O}_3} = \Delta x_{\text{NO}_2}$
- in a well designed flow reactor, the reaction may be driven essentially to completion (> 99.9 %) in a relatively short residence time of < 30 s.

Typically gas phase titration (GPT) is conducted under conditions of excess NO, so that the post-GPT residual ozone mole fraction is virtually zero, and the pre-GPT initial ozone mole fraction is measured indirectly as a change in the NO mole fraction, Δx_{NO} . The measurement of pre-GPT reactant x_{NO} and post-GPT residual x_{NO} is usually achieved using chemiluminescent NO detection.

[†] IUPAC Subcommittee for Gas Kinetic Data Evaluation preferred value; www.iupac-kinetic.ch.cam.ac.uk

In principle, the ozone mole fraction might also be measured in terms of changes of nitrogen dioxide mole fraction, Δx_{NO_2} . Measuring ozone mole fraction in terms of Δx_{NO_2} has some particular challenges but is likely to be achievable and may provide a potentially valuable check on the more frequently attempted measurement of nitrogen monoxide mole fraction changes.

The chemical literature reports a number of attempts to measure ozone mole fraction quantitatively using GPT. To date reported standard uncertainties for GPT as a reference method for ozone mole fraction determination are typically ~2% or often higher.

The importance of developing a practical GPT method for the measurement of ozone mole fractions with overall standard uncertainties of the order of 0.5% or better is that such a method may serve as an independent reference method to conventional UV-photometry methods. The GPT method has the potential to achieve SI traceable values for ozone mole fraction that do not rely on the ozone UV absorption cross section value, and its associated uncertainty of 1.5 %.

Two laboratories, NIES and BIPM, have participated in the study with GPT instruments. Both laboratories used Protocol B as their guide, however strict adherence was not possible because of the differences between the GPT and UV-photometry approaches. The overall approach taken by the two labs was similar in several ways:

- GPT was conducted in conditions of excess NO;
- quantification of x_{O_3} was in terms of Δx_{NO} only;
- nitrogen monoxide mole fraction analysis was done by chemiluminescence;
- gas flow measurement was achieved using molblocTM laminar flow elements;
- traceability was achieved via a primary gravimetric NO/N₂ gas standard;

There were also some differences in the two laboratories' realisation of a practical GPT instrument:

- the NIES-GPT brings together the reactant streams of ozone in air and nominally 100 $\mu\text{mol/mol}$ NO, and subsequently dilutes the product stream with zero air to achieve measurements of ozone mole fractions in the range (80-430) nmol/mol;
- the BIPM-GPT first dilutes a stream of nominally 50 $\mu\text{mol/mol}$ NO with zero air to < 2 $\mu\text{mol/mol}$ NO and subsequently combines this with ozone/zero air to achieve measurements of ozone mole fraction in the range (200-1000) nmol/mol;
- the NIES-GPT was not automated and ultimately their submitted result consisted of 11 individual point measurements acquired over an extended time period;
- the BIPM-GPT was automated and the submitted result consisted of 5 points acquired in a single automated run of 8 hours duration.

The two sets of GPT results are discussed briefly in Section 22.

16. Measurement results and uncertainties of the individual participants

The measurement results for all participants are given in two separate documents depending on the measurement protocol followed: Appendix 4 -Individual Results Protocol A.pdf and Appendix 5 - Individual Results Protocol B.pdf. For each participant, the three sets of comparison data are displayed, together with the results of the linear regression.

17. Linear regression parameters

Each comparison is characterised by the two parameters (slope a and intercept b) of the linear regression and their associated uncertainty (at a 95% level of confidence). For completeness the covariance term between the two parameters should also be included. It is displayed with the parameters in the table below. These parameters have been computed with the software B_Least recommended by the standard ISO 6143 [5].

17.1 Protocol A

Institute	a	$u(a)$	$U(a)$ ($k=2$)	b (nmol/mol)	$u(b)$ (nmol/mol)	$U(b)$ ($k=2$) (nmol/mol)	Covariance (nmol/mol)
CHMI	1.0040	0.0008	0.0016	-0.12	0.19	0.38	-1.0×10^{-4}
CSIR-NML (1)	1.0064			-2.23			
CSIR-NML (2)	1.0071	0.0032	0.0064	-0.63	0.38	0.76	-7.0×10^{-4}
WMO/WCC - EMPA	1.0033	0.0013	0.0026	-0.17	0.22	0.44	-2.0×10^{-4}
Env Canada	1.0028	0.0008	0.0016	-0.16	0.19	0.38	-1.1×10^{-4}
FMI	0.9960	0.0020	0.0040	-0.63	0.27	0.53	-8.0×10^{-4}
INRIM (1)	0.9931	0.0007	0.0014	-0.28	0.16	0.32	-8.5×10^{-5}
INRIM (2)	0.9970	0.0020	0.0040	-0.28	0.36	0.72	-4.9×10^{-4}
KRISS	0.9952	0.0009	0.0018	-0.12	0.16	0.32	-9.2×10^{-5}
METAS (SRP18)	1.0034	0.0008	0.0016	0.11	0.19	0.38	-1.1×10^{-4}
NIES (SRP35)	1.0000	0.0008	0.0016	-0.13	0.19	0.38	-1.0×10^{-4}
NILU	1.0015	0.0022	0.0044	-0.24	0.22	0.44	-2.0×10^{-4}
NMi-VSL	1.0007	0.0013	0.0026	-0.26	0.22	0.44	-2.0×10^{-4}
NPL	1.0023	0.0008	0.0016	-0.05	0.16	0.32	-1.0×10^{-4}
SP	0.9976	0.0012	0.0024	0.04	0.24	0.48	-2.0×10^{-4}
UBA (A)	1.0005	0.0008	0.0016	-0.06	0.19	0.38	-1.0×10^{-4}
UBA (D)	0.9977	0.0008	0.0016	-0.08	0.19	0.38	-1.0×10^{-4}
VNIIM	0.9944	0.0032	0.0064	-5.27	0.50	1.00	-1.0×10^{-3}

17.2 Protocol B

For protocol B the linear regression parameters are calculated in two steps using the software B_Least: a first calibration of the transfer standard values with BIPM-SRP27 is performed. Then the comparison between the national standard and the calibrated transfer standard is performed. This gives the parameters of the linear regression between the national standard and BIPM-SRP27. This process is applied for the two comparisons performed before (1) and after (2) measurements at the BIPM. The results are shown in the table below.

Institute	<i>a</i>	<i>u(a)</i>	<i>U(a) (k=2)</i>	<i>b (nmol/mol)</i>	<i>u(b) (nmol/mol)</i>	<i>U(b) (k=2) (nmol/mol)</i>	Covariance (nmol/mol)
ERLAP (1)	0.9959	0.0032	0.0064	0.34	0.69	1.38	-9.3×10 ⁻³
ERLAP (1b)	0.9958	0.0027	0.0054	0.35	0.56	1.12	-1.1×10 ⁻³
ERLAP (2)	0.9944	0.0032	0.0064	0.49	0.69	1.38	-9.2×10 ⁻³
ERLAP (2b)	0.9938	0.0025	0.0050	0.63	0.57	1.14	-1.1×10 ⁻³
ISCIII (1)	1.0080	0.0008	0.0016	-0.58	0.13	0.26	-1.0×10 ⁻⁴
ISCIII (2)	1.0016	0.0007	0.0014	-0.31	0.13	0.26	-1.0×10 ⁻⁴
LNE (1)	0.9973	0.0010	0.0020	0.19	0.20	0.40	-1.3×10 ⁻⁴
LNE (2)	0.9980	0.0009	0.0018	-0.14	0.20	0.40	-1.3×10 ⁻⁴
METAS SRP14 (1)	1.0009	0.0008	0.0015	0.34	0.27	0.53	-1.5×10 ⁻⁴
METAS SRP14 (2)	1.0015	0.0010	0.0019	0.55	0.24	0.48	-1.8×10 ⁻⁴
NDENW (1)	1.0004	0.0066	0.0132	-1.55	0.65	1.30	-2.4×10 ⁻³
NDENW (2)	0.9962	0.0065	0.0130	-1.11	0.65	1.30	-2.4×10 ⁻³
NERI (1)	0.9836	0.0059	0.0118	1.18	0.86	1.72	-3.2×10 ⁻³
NERI (2)	0.9738	0.0059	0.0118	1.97	0.80	1.60	-2.8×10 ⁻³
NIST (1)	0.9999	0.0009	0.0018	0.25	0.21	0.42	-1.0×10 ⁻⁴
NIST (2)	0.9987	0.0009	0.0018	0.21	0.21	0.42	-1.0×10 ⁻⁴
NIES GPT	1.0214	0.0086	0.0172	0.20	0.54	1.08	-2.0×10 ⁻³
BIPM GPT	1.0285	0.0082	0.0164	0.26	1.20	2.40	-2.9×10 ⁻³

The results of the comparison are most readily displayed using two graphs, one for the slope (Figure 1) and the other for intercept (Figure 2). The error bars represent the expanded uncertainties (*k*=2). For participants that have followed protocol B, two sets of regression parameters are given, and allow the stability of the transfer standard to be assessed. Participants are sorted in order of their participation date (at the BIPM).

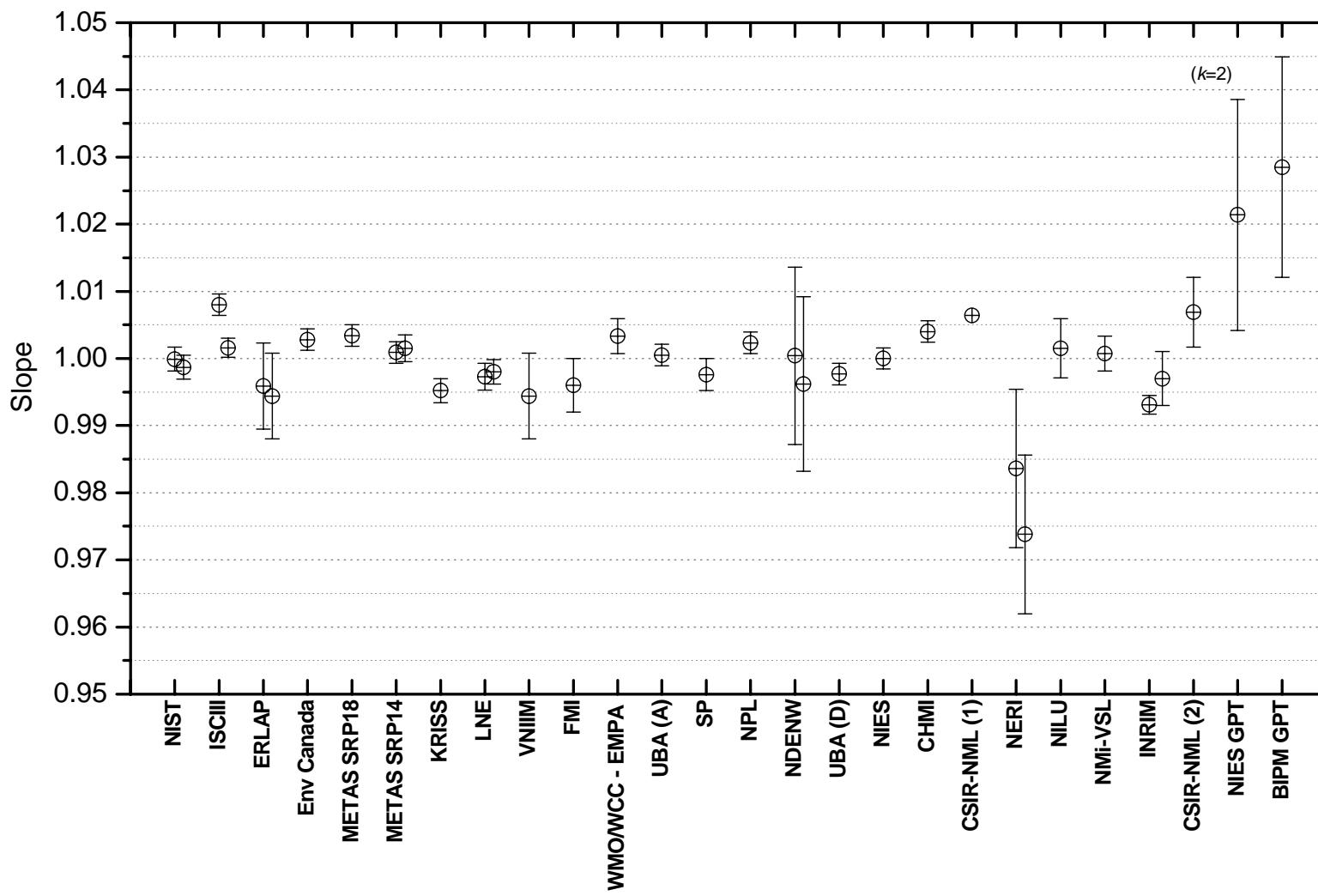


Figure 1 : Slopes of the regression

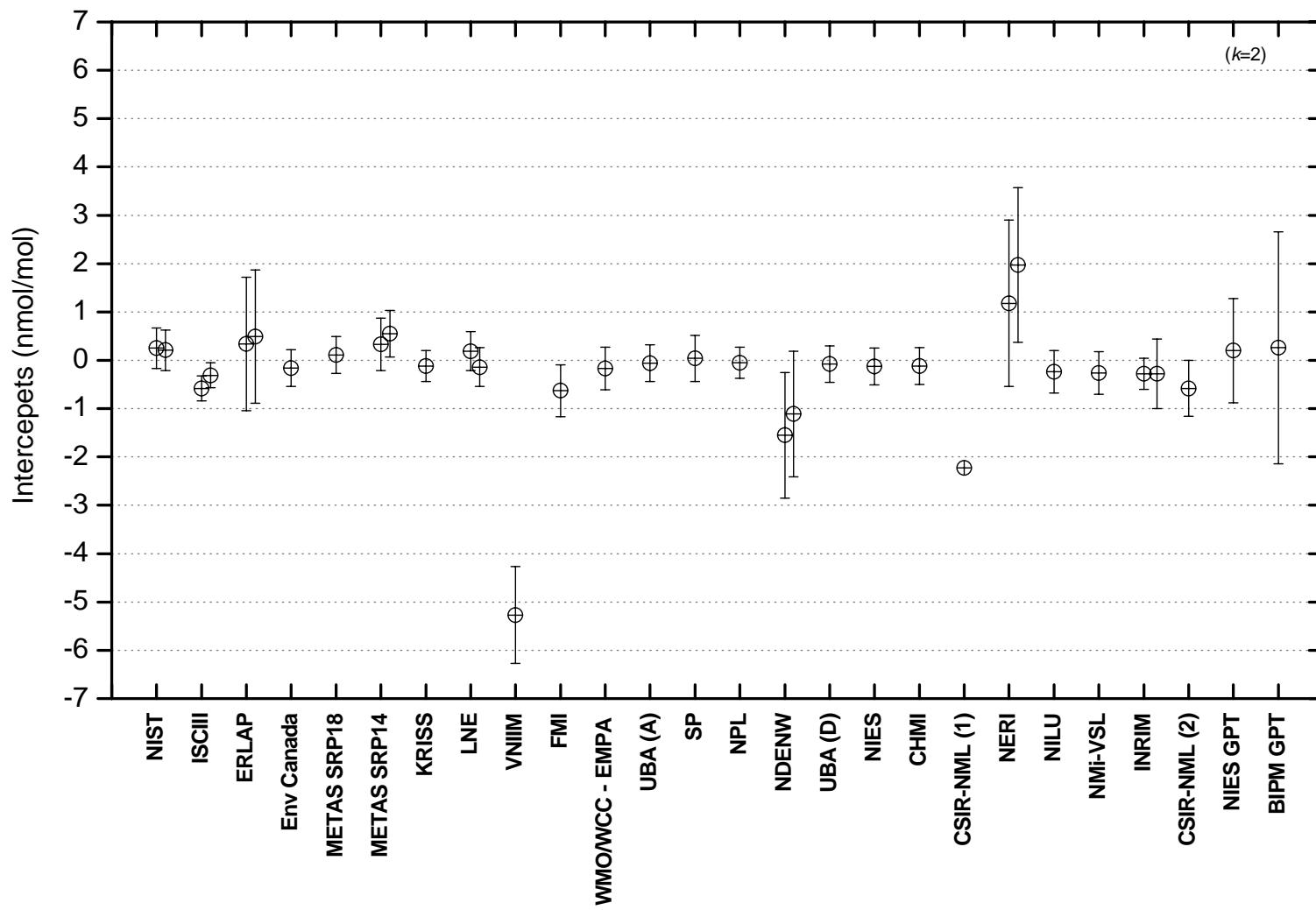


Figure 2 : Intercepts of the regression

18. BIPM-SRP27 stability

Over the period of the pilot study, the measurement standard BIPM-SRP28 has been included in the comparisons to analyse the stability of the comparison common reference, BIPM-SRP27. The results are displayed in Figure 3 (only one comparison result among the cycle of comparisons recorded with each participant). As can be seen in the figure, the standard deviation on the two regression parameters (slope and intercept) are comparable with their standard uncertainty ($u(a)=0.0008$, $u(b)=0.19$ nmol/mol), showing a good stability of both instruments.

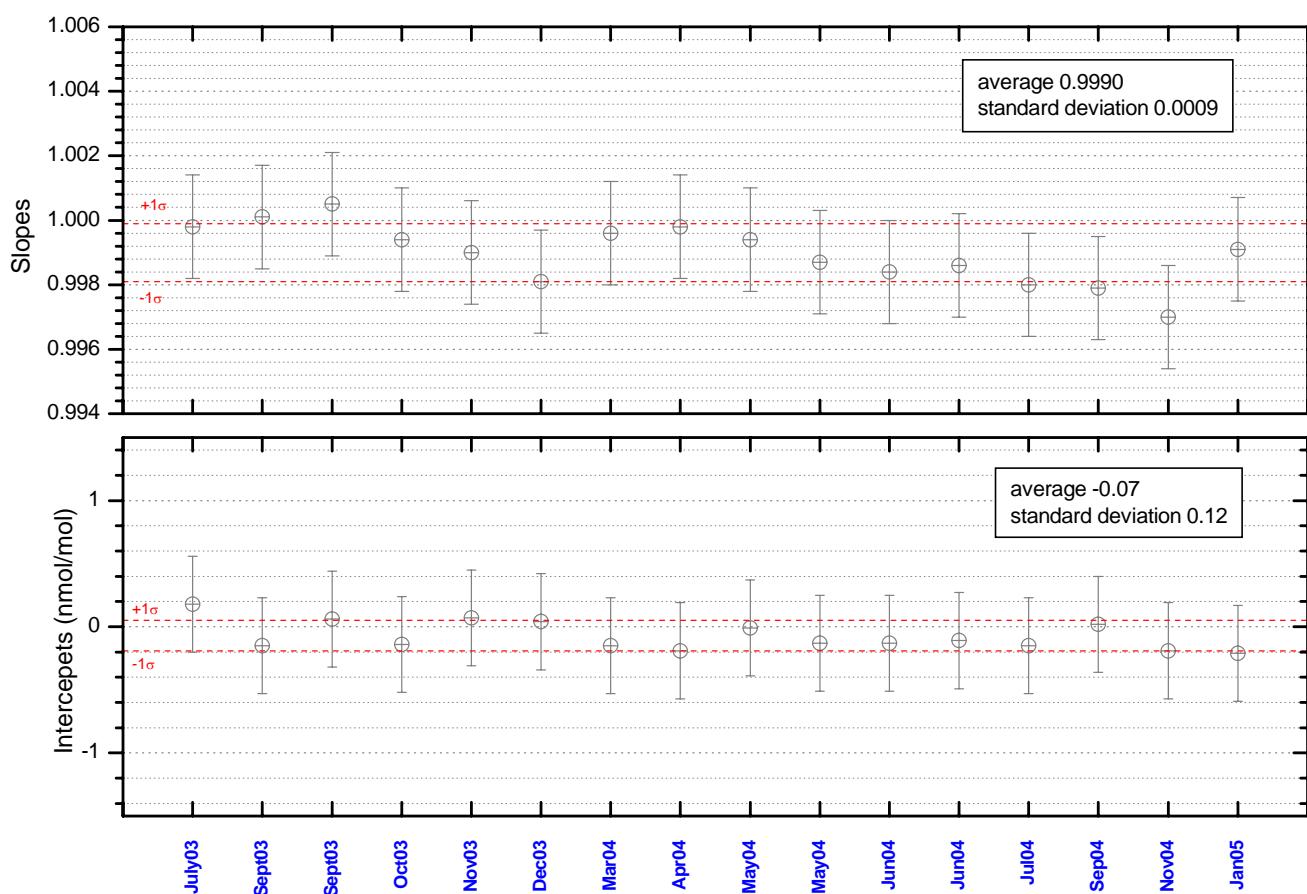


Figure 3 : Results of BIPM-SRP28 versus BIPM-SRP27 comparisons performed during the pilot study

19. Discussion of UV photometer results

19.1 Overall comparability, Birge ratio calculation

In an initial analysis of the UV photometer comparisons results, the two regression parameters are considered separately.

The intercept is closely linked with the ability of the instruments to actually measure zero nmol/mol when no ozone is present in the reference air. It is clear from Figure 2 that almost

all UV photometers are close to zero within the stated uncertainties. The VNIIM photometer measured a negative signal of -6 nmol/mol. The VNIIM reported that this shift in zero value had occurred during transportation to the BIPM. The results of a VNIIM and FMI comparison (dated 2003 and submitted with the VNIIM CCQM-P28 results) demonstrate that the FMI and VNIIM instruments agreed to within 0.7 %, and that the zero offset was not present.

CSIR-NML participated twice in the CCQM-P28 comparison, once in September 2004 and for a second time in March 2005. The first comparison resulted in a negative intercept of -2.23 nmol/mol. No uncertainty budget was provided for these measurements, and a second comparison was requested and performed in March 2005, for which the uncertainty budget is provided.

Calculation of the Birge ratio provides a means of assessing the agreement of the measurement results taking into account their stated uncertainties. The Birge ratio R can be computed from :

$$R^2 = \frac{\sum_{i=1}^n w_i (x_i - m)^2}{v} \quad (7)$$

Where :

x_i are the data points ,

w_i are the weights associated with each data point : $w_i = \frac{1}{u_i^2}$, where the u_i are the standard uncertainties,

m is the weighted mean of the data set :

$$m = \frac{\sum_{i=1}^n w_i x_i}{\sum_{i=1}^n w_i} \quad (8)$$

v is the degree of freedom : $v = n-1$, where n is the total number of points.

The Birge ratio computed on the 27 intercepts (excluding the VNIIM result and first CSIR-NML result) and their associated standard uncertainties is $R=1.37$ (weighted mean -0.16 nmol/mol). The Birge ratio is close to 1, which shows that the weights are not over evaluated, or alternatively that the uncertainties on the intercepts are not under evaluated.

The Birge ratio computed on the 27 slope data points (again, removing VNIIM and CSIR-NML first comparison), is $R=3.77$. This is significantly larger than 1, showing an underestimation of the uncertainties of this regression parameter. The Birge ratio for the slopes reported for the group of NIST SRPs (14 instruments) has also been computed, and is equal to 3.51, indicating that the uncertainties for the NIST SRPs are being underestimated.

A study of the sources of measurement uncertainty and systematic bias in NIST SRPs has been undertaken as part of a collaboration between the NIST and the BIPM, and the results will be published in a separate paper [6].

The two KRISS O₃-SRPs agree with each other (non-corrected measurement results are considered for the INRIM O₃-SRP), but the values of their calculated slope regression parameters are shifted by about -0.5 % compared to the NIST SRPs. The NIST and KRISS designed photometers are similar in design except that the optics in the KRISS SRPs are tilted by an angle of ~3° to avoid multiple reflections of the light in the gas cells. This has a consequence on the optical path length, hence on the calculated ozone mole fraction. The effect has been evaluated by the BIPM and will be treated in detail in a forthcoming paper [6].

Four participants maintain a UMEG photometer as a national (or reference) standard. The measurement results of three of these participants appear to be in good agreement with the reference value, with larger measurement uncertainties than estimated for NIST SRP or KRISS O₃-SRP instruments.

It is important to recall that measurement uncertainties associated with the UV photometers measurements did not include the ozone absorption cross-section. This component of the uncertainty budget cannot be used to explain a discrepancy between two photometers (since all instruments use the same conventional value).

19.2 Use of transfer standards

In the comparisons performed with a transfer standard, the transfer standard uncertainty must be included, enlarging the total uncertainty of the final result of the comparison. Laboratories using a transfer standard were required to perform measurements before and after those performed at the BIPM within a six week period of their measurements at the BIPM. The protocol was designed in this way so that the influence of the stability of the transfer standard on the comparison results could be assessed. Six laboratories used a transfer standard (protocol B). Only in one case did the two sets of regression parameters calculated for a given laboratory not agree within its stated uncertainties, indicating a possible underestimation of the uncertainty arising from the use of the transfer standard.

19.3 Repeatability of the comparisons

Each single comparison run was repeated at least two times, and often more (around 10 times) when the comparisons took place at the BIPM. In most cases, the instruments compared under these conditions appeared stable, and only one set of data was reported in the final result. In some cases, there is some variability or drift in the repeat measurements. In these cases the comparisons were repeated until stable measurements and repeatable results were achieved.

19.4 Comments on the statistical treatment of the comparison data

The data presented have been analysed using Generalised Least Squares (B_Least software) and their level of comparability assessed by calculating the Birge Ratio. This pilot study has given the opportunity to look at different statistical treatments of ozone measurement data. Ozone measurements are serially correlated and input quantities for the linear regression are also correlated, rendering the statistical analysis not straightforward. For example, the standard deviation of the mean cannot be used as an estimator of uncertainty due to the data being serially correlated. Similarly, the generalised least-square regression, as implemented in B_Least software, will underestimate the uncertainty of the regression parameters if correlations in input quantities are neglected. The statistical treatment of data has been

evaluated in a collaboration between the BAM and the BIPM and is the subject of a publication in preparation [7].

20. Discussion of GPT Results

In Figures 1 and 2 the two GPT results may be seen in relation to the reference value defined by the SRP27 measurements. In order to compare the two reference methods for ozone mole fractions, the uncertainty of the ozone UV absorption cross section has been included for the SRP27 measurements in the calculation of the regression parameters. It is evident in Figure 1, (slopes of regression lines), that the two GPT results stand well apart from the overwhelming consensus of the other instruments, having slopes 2-3 % greater than is typical for the UV-photometry method. It is important to realise that in Figure 1 there is a large contribution from the ozone cross-section uncertainty to the uncertainties ascribed to the GPT data points, arguably obscuring optimal interpretation of the GPT results.

The GPT and SRP27 data have been reanalysed, and regression parameters and uncertainties calculated with the BIPM-GPT measurements as reference values, and are replotted in Figure 4. In this format, the large ozone cross-section uncertainty is associated with the SRP27 data point, making a comparison of the two methods, UV-photometry and GPT, more straightforward.

In Figure 4 it is evident that the regression y -intercepts determined by the two GPT instruments were virtually identical and entirely consistent with that determined by SRP27. In no case was the intercept significantly different from $x_{O_3} = 0$ nmol/mol. The relatively large uncertainties associated with the GPT y -intercepts arise from the fact that neither instrument actually measures close to $x_{O_3} = 0$ but extrapolates from a higher measurement range. The NIES-GPT measured over the range (80-430) nmol/mol and the BIPM-GPT over the range (200-1000) nmol/mol.

Some conclusions may be drawn from the slopes graph, Figure 4:

- there is quite good agreement of the two independent GPT results. They differ from each other by ~0.7 % but agree within their stated uncertainties;
- the SRP27 result differs from the BIPM-GPT result by ~2.8 %;
- the UV-photometry result has a combined standard uncertainty approximately twice that of either GPT result (when all uncertainty components of the UV photometry reference method are considered).

The consistency of the two GPT results, the small overall uncertainty of this method, and the as yet unresolved large discrepancy between GPT and UV-photometry approaches raises the question of an unidentified bias in either GPT or UV-photometry, requiring further investigation. For the UV-photometry the assumed ozone cross-section is one possible candidate for further investigation.

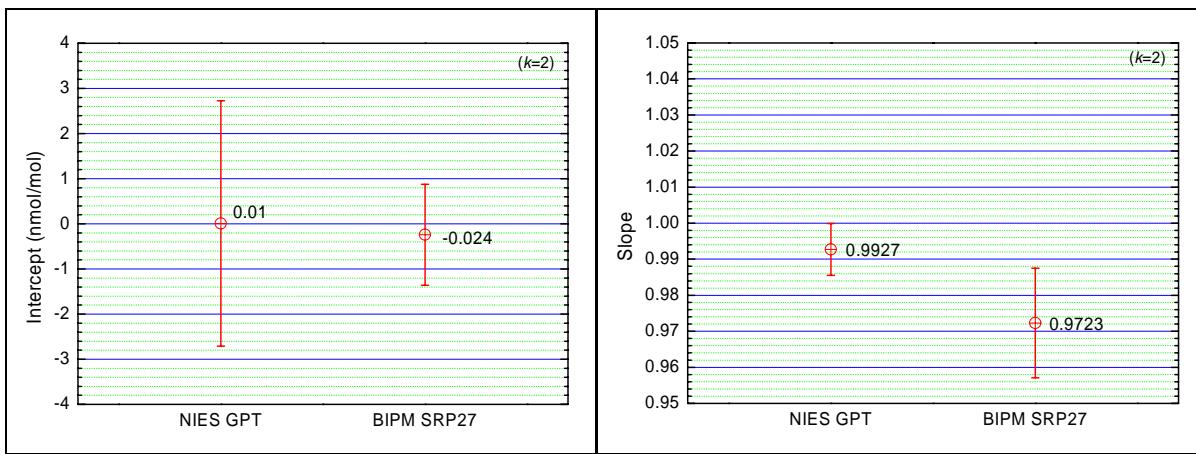


Figure 4 : NIES GPT and BIPM SRP27against the BIPM GPT-reference

Institute	slope <i>a</i>	<i>u(a)</i>	<i>U(a)</i> (k=2)	Intercept <i>b</i> (nmol/mol)	<i>u(b)</i> (nmol/mol)	<i>U(b)</i> (k=2) (nmol/mol)	Covariance (nmol/mol)
NIES GPT	0.9927	0.0036	0.0072	0.01	1.36	2.72	-4.1×10 ⁻³
BIPM SRP27	0.9723	0.0076	0.0152	-0.24	0.56	1.12	-1.1×10 ⁻³

21. Differences from the reference value

Following a workshop with CCQM-28 participants (BIPM, April 2005) and as agreed with the Gas Analysis Working Group, differences from the reference value are calculated at two nominal ozone mole fractions among the twelve measured in each comparison, in the range (0-500) 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 mole 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 differences from the reference value calculated for all the participants at the same nominal value. In each case the reference value is the value measured by SRP27.

21.1 Difference from the reference value for participants who followed protocol A

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

$$D_i = x_i - x_{\text{SRP27}} \quad (9)$$

where x_i and x_{SRP27} are the measurement result of the participant *i* and of SRP27 at the nominal value x_{nom} during a direct comparison of a national ozone standard at the BIPM.

Its associated standard uncertainty is:

$$u(D_i) = \sqrt{u^2(x_i) + u^2(x_{\text{SRP27}})} \quad (10)$$

where $u(x_i)$ and $u(x_{SRP27})$ are the uncertainties assigned to their reference standard measurements by the participants and the BIPM respectively.

21.2 Difference from the reference value for participants who followed protocol B

The difference from the reference value of the participant i , at the nominal value x_{nom} is the following:

$$D_i = \hat{x}_i - x_{SRP27} \quad (11)$$

With an associated standard uncertainty :

$$u(D_i) = \sqrt{u^2(\hat{x}_i) + u^2(x_{SRP27})} \quad (12)$$

where x_{SRP27} is the measurement result of SRP27 at the nominal value x_{nom} , and \hat{x}_i is the value of the participant i , at the same nominal value, deduced for the participant's national standard from the measurement result $x_{i,T}$ of the transfer standard during the comparison at the BIPM, and the parameters of the comparison performed between the transfer standard and the national standard in the participant laboratory (intercept $b_{NS,T}$ and slope $a_{NS,T}$) :

$$\hat{x}_i = a_{NS,T} \cdot x_{i,T} + b_{NS,T} \quad (13)$$

Following equation 12, the uncertainty on \hat{x}_i is :

$$u(\hat{x}_i) = \sqrt{u^2(b_{NS,T}) + x_{i,T}^2 \cdot u^2(a_{NS,T}) + a_{NS,T}^2 \cdot u^2(x_{i,T}) + 2x_{i,T} \cdot u(a_{NS,T}, b_{NS,T})} \quad (14)$$

where $u(x_{i,T})$ is the uncertainty assigned to their transfer standard measurements by the participants. The values $a_{NS,T}$, $b_{NS,T}$, $u(a_{NS,T})$, $u(b_{NS,T})$ and $u(a_{NS,T}, b_{NS,T})$ are the regression parameters and associated uncertainties calculated by the software B_Least from the measurement results and the associated uncertainties of the comparison between the national and the transfer standards, performed in the participants laboratory.

As protocol B includes two comparisons between the national standard and the transfer standard (before and after the comparison at the BIPM), two differences from the reference value are calculated for one nominal value x_{nom} .

21.3 Differences from the reference value at the nominal ozone mole fraction of 80 nmol/mol

Table 2 displays the differences from the reference value at a nominal value 80 nmol/mol, for participants who followed protocol A. The measurement results of the common reference SRP27 and of the national standard are also indicated, as well as the associated uncertainties.

Table 2 : Differences from the reference value at a nominal mole fraction of 80 nmol/mol, protocol A

Institute	x_{SRP27} (nmol/mol)	$u(x_{SRP27})$ (nmol/mol)	x_i (nmol/mol)	$u(x_i)$ (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (k=2) (nmol/mol)
CHMI	81.27	0.28	81.37	0.28	0.10	0.40	0.79
CSIR-NML (1)	81.84	0.28	80.07		-1.77		
CSIR-NML (2)	80.04	0.28	80.04	0.59	0.00	0.65	1.31
EMPA	82.44	0.28	82.56	0.37	0.12	0.46	0.93
Environment Canada	84.77	0.28	84.90	0.28	0.13	0.40	0.79
FMI	78.94	0.28	77.84	0.58	-1.10	0.64	1.29
INRIM (1)	80.88	0.28	79.97	0.19	-0.91	0.34	0.68
INRIM (2)	80.88	0.28	80.29	0.69	-0.59	0.74	1.48
KRISS	79.31	0.28	78.93	0.26	-0.38	0.38	0.76
METAS SRP18	78.76	0.28	79.13	0.28	0.37	0.40	0.79
NIES (SRP35)	80.60	0.28	80.44	0.28	-0.16	0.40	0.79
NILU	81.70	0.28	81.29	0.50	-0.41	0.57	1.15
NMi-VSL	81.06	0.28	80.71	0.35	-0.35	0.45	0.90
NPL	80.80	0.28	81.14	0.16	0.34	0.32	0.64
SP	81.95	0.28	81.55	0.42	-0.40	0.50	1.00
UBA (A)	81.90	0.28	81.97	0.28	0.07	0.40	0.79
UBA (D)	80.73	0.28	80.54	0.28	-0.19	0.40	0.79
VNIIM	77.13	0.28	71.53	1.01	-5.60	1.05	2.10

Table 3 displays the differences from the reference value at a nominal value of 80 nmol/mol, for participants who followed protocol B. The measurement results of the reference SRP27 and the corresponding calculated values of the national standard are also indicated, as well as the associated uncertainties.

Table 3 : Differences from the reference value at the nominal mole fraction of 80 nmol/mol, protocol B

Institute	x_{SRP27} (nmol/mol)	$u(x_{\text{SRP27}})$ (nmol/mol)	\hat{x}_i (nmol/mol)	$u(\hat{x}_i)$ (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (k=2) (nmol/mol)
ERLAP (1)	83.23	0.28	83.30	1.00	0.07	1.03	2.07
ERLAP (2)	83.23	0.28	83.41	1.00	0.18	1.04	2.07
ISCIII (1)	78.27	0.28	78.42	0.11	0.15	0.30	0.61
ISCIII (2)	78.27	0.28	78.18	0.11	-0.09	0.30	0.60
LNE (1)	79.15	0.28	78.87	0.26	-0.28	0.38	0.76
LNE (2)	79.15	0.28	78.57	0.26	-0.58	0.38	0.76
METAS SRP14 (1)	78.76	0.28	79.16	0.38	0.40	0.47	0.94
METAS SRP14 (2)	78.76	0.28	79.20	0.36	0.44	0.46	0.91
NDENW (1)	81.10	0.28	79.58	1.30	-1.52	1.33	2.66
NDENW (2)	81.10	0.28	79.67	1.30	-1.43	1.33	2.65
NERI (1)	81.80	0.28	81.71	1.41	-0.09	1.44	2.88
NERI (2)	81.80	0.28	81.57	1.39	-0.23	1.42	2.83
NIST (1)	82.25	0.28	82.53	0.32	0.28	0.42	0.84
NIST (2)	82.25	0.28	82.39	0.32	0.14	0.42	0.85
BIPM GPT	80.83	0.67	83.28	1.00	2.45	1.20	2.41
NIES GPT	80.60	0.67	82.50	0.57	1.90	0.88	1.76

21.4 Differences from the reference value at the nominal ozone mole fraction of 420 nmol/mol

Table 4 displays the differences from the reference value at a nominal value 420 nmol/mol, for participants who followed protocol A. The measurement results of the reference SRP27 and of the national standard are also indicated, as well as the associated uncertainties.

Table 4 : Differences from the reference value at a nominal mole fraction of 420 nmol/mol, protocol A

Institute	x_{SRP27} (nmol/mol)	$u(x_{SRP27})$ (nmol/mol)	x_i (nmol/mol)	$u(x_i)$ (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ ($k=2$) (nmol/mol)
CHMI	422.02	0.34	423.69	0.33	1.67	0.47	0.95
CSIR-NML (1)	419.68	0.34	420.03		0.35		
CSIR-NML (2)	418.60	0.34	420.02	3.24	1.42	3.26	6.52
EMPA	415.94	0.34	417.28	1.01	1.34	1.07	2.13
Environment Canada	426.27	0.34	427.20	0.34	0.93	0.48	0.96
FMI	411.61	0.34	409.50	1.79	-2.11	1.82	3.64
INRIM (1)	418.85	0.34	415.63	0.26	-3.22	0.43	0.86
INRIM (2)	418.85	0.34	417.28	1.56	-1.57	1.60	3.20
KRISS	421.94	0.34	419.81	1.25	-2.13	1.30	2.59
METAS SRP18	420.82	0.34	422.37	0.34	1.55	0.48	0.96
NIES (SRP35)	424.58	0.34	424.37	0.34	-0.21	0.48	0.96
NILU	423.12	0.34	423.45	2.25	0.33	2.28	4.55
NMi-VSL	418.36	0.34	418.34	0.97	-0.02	1.03	2.06
NPL	409.39	0.34	410.16	0.38	0.77	0.51	1.02
SP	417.17	0.34	416.20	0.83	-0.97	0.90	1.79
UBA (A)	416.62	0.34	416.70	0.34	0.08	0.48	0.96
UBA (D)	407.32	0.34	406.37	0.34	-0.95	0.48	0.96
VNIIM	409.43	0.34	400.46	2.59	-8.97	2.61	5.22

Table 5 displays the differences from the reference value at a nominal value 420 nmol/mol, for participants following the protocol B. The measurement results of the reference SRP27 and of the national standard are also indicated, as well as the associated uncertainties.

Table 5 : Differences from the reference value at a nominal mole fraction of 420 nmol/mol, protocol B

Institute	x_{SRP27} (nmol/mol)	$u(x_{SRP27})$ (nmol/mol)	\hat{x}_i (nmol/mol)	$u(\hat{x}_i)$ (nmol/mol)	D_i (nmol/mol)	$u(D_i)$ (nmol/mol)	$U(D_i)$ (k=2) (nmol/mol)
ERLAP (1)	417.14	0.34	415.77	1.42	-1.37	1.46	2.93
ERLAP (2)	417.14	0.34	415.18	1.37	-1.96	1.41	2.82
ISCIII (1)	420.19	0.34	422.92	0.26	2.73	0.43	0.86
ISCIII (2)	420.19	0.34	420.47	0.25	0.28	0.42	0.85
LNE (1)	414.26	0.34	413.49	0.60	-0.77	0.69	1.38
LNE (2)	414.26	0.34	413.41	0.59	-0.85	0.68	1.37
METAS SRP14 (1)	420.82	0.34	421.57	0.58	0.75	0.68	1.35
METAS SRP14 (2)	420.82	0.34	422.01	0.71	1.19	0.79	1.58
NDENW (1)	409.19	0.34	407.70	6.55	-1.49	6.56	13.11
NDENW (2)	409.19	0.34	406.48	6.52	-2.71	6.53	13.06
NERI (1)	424.48	0.34	418.83	4.30	-5.65	4.31	8.63
NERI (2)	424.48	0.34	415.62	4.28	-8.86	4.29	8.59
NIST (1)	410.41	0.34	410.58	0.38	0.17	0.51	1.02
NIST (2)	410.41	0.34	410.05	0.40	-0.36	0.53	1.06
BIPM GPT	417.33	3.14	429.59	0.78	12.26	3.24	6.48
NIES GPT	424.58	3.20	433.95	2.40	9.36	4.00	7.99

21.5 Graphs of the differences from the reference value

Graphs showing the differences from the reference value have been constructed for both nominal ozone mole fraction values. There are shown in the following pages. The error bars represent the expanded uncertainties ($k=2$). For participants that followed protocol B, two values are given, and allow the stability of the transfer standard to be assessed. The institutes are sorted in the order of their visiting date at the BIPM.

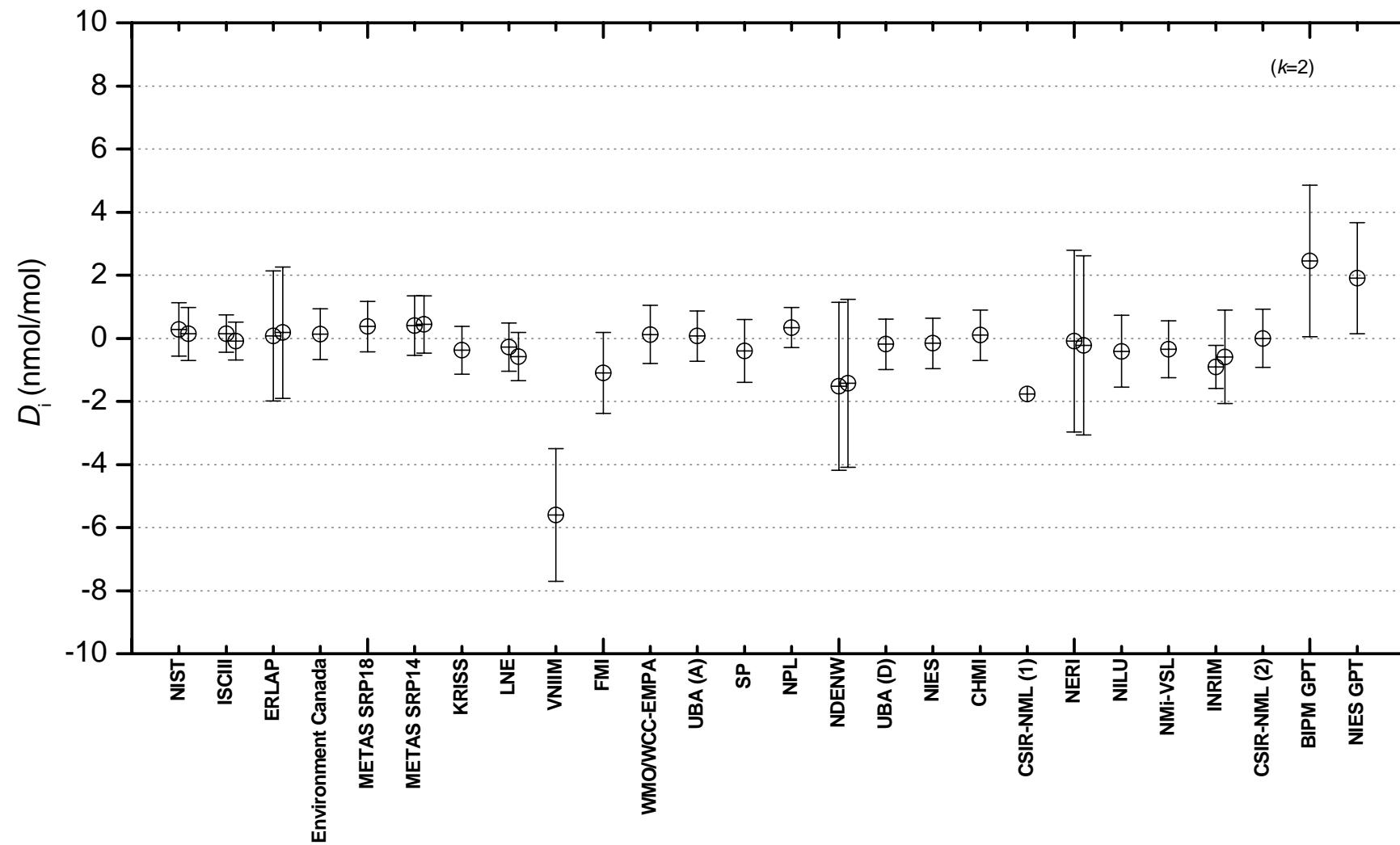


Figure 5 : Differences from the reference value at a nominal ozone mole fraction of 80 nmol/mol

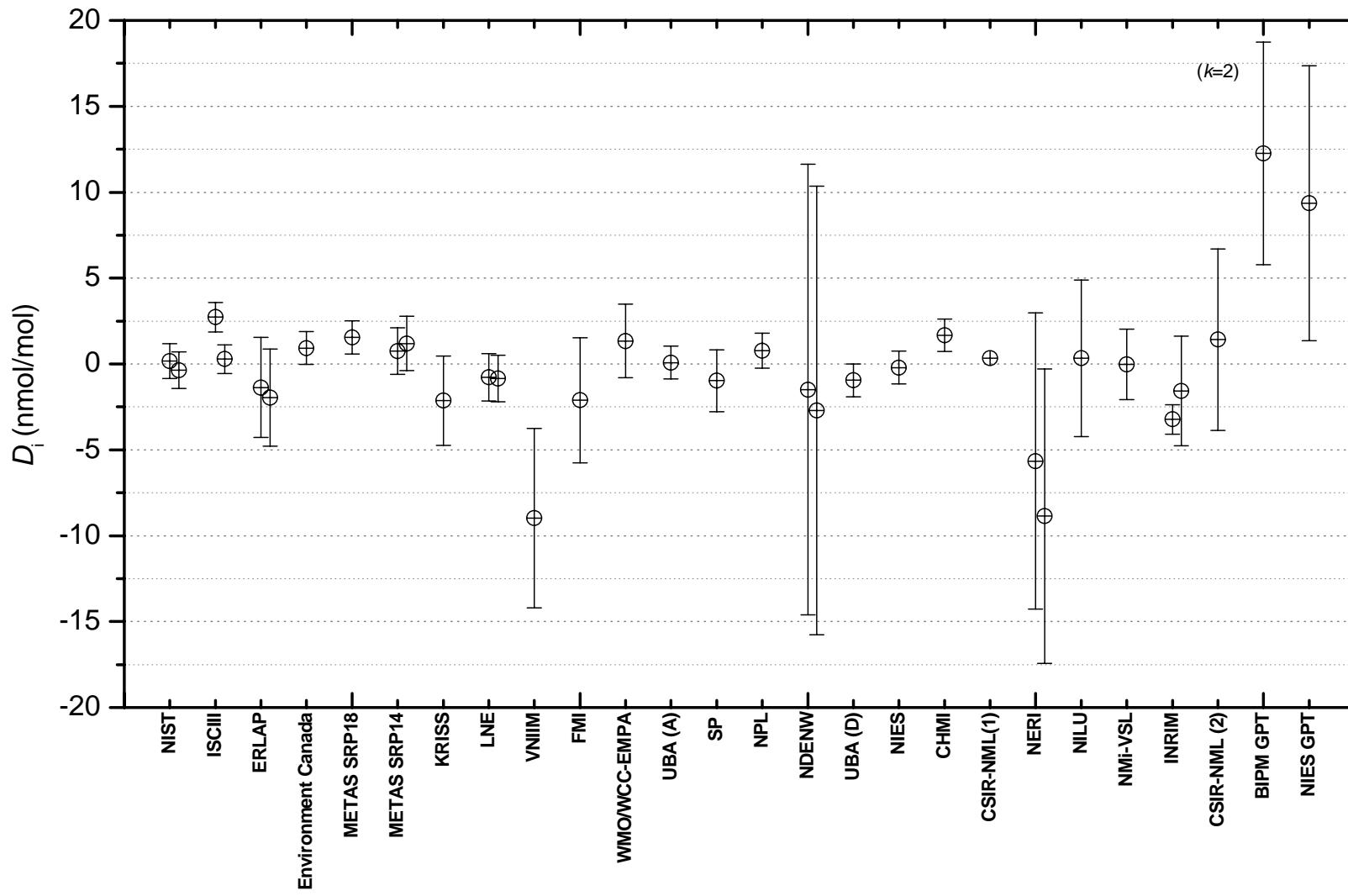


Figure 6 : Differences from the reference value at a nominal ozone mole fraction of 420 nmol/mol

22. Interpretation of future key comparison results in relation to Appendix C CMC claims

This section is aimed at clarifying the relationship between the future key comparison BIPM.QM-K1 results and an institutes' Calibration and Measurement Capabilities (CMC) claims, as expressed in the Appendix C of the BIPM key comparison database (KCDB). The CMC statement for an ozone reference standard is described, introducing the concept of the limit of quantification. Secondly, the absorption cross-section uncertainty is considered, and finally the relationship between an institute's performance and CMC statement is discussed.

22.1 CMC statements

CMC statements on ozone in air for an institute are generally displayed in Appendix C of the KCDB in two tables, corresponding to two distinct ranges of ozone mole fractions (see tables below). In the first range $[x_1 - x_2]$, the absolute expanded uncertainty U_1 (or uncertainty range U_1 to U_2) is given in nmol/mol. In the second range $[x_2 - x_3]$, the relative expanded uncertainty is given in %. The value x_2 is generally equal to 100 nmol/mol.

Matrix or material	Analyte or component	Dissemination range of measurement capability	
		Amount of substance fraction in nmol/mol	Absolute expanded uncertainty in nmol/mol
air	ozone	x_1 to x_2	U_1 to U_2

Matrix or material	Analyte or component	Dissemination range of measurement capability	
		Amount of substance fraction in nmol/mol	Relative expanded uncertainty in %
air	ozone	x_2 to x_3	U_2 to U_3

It is recommended that a comment should be added to CMC claims clarifying the contribution of the absorption cross section to the overall stated uncertainty.

22.2 Value of x_1

x_1 may be expressed as the limit of quantification L_Q of the ozone reference standard, this term being defined as 10 times the standard deviation calculated on at least 10 repeats of the instrument measurement result when no ozone is present in the reference air :

$$L_Q = 10\sigma \quad (15)$$

For example, the BIPM reference standard SRP27 shows a typical standard deviation equal to 0.2 nmol/mol when only dry air is measured. Its limit of quantification is thus equal to 2 nmol/mol.

22.3 Uncertainty on the absorption cross-section

All currently published ozone CMCs in the Appendix C of the KCDB are based on instrument standards which are realisations of the UV photometry method to measure ozone mole fractions in air. This method is based on the knowledge of the ozone absorption cross section α at the particular wavelength of 253.65 nm. In consequence, the measurement uncertainty of these instrument standards includes the uncertainty on α . It can always be expressed as :

$$u = \sqrt{u_\alpha^2 + u_{inst}^2} \quad (16)$$

However, as α takes a conventional value used by all participants in this comparison, the uncertainty on α cancels out in the expression of the uncertainty on the difference from the reference value.

In the key comparison BIPM.QM-K1, the difference from the reference value, D_i , will be termed the degree of equivalence. Its standard uncertainty will be expressed by

$$u(D_i) = \sqrt{u^2(x_i) + u^2(x_{SRP27})} \quad (17)$$

where $u(x_i)=u_{inst}(x_i)$ and $u(x_{SRP27})=u_{inst}(x_{SRP27})$.

It follows that CMCs and degrees of equivalence can only be compared if the standard uncertainty used for the absorption cross-section is known. At the present time, there is no international agreement on the magnitude of this uncertainty, and different values have been used by different institutes (expanded uncertainty of 1% recommended by NIST [3], 1.5% by the ISO standard 13964 [1]). In a forthcoming paper [6], the BIPM and the NIST will propose an uncertainty value of 2.1%, based on the published values in the literature.

22.4 Relation between degrees of equivalence and CMC statements in future rounds of BIPM.QM-K1

For an institute i participating in the ozone comparison BIPM.QM-K1, their measurements can be assumed to be consistent with the reference value at the nominal ozone mole fraction x_{nom} if the following equation is fulfilled:

$$|D_i| \leq k \cdot u(D_i) \quad (18)$$

Following equation (16), we assume that the expanded absolute uncertainty U associated with the measurement result x_i declared by the participant i in the CMC statement can be written :

$$U = k \cdot \sqrt{u_\alpha^2 + u_{inst}^2(x_i)} \quad (19)$$

The standard uncertainty of the degree of equivalence $u(D_i)$ is thus linked with the declared expanded uncertainty by :

$$u(D_i) = \sqrt{u_{inst}^2(x_i) + u^2(x_{SRP27})} = \sqrt{\left(\frac{U}{k}\right)^2 - u_\alpha^2 + u^2(x_{SRP27})} \quad (20)$$

From (18), it follows a condition on the declared expanded uncertainty U :

$$U \geq k' \sqrt{\left(\frac{D_i}{k}\right)^2 + u_\alpha^2 - u^2(x_{SRP27})} \quad (21)$$

The above condition should be fulfilled for the two degrees of equivalence statements defined in future ozone comparisons, evaluated at the two ozone mole fraction nominal values 80 nmol/mol and 420 nmol/mol.

The equations presented in this paragraph should not be applied directly to the results of CCQM-P28, as measurement biases with the common reference SR27 as well as other SRPs need to be corrected, and related measurement uncertainties modified, as described in [6].

23. Conclusion

The pilot study has allowed the comparability between ozone reference standards to be evaluated over the ozone mole fraction range (0-500) nmol/mol, and has also demonstrated that such comparisons can be meaningfully performed using transfer standards, provided the stability of the transfer standard is well characterized.

All participants maintaining ozone reference standards used the same conventional value for the ozone absorption cross section, and for the purposes of this comparison the uncertainty of this component was conventionally set to zero. The uncertainties quoted for non-SRP instruments were in general a factor or more larger than for SRP instruments, and in the majority of cases provided results which were consistent with the reference values. In the case of SRP instruments, analysing the remaining uncertainty budget components, the discrepancy between SRPs should be smaller than 0.2 % of the ozone mole fraction analysed, for mole fractions over 100 nmol/mol. Analysis of the results of the comparison indicates that agreement is somewhat worse than this with a maximum discrepancy of 0.7 % in measurements of ozone mole fraction observed between NIST SRPs. This has led to further work by the BIPM and the NIST to analyse the sources of the observed differences.

Two laboratories reported results based on a gas phase titration reference method for ozone measurement. The results of the two laboratories agreed to within 0.7 % on the ozone mole fractions measured. However, the comparisons of the gas phase titration and UV photometry reference methods have shown a discrepancy of 2 % to 3 % which still needs more investigation. Further work is required on both methods, to identify and characterize possible sources of this bias.

An on-going BIPM coordinated key comparison with an improved protocol and a re-evaluated uncertainty budget for the reference instrument standard BIPM-SRP27, will be proposed.

24. References

- [1] ISO 13964: 1998, *Ambient air - Determination of ozone - Ultraviolet photometric method*, International Organization for Standardization
- [2] ISO 10313: 1993, *Ambient air - Determination of the mass concentration of ozone - chemiluminescence method*, International Organization for Standardization
- [3] Paur R J, Bass A M, Norris J E and Buckley T J, Standard reference photometer for the assay of ozone in calibration atmospheres, 2003, *NISTIR 6369*, 25 pp.

- [4] ISO 13964: 1996, *Ambient air - Determination of ozone - Ultraviolet photometric method*, ISO
- [5] ISO 6143: 2001, *Gas analysis - Determination of the composition of calibration gas mixtures - Comparison methods*, International Organization for Standardization
- [6] Viallon J, Moussay P, Norris J E, Guenther F R and Wielgosz R I, "A study of systematic biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard Reference Photometer", in preparation.
- [7] Bremser W, Viallon J and Wielgosz R I, in preparation.

Appendix 1 - Pilot study organisation

Date of comparison	Institute	Country / organisation	National Standard model	Prot.	Transfer Standard model	Traceable to
July 2003	NIST National Institute for Standards and Technology	United States of America	SRP	B	SRP	
Sept 8-12, 2003	ISC III Institute de Salud Carlos III	Spain	SRP	B	TEI 49C	SRP2 (NIST)
Sept 22-26, 2003	ERLAP (JRC) European Reference Laboratory of Air Pollution	European Community	UMEG	B	TEI 49CPS	
Oct 20-24, 2003	Environment Canada	Canada	SRP	A		
Nov 17-21, 2003	METAS Swiss Federal Office of Metrology and Accreditation	Switzerland	SRP	A/B	SRP	
Dec 1-5, 2003	KRISS Korean Research Institute of Standards and Science	Korea	O3-SRP	A		
Feb 2-6, 2004	LNE Laboratoire National D'Essais	France	SRP	B	TEI 49CPS	
Feb 16-20, 2004	VNIIM Mendeleyev Institute for Metrology	Russia	Dasibi 1003AH	A		
Mar 1-5, 2004	FMI Finnish Meteorological Institute	Finland	TEI 49CPS	A		SRP24 (LNE)
Mar 15-19, 2004	WMO/WCC-EMPA World Calibration Center for Surface Ozone	World Meteorological Organisation	SRP	A		

Mar 29- Apr 2, 2004	UBA (A) Federal Environmental Agency	Austria	SRP	A		
May 3-7, 2004	SP Swedish National Testing and Research Institute	Sweden	Environment SA 42M	A		SRP11 (Stockholm)
May 24-28, 2004	NPL National Physical Laboratory	United Kingdom	SRP	A		
June 7-11, 2004	NDENW National Directorate for Environment, Nature and Water	Hungary	UMEG	B	TEI 49C	
June 21-25, 2004	UBA (D) Federal Environmental Agency	Germany	SRP	A		
July 26-30, 2004	NIES National Institute for Environmental Studies	Japan	SRP / GPT	A/B	SRP	
Sept 20-24, 2004	CHMI Czech Hydro Meteorological Institute	Czech Republic	SRP	A		
Sep 27 – Oct 1, 2004 March 14-16, 2005	CSIR-NML National Metrology Institute	South Africa	API 401	A		SRP2 (NIST)
Nov 22-26, 2004	NERI National Environmental Research Institute	Denmark	UMEG	B	API 400A	
Nov 29 – Dec 3, 2004	NILU Norwegian Institute for Air Research	Norway	API 400E	A		SRP11 (Stockholm)
Jan 11-13, 2005	NMI-VSL NMi van Swinden Laboratory	Nederland	UMEG	A		
Jan 24-26, 2005	INRIM Istituto Nazionale di Ricerca Metrologica	Italy	O3-SRP	A		
Feb 3, 2005	BIPM Bureau International des Poids et Mesures		GPT	B	TEI 49C	

Mar 29- Apr 2, 2004	UBA (A) Federal Environmental Agency	Austria	SRP	A		
May 3-7, 2004	SP Swedish National Testing and Research Institute	Sweden	Environment SA 42M	A		SRP11 (Stockholm)
May 24-28, 2004	NPL National Physical Laboratory	United Kingdom	SRP	A		
June 7-11, 2004	NDENW National Directorate for Environment, Nature and Water	Hungary	UMEG	B	TEI 49C	
June 21-25, 2004	UBA (D) Federal Environmental Agency	Germany	SRP	A		
July 26-30, 2004	NIES National Institute for Environmental Studies	Japan	SRP / GPT	A/B	SRP	
Sept 20-24, 2004	CHMI Czech Hydro Meteorological Institute	Czech Republic	SRP	A		
Sep 27 – Oct 1, 2004 March 14-16, 2005	CSIR-NML National Metrology Institute	South Africa	API 401	A		SRP2 (NIST)
Nov 22-26, 2004	NERI National Environmental Research Institute	Denmark	UMEG	B	API 400A	
Nov 29 – Dec 3, 2004	NILU Norwegian Institute for Air Research	Norway	API 400E	A		SRP11 (Stockholm)
Jan 11-13, 2005	NMI-VSL NMi van Swinden Laboratory	Nederland	UMEG	A		
Jan 24-26, 2005	INRIM Istituto Nazionale di Ricerca Metrologica	Italy	O3-SRP	A		
Feb 3, 2005	BIPM Bureau International des Poids et Mesures		GPT	B	TEI 49C	

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Appendix 2 - UV Photometers uncertainty budgets

1. CHMI (SRP17)

Component (y)	standard uncertainty $u(y)$	Sensitivity coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to $u(x)$ $ c_i \cdot u(y)$
Optical Path $2L$	0.02 cm	$-\frac{x}{2L}$	$\frac{u(2L) \cdot x}{2L}$
Temperature T	0.07 K	$-\frac{x}{T}$	$\frac{u(T) \cdot x}{T}$
Pressure P	0.034 kPa	$-\frac{x}{P}$	$\frac{u(P) \cdot x}{P}$
Ratio of intensities D	1.43×10^{-5}	$\frac{x}{D \ln(D)}$	$\frac{u(D) \cdot x}{D \ln(D)}$
Uncertainty expression	$u(x) = \sqrt{0.28^2 + (3.98 \cdot 10^{-4} x)^2}$		

2. CSIR-NML

At 0-100 nmol/mol :

Parameter	Estimate	Specification	Probability distribution	Divisor	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty contribution $c_i \times u(x_i)$	Degrees of freedom	Type A or B
SRP	x	0,42 nmol/mol	Normal	2	$\frac{0,42}{2}$	1	$\frac{0,42}{2}$	∞	B
Zero drift	x	< 1,0 nmol/mol	Rectangular	$\sqrt{3}$	$\frac{0,5}{\sqrt{3}}$	1	$\frac{0,5}{\sqrt{3}}$	∞	B
Repeatability	x				Standard deviation	1	Standard deviation	$n - 1 = 9$	A

At 100-500 nmol/mol

Parameter	Estimate	Specification	Probability distribution	Divisor	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty contribution $c_i \times u(x_i)$	Degrees of freedom	Type A or B
SRP	x	0,42 % relative	Normal	2	$x \times \frac{0,42}{100} / 2$	1	$\frac{0,42 \times x}{200}$	∞	B
Span drift	x	1% of reading	Rectangular	$\sqrt{3}$	$\frac{1}{\sqrt{3}} \times x$	1	$\frac{x}{100 \times \sqrt{3}}$	∞	B
Repeatability	x				Standard deviation	1	Standard deviation	$n - 1 = 9$	A

Calculate the effective degrees of freedom with the Welch-Satterthwaite formula: $v_{eff} = \frac{u_c^4(y)}{\sum_{i=1}^N \frac{u_i^4(y)}{v_i}}$

3. ERLAP

3.1 National standard UMEG

Model equation:

$$Ozone = -po/p * T/To * I/(k*L) * \ln(I/Io) * 0.466893;$$

List of quantities:

Quantity	Unit	Definition
Ozone	ppb	Concentration of ozone
po	kPa	Pressure at standard conditions
p	kPa	Pressure during measurement
T	°K	Temperature in the measurement cell
To	°K	Temperature at standard conditions
k	1/m/kPa	Coefficient of absorption of ozone in the air at the wavelength of measurement
L	m	Length of path beam
I	mV	Voltage corresponding to the lamp emission after ozone absorption
Io	mV	Voltage corresponding to the lamp emission

Ozone:

Result

po:

Constant

Value: 101.3 kPa

p:

Type B rectangular distribution

Value: 98.95 kPa

Half-width of distribution: 0.05 kPa

T:

Type B rectangular distribution

Value: 302.35 °K

Half-width of distribution: 0.3 °K

To:

Constant

Value: 273.15 °K

k:

Constant

Value: 0.0000144 1/m/kPa

L:

Type B rectangular distribution

Value: 2.655 m

Half-width of distribution: 0.006 m

I:

Type A

Method of observation: Direct

Number of observation: 10

No.	Observation
1	19273
2	19271
3	19272
4	19271
5	19272
6	19272
7	19270
8	19270
9	19272
10	19275

Arithmetic mean: 19271.800 mV

Standard deviation: 1.48 mV

Standard uncertainty: 0.467 mV

Degrees of freedom: 9

Io:

Type A

Method of observation: Direct

Number of observation: 10

No.	Observation
1	19567
2	19566
3	19564
4	19565
5	19567
6	19566
7	19566
8	19566
9	19563
10	19569

Arithmetic mean: 19565.900 mV
 Standard deviation: 1.66 mV
 Standard uncertainty: 0.526 mV
 Degrees of freedom: 9

Uncertainty budget:

Quantity	Value	Standard uncertainty	Degrees of freedom	Sensitivity coefficient	Uncertainty contribution	Corr.-coeff.	Index
po	101.3 kPa						
p	98.9500 kPa	0.0289 kPa	∞	-2.12	-0.0611 ppb	-0.10	0.011
T	302.350 °K	0.173 °K	∞	0.693	0.120 ppb	0.20	0.042
To	273.15 °K						
k	$14.4 \cdot 10^{-6}$ 1/m/kPa						
L	2.65500 m	$3.46 \cdot 10^{-3}$ m	∞	-78.9	-0.273 ppb	-0.47	0.218
I	19271.800 mV	0.467 mV	9	-0.718	-0.335 ppb	-0.57	0.327
Io	19565.900 mV	0.526 mV	9	0.707	0.372 ppb	0.63	0.403
Ozone	209.591 ppb	0.586 ppb	33				

Result:

Quantity: Ozone
 Value: 209.6 ppb
 Expanded uncertainty: ± 1.2 ppb
 Coverage factor: 2.1
 Coverage probability: 95.45%

3.2 Transfer standard TEI 49CPS

Model equation:

$$\text{Ozone} = -\frac{po}{p} \cdot \frac{T}{To} \cdot \frac{1}{k \cdot L} \cdot \text{LogRatioI-zero};$$

List of quantities:

Quantity	Unit	Definition
Ozone	ppb	Concentration of ozone
po	mbar	Pressure at standard conditions
p	mbar	Pressure during measurement
T	°K	Temperature in the measurement cell
To	°K	Temperature at standard conditions
k	1/m/kPa	Coefficient of absorption of ozone in the air at the wavelength of measurement

Quantity	Unit	Definition
L	m	Length of path beam
LogRatioI	None	$\log(I/I_0)$ measured by the equipment
zero	ppb	zero before measuring

Ozone:

Result

po:

Constant

Value: 1013 mbar

p:

Type B rectangular distribution

Value: 995 mbar

Half-width of distribution: 0.3 mbar

criteria for acceptance of pressure sensor of 49 PS: deviation between 49 PS and certified sensor smaller than U of sensor.

The "Value" inserted here is an approximation to the ambient pressure during the ozone measurements.

T:

Type B rectangular distribution

Value: 305 °K

Half-width of distribution: 0.6 °K

criteria for acceptance of temperature sensor of 49 PS: deviation between 49 PS and certified sensor smaller than U of sensor.

The "value" is an approximation to the temperature usually measured at the 49 PS bench during measurements.

To:

Constant

Value: 273.15 °K

k:

Constant

Value: 0.0001004 1/m/kPa

1.5 % value used for UMEG 0.0000144 corrected for path length 2.65 m for UMEG to 0.38 m for 49 PS

L:

Type B rectangular distribution

Value: 0.38 m

Half-width of distribution: 0.001 m

we estimated 1 mm

LogRatioI:

Type B rectangular distribution

Value: -0.0070476 None

Half-width of distribution: 0.00005 None

Uncertainty was chosen according to life cycle of 49PS (Performance tests) where reproducibility was identified as 0.5 % on 200 ppb

zero:

Type B rectangular distribution

Value: 0 ppb

Half-width of distribution: 0.4 ppb

life cycle of 49 PS (Performance test) LDL evaluation 0.4 ppb

The "value" defaults to "0" if the 49 PS is compared in a multipoint calibration to another Primary Standard

Uncertainty budget:

Quantity	Value	Standard uncertainty	Degrees of freedom	Sensitivity coefficient	Uncertainty contribution	Corr.-coeff.	Index
po	1013.0 mbar						
p	995.000 mbar	0.173 mbar	∞	-0.211	-0.0366 ppb	-0.04	0.001
T	305.000 °K	0.346 °K	∞	0.689	0.239 ppb	0.24	0.060
To	273.15 °K						
k	$100.4 \cdot 10^{-6}$ 1/m·kPa						
L	0.380000 m	$577 \cdot 10^{-6}$ m	∞	-553	-0.319 ppb	-0.33	0.107
LogRatioI	$-7.0476 \cdot 10^{-3}$ None	$28.9 \cdot 10^{-6}$ None	∞	-29800	-0.860 ppb	-0.88	0.776
zero	0.0 ppb	0.231 ppb	∞	-1.00	-0.231 ppb	-0.24	0.056
Ozone	209.995 ppb	0.976 ppb	∞				

Result:

Quantity: Ozone

Value: 210.0 ppb

Expanded uncertainty: ± 2.0 ppb

Coverage factor: 2.0

Coverage probability: 95.45%

4. FMI (TEI 49CPS)

The uncertainty associated with the TEI 49CPS ozone mole fraction measurement is modelled by the equation $u(x)=2.5 \times 10^{-6}x^2+2.45 \times 10^{-3}x+0.3714$. It comes from the following budget :

Uncertainty components	Source of uncertainty	standard uncertainty u
SRP24 uncertainty	Systematic uncertainty ¹	0.25 nmol/mol
	Transmittance ²	0.14% at 199.27 nmol/mol
	Pressure ²	0.03%
	Temperature ²	0.03%
	Path Length ²	0.01%
Performance characteristics of the TEI 49CPS	Zero repeatability	0.1 nmol/mol
	Span repeatability	0.18 nmol/mol
	Lower detection limit	0.3 nmol/mol
	Zero drift	0.1 nmol/mol
	Linearity	0.4 %
	Span drift	0.3 nmol/mol

5. INRIM (O3-SRP 2)

Uncertainty budget associated with the measurement results of the INRIM O3-SRP, without the temperature correction.

Component (y)	Uncertainty $u(y)$				Sensibility coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to $u(x)$ $ c_i \cdot u(y)$
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$		
Optical Path $2L$	Measurement Scale	Rect.	0.0011 cm	0.058 cm	$-\frac{x}{2L}$	$\frac{u(2L) \cdot x}{2L}$
	Repeatability	Normal	0.058 cm			
Pressure P	Pressure gauge certificate	Normal	0.020 kPa	0.028 kPa	$-\frac{x}{P}$	$\frac{u(P) \cdot x}{P}$
	Repeatability	Normal	0.010 kPa			
	Difference between cells	Rect	0.017 kPa			
Temperature T	Temperature probe certificate	Normal	0.01 K	0.011 K	$\frac{x}{T}$	$\frac{u(T) \cdot x}{T}$
	repeatability	Normal	0.005 K			
Ratio of intensities D	Scalers resolution	Rect.	8×10^{-6}	9.5×10^{-6}	$\frac{I}{2\sigma} \frac{T}{L} \frac{R}{P} \frac{N_A}{N_A}$	
	Repeatability	Normal	5.2×10^{-6}			
Uncertainty expression $u(x) = \sqrt{0.19^2 + (4.28 \cdot 10^{-4} x)^2}$						

¹ From EMPA-WCC Report 98/5 by P. Hofer, B. Buchmann, and A. Hertzog

² From BIPM report BIPM/03-03 by R.I. Wielgosz, J. Viallon, J. Novak and M. Vokun

Uncertainty budget associated with the measurement results of the INRIM O3-SRP, with the temperature correction :

Component (y)	Uncertainty $u(y)$				Sensibility coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to $u(x)$ $ c_i \cdot u(y)$
	Source	Distribution	Standard Uncertainty y	Combined standard uncertainty $u(y)$		
Optical Path $2L$	Measurement Scale	Rect.	0.0011 cm	0.058 cm	$-\frac{x}{2L}$	$\frac{u(2L) \cdot x}{2L}$
	Repeatability	Normal	0.058 cm			
Pressure P	Pressure gauge certificate	Normal	0.020 kPa	0.028 kPa	$-\frac{x}{P}$	$\frac{u(P) \cdot x}{P}$
	Repeatability	Normal	0.010 kPa			
	Difference between cells	Rect.	0.010 kPa			
Temperature T	Temperature probe certificate	Normal	0.01 K	1.00 K	$\frac{x}{T}$	$\frac{u(T) \cdot x}{T}$
	T meas. repeatability	Normal	0.005 K			
	T gradient along the gas in the cells after correction	Normal	1 K			
	reproducibility	Normal	0.			
Ratio of intensities D	Scalers resolution	Rect.	8×10^{-6}	9.5×10^{-6}	$\frac{1}{2\sigma L} \frac{T}{P} \frac{R}{N_A}$	
	Repeatability	Normal	5.2×10^{-6}			
Ozone losses	max value			0.6 nmol/mol	1	
Absorption Cross section α	Conventional value	-	-	-		-
Uncertainty expression $u(x) = \sqrt{0.63^2 + (3.47 \cdot 10^{-3} x)^2}$						

6. ISCIII

6.1 National standard SRP22

NATIONAL STANDARD UNCERTAINTY:		
Component (y):	Standard uncertainty	Expanded uncertainty
Optical path $2L$	$U_{OP} = 0,06 \% * C$	$U_{op} = k * U_{OP} (k = 2)$
Pressure P	$U_P = 0,1 \% * C$	$U_P = k * U_P (k = 2)$
Temperature T	$U_T = 0,04 \% * C$	$U_T = k * U_T (k = 2)$
Interferences	$U_I = 0,2 \text{ ppb}$	$U_I = k * U_I (k = 2)$
C = ozone concentration		

6.2 Transfert standard TEI 49C

TRANSFER STANDARD UNCERTAINTY			
Component (y):	Source	Standard uncertainty	Expanded uncertainty
Measured value	Scale division	$U_{MV} = \text{scale division} / 2 * \sqrt{3}$	$u_{MV} = k * U_{MV} \quad (k = 2)$
Repeatability	Standard deviation (s)	$U_{rep} = s / \sqrt{n}$ n = number of measurements	$u_{rep} = k * U_{rep} \quad (k = 2)$

7. KRISS (O3-SRP)

KRISS uncertainty budget is given at the end of this document.

8. LNE

8.1 National standard : SRP24

Standard uncertainty component $u(y)$	Source of uncertainty	Value of standard uncertainty $u(y)$	Sensibility coefficient $C_i = \left \frac{\partial x}{\partial y} \right $	Contribution to $u(x)$ $C_i \times u(y)$
$u(L)$	Optical Path	0.028 cm	$\frac{\partial x}{\partial L} = \frac{-10^9}{2 \times 308.32 \times L^2} \times \frac{P_0 \times T}{P \times T_0} \times \ln \frac{l_1 \times l_2}{l_3 \times l_4}$	$u(L) \times \frac{\partial x}{\partial L}$
$u(T)$	Temperature	0.15 K	$\frac{\partial x}{\partial T} = \frac{-10^9}{2 \times 308.32 \times L} \times \frac{P_0}{P \times T_0} \times \ln \frac{l_1 \times l_2}{l_3 \times l_4}$	$u(T) \times \frac{\partial x}{\partial T}$
$u(P)$	Pressure	0.15 hPa	$\frac{\partial x}{\partial P} = \frac{-10^9}{2 \times 308.32 \times L} \times \frac{P_0 \times T}{P^2 \times T_0} \times \ln \frac{l_1 \times l_2}{l_3 \times l_4}$	$u(P) \times \frac{\partial x}{\partial P}$
$u(I_1)$	Intensity	0.577	$\frac{\partial x}{\partial I_1} = \frac{-10^9}{2 \times 308.32 \times L} \times \frac{1}{I_1}$	$u(I_1) \times \frac{\partial x}{\partial I_1}$
$u(I_2)$	Intensity	0.577	$\frac{\partial x}{\partial I_2} = \frac{-10^9}{2 \times 308.32 \times L} \times \frac{1}{I_2}$	$u(I_2) \times \frac{\partial x}{\partial I_2}$
$u(I_3)$	Intensity	0.577	$\frac{\partial x}{\partial I_3} = \frac{-10^9}{2 \times 308.32 \times L} \times \frac{1}{I_3}$	$u(I_3) \times \frac{\partial x}{\partial I_3}$
$u(I_4)$	Intensity	0.577	$\frac{\partial x}{\partial I_4} = \frac{-10^9}{2 \times 308.32 \times L} \times \frac{1}{I_4}$	$u(I_4) \times \frac{\partial x}{\partial I_4}$

8.2 Transfert standard : TEI 49CPS

Source of uncertainty	standard uncertainty $u(y)$
Repeatability	Experimental standard deviation

9. METAS (SRP14 and SRP18)

Uncertainty evaluation for ozone calibration results in CCQM P28

Bernhard Niederhauser, METAS (CH)

Taking Lambert-Beer's law as a model and assuming gas behaviour to be ideal, the model equation for the amount of substance fraction of ozone in air is:

$$x_{O_3} = \frac{-1}{2 \cdot \alpha_x \cdot L} \cdot \frac{T_{mes} \cdot P_{std}}{T_{std} \cdot P_{mes}} \cdot \ln(D) \quad (1)$$

where

- x_{O_3} is the amount of substance fraction of ozone in air
- α_x is the linear absorption coefficient of ozone at 253.7 nm at standard conditions of temperature and pressure. The value used is: 308.32 cm^{-1} .
- L is the optical path length of one of the cells,
- T_{mes} is the temperature measured in the cells,
- T_{std} is the standard temperature (273.15 K),
- P_{mes} is the pressure measured in the cells,
- P_{std} is the standard pressure (101.325 kPa),
- D is the product of transmittances of two cells, with the transmittance (T_A, T_B) of cell A, B defined as

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

where

- I_{ozone} is the UV radiation intensity measured in the cell when containing ozonized air, and
- I_{air} is the UV radiation intensity measured in the cell when containing pure air.

Two examples of uncertainty budgets at molar fractions of 80 nmol/mol and 420 nmol/mol are shown in the following tables:

Quantity	Value	Standard Uncertainty rel. or abs.	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
L	89.2600 cm	0.065 %	∞	rectangular	$-900 \cdot 10^{-12}$	$-52 \cdot 10^{-12} \text{ mol/mol}$	3.4 %
p_{mes}	95.0000 kPa	0.030 %	∞	rectangular	$-840 \cdot 10^{-12}$	$-24 \cdot 10^{-12} \text{ mol/mol}$	0.8 %
T_{mes}	293.000 K	0.25 K	50	normal	$270 \cdot 10^{-12}$	$68 \cdot 10^{-12} \text{ mol/mol}$	6.0 %
T_{A1}	0.998080	0.000009	9	normal	$-21 \cdot 10^{-6}$	$-190 \cdot 10^{-12} \text{ mol/mol}$	44.9 %
T_{B1}	0.998070	0.000009	9	normal	$-21 \cdot 10^{-6}$	$-190 \cdot 10^{-12} \text{ mol/mol}$	44.9 %
α_x	308.32 cm^{-1}						
p_{std}	101.325 kPa						
T_{std}	273.15 K						
D_I	0.9961537	0.0000127	18				
$x_{O_3 I}$	$80 \cdot 10^{-9} \text{ mol/mol}$	$0.280 \cdot 10^{-9} \text{ mol/mol}$	22				

Quantity	Value	Expanded Uncertainty	Rel. Expanded Uncertainty	Coverage factor	Coverage
$x_{O_3 \text{ 1}}$	$80.10 \cdot 10^{-9} \text{ mol/mol}$	$0.60 \cdot 10^{-9} \text{ mol/mol}$	0.74 %	2.1	95% (t-table 95.45%)

Quantity	Value	Standard Uncertainty rel. or abs.	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
L	89.2600 cm	0.065 %	∞	rectangular	$-4.7 \cdot 10^{-9}$	$-270 \cdot 10^{-12} \text{ mol/mol}$	25.5 %
P_{mes}	95.0000 kPa	0.030 %	∞	rectangular	$-4.4 \cdot 10^{-9}$	$-130 \cdot 10^{-12} \text{ mol/mol}$	5.6 %
T_{mes}	293.000 K	0.25 K	50	normal	$1.4 \cdot 10^{-9}$	$360 \cdot 10^{-12} \text{ mol/mol}$	44.3 %
T_{A2}	0.989950	0.000009	9	normal	$-21 \cdot 10^{-6}$	$-190 \cdot 10^{-12} \text{ mol/mol}$	12.3 %
T_{B2}	0.989950	0.000009	9	normal	$-21 \cdot 10^{-6}$	$-190 \cdot 10^{-12} \text{ mol/mol}$	12.3 %
α_x	308.32 cm^{-1}						
P_{std}	101.325 kPa						
T_{std}	273.15 K						
D_2	0.9800010	0.0000126	18				
$x_{O_3 \text{ 2}}$	$419.912 \cdot 10^{-9} \text{ mol/mol}$	$0.538 \cdot 10^{-9} \text{ mol/mol}$	140				

Quantity	Value	Expanded Uncertainty	Rel. Expanded Uncertainty	Coverage factor	Coverage
$x_{O_3 \text{ 2}}$	$419.9 \cdot 10^{-9} \text{ mol/mol}$	$1.1 \cdot 10^{-9} \text{ mol/mol}$	0.26 %	2.0	95% (t-table 95.45%)

Expanded Uncertainties of amount of substance fraction values measured by SRP 14 or 18 with α_x as a conventional value can be expressed over the whole range (0...500) nmol/mol by:

$$U(x_{O_3}) = \sqrt{\left(0.6 \frac{\text{nmol}}{\text{mol}}\right)^2 + (2.2 \cdot 10^{-3} \cdot x_{O_3})^2} \quad (3)$$

10. NDENW

10.1 National standard : UMEG

The table below summarises the uncertainty components.

Component (y)	Value	standard uncertainty $u(y)$
Optical Path L	265.5 cm	0.35 cm
Temperature T		0.29 K
Pressure P		0.29 kPa
Optical ratio Y		s_Y

10.2 Transfert standard : TEI 49C

Source of uncertainty	standard uncertainty $u(y)$
Instrument parameters accuracy	1 nmol/mol
Linearity	1 %
Detection limit	1 nmol/mol
Uncertainty expression	maximum between 1 nmol/mol and $0.015x$

11. NERI

11.1 National standard : UMEG

Component (y)	Value	Source of uncertainty	standard uncertainty $u(y)$
Optical Path L	265.5 cm		0.05 cm
Temperature T	300 K		2 K
Pressure P	100 kPa		0.4 kPa
Optical ratio	1.0373 (at 500 nmol/mol)	Detector noise	6.67×10^{-5}
Uncertainty expression	$u(x) = \sqrt{0.9^2 + 6.4 \cdot 10^{-5} x^2}$		

11.2 Transfert standard : API M401

Component (y)	Value	Source of uncertainty	standard uncertainty $u(y)$
Optical Path L	42.1 cm		0.2 cm
Temperature T	309 K		2 K
Pressure P	100 kPa		0.4 kPa
Optical ratio		Detector noise	1.25×10^{-5}
Uncertainty expression			$u(x) = \sqrt{1.11^2 + 8.05 \cdot 10^{-5} x^2}$

12. NILU (API 400E)

Uncertainty budget of NILUs API M400E ozone monitor for the CCQM P28 pilot study

Source of uncertainty	Uncertainty contribution ($nmol\ mol^{-1}$)	Comment
Intensity fluctuations	0.25	Experimental standard deviation in the worth case.
Pressure	$0.00013x$	Used value from paper ³ since instrument supplier have not given any information on pressure
Temperature	$0.0023x$	Used value from paper ³ adjusted to our cell length.
Cell length	$0.00476x$	
Combined uncertainty	$u(x) = \sqrt{(0.25)^2 + (5.28 \cdot 10^{-3} x)^2}$	

³ "A comprehensive analysis of the uncertainty of a commercial ozone photometer" written by M. Zucco, S. Curci, G. Castorfino and M.P. Sassi, JGR, 108, D19, 4622, 2003

13. NMi-VSL (UMEG 26)

The equation used for assessing the measured ozone concentration in ppb (nmol/mol) is ⁴:

$$C = \frac{10^5}{\alpha L} \left(\frac{P_{ref}}{P_M} \right) \left(\frac{T_M}{T_{ref}} \right) \log \left(\frac{I_0}{I_t} \right)$$

C	Ozone concentration (ppb)
α	Absorption cross section
L	Optical path length
P	Pressure (M = measured, ref = standard pressure 101,325 kPa)
T	Temperature (M = measured, ref = standard temperature 293,15 K)
I	Intensity of signal (0 = zero air; t = ozone air mixture)

13.1 Analyses of the uncertainty in the calibration of the UMEG photometer

1.1) Temperature

The UMEG photometer has a built-in sensor. This is checked annually against a calibrated thermistor with a readability of 0,01 K. The probability distribution of the readings is rectangular resulting in a standard uncertainty of 0,0058 K. The thermistors are calibrated every two years. The total or expanded uncertainty given in the calibration certificate is $\leq 0,01$ K. This implies a standard uncertainty of 0,005 K. The differences in reading between the calibrated thermistor and the UMEG temperature sensor in the measuring cell are between 0 and 0,2 K, with an approximately triangular distribution; this results in a standard uncertainty of 0,082 K. The combined standard uncertainty in the readings of the temperature of the UMEG primary UV photometer is:

$$u_T = \sqrt{(0,0058)^2 + (0,005)^2 + (0,082)^2} = 0,082 \text{ K} \quad (1)$$

1.2) Optical path length

The UMEG measuring cell consists of two glass tubes with an inner diameter of 8,5 mm and a length of 130 cm. These tubes are connected via deviating mirrors so that an optical path length (L) of 265,5 cm is obtained. The standard uncertainty for the optical path length is 0,5 cm.

$$u_L = 0,005 \text{ m} \quad (2)$$

1.3) Pressure

The pressure indicator located on the UMEG primary photometer is checked for consistency every year against a calibrated pressure indicator. The pressure indicator in the lab is calibrated once every year. The total or expanded uncertainty given in the calibration certificate is $\leq 0,1$ hPa, giving a standard uncertainty of 0,05 hPa. The pressure indicator on the photometer has a scale division of 0,1 hPa and a readability of 0,1 hPa. The probability distribution of the readings is rectangular with a standard deviation of 0,058 hPa. The differences in the readings of the calibrated barometer and the pressure sensor in the

⁴ UMEG UV Photometer instruction manual

measuring cell are always between 0 and 3 hPa, with an approximately triangular distribution; this results in a standard uncertainty of 1,22 hPa. The combined uncertainty in the readings of the reference barometer is:

$$u_p = \sqrt{(0.06 \text{ hPa})^2 + (0.05 \text{ hPa})^2 + (1.22 \text{ hPa})^2} = 1.22 \text{ hPa} \quad (3)$$

1.4) Ozone losses

Ozone can be lost in the photometer because of reaction with the cell walls and gas handling components. In the publication of Zucco et al.⁵ the losses are quantified with a photometer of different type over the range 0 to 450 ppb ozone. The standard uncertainty given in this article for Ozone loss is 0,16 ppb. Assuming the UMEG photometer to behave similarly – for lack of alternative information – the figure of 0,16 ppb is used (type B uncertainty).

1.5) Reading uncertainty

The extinction term in the Lambert-Beer (1) equation expressing the ozone concentration is calculated as

$$E = -\ln\left(\frac{I_t}{I_0}\right) \quad (4)$$

or, alternatively as

$$E = \ln(I_0) - \ln(I_t) \quad (5)$$

The intensities I_t and I_0 are determined experimentally by taking alternate readings of I_t and I_0 until 10 readings of each parameter have been obtained.

Of these 10 readings the mean and the standard deviation of the mean are calculated, assuming the readings to be approximately normally distributed. The standard deviation of the mean incorporates the reading uncertainty (the intensities are readable to 5 digits).

In practice, the standard deviation of the mean of I_0 is approximately $\pm 0,15$ units; the standard deviation of I_t is slightly higher, but this may be attributed to variations in the concentration of the ozone calibration gas mixtures sampled by the photometer.

We may therefore safely assume that for all mean readings the standard deviation s is $\pm 0,15$ units.

The uncertainty in equation (6) is given by

$$u^2(E) = u^2[\ln(I_t)] + u^2[\ln(I_0)] \quad (6)$$

As the uncertainties in the logarithms cannot be expressed directly as standard uncertainties, an alternative approach is applied in which the extremes of E are calculated. The uncertainty in E is subsequently obtained by assuming E to follow – approximately - a triangular distribution.

⁵

$$E_{\max} = \ln(I_{0,\max}) - \ln(I_{t,\min}) \Rightarrow E_{\min} = \ln(I_{0,\min}) - \ln(I_{t,\max}) \quad (7)$$

$$I_{\max} = I + k \cdot s; I_{\min} = I - k \cdot s \quad (8)$$

$$u^2(E) = \frac{E_{\max} - E_{\min}}{(2\sqrt{6})^2} \quad (9)$$

k is the coverage factor for a 99% confidence interval; in this case (10 readings) $k=3,25$.

Application of eq. (10) leads to the relationship between the reading uncertainty and the ozone concentration represented in Figure 1. Here, an I_0 of 19960 is assumed.

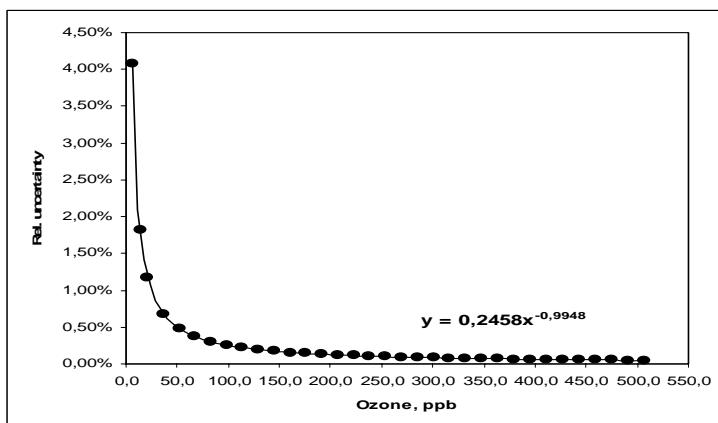


Figure 1: Relative reading uncertainty as a function of concentration

13.2 Combined uncertainty

Component	Unit	Value	Distribution	Standard uncertainty	Sensitivity coefficient	Contribution
Optical path length L	m	2,655	normal	0,005	-x/L	0,0019x
Pressure P	kPa	101,325	triangular	0,122	-x/P	0,0012x
Temperature T	K	299	triangular	0,082	x/T	0,0003x
Cross section α	atm ⁻¹ .m ⁻¹	1,34	normal	0,010	x/ α	not relevant here
Extinction E	-			0,246x ^{0,0052}	1	0,246x ^{0,0052}
Ozone losses	ppb	0,16	normal	0,16	1	0,16

$$u_c^2(x) = (0,16)^2 + (0,246)^2 \cdot x^{0,01} + (0,0023x)^2 \cong (0,30)^2 + (0,0023x)^2$$

Without the contribution for ozone losses, the combined uncertainty is

$$u_c^2(x) = (0,25)^2 + (0,0023x)^2$$

14. NPL (SRP20)

Analysis of Uncertainties in Ozone Calibrations for CCQM P-28

Bryan Sweeney, Paul Quincey, Martin Milton, Peter Woods NPL, UK

Assuming the Beer-Lambert law, the measurement equation is:

$$x = -\frac{1}{\alpha L} \frac{kT}{P} \ln\left(\frac{I}{I_0}\right)$$

Where x is the ozone amount fraction, ozone in air (mol/mol)
 α is the absorption cross-section for an ozone molecule at 253.7 nm (m^2 – see below)
 L is the path length (~ 0.9 m)
 k is Boltzmann's constant ($1.381 \times 10^{-23} \text{ J.K}^{-1}$)
 T is the cell gas temperature (~300 K)
 P is the cell gas pressure (~ 10^5 Pa)
 I is the light intensity (253.7 nm) with ozone in the cell (arb. units)
 I_0 is the light intensity with no ozone in the cell (as for I)
 I/I_0 lies in the range 0.99 to 1

α is an input parameter that was standardised for all photometers involved in the comparison at $1.1476 \times 10^{-21} \text{ m}^2$. For these purposes its uncertainty is set to zero.

By defining the “constant” terms as B , we have

$$x = -B \ln\left(\frac{I}{I_0}\right), \text{ where } B \sim 4.8 \times 10^{-5}$$

Factors affecting the result are itemised as follows:

Term	Factors affecting uncertainty	Means of evaluating	component
L	Measurement uncertainty Environmental factors (thermal expansion)	Estimate Estimate	$u(L)$ negligible
T	Measurement uncertainty, including temperature gradients Drift	Estimate From repeat measurements	$u(T)$ included in $u(\text{rep})$
P	Measurement uncertainty, including pressure gradients Drift	Estimate From repeat measurements	$u(P)$ included in $u(\text{rep})$
I/I_0	Measurement uncertainty, including source and detectors repeatability and drift Instrument resolution Environmental factors (effect of temperature on source and detectors) Detector non-proportionality	From repeat measurements Estimate Estimate Estimate	$u(\text{rep})$ negligible $u(E)$ $u(\text{NP})$

Quantification of some individual terms

Repeatability, u(rep)

Analysis of 10 repeat measurements at all concentrations gives a standard deviation, independent of concentration, of about 0.3 nmol/mol.

The standard deviation of the mean of these 10 repeat measurements, u(rep), is taken to be 0.1 nmol/mol.

Environmental effects on source and detectors, u(E)

In the absence of independent data, the systematic effects of ambient temperature and pressure are taken to be similar to the random effects evaluated as u(rep), ie u(E) has a value of 0.1 nmol/mol with a Gaussian distribution.

Detector non-proportionality, u(NP)

The measurement equation assumes that the ratio of the two measured intensities is equal to the true ratio. This assumes that the output of the detector is proportional to the input. Errors due to non-proportionality are generally small providing the two measurement points are close together (as is the case here).

From the manufacturers specification for non-linearity of the converter, errors in the ratio I/I_0 are expected to be $4 \times 10^{-4} x/B$, with a rectangular distribution.

Uncertainty calculation

Term	size	distribution	Standard u/c	Sensitivity coeff	Contribution to uncertainty
u(L)	2×10^{-4} m	Rect	1.2×10^{-4} m	$-x/L$	$1.3 \times 10^{-4} x$
u(T)	0.3 K	rect	0.17 K	x/T	$5.7 \times 10^{-4} x$
u(P)	100 Pa	rect	58 Pa	x/P	$5.8 \times 10^{-4} x$
u(E)	0.1 nmol/mol	gaussian	0.1 nmol/mol	1	0.1 nmol/mol
u(rep)	0.1 nmol/mol	gaussian	0.1 nmol/mol	1	0.1 nmol/mol
u(NP)	$4 \times 10^{-4} x/B$ [I/I_0]	rect	$2.3 \times 10^{-4} x/B$ [I/I_0]	$\sim B$	$2.3 \times 10^{-4} x$

Combined 1 σ uncertainty:

$$0.086 \% + 0.14 \text{ nmol/mol} \text{ (to be added in quadrature)}$$

$$\text{ie } u(x) = \sqrt{(0.14)^2 + 7.4 \cdot 10^{-7} x^2} \text{ nmol/mol}$$

15. SP (Environment SA 42M)

15.1 Method proposed by SP

- calibration of SP-42M with SRP11 : the relationship is calculated with excel. The result is

$$x_{42M} = 0.9818 x_{SRP11}$$

- Deduction of the bias of SP-42M : $Bias = x_{42M} (1 - 0.9818)$

- Calculation of SP-42M corrected values in Stockholm : $x'_{42M} = \frac{x_{42M}}{0.9818}$

- Calculation of the residual bias : $res = x'_{42M} - x_{SRP11}$

- Fit of SP-42M uncertainty to evaluate the bias uncertainty, the SP-42M uncertainty associated with each measurement result being the standard deviation of the mean : $u(bias) = 0.22e^{0.0029x_{42M}}$

- Application to the comparison at the BIPM : $bias = -x_{42M} (1 - 0.9818)$ and corrected value $x'_{42M} = x_{42M} - bias$

- Calculation of the associated uncertainty, the variance expression being :

$$u^2(x'_{42M}) = (0.22e^{0.0029x_{42M}})^2 + u^2(x_{SRP27}) + \frac{s^2}{10},$$

where s is the experimental standard deviation of SP-42M measurements.

- A linear regression is then performed, as for other comparisons, with the B_Least software.

The table below shows the calculations performed on the comparison at BIPM.

Paris			Stockholm				Paris - corrected values		
Measured	s	$u(meas.)$	Bias	$u(ref)$	$u(bias\ meas)$	$u(bias)$	Corr value	$u(corr)$	U
ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
0.18	0.3	0.09	0.00	0.28	0.22	0.36	0.18	0.37	0.7
219.58	0.5	0.15	-4.00	0.30	0.42	0.51	223.58	0.53	1.1
80.09	0.6	0.19	-1.46	0.28	0.28	0.40	81.55	0.44	0.9
408.76	0.4	0.12	-7.44	0.34	0.72	0.79	416.20	0.80	1.6
117.26	0.3	0.11	-2.13	0.29	0.31	0.42	119.39	0.43	0.9
309.57	0.3	0.10	-5.63	0.31	0.54	0.62	315.20	0.63	1.3
26.16	0.4	0.13	-0.48	0.28	0.24	0.37	26.64	0.39	0.8
354.28	0.3	0.10	-6.45	0.32	0.61	0.69	360.73	0.70	1.4
164.20	0.4	0.12	-2.99	0.29	0.35	0.46	167.19	0.47	0.9
487.08	0.6	0.20	-8.86	0.36	0.90	0.97	495.94	0.99	2.0
265.22	0.5	0.15	-4.83	0.31	0.47	0.56	270.05	0.58	1.2
0.12	0.3	0.09	0.00	0.28	0.22	0.36	0.12	0.37	0.7

15.2 Method proposed by BIPM : Calculation of SRP27 and SP-42M comparison results with B Least (ISO 6143:2001), SP-42M being calibrated by SRP11

2.1) First Step: calibration of SP-42M with SRP11

The data set is :

x=SRP11	u(x)	y=SP-42M	u(y)
0.17	0.28	0.27	0.13
215.28	0.30	211.56	0.33
78.8	0.28	77.54	0.36
427.45	0.34	418.26	0.62
125.93	0.29	118.16	0.10
326.43	0.32	320.12	0.45
19.52	0.28	18.23	0.39
370.52	0.33	364.36	1.12
149.93	0.29	144.78	2.15
506.97	0.36	501.7	0.85
0.08	0.28	0.15	0.09
273.48	0.31	266.86	0.80

B_Least is used to perform SP-42M calibration (fit x vs y) :

```
Results of ISO 6143 method:
b0          b1          u (b0)        u (b1)      cov:
1.0923E+00  1.0187E+00  1.7354E-01  1.0418E-03 -1.1365E-04

Remaining SSD is:      294.1437
Weighted distances:
#           x-value    x-dist.    y-dist.
1.00E+00   8.00E-02  -3.76E+00  1.23E+00
2.00E+00   1.70E-01  -3.49E+00  1.65E+00
3.00E+00   1.95E+01  -1.70E-01  2.41E-01
4.00E+00   7.88E+01  -1.69E+00  2.21E+00
5.00E+00   1.26E+02  1.37E+01  -4.82E+00
6.00E+00   1.50E+02  8.00E-02  -6.05E-01
7.00E+00   2.15E+02  -1.97E+00  2.21E+00
8.00E+00   2.73E+02  2.17E-01  -5.70E-01
9.00E+00   3.26E+02  -7.94E-01  1.14E+00
1.00E+01   3.71E+02  -4.10E-01  1.42E+00
1.10E+01   4.27E+02  1.77E-01  -3.28E-01
1.20E+01   5.07E+02  -2.13E+00  5.13E+00
Goodness-of-fit measure: 13.7071
```

The fit is not acceptable : remaining SSD > 10 (number of points – number of parameters) and goodness-of-fit>2.

The regression parameters are recalculated after removal of point n°5, which is an clear outlier : $x\text{-dist} > 2u(x_{mes})$ and $y\text{-dist} > 2u(y_{mes})$.

```

Results of ISO 6143 method:
b0           b1           u  (b0)        u  (b1)        cov:
1.1232E-01   1.0179E+00   1.8399E-01   1.0364E-03  -1.1017E-04

Remaining SSD is:          31.9850
Weighted distances:
#      x-value      x-dist.      y-dist.
1.00E+00  8.00E-02  -5.97E-01  1.95E-01
2.00E+00  1.70E-01  -6.34E-01  3.00E-01
3.00E+00  1.95E+01   1.01E+00  -1.43E+00
4.00E+00  7.88E+01  -3.14E-01  4.11E-01
5.00E+00  1.50E+02   1.46E-01  -1.10E+00
6.00E+00  2.15E+02  -2.57E-01  2.88E-01
7.00E+00  2.73E+02   7.10E-01  -1.86E+00
8.00E+00  3.26E+02   4.88E-01  -6.98E-01
9.00E+00  3.71E+02  -1.09E-01  3.76E-01
1.00E+01  4.27E+02   1.06E+00  -1.97E+00
1.10E+01  5.07E+02  -1.56E+00  3.75E+00
Goodness-of-fit measure:  3.7536

```

The fit is better, but still not acceptable. As there is no other clear outliers, the stated uncertainties for SP-42M have been enlarged so that, $u(y)$ = measured standard deviation (and not the standard deviation of the mean). Indeed, the standard deviation of the mean is believed to be an inappropriate estimate of the uncertainty of the measurement results since successive ozone measurements are serially correlated.

```

Results of ISO 6143 method:
b0           b1           u  (b0)        u  (b1)        cov:
4.2457E-03   1.0183E+00   2.4824E-01   1.8739E-03  -2.0736E-04

Remaining SSD is:          7.6501
Weighted distances:
#      x-value      x-dist.      y-dist.
1.00E+00  8.00E-02  -1.80E-01  1.31E-01
2.00E+00  1.70E-01  -1.78E-01  1.94E-01
3.00E+00  1.95E+01   3.09E-01  -9.77E-01
4.00E+00  7.88E+01  -6.04E-02  1.78E-01
5.00E+00  1.50E+02   3.02E-02  -5.09E-01
6.00E+00  2.15E+02  -7.15E-02  1.80E-01
7.00E+00  2.73E+02   1.55E-01  -9.18E-01
8.00E+00  3.26E+02   1.25E-01  -3.99E-01
9.00E+00  3.71E+02  -2.57E-02  1.98E-01
1.00E+01  4.27E+02   2.45E-01  -1.02E+00
1.10E+01  5.07E+02  -3.64E-01  1.96E+00
Goodness-of-fit measure:  1.9571

```

The fit is now acceptable. Furthermore, the intercept is $b_0 = 0.004$, which is more consistent with the experimental results at 0 nmol/mol.

As another measurement around 100 nmol/mol was recorded by SP before conducting the comparison it has been added to the data set, and the data set reanalysed. The resulting regression parameters are:

x=SRP11	u(x)	y=SP-42M	u(y)
117.2	0.28	113.8	0.67

2.2) Results of B_Least :

```

Results of ISO 6143 method:
b0          b1          u (b0)        u (b1)        cov:
8.6378E-02  1.0187E+00  2.4350E-01  1.8590E-03  -2.1997E-04

Remaining SSD is:      10.5021
Weighted distances:
#      x-value      x-dist.      y-dist.
1.00E+00  8.00E-02  -3.72E-01  2.70E-01
2.00E+00  1.70E-01  -3.12E-01  3.41E-01
3.00E+00  1.95E+01  2.79E-01  -8.84E-01
4.00E+00  7.88E+01  -1.03E-01  3.03E-01
5.00E+00  1.17E+02  6.08E-01  -1.48E+00
6.00E+00  1.50E+02  2.84E-02  -4.79E-01
7.00E+00  2.15E+02  -1.50E-01  3.77E-01
8.00E+00  2.73E+02  1.38E-01  -8.14E-01
9.00E+00  3.26E+02  6.39E-02  -2.03E-01
1.00E+01  3.71E+02  -3.76E-02  2.90E-01
1.10E+01  4.27E+02  2.03E-01  -8.48E-01
1.20E+01  5.07E+02  -3.91E-01  2.10E+00
Goodness-of-fit measure:  2.1041

```

The fit parameters are not as good as without this added measurement point. Furthermore, as this point was taken in the preliminary testing period, it is not appropriate to add it to the dataset.

2.3) Second step : calculation of SP-42M corrected values

B_Least can be used to calculate corrected values fore SP-42M in the comparison with SRP27. We use the values of the run n°1, with the standard deviation of measurements used as an estimate of the uncertainty for consistency.

Data set :

x_{SRP27} nmol/mol	$u(x_{SRP27})$ nmol/mol	x_{SP} nmol/mol	$u(x_{SP})$ nmol/mol
-0.08	0.28	0.18	0.3
224.36	0.30	219.58	0.5
81.95	0.28	80.09	0.6
417.17	0.34	408.76	0.4
119.98	0.29	117.26	0.3
315.85	0.32	309.57	0.3
26.68	0.28	26.16	0.4
361.64	0.33	354.28	0.3
167.48	0.29	164.20	0.4
496.60	0.36	487.08	0.6
270.36	0.31	265.22	0.5
-0.09	0.28	0.12	0.3

From SP-42M measured values ("response"), B_Least calculates the following corrected values ("calc.") :

calc. x	$u(x)$	response y	$u(y)$
1.8754E-01	3.9354E-01	1.8000E-01	3.0000E-01
2.2360E+02	6.3174E-01	2.1958E+02	5.0000E-01
8.1560E+01	6.5133E-01	8.0090E+01	6.0000E-01
4.1625E+02	8.0294E-01	4.0876E+02	4.0000E-01
1.1941E+02	3.9319E-01	1.1726E+02	3.0000E-01
3.1524E+02	6.0255E-01	3.0957E+02	3.0000E-01
2.6643E+01	4.6807E-01	2.6160E+01	4.0000E-01
3.6077E+02	6.6989E-01	3.5428E+02	3.0000E-01
1.6721E+02	5.0409E-01	1.6420E+02	4.0000E-01
4.9600E+02	1.0325E+00	4.8708E+02	6.0000E-01
2.7008E+02	6.7666E-01	2.6522E+02	5.0000E-01
1.2644E-01	3.9357E-01	1.2000E-01	3.0000E-01

Final step : fit of SRP27 vs. SP-42M-corrected values

B_Least is used to perform a fit (y vs x) on the values of SRP27 (x) and the corrected values of SP-42M (y):

New data set :

x_{SRP27} nmol/mol	$u(x_{SRP27})$ nmol/mol	x_{SP} nmol/mol	$u(x_{SP})$ nmol/mol
-0.08	0.28	0.19	0.39
224.36	0.30	223.60	0.63
81.95	0.28	81.56	0.65
417.17	0.34	416.25	0.80
119.98	0.29	119.41	0.39
315.85	0.32	315.24	0.60
26.68	0.28	26.64	0.47
361.64	0.33	360.77	0.67
167.48	0.29	167.21	0.50
496.60	0.36	496.00	1.03
270.36	0.31	270.08	0.68
-0.09	0.28	0.13	0.39

```

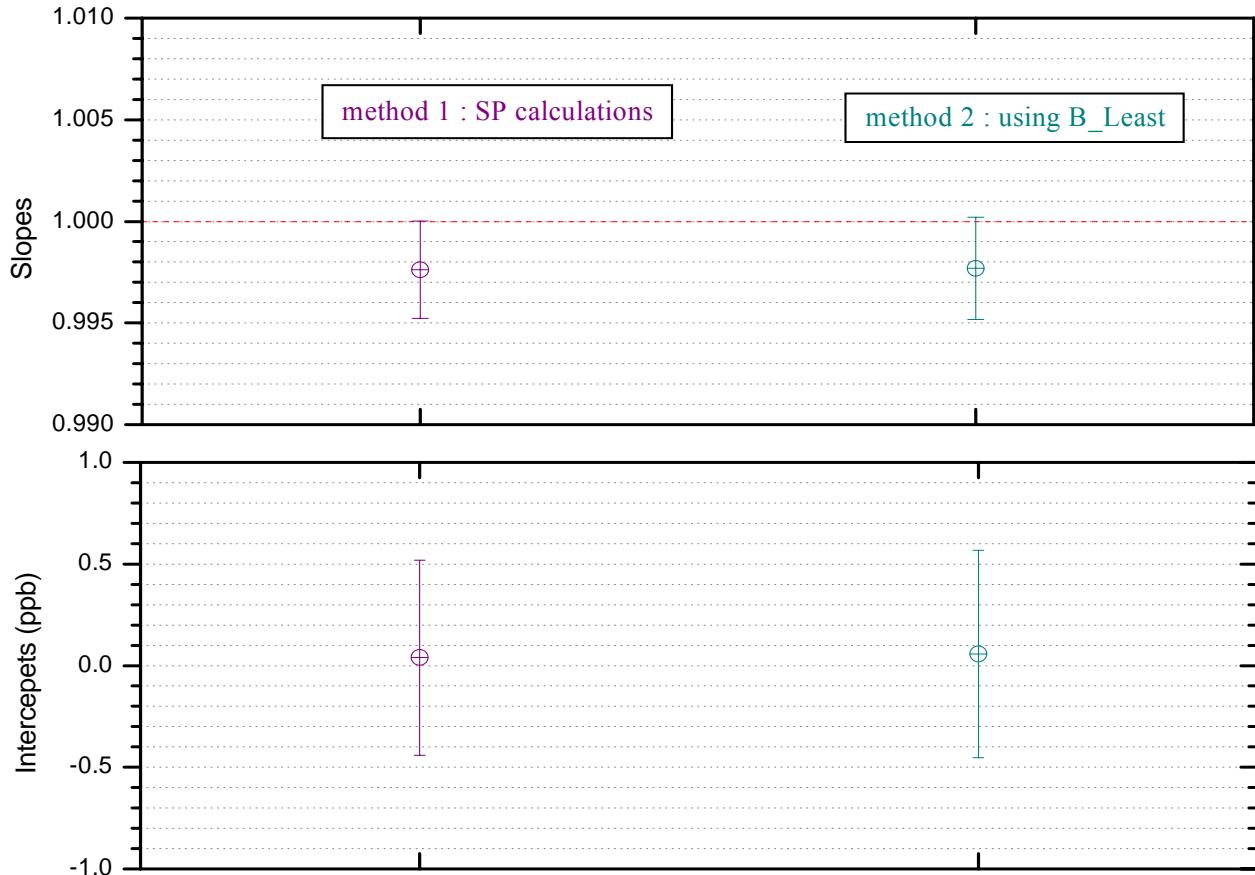
Results of ISO 6143 method:
a0           a1           u (a0)        u (a1)        cov:
5.6991E-02   9.9768E-01   2.5493E-01   1.2578E-03  -2.2842E-04

Remaining SSD is:          1.5357
Weighted distances:
#      x-value    x-dist.    y-dist.
1.00E+00 -9.00E-02 -1.98E-01  2.76E-01
2.00E+00 -8.00E-02 -2.58E-01  3.61E-01
3.00E+00  2.67E+01  3.28E-02  -5.52E-02
4.00E+00  8.20E+01  1.43E-01  -3.34E-01
5.00E+00  1.20E+02  4.28E-01  -5.77E-01
6.00E+00  1.67E+02  -5.32E-02  9.19E-02
7.00E+00  2.24E+02  1.83E-01  -3.84E-01
8.00E+00  2.70E+02  -1.61E-01  3.53E-01
9.00E+00  3.16E+02  -4.51E-02  8.48E-02
1.00E+01  3.62E+02  5.23E-02  -1.06E-01
1.10E+01  4.17E+02  4.40E-03  -1.04E-02
1.20E+01  4.97E+02  -1.49E-01  4.28E-01
Goodness-of-fit measure:  0.5769

```

The fit is acceptable.

The following graph shows the fit parameters calculated with the data obtained here, in comparison with the data treatment used by the SP.



16. VNIIM (Dasibi 1003AH)

Component	Uncertainty			Coefficient of sensitivity	Contribution
	Source	Distribution	Standard uncertainty		
Calibration	Uncertainty of calibration	Rectangular	0,006	x	0,006· x ppb
Measurement	Repeatability	Normal	0,9 ppb	1	0,9 ppb

17. WCC-EMPA (SRP15)

The complete WCC-EMPA uncertainty budget is reproduced here. The table below summarises the uncertainty components.

Parameter	Reason for the uncertainty	Type	Determination of the uncertainty	Standard uncertainty u	Contribution to the uncertainty
I, I_0	Resolution of the detector incl. the electronics and the display	A	Comparison with two instruments of identical construction under repeatability conditions		0.25 nmol/mol
L	Uncertainty of the measurement of the length	B	Statement of the producer	0.82 mm	$5 \times 10^{-4}x$
T_a	Uncertainty of the adjustment	B	Determination of the maximum deviation	0.5 K	$2 \times 10^{-3}x$
p_a	Uncertainty of the adjustment	B	Determination of the maximum deviation	0.1 kPa	$10^{-3}x$
U_G	Non-ideal realisation of the comparison	B	Several comparisons over several years	0.20 nmol/mol	0.20 nmol/mol
Uncertainty expression		$u(x) = \sqrt{0.32^2 + (2.3 \cdot 10^{-3} x)^2}$			

17.1 The Standard Reference Photometer (SRP)

The primary ozone standard used by the EMPA is a UV-photometer designed and distributed by the U.S. National Institute of Standards and Technology (NIST), a so called Standard Reference Photometer (SRP). This instrument is regularly compared with an identical instrument of the NIST. The goal of such an comparison is not a calibration of our instrument but a check of conformity. If the measured deviations between two SRPs are larger than the

maximum deviations calculated in section 3.6 (see Fig. 5) the reason for these deviations must be found and eliminated.

17.2 The Physical Model of the Measurement Process

$$\ln \frac{I}{I_0} = -c \cdot L \cdot \alpha \cdot \frac{p_a \cdot T_n}{T_a \cdot p_n} \quad \text{resp.}$$

$$c = \ln \frac{I_0}{I} \cdot \frac{1}{\alpha \cdot L} \cdot \frac{T_a \cdot p_n}{p_a \cdot T_n} \quad (3 \text{ a,b})$$

c concentration of ozone

I, I_0 measured light intensity with presence and absence of ozone

α absorption coefficient

L length of the measurement cell

T_a, p_a measured temperature and measured pressure

T_n, p_n pressure and temperature at standard conditions (1013 mbar, 273.16 K)

2.1) The different components of the uncertainty

Parameter	Reason for the uncertainty	Type	Determination of the uncertainty
I, I_0	Resolution of the detector incl. the electronics and the display	A	Comparison with two instruments of identical construction under repeatability conditions
α	Uncertainty of the determination	B	Literature
L	Uncertainty of the measurement of the length	B	Statement of the producer
T_a	Uncertainty of the adjustment	B	Determination of the maximum deviation
p_a	Uncertainty of the adjustment	B	Determination of the maximum deviation
U_G	Non-ideal realisation of the comparison	B	Several comparisons over several years

2.2) Uncertainty u_A

The determination of the uncertainty of type A is done by an comparison with another SRP and a linear regression analysis of the results. Because the parameters α, L, p_a, T_a are constant during the measurement the result characterises the term $\ln(I/I_0)$.

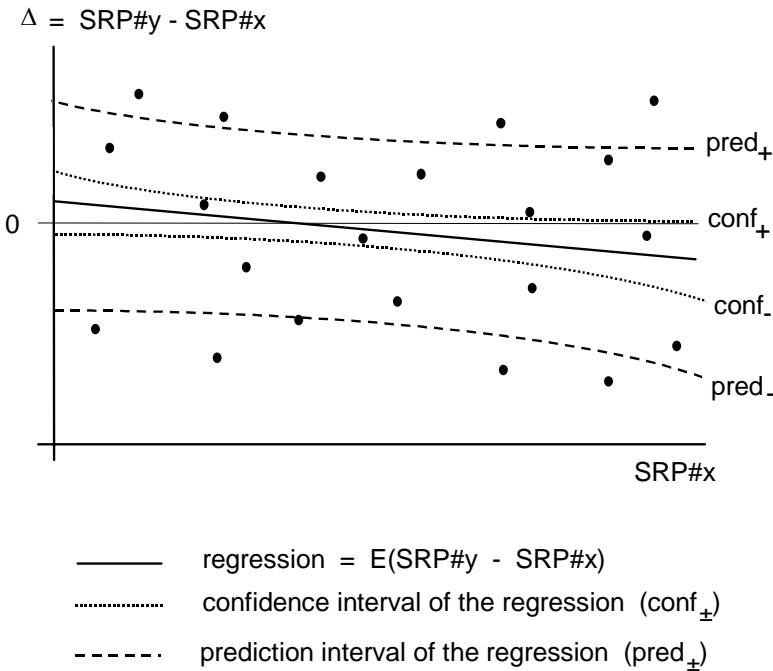


Fig. 2 Linear regression analysis for the determination of u_A

linear regression $E(\text{SRP}\#y - \text{SRP}\#x) = \hat{\Delta}(x) = a \cdot x + b \quad x = \text{SRP}\#x \quad (4)$

$\hat{\Delta}(x)$ = expectation value

confidence interval the expectation value $\hat{\Delta}(x)$ is with a probability of 68 % within that interval

$$\text{conf}_{\pm}(x) = \hat{\Delta} \pm t_{(n-2)} \cdot s_{\Delta \cdot x} \sqrt{\frac{1}{n} + \frac{(x - \bar{x})^2}{\sum(x - \bar{x})^2}} \quad (5)$$

prediction interval 68 % of the measured values are within that interval ($t_{(n-2)} \approx 1$ for 1σ)

$$\text{pred}_{\pm}(x) = \hat{\Delta} \pm t_{(n-2)} \cdot s_{\Delta \cdot x} \sqrt{1 + \frac{1}{n} + \frac{(x - \bar{x})^2}{\sum(x - \bar{x})^2}} \quad (6)$$

$s_{\Delta \cdot x}$: standard deviation of the difference Δ under the assumption, that the values of x are exact values with no uncertainty (which of course is not the case).

$s_{\Delta \cdot x}$ should be constant over the whole range. If this is not the case, the regression has to be performed for several sections.

$$s_{\Delta \cdot x} = \sqrt{\frac{\sum(\Delta - \hat{\Delta})^2}{n - 2}} \quad n - 2, \text{ because 2 parameters (a, b) are determined by the regression analysis}$$

The prediction interval is the result of the uncertainties u_A of SRP#y **and** SRP#x. Under the assumption that the uncertainties of these two identical instruments are equal we obtain the **standard uncertainty u_A of a single SRP**:

$$u_A(x) = \frac{1}{\sqrt{2}} \cdot (pred_{\pm}(x) - \hat{\Delta}(x)) \quad (7)$$

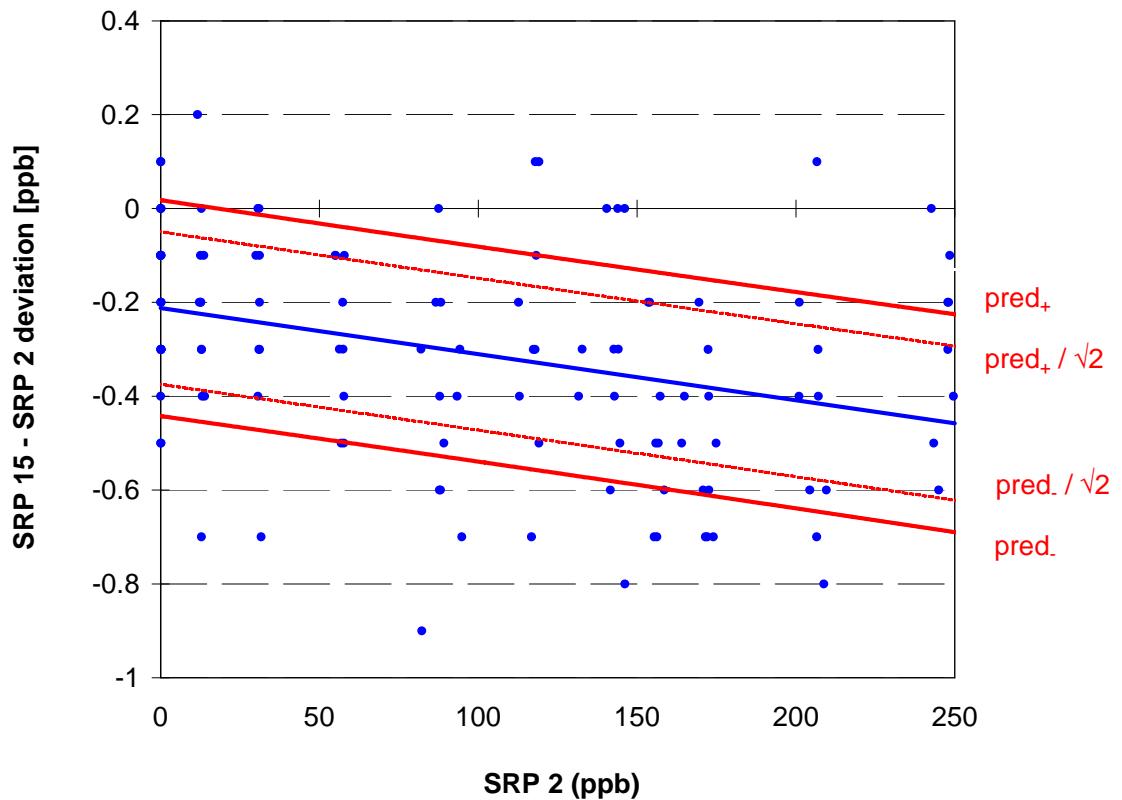


Fig. 3 Comparison of SRP#2 and SRP#15 1997 (123 pairs of data)

Figure 3 shows that the standard deviation $s_{\Delta \cdot x}$ and the difference $(pred_{\pm}(x) - \hat{\Delta}(x))$ of the two SRPs is fairly constant in the range 0 - 250 ppb. The standard uncertainty therefore is also constant; several comparisons performed from 1994 to 1997 have given values from 0.10 to 0.20 ppb. Because the standard uncertainty of a SRP between two comparisons might be slightly greater than the measured values, the value used in practical work was enlarged to 0.25 ppb:

Standard uncertainty

$$u_A = 0.25 \text{ ppb}$$

Expanded uncertainty

$$U_A = 0.50 \text{ ppb} \quad (\text{coverage factor } k = 2)$$

2.3) Uncertainty u_B

The uncertainty of the type B is composed of the following elements:

- **Uncertainty of the absorption coefficient u_α**

Absorption coefficient $\alpha = 308.32 \pm 3 \text{ cm}^{-1}$ (error limits)

$$u_\alpha = 3\text{cm}^{-1}/\sqrt{3} = 1.73\text{cm}^{-1} \triangleq 0.58 \%$$

This term may be neglected in projects where only the UV-absorption technique is used.

- **Uncertainty of the length of the photometric path u_L (SRP#15)**

Length of the photometric path = twice the length of a single cell = $2 \cdot 896,5 \text{ mm}$

Error limit of a single cell $\approx 1 \text{ mm}$ (rectangular distribution)

Standard uncertainties

of a single cell $u_{\text{cell}} = 0,2\text{mm}/\sqrt{3}$

of the photometric path $u_L = \sqrt{2} \cdot u_{\text{cell}} = \sqrt{\frac{2}{3}} \cdot 1\text{mm} = 0.82 \text{ mm} \triangleq 0.05 \%$

- **Uncertainty of the pressure sensor u_p**

The pressure is measured with an instrument of defined uncertainty:

$$u_p = 1 \text{ mbar} \triangleq 0.1 \%$$

- **Uncertainty of the temperature sensor u_T**

This value was estimated to be:

$$u_T = 0.5 \text{ K} \triangleq 0.2 \%$$

- **Uncertainties because of unknown interferences u_G**

All the components of u_B discussed above lead to uncertainties, which disappear when no ozone is present (zero air). Thus two different SRPs should show the same value at the absence of ozone. However a lot of comparisons with the NIST and the Swiss Federal Office of Metrology have shown that there remains a difference (Fig. 6). These deviations the technical reason of which has not been studied in detail lead to the following uncertainty:

$$u_G = 0.20 \text{ ppb}$$

Standard uncertainty u_B of the reference photometer:

$$u_B = \sqrt{u_\alpha^2 + u_L^2 + u_p^2 + u_T^2 + u_G^2} \quad (8)$$

Depending whether the UV-absorption is just one method among others or whether it is accepted as the method which measures the conventional correct value the uncertainty of the absorption coefficient u_α has to be considered or not:

if $u_\alpha = 0,58\%$	$u_B = \sqrt{(0,62\%)^2 + (0,20\text{ppb})^2}$
if $u_\alpha = 0$	$u_B = \sqrt{(0,23\%)^2 + (0,20\text{ppb})^2}$

17.3 Combined Uncertainty of the SRP

standard uncertainty $u_{SRP} = \sqrt{u_A^2 + u_B^2}$ (9)

expanded uncertainty $U_{SRP} = k \cdot u_{SRP}$ $k = 2$ (10)

Based on the formulas above the uncertainty for SRP#15 can be calculated as follows:

concentration [ppb]	$u_\alpha = 0,58\%$		$u_\alpha = 0$	
	u_{SRP} [ppb]	U_{SRP} [ppb] $k = 2$	u_{SRP} [ppb]	U_{SRP} [ppb] $k = 2$
0	0.32	0.64	0.32	0.64
20	0.34	0.69	0.32	0.65
40	0.41	0.81	0.33	0.67
60	0.49	0.98	0.35	0.70
80	0.59	1.19	0.37	0.74
100	0.70	1.40	0.39	0.79
150	0.99	1.98	0.47	0.94
200	1.29	2.58	0.56	1.12
250	1.59	3.18	0.66	1.31

Table 1: Standard uncertainty u and expanded uncertainty U of the SRP#15

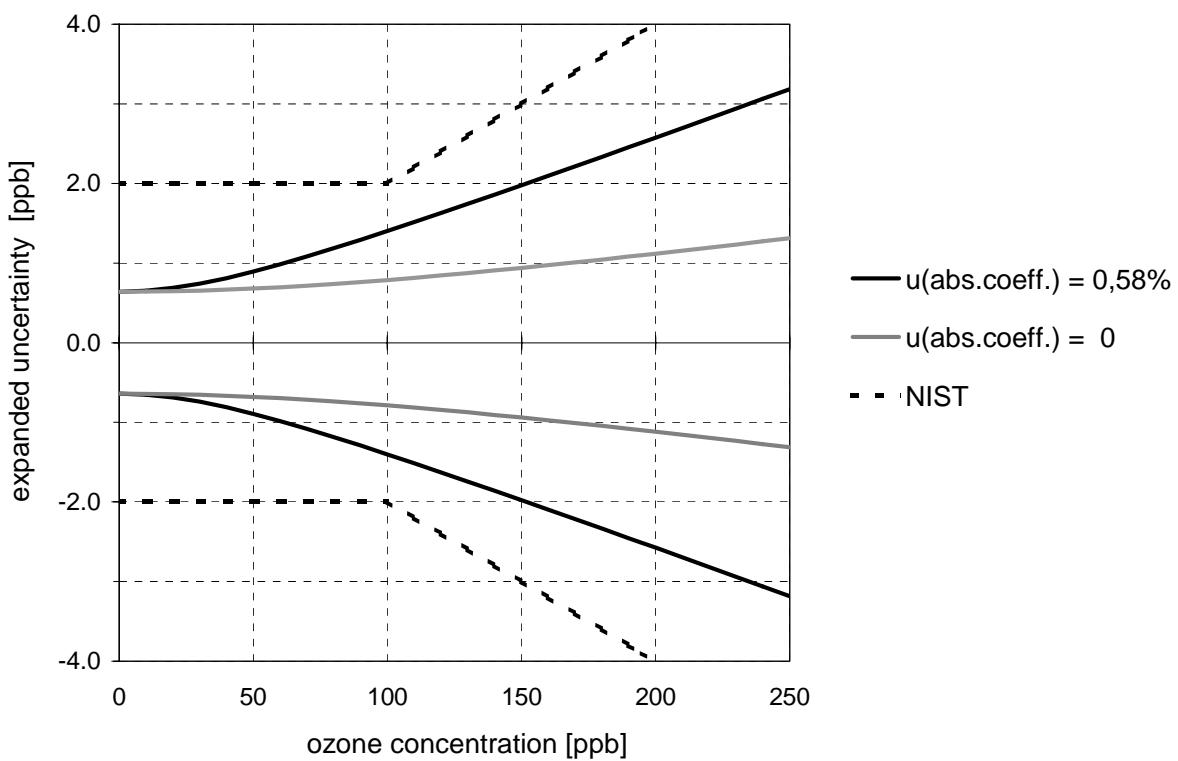


Fig. 4 Expanded uncertainty U_{SRP} of the SRP#15 (coverage factor = 2)

KRISS-SRP1 Uncertainty budget

Jan. 3. 2004.

Jin-Chun Woo, Yong-Doo Kim

We provided following four steps for the KRISS-SRP1 uncertainty budget, which is generally adopted in the calculation of uncertainty.

- 1) Setting up an equation of analytical model,
- 2) Quantification of standard uncertainties and degree of freedom,
- 3) Calculation of combined uncertainty,
- 4) Calculation of expanded uncertainty at 95 % confidence level with effective degrees of freedom.

As an explanation, a data set obtained for the ozone concentration, 419.81 nmol/mol is presented in this paper. This value is one of the data obtained in the comparison(refered to data point no. 4 of BIPM-KRISS comparison data).

1) Equation of analytical model

The concentration of ozone with the unit of nmol/mol is calculated by following equation of light absorption(referred to Table 1);

$$c = \frac{-\ln F}{2\alpha L} \cdot \frac{t}{273.15} \cdot \frac{103.125}{P} \times 10^9 \quad \dots \dots \dots \quad (1)$$

The equation of model was slightly changed by adding dummy input quantities for the uncertainty budget because more then one source of uncertainty are associated with an input quantity at the equation 1. The final modified equation of model is as a following (referred to Table 1);

$$c = \left(\frac{-\ln F}{2\alpha(L + \Delta_L)} \right) \cdot \left(\frac{t + \Delta_t}{273.15} \right) \cdot \left(\frac{103.125}{P + \Delta_P} \right) \cdot f_{c-path} \cdot f_{c-lin} \cdot f_{c-leak} \times 10^9 \quad \dots \dots \dots \quad (2)$$

, where a Δ or f means an error or relative error quantity due to additional source of uncertainty at the associated input quantity or measurand(c). The values of input and output(measurand) quantities as an example and their meaning are summarized at the Table 1.

Table 1. Input and output(measurand) quantity and value.

Symbol	Meaning	Value	Unit
	Absorption coefficient	308.32	cm ⁻¹
F	$F = I_1 I_2 / I_{01} I_{02}$	0.978927	-
L	Cell length	90.18	cm
ΔL	Error of light path length due to dispersed light.	0	cm
t	Temperature	295.84	K
Δt	Error shown at the calibration sheet of temperature sensor	0	K
P	Pressure	1001.21	hPa
ΔP	Error shown at calibration sheet of pressure sensor	0	hPa
f_{c-path}	Relative error of concentration due to multi-pass of light	1	-
f_{c-lin}	Relative Difference of concentration due to non-linear response of detectors and signal processing electronics	1	-
f_{c-leak}	Relative Difference of concentration due to leak at flow lines	1	-
c	Concentration of ozone (measurand)	419.8	nmol/mol

2) Quantification of standard uncertainties

The procedure of the quantification for the individual uncertainty is summarized at table 2. And the value, type of distribution, and degrees of freedom are also summarized at table 3, which are related to data of measurand shown at Table 1.

Table 2. Quantification of Standard uncertainty

Standard uncertainty	Quantification of Standard uncertainty
$u(\)$	Uncertainty from literature. Ignored by the purpose of this comparison.
$u(F)$	Standard deviation of the mean from the 10 determination results of F .
$u(L)$	Minimum scale(1 mm) of rule used for the determination of length.
$u(\ L)$	Increment of length of light path more then cell length, because of some portion of dispersed light. We calculated it as $u(\ L)=0.26$ cm, because, in the configuration of KRISS-SRP1, a parallelizer(with 7 holes of 5 x50 mm) blocks some portion of the dispersed light.
$u(t)$	Standard deviation of the 10 determination results of temperature.
$u(\ t)$	Uncertainty from the certification sheet of calibration of the temperature sensor.
$u(P)$	Standard deviation of the 10 determination results of pressure.
$u(\ p)$	Uncertainty from the certification sheet of calibration of the pressure sensor.
$u(f_{c-path})$	Increment of concentration due to multi-path of light; by reflection of light between the windows of cells, filters and detectors. We assume $u(f_{c-path})=0$, because, in the configuration of KRISS-SRP1, multi-passing light cannot enter the detector by a parallelizer and by optical windows, filters and detectors set with 3°angle to vertical plane.
$u(f_{c-lin})$	Difference of concentration due to non-linear response of detector and signal processing electronics. We assume $u(f_{c-lin})=0$, because we tested the difference between concentrations obtained at normal and half of light intensity of Hg lamp. And, we did not observed any significant statistical difference of ozone concentrations. The test was performed at the same concentration and assisted by another ozone analyzer.
$u(f_{c-leak})$	Uncertainty of concentration due to leak. It is our future work, but we assume $u(f_{c-leak})=0$.

Table 3. Standard uncertainty

Input quantity			Standard uncertainty				
Sym -bol	Value	Unit	Symbol	Value	Degrees of freedom	Assumed Distribu-tion	Contribution to combined variance of uncertainty
	308.32	cm ⁻¹	$u(\)$	-	-	-	-
F	0.978927	-	$u(F)$	0.0000072	9	t	1.4 %
L	90.18	cm	$u(L)$	0.058	50	rectangle	4.6 %
L	0	cm	$u(L)$	0.26	50	rectangle	96.0 %
t	295.84	K	$u(t)$	0.000	50	t	0.0 %
t	0	K	$u(t)$	0.0012	50	rectangle	0.0 %
P	1001.21	hPa	$u(P)$	0.002	9	t	0.0 %
P	0	hPa	$u(P)$	0.062	50	rectangle	0.0 %
f_{c-path}	1	-	$u(f_{c-path})$	0	9	rectangle	0.0 %
f_{c-lin}	1	-	$u(f_{c-lin})$	0	50	rectangle	0.0 %
f_{c-leak}	1	-	$u(f_{c-leak})$	0	50	rectangle	0.0 %

3) Calculation of combined uncertainty

Combined uncertainty($u_c(c)$) can be obtained with the following uncertainty propagation principle(refered to ISO guide);

$$u_c^2(c) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) \quad \text{-----} (3)$$

With some mathematical treatment, simplified form of following combined uncertainty ($u_c(c)$) can be obtained from the equation 2 and 3;

$$\left(\frac{u_c(c)}{c}\right)^2 = \left(\frac{u(F)}{F \cdot \ln F}\right)^2 + \left(\frac{u(\alpha)}{\alpha}\right)^2 + \left(\frac{u(L)}{L}\right)^2 + \left(\frac{u(\Delta_L)}{L}\right)^2 + \left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(\Delta_P)}{P}\right)^2 + \left(\frac{u(t)}{t}\right)^2 + \left(\frac{u(\Delta_t)}{t}\right)^2 + \left(\frac{u(f_{c-path})}{f_{c-path}}\right)^2 + \left(\frac{u(f_{c-lin})}{f_{c-lin}}\right)^2 + \left(\frac{u(f_{c-leak})}{f_{c-leak}}\right)^2 \quad \text{----(4)}$$

In the actual calculation, commercial program of uncertainty named “PUMA” was used. And, combined standard uncertainty and effective degrees of freedom(referred to ISO guide and following equation 5) were obtained simultaneously and presented at table 4.

$$v_{eff} = \frac{u_c^4(y)}{\sum_{i=1}^n \frac{u_i^4(y)}{v_i}} \quad \text{-----(5)}$$

4) Calculation of expanded uncertainty

Expanded uncertainty and coverage factor were obtained at 95% level of confidence used also with “PUMA.” They are presented at table 4. The contribution of individual variance to combined variance of uncertainty was obtained by “PUMA” and presented at Table 3.

Table 4. The combined standard and expanded uncertainties

c , Measurand (output quantity)		$u(c)$, Combined standard uncertainty			U , Expanded uncertainty @ 95 %level of confidence	
Value	unit	Value	Degrees of freedom	Assumed Distribu- tion	value	k , Coverage factor
419.81	nmol/mol	1.25	56	t	2.50	2.0

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Appendix 3 - GPT systems uncertainty budgets

1. BIPM

1.1 Uncertainty Budget for BIPM-GPT for measurement of Ozone (M.B. Esler 22/03/05)

The measurement equation for the measurement by the BIPM-GPT of an ozone mole fraction in dry air, x_{O_3} , may be expressed as:

$$\begin{aligned}x_{O_3} &= \Delta[NO] \\&= [NO]_{reactant} - [NO]_{untitrated} \\&= \left(\frac{C \cdot F_{NO,Titr}}{F_{NO,Titr} + F_{ZA,Titr}} \right) - [NO]_{untitrated}\end{aligned}$$

where,

$[NO]_{reactant}$ is the mole fraction of NO input to the GPT reaction vessel, and is determined solely by the flows $F_{NO,Titr}$, $F_{ZA,Titr}$ and the NO mole fraction C .

$F_{NO,Titr}$ is the NO standard gas flow measured on molbloc₁ during the titration.

$F_{ZA,Titr}$ is the zero air flow measured on molbloc₄ during the titration.

C is the NO mole fraction value assigned to the 2° standard gas.

$[NO]_{untitrated}$ is the mole fraction of NO remaining after the GPT reaction, and is measured on the TEI42C. The TEI42C reports $[NO]_{42C}$, i.e. an NO mole fraction on an uncalibrated instrumental measurement scale. There is a separate process of calibration (by bracketing) of the TEI42C measurement scale against the 2° standard gas. For full rigour the $[NO]_{untitrated}$ term should be expanded as a function of these bracketing calibration terms. Such a treatment is beyond the scope of this report, but will be detailed fully in a report in preparation dedicated to the BIPM-GPT facility.

The first table below summarises the uncertainty budget for the measurement of the amount fraction of ozone in dry air x_{O_3} using the BIPM-GPT facility over the range (200-1000) nmol/mol. The contribution of $[NO]_{\text{untitrated}}$ to the overall uncertainty in x_{O_3} appears as a single line entry. The second table summarises the uncertainty budget for $[NO]_{\text{untitrated}}$ itself over the same range. There are contributions from the TEI49C calibration process and from the repeatability of the TEI42C measurement.

Experimental investigations on the GPT apparatus have confirmed that, within the uncertainties:

- there are no significant losses of either NO or O₃ taking place due to either wall effects or gas phase chemistry other than the titration reaction itself: NO + O₃ → NO₂ + O₂;
- the two channels of the BIPM-GPT apparatus, (namely the titration and calibration channels) are equivalent. This is required for the form of the measurement equation above to be valid.

Component (y)	Uncertainty $u(y)$			Sensitivity coefficient $c_i = \partial x / \partial y$	Relative Contribution to $u(x)$
	Source	Distribution	Combined Standard Uncertainty $u(y)$		
[NO] in 2° std gas, C (55.11 μmol/mol)	Calibration against 1° std gases	Normal	50 nmol/mol	$\frac{F_{NO,\text{Titr}}}{F_{NO,\text{Titr}} + F_{ZA,\text{Titr}}}$	0.09 %
Std gas flow $F_{NO,\text{Titr}}$ (10-50) ml/min	molbloc #1 (type 1E2)	Rect.	0.09 % $F_{NO,\text{Titr}}$	$\frac{C \cdot F_{ZA,\text{Titr}}}{(F_{NO,\text{Titr}} + F_{ZA,\text{Titr}})^2}$	0.17 %
Zero Air flow, $F_{ZA,\text{Titr}}$ (1250 ml/min)	molbloc #4 (type 5E3)	Rect.	0.1 % $F_{ZA,\text{Titr}}$	$\frac{-C \cdot F_{NO,\text{Titr}}}{(F_{NO,\text{Titr}} + F_{ZA,\text{Titr}})^2}$	0.19 %
$[NO]_{\text{untitrated}}$			0.27 % $[NO]_{\text{untitrated}}$	1	0.14 %
$x_{O_3} = \Delta[NO]$					0.30 %

Component (y)	Uncertainty $u(y)$			Sensitivity coefficient $c_i = \partial x / \partial y$	Relative Contribution to $u(x)$
	Source	Distribution	Combined Standard Uncertainty $u(y)$		
[NO] _{42C} calibration	Calibration of TEI49C against 2° std gas	Normal	0.27 % [NO] _{42C}	1	0.27 %
[NO] _{42C} measurement	TEI49C repeatability	Normal	0.03 % [NO] _{42C}	1	0.03 %
$x = [\text{NO}]_{\text{untitrated}}$					0.27 %

1.2 Uncertainty Budget for use of BIPM-TEI49C as Transfer Standard in comparison of BIPM-GPT with SRP27 (M.B. Esler 21/03/05)

The comparison of the BIPM-GPT instrument with SRP-27 is a two step process that proceeds via the use of the BIPM's TEI49C as a transfer standard:

- first the comparison TEI49C vs BIPM-GPT is performed experimentally.
- second, the comparison TEI49C vs SRP27 is performed experimentally.

From these two experimental comparisons the further comparison of BIPM-GPT vs SRP27 can be deduced analytically, provided that due care is taken in characterising and propagating the uncertainties of the three instruments involved.

Only the components of the uncertainty corresponding to the repeatability and reproducibility of the TEI49C's measurements are considered, since it is assumed that any causes of bias in the TEI49C's measurement remains constant over the time period of the comparisons.

The repeatability and reproducibility of the TEI49C measurements has been evaluated independently for the two comparisons, as the measurement conditions of the TEI49C are somewhat different in each (in terms of averaging time and measurement range).

TEI49C vs BIPM GPT:

Repeatability: In the TEI49C vs BIPM-GPT comparison, the TEI49C measurements of x_{O_3} are the result of a five minute averaging period, τ , and the measurement range is 0 nmol/mol to 1000 nmol/mol.

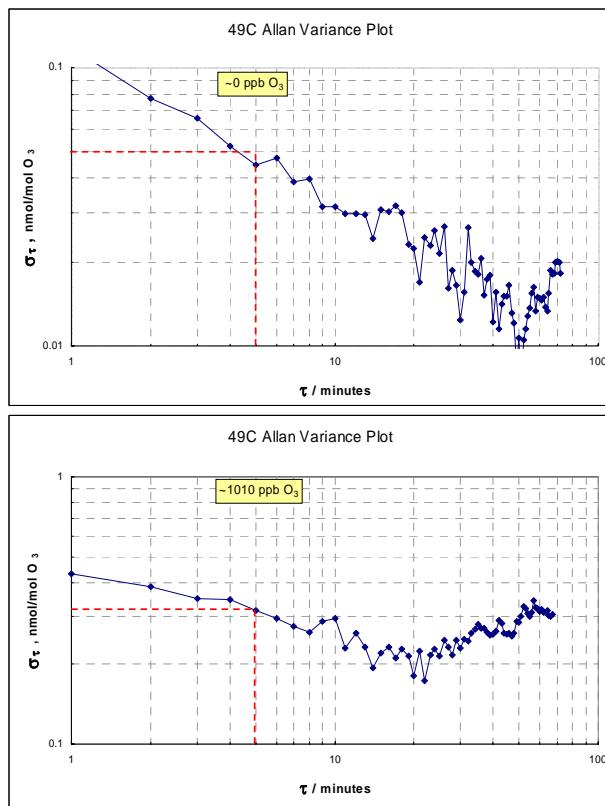
To assess short term repeatability, several time series analyses of the behaviour of the TEI49C were performed and analysed using an Allan Variance approach. The table below summarises the results:

[O ₃] nmol/mol	Averaging time, τ min	Allan Deviation σ_y nmol/mol
0	5	0.05
1000	5	0.32

When the TEI 49C was analysing zero air ([O₃]=0 nmol/mol) it was observed that the Allan Deviation, σ_y , continued to diminish in proportion to $\tau^{-\frac{1}{2}}$ until $\tau>15$ min. However, when the analyte was 1000 nmol/mol O₃, generated by the Environics O₃ generator, σ_y reached a minimum of 0.2 nmol/mol at $\tau \approx 11$ min after which it climbed, indicating the presence of drift in the system for the higher ozone levels not seen when the analyte is zero air.

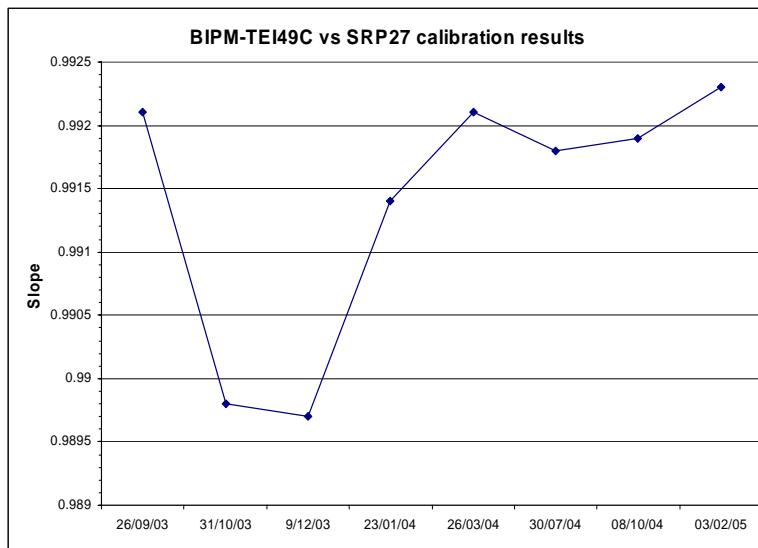
Assuming that the Allan Deviation observed can be attributed to the TEI49C, and that it increases linearly over the measurement range (0 nmol/mol and at 1000 nmol/mol), the TEI49C measurement uncertainty due to repeatability for a 5 minute average measurement may be estimated from the numerical equation (where the numerical values are expressed in units of nmol/mol):

$$u_{\text{repeat}}(x_{O_3}) = 2.7 \times 10^{-4} \cdot x_{O_3} + 5.0 \times 10^{-2}$$



Reproducibility: To assess the TEI49C measurement uncertainty contributions due to longer term reproducibility, we make use of the fact that the BIPM's TEI49C has been calibrated against SRP27 on eight occasions between September 2003 and February 2005. The table below contains the slope and intercept parameters resulting from these TEI49C vs SRP27 comparisons:

Calibration Date	Slope	y-intercept nmol/mol
26/09/03	0.9921	-0.11
31/10/03	0.9898	-0.07
9/12/03	0.9897	-0.01
23/01/04	0.9914	-0.09
26/03/04	0.9921	-0.17
30/07/04	0.9918	-0.03
08/10/04	0.9919	-0.12
03/02/05	0.9923	0.04
Max-Min	0.0026	0.21
Mean	0.9914	-0.08
Std Dev.	0.0010	0.06



By considering a rectangular distribution over the interval of all eight TEI49C vs SRP27 slope results, the uncertainty in the calibration slope may be estimated as:

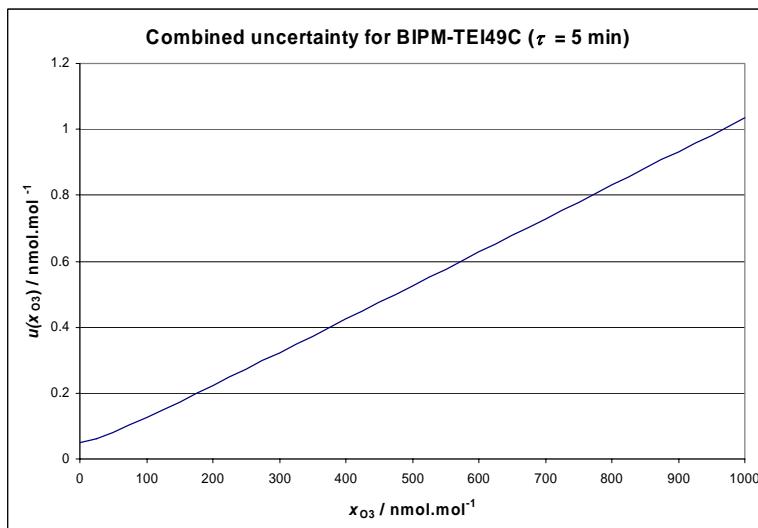
$$u(\text{slope}) = \frac{0.0026}{2\sqrt{3}} = 0.00075$$

and the the TEI49C measurement uncertainty contribution from reproducibility may be estimated as:

$$u_{\text{reprod}}(x_{O_3}) = 7.5 \times 10^{-4} \cdot x_{O_3}$$

Combined Uncertainty: Adding the two contributions in quadrature gives the numerical expression (where the numerical values are expressed in units of nmol/mol):

$$\begin{aligned} u_c(x_{O_3}) &= \sqrt{(2.7 \times 10^{-4} \cdot x_{O_3} + 5 \times 10^{-2})^2 + (7.5 \times 10^{-4} x_{O_3})^2} \\ &= \sqrt{1.04 \times 10^{-6} \cdot x_{O_3}^2 + 2.7 \times 10^{-5} \cdot x_{O_3} + 2.5 \times 10^{-3}} \end{aligned}$$



TEI49C vs SRP27:

Repeatability: In the TEI49C vs SRP comparison, the TEI49C measurements of x_{O_3} are the result of a 10 s averaging period, τ , performed at 30 s intervals; and the measurement range is 0 nmol/mol to 500 nmol/mol. We know from the behaviour of SRPs that measurements of x_{O_3} are serially correlated under such operating conditions and that the experimental standard deviation is a suitable estimate for their repeatability. We estimate the repeatability of TEI49C x_{O_3} measurements in the same way:

$$u_{\text{repeat}}(x_{O_3}) = s(x_{O_3})$$

Reproducibility: The measurement uncertainty due to longer term reproducibility in the TEI49C will be the same as discussed above, namely:

$$u_{\text{reprod}}(x_{O_3}) = 7.5 \times 10^{-4} \cdot x_{O_3}$$

Combined Uncertainty: Adding the two contributions in quadrature gives:

$$u_C(x_{O_3}) = \sqrt{(s^2(x_{O_3}) + (7.5 \times 10^{-4} x_{O_3})^2)}$$

Summary

The table below summarises the proposed estimates of uncertainty in the TEI49C analysis of ozone.

Comparison Type	$u_{\text{repeat}}(x_{O_3})$	$u_{\text{reprod}}(x_{O_3})$	$u_C(x_{O_3})$
TEI49C vs BIPM-GPT	$2.7 \times 10^{-4} \cdot x_{O_3} + 5.0 \times 10^{-2}$	$7.5 \times 10^{-4} \cdot x_{O_3}$	$\sqrt{1.04 \times 10^{-6} \cdot x_{O_3}^2 + 2.7 \times 10^{-5} \cdot x_{O_3} + 2.5 \times 10^{-3}}$
TEI49C vs SRP27	$s(x_{O_3})$	$7.5 \times 10^{-4} \cdot x_{O_3}$	$\sqrt{(s(x_{O_3})^2 + (7.5 \times 10^{-4} x_{O_3})^2)}$

2. NIES

NIES excess NO + O₃ GPT uncertainty budget

The following is an uncertainty budget that is applicable for the measurement of an ozone mole fraction in dry air (x) by the NIES excess NO + O₃ GPT system in the range (0-500) nmol/mol.

Component (y)	Value	Uncertainty $u(y)$				Relative Contribution to $u(x)$
		Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$	
NO/N ₂ gas C	99.88 umol/mol	Gravimetric Preparation	Rect.	0.05 umol/mol	0.05 umol/mol	$x^*u(C)/C, 0.050 \%$
Dilution Factor D	200 ~ 500	Flow (NO), F_{NO}	Rect.	0.2 % reading (0.04-0.1 sccm @20-50 sccm)	1.0 ~ 2.5	$x^*u(D)/D, 0.36 \%$
		Flow (ZA), F_{ZA}	Rect.	0.3 % reading (0.03 slm @10 slm)		
δ[NO] Measurement M	50 ~ 500 nmol/mol	Repeatability	Normal	0.10 nmol/mol	0.10 nmol/mol	$u(M), 0.10$

The measurement equation can be written in:

$$x = (M_{\text{beforeSRPmeas}} + M_{\text{afterSRPmeas}})/2,$$

where $M = \delta [NO]$ ($= [NO]_{\text{MIX}} - [NO]_{\text{GPT}}$),

and $[NO]_i = C / D$, $D = (F_{NO} + F_{ZA}) / F_{NO} \approx F_{ZA}/F_{NO}$ ($F_{ZA} \gg F_{NO}$)

The combined standard uncertainty $u(x)$:

$$u(x) = \text{SQRT}[\{(u(C)/C)^2 + (u(D)/D)^2\} * x^2 + u(M)^2]$$

Note:

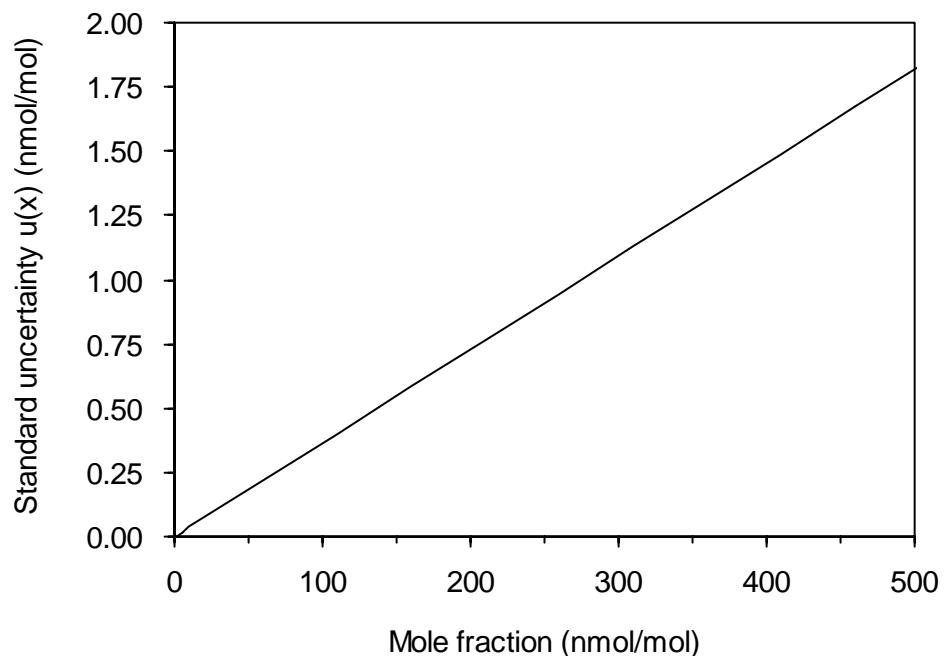
NO/N₂ standard gas (3MK-76158) from CERI (NMIJ traceable)

Flow measurement by Molbloc (5E-VCR-V-Q (50sccm N₂ F.S.), 3E4-VCR-V-Q (30 slm N₂ F.S.))

NO measurement by TEI model 42, and Eco Physics model 88x

Figure 1 depicts the estimated value of $u(x)$ as a function of the ozone mole fraction x .

Figure 1 : Combined standard uncertainty associated with the measured mole fraction of ozone in dry air for NIES GPT.



Pilot Study CCQM-P28, Ozone at ambient level

Individual results of the comparisons following the protocol A

Page	Participant
2	CHMI
3	CSIR-NML
4	EMPA
5	Env Canada
6	FMI
7	INRIM (1)
8	INRIM (2)
9	KRISS
10	METAS (SRP18)
11	NIES (SRP35)
12	NILU
13	NMi-VSL
14	NPL
15	SP
16	SP (2)
17	UBA (A)
18	UBA (D)
19	VNIIM

Note : cells highlighted in yellow corresponds to ozone mole fractions that differ from the nominal value by more than 15 nmol/mol

Comparison at the BIPM: CHMI SRP17 versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			CHMI SRP17			SRP17 vs SRP27				
			x_{SRP27}	s_{SRP27}	$u(x_{\text{SRP27}})$	x_{NS}	s_{NS}	$u(x_{\text{NS}})$	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$	$u(b_{\text{NS,SRP27}})$	Cov
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol			nmol/mol	nmol/mol	
1 09/20/04 (C0920005)	1	0	-0.03	0.29	0.28	0.06	0.22	0.28	1.0040	0.0008	-0.12	0.19	-1.13E-04
	2	220	220.61	0.19	0.30	221.12	0.83	0.29					
	3	80	81.27	0.20	0.28	81.37	0.34	0.28	Goodness-of-fit measure: 0.44				
	4	420	422.02	0.28	0.34	423.69	0.35	0.33					
	5	120	118.19	0.37	0.29	118.77	0.22	0.28					
	6	320	323.39	0.18	0.32	324.60	0.22	0.31					
	7	30	31.39	0.36	0.28	31.25	0.17	0.28					
	8	370	372.67	0.20	0.33	374.08	0.24	0.32					
	9	170	169.86	0.12	0.29	170.39	0.23	0.29					
	10	500	504.24	0.36	0.36	506.12	0.32	0.35					
	11	270	270.67	0.16	0.31	271.63	0.23	0.30					
	12	0	0.07	0.18	0.28	-0.09	0.14	0.28					
2 09/20/04 (c0920006)	1	0	0.00	0.25	0.28	-0.11	0.22	0.28	1.0039	0.0008	-0.14	0.19	-1.13E-04
	2	220	220.63	0.23	0.30	221.00	0.65	0.29					
	3	80	81.47	0.24	0.28	81.82	0.38	0.28	Goodness-of-fit measure: 1.01				
	4	420	421.95	0.27	0.34	423.54	0.35	0.33					
	5	120	118.07	0.19	0.29	118.65	0.26	0.28					
	6	320	323.62	0.16	0.32	324.41	0.26	0.31					
	7	30	31.46	0.24	0.28	31.54	0.21	0.28					
	8	370	372.32	0.19	0.33	374.28	0.79	0.32					
	9	170	169.54	0.24	0.29	169.95	0.13	0.29					
	10	500	504.01	0.24	0.36	505.68	0.26	0.35					
	11	270	270.36	0.18	0.31	271.17	0.25	0.30					
	12	0	0.14	0.20	0.28	-0.22	0.32	0.28					
3 09/20/04 (c0920007)	1	0	-0.18	0.27	0.28	-0.05	0.23	0.28	1.0033	0.0008	-0.06	0.19	-1.13E-04
	2	220	220.83	0.15	0.30	221.67	0.17	0.29					
	3	80	81.77	0.22	0.28	81.96	0.17	0.28	Goodness-of-fit measure: 0.36				
	4	420	422.40	0.13	0.34	423.88	0.22	0.33					
	5	120	118.34	0.25	0.29	118.49	0.21	0.28					
	6	320	323.55	0.20	0.32	324.71	0.23	0.31					
	7	30	31.45	0.23	0.28	31.39	0.34	0.28					
	8	370	372.89	0.33	0.33	373.84	0.73	0.32					
	9	170	169.51	0.16	0.29	169.98	0.15	0.29					
	10	500	504.28	0.40	0.36	505.92	0.33	0.35					
	11	270	270.60	0.15	0.31	271.36	0.19	0.30					
	12	0	-0.02	0.14	0.28	-0.06	0.28	0.28					

Comparison at the BIPM: CHMI SRP17 versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			CSIR-NML			CSIR-NML vs SRP27				
			x_{SRP27}	s_{SRP27}	$u(x_{\text{SRP27}})$	x_{NS}	s_{NS}	$u(x_{\text{NS}})$	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$	$u(b_{\text{NS,SRP27}})$	Cov
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol					
1 03/12/05 (c0311015)	1	0	0.65	0.25	0.28	0.26	0.19	0.40	1.0069	0.0026	-0.58	0.29	-4.23E-04
	2	220	218.83	0.94	0.30	220.18	0.15	1.36					
	3	80	80.04	0.85	0.28	80.04	0.10	0.37	Goodness-of-fit measure:				
	4	420	418.60	1.06	0.34	420.02	0.45	2.62					
	5	120	119.61	0.76	0.29	119.96	0.19	0.76					
	6	320	318.27	0.96	0.32	320.09	0.23	1.98					
	7	30	1.98	1.31	0.28	0.29	0.87	0.94					
	8	370	378.29	0.78	0.33	380.11	0.26	2.35					
	9	170	179.29	0.68	0.29	179.99	0.08	1.11					
	10	500	497.44	1.29	0.36	499.88	0.44	3.10					
	11	270	278.87	0.75	0.31	280.02	0.20	1.73					
	12	0	0.67	0.15	0.28	0.10	0.16	0.39					
2 03/12/05 (c0311016)	1	0	0.68	0.17	0.28	0.21	0.13	0.38	1.0053	0.0025	-0.41	0.27	-3.54E-04
	2	220	219.07	0.79	0.30	219.89	0.19	1.36					
	3	80	79.96	0.71	0.28	79.98	0.18	0.40	Goodness-of-fit measure:				
	4	420	417.60	1.12	0.34	420.20	0.19	2.59					
	5	120	119.60	0.59	0.29	119.98	0.17	0.76					
	6	320	318.69	0.64	0.32	320.05	0.29	1.99					
	7	30	1.37	1.04	0.28	0.63	0.40	0.54					
	8	370	378.59	0.95	0.33	379.94	0.37	2.36					
	9	170	180.17	0.82	0.29	180.05	0.23	1.13					
	10	500	496.91	0.94	0.36	499.84	0.26	3.08					
	11	270	279.15	0.87	0.31	279.92	0.20	1.73					
	12	0	0.54	0.14	0.28	0.41	0.10	0.37					
3 03/13/05 (c0311017)	1	0	0.54	0.17	0.28	0.32	0.39	0.53	1.0058	0.0026	-0.60	0.30	-4.61E-04
	2	220	219.19	0.52	0.30	219.95	0.22	1.37					
	3	80	80.14	0.58	0.28	79.95	0.14	0.38	Goodness-of-fit measure:				
	4	420	418.24	1.02	0.34	419.90	0.26	2.59					
	5	120	119.97	0.53	0.29	120.03	0.10	0.74					
	6	320	318.55	1.14	0.32	319.96	0.24	1.98					
	7	30	1.62	1.35	0.28	0.34	0.66	0.75					
	8	370	377.66	0.61	0.33	379.92	0.27	2.35					
	9	170	179.51	0.96	0.29	179.97	0.25	1.13					
	10	500	497.68	1.12	0.36	499.92	0.29	3.08					
	11	270	279.23	1.26	0.31	279.95	0.25	1.74					
	12	0	0.69	0.32	0.28	0.16	0.17	0.40					

Comparison at the BIPM: EMPA SRP15 versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			EMPA SRP15			SRP15 vs SRP27					
			x_{SRP27}	s_{SRP27}	$u(x_{\text{SRP27}})$	x_{NS}	s_{NS}	$u(x_{\text{NS}})$	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$	$u(b_{\text{NS,SRP27}})$	cov	
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol			nmol/mol	nmol/mol		
1 03/17/04 (c0316007)	1	0	0.10	0.17	0.28		0.01	0.44	0.32	1.0033	0.0013	-0.17	0.22	-1.97E-04
	2	220	224.04	0.34	0.30		224.38	0.34	0.61					
	3	80	82.44	0.33	0.28		82.56	0.48	0.37					
	4	420	415.94	0.27	0.34		417.28	0.41	1.01					
	5	120	119.47	0.31	0.29		119.79	0.26	0.42					
	6	320	315.53	0.35	0.32		316.42	0.36	0.80					
	7	30	26.82	0.28	0.28		26.60	0.45	0.33					
	8	370	360.89	0.37	0.33		362.03	0.45	0.89					
	9	170	167.45	0.21	0.29		167.89	0.35	0.50					
	10	500	494.94	0.29	0.36		496.42	0.61	1.19					
	11	270	270.25	0.27	0.31		270.85	0.18	0.70					
	12	0	0.19	0.27	0.28		0.05	0.23	0.32					
2 03/17/04 (c0316008)	1	0	0.26	0.22	0.28		-0.08	0.38	0.32	1.0028	0.0013	-0.15	0.22	-1.97E-04
	2	220	224.21	0.24	0.30		224.53	0.24	0.61					
	3	80	82.42	0.20	0.28		82.51	0.53	0.37					
	4	420	416.02	0.31	0.34		416.99	0.37	1.01					
	5	120	119.58	0.28	0.29		119.95	0.31	0.42					
	6	320	315.92	0.27	0.32		316.74	0.19	0.80					
	7	30	26.56	0.14	0.28		26.58	0.29	0.33					
	8	370	361.01	0.36	0.33		362.14	0.19	0.89					
	9	170	167.49	0.28	0.29		167.61	0.25	0.50					
	10	500	495.05	0.33	0.36		496.34	0.39	1.19					
	11	270	270.75	0.35	0.31		271.18	0.27	0.70					
	12	0	0.16	0.17	0.28		0.11	0.21	0.32					
3 03/17/04 (c0316009)	1	0	0.24	0.19	0.28		0.05	0.40	0.32	1.0024	0.0013	-0.06	0.22	-1.96E-04
	2	220	224.09	0.27	0.30		224.57	0.31	0.61					
	3	80	82.11	0.23	0.28		82.57	0.47	0.37					
	4	420	416.34	0.36	0.34		417.35	0.22	1.01					
	5	120	119.53	0.34	0.29		119.81	0.19	0.42					
	6	320	315.94	0.22	0.32		316.51	0.24	0.80					
	7	30	26.77	0.10	0.28		26.72	0.18	0.33					
	8	370	361.47	0.32	0.33		361.87	0.16	0.89					
	9	170	167.36	0.17	0.29		167.74	0.36	0.50					
	10	500	494.97	0.36	0.36		495.99	0.30	1.18					
	11	270	270.45	0.22	0.31		271.21	0.24	0.70					
	12	0	0.15	0.63	0.28		0.01	0.28	0.32					

Comparison at the BIPM: Environment Canada SRP16 versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			Environment Canada SRP16			SRP16 vs SRP27					
			x_{SRP27}	s_{SRP27}	$u(x_{\text{SRP27}})$	x_{NS}	s_{NS}	$u(x_{\text{NS}})$	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$	$u(b_{\text{NS,SRP27}})$	Cov	
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol			nmol/mol	nmol/mol		
1 10/21/03 (c1021003)	1	0	0.23	0.20	0.28	Goodness-of-fit measure: 0.29	0.05	0.17	0.28	1.0028	0.0008	-0.16	0.19	-1.15E-04
	2	220	229.69	0.17	0.30		230.35	0.56	0.30					
	3	80	84.77	0.22	0.28		84.90	0.12	0.28					
	4	420	426.27	0.26	0.34		427.20	0.17	0.34					
	5	120	123.32	0.15	0.29		123.60	0.16	0.29					
	6	320	323.48	0.20	0.32		324.22	0.75	0.32					
	7	30	27.48	0.12	0.28		27.31	0.31	0.28					
	8	370	370.25	0.19	0.33		371.13	0.25	0.33					
	9	170	171.91	0.10	0.29		172.13	0.25	0.29					
	10	500	506.44	0.16	0.37		507.79	0.16	0.37					
	11	270	276.80	0.19	0.31		277.31	0.25	0.31					
	12	0	0.12	0.21	0.28		-0.03	0.15	0.28					
2 10/22/03 (c1022003)	1	0	0.27	0.19	0.28	Goodness-of-fit measure: 0.42	-0.04	0.19	0.28	1.0033	0.0008	-0.28	0.19	-1.15E-04
	2	220	230.23	0.24	0.30		230.74	0.25	0.30					
	3	80	85.12	0.24	0.28		85.13	0.13	0.28					
	4	420	427.77	0.26	0.34		428.62	0.20	0.34					
	5	120	123.91	0.16	0.29		123.80	0.23	0.29					
	6	320	324.58	0.26	0.32		325.36	0.21	0.32					
	7	30	27.59	0.15	0.28		27.56	0.16	0.28					
	8	370	371.01	0.18	0.33		372.20	0.43	0.33					
	9	170	172.34	0.15	0.29		172.79	0.56	0.29					
	10	500	507.88	0.17	0.37		509.39	0.24	0.37					
	11	270	277.73	0.22	0.31		278.28	0.23	0.31					
	12	0	0.28	0.12	0.28		-0.04	0.17	0.28					
3 10/22/03 (c1022009)	1	0	0.30	0.17	0.28	Goodness-of-fit measure: 0.46	0.15	0.19	0.28	1.0031	0.0008	-0.24	0.19	-1.15E-04
	2	220	230.15	0.28	0.30		230.72	0.25	0.30					
	3	80	84.90	0.17	0.28		84.87	0.13	0.28					
	4	420	427.15	0.21	0.34		428.23	0.18	0.34					
	5	120	123.44	0.14	0.29		123.62	0.34	0.29					
	6	320	324.48	0.16	0.32		325.17	0.26	0.32					
	7	30	27.53	0.19	0.28		27.25	0.12	0.28					
	8	370	371.28	0.26	0.33		371.90	0.17	0.33					
	9	170	172.22	0.15	0.29		172.51	0.26	0.29					
	10	500	507.87	0.27	0.37		509.35	0.36	0.37					
	11	270	277.56	0.19	0.31		278.45	0.24	0.31					
	12	0	0.30	0.12	0.28		0.06	0.17	0.28					

Comparison at the BIPM: FMI TEI 49CPS versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			TEI 49CPS			TEI 49CPS vs SRP27				
			x_{SRP27}	s_{SRP27}	$u(x_{SRP27})$	x_{NS}	s_{NS}	$u(x_{NS})$	$a_{NS,SRP27}$	$u(a_{NS,SRP27})$	$b_{NS,SRP27}$	$u(b_{NS,SRP27})$	cov
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol			nmol/mol	nmol/mol	
1 03/03/04 (C0303007)	1	0	0.14	0.28	0.28	-0.56	0.14	0.37	0.9960	0.0020	-0.63	0.27	-3.08E-04
	2	220	216.14	0.26	0.30	214.52	0.18	1.01	Goodness-of-fit measure:				
	3	80	78.94	0.27	0.28	77.84	0.15	0.58					
	4	420	411.61	0.41	0.34	409.50	0.39	1.79					
	5	120	118.60	0.25	0.29	117.35	0.15	0.69					
	6	320	313.95	0.27	0.32	312.18	0.21	1.38					
	7	30	30.17	0.21	0.28	29.55	0.26	0.45					
	8	370	362.61	0.60	0.33	360.59	0.46	1.58					
	9	170	167.26	0.21	0.29	165.99	0.20	0.85					
	10	500	490.24	0.38	0.36	487.90	0.37	2.16					
	11	270	265.43	0.26	0.31	263.68	0.23	1.19					
	12	0	0.00	0.19	0.28	-0.55	0.11	0.37					
2 03/03/04 (C0303008)	1	0	0.07	0.24	0.28	-0.43	0.13	0.37	0.9961	0.0020	-0.62	0.27	-3.08E-04
	2	220	216.03	0.24	0.30	214.48	0.17	1.01	Goodness-of-fit measure:				
	3	80	78.85	0.24	0.28	77.88	0.21	0.58					
	4	420	411.54	0.43	0.34	409.43	0.41	1.79					
	5	120	118.44	0.22	0.29	117.25	0.18	0.69					
	6	320	313.95	0.38	0.32	312.12	0.22	1.38					
	7	30	30.19	0.16	0.28	29.51	0.14	0.45					
	8	370	362.49	0.31	0.33	360.56	0.40	1.58					
	9	170	167.31	0.27	0.29	165.97	0.16	0.85					
	10	500	490.22	0.34	0.36	487.85	0.33	2.16					
	11	270	265.30	0.20	0.31	263.63	0.20	1.19					
	12	0	0.13	0.17	0.28	-0.58	0.09	0.37					
3 03/03/04 (C0303009)	1	0	0.05	0.18	0.28	-0.58	0.09	0.37	0.9964	0.0020	-0.66	0.27	-3.08E-04
	2	220	215.96	0.29	0.30	214.55	0.21	1.01	Goodness-of-fit measure:				
	3	80	78.93	0.17	0.28	77.84	0.18	0.58					
	4	420	411.51	0.57	0.34	409.44	0.43	1.79					
	5	120	118.53	0.23	0.29	117.34	0.24	0.69					
	6	320	313.93	0.22	0.32	312.15	0.25	1.38					
	7	30	30.30	0.24	0.28	29.55	0.24	0.45					
	8	370	362.46	0.45	0.33	360.61	0.30	1.58					
	9	170	167.32	0.26	0.29	165.95	0.23	0.85					
	10	500	489.92	0.24	0.36	487.79	0.37	2.16					
	11	270	265.25	0.24	0.31	263.71	0.24	1.19					
	12	0	0.07	0.14	0.28	-0.54	0.19	0.37					

Comparison at the BIPM: INRIM O3-SRP2 versus BIPM-SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			INRIM O3-SRP			INRIM O3-SRP vs SRP27				
			x_{SRP27}	s_{SRP27}	$u(x_{\text{SRP27}})$	x_{NS}	s_{NS}	$u(x_{\text{NS}})$	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$	$u(b_{\text{NS,SRP27}})$	cov
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol			nmol/mol	nmol/mol	
1 01/24/05 (c0124002)	1	0	0.25	0.18	0.28	0.00	0.05	0.19	0.9931	0.0007	-0.28	0.16	-8.52E-05
	2	220	218.62	0.24	0.30	216.97	0.11	0.21					
	3	80	80.88	0.20	0.28	79.97	0.11	0.19					
	4	420	418.85	0.14	0.34	415.63	0.11	0.26					
	5	120	117.60	0.26	0.29	116.26	0.18	0.20					
	6	320	320.99	0.20	0.32	318.41	0.14	0.23					
	7	30	31.68	0.15	0.28	31.22	0.13	0.19					
	8	370	369.81	0.35	0.33	367.03	0.12	0.25					
	9	170	168.18	0.21	0.29	166.79	0.09	0.20					
	10	500	500.54	0.18	0.36	496.91	0.18	0.29					
	11	270	268.26	0.32	0.31	266.17	0.13	0.22					
	12	0	0.16	0.19	0.28	-0.04	0.09	0.19					
2 01/24/05 (c0124004)	1	0	0.31	0.12	0.28	-0.07	0.15	0.19	0.9931	0.0007	-0.29	0.16	-8.52E-05
	2	220	218.89	0.35	0.30	217.16	0.13	0.21					
	3	80	81.11	0.35	0.28	80.22	0.19	0.19					
	4	420	418.95	0.30	0.34	415.92	0.15	0.26					
	5	120	117.34	0.19	0.29	116.20	0.15	0.20					
	6	320	321.11	0.21	0.32	318.65	0.08	0.23					
	7	30	31.45	0.12	0.28	30.98	0.11	0.19					
	8	370	369.78	0.26	0.33	366.79	0.12	0.25					
	9	170	168.39	0.22	0.29	166.85	0.12	0.20					
	10	500	500.55	0.20	0.36	496.81	0.22	0.29					
	11	270	268.41	0.13	0.31	266.17	0.18	0.22					
	12	0	0.25	0.17	0.28	0.11	0.09	0.19					
3 01/24/05 (c0124005)	1	0	0.20	0.14	0.28	-0.02	0.07	0.19	0.9930	0.0007	-0.28	0.16	-8.52E-05
	2	220	218.80	0.16	0.30	216.98	0.15	0.21					
	3	80	81.07	0.13	0.28	80.16	0.16	0.19					
	4	420	418.76	0.26	0.34	415.57	0.14	0.26					
	5	120	116.94	0.21	0.29	115.93	0.14	0.20					
	6	320	320.85	0.24	0.32	318.35	0.12	0.23					
	7	30	31.74	0.14	0.28	31.20	0.14	0.19					
	8	370	369.94	0.22	0.33	367.03	0.11	0.25					
	9	170	168.47	0.18	0.29	166.94	0.21	0.20					
	10	500	500.55	0.30	0.36	496.89	0.13	0.29					
	11	270	268.41	0.18	0.31	266.19	0.11	0.22					
	12	0	0.30	0.20	0.28	0.05	0.11	0.19					

Comparison at the BIPM: INRIM O3-SRP2 (corrected) versus BIPM-SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			INRIM O3-SRP (corrected)			INRIM O3-SRP vs SRP27					
			x_{SRP27}	s_{SRP27}	$u(x_{\text{SRP27}})$	x_{NS}	s_{NS}	$u(x_{\text{NS}})$	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$	$u(b_{\text{NS,SRP27}})$	cov	
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol			nmol/mol	nmol/mol		
1 01/24/05 (c0124002)	1	0	0.25	0.18	0.28	Goodness-of-fit measure: 0.4	0.00	0.05	0.63	0.9969	0.0016	-0.26	0.19	-1.69E-04
	2	220	218.62	0.24	0.30		217.83	0.11	0.98					
	3	80	80.88	0.20	0.28		80.29	0.11	0.69					
	4	420	418.85	0.14	0.34		417.28	0.11	1.56					
	5	120	117.60	0.26	0.29		116.72	0.17	0.75					
	6	320	320.99	0.20	0.32		319.68	0.14	1.26					
	7	30	31.68	0.15	0.28		31.35	0.14	0.64					
	8	370	369.81	0.35	0.33		368.50	0.11	1.41					
	9	170	168.18	0.21	0.29		167.45	0.10	0.85					
	10	500	500.54	0.18	0.36		498.89	0.18	1.82					
	11	270	268.26	0.32	0.31		267.22	0.12	1.11					
	12	0	0.16	0.19	0.28		-0.04	0.09	0.63					

Comparison at the BIPM: KRISS O3-SRP versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			KRISS O3-SRP			KRISS O3-SRP vs SRP27				
			x_{SRP27}	s_{SRP27}	$u(x_{\text{SRP27}})$	x_{NS}	s_{NS}	$u(x_{\text{NS}})$	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$	$u(b_{\text{NS,SRP27}})$	Cov
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol			nmol/mol	nmol/mol	
1 12/02/03 c1202001	1	0	-0.04	0.28	0.28	-0.07	0.38	0.12	0.9952	0.0009	-0.12	0.16	-9.23E-05
	2	220	223.99	0.24	0.30	222.85	0.55	0.68	Goodness-of-fit measure:	0.56			
	3	80	79.31	0.22	0.28	78.93	0.36	0.26					
	4	420	421.94	0.13	0.34	419.81	0.46	1.25					
	5	120	122.57	0.17	0.29	121.69	0.53	0.40					
	6	320	323.33	0.19	0.32	321.29	0.32	0.37					
	7	30	29.08	0.17	0.28	28.71	0.43	0.16					
	8	370	371.44	0.12	0.33	369.72	0.32	0.10					
	9	170	170.97	0.25	0.29	169.93	0.38	0.52					
	10	500	502.02	0.28	0.36	499.00	0.55	1.48					
	11	270	271.76	0.23	0.31	270.47	0.59	0.82					
	12	0	0.00	0.09	0.28	-0.13	0.29	0.09					
2 12/02/03 c1202003	1	0	-0.06	0.28	0.28	0.24	0.34	0.11	Goodness-of-fit measure:	0.94			
	2	220	224.44	0.42	0.30	222.98	0.64	0.69					
	3	80	79.55	0.18	0.28	79.31	0.98	0.39					
	4	420	422.01	0.27	0.34	420.11	0.31	1.60					
	5	120	122.99	0.20	0.29	121.97	0.35	0.38					
	6	320	323.54	0.27	0.32	321.54	0.46	0.96					
	7	30	28.90	0.19	0.28	28.77	0.38	0.15					
	8	370	372.06	0.14	0.33	369.89	0.22	1.09					
	9	170	171.65	0.25	0.29	170.60	0.49	0.53					
	10	500	502.55	0.22	0.36	500.10	0.45	1.48					
	11	270	272.49	0.28	0.31	271.07	0.28	0.81					
	12	0	0.15	0.17	0.28	-0.14	0.29	0.09					
3 12/02/03 c1202006	1	0	0.14	0.17	0.28	-0.26	0.56	0.18	Goodness-of-fit measure:	1.13			
	2	220	224.72	0.16	0.30	223.50	0.43	0.67					
	3	80	79.82	0.26	0.28	79.83	0.49	0.28					
	4	420	422.15	0.35	0.34	419.98	0.64	1.25					
	5	120	122.94	0.20	0.29	122.22	0.32	0.38					
	6	320	323.77	0.14	0.32	322.37	0.35	0.96					
	7	30	28.85	0.25	0.28	28.81	0.02	0.09					
	8	370	372.25	0.25	0.33	370.73	0.32	1.10					
	9	170	171.72	0.22	0.29	171.42	0.35	0.53					
	10	500	502.96	0.25	0.36	500.47	0.82	0.63					
	11	270	272.69	0.18	0.31	271.42	0.55	0.82					
	12	0	0.00	0.24	0.28	0.40	0.35	0.35					

Comparison at the BIPM: METAS SRP18 versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			METAS SRP18			SRP18 vs SRP27				
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{\text{SRP27}})$ nmol/mol	x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{\text{NS}})$ nmol/mol	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$ nmol/mol	$u(b_{\text{NS,SRP27}})$ nmol/mol	cov
1 18/11/03 (c1118003)	1	0	-0.04	0.23	0.28				1.0034	0.0008	0.11	0.19	-1.14E-04
	2	220	223.89	0.14	0.30								
	3	80	78.76	0.19	0.28								
	4	420	420.82	0.26	0.34								
	5	120	122.32	0.15	0.29								
	6	320	322.75	0.18	0.32								
	7	30	28.79	0.16	0.28								
	8	370	371.16	0.18	0.33								
	9	170	171.00	0.28	0.29								
	10	500	501.03	0.15	0.36								
	11	270	271.51	0.18	0.31								
	12	0	-0.11	0.20	0.28								
2 18/11/03 (c1118004)	1	0	0.00	0.24	0.28				1.0033	0.0008	0.05	0.19	-1.14E-04
	2	220	224.14	0.23	0.30								
	3	80	79.20	0.23	0.28								
	4	420	420.98	0.27	0.34								
	5	120	122.64	0.14	0.29								
	6	320	322.85	0.20	0.32								
	7	30	28.80	0.22	0.28								
	8	370	371.37	0.22	0.33								
	9	170	171.23	0.19	0.29								
	10	500	501.30	0.22	0.36								
	11	270	271.76	0.23	0.31								
	12	0	0.11	0.14	0.28								
3 18/11/03 (c1118005)	1	0	-0.02	0.37	0.28				1.0034	0.0008	0.07	0.19	-1.14E-04
	2	220	224.36	0.23	0.30								
	3	80	79.63	0.20	0.28								
	4	420	421.05	0.24	0.34								
	5	120	122.53	0.21	0.29								
	6	320	322.76	0.20	0.32								
	7	30	29.31	0.15	0.28								
	8	370	371.51	0.22	0.33								
	9	170	171.35	0.21	0.29								
	10	500	501.89	0.26	0.36								
	11	270	271.71	0.21	0.31								
	12	0	-0.12	0.14	0.28								

Comparison at the BIPM: NIES SRP35 versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			NIES SRP35			SRP35 vs SRP27				
			x_{SRP27}	s_{SRP27}	$u(x_{\text{SRP27}})$	x_{NS}	s_{NS}	$u(x_{\text{NS}})$	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$	$u(b_{\text{NS,SRP27}})$	cov
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol			nmol/mol	nmol/mol	
1 07/27/04 (c0727001)	1	0	0.16	0.31	0.28	0.14	0.19	0.28	1.0000	0.0008	-0.13	0.19	-1.14E-04
	2	220	223.71	0.29	0.30	223.32	0.17	0.30					
	3	80	80.60	0.20	0.28	80.44	0.16	0.28	Goodness-of-fit measure: 0.43				
	4	420	424.58	0.16	0.34	424.37	0.25	0.34					
	5	120	121.66	0.27	0.29	121.65	0.18	0.29					
	6	320	321.85	0.27	0.32	321.76	0.14	0.32					
	7	30	30.84	0.20	0.28	30.61	0.18	0.28					
	8	370	375.33	0.19	0.33	375.09	0.21	0.33					
	9	170	168.26	0.20	0.29	168.14	0.14	0.29					
	10	500	505.35	0.16	0.37	505.33	0.16	0.37					
	11	270	268.25	0.20	0.31	268.32	0.16	0.31					
	12	0	0.24	0.14	0.28	0.08	0.22	0.28					
2 07/27/04 (c0727005)	1	0	0.23	0.25	0.28	0.01	0.19	0.28	1.0004	0.0008	-0.19	0.19	-1.14E-04
	2	220	224.04	0.35	0.30	224.02	0.24	0.30					
	3	80	80.63	0.13	0.28	80.40	0.26	0.28	Goodness-of-fit measure: 0.32				
	4	420	425.09	0.27	0.34	425.08	0.23	0.34					
	5	120	122.32	0.29	0.29	122.06	0.26	0.29					
	6	320	322.28	0.19	0.32	322.12	0.29	0.32					
	7	30	30.75	0.31	0.28	30.51	0.25	0.28					
	8	370	375.48	0.10	0.33	375.54	0.16	0.33					
	9	170	168.64	0.31	0.29	168.44	0.19	0.29					
	10	500	505.77	0.32	0.37	505.68	0.33	0.37					
	11	270	268.90	0.16	0.31	268.92	0.12	0.31					
	12	0	0.15	0.13	0.28	0.14	0.18	0.28					
3 07/27/04 (c0727009)	1	0	0.15	0.20	0.28	0.09	0.16	0.28	1.0004	0.0008	-0.17	0.19	-1.14E-04
	2	220	224.36	0.18	0.30	224.32	0.30	0.30					
	3	80	80.93	0.13	0.28	80.60	0.27	0.28	Goodness-of-fit measure: 0.38				
	4	420	425.85	0.17	0.34	425.73	0.28	0.34					
	5	120	122.54	0.32	0.29	122.49	0.21	0.29					
	6	320	322.75	0.23	0.32	322.65	0.17	0.32					
	7	30	30.76	0.24	0.28	30.56	0.28	0.28					
	8	370	376.50	0.28	0.33	376.28	0.54	0.33					
	9	170	168.76	0.19	0.29	168.73	0.14	0.29					
	10	500	507.22	0.12	0.37	507.52	0.23	0.37					
	11	270	269.46	0.27	0.31	269.37	0.22	0.31					
	12	0	0.26	0.17	0.28	0.11	0.16	0.28					

Comparison at the BIPM: NILU API M400E versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			NILU API M400E			API M400E vs SRP17				
			x_{SRP27}	s_{SRP27}	$u(x_{\text{SRP27}})$	x_{NS}	s_{NS}	$u(x_{\text{NS}})$	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$	$u(b_{\text{NS,SRP27}})$	cov
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol			nmol/mol	nmol/mol	
c12030016	1	0	0.22	0.28	0.28	0.09	0.21	0.25	1.0015	0.0022	-0.24	0.22	-2.46E-04
	2	220	220.64	0.26	0.30	220.85	0.23	1.19					
	3	80	81.70	0.24	0.28	81.29	0.19	0.50	Goodness-of-fit measure:				
	4	420	423.12	0.14	0.34	423.45	0.12	2.25			0.446		
	5	120	118.10	0.17	0.29	118.05	0.21	0.67					
	6	320	324.28	0.31	0.32	324.42	0.14	1.73					
	7	30	31.42	0.20	0.28	31.12	0.20	0.30					
	8	370	373.79	0.33	0.33	374.49	0.35	2.00					
	9	170	169.46	0.28	0.29	169.59	0.10	0.93					
	10	500	505.99	0.21	0.37	506.50	0.27	2.69					
	11	270	270.93	0.31	0.31	271.33	0.12	1.46					
	12	0	0.17	0.17	0.28	-0.01	0.15	0.25					
c12030026	1	0	0.29	0.13	0.28	-0.08	0.09	0.25	1.0015	0.0022	-0.18	0.22	-2.46E-04
	2	220	220.93	0.26	0.30	220.97	0.37	1.19					
	3	80	81.72	0.21	0.28	81.68	0.18	0.50	Goodness-of-fit measure:				
	4	420	423.26	0.31	0.34	423.85	0.07	2.26			0.401		
	5	120	118.25	0.21	0.29	118.07	0.12	0.67					
	6	320	324.29	0.23	0.32	324.46	0.18	1.73					
	7	30	31.20	0.22	0.28	31.29	0.15	0.30					
	8	370	373.51	0.21	0.33	373.85	0.31	1.99					
	9	170	169.83	0.16	0.29	169.92	0.21	0.93					
	10	500	506.51	0.27	0.37	507.08	0.33	2.69					
	11	270	271.06	0.29	0.31	271.42	0.15	1.46					
	12	0	0.20	0.14	0.28	0.06	0.25	0.25					
c12030029	1	0	0.26	0.40	0.28	-0.02	0.12	0.25	1.0014	0.0022	-0.18	0.22	-2.46E-04
	2	220	220.65	0.18	0.30	220.93	0.17	1.19					
	3	80	81.54	0.25	0.28	81.50	0.22	0.50	Goodness-of-fit measure:				
	4	420	423.12	0.16	0.34	423.72	0.18	2.25			0.283		
	5	120	118.22	0.17	0.29	118.08	0.17	0.67					
	6	320	324.62	0.28	0.32	324.59	0.23	1.73					
	7	30	31.39	0.15	0.28	31.20	0.11	0.30					
	8	370	373.89	0.17	0.33	374.11	0.14	1.99					
	9	170	169.86	0.26	0.29	169.93	0.25	0.93					
	10	500	506.02	0.24	0.37	506.74	0.13	2.69					
	11	270	271.17	0.15	0.31	271.46	0.17	1.46					
	12	0	0.21	0.17	0.28	0.17	0.13	0.25					

Comparison at the BIPM: NMi-VSL UMEG26 versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			NMi-VSL UMEG26			#NAME?				
			x_{SRP27}	s_{SRP27}	$u(x_{\text{SRP27}})$	x_{NS}	s_{NS}	$u(x_{\text{NS}})$	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$	$u(b_{\text{NS,SRP27}})$	cov
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol			nmol/mol	nmol/mol	
1 01/11/05 c0111001	1	0	0.35	0.42	0.28	0.00	0.57	0.30	1.0007	0.0013	-0.26	0.22	-1.84E-04
	2	220	218.38	0.32	0.30	218.40	0.51	0.57					
	3	80	81.06	0.22	0.28	80.71	0.34	0.35	Goodness-of-fit measure:				
	4	420	418.36	0.23	0.34	418.34	0.36	0.97					
	5	120	117.05	0.20	0.29	117.05	0.42	0.40					
	6	320	320.71	0.23	0.32	320.53	0.39	0.77					
	7	30	31.75	0.16	0.28	31.67	0.40	0.31					
	8	370	369.28	0.28	0.33	369.53	0.49	0.87					
	9	170	167.91	0.25	0.29	167.86	0.53	0.48					
	10	500	499.66	0.28	0.36	499.57	0.47	1.15					
	11	270	267.74	0.39	0.31	267.47	0.61	0.67					
	12	0	0.18	0.18	0.28	-0.14	0.44	0.30					
2 01/11/05 c0112001	1	0	0.31	0.21	0.28	0.28	0.49	0.30	1.0000	0.0013	-0.15	0.22	-1.83E-04
	2	220	218.56	0.20	0.30	218.49	0.47	0.57					
	3	80	80.92	0.24	0.28	80.75	0.49	0.35	Goodness-of-fit measure:				
	4	420	418.56	0.33	0.34	418.89	0.34	0.97					
	5	120	117.08	0.41	0.29	116.77	0.40	0.40					
	6	320	320.89	0.22	0.32	320.62	0.36	0.77					
	7	30	31.33	0.22	0.28	31.23	0.53	0.31					
	8	370	369.50	0.26	0.33	369.16	0.44	0.87					
	9	170	167.80	0.21	0.29	167.46	0.30	0.48					
	10	500	500.53	0.28	0.36	500.24	0.52	1.15					
	11	270	267.95	0.27	0.31	267.96	0.44	0.67					
	12	0	0.21	0.10	0.28	0.00	0.33	0.30					
3 01/11/05 c0112002	1	0	0.27	0.37	0.28	0.00	0.57	0.30	1.0011	0.0013	-0.21	0.22	-1.84E-04
	2	220	218.69	0.52	0.30	218.81	0.66	0.57					
	3	80	80.67	0.30	0.28	80.78	0.49	0.35	Goodness-of-fit measure:				
	4	420	418.65	0.31	0.34	419.08	0.48	0.97					
	5	120	117.25	0.25	0.29	116.83	0.46	0.40					
	6	320	320.67	0.14	0.32	320.99	0.51	0.77					
	7	30	31.32	0.15	0.28	31.32	0.36	0.31					
	8	370	369.11	0.24	0.33	369.39	0.34	0.87					
	9	170	167.82	0.20	0.29	167.53	0.35	0.48					
	10	500	499.85	0.28	0.36	499.91	0.76	1.15					
	11	270	267.90	0.18	0.31	268.09	0.53	0.67					
	12	0	0.27	0.18	0.28	0.00	0.47	0.30					

Comparison at the BIPM: NPL SRP20 versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			NPL SRP20			SRP20 vs SRP27				
			x_{SRP27}	s_{SRP27}	$u(x_{\text{SRP27}})$	x_{NS}	s_{NS}	$u(x_{\text{NS}})$	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$	$u(b_{\text{NS,SRP27}})$	cov
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol			nmol/mol	nmol/mol	
1 05/26/04 (c0526002)	1	0	0.25	0.36	0.28	0.15	0.27	0.14	1.0023	0.0008	-0.05	0.16	-8.62E-05
	2	220	219.98	0.16	0.30	220.25	0.31	0.24					
	3	80	80.80	0.15	0.28	81.14	0.33	0.16	Goodness-of-fit measure:				
	4	420	409.39	0.20	0.34	410.16	0.29	0.38	0.87				
	5	120	117.59	0.28	0.29	117.48	0.11	0.17					
	6	320	310.03	0.22	0.31	310.56	0.23	0.30					
	7	30	26.19	0.09	0.28	26.12	0.26	0.14					
	8	370	355.70	0.20	0.32	356.42	0.23	0.34					
	9	170	164.88	0.17	0.29	165.45	0.22	0.20					
	10	500	487.03	0.36	0.36	488.36	0.21	0.44					
	11	270	265.81	0.16	0.31	266.64	0.27	0.27					
	12	0	0.19	0.20	0.28	0.27	0.25	0.14					
2 05/26/04 (c0526003)	1	0	0.07	0.40	0.28	0.03	0.24	0.14	1.0026	0.0008	-0.19	0.16	-8.62E-05
	2	220	220.36	0.24	0.30	220.62	0.19	0.24					
	3	80	80.86	0.18	0.28	80.50	0.21	0.16	Goodness-of-fit measure:				
	4	420	409.42	0.24	0.34	410.10	0.12	0.38	1.05				
	5	120	117.51	0.28	0.29	117.47	0.24	0.17					
	6	320	310.36	0.19	0.31	311.41	0.10	0.30					
	7	30	26.09	0.19	0.28	26.33	0.29	0.14					
	8	370	355.67	0.30	0.32	356.68	0.14	0.34					
	9	170	164.86	0.18	0.29	164.92	0.19	0.20					
	10	500	486.95	0.28	0.36	488.05	0.14	0.44					
	11	270	266.01	0.18	0.31	266.28	0.19	0.27					
	12	0	0.07	0.23	0.28	-0.17	0.17	0.14					
3 05/26/04 (c0526005)	1	0	0.12	0.23	0.28	-0.15	0.23	0.14	1.0030	0.0008	-0.09	0.16	-8.63E-05
	2	220	220.89	0.18	0.30	221.15	0.15	0.24					
	3	80	80.94	0.25	0.28	80.75	0.18	0.16	Goodness-of-fit measure:				
	4	420	409.98	0.33	0.34	410.76	0.14	0.38	1.05				
	5	120	117.77	0.23	0.29	117.96	0.18	0.17					
	6	320	311.10	0.11	0.31	311.79	0.20	0.30					
	7	30	26.45	0.19	0.28	26.51	0.17	0.14					
	8	370	355.98	0.19	0.33	357.21	0.27	0.34					
	9	170	165.10	0.26	0.29	165.70	0.26	0.20					
	10	500	487.73	0.16	0.36	489.35	0.20	0.44					
	11	270	266.12	0.24	0.31	267.16	0.17	0.27					
	12	0	0.14	0.30	0.28	0.42	0.20	0.14					

Comparison at the BIPM: SP Environment SA 42M versus SRP27 results (measured values)

Run/Date	Point number	nominal value nmol/mol	SRP27			SP Environment SA 42M (measured values)			Environment SA 42M vs SRP27				
			x_{SRP27}	s_{SRP27}	$u(x_{SRP27})$	x_{NS}	s_{NS}	$u(x_{NS})$	$a_{NS,SRP27}$	$u(a_{NS,SRP27})$	$b_{NS,SRP27}$	$u(b_{NS,SRP27})$	
05/05/04 c0504006	1	0	-0.08	0.21	0.28	0.18	0.28	0.09	0.9800	0.0006	0.02	0.14	-6.58E-05
	2	220	224.36	0.28	0.30	219.58	0.46	0.15					
	3	80	81.95	0.30	0.28	80.09	0.61	0.19	Goodness-of-fit measure: 1.03				
	4	420	417.17	0.33	0.34	408.76	0.37	0.12					
	5	120	119.98	0.12	0.29	117.26	0.34	0.11					
	6	320	315.85	0.24	0.32	309.57	0.33	0.10					
	7	30	26.68	0.24	0.28	26.16	0.40	0.13					
	8	370	361.64	0.17	0.33	354.28	0.31	0.10					
	9	170	167.48	0.21	0.29	164.20	0.38	0.12					
	10	500	496.60	0.72	0.36	487.08	0.64	0.20					
	11	270	270.36	0.23	0.31	265.22	0.46	0.15					
	12	0	-0.09	0.16	0.28	0.12	0.28	0.09					
05/05/04 c0504007	1	0	0.02	0.36	0.28	0.16	0.16	0.05	0.9805	0.0006	-0.13	0.14	-6.36E-05
	2	220	224.56	0.23	0.30	219.97	0.61	0.19					
	3	80	82.05	0.15	0.28	79.98	0.43	0.14	Goodness-of-fit measure: 1.27				
	4	420	416.82	0.25	0.34	408.49	0.41	0.13					
	5	120	119.75	0.25	0.29	117.24	0.46	0.15					
	6	320	315.88	0.28	0.32	309.39	0.47	0.15					
	7	30	26.61	0.28	0.28	25.46	0.60	0.19					
	8	370	361.67	0.28	0.33	354.47	0.35	0.11					
	9	170	167.61	0.16	0.29	164.12	0.17	0.05					
	10	500	496.17	0.27	0.36	486.61	0.39	0.12					
	11	270	270.68	0.34	0.31	265.53	0.44	0.14					
	12	0	-0.15	0.32	0.28	0.08	0.16	0.05					
05/05/04 c0504008	1	0	0.14	0.27	0.28	0.25	0.37	0.12	0.9805	0.0006	-0.16	0.14	-6.55E-05
	2	220	224.14	0.22	0.30	219.65	0.42	0.13					
	3	80	82.14	0.23	0.28	80.12	0.40	0.13	Goodness-of-fit measure: 1.60				
	4	420	417.02	0.32	0.34	408.46	0.75	0.24					
	5	120	119.99	0.29	0.29	116.94	0.43	0.14					
	6	320	316.19	0.26	0.32	309.70	0.53	0.17					
	7	30	26.46	0.26	0.28	25.89	0.47	0.15					
	8	370	361.64	0.29	0.33	354.20	0.49	0.15					
	9	170	167.37	0.24	0.29	163.96	0.72	0.23					
	10	500	496.34	0.21	0.36	487.12	0.35	0.11					
	11	270	270.57	0.28	0.31	265.23	0.49	0.15					
	12	0	0.00	0.18	0.28	0.09	0.17	0.05					

Comparison at the BIPM: SP Environment SA 42M versus BIPM SRP27 results (corrected values)

Run/Date	Point number	nominal value nmol/mol	SRP27			SP Environment SA 42M (corrected values)			Environment SA 42M vs SRP27				
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{\text{SRP27}})$ nmol/mol	x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{\text{NS}})$ nmol/mol	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$ nmol/mol	$u(b_{\text{NS,SRP27}})$ nmol/mol	cov
05/05/04	1	0	-0.08	0.21	0.28	0.18	0.28	0.37	0.9976	0.0012	0.04	0.24	-2.05E-04
	2	220	224.36	0.28	0.30	223.58	0.46	0.53	Goodness-of-fit measure: 0.55				
	3	80	81.95	0.30	0.28	81.55	0.61	0.42					
	4	420	417.17	0.33	0.34	416.20	0.37	0.83					
	5	120	119.98	0.12	0.29	119.39	0.34	0.44					
	6	320	315.85	0.24	0.32	315.20	0.33	0.65					
	7	30	26.68	0.24	0.28	26.64	0.40	0.40					
	8	370	361.64	0.17	0.33	360.73	0.31	0.71					
	9	170	167.48	0.21	0.29	167.19	0.38	0.51					
	10	500	496.60	0.72	0.36	495.94	0.64	0.98					
	11	270	270.36	0.23	0.31	270.05	0.46	0.58					
	12	0	-0.09	0.16	0.28	0.12	0.28	0.36					
05/05/04	1	0	0.02	0.36	0.28	0.16	0.16	0.36	0.9982	0.0012	-0.14	0.24	-2.03E-04
	2	220	224.56	0.23	0.30	223.97	0.61	0.55	Goodness-of-fit measure: 0.84				
	3	80	82.05	0.15	0.28	81.44	0.43	0.42					
	4	420	416.82	0.25	0.34	415.92	0.41	0.80					
	5	120	119.75	0.25	0.29	119.37	0.46	0.44					
	6	320	315.88	0.28	0.32	315.02	0.47	0.64					
	7	30	26.61	0.28	0.28	25.92	0.60	0.41					
	8	370	361.67	0.28	0.33	360.92	0.35	0.70					
	9	170	167.61	0.16	0.29	167.11	0.17	0.46					
	10	500	496.17	0.27	0.36	495.47	0.39	0.98					
	11	270	270.68	0.34	0.31	270.36	0.44	0.58					
	12	0	-0.15	0.32	0.28	0.08	0.16	0.36					
05/05/04	1	0	0.14	0.27	0.28	0.25	0.37	0.37	0.9979	0.0012	-0.11	0.24	-2.05E-04
	2	220	224.14	0.22	0.30	223.64	0.42	0.53	Goodness-of-fit measure: 0.89				
	3	80	82.14	0.23	0.28	81.58	0.40	0.42					
	4	420	417.02	0.32	0.34	415.90	0.75	0.83					
	5	120	119.99	0.29	0.29	119.07	0.43	0.44					
	6	320	316.19	0.26	0.32	315.33	0.53	0.65					
	7	30	26.46	0.26	0.28	26.36	0.47	0.40					
	8	370	361.64	0.29	0.33	360.64	0.49	0.71					
	9	170	167.37	0.24	0.29	166.95	0.72	0.51					
	10	500	496.34	0.21	0.36	495.99	0.35	0.98					
	11	270	270.57	0.28	0.31	270.06	0.49	0.58					
	12	0	0.00	0.18	0.28	0.09	0.17	0.36					

Comparison at the BIPM: UBA (A) SRP26 versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			UBA (A) SRP26			SRP26 vs SRP27				
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{\text{SRP27}})$ nmol/mol	x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{\text{NS}})$ nmol/mol	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$ nmol/mol	$u(b_{\text{NS,SRP27}})$ nmol/mol	cov
1 03/30/04 (c0330004)	1	0	0.21	0.18	0.28	0.06	0.19	0.28	1.0005	0.0008	-0.06	0.19	-1.16E-04
	2	220	223.83	0.18	0.30	223.89	0.23	0.30	Goodness-of-fit measure: 0.17				
	3	80	81.90	0.21	0.28	81.97	0.14	0.28					
	4	420	416.62	0.26	0.34	416.70	0.23	0.34					
	5	120	119.66	0.29	0.29	119.73	0.17	0.29					
	6	320	315.97	0.29	0.32	316.11	0.20	0.32					
	7	30	26.96	0.16	0.28	26.91	0.24	0.28					
	8	370	361.06	0.27	0.33	361.20	0.29	0.33					
	9	170	167.29	0.21	0.29	167.25	0.18	0.29					
	10	500	494.92	0.27	0.36	495.09	0.29	0.36					
	11	270	270.30	0.38	0.31	270.32	0.24	0.31					
	12	0	0.18	0.18	0.28	0.13	0.20	0.28					
2 03/31/04 (c0330006)	1	0	0.19	0.21	0.28	0.14	0.18	0.28	1.0003	0.0008	-0.02	0.19	-1.16E-04
	2	220	224.35	0.23	0.30	224.47	0.14	0.30	Goodness-of-fit measure: 0.25				
	3	80	82.42	0.22	0.28	82.49	0.46	0.28					
	4	420	416.71	0.22	0.34	416.78	0.26	0.34					
	5	120	119.44	0.19	0.29	119.51	0.23	0.29					
	6	320	315.95	0.21	0.32	316.08	0.24	0.32					
	7	30	26.78	0.25	0.28	26.63	0.15	0.28					
	8	370	361.50	0.25	0.33	361.67	0.22	0.33					
	9	170	167.41	0.27	0.29	167.48	0.19	0.29					
	10	500	495.61	0.25	0.36	495.57	0.22	0.36					
	11	270	270.40	0.37	0.31	270.48	0.19	0.31					
	12	0	0.13	0.27	0.28	0.11	0.19	0.28					
3 03/31/04 (c0330007)	1	0	0.25	0.41	0.28	0.12	0.17	0.28	1.0004	0.0008	-0.09	0.19	-1.16E-04
	2	220	224.62	0.29	0.30	224.61	0.14	0.30	Goodness-of-fit measure: 0.19				
	3	80	82.21	0.16	0.28	82.19	0.31	0.28					
	4	420	416.56	0.34	0.34	416.58	0.20	0.34					
	5	120	119.47	0.29	0.29	119.53	0.17	0.29					
	6	320	315.84	0.14	0.32	315.99	0.20	0.32					
	7	30	26.90	0.18	0.28	26.73	0.22	0.28					
	8	370	361.85	0.18	0.33	361.86	0.23	0.33					
	9	170	167.47	0.28	0.29	167.41	0.26	0.29					
	10	500	495.98	0.35	0.36	496.02	0.29	0.36					
	11	270	270.98	0.14	0.31	270.99	0.22	0.31					
	12	0	0.14	0.19	0.28	0.05	0.19	0.28					

Comparison at the BIPM: UBA (D) SRP29 versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			UBA (D) SRP29							
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{\text{SRP27}})$ nmol/mol	x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{\text{NS}})$ nmol/mol	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$ nmol/mol	$u(b_{\text{NS,SRP27}})$ nmol/mol	cov
1 06/22/04 (c0622002)	1	0	0.03	0.31	0.28	0.06	0.33	0.28	0.9977	0.0008	-0.08	0.19	-1.18E-04
	2	220	219.40	0.21	0.30	218.83	0.21	0.30					
	3	80	80.73	0.13	0.28	80.54	0.19	0.28					
	4	420	407.32	0.25	0.34	406.37	0.18	0.34					
	5	120	117.57	0.19	0.29	117.26	0.18	0.29					
	6	320	309.00	0.27	0.31	308.15	0.29	0.31					
	7	30	26.34	0.17	0.28	26.10	0.22	0.28					
	8	370	353.63	0.25	0.32	352.68	0.18	0.32					
	9	170	164.20	0.14	0.29	163.72	0.28	0.29					
	10	500	484.61	0.37	0.36	483.38	0.22	0.36					
	11	270	264.47	0.16	0.31	263.82	0.15	0.31					
	12	0	0.18	0.28	0.28	0.01	0.23	0.28					
2 06/22/04 (c0622004)	1	0	0.08	0.23	0.28	-0.01	0.21	0.28	0.9976	0.0008	-0.05	0.19	-1.18E-04
	2	220	220.12	0.28	0.30	219.51	0.38	0.30					
	3	80	80.79	0.37	0.28	80.62	0.28	0.28					
	4	420	408.53	0.22	0.34	407.37	0.19	0.34					
	5	120	117.65	0.17	0.29	117.24	0.25	0.29					
	6	320	309.94	0.33	0.31	309.23	0.16	0.31					
	7	30	26.19	0.22	0.28	26.08	0.14	0.28					
	8	370	354.56	0.35	0.32	353.85	0.27	0.32					
	9	170	164.99	0.65	0.29	164.12	0.18	0.29					
	10	500	485.78	0.17	0.36	484.82	0.23	0.36					
	11	270	265.30	0.21	0.31	264.48	0.17	0.31					
	12	0	-0.33	0.82	0.28	-0.08	0.21	0.28					
3 06/22/04 (c0622007)	1	0	-0.24	0.84	0.28	0.12	0.35	0.28	0.9977	0.0008	-0.08	0.19	-1.18E-04
	2	220	220.79	0.21	0.30	220.25	0.26	0.30					
	3	80	81.18	0.23	0.28	80.63	0.25	0.28					
	4	420	410.01	0.25	0.34	409.00	0.20	0.34					
	5	120	118.20	0.23	0.29	117.77	0.21	0.29					
	6	320	311.01	0.33	0.31	310.28	0.15	0.31					
	7	30	26.58	0.21	0.28	26.18	0.22	0.28					
	8	370	355.49	0.31	0.32	354.72	0.23	0.32					
	9	170	165.01	0.29	0.29	164.47	0.23	0.29					
	10	500	487.19	0.29	0.36	485.88	0.20	0.36					
	11	270	266.16	0.17	0.31	265.63	0.27	0.31					
	12	0	0.09	0.25	0.28	0.05	0.20	0.28					

Comparison at the BIPM: VNIIM Dasibi 1003AH versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	SRP27			VNIIM Dasibi 1003AH			DASIBI 1003AH vs SRP27				
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{\text{SRP27}})$ nmol/mol	x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{\text{NS}})$ nmol/mol	$a_{\text{NS,SRP27}}$	$u(a_{\text{NS,SRP27}})$	$b_{\text{NS,SRP27}}$ nmol/mol	$u(b_{\text{NS,SRP27}})$ nmol/mol	cov
02/18/04 c0218004	1	0	0.37	0.39	0.28	-5.05	0.82	0.90	0.9944	0.0032	-5.27	0.50	-1.03E-03
	2	220	218.39	0.27	0.30	212.63	0.69	1.59	Goodness-of-fit measure: 0.53				
	3	80	77.13	0.20	0.28	71.53	0.83	1.01					
	4	420	409.43	0.24	0.34	400.46	0.77	2.59					
	5	120	119.22	0.24	0.29	113.15	1.46	1.15					
	6	320	313.89	0.23	0.32	306.64	0.90	2.08					
	7	30	28.43	0.24	0.28	23.13	0.72	0.92					
	8	370	361.08	0.24	0.33	353.90	0.97	2.33					
	9	170	166.49	0.19	0.29	160.51	1.02	1.34					
	10	500	487.21	0.24	0.36	479.01	0.67	3.04					
	11	270	264.30	0.30	0.31	257.84	0.58	1.82					
	12	0	0.13	0.19	0.28	-5.32	0.95	0.90					
02/18/04 c0218005	1	0	0.17	0.28	0.28	-5.02	0.72	0.90	0.9942	0.0032	-5.10	0.50	-1.03E-03
	2	220	218.50	0.29	0.30	212.37	1.17	1.59	Goodness-of-fit measure: 0.46				
	3	80	77.10	0.26	0.28	71.71	0.64	1.01					
	4	420	409.93	0.23	0.34	401.58	0.71	2.59					
	5	120	119.17	0.23	0.29	113.51	0.87	1.15					
	6	320	314.45	0.24	0.32	307.54	0.79	2.08					
	7	30	28.45	0.23	0.28	22.96	0.64	0.92					
	8	370	361.60	0.31	0.33	353.79	0.71	2.33					
	9	170	166.73	0.30	0.29	160.94	0.46	1.34					
	10	500	488.35	0.30	0.36	479.90	0.93	3.04					
	11	270	264.70	0.23	0.31	258.95	0.51	1.82					
	12	0	0.17	0.14	0.28	-4.97	0.73	0.90					
02/18/04 c0218006	1	0	0.07	0.13	0.28	-5.51	1.34	0.90	0.9947	0.0032	-5.24	0.50	-1.03E-03
	2	220	218.84	0.20	0.30	213.35	1.07	1.59	Goodness-of-fit measure: 0.55				
	3	80	77.42	0.27	0.28	71.96	1.29	1.01					
	4	420	410.36	0.42	0.34	402.19	0.74	2.59					
	5	120	119.25	0.26	0.29	113.28	0.75	1.15					
	6	320	314.73	0.36	0.32	307.70	0.65	2.08					
	7	30	28.25	0.17	0.28	22.90	1.06	0.92					
	8	370	361.69	0.34	0.33	354.05	0.80	2.33					
	9	170	166.94	0.21	0.29	161.57	1.03	1.34					
	10	500	488.49	0.22	0.36	479.51	0.58	3.04					
	11	270	264.86	0.30	0.31	258.25	0.63	1.82					
	12	0	0.30	0.28	0.28	-5.07	0.83	0.90					

Pilot Study CCQM-P28, Ozone at ambient level

Individual results of the comparisons following the protocol B

Page	Participant
2-3	BIPM (GPT)
4-6	ERLAP
7-9	ISCIII
10-12	LNE
13-15	METAS (SRP14)
16-18	NDENW
19-21	NERI
22-23	NIES (GPT)
24-26	NIST

1) Comparison at the BIPM: TEI 49C versus SRP27 results

note : B_Least has been used at that point, in order to calibrate TEI 49C versus SRP27

Run/Date	Point number	nominal value nmol/mol	SRP27			TEI 49C		
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{SRP27})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol
4-janv-05 (c0202009)	1	0	0.51	0.19	0.28	0.15	0.19	0.19
	2	220	218.07	0.25	0.30	216.24	0.25	0.30
	3	80	80.83	0.15	0.28	79.81	0.12	0.14
	4	420	417.33	0.23	0.34	414.17	0.20	0.37
	5	120	116.85	0.23	0.29	115.69	0.16	0.18
	6	320	319.84	0.25	0.32	317.21	0.18	0.30
	7	30	31.53	0.14	0.28	30.96	0.15	0.15
	8	370	368.37	0.23	0.33	365.46	0.16	0.32
	9	170	167.86	0.23	0.29	166.34	0.25	0.28
	10	500	498.76	0.15	0.37	494.96	0.18	0.41
	11	270	267.19	0.20	0.31	264.98	0.19	0.28
	12	0	0.41	0.29	0.28	0.14	0.17	0.17

2) calculation of TEI49C corrected values in the GPT-TEI 49C comparison

calculation performed with B_Least, the absorption cross-section uncertainty is introduced in the TEI 49C

Run/ Date	Point number	TEI 49C			TEI 49C calibrated with SRP27		
		x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	x_T nmol/mol	$u(x_T)$ nmol/mol	$u'(x_T)$ nmol/mol
2-sept-04	1	1032.70	0.25	1.08	1040.30	1.28	7.91
	2	838.75	0.06	0.89	844.96	1.04	6.42
	3	643.53	0.22	0.69	648.37	0.80	4.93
	4	425.61	0.09	0.48	428.94	0.54	3.26
	5	197.47	0.08	0.25	199.20	0.28	1.52

3) calculation of BIPM-GPT and SRP27 comparison

calculation performed with OzonE, including the correlation factor from the absorption cross-section in between the SRP points

Run/ Date	Point number	BIPM GPT			TEI 49C calibrated with SRP27		BIPM GPT vs SRP27						
		x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol			x_T nmol/mol	$u(x_T)$ nmol/mol	a	$u(a)$	b nmol/mol		
2-sept-04	1	1069.00	0.50	3.40			1040.30	7.91	1.0285	0.0082	0.26		
	2	871.22	0.18	2.70			844.96	6.42			1.20		
	3	666.34	0.12	2.04			648.37	4.93			-2.94E-03		
	4	441.53	0.15	1.39			428.94	3.26					
	5	205.14	0.21	0.77			199.20	1.52					
Goodness-of-fit measure													
0.24													

First comparison at ERLAP: ERLAP TEI49CPS versus ERLAP UMEG results

Run/Date	Point number	nominal value nmol/mol	ERLAP UMEG			ERLAP TEI 49CPS-56685			TEI 49CPS vs UMEG				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a_{T,NS}$	$u(a_{T,NS})$	$b_{T,NS}$ nmol/mol	$u(b_{T,NS})$ nmol/mol	$cov(a_{T,NS}, b_{T,NS})$
09/12/03	1	0	0.07	0.52	0.49	0.70	0.13	0.90	0.9996	0.0025	0.44	0.52	
	2	220	213.10	1.70	0.46	213.40	0.52	1.00					
	3	80	77.60	0.84	1.10	77.90	0.28	0.90	Goodness-of-fit measure: 0.41				
	4	420	417.60	1.26	1.45	417.30	0.86	1.20					
	5	120	116.50	0.93	0.44	116.60	0.21	0.90					
	6	320	314.30	1.68	1.35	315.10	0.64	1.05					
	7	30	31.20	0.40	0.55	31.70	0.14	0.90					
	8	370	368.40	1.12	1.15	368.90	0.61	1.15					
	9	170	168.50	0.92	1.00	168.60	0.23	0.95					
	10	500	498.20	2.47	1.10	498.40	0.46	1.30					
	11	270	270.30	1.25	1.75	271.60	0.44	1.05					
	12	0	0.18	0.45	0.46	0.60	0.22	0.90					
09/15/03	1	0	0.00	0.00	0.46	0.70	0.15	0.90	1.0011	0.0025	0.33	0.53	
	2	220	213.50	0.83	0.65	214.50	0.47	1.00					
	3	80	78.00	0.70	0.85	78.30	0.26	0.90	Goodness-of-fit measure: 0.41				
	4	420	419.10	1.19	1.30	418.90	0.94	1.20					
	5	120	116.50	1.32	1.05	116.80	0.16	0.90					
	6	320	316.80	1.26	1.05	317.60	0.55	1.10					
	7	30	32.50	0.73	0.80	32.40	0.22	0.90					
	8	370	371.50	1.70	2.10	372.10	0.77	1.15					
	9	170	171.50	1.65	1.15	171.60	0.33	0.95					
	10	500	499.10	0.88	1.10	500.70	0.41	1.30					
	11	270	276.20	0.75	1.25	276.70	0.48	1.05					
	12	0	0.21	0.48	0.35	0.60	0.22	0.90					
09/16/03	1	0	0.00	0.33	0.36	0.60	0.09	0.90	1.0012	0.0025	0.37	0.56	
	2	220	211.50	1.32	0.70	212.00	0.28	1.00					
	3	80	76.80	1.31	1.65	77.60	0.17	0.90	Goodness-of-fit measure: 0.23				
	4	420	417.00	1.10	0.95	417.70	0.41	1.20					
	5	120	116.10	0.61	0.48	116.40	0.20	0.90					
	6	320	314.60	1.20	0.95	315.70	0.48	1.05					
	7	30	32.10	0.71	1.80	32.00	0.23	0.90					
	8	370	370.30	1.38	1.05	371.20	0.34	1.15					
	9	170	169.60	0.68	1.05	170.00	0.36	0.95					
	10	500	497.10	0.76	1.55	498.30	0.25	1.30					
	11	270	269.10	0.84	0.95	269.60	0.37	1.05					
	12	0	0.21	0.68	0.43	0.60	0.22	0.90					

Comparison at BIPM : ERLAP TEI49CPS versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	BIPM SRP27			ERLAP TEI 49CPS-56685			TEI 49CPS vs UMEG				
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{SRP27})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a_{T,SRP27}$	$u(a_{T,SRP27})$	$b_{T,SRP27}$ nmol/mol	$u(b_{T,SRP27})$ nmol/mol	$cov(a_{T,SRP27}, b_{T,SRP27})$
4 09/23/03	1	0	-0.01	0.23	0.28	0.76	0.11	0.90	0.9955	0.0020	0.78	0.46	
	2	220	223.81	0.44	0.30	223.48	0.26	0.99					
	3	80	83.23	0.15	0.28	83.71	0.19	0.91	Goodness-of-fit measure: 0.16				
	4	420	417.14	0.61	0.34	416.04	0.76	1.19					
	5	120	128.36	0.19	0.29	128.50	0.15	0.92					
	6	320	323.20	0.24	0.32	322.60	0.25	1.08					
	7	30	32.37	0.22	0.28	32.92	0.13	0.89					
	8	370	369.71	0.64	0.33	369.00	0.54	1.13					
	9	170	174.29	0.19	0.29	174.17	0.17	0.95					
	10	500	501.14	0.70	0.36	499.53	0.73	1.30					
	11	270	276.20	0.24	0.31	275.69	0.13	1.03					
	12	0	-0.04	0.23	0.28	0.85	0.15	0.89					
5 09/24/03	1	0	0.11	0.21	0.28	0.81	0.11	0.89	0.9958	0.0020	0.56	0.46	
	2	220	225.21	0.53	0.30	224.56	0.41	0.99					
	3	80	83.53	0.28	0.28	83.76	0.21	0.91	Goodness-of-fit measure: 0.25				
	4	420	420.11	0.64	0.34	418.91	0.65	1.20					
	5	120	128.60	0.14	0.29	128.67	0.13	0.92					
	6	320	324.28	0.22	0.32	323.40	0.21	1.08					
	7	30	32.72	0.21	0.28	33.02	0.20	0.89					
	8	370	370.94	0.46	0.33	370.04	0.55	1.14					
	9	170	174.68	0.14	0.29	174.61	0.18	0.95					
	10	500	503.27	0.82	0.36	501.88	0.73	1.31					
	11	270	276.67	0.13	0.31	276.06	0.22	1.03					
	12	0	0.21	0.21	0.28	0.77	0.19	0.89					
6 09/24/03	1	0	0.11	0.19	0.28	0.86	0.27	0.89	0.9953	0.0020	0.73	0.46	
	2	220	225.24	0.45	0.30	224.69	0.66	0.99					
	3	80	83.53	0.18	0.28	83.92	0.14	0.91	Goodness-of-fit measure: 0.20				
	4	420	420.10	0.76	0.34	418.82	0.91	1.20					
	5	120	128.77	0.18	0.29	128.79	0.21	0.92					
	6	320	324.51	0.29	0.32	323.66	0.25	1.08					
	7	30	32.52	0.25	0.28	33.06	0.15	0.89					
	8	370	371.66	0.44	0.33	370.70	0.55	1.14					
	9	170	174.86	0.17	0.29	174.84	0.15	0.95					
	10	500	504.22	0.78	0.36	502.76	0.72	1.31					
	11	270	277.04	0.29	0.31	276.40	0.27	1.03					
	12	0	0.16	0.13	0.28	0.99	0.19	0.89					

Second comparison at ERLAP: ERLAP TEI49CPS versus ERLAP UMEG results

Run/Date	Point number	nominal value nmol/mol	ERLAP UMEG			ERLAP TEI 49CPS-56685			TEI 49CPS vs UMEG				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{\text{NS}})$ nmol/mol	x_{T} nmol/mol	s_{T} nmol/mol	$u(x_{\text{T}})$ nmol/mol	$a2_{\text{T,NS}}$	$u(a2_{\text{T,NS}})$	$b2_{\text{T,NS}}$ nmol/mol	$u(b2_{\text{T,NS}})$ nmol/mol	$\text{cov}(a2_{\text{T,NS}}, b2_{\text{T,NS}})$
09/30/03	1	0	0.00	0.58	0.50	0.30	0.11	0.89	1.0017	0.0023	0.16	0.53	
	2	270	266.80	1.18	0.82	267.90	0.78	1.03					
	3	500	490.70	1.01	1.01	491.70	0.48	1.29	Goodness-of-fit measure: 0.33				
	4	170	165.70	0.59	0.75	165.90	0.21	0.95					
	5	370	363.50	0.99	0.78	364.00	0.86	1.13					
	6	30	30.70	0.60	0.28	30.90	0.15	0.89					
	7	320	313.70	1.32	0.97	314.50	0.41	1.07					
	8	120	116.80	1.34	1.38	116.50	0.39	0.92					
	9	420	414.00	0.77	0.69	415.00	0.24	1.19					
	10	80	76.00	1.15	1.22	76.20	0.18	0.90					
	11	220	209.60	1.14	0.59	210.00	0.16	0.98					
	12	0	0.10	0.52	0.63	0.40	0.26	0.89					
10/01/03	1	0	0.07	0.40	0.30	0.30	0.11	0.89	1.0008	0.0023	0.21	0.51	
	2	270	266.90	0.78	0.77	267.10	0.21	1.03					
	3	500	492.40	1.26	1.06	493.20	0.54	1.29	Goodness-of-fit measure: 0.64				
	4	170	167.10	0.69	0.45	167.20	0.32	0.95					
	5	370	366.20	1.41	0.70	366.70	0.47	1.13					
	6	30	31.26	1.08	1.13	31.80	0.23	0.89					
	7	320	314.10	0.96	1.00	314.50	0.24	1.07					
	8	120	116.60	0.94	0.43	116.20	0.45	0.92					
	9	420	411.70	0.78	0.66	412.40	0.52	1.19					
	10	80	76.00	0.67	0.41	76.50	0.31	0.90					
	11	220	209.00	1.30	0.54	209.90	0.41	0.98					
	12	0	0.00	0.47	0.56	0.40	0.26	0.89					
10/02/03	1	0	-0.14	0.45	0.50	0.50	0.19	0.89	1.0001	0.0024	0.38	0.52	
	2	270	267.10	1.03	0.62	267.70	0.41	1.03					
	3	500	489.70	1.23	1.40	490.90	0.32	1.29	Goodness-of-fit measure: 0.39				
	4	170	166.20	1.51	0.88	166.10	0.29	0.95					
	5	370	364.60	1.78	1.11	365.20	0.34	1.13					
	6	30	31.16	1.25	0.79	31.90	0.29	0.89					
	7	320	314.70	1.34	1.08	314.90	0.24	1.07					
	8	120	116.70	0.75	0.86	117.00	0.18	0.92					
	9	420	413.00	1.28	0.78	413.80	0.54	1.19					
	10	80	77.20	1.11	0.64	77.10	0.12	0.90					
	11	220	211.10	0.40	0.85	211.90	0.21	0.98					
	12	0	0.00	0.47	0.27	0.50	0.19	0.89					

First comparison at ISCIII : ISCIII TEI49C versus ISCIII SRP22 results

Run/Date	Point number	nominal value nmol/mol	ISCIII SRP22			ISCIII TEI 49C			TEI 49C vs SRP22				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a1_{T,NS}$	$u(a1_{T,NS})$	$b1_{T,NS}$ nmol/mol	$u(b1_{T,NS})$ nmol/mol	$cov(a1_{T,NS}, b1_{T,NS})$
08/25/03	1	0	-0.32	0.20	0.20	0.16	0.13	0.10	0.9924	0.0007	0.36	0.12	-5.91E-05
	2	220	219.22	0.30	0.34	217.66	0.18	0.11					
	3	80	80.43	0.30	0.22	80.08	0.17	0.10	Goodness-of-fit measure: 0.71				
	4	420	420.06	0.40	0.56	417.16	0.36	0.12					
	5	120	122.57	0.20	0.25	121.96	0.18	0.10					
	6	320	321.20	0.20	0.44	319.06	0.09	0.11					
	7	30	29.95	0.30	0.20	30.06	0.14	0.10					
	8	370	377.42	0.30	0.51	375.16	0.13	0.11					
	9	170	172.76	0.30	0.29	172.04	0.23	0.10					
	10	500	504.33	0.30	0.65	501.00	0.21	0.12					
	11	270	265.98	0.20	0.38	264.30	0.23	0.11					
	12	0	-0.12	0.20	0.20	0.23	0.15	0.10					
08/28/03	1	0	-0.12	0.24	0.20	0.10	0.13	0.08	0.9944	0.0007	0.29	0.12	-4.97E-05
	2	220	225.30	0.18	0.34	224.45	0.22	0.09					
	3	80	80.05	0.34	0.22	79.83	0.15	0.08	Goodness-of-fit measure: 0.61				
	4	420	425.12	0.40	0.56	423.18	0.29	0.10					
	5	120	121.20	0.27	0.25	120.68	0.16	0.08					
	6	320	326.32	0.28	0.45	324.68	0.24	0.09					
	7	30	29.77	0.28	0.20	29.88	0.16	0.08					
	8	370	371.23	0.22	0.50	369.32	0.19	0.09					
	9	170	169.70	0.26	0.29	169.22	0.25	0.08					
	10	500	505.47	0.25	0.65	502.81	0.19	0.10					
	11	270	271.74	0.21	0.39	270.41	0.24	0.09					
	12	0	-0.17	0.24	0.20	0.23	0.21	0.08					
08/29/03	1	0	0.02	0.28	0.20	0.32	0.12	0.07	0.9942	0.0007	0.37	0.11	-4.84E-05
	2	220	226.89	0.23	0.34	225.80	0.09	0.08					
	3	80	80.33	0.30	0.22	80.12	0.11	0.07	Goodness-of-fit measure: 0.83				
	4	420	427.43	0.34	0.56	425.43	0.28	0.10					
	5	120	121.96	0.20	0.25	121.39	0.17	0.08					
	6	320	328.07	0.25	0.45	326.43	0.16	0.09					
	7	30	29.79	0.22	0.20	30.08	0.10	0.07					
	8	370	373.41	0.33	0.50	371.58	0.28	0.09					
	9	170	170.89	0.21	0.29	170.41	0.22	0.08					
	10	500	500.68	0.23	0.65	498.28	0.18	0.10					
	11	270	273.86	0.20	0.39	272.81	0.14	0.09					
	12	0	-0.12	0.33	0.20	0.39	0.14	0.07					

Comparison at BIPM : ISCIII TEI49C versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	BIPM SRP27			ISCIII TEI49C			TEI 49C vs SRP27				
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{SRP27})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a_{T,SRP27}$	$u(a_{T,SRP27})$	$b_{T,SRP27}$ nmol/mol	$u(b_{T,SRP27})$ nmol/mol	$cov(a_{T,SRP27}, b_{T,SRP27})$
4 09/10/03	1	0	0.05	0.21	0.28	-0.22	0.13	0.04	1.0004	0.0006	-0.21	0.14	-6.01E-05
	2	220	224.30	0.24	0.30	224.17	0.13	0.04					
	3	80	78.27	0.21	0.28	78.19	0.22	0.07	Goodness-of-fit measure: 0.78				
	4	420	420.19	0.55	0.34	420.07	0.35	0.11					
	5	120	120.22	0.15	0.29	119.82	0.14	0.05					
	6	320	317.22	0.34	0.32	317.15	0.19	0.06					
	7	30	30.90	0.16	0.28	30.70	0.17	0.06					
	8	370	373.30	0.37	0.33	373.25	0.23	0.07					
	9	170	166.52	0.19	0.29	166.31	0.15	0.05					
	10	500	500.01	0.37	0.36	500.08	0.36	0.11					
	11	270	273.74	0.24	0.31	273.71	0.19	0.06					
	12	0	0.02	0.23	0.28	-0.04	0.19	0.06					
5 09/10/03	1	0	0.29	0.20	0.28	-0.17	0.14	0.04	1.0003	0.0006	-0.33	0.14	-6.13E-05
	2	220	224.55	0.14	0.30	224.35	0.15	0.05					
	3	80	78.26	0.19	0.28	77.88	0.20	0.06	Goodness-of-fit measure: 0.76				
	4	420	420.45	0.39	0.34	420.40	0.47	0.15					
	5	120	120.18	0.18	0.29	119.94	0.19	0.06					
	6	320	317.54	0.21	0.32	317.26	0.15	0.05					
	7	30	31.16	0.17	0.28	30.83	0.17	0.05					
	8	370	373.56	0.28	0.33	373.23	0.27	0.09					
	9	170	166.58	0.20	0.29	166.23	0.14	0.05					
	10	500	497.98	0.41	0.36	497.82	0.60	0.19					
	11	270	273.39	0.14	0.31	273.08	0.13	0.04					
	12	0	0.15	0.23	0.28	0.04	0.12	0.04					
6 09/10/03	1	0	0.17	0.22	0.28	-0.11	0.13	0.04	1.0001	0.0006	-0.23	0.14	-6.00E-05
	2	220	224.43	0.20	0.30	224.17	0.20	0.06					
	3	80	77.98	0.19	0.28	77.73	0.14	0.04	Goodness-of-fit measure: 0.54				
	4	420	419.78	0.39	0.34	419.60	0.24	0.08					
	5	120	119.98	0.14	0.29	119.67	0.18	0.06					
	6	320	317.25	0.28	0.32	317.03	0.21	0.07					
	7	30	30.86	0.19	0.28	30.79	0.11	0.04					
	8	370	372.99	0.26	0.33	372.95	0.26	0.08					
	9	170	166.33	0.23	0.29	166.08	0.15	0.05					
	10	500	497.68	0.43	0.36	497.37	0.50	0.16					
	11	270	272.92	0.31	0.31	272.88	0.15	0.05					
	12	0	0.17	0.12	0.28	-0.08	0.12	0.04					

Second comparison at ISCHI : ISCHI TEI 49C vs SRP22 results

Run/Date	Point number	nominal value nmol/mol	ISCHI SRP22			ISCHI TEI 49C			TEI 49C vs SRP22				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a2_{T,NS}$	$u(a2_{T,NS})$	$b2_{T,NS}$ nmol/mol	$u(b2_{T,NS})$ nmol/mol	$cov(a2_{T,NS}, b2_{T,NS})$
09/22/03	1	0	-0.16	0.28	0.20	-0.07	0.11	0.06	0.9988	0.0007	0.10	0.11	-4.97E-05
	2	220	222.40	0.17	0.34	222.06	0.10	0.07	Goodness-of-fit measure: 0.52				
	3	80	80.23	0.43	0.23	80.23	0.15	0.07					
	4	420	425.07	0.80	0.56	424.44	0.21	0.07					
	5	120	126.47	0.49	0.26	126.39	0.16	0.07					
	6	320	324.63	0.50	0.45	324.48	0.16	0.07					
	7	30	34.50	0.23	0.21	34.56	0.12	0.06					
	8	370	375.41	0.52	0.51	374.97	0.15	0.07					
	9	170	170.77	0.30	0.29	170.70	0.08	0.07					
	10	500	506.42	0.45	0.66	506.06	0.12	0.08					
	11	270	264.32	0.39	0.38	264.31	0.14	0.07					
	12	0	-0.27	0.21	0.20	-0.15	0.09	0.06					
09/30/03	1	0	-0.12	0.12	0.20	-0.12	0.13	0.08	0.9990	0.0007	0.00	0.11	-5.18E-05
	2	220	218.33	0.09	0.34	218.06	0.13	0.09	Goodness-of-fit measure: 0.56				
	3	80	78.95	0.16	0.22	78.75	0.08	0.08					
	4	420	427.71	0.30	0.57	427.41	0.23	0.09					
	5	120	112.86	0.18	0.25	112.65	0.14	0.08					
	6	320	318.86	0.13	0.44	318.49	0.18	0.09					
	7	30	33.97	0.08	0.21	33.96	0.17	0.08					
	8	370	368.59	0.21	0.50	368.25	0.14	0.09					
	9	170	167.54	0.21	0.29	167.39	0.24	0.08					
	10	500	506.01	0.26	0.66	505.78	0.23	0.10					
	11	270	259.66	0.17	0.38	259.37	0.24	0.09					
	12	0	-0.26	0.10	0.20	-0.13	0.22	0.08					
10/01/03	1	0	-0.24	0.25	0.20	-0.06	0.10	0.06	0.9991	0.0007	0.01	0.11	-5.01E-05
	2	220	217.79	0.20	0.34	217.64	0.18	0.08	Goodness-of-fit measure: 0.60				
	3	80	78.66	0.30	0.22	78.65	0.17	0.07					
	4	420	416.94	0.32	0.55	416.81	0.30	0.10					
	5	120	123.79	0.23	0.25	123.67	0.13	0.07					
	6	320	318.51	0.25	0.44	318.22	0.18	0.09					
	7	30	33.89	0.23	0.21	33.94	0.08	0.06					
	8	370	368.53	0.22	0.50	368.30	0.21	0.10					
	9	170	167.30	0.27	0.29	167.18	0.18	0.08					
	10	500	506.21	0.32	0.66	505.79	0.29	0.11					
	11	270	259.75	0.29	0.38	259.48	0.17	0.09					
	12	0	-0.14	0.20	0.20	-0.21	0.15	0.06					

First comparison at LNE : LNE TEI49CPS versus SRP24 results

Run/Date	Point number	nominal value nmol/mol	LNE SRP24			LNE TEI 49CPS			TEI 49CPS vs SRP24				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a1_{T,NS}$	$u(a1_{T,NS})$	$b1_{T,NS}$ nmol/mol	$u(b1_{T,NS})$ nmol/mol	$cov(a1_{T,NS}, b1_{T,NS})$
1 01/28/04	1	0	-0.12	0.24	0.29	-0.01	0.22	0.22	1.0150	0.0008	-0.17	0.18	-1.08E-04
	2	220	216.57	0.36	0.32	219.83	0.16	0.16					
	3	80	78.66	0.50	0.29	80.04	0.29	0.29					
	4	420	413.56	0.55	0.39	419.97	0.58	0.58					
	5	120	118.30	0.46	0.30	119.87	0.24	0.24					
	6	320	315.36	0.42	0.35	319.91	0.23	0.23					
	7	30	29.98	0.39	0.29	29.94	0.21	0.21					
	8	370	364.49	0.56	0.37	369.97	0.43	0.43					
	9	170	167.62	0.38	0.31	169.98	0.31	0.31					
	10	500	493.37	0.56	0.42	499.99	0.36	0.36					
	11	270	266.10	0.34	0.34	270.05	0.30	0.30					
	12	0	0.30	0.28	0.29	-0.16	0.15	0.15					
2 01/29/04	1	0	0.14	0.33	0.29	-0.02	0.27	0.27	1.0152	0.0011	-0.04	0.23	-1.81E-04
	2	220	216.25	0.88	0.32	219.80	0.52	0.52					
	3	80	79.20	0.62	0.29	80.12	0.50	0.50					
	4	420	413.95	0.96	0.39	419.98	0.92	0.92					
	5	120	118.21	0.58	0.30	119.97	0.38	0.38					
	6	320	315.15	0.51	0.35	319.92	0.57	0.57					
	7	30	29.46	0.80	0.29	29.86	0.80	0.80					
	8	370	364.50	0.76	0.37	370.06	0.64	0.64					
	9	170	167.69	0.40	0.31	169.97	0.41	0.41					
	10	500	492.38	0.84	0.42	499.80	0.49	0.49					
	11	270	265.77	0.47	0.34	269.95	0.41	0.41					
	12	0	0.15	0.29	0.29	0.34	0.30	0.30					
3 01/30/04	1	0	0.44	0.49	0.29	-0.06	0.31	0.31	1.0165	0.0009	-0.43	0.23	-1.70E-04
	2	220	216.69	0.63	0.32	219.80	0.30	0.30					
	3	80	79.36	0.58	0.29	79.97	0.43	0.43					
	4	420	413.52	0.67	0.39	419.97	0.48	0.48					
	5	120	118.34	0.35	0.30	120.01	0.21	0.21					
	6	320	315.60	0.46	0.35	319.93	0.30	0.30					
	7	30	29.78	0.64	0.29	30.01	0.45	0.45					
	8	370	364.33	0.53	0.37	369.92	0.16	0.16					
	9	170	167.77	0.74	0.31	170.07	0.44	0.44					
	10	500	491.84	0.76	0.42	499.05	0.52	0.52					
	11	270	265.86	0.35	0.34	269.81	0.32	0.32					
	12	0	0.33	0.87	0.29	0.10	0.42	0.42					

Comparison at BIPM : LNE TEI 49CPS versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	BIPM SRP27			LNE TEI 49CPS			TEI 49CPS vs SRP27				
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{SRP27})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a_{T,SRP27}$	$u(a_{T,SRP27})$	$b_{T,SRP27}$ nmol/mol	$u(b_{T,SRP27})$ nmol/mol	$cov(a_{T,SRP27}, b_{T,SRP27})$
4 02/03/04	1	0	-0.07	0.33	0.28	0.23	0.29	0.29	1.0123	0.0008	0.03	0.18	-1.06E-04
	2	220	216.96	0.34	0.30	219.69	0.27	0.27					
	3	80	79.15	0.58	0.28	79.88	0.22	0.22					
	4	420	414.26	0.78	0.34	419.53	0.56	0.56					
	5	120	118.20	0.22	0.29	119.94	0.21	0.21					
	6	320	316.12	0.31	0.32	319.96	0.23	0.23					
	7	30	29.81	0.35	0.28	30.35	0.54	0.54					
	8	370	365.23	0.37	0.33	369.83	0.34	0.34					
	9	170	168.21	0.39	0.29	170.00	0.20	0.20					
	10	500	493.63	0.63	0.36	499.90	0.20	0.20					
	11	270	266.72	0.36	0.31	269.89	0.37	0.37					
	12	0	-0.11	0.26	0.28	-0.06	0.14	0.14					
5 02/04/04	1	0	0.05	0.19	0.28	-0.22	0.37	0.37	1.0120	0.0008	0.06	0.21	-1.41E-04
	2	220	216.99	0.49	0.30	219.66	0.37	0.37					
	3	80	78.65	0.24	0.28	79.82	0.32	0.32					
	4	420	414.92	0.56	0.34	419.73	0.53	0.53					
	5	120	118.32	0.48	0.29	119.96	0.42	0.42					
	6	320	316.01	0.56	0.32	320.00	0.24	0.24					
	7	30	29.59	0.20	0.28	30.07	0.22	0.22					
	8	370	365.54	0.37	0.33	370.02	0.17	0.17					
	9	170	167.96	0.83	0.29	169.96	0.39	0.39					
	10	500	493.84	0.55	0.36	500.00	0.37	0.37					
	11	270	266.91	0.29	0.31	269.84	0.27	0.27					
	12	0	-0.09	0.26	0.28	0.16	0.44	0.44					
6 02/05/04	1	0	0.11	0.26	0.28	-0.02	0.27	0.27	1.0119	0.0008	0.00	0.18	-1.05E-04
	2	220	216.97	0.52	0.30	219.78	0.38	0.38					
	3	80	79.05	0.57	0.28	79.77	0.17	0.17					
	4	420	414.56	0.60	0.34	419.68	0.37	0.37					
	5	120	118.60	0.28	0.29	120.02	0.13	0.13					
	6	320	316.12	0.35	0.32	320.04	0.22	0.22					
	7	30	29.75	0.25	0.28	30.24	0.26	0.26					
	8	370	365.70	0.40	0.33	369.89	0.33	0.33					
	9	170	168.03	0.46	0.29	169.92	0.29	0.29					
	10	500	494.22	0.54	0.36	499.88	0.40	0.40					
	11	270	266.85	0.38	0.31	269.97	0.17	0.17					
	12	0	-0.09	0.19	0.28	0.05	0.22	0.22					

Second comparison at LNE : LNE TEI 49CPS vs SRP24 results

Run/Date	Point number	nominal value nmol/mol	LNE SRP24			LNE TEI 49CPS			TEI 49CPS vs SRP24				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a2_{T,NS}$	$u(a2_{T,NS})$	$b2_{T,NS}$ nmol/mol	$u(b2_{T,NS})$ nmol/mol	$cov(a2_{T,NS}, b2_{T,NS})$
7 02/11/04	1	0	-0.45	0.75	0.29	0.08	0.17	0.17	1.0144	0.0008	0.18	0.18	-1.11E-04
	2	220	216.56	0.33	0.32	219.76	0.18	0.18					
	3	80	79.12	0.81	0.29	80.07	0.22	0.22					
	4	420	413.74	0.64	0.39	419.91	0.24	0.24					
	5	120	118.29	0.72	0.30	119.92	0.26	0.26					
	6	320	315.04	0.64	0.35	320.03	0.25	0.25					
	7	30	29.31	0.71	0.29	30.07	0.23	0.23					
	8	370	364.28	0.63	0.37	370.03	0.17	0.17					
	9	170	167.55	0.81	0.31	170.03	0.38	0.38					
	10	500	492.88	0.58	0.42	499.85	0.37	0.37					
	11	270	266.30	0.58	0.34	270.02	0.40	0.40					
	12	0	0.03	0.40	0.29	0.08	0.35	0.35					
8 02/12/04	1	0	-0.09	0.72	0.29	0.04	0.26	0.26	1.0132	0.0008	0.20	0.19	-1.18E-04
	2	220	216.55	0.64	0.32	219.70	0.17	0.17					
	3	80	79.37	0.39	0.29	79.96	0.46	0.46					
	4	420	414.36	0.82	0.39	419.95	0.30	0.30					
	5	120	117.80	0.55	0.30	119.97	0.50	0.50					
	6	320	315.26	0.56	0.35	320.02	0.22	0.22					
	7	30	29.52	0.53	0.29	30.10	0.16	0.16					
	8	370	365.11	0.60	0.37	369.92	0.24	0.24					
	9	170	167.44	0.51	0.31	169.89	0.27	0.27					
	10	500	493.11	0.75	0.42	499.92	0.36	0.36					
	11	270	266.52	0.62	0.34	270.02	0.16	0.16					
	12	0	-0.17	0.67	0.29	0.21	0.25	0.25					
9 02/13/04	1	0	-0.36	0.18	0.29	-0.23	0.26	0.26	1.0139	0.0010	0.27	0.21	-1.47E-04
	2	220	216.40	0.50	0.32	219.74	0.44	0.44					
	3	80	79.13	0.53	0.29	79.98	0.31	0.31					
	4	420	414.00	0.62	0.39	419.87	0.50	0.50					
	5	120	118.12	0.59	0.30	119.80	0.50	0.50					
	6	320	315.06	0.83	0.35	320.09	0.52	0.52					
	7	30	29.01	0.49	0.29	29.94	0.28	0.28					
	8	370	364.29	0.58	0.37	369.96	0.43	0.43					
	9	170	167.53	0.60	0.31	170.00	0.39	0.39					
	10	500	492.92	0.65	0.42	499.92	0.53	0.53					
	11	270	266.27	0.83	0.34	270.02	0.24	0.24					
	12	0	-0.88	0.86	0.29	-0.07	0.36	0.36					

First comparison at METAS : SRP14 versus SRP18 results

Run/Date	Point number	nominal value nmol/mol	METAS SRP14			METAS SRP18			SRP18 vs SRP14				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{\text{NS}})$ nmol/mol	x_{T} nmol/mol	s_{T} nmol/mol	$u(x_{\text{T}})$ nmol/mol	$a_{1,\text{NS}}$	$u(a_{1,\text{NS}})$	$b_{1,\text{NS}}$ nmol/mol	$u(b_{1,\text{NS}})$ nmol/mol	$\text{cov}(a_{1,\text{NS}}, b_{1,\text{NS}})$
26-juin-03 svh0626.log	1	270	266.06	0.19	0.42	266.45	0.17	0.42	1.0025	0.0007	-0.23	0.25	-1.29E-04
	2	190	192.24	0.15	0.37	192.57	0.30	0.37					
	3	630	634.29	0.23	0.76	635.76	0.26	0.76					
	4	560	562.94	0.19	0.69	564.36	0.27	0.69					
	5	420	415.40	0.28	0.55	416.15	0.25	0.55					
	6	700	703.62	0.25	0.83	704.89	0.36	0.83					
	7	770	771.06	0.22	0.90	772.62	0.25	0.90					
	8	960	962.05	0.26	1.10	964.27	0.33	1.10					
	9	340	340.21	0.25	0.48	340.53	0.27	0.48					
	10	900	900.59	0.40	1.04	902.49	0.49	1.04					
	11	840	837.57	0.26	0.97	839.35	0.29	0.97					
	12	60	62.25	0.25	0.31	62.15	0.19	0.31					
	13	490	489.04	0.18	0.62	490.15	0.31	0.62					
	14	110	113.58	0.23	0.32	113.78	0.28	0.33					
	15	0	-0.07	0.16	0.30	-0.37	0.37	0.30					
26-juin-03 svi0626.log	1	630	633.50	0.40	0.76	634.88	0.75	0.76	1.0026	0.0007	-0.28	0.25	-1.30E-04
	2	340	339.75	0.24	0.48	340.37	0.32	0.48					
	3	110	113.79	0.21	0.33	113.65	0.22	0.33					
	4	700	701.83	0.47	0.83	703.36	0.53	0.83					
	5	270	266.56	0.26	0.42	267.01	0.36	0.42					
	6	900	899.21	0.37	1.03	901.30	0.49	1.04					
	7	940	836.09	0.23	0.97	838.06	0.31	0.97					
	8	60	62.24	0.18	0.31	62.16	0.29	0.31					
	9	490	488.48	0.22	0.62	489.70	0.34	0.62					
	10	400	414.68	0.26	0.55	415.54	0.19	0.55					
	11	190	192.81	0.21	0.37	192.75	0.32	0.37					
	12	560	561.30	0.25	0.69	562.36	0.43	0.69					
	13	960	958.87	0.44	1.10	960.96	0.32	1.10					
	14	770	769.37	0.25	0.90	771.13	0.26	0.90					
	15	0	-0.04	0.10	0.30	-0.15	0.29	0.30					
27-juin-03 svj0627.log	1	20	16.86	0.15	0.30	16.51	0.29	0.30	1.0022	0.0011	-0.35	0.21	-1.84E-04
	2	130	127.55	0.18	0.33	127.46	0.24	0.33					
	3	220	220.31	0.16	0.39	220.37	0.30	0.39					
	4	250	250.40	0.23	0.41	250.71	0.27	0.41					
	5	40	36.99	0.19	0.30	36.55	0.19	0.30					
	6	370	368.15	0.30	0.50	368.63	0.35	0.50					
	7	400	397.92	0.19	0.53	398.49	0.21	0.53					
	8	280	280.71	0.15	0.43	281.17	0.14	0.43					
	9	190	190.49	0.16	0.37	190.66	0.25	0.37					
	10	310	310.28	0.18	0.45	310.49	0.16	0.45					
	11	60	64.04	0.17	0.31	63.81	0.39	0.31					
	12	340	339.25	0.25	0.48	339.53	0.28	0.48					
	13	160	159.03	0.20	0.35	159.07	0.15	0.35					
	14	100	95.40	0.15	0.32	95.29	0.20	0.32					
	15	0	0.03	0.13	0.30	-0.15	0.45	0.30					

Comparison at BIPM : METAS SRP18 versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	BIPM SRP27			METAS SRP18			SRP18 vs SRP27			
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{SRP27})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a_{T,SRP27}$	$u(a_{T,SRP27})$	$b_{T,SRP27}$ nmol/mol	$u(b_{T,SRP27})$ nmol/mol
1 18/11/03 (c1118003)	1	0	-0.04	0.23	0.28	0.01	0.16	0.30	Goodness-of-fit measure: 0.2385	0.19		
	2	220	223.89	0.14	0.30	224.90	0.45	0.39				
	3	80	78.76	0.19	0.28	79.13	0.29	0.31				
	4	420	420.82	0.26	0.34	422.37	0.18	0.55				
	5	120	122.32	0.15	0.29	122.86	0.25	0.33				
	6	320	322.75	0.18	0.32	323.89	0.23	0.47				
	7	30	28.79	0.16	0.28	28.95	0.22	0.30				
	8	370	371.16	0.18	0.33	372.60	0.28	0.51				
	9	170	171.00	0.28	0.29	171.63	0.16	0.35				
	10	500	501.03	0.15	0.36	502.84	0.33	0.63				
	11	270	271.51	0.18	0.31	272.39	0.18	0.42				
	12	0	-0.11	0.20	0.28	0.13	0.16	0.30				
2 18/11/03 (c1118004)	1	0	0.00	0.24	0.28	-0.12	0.34	0.30	Goodness-of-fit measure: 0.3628	0.19		
	2	220	224.14	0.23	0.30	224.91	0.36	0.39				
	3	80	79.20	0.23	0.28	79.62	0.22	0.31				
	4	420	420.98	0.27	0.34	422.24	0.42	0.55				
	5	120	122.64	0.14	0.29	122.98	0.16	0.33				
	6	320	322.85	0.20	0.32	324.20	0.21	0.47				
	7	30	28.80	0.22	0.28	28.99	0.24	0.30				
	8	370	371.37	0.22	0.33	372.70	0.29	0.51				
	9	170	171.23	0.19	0.29	171.97	0.30	0.35				
	10	500	501.30	0.22	0.36	503.05	0.27	0.63				
	11	270	271.76	0.23	0.31	272.51	0.18	0.42				
	12	0	0.11	0.14	0.28	0.25	0.46	0.30				
3 18/11/03 (c1118005)	1	0	-0.02	0.37	0.28	-0.01	0.27	0.30	Goodness-of-fit measure: 0.4372	0.19		
	2	220	224.36	0.23	0.30	225.18	0.19	0.39				
	3	80	79.63	0.20	0.28	79.83	0.21	0.31				
	4	420	421.05	0.24	0.34	422.83	0.44	0.55				
	5	120	122.53	0.21	0.29	123.08	0.25	0.33				
	6	320	322.76	0.20	0.32	324.18	0.35	0.47				
	7	30	29.31	0.15	0.28	29.45	0.23	0.30				
	8	370	371.51	0.22	0.33	372.55	0.75	0.51				
	9	170	171.35	0.21	0.29	171.94	0.23	0.35				
	10	500	501.89	0.26	0.36	503.58	0.20	0.63				
	11	270	271.71	0.21	0.31	272.58	0.24	0.42				
	12	0	-0.12	0.14	0.28	0.15	0.19	0.30				

Second comparison at METAS : SRP14 vs SRP18 results

Run/Date	Point number	nominal value nmol/mol	LNE SRP24			LNE TEI 49CPS			TEI 49CPS vs SRP24				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{\text{NS}})$ nmol/mol	x_{T} nmol/mol	s_{T} nmol/mol	$u(x_{\text{T}})$ nmol/mol	$a_{2,\text{T,NS}}$	$u(a_{2,\text{T,NS}})$	$b_{2,\text{T,NS}}$ nmol/mol	$u(b_{2,\text{T,NS}})$ nmol/mol	$\text{cov}(a_{2,\text{T,NS}}, b_{2,\text{T,NS}})$
14_18.log	1	190	189.02	0.20	0.37	188.79	0.24	0.36	Goodness-of-fit measure:	0.4693			
	2	100	96.89	0.19	0.32	96.45	0.29	0.32					
	3	500	495.73	0.25	0.62	496.37	0.32	0.62					
	4	410	409.05	0.16	0.54	409.32	0.37	0.54					
	5	320	320.83	0.20	0.46	321.06	0.42	0.46					
	6	280	276.03	0.24	0.43	276.07	0.17	0.43					
	7	540	538.54	0.30	0.66	539.13	0.34	0.66					
	8	230	233.99	0.24	0.40	233.91	0.22	0.40					
	9	580	580.73	0.24	0.71	581.49	0.33	0.71					
	10	360	364.12	0.22	0.50	364.55	0.35	0.50					
	11	450	452.35	0.17	0.58	452.81	0.23	0.58					
	12	60	64.45	0.17	0.31	64.43	0.49	0.31					
	13	140	144.85	0.15	0.34	144.47	0.67	0.34					
	14	40	37.84	0.15	0.30	37.65	0.21	0.30					
	15	0	0.15	0.16	0.30	-0.34	0.18	0.30					
14_18_2.log	1	280	275.60	0.19	0.43	275.59	0.36	0.43	Goodness-of-fit measure:	0.1953			
	2	450	451.85	0.21	0.58	452.07	0.52	0.58					
	3	260	363.99	0.22	0.50	364.14	0.22	0.50					
	4	410	408.11	0.16	0.54	408.44	0.18	0.54					
	5	540	538.19	0.17	0.66	538.86	0.33	0.66					
	6	580	580.60	0.19	0.71	581.29	0.28	0.71					
	7	150	145.27	0.24	0.34	145.08	0.33	0.34					
	8	70	65.58	0.18	0.31	65.33	0.24	0.31					
	9	40	37.89	0.21	0.30	37.73	0.15	0.30					
	10	230	233.64	0.18	0.40	233.57	0.30	0.39					
	11	190	190.41	0.18	0.37	190.39	0.25	0.37					
	12	490	494.87	0.26	0.62	495.39	0.31	0.62					
	13	320	319.59	0.22	0.46	319.89	0.26	0.46					
	14	100	98.10	0.14	0.32	97.88	0.19	0.32					
	15	0	0.23	0.16	0.30	-0.09	0.30	0.30					
14_18_05.log	1	190	193.97	0.14	0.37	194.35	0.35	0.37	Goodness-of-fit measure:	0.3809			
	2	240	239.24	0.19	0.40	239.61	0.34	0.40					
	3	460	461.39	0.16	0.59	462.32	0.22	0.59					
	4	40	38.77	0.20	0.30	38.58	0.27	0.30					
	5	510	505.37	0.30	0.63	506.60	0.43	0.63					
	6	370	371.25	0.18	0.51	371.59	0.97	0.51					
	7	100	99.97	0.16	0.32	100.02	0.24	0.32					
	8	550	548.37	0.31	0.67	549.67	0.31	0.67					
	9	290	281.69	0.22	0.43	282.19	0.44	0.43					
	10	150	147.69	0.19	0.34	147.76	0.33	0.34					
	11	70	67.41	0.24	0.31	67.53	0.29	0.31					
	12	420	415.67	0.17	0.55	416.53	0.33	0.55					
	13	590	590.99	0.33	0.72	592.26	0.39	0.72					
	14	330	325.62	0.16	0.47	326.19	0.23	0.47					
	15	0	0.19	0.19	0.30	-0.33	0.42	0.30					

First comparison at NDENW : NDENW TEI49C versus UMEG results

Run/Date	Point number	nominal value nmol/mol	NDENW UMEG 18			NDENW TEI 49C			TEI 49C vs UMEG18				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a1_{T,NS}$	$u(a1_{T,NS})$	$b1_{T,NS}$ nmol/mol	$u(b1_{T,NS})$ nmol/mol	$cov(a1_{T,NS}, b1_{T,NS})$
05/07/04	1	0	-0.20	0.40	0.08	0.60	0.60	1.00	1.0066	0.0061	1.63	0.57	-1.84E-03
	2	220	218.40	0.40	0.97	220.80	0.60	3.30					
	3	80	81.00	0.60	0.38	83.10	0.30	1.20	Goodness-of-fit measure: 2.13				
	4	420	414.40	0.50	1.86	419.50	0.60	6.30					
	5	120	117.40	0.80	0.55	119.20	0.20	1.80					
	6	320	327.50	0.50	1.47	331.10	0.00	5.00					
	7	30	27.10	0.40	0.16	31.10	0.30	1.00					
	8	370	365.10	0.50	1.64	368.90	0.50	5.50					
	9	170	167.90	0.50	0.75	170.10	0.20	2.60					
	10	500	496.40	0.60	2.24	500.90	0.50	7.50					
	11	270	269.10	0.50	1.20	272.00	0.10	4.10					
	12	0	-0.30	0.50	0.12	0.40	0.50	1.00					
05/12/04	1	0	-0.50	0.30	0.08	0.90	0.50	1.00	1.0091	0.0062	1.30	0.58	-1.84E-03
	2	220	220.60	0.40	0.99	223.50	0.50	3.40					
	3	80	81.40	0.90	0.42	84.10	0.20	1.30	Goodness-of-fit measure: 0.59				
	4	420	418.30	1.00	1.92	423.30	0.50	6.30					
	5	120	118.20	0.90	0.56	120.60	0.50	1.80					
	6	320	329.20	0.40	1.49	333.00	0.10	5.00					
	7	30	29.30	0.90	0.23	31.20	0.20	1.00					
	8	370	365.80	0.50	1.66	370.10	0.10	5.60					
	9	170	169.00	0.70	0.77	171.10	0.30	2.60					
	10	500	496.90	0.80	2.28	503.20	0.50	7.50					
	11	270	270.30	0.50	1.22	273.60	0.60	4.10					
	12	0	-0.50	0.50	0.11	0.20	0.50	1.00					
05/13/04	1	0	-0.40	0.40	0.09	0.80	0.40	1.00	1.0084	0.0061	1.16	0.57	-1.86E-03
	2	220	219.80	0.60	0.99	222.10	0.17	3.30					
	3	80	80.00	0.50	0.38	83.00	0.18	1.20	Goodness-of-fit measure: 0.88				
	4	420	417.00	0.60	1.89	421.60	0.60	6.30					
	5	120	118.80	0.50	0.54	120.10	0.10	1.80					
	6	320	329.30	0.80	1.49	332.80	0.40	5.00					
	7	30	29.60	0.70	0.21	31.20	0.20	1.00					
	8	370	366.20	0.60	1.65	370.10	0.30	5.60					
	9	170	168.80	0.70	0.77	171.10	0.20	2.60					
	10	500	496.30	0.60	2.26	502.40	0.50	7.50					
	11	270	270.30	0.60	1.21	272.90	0.30	4.10					
	12	0	-0.30	0.50	0.11	0.30	0.50	1.00					

Comparison at BIPM : NDENW TEI49C versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	BIPM SRP27			NDENW TEI 49C			TEI 49C vs SRP27				
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{SRP27})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a_{T,SRP27}$	$u(a_{T,SRP27})$	$b_{T,SRP27}$ nmol/mol	$u(b_{T,SRP27})$ nmol/mol	$cov(a_{T,SRP27}, b_{T,SRP27})$
4 06/08/04 c0608006	1	0	0.14	0.20	0.28	0.29	0.12	1.00	1.0067	0.0060	0.10	0.58	-1.91E-03
	2	220	220.67	0.29	0.30	222.21	0.14	3.30					
	3	80	81.10	0.13	0.28	81.74	0.08	1.20	Goodness-of-fit measure: 0.03				
	4	420	409.19	0.23	0.34	412.03	0.23	6.20					
	5	120	117.73	0.19	0.29	118.61	0.20	1.80					
	6	320	310.74	0.19	0.31	313.00	0.14	4.70					
	7	30	26.44	0.30	0.28	26.72	0.15	1.00					
	8	370	355.29	0.16	0.32	357.79	0.14	5.40					
	9	170	164.81	0.16	0.29	166.02	0.14	2.50					
	10	500	486.51	0.28	0.36	489.88	0.27	7.30					
	11	270	265.79	0.28	0.31	267.72	0.13	4.00					
	12	0	0.21	0.20	0.28	0.32	0.08	1.00					
5 06/08/04 c0608007	1	0	0.31	0.23	0.28	0.38	0.11	1.00	1.0066	0.0060	0.12	0.58	-1.91E-03
	2	220	220.47	0.24	0.30	222.13	0.29	3.30					
	3	80	81.13	0.09	0.28	81.83	0.13	1.20	Goodness-of-fit measure: 0.04				
	4	420	408.82	0.25	0.34	411.74	0.21	6.20					
	5	120	117.59	0.14	0.29	118.46	0.13	1.80					
	6	320	310.18	0.27	0.31	312.25	0.13	4.70					
	7	30	26.34	0.18	0.28	26.60	0.09	1.00					
	8	370	354.88	0.18	0.32	357.37	0.18	5.40					
	9	170	164.69	0.23	0.29	165.80	0.13	2.50					
	10	500	486.24	0.21	0.36	489.64	0.33	7.30					
	11	270	265.58	0.10	0.31	267.35	0.20	4.00					
	12	0	0.14	0.16	0.28	0.28	0.10	1.00					
6 06/08/04 c0608008	1	0	0.31	0.20	0.28	0.33	0.10	1.00	1.0066	0.0060	0.08	0.58	-1.91E-03
	2	220	220.41	0.28	0.30	221.84	0.20	3.30					
	3	80	80.97	0.16	0.28	81.60	0.11	1.20	Goodness-of-fit measure: 0.08				
	4	420	408.45	0.23	0.34	411.22	0.19	6.20					
	5	120	117.68	0.24	0.29	118.45	0.16	1.80					
	6	320	309.90	0.18	0.31	312.01	0.15	4.70					
	7	30	26.15	0.29	0.28	26.49	0.08	1.00					
	8	370	354.51	0.24	0.32	357.07	0.21	5.40					
	9	170	164.49	0.15	0.29	165.69	0.15	2.50					
	10	500	485.92	0.31	0.36	489.27	0.25	7.30					
	11	270	265.28	0.21	0.31	267.16	0.11	4.00					
	12	0	0.26	0.20	0.28	0.34	0.07	1.00					

Second comparison at NDENW : NDENW TEI 49C vs UMEG18 results

Run/Date	Point number	nominal value nmol/mol	NDENW UMEG 18			NDENW TEI 49C			TEI 49C vs UMEG18				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a2_{T,NS}$	$u(a2_{T,NS})$	$b2_{T,NS}$ nmol/mol	$u(b2_{T,NS})$ nmol/mol	$cov(a2_{T,NS}, b2_{T,NS})$
7 07/09/04	1	0	-0.60	0.50	0.10	0.60	0.60	1.00	1.0106	0.0062	1.22	0.58	-1.86E-03
	2	220	216.40	0.30	1.00	220.70	0.40	3.30					
	3	80	80.90	0.20	0.40	83.50	0.10	1.30	Goodness-of-fit measure: 0.41				
	4	420	413.10	0.40	1.90	419.10	0.60	6.30					
	5	120	118.50	0.50	0.50	120.40	0.30	1.80					
	6	320	324.50	0.20	1.50	328.90	0.20	4.90					
	7	30	29.70	0.50	0.20	31.60	0.20	1.00					
	8	370	364.10	0.40	1.70	368.10	0.60	5.50					
	9	170	168.60	0.30	0.80	171.50	0.30	2.60					
	10	500	492.40	0.50	2.30	499.20	0.60	7.50					
	11	270	268.80	0.40	1.20	271.80	0.20	4.10					
	12	0	-0.10	0.40	0.10	0.70	0.10	1.00					
8 07/13/04	1	0	-0.60	0.40	0.10	0.80	0.10	1.00	1.0110	0.0062	1.26	0.58	-1.87E-03
	2	220	216.50	0.50	1.00	220.30	0.10	3.30					
	3	80	80.50	0.50	0.40	83.40	0.20	1.30	Goodness-of-fit measure: 0.65				
	4	420	414.40	0.30	1.90	418.60	0.60	6.30					
	5	120	117.50	0.40	0.50	120.50	0.20	1.80					
	6	320	323.70	0.20	1.50	328.50	0.30	4.90					
	7	30	29.90	0.40	0.20	31.60	0.20	1.00					
	8	370	363.50	0.80	1.70	367.40	0.50	5.50					
	9	170	168.20	0.40	0.80	171.10	0.30	2.60					
	10	500	493.10	0.40	2.30	498.50	0.50	7.50					
	11	270	268.00	0.20	1.20	271.50	0.20	4.10					
	12	0	0.00	0.50	0.10	0.60	0.10	1.00					
9 07/14/04	1	0	-0.40	0.50	0.10	0.80	0.10	1.00	1.0101	0.0062	1.50	0.58	-1.85E-03
	2	220	218.30	0.30	1.00	221.60	0.10	3.30					
	3	80	80.80	0.40	0.40	83.90	0.20	1.30	Goodness-of-fit measure: 0.55				
	4	420	415.90	0.30	1.90	420.80	0.60	6.30					
	5	120	118.40	0.30	0.50	121.30	0.20	1.80					
	6	320	326.70	0.40	1.50	331.20	0.10	5.00					
	7	30	29.60	0.40	0.20	31.70	0.20	1.00					
	8	370	365.50	0.60	1.70	369.40	0.60	5.50					
	9	170	169.60	0.40	0.80	172.40	0.30	2.60					
	10	500	495.80	0.40	2.30	501.40	0.60	7.50					
	11	270	269.00	0.50	1.20	273.30	0.20	4.10					
	12	0	-0.50	0.50	0.10	0.70	0.10	1.00					

First comparison at NERI : NERI API M401 versus UMEG results

Run/Date	Point number	nominal value nmol/mol	NERI UMEG			NERI API M401			API M401 vs UMEG				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a1_{T,NS}$	$u(a1_{T,NS})$	$b1_{T,NS}$ nmol/mol	$u(b1_{T,NS})$ nmol/mol	$cov(a1_{T,NS}, b1_{T,NS})$
11/10/04	1	0	7.20	0.50	0.90	1.20	0.30	1.11	0.9836	0.0059	1.18	0.86	-3.18E-03
	2	220	41.20	0.40	0.96	53.20	0.30	1.21					
	3	80	89.10	0.80	1.14	102.80	0.20	1.44	Goodness-of-fit measure:				
	4	420	138.80	0.60	1.41	153.60	0.20	1.77					
	5	120	186.60	0.70	1.72	202.90	0.50	2.13					
	6	320	235.50	1.20	2.05	253.20	0.30	2.53					
	7	30	285.60	1.30	2.41	302.20	1.10	2.93					
	8	370	334.90	1.60	2.78	353.50	0.60	3.36					
	9	170	383.20	1.10	3.14	403.70	0.80	3.79					
	10	500	433.60	2.20	3.52	451.70	3.40	4.20					
	11	270	484.10	1.40	3.90	504.00	3.40	4.66					
	12	0	9.30	0.60	0.90	1.10	0.30	1.11					
11/10/04	1	0	9.70	0.60	0.90	0.60	0.20	1.11	1.0658	0.0060	-0.85	0.86	-3.21E-03
	2	220	41.00	0.40	0.96	52.80	0.10	1.21					
	3	80	89.00	0.70	1.14	102.10	0.50	1.44	Goodness-of-fit measure:				
	4	420	138.40	0.60	1.41	153.30	0.40	1.77					
	5	120	189.20	0.70	1.74	202.90	0.50	2.13					
	6	320	237.80	1.00	2.07	253.50	0.60	2.53					
	7	30	287.30	1.10	2.43	302.90	1.40	2.94					
	8	370	338.30	1.40	2.80	351.30	3.00	3.34					
	9	170	386.70	1.00	3.16	404.30	0.90	3.79					
	10	500	438.10	1.50	3.55	457.00	1.00	4.25					
	11	270	485.80	2.00	3.91	502.10	1.70	4.64					
	12	0	6.50	0.50	0.90	1.40	0.40	1.11					
11/11/04	1	0	6.50	0.50	0.90	6.50	0.50	1.11	0.9452	0.0054	-1.64	0.82	-2.77E-03
	2	220	53.60	0.40	0.99	44.10	0.20	1.18					
	3	80	102.70	0.20	1.21	91.10	0.70	1.38	Goodness-of-fit measure:				
	4	420	154.10	0.20	1.51	140.90	0.60	1.68					
	5	120	203.20	1.10	1.83	189.60	1.20	2.03					
	6	320	254.70	0.50	2.19	239.40	1.00	2.42					
	7	30	306.10	0.50	2.56	287.30	1.30	2.81					
	8	370	354.90	0.40	2.93	337.00	1.40	3.22					
	9	170	406.90	0.30	3.32	385.70	1.70	3.63					
	10	500	454.60	0.30	3.68	435.60	1.70	4.06					
	11	270	505.70	0.80	4.07	484.50	2.10	4.49					
	12	0	3.00	0.40	0.90	6.00	0.30	1.11					

Comparison at BIPM : NERI API M401 versus BIPM SRP27 results

Run/Date	Point number	nominal value nmol/mol	BIPM SRP27			NERI API M401			API M401 vs SRP27				
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{SRP27})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a_{T,SRP27}$	$u(a_{T,SRP27})$	$b_{T,SRP27}$ nmol/mol	$u(b_{T,SRP27})$ nmol/mol	$cov(a_{T,SRP27}, b_{T,SRP27})$
4 11/23/04 c1123005	1	0	0.29	0.21	0.28	0.96	0.25	1.11	1.0545	0.0046	0.68	0.63	-1.73E-03
	2	220	221.94	0.09	0.30	234.40	0.33	2.38					
	3	80	81.80	0.18	0.28	86.78	0.23	1.36	Goodness-of-fit measure:	0.13			
	4	420	424.48	0.17	0.34	448.76	0.42	4.18					
	5	120	118.48	0.21	0.29	125.70	0.31	1.58					
	6	320	325.48	0.13	0.32	343.98	0.26	3.28					
	7	30	31.47	0.18	0.28	33.79	0.32	1.15					
	8	370	375.19	0.32	0.33	396.24	0.36	3.72					
	9	170	170.61	0.27	0.29	180.86	0.35	1.97					
	10	500	507.50	0.35	0.37	535.77	0.37	4.93					
	11	270	272.03	0.24	0.31	287.45	0.49	2.81					
	12	0	0.11	0.13	0.28	0.94	0.38	1.11					
5 11/23/04 c1123007	1	0	0.32	0.23	0.28	0.88	0.38	1.11	1.0545	0.0046	0.70	0.63	-1.73E-03
	2	220	221.70	0.19	0.30	234.43	0.30	2.38					
	3	80	81.98	0.25	0.28	87.27	0.32	1.36	Goodness-of-fit measure:	0.1999			
	4	420	424.72	0.18	0.34	448.65	0.31	4.18					
	5	120	118.71	0.21	0.29	126.05	0.39	1.58					
	6	320	325.21	0.18	0.32	343.68	0.30	3.28					
	7	30	31.55	0.17	0.28	33.74	0.28	1.15					
	8	370	375.15	0.17	0.33	396.20	0.44	3.72					
	9	170	170.57	0.27	0.29	180.50	0.30	1.96					
	10	500	507.48	0.25	0.37	535.70	0.25	4.93					
	11	270	271.91	0.16	0.31	287.34	0.47	2.81					
	12	0	0.09	0.15	0.28	1.03	0.29	1.11					
6 11/24/04 c1123010	1	0	0.29	0.16	0.28	0.67	0.29	1.11	1.0548	0.0046	0.61	0.63	-1.74E-03
	2	220	221.64	0.20	0.30	234.26	0.23	2.38					
	3	80	81.91	0.21	0.28	86.94	0.28	1.36	Goodness-of-fit measure:	0.2247			
	4	420	424.69	0.19	0.34	448.52	0.26	4.17					
	5	120	118.53	0.12	0.29	125.80	0.39	1.58					
	6	320	325.32	0.19	0.32	343.61	0.48	3.28					
	7	30	31.64	0.21	0.28	34.26	0.34	1.15					
	8	370	374.73	0.17	0.33	396.09	0.40	3.72					
	9	170	170.54	0.13	0.29	180.38	0.34	1.96					
	10	500	507.73	0.35	0.37	536.06	0.37	4.94					
	11	270	272.16	0.19	0.31	287.72	0.27	2.81					
	12	0	0.31	0.18	0.28	0.96	0.37	1.11					

Second comparison at NERI : NERI API M401 vs UMEG results

Run/Date	Point number	nominal value nmol/mol	NERI UMEG			NERI API M401			API M401 vs UMEG				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a2_{T,NS}$	$u(a2_{T,NS})$	$b2_{T,NS}$ nmol/mol	$u(b2_{T,NS})$ nmol/mol	$cov(a2_{T,NS}, b2_{T,NS})$
01/14/05	7	0	4.20	1.66	0.90	-0.54	0.28	1.11	1.0836	0.0062	-1.62	0.81	-3.05E-03
	1	220	206.70	2.29	1.85	224.31	0.49	2.30					
	2	80	73.24	2.14	1.07	80.48	0.62	1.32	Goodness-of-fit measure:				
	3	420	407.34	2.14	3.32	432.49	1.34	4.04					
	4	120	109.81	2.06	1.25	122.39	0.47	1.56					
	5	320	306.79	1.36	2.57	329.80	0.27	3.16					
	6	30	23.25	0.79	0.92	29.33	0.29	1.14					
	7	370	353.61	1.22	2.92	381.29	0.29	3.60					
	8	170	163.62	1.85	1.57	174.63	0.22	1.92					
	9	500	490.95	2.05	3.95	516.61	0.59	4.77					
	10	270	257.20	1.19	2.21	278.16	0.73	2.73					
	11	0	5.65	1.11	0.90	-0.84	0.36	1.11					
01/14/05	8	0	5.65	1.11	0.90	-0.84	0.36	1.11	1.0669	0.0061	-2.24	0.81	-2.98E-03
	1	220	213.00	1.32	1.90	226.42	0.50	2.31					
	2	80	71.05	2.06	1.06	81.29	0.55	1.33	Goodness-of-fit measure:				
	3	420	412.05	2.16	3.35	433.04	0.92	4.04					
	4	120	115.99	2.78	1.28	123.15	0.42	1.57					
	5	320	308.95	1.92	2.58	331.40	0.44	3.17					
	6	30	29.45	1.56	0.93	29.95	0.29	1.14					
	7	370	368.82	1.59	3.03	383.39	0.96	3.61					
	8	170	169.74	2.06	1.61	175.56	0.75	1.93					
	9	500	490.91	1.70	3.95	518.18	1.01	4.78					
	10	270	265.46	3.83	2.27	279.53	1.08	2.74					
	11	0	2.12	1.23	0.90	-0.66	0.72	1.11					
01/14/05	9	0	2.12	1.23	0.90	-0.66	0.72	1.11	1.0557	0.0060	-4.26	0.81	-3.01E-03
	1	220	214.54	3.39	1.91	226.77	0.93	2.32					
	2	80	81.34	1.37	1.10	80.70	0.38	1.33	Goodness-of-fit measure:				
	3	420	421.75	1.33	3.43	433.68	1.20	4.05					
	4	120	119.46	1.14	1.30	122.75	0.32	1.56					
	5	320	315.59	1.27	2.63	329.92	0.71	3.16					
	6	30	35.16	1.37	0.94	30.15	0.43	1.14					
	7	370	368.55	1.36	3.03	382.81	1.25	3.61					
	8	170	171.11	1.60	1.62	174.54	0.58	1.92					
	9	500	488.64	1.86	3.94	517.39	0.81	4.77					
	10	270	266.82	1.84	2.28	278.64	0.83	2.74					
	11	0	2.24	1.67	0.90	-0.92	0.27	1.11					

First comparison at NIST : NIST SRP0 versus SRP2 results

Run/Date	Point number	nominal value nmol/mol	NIST SRP2			NIST SRP0			SRP0 vs SRP2					
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a_{T,NS}$	$u(a_{T,NS})$	$b_{T,NS}$ nmol/mol	$u(b_{T,NS})$ nmol/mol	$cov(a_{T,NS}, b_{T,NS})$	
06/02/03	1	0	0.28	0.29	0.28	Goodness-of-fit measure: 0.40	0.10	0.21	0.28	0.9978	0.0006	-0.19	0.17	-6.72E-05
	2	220	252.37	0.32	0.30		251.86	0.32	0.30					
	3	80	76.19	0.12	0.28		75.70	0.21	0.28					
	4	420	535.58	0.30	0.37		534.08	0.31	0.37					
	5	120	613.79	0.22	0.39		611.99	0.28	0.39					
	6	320	170.14	0.21	0.29		169.54	0.21	0.29					
	7	30	684.95	0.63	0.42		683.51	0.74	0.42					
	8	370	12.91	0.33	0.28		12.91	0.34	0.28					
	9	170	34.90	0.34	0.28		34.59	0.23	0.28					
	10	500	448.42	0.35	0.35		447.22	0.28	0.35					
	11	270	345.01	0.23	0.32		344.02	0.29	0.32					
	12	0	0.30	0.12	0.28		-0.02	0.20	0.28					
06/04/03	1	0	0.12	0.18	0.28	Goodness-of-fit measure: 0.55	0.02	0.18	0.28	0.9978	0.0006	-0.06	0.17	-6.77E-05
	2	220	250.58	0.24	0.30		249.63	0.13	0.30					
	3	80	533.11	0.43	0.37		531.95	0.35	0.37					
	4	420	34.50	0.16	0.28		34.34	0.21	0.28					
	5	120	342.88	0.40	0.32		342.03	0.34	0.32					
	6	320	168.64	0.26	0.29		168.32	0.16	0.29					
	7	30	74.74	0.17	0.28		74.62	0.17	0.28					
	8	370	678.64	0.25	0.42		677.15	0.19	0.42					
	9	170	13.09	0.12	0.28		13.00	0.26	0.28					
	10	500	608.11	0.34	0.39		606.85	0.31	0.39					
	11	270	445.17	0.24	0.35		443.91	0.34	0.34					
	12	0	0.15	0.20	0.28		0.18	0.17	0.28					
06/05/03	1	0	0.16	0.20	0.28	Goodness-of-fit measure: 0.22	0.02	0.25	0.28	0.9979	0.0006	-0.22	0.17	-6.94E-05
	2	220	442.42	0.43	0.34		441.16	0.34	0.34					
	3	80	167.78	0.11	0.29		167.29	0.29	0.29					
	4	420	40.93	0.22	0.28		40.56	0.40	0.28					
	5	120	341.14	0.16	0.32		340.09	0.27	0.32					
	6	320	675.98	0.30	0.42		674.29	0.46	0.41					
	7	30	247.34	0.12	0.30		246.64	0.28	0.30					
	8	370	82.10	0.13	0.28		81.75	0.15	0.28					
	9	170	605.97	0.51	0.39		604.60	0.45	0.39					
	10	500	17.44	0.21	0.28		17.24	0.22	0.28					
	11	270	528.14	0.41	0.37		526.91	0.40	0.37					
	12	0	0.17	0.21	0.28		-0.17	0.47	0.28					

Comparison at BIPM : NIST SRP0 vs BIPM SRP27

Run/Date	Point number	nominal value nmol/mol	BIPM SRP27			NIST SRP0			SRP0 vs SRP27				
			x_{SRP27} nmol/mol	s_{SRP27} nmol/mol	$u(x_{\text{SRP27}})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a_{T,\text{SRP27}}$	$u(a_{T,\text{SRP27}})$	$b_{T,\text{SRP27}}$ nmol/mol	$u(b_{T,\text{SRP27}})$ nmol/mol	$\text{cov}(a_{T,\text{SRP27}}, b_{T,\text{SRP27}})$
4 07/26/03	1	0	-0.14	0.18	0.28	-0.01	0.23	0.28	0.9976	0.0008	0.06	0.19	-1.19E-04
	2	220	220.73	0.19	0.30	220.32	0.12	0.30					
	3	80	82.25	0.13	0.28	82.16	0.19	0.28	Goodness-of-fit measure:				
	4	420	410.41	0.52	0.34	409.48	0.54	0.34	0.7639				
	5	120	120.09	0.10	0.29	119.97	0.24	0.29					
	6	320	313.68	0.17	0.32	312.88	0.12	0.32					
	7	30	33.52	0.36	0.28	33.45	0.16	0.28					
	8	370	357.74	0.29	0.33	357.28	0.37	0.33					
	9	170	167.83	0.11	0.29	167.05	0.39	0.29					
	10	500	488.77	0.26	0.36	487.56	0.27	0.36					
	11	270	260.84	0.57	0.31	260.38	0.61	0.30					
	12	0	-0.13	0.17	0.28	-0.02	0.11	0.28					
5 07/27/03	1	0	-0.10	0.23	0.28	-0.08	0.14	0.28	0.9984	0.0008	0.04	0.19	-1.20E-04
	2	220	219.41	0.16	0.30	219.06	0.35	0.30					
	3	80	81.74	0.13	0.28	81.73	0.27	0.28	Goodness-of-fit measure:				
	4	420	407.25	0.30	0.34	406.72	0.40	0.34	0.3761				
	5	120	119.40	0.09	0.29	119.15	0.18	0.29					
	6	320	311.05	0.13	0.31	310.82	0.36	0.31					
	7	30	33.28	0.21	0.28	33.22	0.24	0.28					
	8	370	354.87	0.46	0.32	354.31	0.39	0.32					
	9	170	166.60	0.19	0.29	166.46	0.25	0.29					
	10	500	484.93	0.53	0.36	484.06	0.46	0.36					
	11	270	259.68	0.58	0.30	259.12	0.50	0.30					
	12	0	-0.13	0.15	0.28	-0.05	0.25	0.28					
6 07/29/03	1	0	-0.05	0.18	0.28	0.05	0.23	0.28	0.9976	0.0008	0.05	0.19	-1.19E-04
	2	220	221.44	0.25	0.30	220.80	0.26	0.30					
	3	80	82.49	0.22	0.28	82.32	0.27	0.28	Goodness-of-fit measure:				
	4	420	411.63	0.37	0.34	410.88	0.42	0.34	0.3761				
	5	120	120.69	0.29	0.29	120.43	0.32	0.29					
	6	320	314.34	0.19	0.32	313.67	0.32	0.32					
	7	30	33.67	0.11	0.28	33.59	0.26	0.28					
	8	370	358.56	0.24	0.33	357.82	0.36	0.33					
	9	170	168.14	0.16	0.29	167.75	0.31	0.29					
	10	500	490.01	0.26	0.36	488.81	0.36	0.36					
	11	270	261.42	0.31	0.31	260.83	0.30	0.31					
	12	0	-0.02	0.07	0.28	0.15	0.24	0.28					

Second comparison at NIST : NIST SRP0 vs SRP2 results

Run/Date	Point number	nominal value nmol/mol	NIST SRP2			NIST SRP0			SRP0 vs SRP2				
			x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_T nmol/mol	s_T nmol/mol	$u(x_T)$ nmol/mol	$a2_{T,NS}$	$u(a2_{T,NS})$	$b2_{T,NS}$ nmol/mol	$u(b2_{T,NS})$ nmol/mol	$cov(a2_{T,NS}, b2_{T,NS})$
08/21/03	7	0	0.40	0.10	0.28	0.20	0.10	0.28	0.9990	0.0008	-0.15	0.19	-1.16E-04
	1	220	223.50	0.20	0.30	223.20	0.20	0.30	Goodness-of-fit measure: 0.42				
	2	80	81.70	0.30	0.28	81.70	0.20	0.28					
	3	420	417.30	0.20	0.34	416.60	0.10	0.34					
	4	120	122.60	0.20	0.29	122.40	0.40	0.29					
	5	320	323.70	0.50	0.32	323.30	0.60	0.32					
	6	30	33.70	0.20	0.28	33.40	0.20	0.28					
	7	370	370.00	0.20	0.33	369.40	0.20	0.33					
	8	170	175.70	0.20	0.29	175.30	0.20	0.29					
	9	500	509.60	0.40	0.37	509.00	0.20	0.37					
	10	270	273.60	0.20	0.31	273.10	0.30	0.31					
	11	0	0.30	0.20	0.28	0.10	0.10	0.28					
08/21/03	8	0	0.20	0.20	0.28	0.10	0.20	0.28	0.9991	0.0008	-0.17	0.19	-1.16E-04
	1	220	221.40	0.30	0.30	220.90	0.20	0.30	Goodness-of-fit measure: 0.48				
	2	80	80.70	0.20	0.28	80.60	0.30	0.28					
	3	420	413.60	0.30	0.34	413.10	0.30	0.34					
	4	120	121.60	0.10	0.29	121.10	0.30	0.29					
	5	320	320.80	0.20	0.32	320.20	0.20	0.32					
	6	30	33.20	0.20	0.28	33.10	0.30	0.28					
	7	370	366.30	0.40	0.33	366.10	0.40	0.33					
	8	170	173.60	0.20	0.29	173.30	0.20	0.29					
	9	500	504.70	0.40	0.36	504.10	0.30	0.36					
	10	270	270.60	0.30	0.31	269.90	0.30	0.31					
	11	0	0.20	0.20	0.28	0.00	0.20	0.28					
08/21/03	9	0	0.10	0.20	0.28	-0.10	0.20	0.28	0.9993	0.0008	-0.26	0.19	-1.16E-04
	1	220	220.40	0.30	0.30	220.00	0.40	0.30	Goodness-of-fit measure: 0.27				
	2	80	80.20	0.30	0.28	80.00	0.40	0.28					
	3	420	411.90	0.20	0.34	411.50	0.30	0.34					
	4	120	120.80	0.10	0.29	120.30	0.20	0.29					
	5	320	319.40	0.20	0.32	319.00	0.20	0.32					
	6	30	33.10	0.20	0.28	32.80	0.20	0.28					
	7	370	366.30	0.20	0.33	365.90	0.30	0.33					
	8	170	173.30	0.20	0.29	172.90	0.20	0.29					
	9	500	503.80	0.30	0.36	503.00	0.20	0.36					
	10	270	270.00	0.20	0.31	269.40	0.20	0.31					
	11	0	0.30	0.20	0.28	0.00	0.20	0.28					

1) Comparison at the BIPM: NIES SRP35 versus SRP27 results

note : B_Least has been used at that point, in order to calibrate SRP35 versus SRP27

Run/Date	Point number	nominal value nmol/mol	SRP27			SRP35		
			x_{SRP27}	s_{SRP27}	$u(x_{SRP27})$	x_T	s_T	$u(x_T)$
			nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol
27-juil-04 (c0727001)	1	0	0.16	0.31	0.28	0.14	0.19	0.28
	2	220	223.71	0.29	0.31	223.32	0.17	0.30
	3	80	80.60	0.20	0.28	80.44	0.16	0.28
	4	420	424.58	0.16	0.39	424.37	0.25	0.34
	5	120	121.66	0.27	0.29	121.65	0.18	0.29
	6	320	321.85	0.27	0.35	321.76	0.14	0.32
	7	30	30.84	0.20	0.28	30.61	0.18	0.28
	8	370	375.33	0.19	0.37	375.09	0.21	0.33
	9	170	168.26	0.20	0.30	168.14	0.14	0.29
	10	500	505.35	0.16	0.43	505.33	0.16	0.37
	11	270	268.25	0.20	0.33	268.32	0.16	0.31
	12	0	0.24	0.14	0.28	0.08	0.22	0.28

2) calculation of SRP35 corrected values in the GPT-SRP35 comparison at NIES

calculation performed with B_Least, the absorption cross-section uncertainty is introduced in SRP35

Run/ Date	Point number	SRP35			SRP35 calibrated with SRP27	
		x_T	s_T	$u(x_T)$	x_T	$u(x_T)$
		nmol/mol	nmol/mol	nmol/mol	nmol/mol	nmol/mol
	1	135.70	0.20	1.06	135.83	1.07
	2	159.20	0.30	1.23	159.33	1.24
	3	94.30	0.30	0.76	94.43	0.77
	4	250.90	0.30	1.91	251.03	1.91
	5	149.50	0.20	1.16	149.63	1.17
	6	144.10	0.20	1.12	144.23	1.13
	7	154.50	0.20	1.19	154.63	1.20
	8	83.90	0.20	0.69	84.03	0.71
	9	109.30	0.10	0.87	109.43	0.88
	10	415.30	0.30	3.13	415.44	3.14
	11	135.60	0.20	1.06	135.73	1.07

3) calculation of NIES-GPT and SRP27 comparison

calculation performed with OzonE, including the correlation factor from the absorption cross-section in between the SRP points

Run/ Date	Point number	NIES GPT			SRP35 calibrated with SRP27		NIES GPT vs SRP27					
		x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{NS})$ nmol/mol	x_T nmol/mol	$u(x_T)$ nmol/mol	a	$u(a)$	b nmol/mol	$u(b)$ nmol/mol	$cov(a,b)$	
	1	139.40	0.40	0.51	135.83	1.07	Goodness-of-fit measure	1.0218	0.0086	0.18	0.54	-1.96E-03
	2	162.80	0.10	0.59	159.33	1.24				0.50		
	3	96.40	0.10	0.35	94.43	0.77						
	4	256.30	0.10	0.93	251.03	1.91						
	5	153.40	0.20	0.56	149.63	1.17						
	6	147.20	0.10	0.54	144.23	1.13						
	7	158.20	0.10	0.57	154.63	1.20						
	8	86.00	0.20	0.31	84.03	0.71						
	9	111.90	0.20	0.41	109.43	0.88						
	10	424.20	0.20	1.54	415.44	3.14						
	11	139.50	0.10	0.51	135.73	1.07						

Protocol for the Pilot Study CCQM-P28 – Ozone at ambient level

1. Introduction

The pilot study is aimed at evaluating the level of comparability of ozone reference standards that are maintained as national standards, or as primary standards within international networks for ambient ozone measurements, and for those laboratories that have completed the CCQM-P28 questionnaire (August 2002). The study is a prelude to an on-going key comparison.

The level of comparability will be determined using the NIST Standard Reference Photometer (BIPM-SRP27) maintained by the BIPM as a common reference. Comparisons will be performed at the BIPM either directly with a visiting laboratory's national standard, or by means of the visiting laboratory's transfer standard. In either case it is expected that staff trained in the operation of their ozone reference standards will accompany their instruments to the BIPM.

This document contains protocols for both these situations.

Laboratories that bring their national ozone standard to the BIPM should follow Protocol A.

Laboratories that bring a transfer standard to the BIPM should follow Protocol B.

Comparisons will be performed over an ozone mole fraction range of 0 nmol/mol to 500 nmol/mol.

An expression for the degree of equivalence between each national standard and BIPM-SRP27 will be calculated by the BIPM, from the comparison results and measurement uncertainties submitted by participating laboratories.

Laboratories wishing to participate in CCQM-P28, should register their interest using the registration form provided and return this to the BIPM by **5 May 2003**.

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.

CCQM-P28 Protocol A

For laboratories that bring their national standard to the BIPM

1. Transport of instruments to and from the BIPM

It is the responsibility of the laboratory visiting the BIPM to organise transport of their instruments to and from the BIPM, and to ensure that proper arrangements are made for local customs formalities. The laboratory shall inform the BIPM of its transport and customs arrangements prior to equipment leaving their laboratory. If an ATA carnet is used, it must be used properly. Upon each movement of the package the person organizing the transit must ensure that the carnet is presented to customs on leaving the country and upon its arrival in the country of destination.

2. Description of the comparison

A direct comparison will be made at the BIPM between BIPM-SRP27 and the national ozone reference standard of the visiting laboratory over 12 mole fractions of ozone in dry air in the range (0-500) nmol/mol. Where possible, BIPM-SRP28 will also be included in the comparison to ensure the stability of BIPM-SRP27.

The BIPM will provide the source of zero air for the comparison. The BIPM will utilise its ozone generator for the comparisons, unless the visiting laboratory's instrument cannot operate in this mode, in which case the visiting laboratory's generator will be used. Data will be acquired using the SRP control software version 4.00 (2002) unless the communication between this programme and the participating laboratory's standard is not possible.

The comparison information form [CCQM-P28-R1](#), as well as the results form [CCQM-P28-R2](#), attached to this protocol, shall be completed and verified by the participating laboratory and the BIPM staff.

3. Quantities and Units

A number of quantities can be used to express the composition of mixtures, and this is true within the field of ambient ozone measurements. In this protocol the measurand is the mole fraction of ozone in air, with measurement results being expressed in units of nmol/mol. The numerical value of a mole fraction of ozone in air expressed in this unit, is equivalent to the numerical value of the volume fraction expressed as ppb (parts per billion, 1 billion = 10^9) or ppbv.

Laboratories are to use $1.1476 \times 10^{-21} \text{ m}^2$ (equivalent to $308.32 \text{ atm}^{-1} \text{ cm}^{-1}$) as the conventional value of the ozone absorption cross section at 253.7 nm, in order to calculate their ozone mole fractions.

4. Pre-comparison requirements

Installation guidelines (for SRPs only)

SRPs will be mounted on stands (provided by the BIPM) and not operated whilst resting on their pneumatic and electronics modules.

Stabilisation of instruments

Prior to the comparison, all the instruments that will be used for the comparison shall be switched on and allowed to stabilise for at least eight hours.

Instrument temperature and pressure measurement systems

The laboratories participating in the comparison will be allowed to check the pressure and temperature measurement systems within their instrument. If any adjustments are required, they will be noted.

Recording of SRP operating characteristics (for laboratories that operate SRPs)

'SRP operating characteristics data sheets' shall be completed for all SRPs after their initial warm up period. The data sheets to be completed will be provided by the BIPM. Copies of the participating institute's data sheet shall be kept by the BIPM. The participating institutes are free to make adjustments to their instrument's operating parameters following their usual operating procedures. Any adjustments made will be noted within the data sheets.

Source of purified air

One common source of pure air will be used to provide the flows of reference air and ozone. This air will be furnished by the BIPM. It is ambient air 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 found to be 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 . The maximum available flow rate is 25 L/min .

Ozone generator

One common ozone generator will be used to generate the ozone to be measured by all the instruments included in the comparison. The ozone generator utilised in the comparison will be capable of producing stable ozone mole fractions over the range (0-500) nmol/mol , at a minimum flow rate equal to 2 L/min plus the flow rate needed by the guest instrument plus an excess flow rate of 1 L/min . When possible, ozone will be generated with one of the BIPM ozone generators.

Gas manifold

The BIPM external dual manifold system will always be used to redistribute the zero air and ozone/air to instruments. If the guest instrument possesses its own manifold, the participating laboratory shall decide whether or not it wishes to make use of it, and note this in form CCQM-P28-R1.

Flow rates

Gas flows shall be provided to photometers with a minimum excess of 1 L/min compared to the combined requirements of the photometers included in the comparison.

5. Comparison procedure

The following procedure will be followed for the comparison.

Conditioning of the photometers and the pneumatic lines before the comparison

At the beginning of the comparison, the photometers as well as interconnecting pneumatic lines will be conditioned with a nominal value of the ozone mole fraction greater than 500 nmol/mol for at least 2 hours.

Ozone mole fraction nominal values

12 nominal values will be measured by the photometers. These values include the measurement of 0 nmol/mol at the beginning and the end of the comparison. The 12 nominal values will be produced in the following sequence: (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270, 0) nmol/mol. Due to the operational characteristics of ozone generators, it is expected that the actual delivered values will be within ± 15 nmol/mol of those nominal values.

Ozone generator stability

For each nominal value of the ozone mole fraction x_{nom} furnished by the ozone generator, it is important to ensure that the photometers are measuring a stable value. To this end, the standard deviation s_{SRP27} on the set of 10 consecutive measurements $x_{\text{SRP27},i}$ recorded by BIPM-SRP27 will be calculated. This set is considered as valid if s_{SRP27} is less than 1 nmol/mol. If s_{SRP27} is found greater than 1 nmol/mol, another set of 10 consecutive measurements of the same nominal values is taken. Repeated instances of unacceptable values of s_{SRP27} indicate that there are instabilities in the ozone generator or in the BIPM-SRP27 measurement system. The reasons for these will be examined and documented prior to continuing the comparison.

Recorded values

For each nominal value x_{nom} , the value recorded for each photometer A is the mean (\bar{x}_A) of 10 consecutive single measurements $x_{A,i}$ taken in a stable regime as defined above.

Comparison repeatability

The comparison procedure will be repeated a further two times to ensure its repeatability. For each comparison, a copy of the report form [CCQM-P28-R2](#) shall be completed.

6. Uncertainty budget

Uncertainties calculation

The uncertainties associated with the twelve values \bar{x}_{NS} measured by the national standard(NS) will be evaluated by the participating laboratory. The visiting laboratory will provide an uncertainty budget used to calculate the values in the report form CCQM-P28-R1.

The uncertainties associated with the twelve values \bar{x}_{SRP27} (and eventually \bar{x}_{SRP28}) measured by the BIPM-SRP27 (and eventually BIPM-SRP28) will be evaluated by the BIPM. Details of the uncertainty budget for the BIPM-SRPs can be found at the end of this document.

Absorption cross section value

Ozone photometers measure ozone mole fractions by the absorption of radiation by ozone at 253.7 nm. As a consequence, the uncertainty on the absorption cross section of ozone at 253.7 nm can be conventionally set to zero if all the instruments use the same value for this parameter. All laboratories shall calculate their ozone mole fractions using the conventional value for the absorption cross section of $1.1476 \times 10^{-21} \text{ m}^2$ (equivalent to $308.32 \text{ atm}^{-1} \text{ cm}^{-1}$). If the laboratory ordinarily uses a different value for the absorption cross section, this should be stated in form [CCQM-P28-R1](#), but not used in the calculation.

7. Linear regression fits

The sets of the twelve data points (\bar{x}_{SRP27} and \bar{x}_{NS}) will be fitted using a generalised least square program, taking into account the associated uncertainties $u(\bar{x}_{\text{SRP27}})$ and $u(\bar{x}_{\text{NS}})$. This will be performed by the BIPM. The parameters $a_{\text{NS},\text{SRP27}}$ and $b_{\text{NS},\text{SRP27}}$ of the linear relationship between x_{NS} and x_{SRP27} ($x_{\text{NS}} = a_{\text{NS},\text{SRP27}} x_{\text{SRP27}} + b_{\text{NS},\text{SRP27}}$) will be calculated as well as their uncertainties.

8. Reporting of results

The BIPM is responsible for the preparation of a report on the comparison. The report passes through a number of stages, and these are referred to here as drafts A and B.

The first draft, draft A, is prepared as soon as all the results have been received from the participants. It includes the results transmitted by the participants, identified by name. It is confidential to the participants.

The second draft, draft B, is subsequently prepared for the Consultative Committee.

In more detail, the procedure is as follows:

- During the comparison, as the results are received by the BIPM, they are kept confidential by the BIPM until all the participants have completed their measurements and all the results have been received, or until the date limit for receipt of results has passed.
- A result from a participant is not considered complete without an associated uncertainty, and is not included in the draft report unless it is accompanied by an uncertainty supported by a complete uncertainty budget.
- If, on examination of the complete set of results, the BIPM finds results that appear to be anomalous, the corresponding institutes are invited to check their results for numerical errors but without being informed as to the magnitude or sign of the apparent anomaly. If no numerical error is found the result stands and the complete set of results is sent to all participants. Note that once all participants have been informed of the results,

individual values and uncertainties may be changed or removed, or the complete comparison abandoned, only with the agreement of all participants and on the basis of a clear failure of the travelling standard or some other phenomenon that renders the comparison or part of it invalid.

- Draft A of the report is sent as soon as possible after completion of the comparison to all the participants for comment, with a reasonable deadline for replies. The date at which this draft is sent to the participants is taken to be the end date for the comparison and is subsequently referred to as such.
- Draft A is considered as confidential to the participants. Copies are not given to nonparticipants, and graphs or other parts of the draft are not used in oral presentations at an outside Conference without the specific agreement of all the participants.
- On receipt of final comments from participants, the second draft, draft B, is prepared which includes an Appendix containing proposals for a reference value and degrees of equivalence.
- Draft B, which supersedes draft A, is not considered confidential, and may be the subject of a publication with the consensus of all participants. The first initiative for publication is with the BIPM. Other participants may publish the results with the agreement of the BIPM. The Draft B report becomes the final report once it has been presented as such to the CCQM.

CCQM-P28 Protocol B

For laboratories that bring a transfer standard to the BIPM

1. Transport of instruments to and from the BIPM

It is the responsibility of the laboratory visiting the BIPM to organise transport of their instruments to and from the BIPM, and to ensure that proper arrangements are made for local customs formalities. The laboratory shall inform the BIPM of its transport and customs arrangements prior to equipment leaving their laboratory. If an ATA carnet is used, it must be used properly. Upon each movement of the package the person organizing the transit must ensure that the carnet is presented to customs on leaving the country and upon its arrival in the country of destination.

2. Stability and Characteristics of Transfer Standards

Laboratories employing a transfer standard should ensure that the standard has good short-term stability and stability during transport. Ozone reference transfer standards should fulfil the requirements described in section 6 of this protocol.

3. Comparison description

A series of comparisons will be performed utilising an ozone reference transfer standard (of the visiting laboratory) in order to determine the degree of equivalence between the participating laboratory's national standard (designated with NS) and the BIPM-SRP27. Comparisons shall be performed over 12 mole fractions of ozone in dry air in the range (0-500) nmol/mol. The comparisons will be in three parts:

1. National standard (NS) vs. Transfer standard (T) comparison at the laboratory of the participating institute: within the six weeks prior to bringing the transfer standard to the BIPM, a direct comparison between the transfer standard and the national standard will be performed in the laboratory of the participating institute. The comparison information form [CCQM-P28-R3](#), as well as the results form [CCQM-P28-R4](#), attached to this protocol, shall be completed by the participating laboratory and sent to the BIPM.
2. Transfer standard (T) vs. BIPM-SRP27 at the BIPM: comparison between the transfer standard (T) and BIPM-SRP27 will be performed at the BIPM. The comparison information form [CCQM-P28-R5](#), as well as the results form [CCQM-P28-R6](#), attached to this protocol, shall be completed and verified by the participating laboratory and the BIPM staff.

3. National standard (NS) vs. Transfer standard (T) comparison at the laboratory of the participating institute: within the six weeks following the comparison at the BIPM, a second comparison between the transfer standard (T) and the national standard (NS) will be performed in the laboratory of the participating institute. Further copies of the comparison information form [CCQM-P28-R3](#), as well as the results from [CCQM-P28-R4](#), attached to this protocol, shall be completed by the participating laboratory and sent to the BIPM.

4. Quantities and Units

A number of quantities can be used to express the composition of mixtures, and this is true within the field of ambient ozone measurements. In this protocol the measurand is the mole fraction of ozone in air, with measurement results being expressed in units of nmol/mol. The numerical value of a mole fraction of ozone in air expressed in this unit, is equivalent to the numerical value of the volume fraction expressed as ppb (parts per billion, 1 billion = 10^9) or ppbv.

Laboratories are to use $1.1476 \times 10^{-21} \text{ m}^2$ (equivalent to $308.32 \text{ atm}^{-1} \text{ cm}^{-1}$) as the conventional value of the ozone absorption cross section at 253.7 nm, in order to calculate their ozone mole fractions.

5. Comparison between the national standard and the transfer standard before travelling with the transfer standard

5.1 Pre-comparison requirements

Stabilisation of instruments

Prior to the comparison, all the instruments that will be used for the comparison shall be switched on and allowed to stabilise for at least 8 hours.

Instruments temperature and pressure measurement systems

The laboratories participating in the comparison should check the pressure and temperature measurement systems within their instruments (national and transfer standards). If any adjustments are required, they will be noted, and the traceability of these measurements documented.

Source of purified air

One common source of pure air shall be used to provide the flows of reference air and ozone. The source of pure air shall be free of ozone, nitrogen oxides and any other interfering substance that can cause an undesired positive or negative response in the UV photometer.

Ozone generator

One common ozone generator will be used to generate the ozone to be measured by the national standard and the transfer standard. This ozone generator should be able to produce a maximum of 500 nmol/mol of ozone mole fractions in dry air at the flow rate needed for the comparison.

Flow rates

All the gas flows provided to the instruments (reference air and/or ozonized air) should have flow rates with a minimum excess of 1 L/min compared to what is needed by the national standard plus the transfer standard.

Gas manifold

The gas manifold used to connect the instruments shall be described in form CCQM-P28-R3.

5.2 Comparison procedure

Conditioning of the photometers and the pneumatic lines before the comparison

At the beginning of the comparison, the photometers as well as interconnecting pneumatic lines will be conditioned with a nominal value of the ozone mole fraction greater than 500 nmol/mol for at least 2 hours.

Ozone mole fraction nominal values

12 nominal values will be measured by the photometers. These values include the measurement of 0 nmol/mol at the beginning and the end of the comparison. The 12 nominal values will be produced in the following sequence: (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270, 0) nmol/mol. Due to the operational characteristics of ozone generators, it is expected that the actual delivered values will be within ± 15 nmol/mol of those nominal values.

Ozone generator stability

For each nominal value of the ozone mole fraction x_{nom} furnished by the ozone generator, it is important to ensure that the photometers are measuring a stable value. To this end, each of the twelve points will be sampled for at least ten minutes by the two photometers. Following this, ten consecutive output values from each instrument will be recorded. The averages \bar{x}_{NS} and \bar{x}_{T} as well as the standard deviations s_{NS} and s_{T} of the recorded values will be evaluated. The two values \bar{x}_{NS} and \bar{x}_{T} are considered as valid if the associated standard deviation s_{NS} and s_{T} do not exceed 2 nmol/mol or 1.5 % of the average value (which ever is the largest). If any of the two values is not valid, the point will be taken again after five minutes of sampling at the same nominal value. Repeated instances of unacceptable values of s_{NS} or s_{T} indicate that there are instabilities in the ozone generator or in the measurement systems. The reasons for these will be examined and documented prior to the comparison continuing.

Laboratories are free to use more restrictive conditions than those described above (see for example the conditions used with an SRP in protocol A). These conditions shall be noted in the comparison information form CCQM-P28-R5.

Comparison repeatability

The comparison procedure will be repeated a further two times to ensure its repeatability. For each comparison, a copy of the results form [CCQM-P28-R6](#) attached to this protocol, which includes the comparison results, shall be completed by the participating laboratory and sent to the BIPM. These results forms must arrive at the BIPM before the measurements of the transfer standard vs. BIPM-SRP27 begin.

5.3 Uncertainty budget

Uncertainty calculation

The uncertainties associated with the twelve values of \bar{x}_{NS} and \bar{x}_{T} measured by the national standard and the transfer standard will be evaluated by the participating laboratory. The participating laboratory will describe the uncertainty budget used to calculate these values in the form CCQM-P28-R3.

Absorption cross section value

Ozone photometers measure ozone mole fractions by the absorption of radiation by ozone at 253.7 nm. As a consequence, the uncertainty on the absorption cross section of ozone at 253.7 nm can be conventionally set to zero if all the instruments use the same value. All laboratories should calculate their ozone mole fractions using the conventional value for the absorption cross section of $1.1476 \times 10^{-17} \text{ m}^2$ (equivalent to $308.32 \text{ atm}^{-1} \text{ cm}^{-1}$). If the laboratory ordinarily uses a different value for the absorption cross section, this should be stated in form CCQM-P28-R3, but the value given here should be used in the calculation.

5.4 Linear regression fit

The sets of the twelve data \bar{x}_{NS} and \bar{x}_{T} will be fitted using a generalised least square program, taking into account the associated uncertainties $u(\bar{x}_{\text{NS}})$ and $u(\bar{x}_{\text{T}})$. This will be performed by the BIPM. The parameters $a_{\text{NS,T}}$ and $b_{\text{NS,T}}$ of the linear relationship between x_{NS} and x_{T} ($x_{\text{NS}} = a_{\text{NS,T}} x_{\text{T}} + b_{\text{NS,T}}$) will be provided as well as their uncertainties.

6. Comparison between the transfer standard and BIPM-SRP27 at the BIPM

6.1 Comparison description

A direct comparison will be made at the BIPM between BIPM-SRP27 and the transfer standard of the visiting laboratory over 12 mole fractions of ozone in dry air in the range (0-500) nmol/mol. Where possible, BIPM-SRP28 will also be included in the comparison to ensure the stability of BIPM-SRP27.

The BIPM will provide the source of zero air for the comparison. The BIPM will utilise its ozone generator for the comparisons, unless the visiting laboratory's instrument cannot operate in this mode, in which case the visiting laboratory's generator will be used. Data will be acquired using the SRP control software version 4.00 (2002) unless the communication between this programme and the participating standard is not possible.

The comparison information form [CCQM-P28-R5](#), as well as the results form [CCQM-P28-R6](#), attached to this protocol, shall be completed and verified by the participating laboratory and the BIPM staff.

6.2 Pre-comparison requirements

Installation guidelines (for SRPs only)

SRPs will be mounted on stands (provided by the BIPM) and not operated whilst resting on their pneumatic and electronics modules.

Stabilisation of instruments

Prior to the comparison, all the instruments that will be used for the comparison shall be switched on and allowed to stabilise for at least eight hours.

Instrument temperature and pressure measurement systems

The laboratories participating in the comparison will be allowed to check their pressure and temperature measurement systems within their instrument. If any adjustments are required, they will be noted.

Records of SRP operating characteristics (for laboratories that operate SRPs)

SRP operating characteristics data sheets shall be completed for all SRPs after their initial warm up period. The data sheets to be completed will be provided by the BIPM. Copies of the participating institute's data sheet shall be kept by the BIPM. The participating institutes are free to make adjustments to their instrument's operating parameters following their usual operating procedures. Any adjustments made will be noted within the data sheets.

Source of purified air

One common source of pure air will be used to provide the flows of reference air and ozone. This air will be furnished by the BIPM. It is ambient air 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 found to be 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. The maximum available flow rate is 25 L/min.

Ozone generator

One common ozone generator will be used to generate the ozone to be measured by all the instruments included in the comparison. The ozone generator utilised in the comparison will be capable of producing stable ozone mole fractions over the range (0-500) nmol/mol, at a minimum flow rate equal to 2 L/min plus the flow rate needed by the guest instrument plus an excess flow rate of 1 L/min. When possible, ozone will be generated with one of the BIPM ozone generators.

Gas manifold

The BIPM external dual manifold system will always be used to redistribute the zero air and ozone/air to the instruments. If the guest instrument possesses its own manifold, the participating laboratory shall decide whether or not it wishes to make use of it, and note this in form CCQM-P28-R5.

Flow rates

Gas flows shall be provided to photometers with a minimum excess of 1 L/min compared to the combined requirements of the photometers included in the comparison.

6.3 Comparison procedure

The following procedure will be followed for the comparison.

Conditioning of the photometers and the pneumatic lines before the comparison

At the beginning of the comparison, the photometers as well as interconnecting pneumatic lines will be conditioned with a nominal value of the ozone mole fraction greater than 500 nmol/mol for at least 2 hours.

Ozone mole fraction nominal values

12 nominal values will be measured by the photometers. These values include the measurement of 0 nmol/mol at the beginning and the end of the comparison. The 12 nominal values will be produced in the following sequence: (0, 220, 80, 420, 120, 320, 30, 370, 170, 500, 270, 0) nmol/mol. Due to the operational characteristics of ozone generators, it is expected that the actual delivered values will be within ± 15 nmol/mol of those nominal values.

Ozone generator stability

For each nominal value of the ozone mole fraction x_{nom} furnished by the ozone generator, it is important to ensure that the photometers are measuring a stable value. To this end, the standard deviation s_{SRP27} on the set of 10 consecutive measurements $x_{\text{SRP27},i}$ performed by BIPM-SRP27 will be calculated. This set is considered as valid if s_{SRP27} is less than 1 nmol/mol. If s_{SRP27} is found greater than 1 nmol/mol, another set of 10 consecutive measurements of the same nominal values is taken. Repeated instances of unacceptable values of s_{SRP27} indicate that there are instabilities in the ozone generator or in the BIPM-SRP27 measurement system. The reasons for these will be examined and documented prior to continuing the comparison.

Recorded values

For each nominal value x_{nom} , the value recorded for each photometer A is the mean (\bar{x}_A) of 10 consecutive single measurements $x_{A,i}$ taken in a stable regime as defined above.

Comparison repeatability

The comparison procedure will be repeated a further two times to ensure its repeatability. A copy of the results form [CCQM-P28-R6](#) shall be completed for each comparison.

6.4 Uncertainty budget

Transfer standard uncertainty calculation

The uncertainties associated with the twelve values \bar{x}_T measured by the transfer standard T will be evaluated by the participating laboratory. The visiting laboratory will provide an uncertainty budget used to calculate the values submitted in the comparison information form [CCQM-P28-R5](#).

The uncertainties associated with the twelve values \bar{x}_{SRP27} (and eventually \bar{x}_{SRP28}) measured by the BIPM-SRP27 (and eventually BIPM-SRP28) will be evaluated by the BIPM. Details of the uncertainty budget for BIPM-SRPs can be found at the end of this document.

Calculation of corresponding values for the national standard

For each value \bar{x}_T measured with the transfer standard, the corresponding value x_{NS} for the national standard will be evaluated using the linear relationship between the two instruments

calculated according to the paragraph 5.4. The twelve obtained values will be reported in the form [CCQM-P28-R6](#).

Calculation of uncertainty of the corresponding values for the national standard

The uncertainties associated with the twelve values x_{NS} obtained above will be evaluated by the participating laboratory and the BIPM. The uncertainty budget used to calculate these values will be described in the comparison information form [CCQM-P28-R5](#).

6.5 Linear regression fits

The sets of the twelve data points (\bar{x}_{SRP27} and x_{NS}) will be fitted using a generalised least square program, taking into account the associated uncertainties $u(\bar{x}_{\text{SRP27}})$ and $u(x_{\text{NS}})$. This will be performed by the BIPM. The parameters $a_{\text{NS},\text{SRP27}}$ and $b_{\text{NS},\text{SRP27}}$ of the linear relationship between x_{NS} and x_{SRP27} ($x_{\text{NS}} = a_{\text{NS},\text{SRP27}} \bar{x}_{\text{SRP27}} + b_{\text{NS},\text{SRP27}}$) will be calculated as well as their uncertainties.

7. Subsequent comparison between the national standard and the transfer standard at the laboratory of the participating institute

The aim of this second comparison between the national and the transfer standard is to demonstrate that no significant drift has occurred in those instruments since the time of their first comparison at the participating institute's laboratory. In consequence, this comparison should be as close as possible of the first comparison.

7.1 Pre-comparison requirements

The requirements are the same as those described for the first comparison in the paragraph 5.1 of this protocol.

7.2 Comparison procedure

The comparison procedure is the same as the one described in the paragraph 5.2 of this protocol. The comparison information form CCQM-P28-R3 attached to this protocol shall be completed by the participating laboratory, as well as three copies of the results form CCQM-P28-R4 for each of the three instances of this comparison. The comparison should be completed and relevant results form received by the BIPM no later than six weeks after the comparison at the BIPM.

7.3 Uncertainty budget

The uncertainty budget shall be described in the form CCQM-P28-R3.

7.4 Linear regression fits

The sets of the twelve data \bar{x}_{NS} and \bar{x}_{T} will be fitted using a generalised least square program, taking the associated uncertainties $u(\bar{x}_{\text{NS}})$ and $u(\bar{x}_{\text{T}})$ as weights. This will be performed by the BIPM. The parameters $a_{\text{NS,T}}$ and $b_{\text{NS,T}}$ of the linear relationship between x_{NS} and x_{T} ($x_{\text{NS}} = a_{\text{NS,T}} x_{\text{T}} + b_{\text{NS,T}}$) will be provided as well as their uncertainties.

8. Reporting of results

The BIPM is responsible for the preparation of a report on the comparison. The report passes through a number of stages, and these are referred to here as drafts A and B.

The first draft, draft A, is prepared as soon as all the results have been received from the participants. It includes the results transmitted by the participants, identified by name. It is confidential to the participants.

The second draft, draft B, is subsequently prepared for the Consultative Committee.

In more detail, the procedure is as follows:

- During the comparison, as the results are received by the BIPM, they are kept confidential by the BIPM until all the participants have completed their measurements and all the results have been received, or until the date limit for receipt of results has passed.
- A result from a participant is not considered complete without an associated uncertainty, and is not included in the draft report unless it is accompanied by an uncertainty supported by a complete uncertainty budget.
- If, on examination of the complete set of results, the pilot institute finds results that appear to be anomalous, the corresponding institutes are invited to check their results for numerical errors but without being informed as to the magnitude or sign of the apparent anomaly. If no numerical error is found the result stands and the complete set of results is sent to all participants. Note that once all participants have been informed of the results, individual values and uncertainties may be changed or removed, or the complete comparison abandoned, only with the agreement of all participants and on the basis of a clear failure of the travelling standard or some other phenomenon that renders the comparison or part of it invalid.
- Draft A of the report is sent as soon as possible after completion of the comparison to all the participants for comment, with a reasonable deadline for replies. The date at which this draft is sent to the participants is taken to be the end date for the comparison and is subsequently referred to as such.
- Draft A is considered as confidential to the participants. Copies are not given to nonparticipants, and graphs or other parts of the draft are not used in oral presentations at an outside Conference without the specific agreement of all the participants.
- On receipt of final comments from participants, the second draft, draft B, is prepared which includes an Appendix containing proposals for a reference value and degrees of equivalence.
- Draft B, which supersedes draft A, is not considered confidential, and may be the subject of a publication with the consensus of all participants. The first initiative for publication is with the BIPM. Other participants may publish the results with the agreement of the BIPM. The Draft B report becomes the final report once it has been presented as such to the CCQM.

BIPM-SRP27 uncertainty budget

The following is an example of a model uncertainty budget that is applicable for the measurement of an ozone mole fraction in dry air (x) by BIPM-SRP27 and BIPM-SRP28 in the range (0-500) nmol/mol.

Component (y)	Uncertainty $u(y)$				Sensibility coefficient $c_i = \frac{\partial x}{\partial y}$	contribution to $u(x)$ $ c_i \cdot u(y)$
	Source	Distribution	Standard Uncertainty	Combined standard uncertainty $u(y)$		
Optical Path $2L$	Measurement Scale	Rect.	0.0011 cm	0.014 cm	- $\frac{x}{2L}$	$\frac{u(2L) \cdot x}{2L}$
	Repeatability	Normal	0.01 cm			
Pressure P	Pressure gauge	Rect.	0.029 kPa	0.034 kPa	- $\frac{x}{P}$	$\frac{u(P) \cdot x}{P}$
	Difference between cells	Rect.	0.017 kPa			
Temperature T	Temperature probe	Rect.	0.087 K	0.087 K	- $\frac{x}{T}$	$\frac{u(T) \cdot x}{T}$
Ratio of intensities D	Scalers resolution	Rect.	8×10^{-6}	1.4×10^{-5}	$\frac{x}{D \ln(D)}$	$\frac{u(D) \cdot x}{D \ln(D)}$
	Repeatability	Triang.	1.1×10^{-5}			
Absorption Cross section α	Conventional value	-	-	-	-	-

Additionally, a comparison will allow Type A uncertainties to be assessed from the measurement data.

The measurement equation can be written

$$x = \frac{-1}{2\alpha L} \frac{R}{N_A} \frac{T_{\text{mes}}}{P_{\text{mes}}} \ln(D) \quad [1]$$

or :

$$x = B \ln(D) \quad [2]$$

where

$$B = \frac{-1}{2\alpha L} \frac{R}{N_A} \frac{T_{\text{mes}}}{P_{\text{mes}}} \quad [3]$$

and is constant for a given temperature and pressure.

The combined standard uncertainty $u(x)$:

$$u(x) = \sqrt{\left(\frac{u(D)x}{D \ln(D)}\right)^2 + \left(\left(\frac{u(2L)}{2L}\right)^2 + \left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(T)}{T}\right)^2\right)x^2} \quad [4]$$

Note that the uncertainty contribution from the ratio of intensities D (to the combined standard uncertainty of x) can be written:

$$u_D = \frac{u(D)x}{D \ln(D)} = \frac{u(D)B}{D} \approx u(D)B \quad [5]$$

Which is approximately constant for a given temperature and pressure, since for the measurement range (0 – 500) nmol/mol:

$$D \approx 1 \quad [6]$$

Applying this to BIPM-SRP27 ($L = 89.8$ cm), with a measured temperature equal to 295 K and a measured pressure equal to 100 kPa gives the numerical equation (where the numerical values of x are for ozone mole fractions given in units of nmol/mol):

$$u(x) = \sqrt{(0.28)^2 + 2.09 \cdot 10^{-7} x^2} \quad [7]$$

Figure 1 depicts the estimated value of $u(x)$ as a function of the ozone mole fraction x .

Figure 1 : Combined standard uncertainty associated with the measured mole fraction of ozone in dry air for BIPM-SRP27.

