Bureau International des Poids et Mesures

Requirements for new measurements of ozone absorption cross-sections for the accurate determination of ozone concentration

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Bureau International des Poids et Mesures

WMO Ozone Theme meeting
Geneva, 11-13 May 2009

Outline

- **The CIPM, the BIPM, the chemistry section**
- International comparisons of ozone standards
- Scientific programme (1) : biases in the reference standard
- Scientific programme (2) : biases in the reference method
- Future programme : new measurements of the ozone absorption cross-section

BUREAU INTERNATIONAL DES POIDS ET MESURES

The BIPM

- It has **headquarters** near Paris, France. It is **financed** jointly by the Member States and Associates, and operates under the exclusive **supervision** of the CIPM.
- Its **mandate** is to provide the basis for a single, coherent system of measurements throughout the world, traceable to the International System of Units (SI). This task takes many forms, from **direct dissemination** of units (as in the case of mass and time) to coordination through **international comparisons** of national measurement standards (as in length, electricity and ionizing radiation).
- It maintains **scientific laboratories** in areas of: mass, time, frequency and gravimetry, electricity, ionizing radiation, and chemistry.
- It has an international **staff** of over 70 and its status vis-à-vis the French Government is similar to that of other **intergovernmental organizations**.
- Its **budget** is over eleven million euros.

COMITÉ INTERNATIONAL DES POIDS ET MESURES

The CIPM

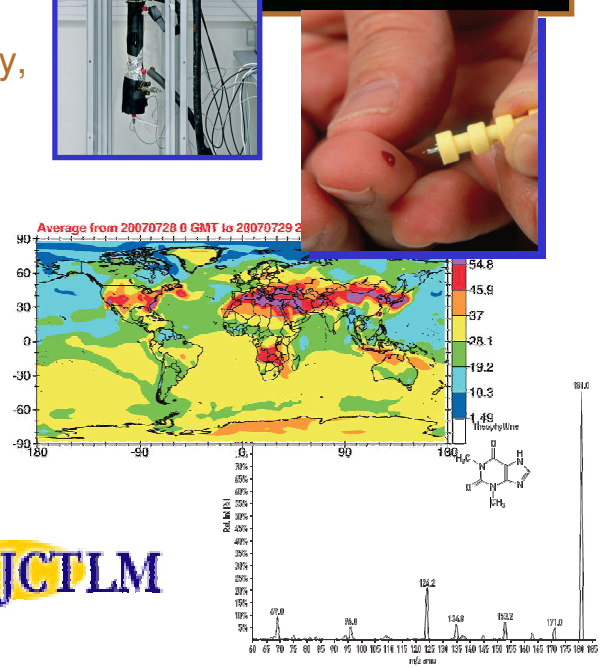
- Is made up of **eighteen individuals**, each from a different State. Its principal task is to **promote worldwide uniformity in units of measurement** by direct action or by submitting draft resolutions to the CGPM.
- **Meets annually** and, its duties include:
  - consideration of the **work of the BIPM**;
  - consideration of reports presented to it by its **Consultative Committees**;
  - consideration of metrological work that Member States decide to do in common and sets up and coordinates **activities between specialists in metrology**;
  - making appropriate **Recommendations**;
  - issuing an **Annual Report** on the **administrative and financial position of the BIPM** to the Member States;
  - commissioning **reports** in preparation for CGPMs, and others such as the SI Brochure.

CIPM 1894

CIPM 2007

CHEMISTRY

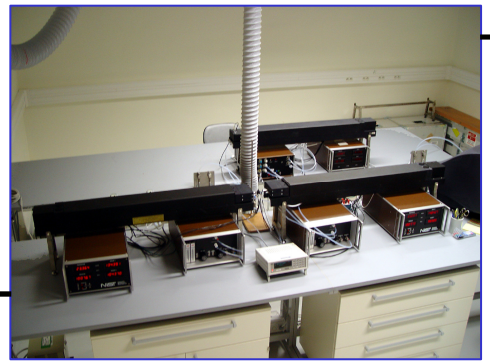
- **Chemical metrology** is important in national measurement infrastructures to improve industrial competitiveness, facilitate trade, implement regulations, ensure the safety of products, protect the environment and enhance the quality of life.
- The BIPM organizes **international comparisons** of:
  - **gas standards for air quality and greenhouse gas monitoring**;
  - and of **primary calibrators for laboratory medicine, food analysis and forensics**.
- The BIPM maintains a central **O_3 reference standard** comparison facility, facilities for **NO and NO_2** gas standard comparisons, and is developing facilities for **CH_4 and CH_2O** gas standard comparisons.
- The BIPM is coordinating comparisons on the **purity of monitored therapeutic drugs and steroid hormones** to underpin reference measurement systems for **clinical analytes**. Future comparisons will underpin systems for **contaminants and residues in food** as well as **forensic** applications.
- The BIPM maintains the database of the **Joint Committee on Traceability in Laboratory Medicine**, which lists certified reference materials and methods of higher order which have been reviewed by the Committee against ISO standards.



JCTLM

Gas Metrology Programme (2005-2008)

Ozone reference standard comparison facility



CCQM-P28

BIPM.QM-K1

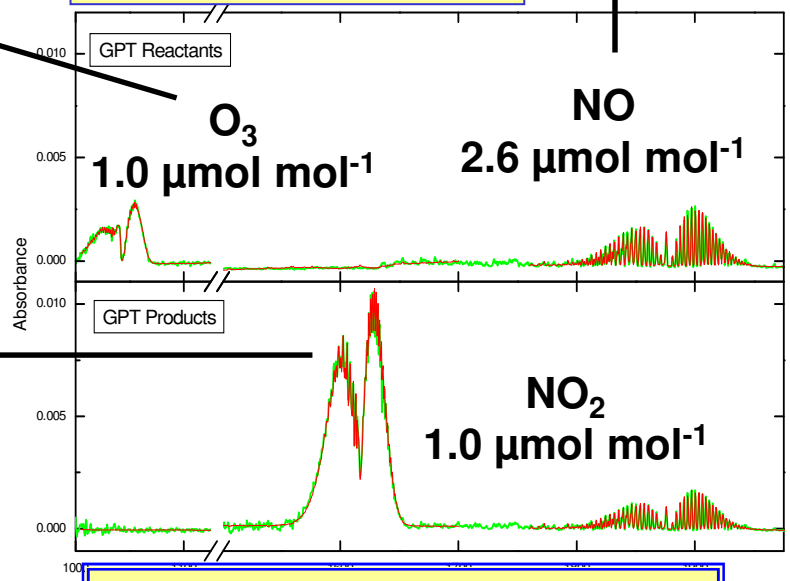
Ozone (2-1000) nmol/mol

CCQM-P73

NO (30-70) µmol/mol

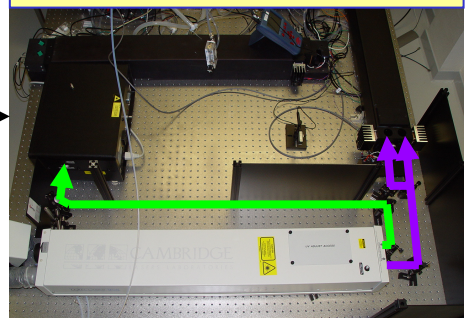
NO standard comparison facility

Gas Phase Titration



$NO + O_3 \rightarrow NO_2 + O_2$

Laser based SRP



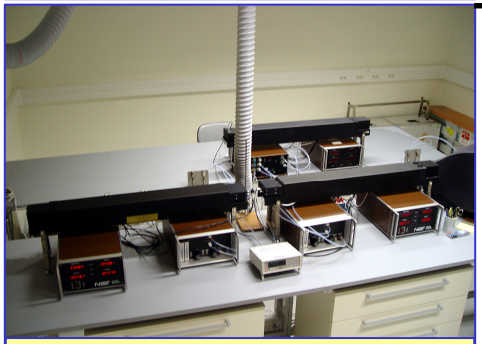
NO_2 primary facility (dynamic preparation)

Method development and validation at

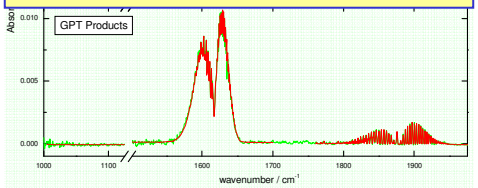
10 µmol/mol

Gas Metrology Programme (2009-2012)

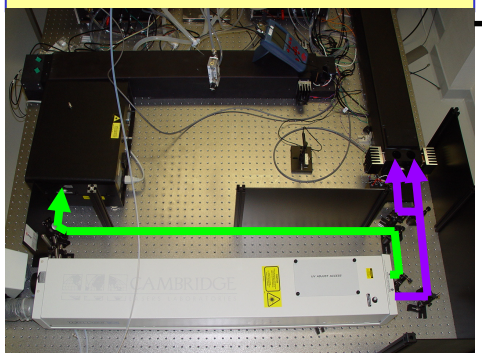
Ozone reference standard comparison facility



Gas Phase Titration



O_3 absorption cross section



BIPM.QM-K1

Ozone (2-1000) nmol/mol

Core Comparison

CH_4 / air

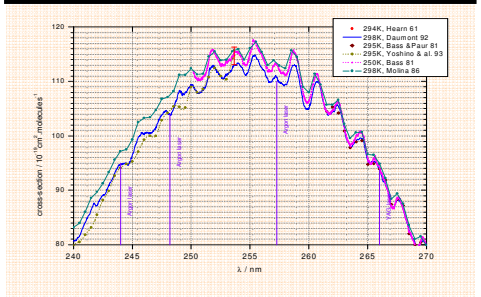
CCQM-P110

NO_2 /N_2 10 µmol/mol

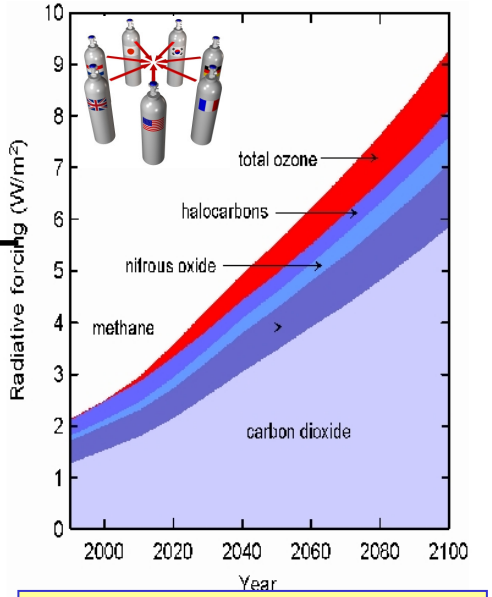
Analytical Challenge Comparison

CH_2O 10 µmol/mol

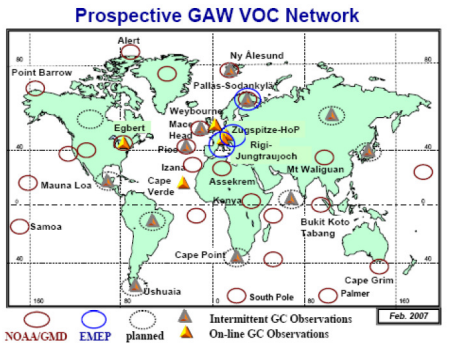
α_{O3}



Green House Gas comparison facility



Formaldehyde (ozone precursor) facility



Outline

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- **International comparisons of ozone standards**
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The reference method for ozone at ambient level: UV photometry

T Temperature in the cells

P Pressure in the cells

L_{opt} light path length

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

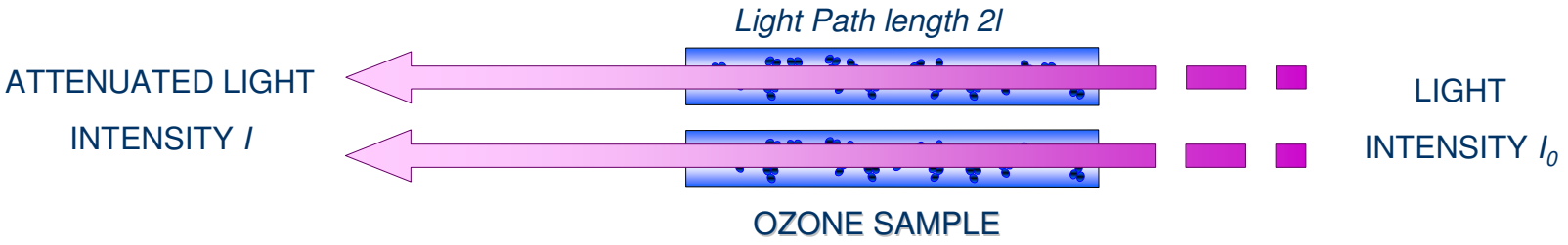
R Gas constant

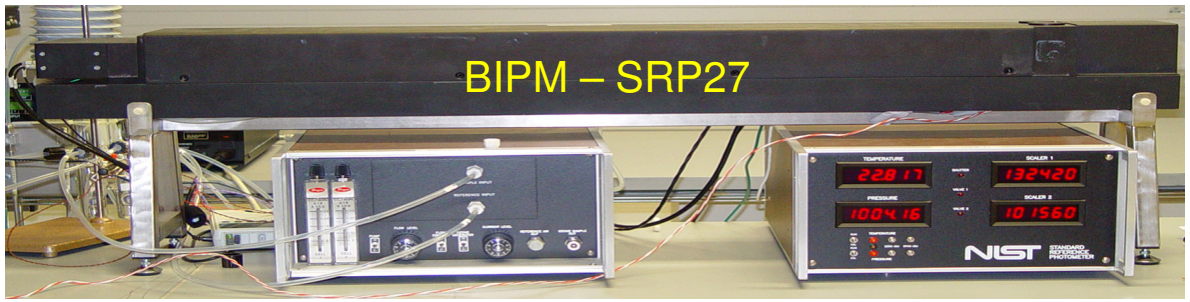
N_A Avogadro constant

D Product of transmittance of the two cells

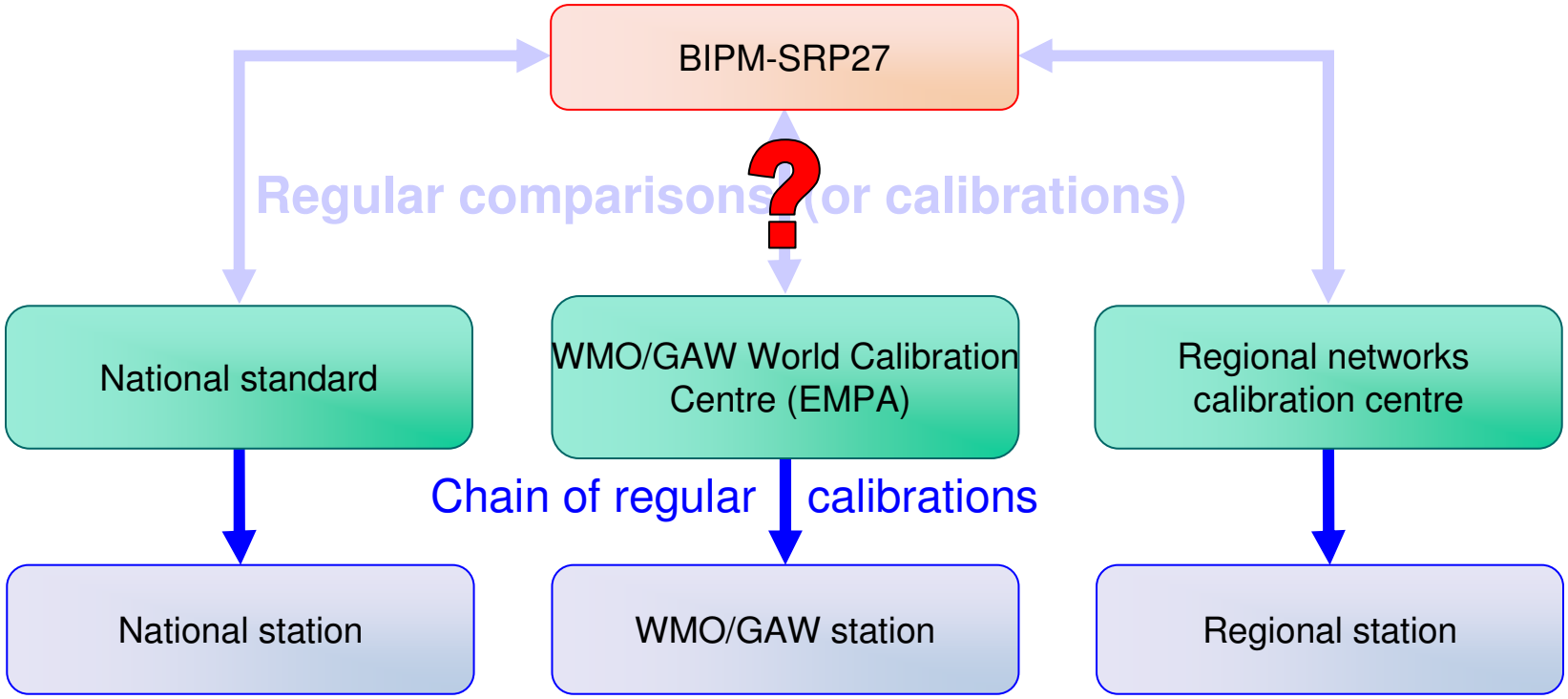
σ Ozone absorption cross-section at 253.64 nm under standard conditions of temperature and pressure

➡ ***x* mole fraction of ozone in dry air (nmol/mol)**



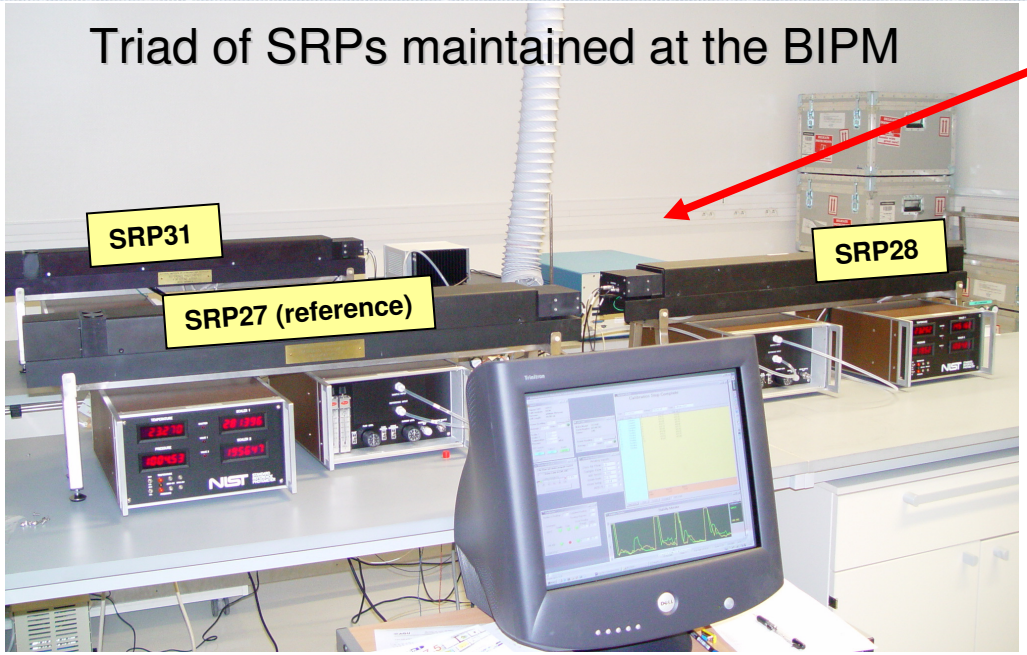


Scheme for international comparisons



Stations around the world monitoring ozone at ambient level….

Comparisons at the BIPM

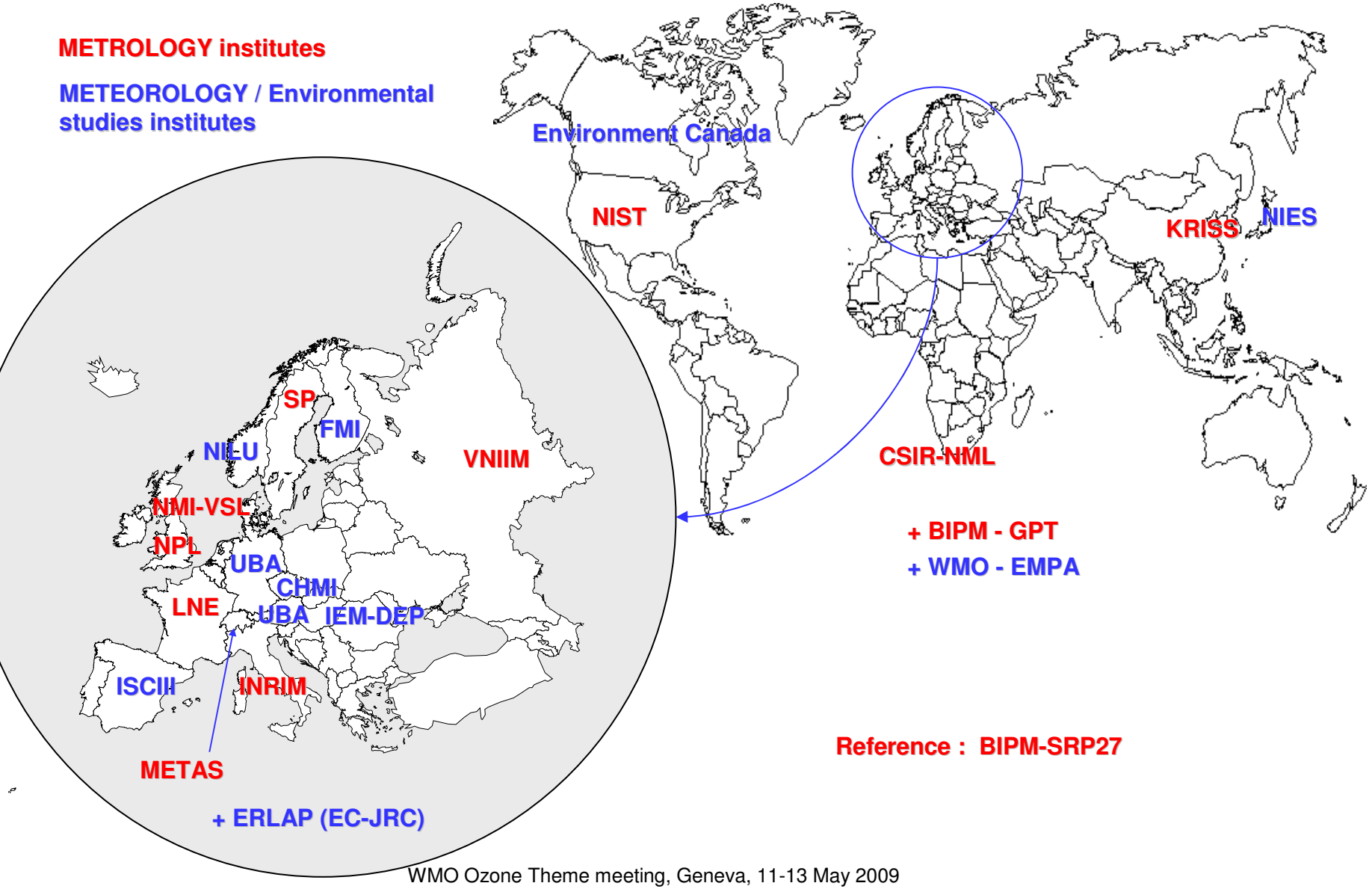


One comparison = 2 ozone standards measuring different O_3 concentration from the same source

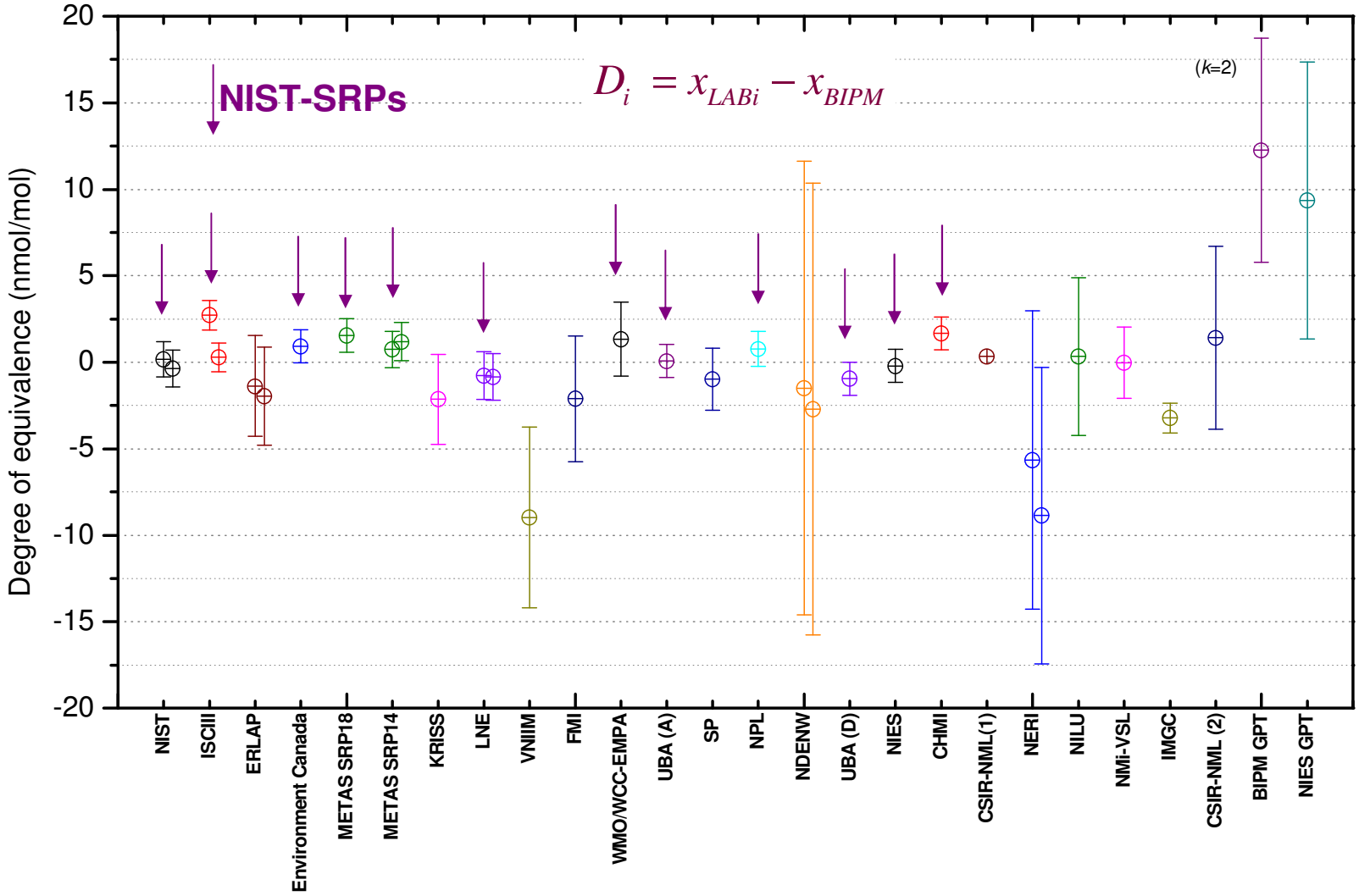
range : 0 to 1000 nmol/mol

One common reference standard : SRP27

Comparison CCQM-P28, 23 participants, 18 months



Comparison CCQM-P28 Final results - D_i at 420 nmol/mol



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Biases in the SRPs

Temperature not uniform

Solution : avoid the heating

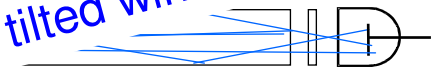
as temperature gradient

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

Optical path ≠ cell length

lamp

Partial solution : avoid multiple reflections with tilted windows



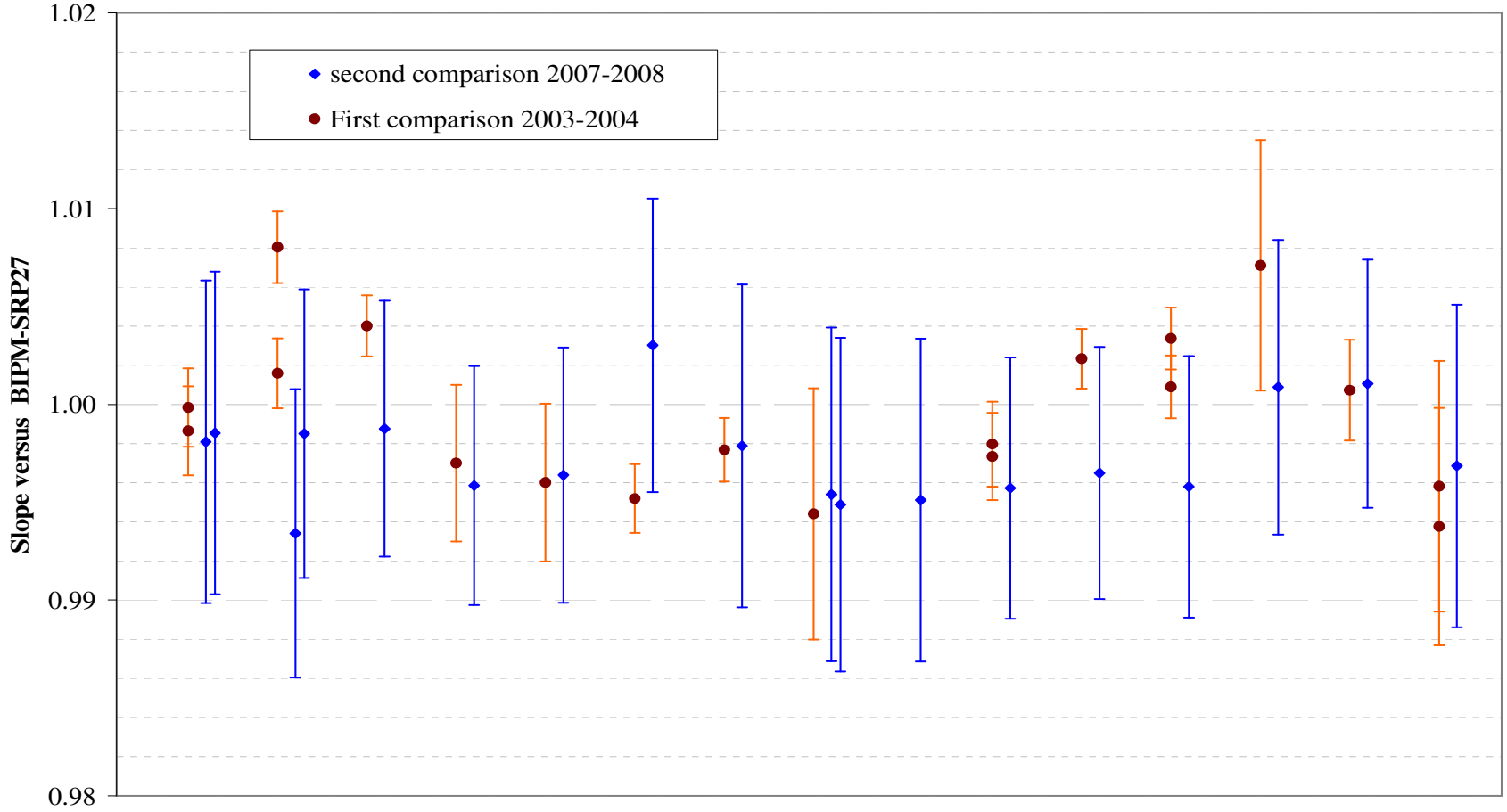
Optical path $L_{opt} > Lc$

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

Improved comparability

Upgraded SRPs (biases reduced) + Revised uncertainty budget

= improved comparability among National Metrology Institutes



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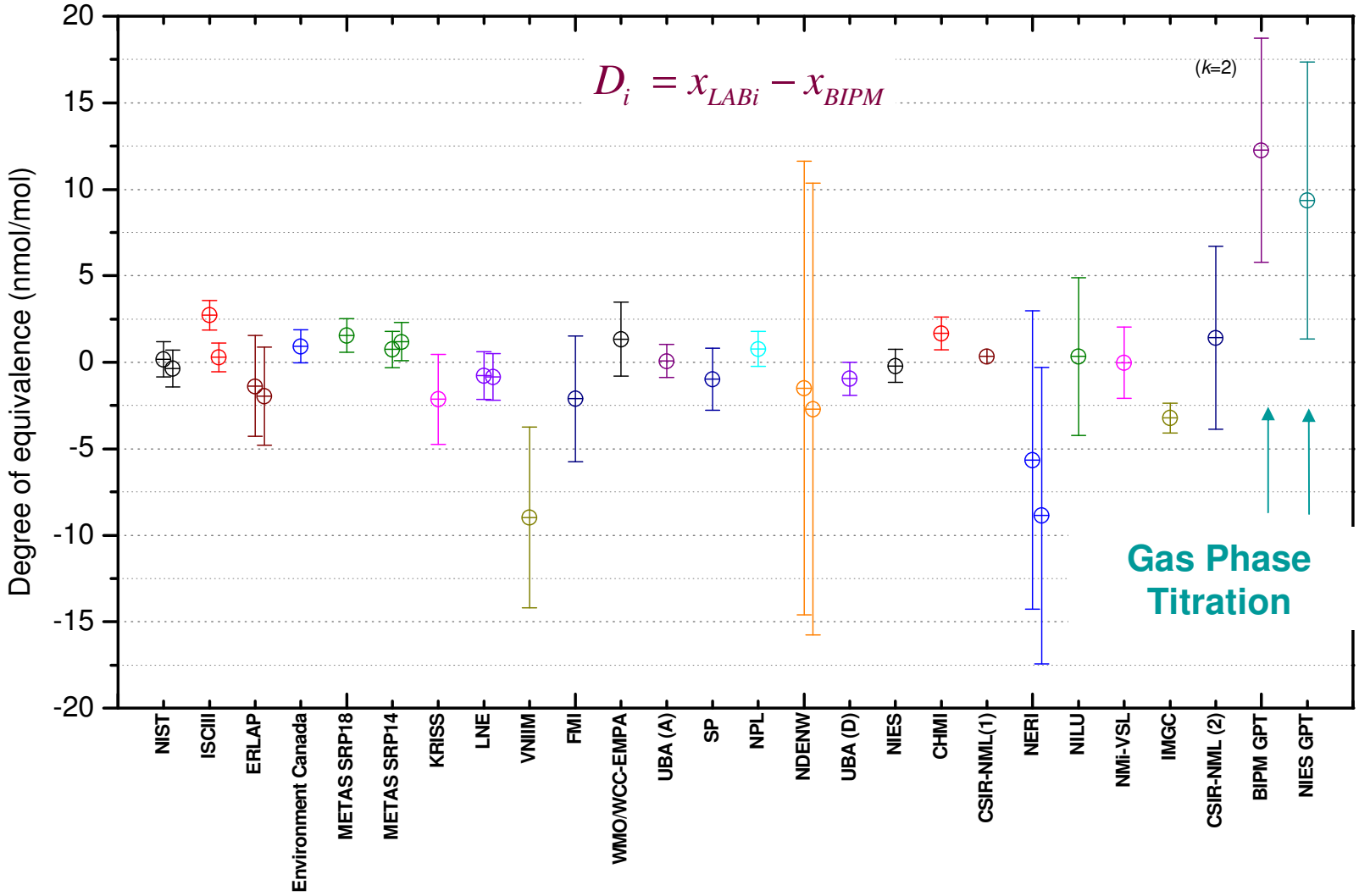
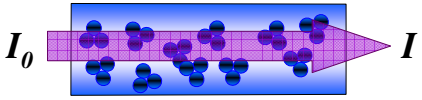
Pilot study CCQM-P28 Final results - D_i at 420 nmol/mol



UV photometry and GPT traceability chains

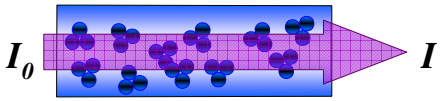
Pure ozone concentration *c* assessed by pressure measurements



$$\sigma(\lambda) = -\frac{1}{L_{opt} \cdot c} \ln\left(\frac{I}{I_0}\right)$$

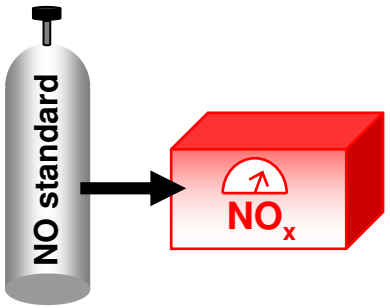
$\sigma(\lambda)$

Primary UV photometer



$$c' = -\frac{1}{L_{opt} \cdot \sigma(\lambda)} \ln\left(\frac{I}{I_0}\right)$$

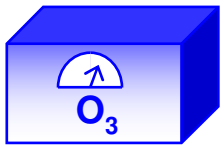
Calibration by comparison of measurement results *c'* on an unknown sample



Chemiluminscence NO_x analyser calibrated by gravimetric NO standard

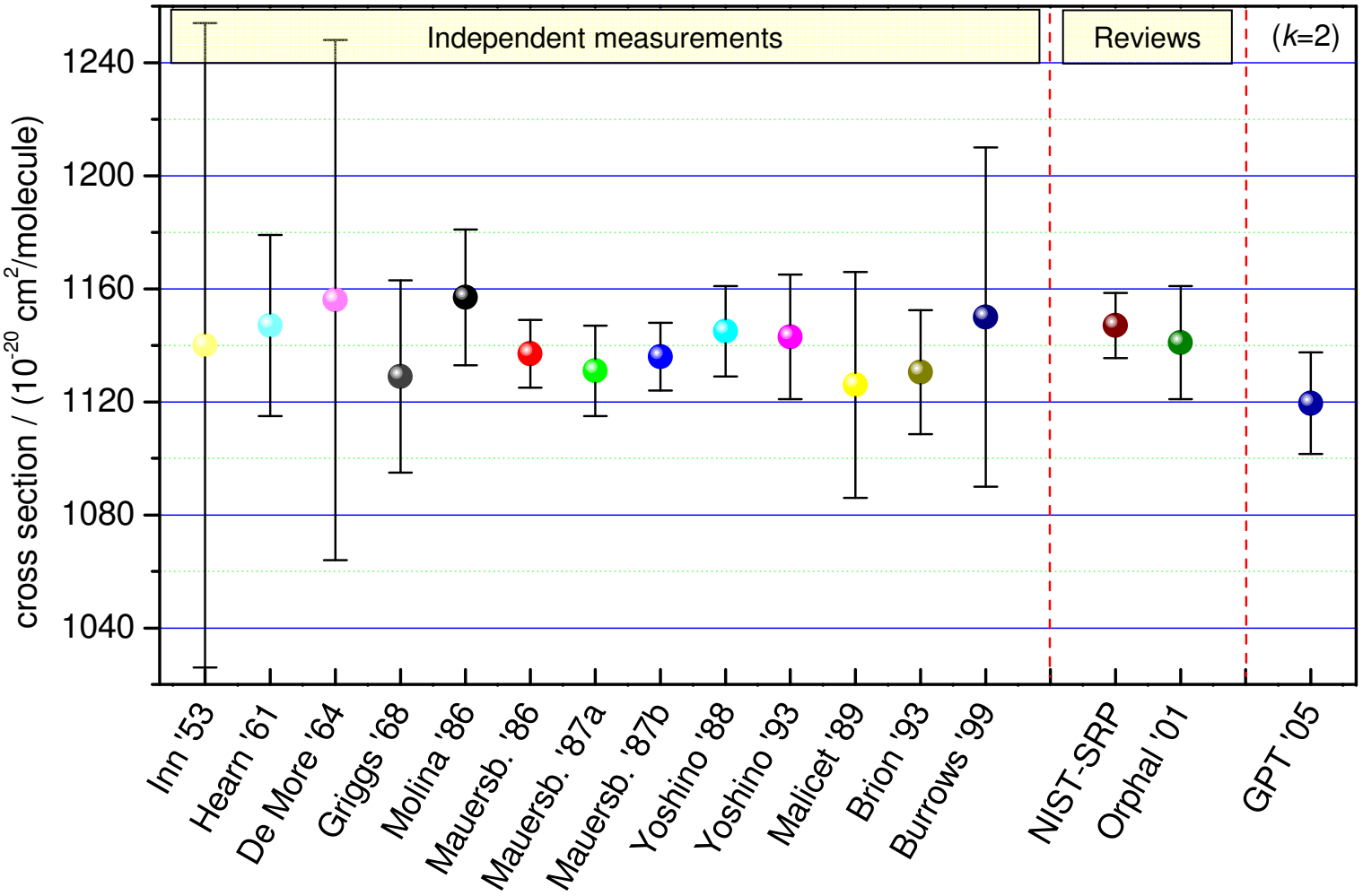
GPT stochiometric reaction

$$NO + O_3 \rightarrow NO_2 + O_2$$

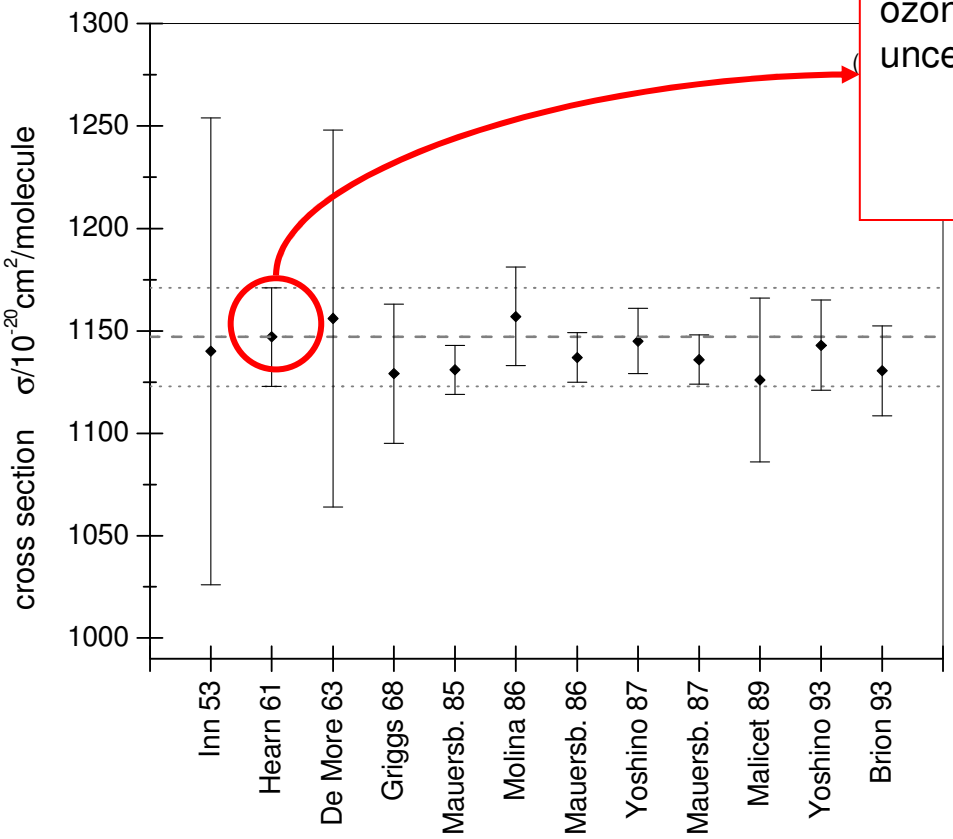


Calibration of any O_3 analyser

GPT results put the question mark on the cross-section



Harmonisation issue solved



Up to now : conventional value used in all ozone photometers, with a relative standard uncertainty equals to:

0.58% (NIST/NASA)
0.75% (ISO standard)
1% (some institutes)

2009 : NMIs adopt a conventional uncertainty for the cross-section based on Hearn uncertainty budget with *GUM*[1] principles

Standard deviation of the mean (%)	0.43
Tube length (%)	0.54
McLeod gauge (%)	0.81
Combined relative uncertainty (%)	1.06
Expanded relative uncertainty (k=2) (%)	2.12

[1] BIPM, CEI, FICC, ISO, OIML, UICPA, and UIPPA, *Guide to the Expression of Uncertainty in Measurement*. 1995, Geneva: International Organization for Standardization. 101.

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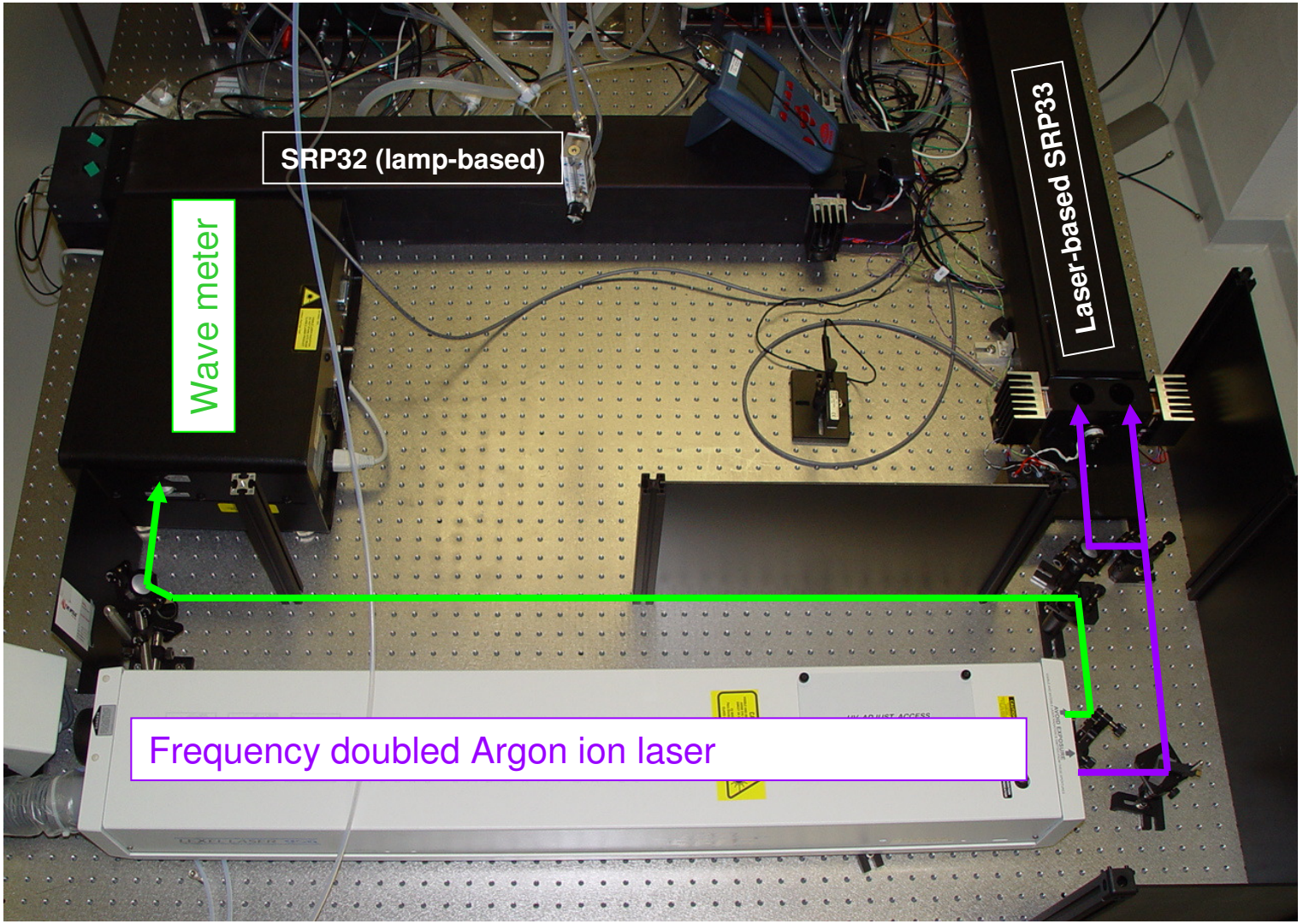
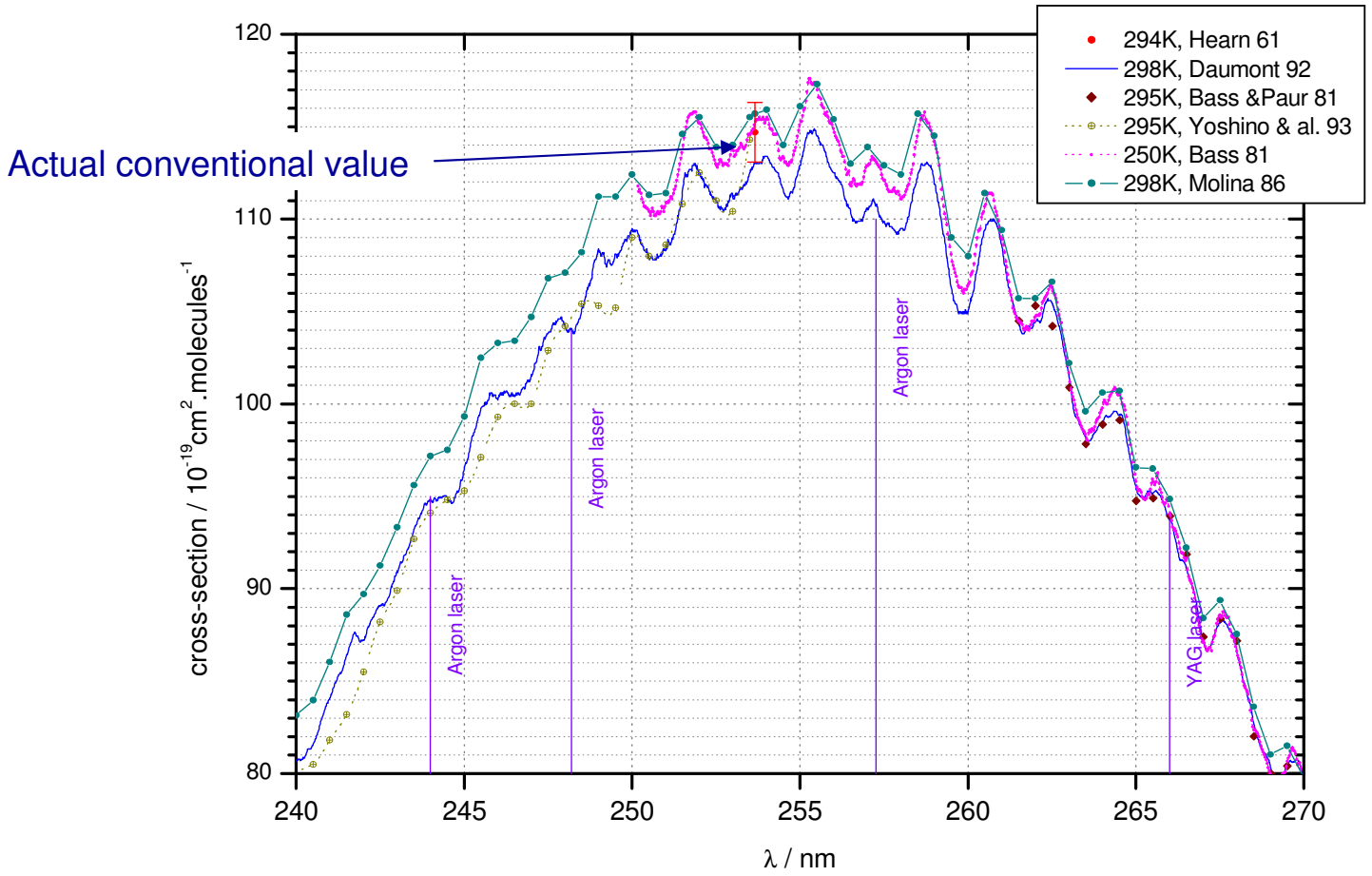
The laser-based SRP - a potential new primary standard



Ozone cross-section to be measured again in the Hartley band

Three laser lines close to the ozone absorption cross-section maximum



Conclusion

- **The BIPM provides the basis for a single, coherent system of measurements throughout the world, traceable to the International System of Units (SI).**
- **For ozone at ambient level, comparability is insured through International comparisons of ozone standard instruments (UV photometers)**
- **Traceability to the SI is under question as two reference methods do not agree**
- **To resolve this issue, new (more accurate) measurements of the ozone absorption cross-section in the Hartley band are undertaken**

THANK YOU

www.bipm.org

www.metrologyinfo.org