Improving the accuracy of NO_2 and Ozone monitoring

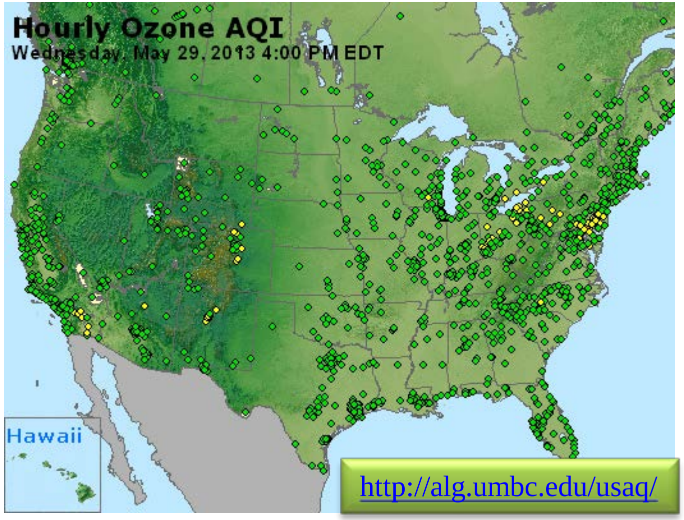
J. Viallon, E. Flores, F. Idrees, P. Moussay, and R.I. Wielgosz

Standards and Measurements for Clean Air
14 October 2016, IPQ – Caparica, Portugal

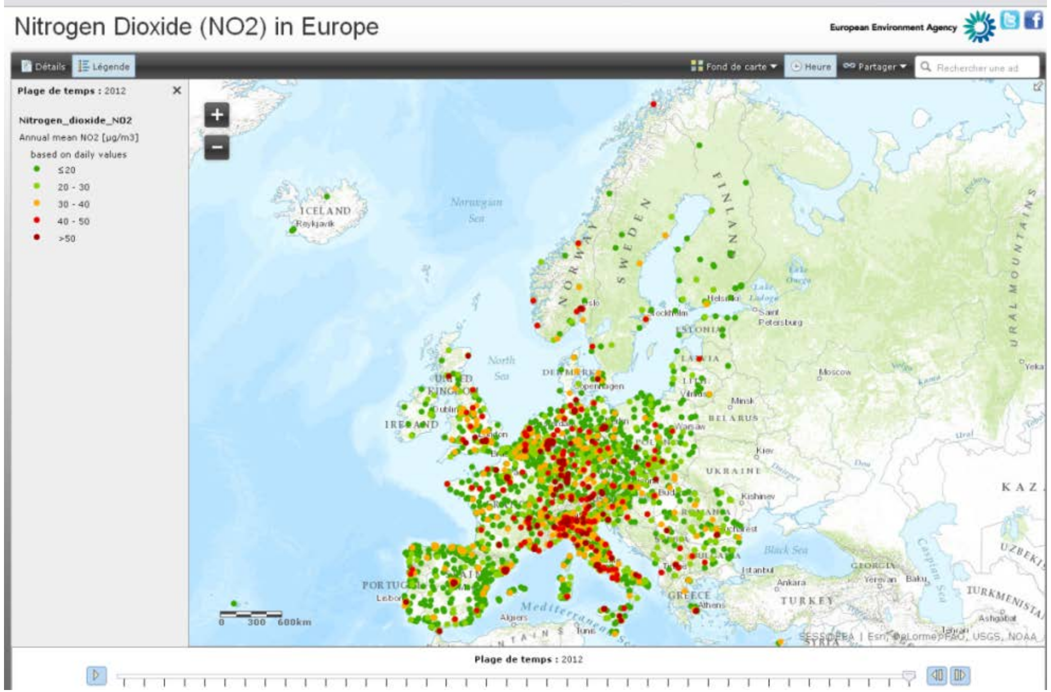
Bureau
International des
Poids et
Mesures

Air Quality, NO_2 and O_3 measurements

Pollutant	*Concentration*	*Averaging period*
Ozone	60 nmol/mol	Maximum daily 8 hour mean
Nitrogen dioxide (NO_2)	100 nmol/mol	1 hour
	20 nmol/mol	1 year

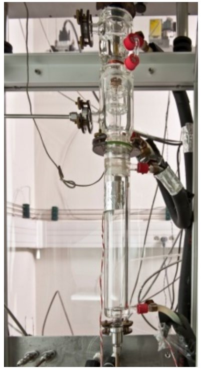


http://alg.umbc.edu/usaq/

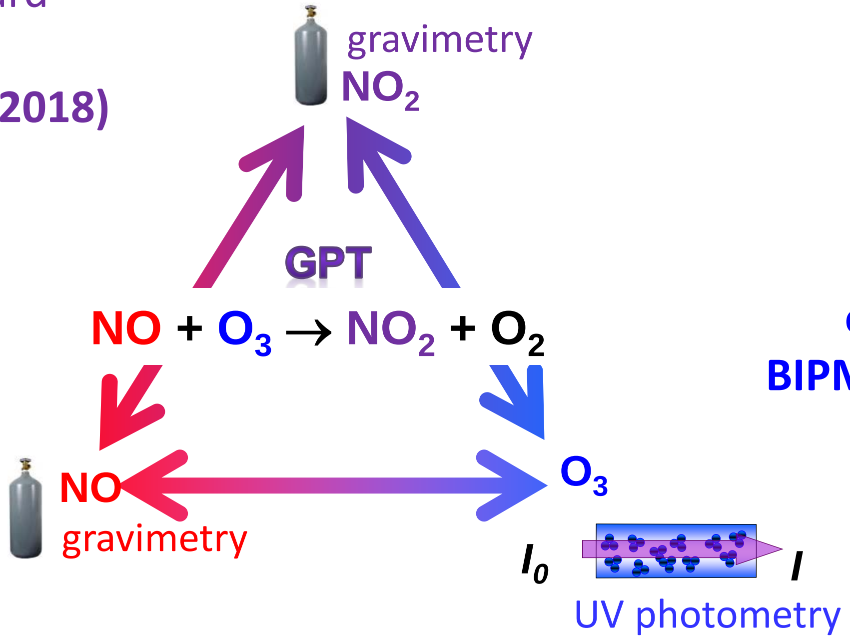


Typical ambient levels nmol mol^{-1}

NO_2 and O_3 at BIPM



Dynamic gas standard generation
CCQM-K74.2010 (+2018)

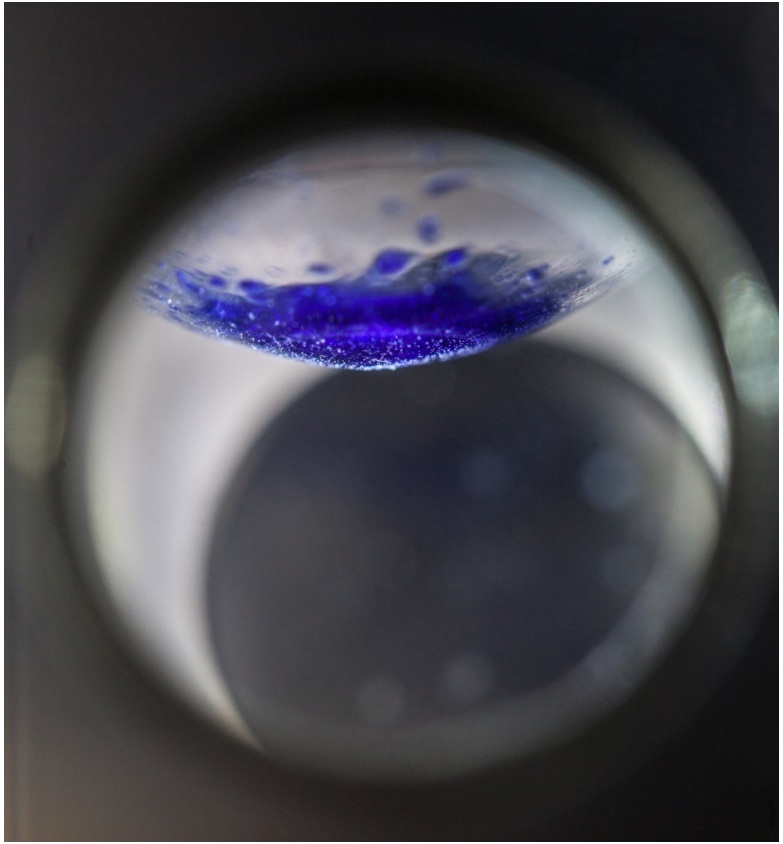


Triad of reference ozone photometers
BIPM.QM-K1 (2007-….)

NO analyzers under repeatability conditions
CCQM-P73 (2006) / CCQM-K137 (2017)

Ozone cross-section measurement by gas phase titration
Joele Viallon, Philippe Moussay, Edgar Flores, and Robert Ian Wielgosz
Analytical Chemistry Just Accepted Manuscript
DOI: 10.1021/acs.analchem.6b03299

Ozone



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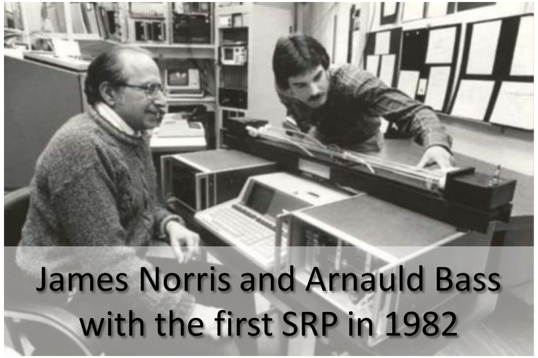
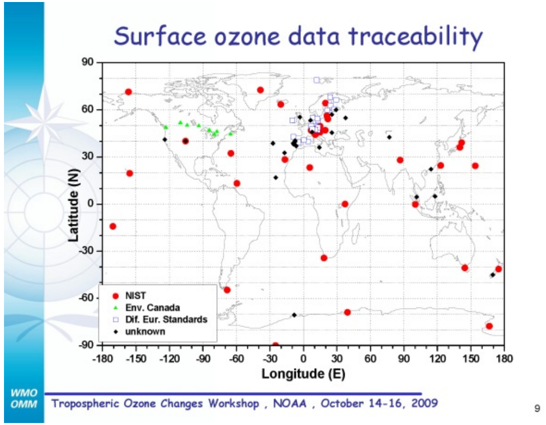
Ozone SRP, from US to the world



James Norris and Arnauld Bass with the first SRP in 1982

2016: 55 SRPs acting as ozone standard for national, regional or global networks

NIST acting as Central Calibration Laboratory for WMO/GAW



SRP54 installed at DMDM (Serbia) in 2014

http://www.dmdm.rs/en/Vesti.php

International Bureau of Weights and Measures BIPM has published in the International database new calibration capabilities (CMC) in the field of chemistry (gas analysis)

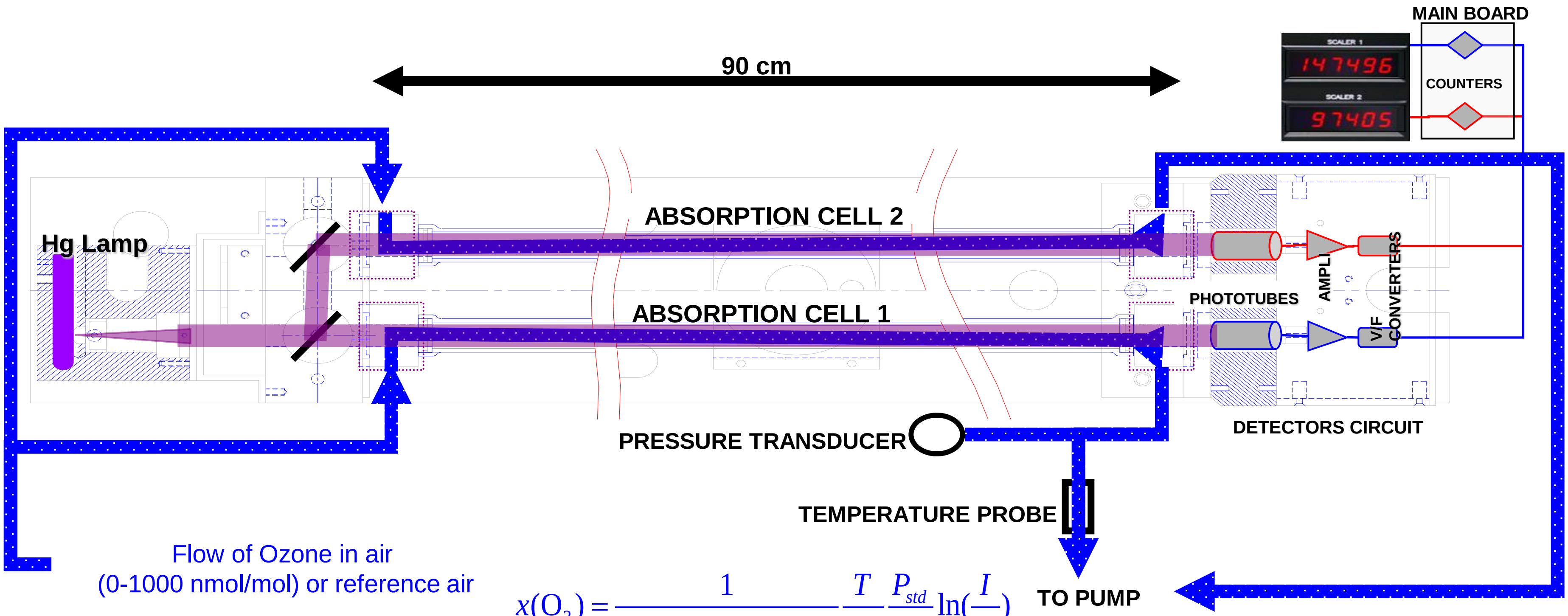
July 14, 2016

International Bureau of Weights and Measures (BIPM) published in International database new calibration capabilities (CMC) in the field of chemistry (gas analysis) of the Directorate of Measures and Precious Metals (DMDM), Group for metrology in chemistry. Capabilities of calibration in the field of chemistry (gas analysis) for measurement of the concentration of ozone in the atmosphere by applying new national standard – the standard photometer for ozone SRP 54 can be found at:

http://kcdb.bipm.org/appendixC/QM/RS/QM_RS_4.pdf

Operating principal of the NIST Standard Reference Photometer

Ozone, at ambient level... absorbs UV light at 253.64 nm

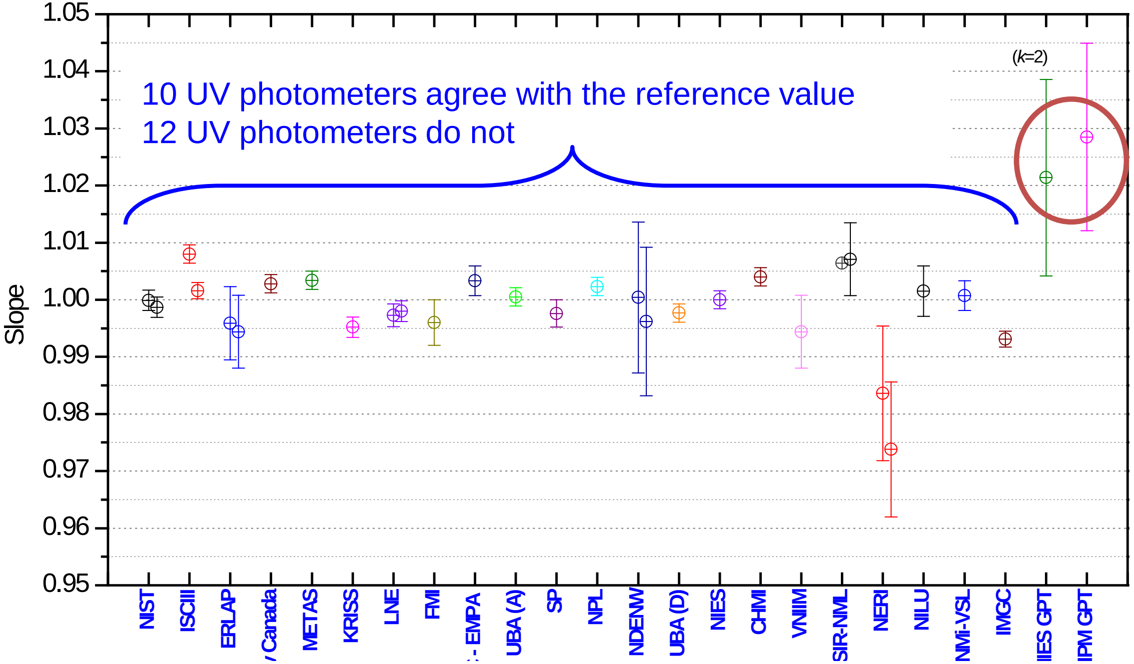


Flow of Ozone in air
(0-1000 nmol/mol) or reference air

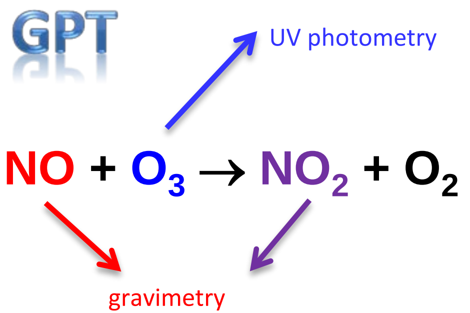
$$x(O_3) = \frac{1}{\alpha(\lambda = 254\text{nm})L_{opt}} \frac{T}{T_{std}} \frac{P_{std}}{P} \ln\left(\frac{I}{I_0}\right)$$

BIPM-NIST program to maintain the comparability of the worldwide network of ozone reference standards

2003-2005 : first international comparions CCQM-P28



2 systems based on Gas Phase Titration of ozone with NO already showed discrepancy between methods



Uncertainty budget revised in 2006

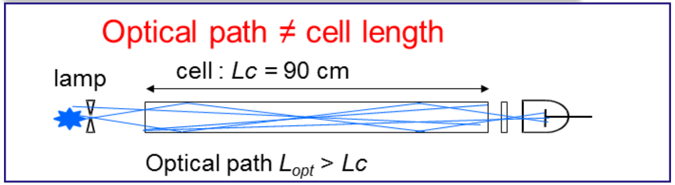
Measurement range [0-1000] nmol mol^{-1}

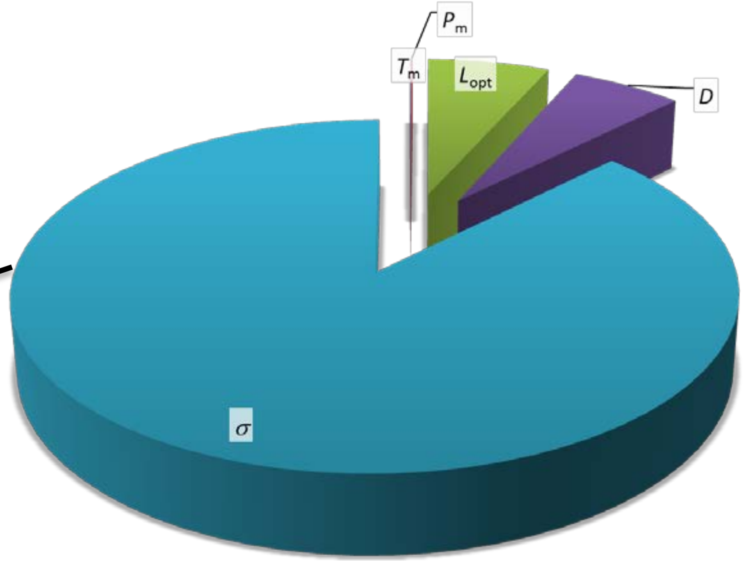
Typical standard uncertainty 1.12%

Dominated by ozone absorption cross-section

$$x(O_3) = \frac{1}{\alpha(\lambda = 254\text{nm}) L_{opt}} \frac{T}{T_{std}} \frac{P_{std}}{P} \ln\left(\frac{I}{I_0}\right)$$

Light path cell inside the gas cell



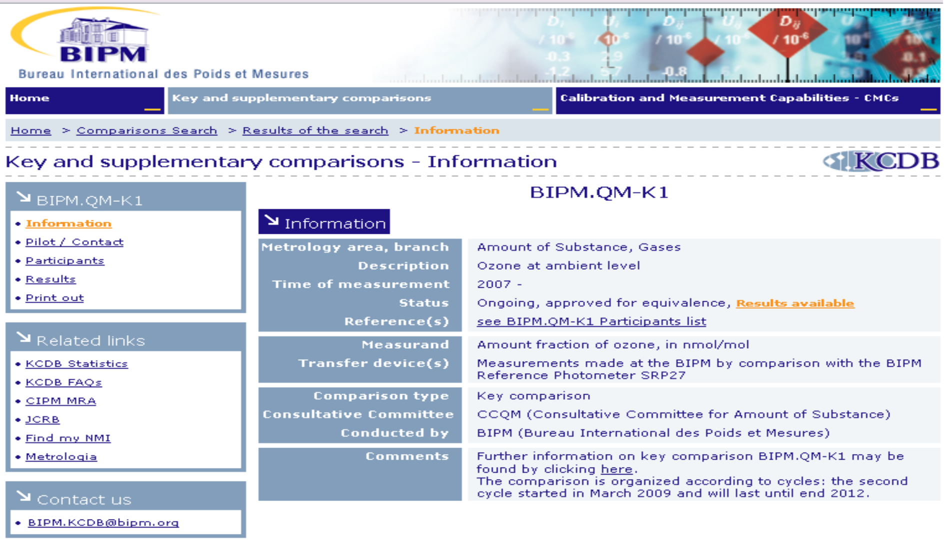


Absorption cross-section

Fundamental property of the molecule
Measured separately on known amount fractions
Measured by ~ 15 groups
Conventional value to be adopted

2007: launch of International Comparison BIPM.QM.K1

http://kcdb.bipm.org/appendixB/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Home | Key and supplementary comparisons | Calibration and Measurement Capabilities - CMCs

Home > Comparisons Search > Results of the search > Information

Key and supplementary comparisons - Information   KCDB

BIPM.QM-K1
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- Metrologia

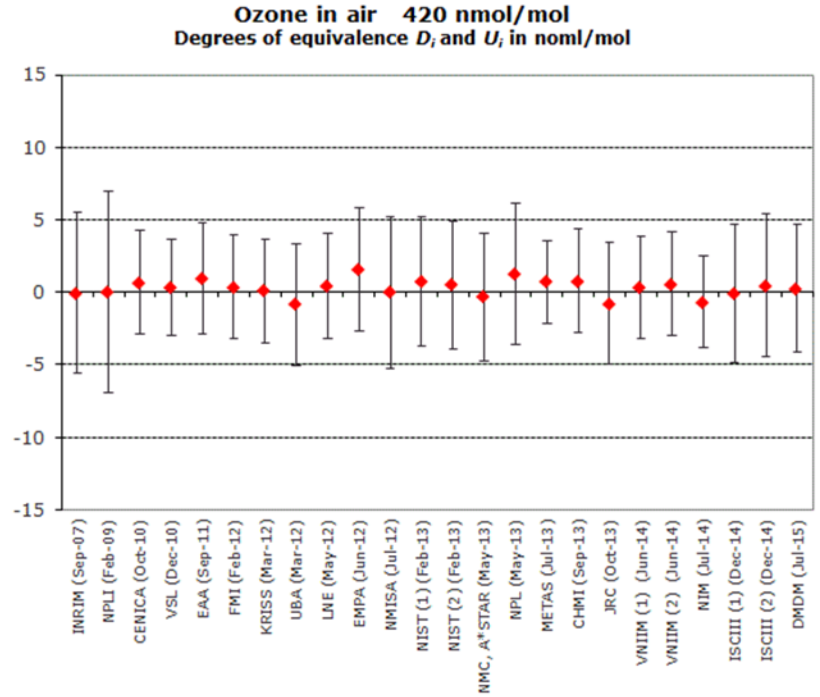
Contact us
- BIPM.KCDB@bipm.org

BIPM.QM-K1

Information

Metrology area, branch	Amount of Substance, Gases
Description	Ozone at ambient level
Time of measurement	2007 -
Status	Ongoing, approved for equivalence, Results available
Reference(s)	see BIPM.QM-K1 Participants list
Measurand	Amount fraction of ozone, in nmol/mol
Transfer device(s)	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	Further information on key comparison BIPM.QM-K1 may be found by clicking here. The comparison is organized according to cycles: the second cycle started in March 2009 and will last until end 2012.

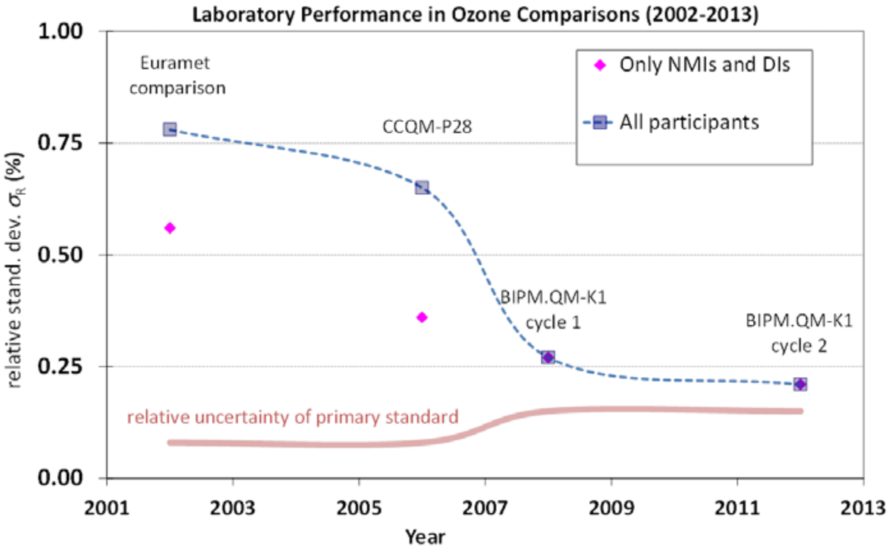
Degrees of equivalence at 420 nmol/mol of ozone in air:



On-going = series of bilateral comparisons between BIPM and participants, directly or using transfer standards

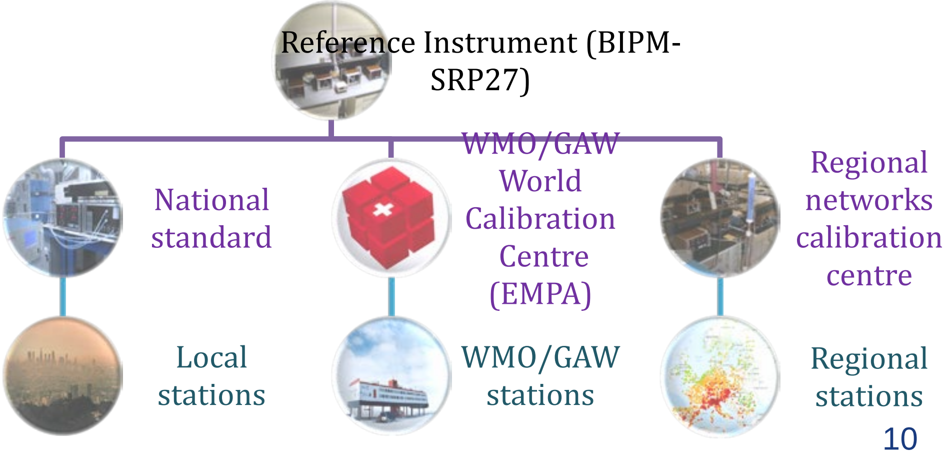
Improved comparability and traceability

2002-2013: improved comparability between institutes taking part in BIPM comparisons

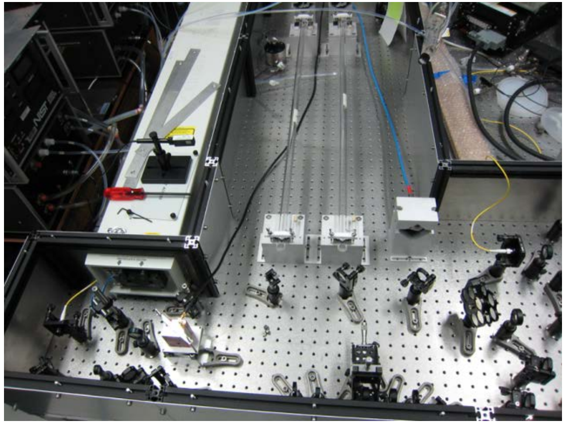


GAW Report No. 209

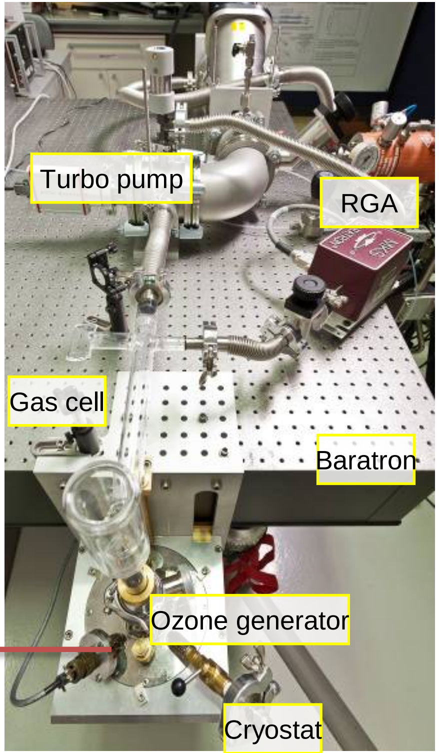
2013: BIPM.QM-K1 comparison recognised as the way to demonstrate metrological traceability in surface ozone measurements for WMO



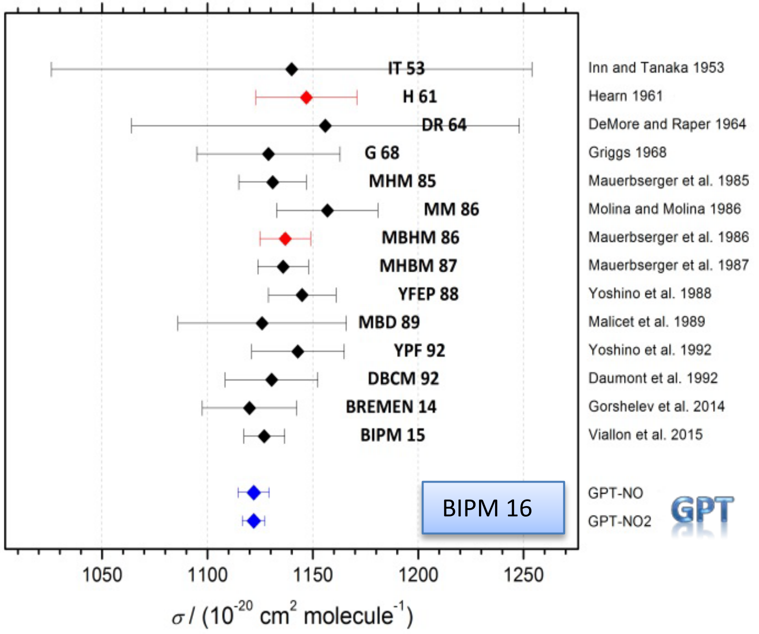
Measuring Ozone Cross-Sections at the BIPM



A laser ozone photometer measuring at 244,nm, 248 nm, 257 nm



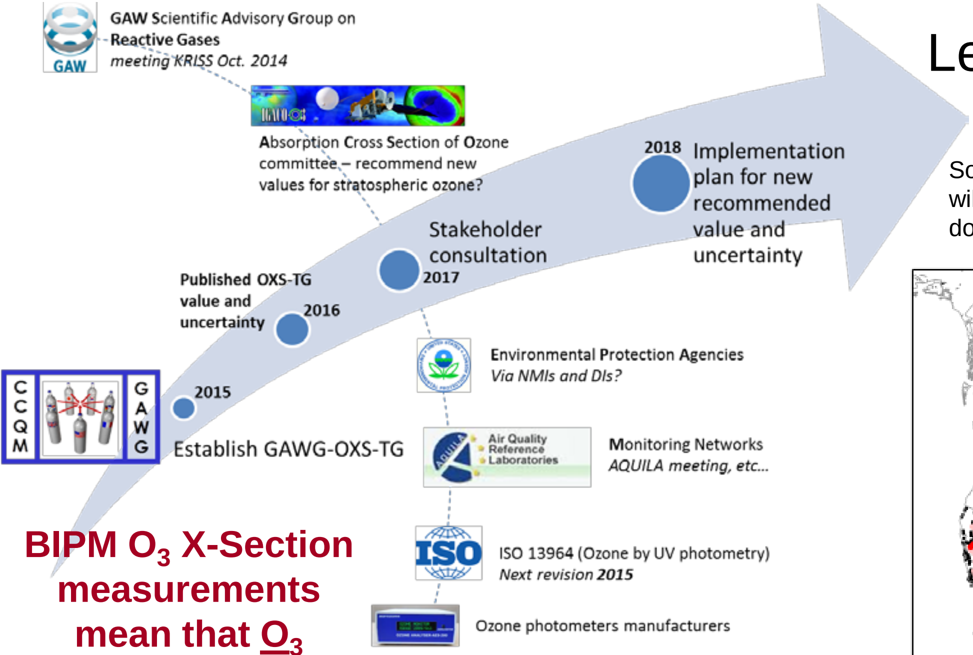
Setup for (absolute) cross-section measurements on pure ozone at low pressure



Values of the ozone absorption cross-section at 253.65 nm reported in the literature

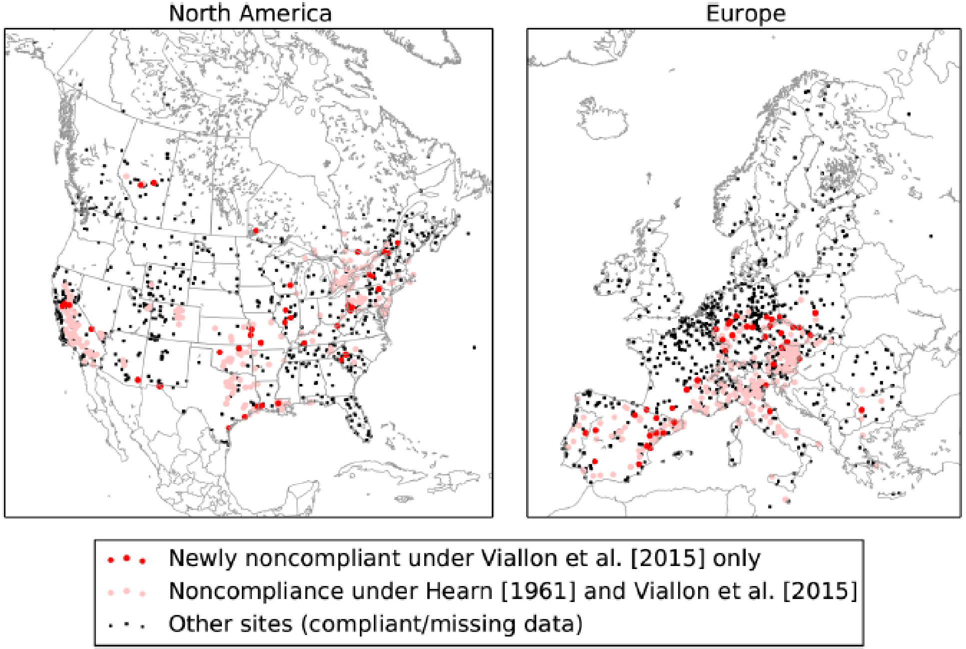
Viallon, J., Lee, S., Moussay, P., Tworek, K., Petersen, M., and Wielgosz, R. I. Accurate measurements of ozone absorption cross-sections in the Hartley band, Atmos. Meas. Tech., 8, 1245-1257, doi:10.5194/amt-8-1245-2015, **2015**.

Impact of Ozone Cross Sections on Monitoring Programs



Lead to actions for improved air quality* for the World's Population

Sofen, E. D., Evans, M. J., and Lewis, A. C.: Updated ozone absorption cross section will reduce air quality compliance, Atmos. Chem. Phys. Discuss., 15, 19537-19551, doi:10.5194/acpd-15-19537-2015, 2015.

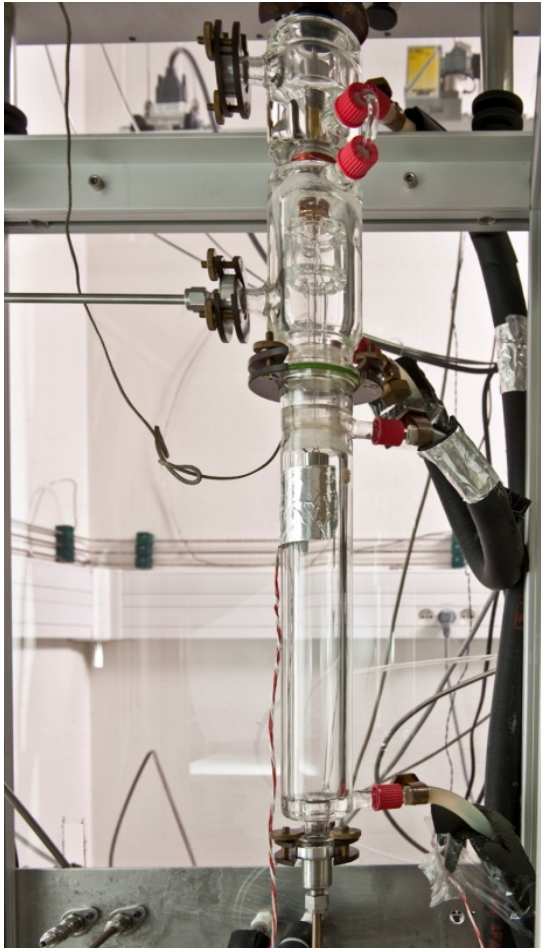


BIPM O_3 X-Section measurements mean that O_3 values are 1.8% higher than historically reported

www.bipm.org

*20 % increase in the number of sites that are out of compliance with current US, Canadian, and European ozone air quality health standards for the year 2012

Nitrogen dioxide



Gas Standards for long term monitoring of nitrogen oxides

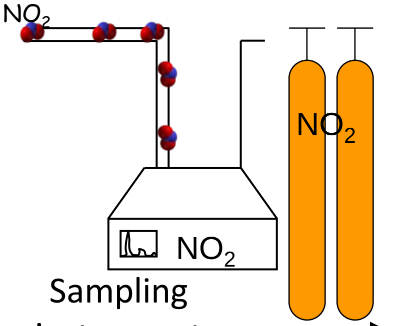
NPL is WMO/GAW Central Calibration Laboratory for NO

http://www.wmo.int/pages/prog/arep/gaw/documents/Final_GAW_195_TD_No_1570_web.pdf

Table 2 - Data Quality Objectives (DQOs) for NO and NO_2 under differing conditions

Level	1 (basic)	2 (enhanced)	3 (high)
Site characteristics	Continental basic	Continental background	Pristine, marine background, free troposphere
Mean mixing ratio NO_x	> 1 ppb	0.1 – 1 ppb	< 0.1 ppb
Scope (corresponding time resolution)	long term monitoring, trends (1 hour) source-receptor-relationship, transport processes (hour-minute) photochemical process studies (minute)		
Detection Limit (1 hour, 3-σ)	NO: 50 ppt NO_2:100 ppt	NO: 10 ppt NO_2:20 ppt	NO: 1 ppt NO_2:5 ppt
uncertainty (1 hour, 2-σ)[1]	NO: 40 ppt or 3% NO_2:80 ppt or 5%	NO: 8 ppt or 3% NO_2:15 ppt or 5%	NO: 1 ppt or 3% NO_2:3 ppt or 5%
uncertainty (1 month, 2-σ)[2]	NO: 2.5% NO_2: 3%	NO: 2.5% NO_2: 3%	NO: 1 ppt or 2.5% NO_2:3 ppt or 3%
data coverage	66%		
suggested method	CLD / PLC	CLD / PLC	CLD / PLC
alternative method (backup or QC reasons)	CRDS, LIF ; DOAS ; TDLAS	CRDS, LIF ; TDLAS	LIF

Nitrogen dioxide measurements



Sampling instrument

Calibration with Reference Materials

Chemiluminescence detectors (**CLD**)

GPT

$$NO + O_3 \longrightarrow NO_2^* + O_2$$
$$NO_2^* \longrightarrow NO_2 + \text{light}$$

Most used, recommended method
indirect method

Interferences (HNO_3, O_3, etc.)

Non-dispersive ultraviolet analyzers (**NUA**)
Cavity Attenuated Phase Shift (**CAPS**)
Differencial Optical Absorption Spectroscopy (**DOAS**)

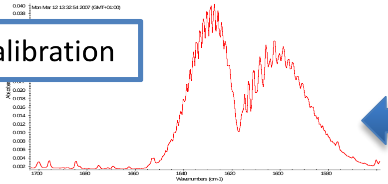
UV absorption

Open path instrument

Synthetic calibration

Fourier Transform Infrared Spectroscopy (**FTIR**)
Tunable Infrared Laser Differential Absorption Spectroscopy (**TILDAS**)

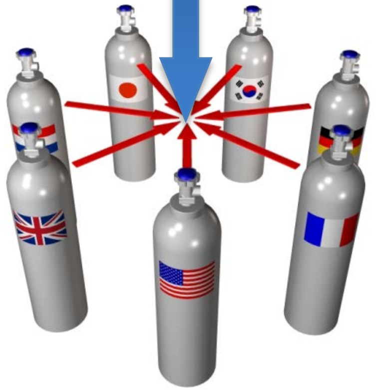
IR absorption

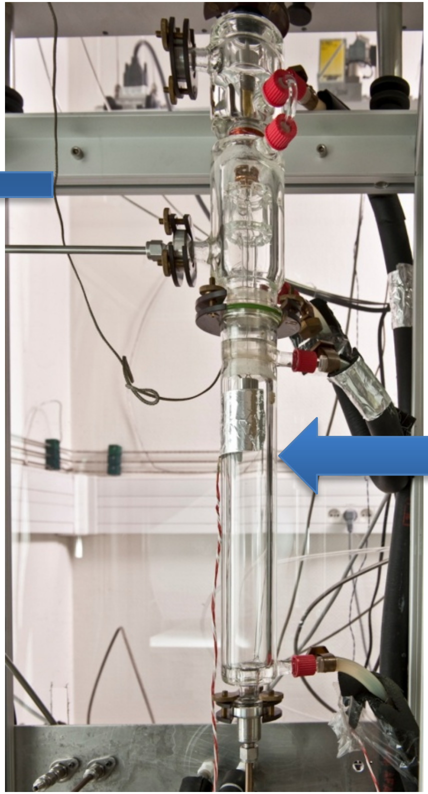


Database of spectroscopic parameters
(**HITRAN** or PNNL or NIST library)

Dynamic gas standards to underpin international comparisons

Reference = NO_2 mole fraction as generated + measured by BIPM dynamic system

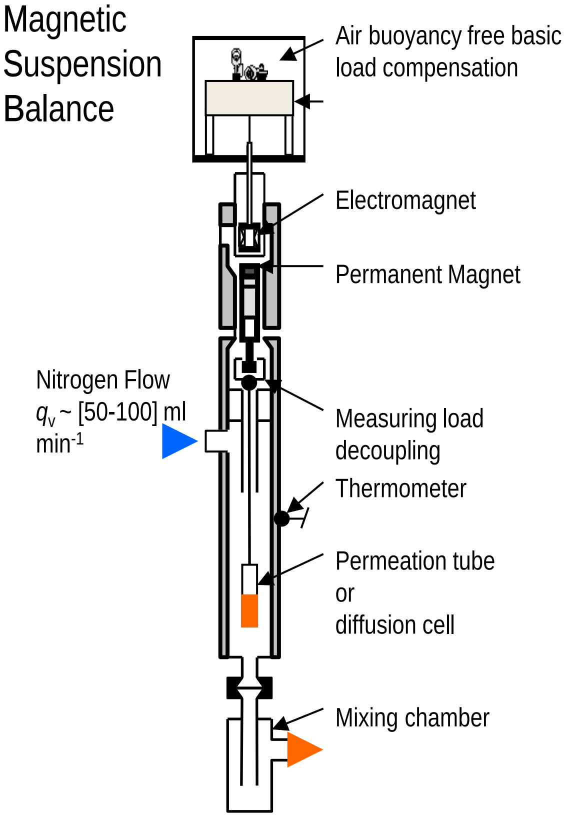




Permeation/diffusion tubes as sources

- Regular/constant weighing
- Matrix gas flow control
- Purity analysis

Magnetic Suspension Balance



Magnetic **S**uspension **B**alance:

- Mass load 20 g
- Resolution 2 µg
- Stability over 3 days ~ 0.5 µg

Measurement of the **mass** of the permeation tube emitting the analyte

Deduction of the **permeation rate q_m / (ng min^{-1})**
= mass loss per unit of time

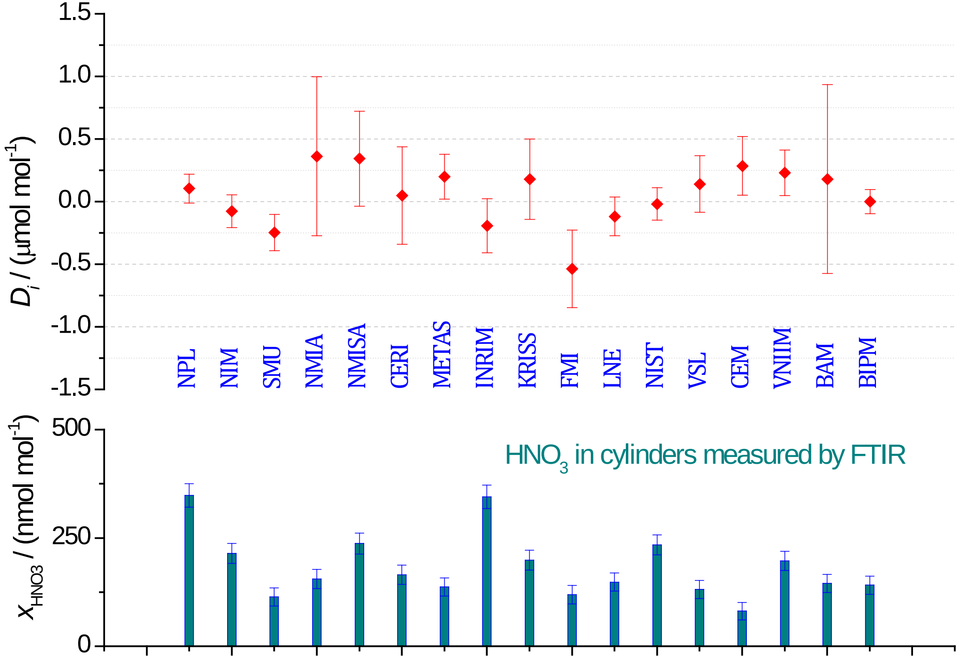
$$q_m = \frac{dm}{dt}$$

And the amount of substance fraction

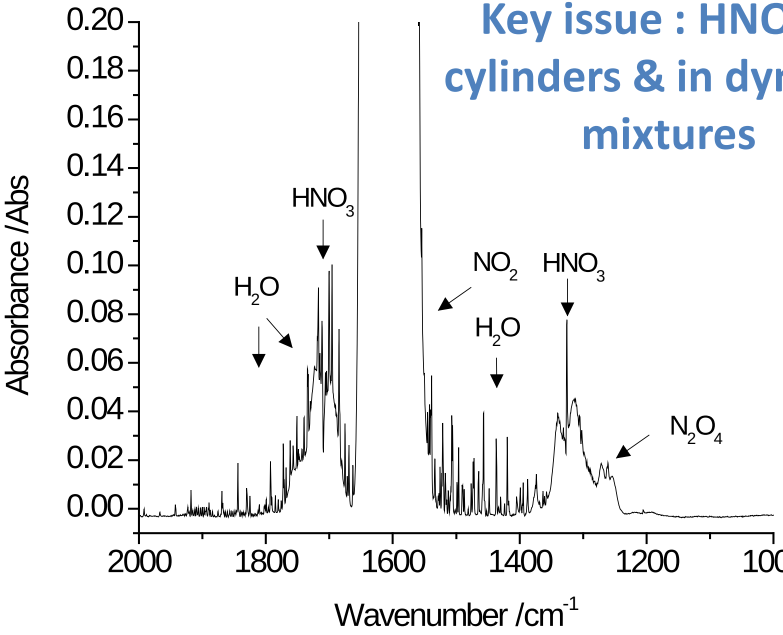
$$x_A = \frac{q_m V_m}{q_v M_A}$$

CCQM-K74 International comparison of nitrogen dioxide in nitrogen standards (2010)

- NO_2/N_2, nominal amount fraction 10 µmol mol^{-1}
- Set of 17 transfer standards prepared by VSL
- Analysis using **FTIR** & **UV absorption**



Key issue : HNO_3 in cylinders & in dynamic mixtures



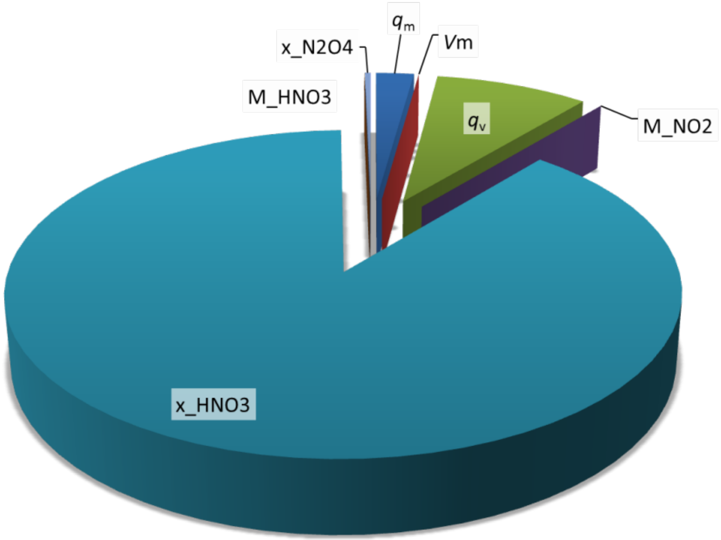
Flores E., Viallon J., Moussay P., Idrees F. and Wielgosz R.I.,2012, *Analytical Chemistry* Highly Accurate Nitrogen Dioxide (NO_2) in Nitrogen Standards Based on Permeation,

CCQM-K74 BIPM typical uncertainties

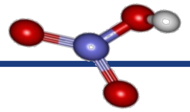
Quantity	Value	unit	Standard relative uncertainty
q_m	8357.30	ng min^{-1}	5.00×10^{-4}
Vm	22.40037	L mol^{-1}	1.52×10^{-5}
q_v	0.452	L min^{-1}	1.00×10^{-3}
M_{NO2}	46.0055	g mol^{-1}	3.04×10^{-5}
x_{HNO3}	104.00	nmol mol^{-1}	2.02×10^{-1}
M_{HNO3}	63.013	g mol^{-1}	1.86×10^{-5}
x_{N2O4}	0	µmol mol^{-1}	0.866 nmol/mol

HNO_3 quantification by FTIR referenced to molecular parameters (HITRAN)

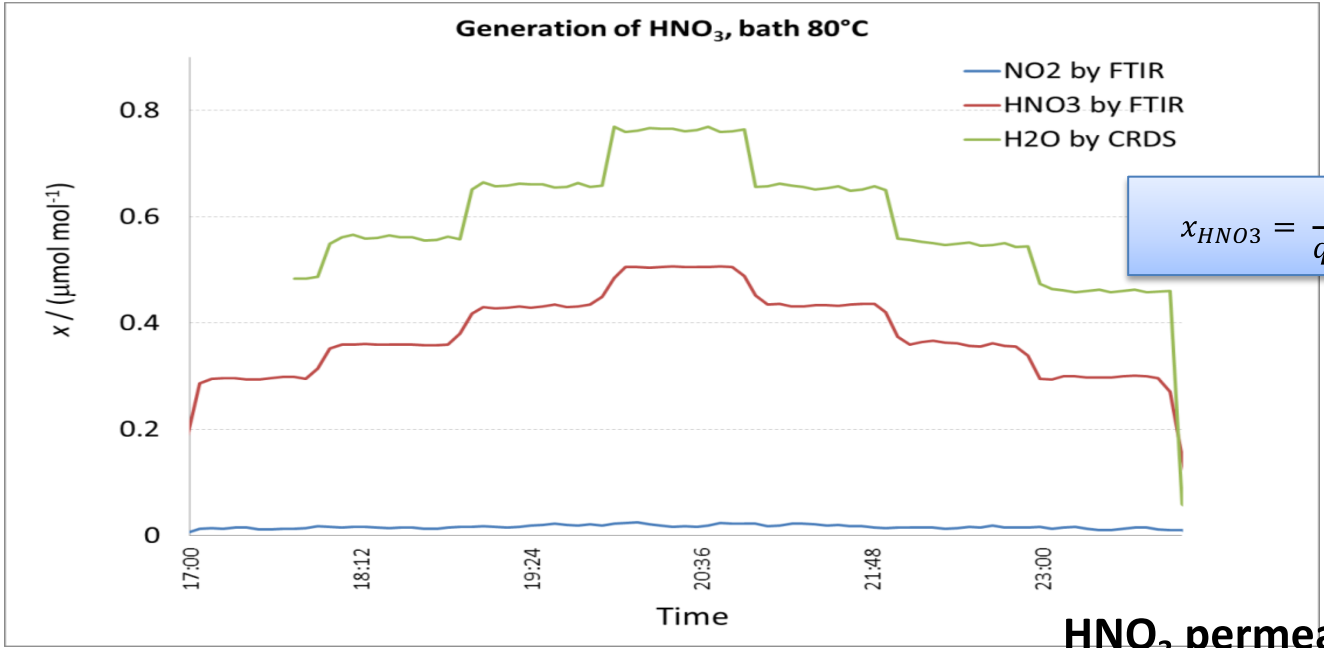
Quantity	Value	Standard Uncertainty
$x(NO_2)$	8.86 µmol mol^{-1}	0.03 µmol mol^{-1}



Preparing for a repeat comparison **CCQM-K74.2018**



Generation of dynamic mixtures of HNO_3 in nitrogen by permeation



$$x_{HNO3} = \frac{q_m \, Vm}{q_v \, M_{HNO3}} - \frac{M_{NO2} x_{NO2}}{M_{HNO3}} - \frac{M_{H2O} x_{H2O}}{M_{HNO3}}$$

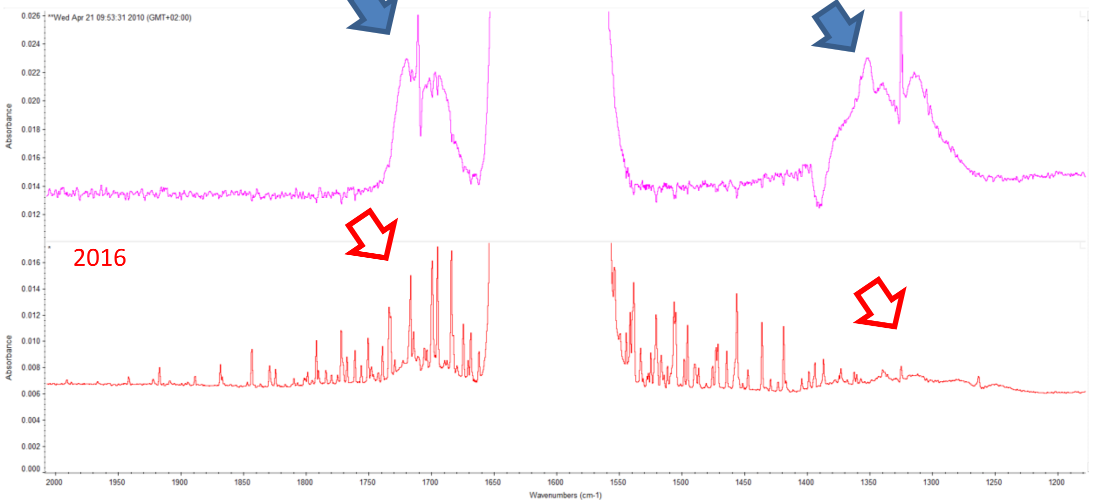
HNO_3 permeation [200-500] nmol mol^{-1}
Permeation rate ~ 30 % H_2O
H_2O accurate quantification is crucial

BIPM and VSL agreed to work together again to coordinate **CCQM-K74.2018**

Levels of HNO_3 in recent standards much lower than in 2010

VSL
Dutch Metrology Institute

2010



K74.2010 key results

- *u*(KCRV)=0.4 %
- Consistency between participants ± 3 %

Conclusions

- Standards for air quality are challenging due to the reactivity of target compounds
- Maintenance of dynamic standards is a valuable solution, either based on spectroscopy or continuous weighing of a source material
- The BIPM has been maintaining dynamic generation facilities to underpin international comparisons to demonstrate NMIs comparability
- Within the last 15 years, important progress have been made in global comparability of standards at the national level

Acknowledgements

NIST

James Norris, Frank Guenther, Joseph Hodges

BIPM

Philippe Moussay, Faraz Idrees, Edgar Flores, Robert Wielgosz

Secondees from NMIs

M. Sega (INRIM, Italy), A. Rakowska (GUM, Poland), C. Pascale (METAS)

S.Lee (KRISS, Korea), K. Tworek (GUM, Poland)