Primary Surface Ozone Standard
Reference Photometers and BIPM.QM-K1

J. Viallon, BIPM

Accurate Monitoring of Surface Ozone
Virtual Workshop
6 October 2020

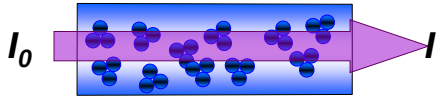
Bureau International des Poids et Mesures

www.bipm.org

All SRPs are equivalent and linked to the SI

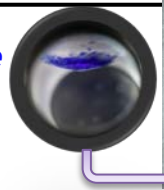
The ozone absorption cross-section is what links the SRP to the SI

Measurement of the absorption cross-section of *pure ozone* in laboratory



$$\sigma(\lambda) = \frac{-1}{L_{opt}} \frac{T}{P(O_3)} \frac{R}{Na} \ln\left(\frac{I}{I_0}\right)$$

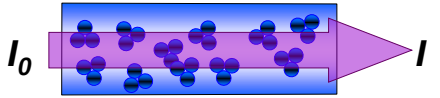
pure ozone
(liquid before evaporation)



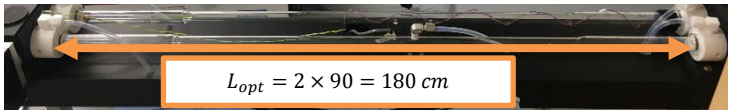
$\sigma(\lambda)$

λ = 253.65 nm

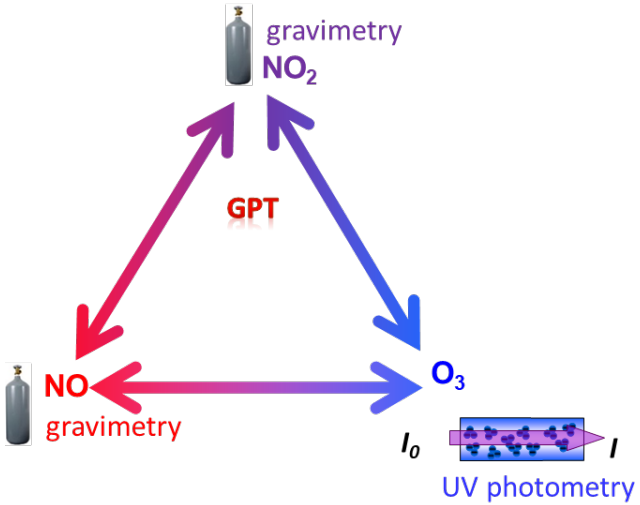
Measurement of the amount fraction of ozone in air inside the SRP (Ozone UV analyser)



$$x(O_3) = \frac{-1}{L_{opt}\,\sigma(\lambda)} \frac{R}{N_a} \frac{T}{P} \ln\left(\frac{I}{I_0}\right)$$



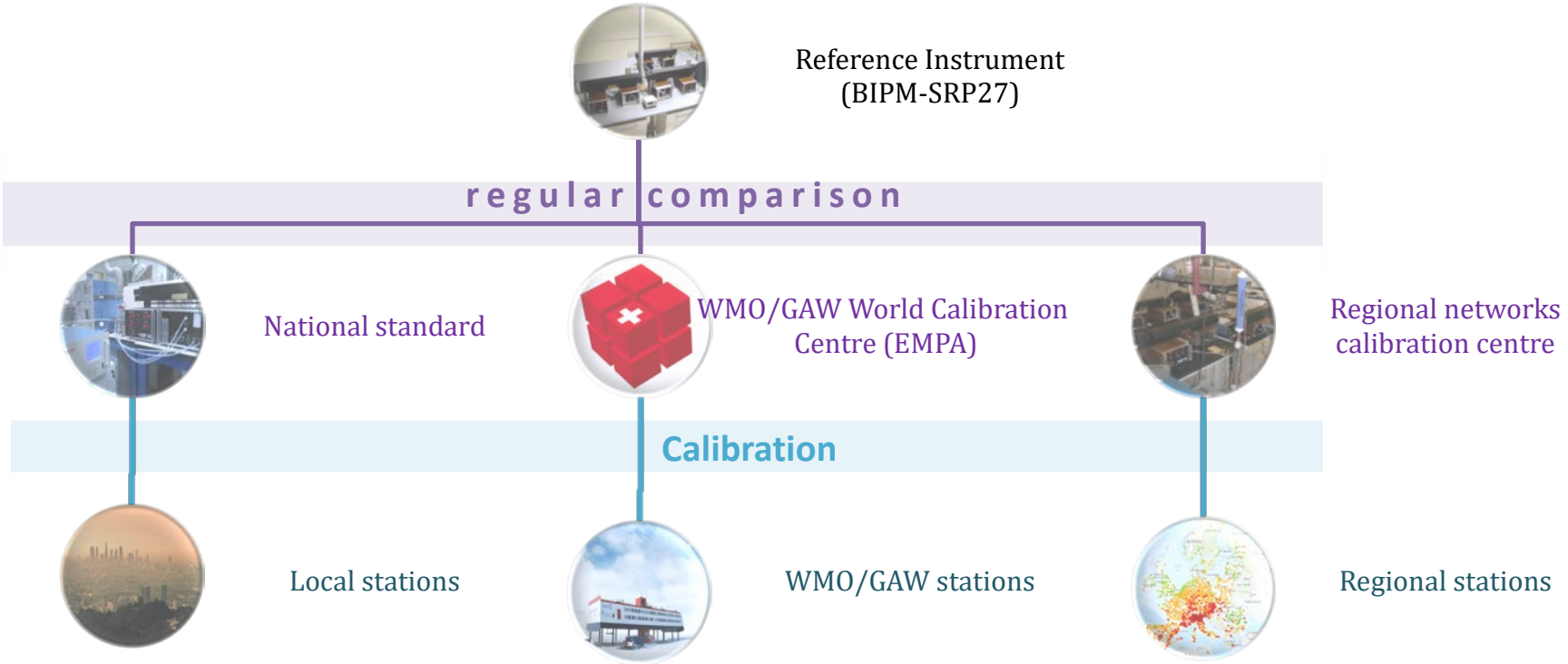
BIPM mission since 2002 : improved accuracy



Gas Phase Titration : $NO + O_3 \rightarrow NO_2$

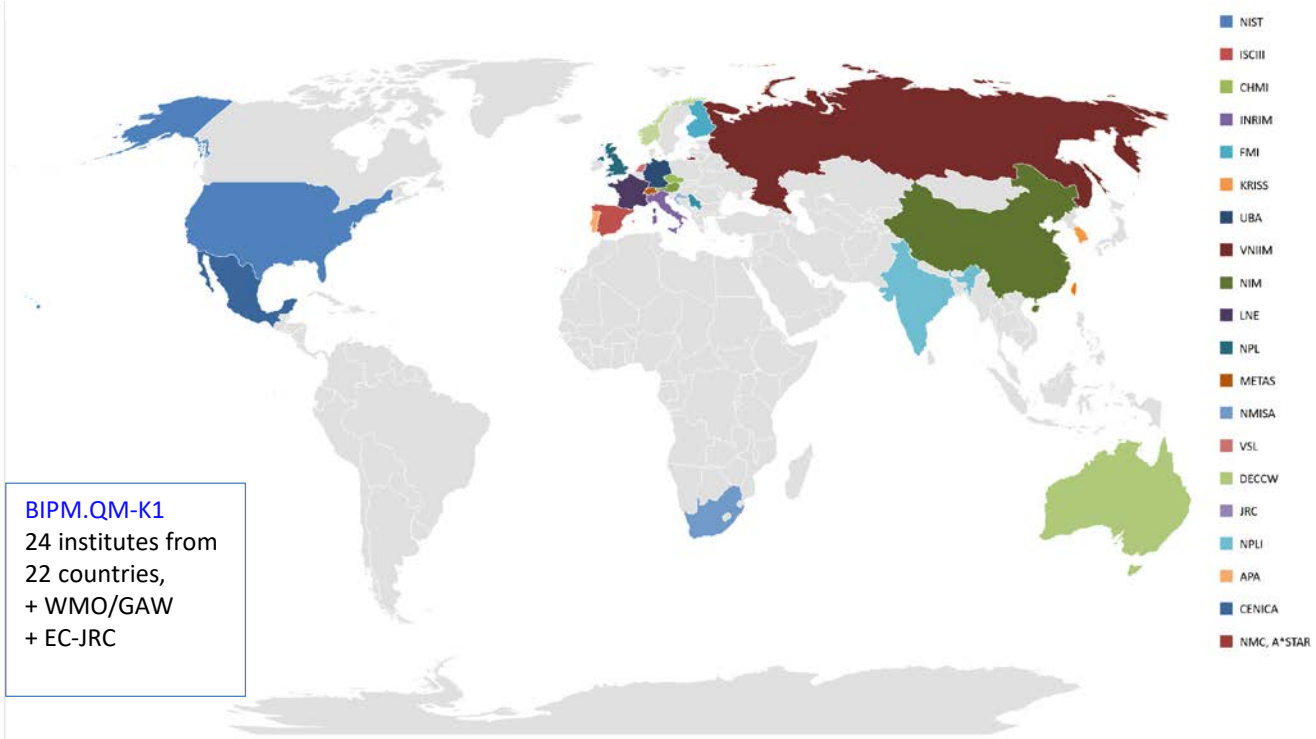
- 2002 : the BIPM installs 3 SRPs and starts a Gas Phase Titration experiment
- 2005 : BIPM and NIES GPT measurements during CCQM-P28 : ~ 2% bias
- 2007: launch of BIPM.QM-K1
- 2012 : laser-based SRP to perform relative measurements of the absorption cross-section
- 2015 : absorption cross-section measurements in pure ozone results in lower value than Hearn
- 2016 : improved GPT with traceability to NO and NO_2 agrees better with 2015 value

Metrological Traceability of surface ozone measurements



Comparisons at the BIPM since 2003

2003-2005 : Pilot Study CCQM-P28, 23 participants
Since 2007 : On-going Key Comparison BIPM.QM-K1



BIPM.QM-K1
24 institutes from
22 countries,
+ WMO/GAW
+ EC-JRC

Comparisons of SRPs at the BIPM

Comparison Protocol

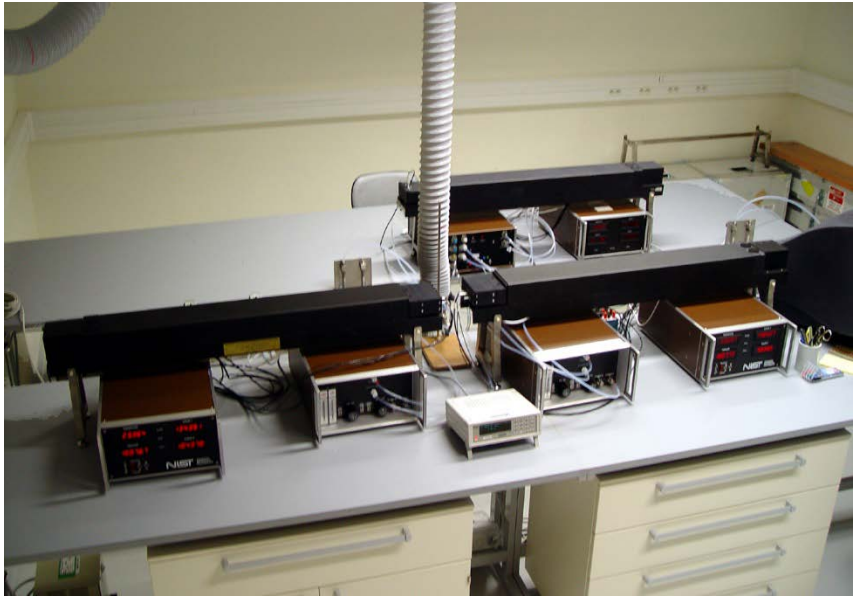
One comparison : 2 SRPs measuring different O_3 concentration from the same source

Range of O_3 : 0 to 500 nmol/mol

One main instrument : SRP27

Number of points : 10

Triad of SRPs maintained at the BIPM



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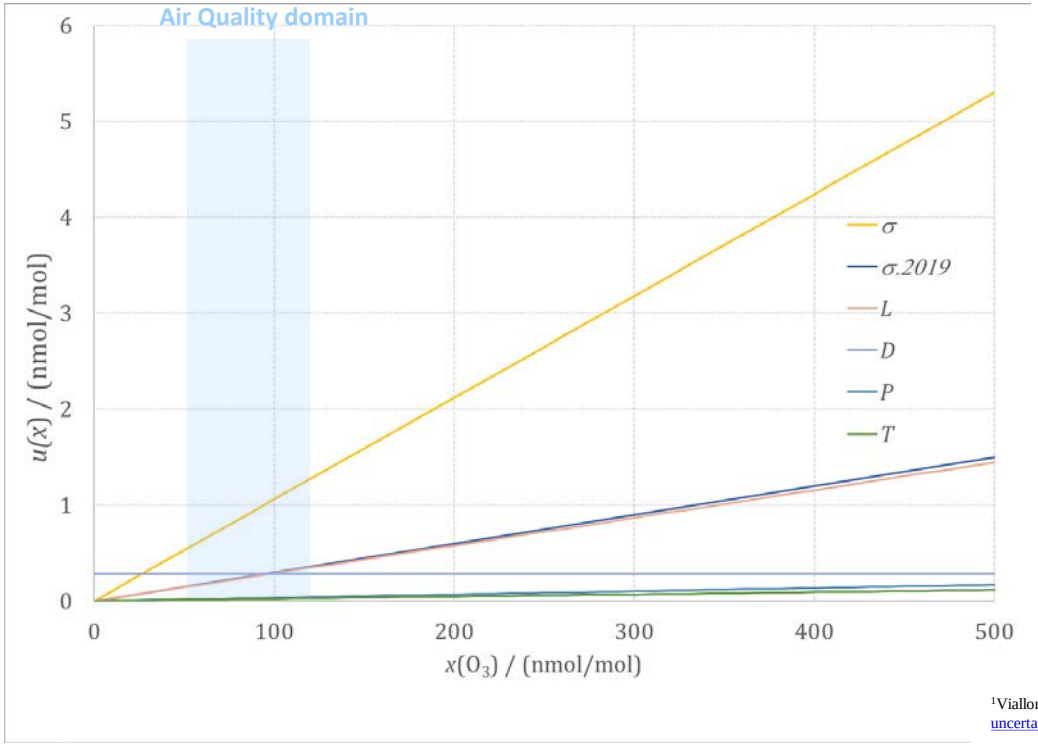
Uncertainties (of BIPM maintained SRPs)

Standard uncertainty for the range of one ozone amount fractions measured during a comparison of SRPs



$$x(O_3) = \frac{-1}{L\sigma(\lambda)} \frac{R}{N_a} \frac{T}{P} \ln(D)$$

Major uncertainty: absorption cross-section, currently 1.06 % (standard)

Light path length: 0.3 % (increased in 2006 after BIPM work on biases[1])

Pressure: 0.04 %

Temperature: 0.03 %

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

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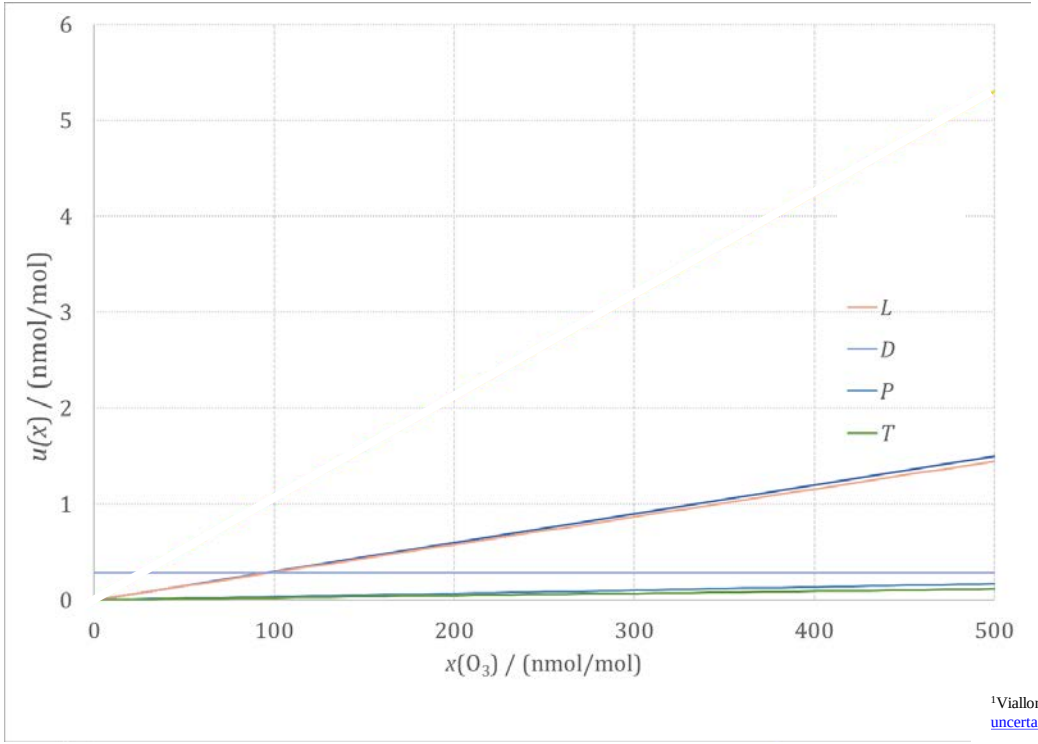


$$x(O_3) = \frac{-1}{L\sigma(\lambda)} \frac{R}{N_a} \frac{T}{P} \ln(D)$$

Major uncertainty: absorption cross-section, currently 1.06 % (standard)

No uncertainty on the absorption cross-section when comparing instruments (fully correlated component)

Note for calibration : include $u(\sigma)$ just once!

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

Degrees of Equivalence

By definition: $D = x_{\mathrm{NS}} - x_{\mathrm{RS}}$

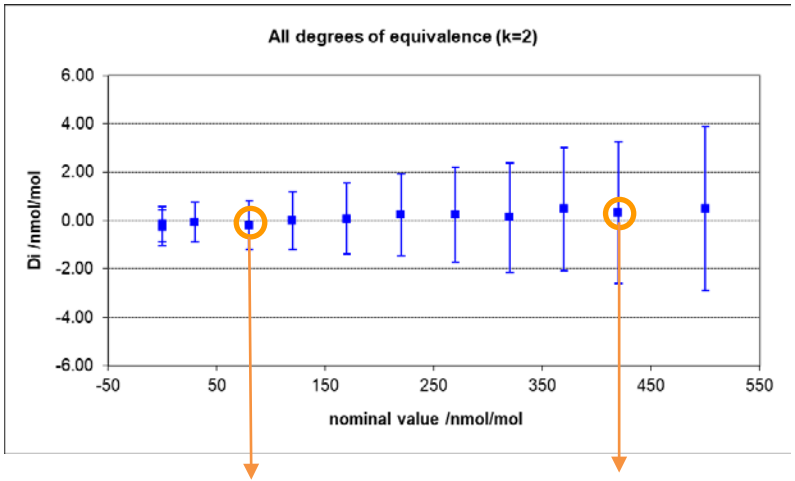
$u(D) = \sqrt{u(x_{\mathrm{NS}})^2 + u(x_{\mathrm{RS}})^2}$

RS = Reference Instrument = BIPM-SRP27 by convention

10 nominal ozone amount fractions measured during a comparison :

	Reference Standard (RS)			National standard (NS)		
Nominal value	x_{RS} nmol/mol	s_{RS} nmol/mol	$u(x_{\mathrm{RS}})$ nmol/mol	x_{NS} nmol/mol	s_{NS} nmol/mol	$u(x_{\mathrm{NS}})$ nmol/mol
0	0.01	0.22	0.28	-0.29	0.27	0.24
220	206.50	0.22	0.66	206.74	0.27	0.53
80	76.63	0.17	0.36	76.44	0.20	0.35
420	407.25	0.44	1.22	407.58	0.33	0.81
120	119.08	0.18	0.45	119.08	0.30	0.41
320	298.71	0.18	0.92	298.84	0.31	0.66
30	29.49	0.17	0.29	29.42	0.17	0.28
370	346.30	0.24	1.05	346.77	0.31	0.73
170	163.88	0.24	0.55	163.97	0.30	0.47
500	480.25	0.42	1.43	480.74	0.36	0.91
270	251.15	0.09	0.79	251.39	0.30	0.59
0	-0.08	0.23	0.28	-0.23	0.29	0.24

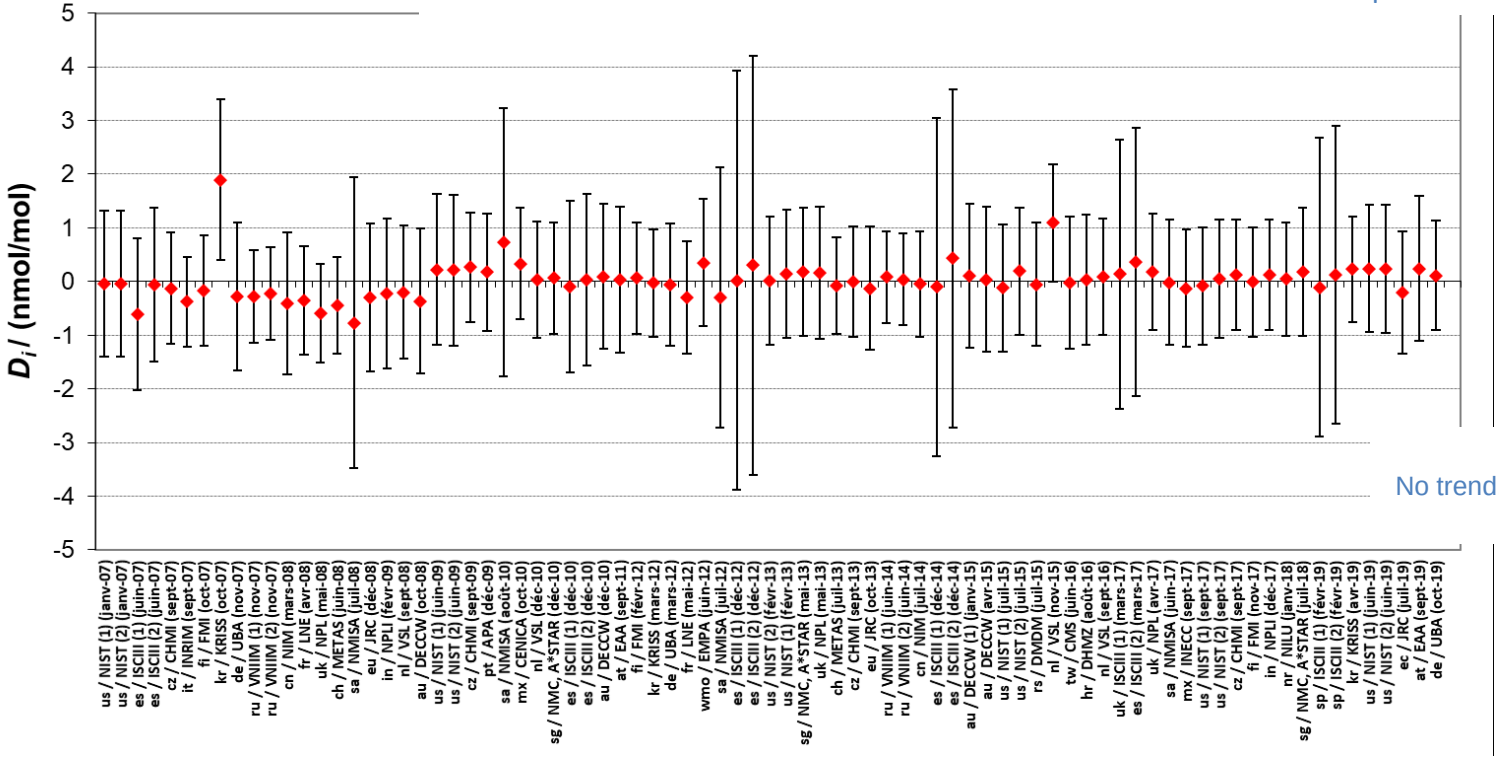
2 out of 10 chosen to calculate Degrees of Equivalence



Values chosen as representative of the range (CCQM/GAWG Workshop 2005)

On-going comparison since 2007

One bilateral comparison -> one report + results in KCDB
(D_i at 80 and 420 nmol/mol)



Maintained agreement
No trend, stability maintained over years

Results in the BIPM **K**ey **C**omparison **D**ata **B**ase

https://www.bipm.org/kcdb/comparison?id=1428

KCDB

All data listed in the KCDB have been reviewed and approved within the CIPM Mutual Recognition Arrangement

CMCS | COMPARISONS | NEWS | STATISTICS

Home > Comparisons

INFORMATION | GRAPHS OF EQUIVALENCE | DEGREES OF EQUIVALENCE | EQUIVALENCE STATEMENTS | LABORATORY MEASUREMENTS

BIPM comparison

→ BIPM.QM-K1

Linked comparison

BIPM.QM-K1

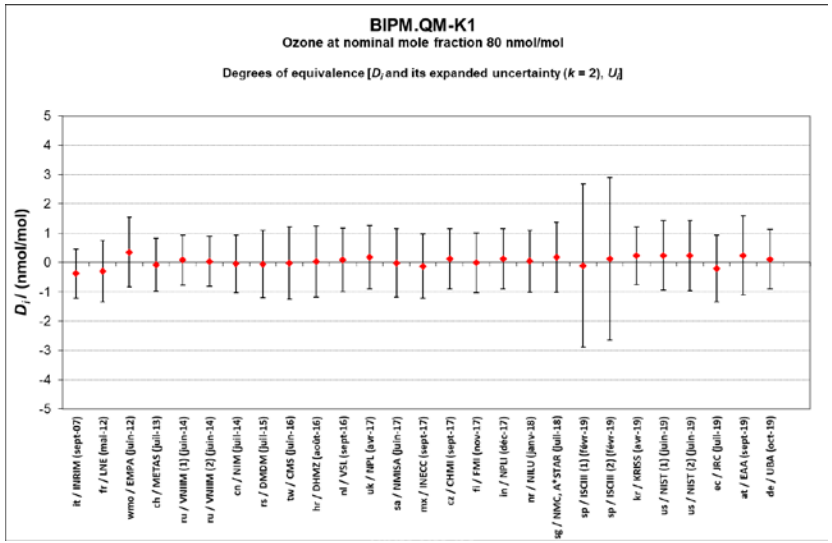
PRINT OUT

INFORMATION & CONTACT | PARTICIPANTS

Metrology area, Sub-field	Chemistry and Biology, Gases
Description	Ozone at ambient level
Time of measurements	2007 -
Status	Continuous, approved for equivalence
Measurand	Amount fraction of ozone in dry air 80 nmol/mol and 420 nmol/mol
Transfer device	Measurements made at the BIPM by comparison with the BIPM Reference Photometer SRP27
Comparison type	Key Comparison
Consultative Committee	CCQM (Consultative Committee for Amount of Substance)
Conducted by	BIPM (Bureau International des Poids et Mesures)
Comments	First results published on 09 April 2008 *The Final Report for each bi-lateral comparsion is listed in the tab "Participants"* **Last update: 5 June 2020**

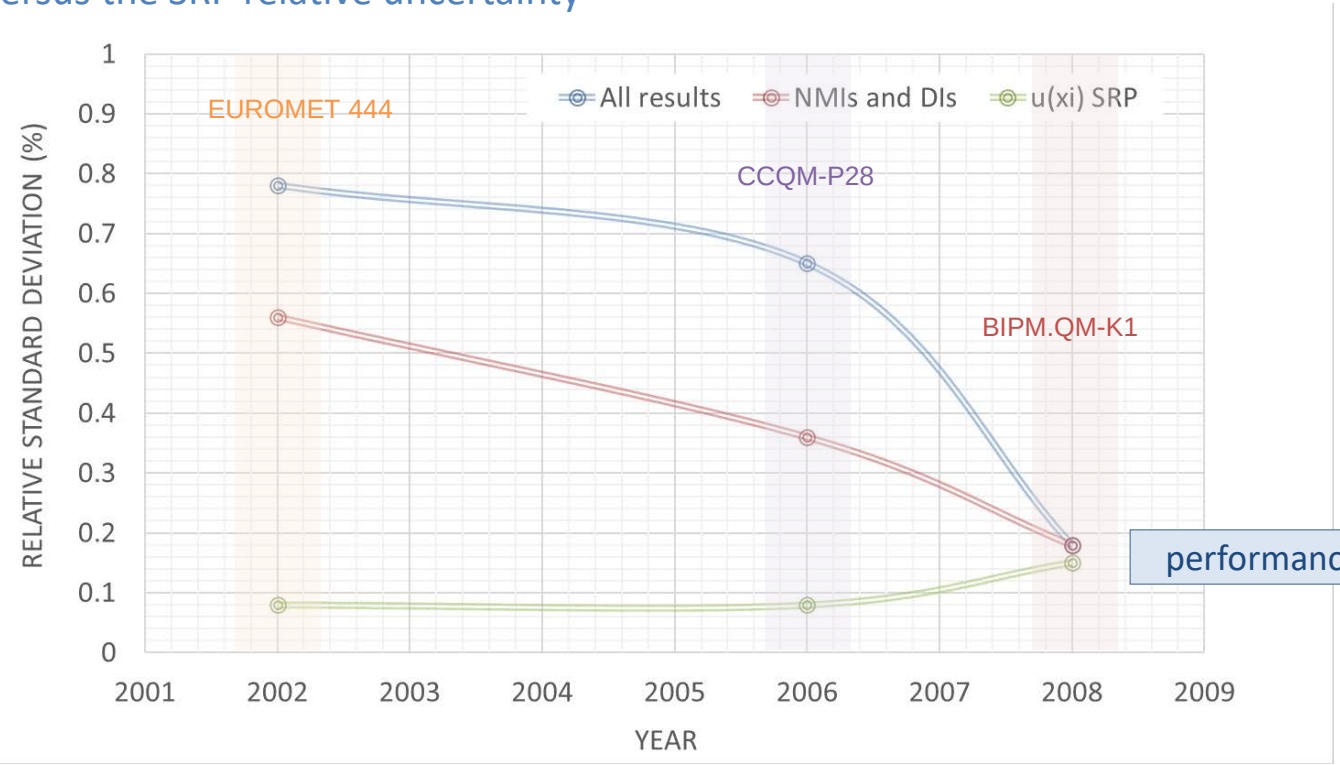
Some rules

- Maximum period between repeats of 8 years
- Laboratories can send their national standard or a transfer standard



Laboratory performance in Ozone comparisons since 2002

Looking at the spread amongst standards in International Comparisons versus the SRP relative uncertainty



performance maintained until now

Acknowledgements

BIPM Staff performing the comparison measurements
F. Idrees, P. Moussay

All participants in BIPM.QM-K1

The CCQM / Gas Analysis Working Group
http://www.bipm.org/en/committees/cc/wg/gawg.html