CCQM Activities and Impact in Environment and Climate

R.I. Wielgosz (BIPM)

Bureau
International des
Poids et
Mesures

Outline

NMI activities in the CCQM Gas Analysis Working Group

Ozone Standards and comparisons

Comparisons of nitrogen dioxide standards

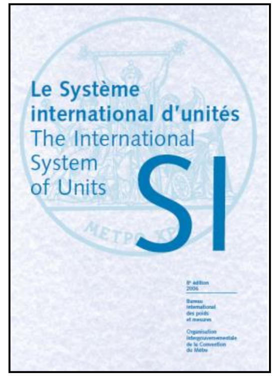
Progress with methane and CO_2 standards and comparisons

Conclusions

Bureau International des Poids et Mesures

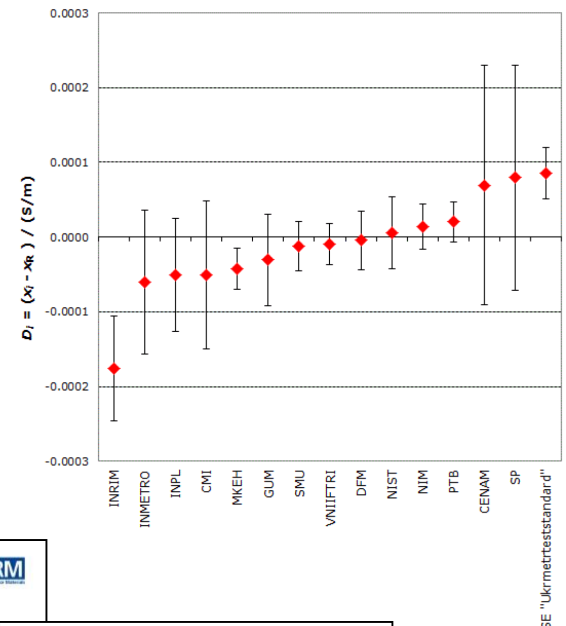
CIPM Mutual Recognition Arrangement: CCQM GAWG Activities

Definition

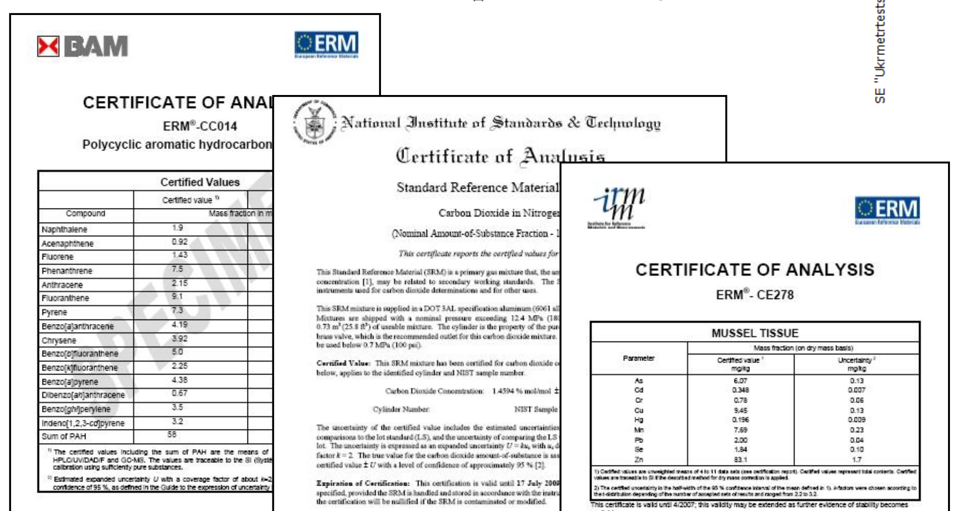


Realization

Comparisons



Dissemination



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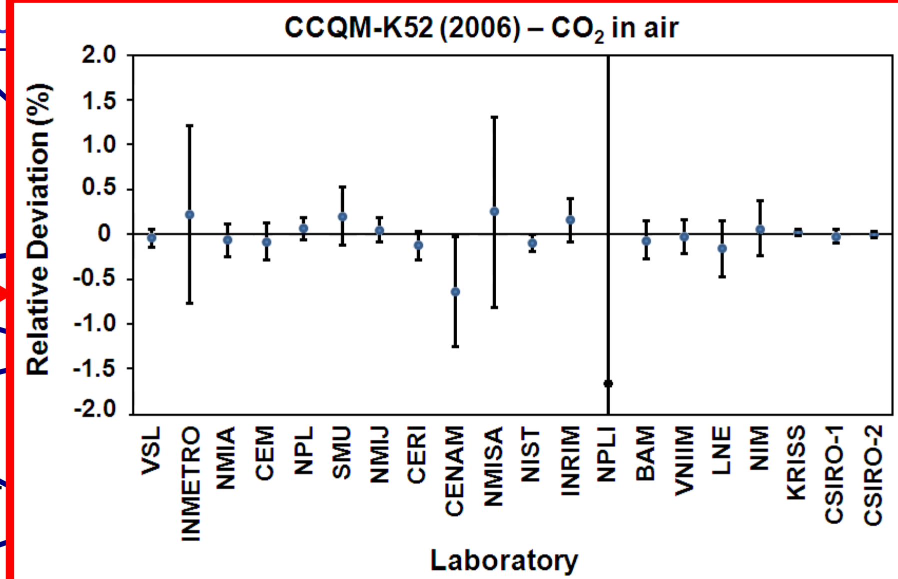
Traceability Chain for Gas Concentration Measurements

Mole fraction of CO_2 in air
SI-Unit: µmol/mol

Measurand and U

INTERNATIONAL STANDARD ISO 6142

INTERNATIONAL STANDARD ISO 6143



NMIs

Primary Reference Gas Mixtures
ISO Guide 34

CRMs or SRMs
ISO Guide 34

Specialty Gas Industry

Speciality Gas Industry Master Standards

ISO 6143 Compliant Calibration Procedure

Commercially Available Standards

End User

Customer's Measurement Procedure

RESULT
CO_2 in µmol/mol

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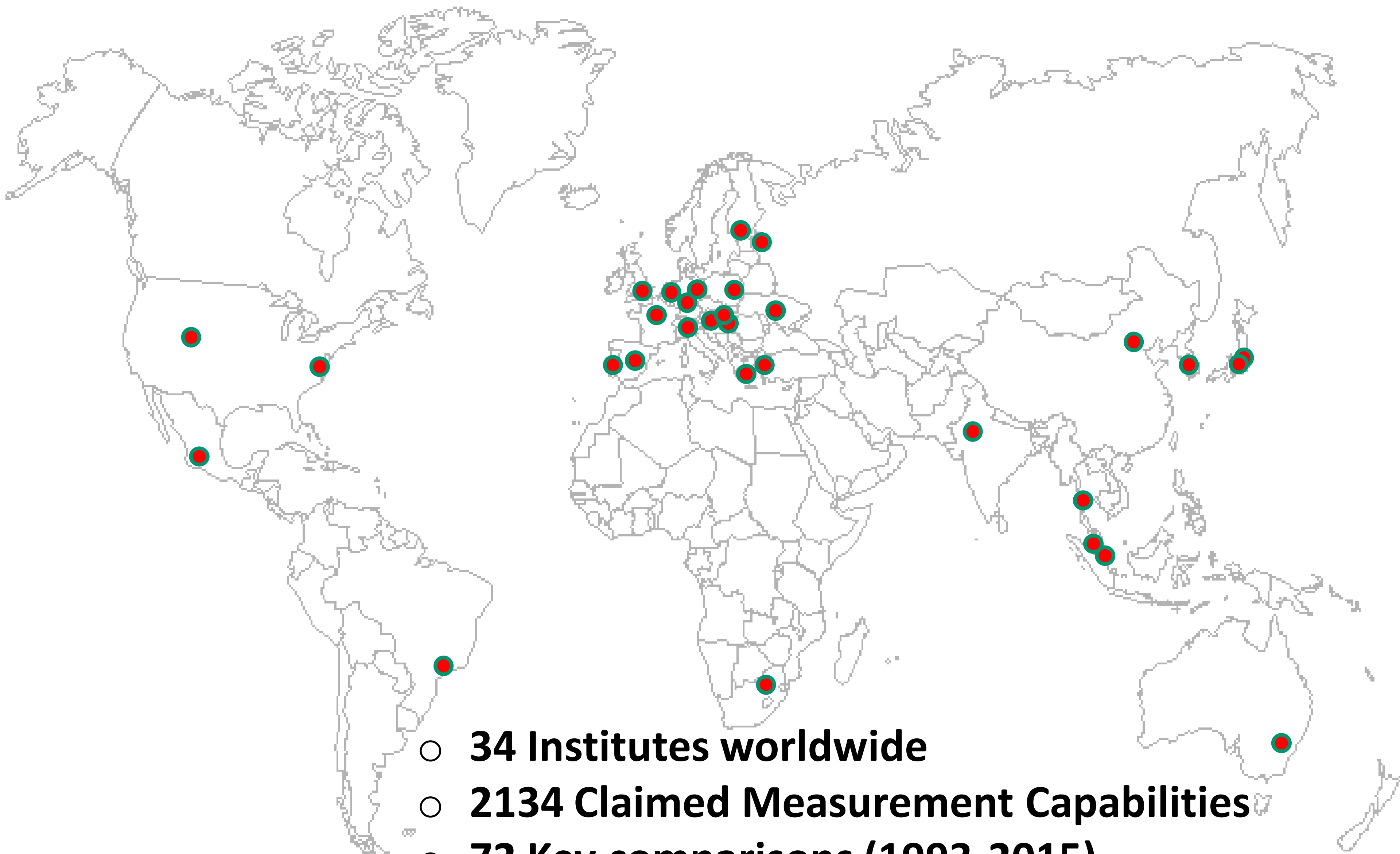
NMIs active in the CCQM Gas Analysis Working Group (GAWG)



- 34 Institutes worldwide
- 2134 Claimed Measurement Capabilities
- 72 Key comparisons (1993-2015)

Bureau International des Poids et Mesures (BIPM)

The BIPM is an intergovernmental organization established by the Metre Convention, through which Member States act together on matters related to measurement science and measurement standards.

www.bipm.org

The mission of the BIPM is to ensure and promote the global comparability of measurements, including providing a coherent international system of units for:

- Scientific discovery and innovation,
- Industrial manufacturing and international trade,
- Sustaining the quality of life and the global environment.

BIPM Chemistry Department programme on:

International equivalence of gas standards for air quality and climate change monitoring

Coordinating comparisons of gas standards with the National Metrology Institutes and Designated Institutes within the CCQM Gas Analysis Working Group

Bureau International des Poids et Mesures

International Gas Standard Comparisons coordinated by the BIPM Chemistry Department within CCQM GAWG

Comparison	Description	Nominal mole fraction	Year
CCQM-P28	Ozone (ground-level)	80 nmol/mol; 400 nmol/mol	2003
CCQM-P73	Nitrogen Monoxide	50 µmol/mol	2006
BIPM.QM-K1	Ozone (ground-level)	80 nmol/mol; 400 nmol/mol	2007
CCQM-K74	Nitrogen Dioxide	10 µmol/mol	2009
CCQM-P110.B1 CCQM-P110.B2	Nitrogen Dioxide : Spectroscopic Studies	10 µmol/mol	2009
CCQM-K82†	Methane	2000 nmol/mol	2012
CCQM-K90	Formaldehyde	2000 nmol/mol	2014
CCQM-K120.a†	Carbon dioxide	380 µmol/mol – 480 µmol/mol	2016
CCQM-K120.b†	Carbon dioxide	480 µmol/mol – 800 µmol/mol	2016
CCQM-KXX**	CO_2 isotope ratios	$\delta^{13}C$, $\delta^{18}O$ (Pure CO_2)	2019

† with **NIST** ‡ with **KRISS** ** with **IAEA**

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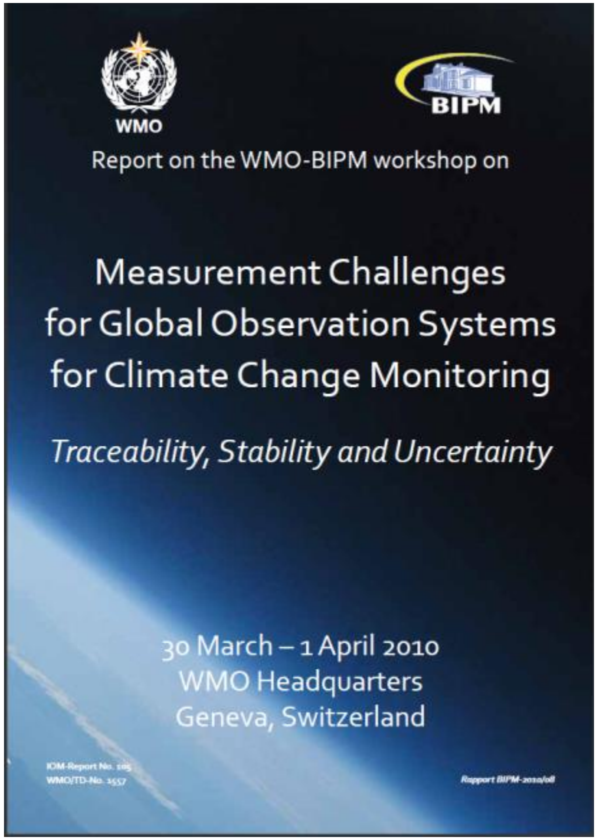
BIPM-WMO joint activities



2010 WMO-BIPM workshop on

"Measurements Challenges for Global Observation Systems for Climate Change Monitoring"

Signature of CIPM-MRA by WMO

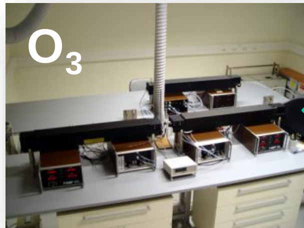
Wielgosz R., Calpini B., (Editors), Report on the WMO-BIPM workshop on Measurement Challenges for Global Observation Systems for Climate Change Monitoring: Traceability, Stability and Uncertainty, Rapport BIPM-2010/08, 100 pp

Global comparisons related to air quality and greenhouse gases

BIPM

GAW

Ozone Reference Standards Comparison Facility

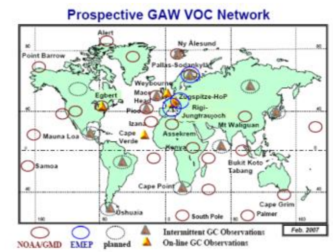


GAW World Calibration Centre for Ozone participates in BIPM comparison

BIPM.QM-K1

Formaldehyde facility

GAW-VOCs workshops



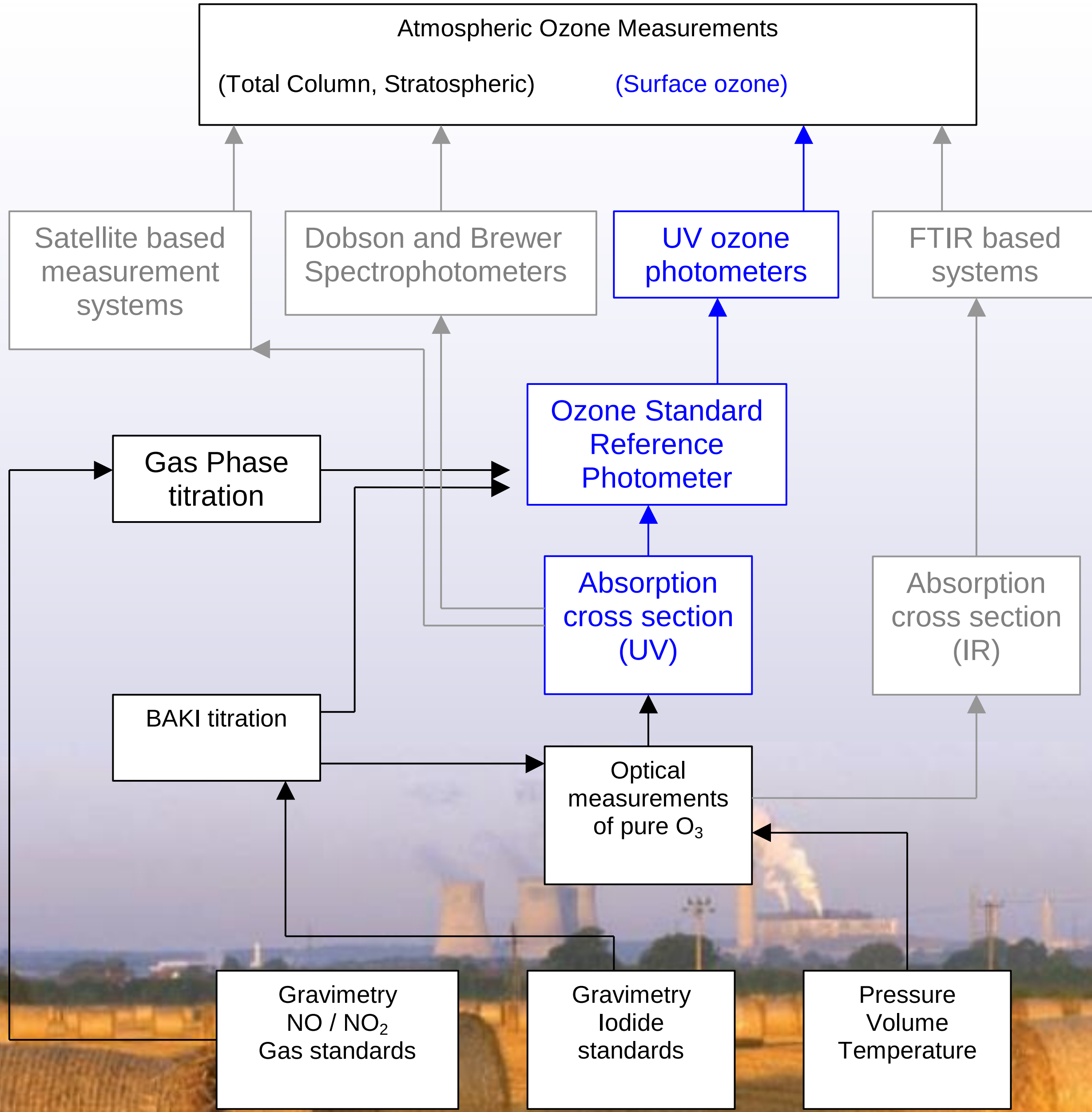
Dynamic Gas Standard Facility

GAW workshops to establish nitrogen oxides network

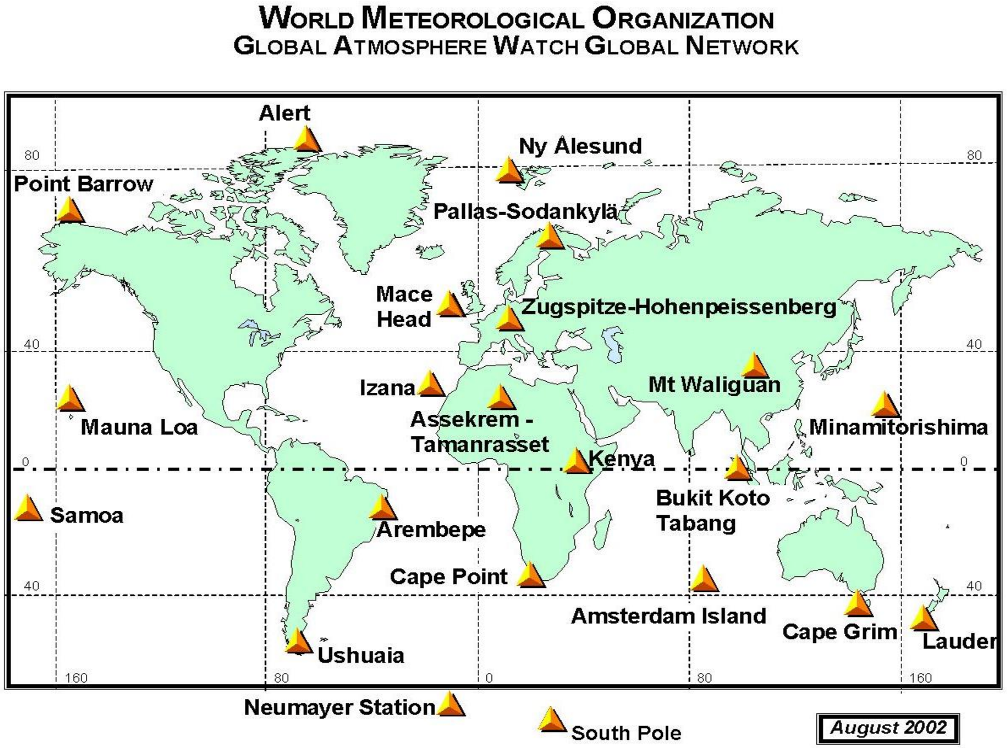
Green House Gas comparison facility

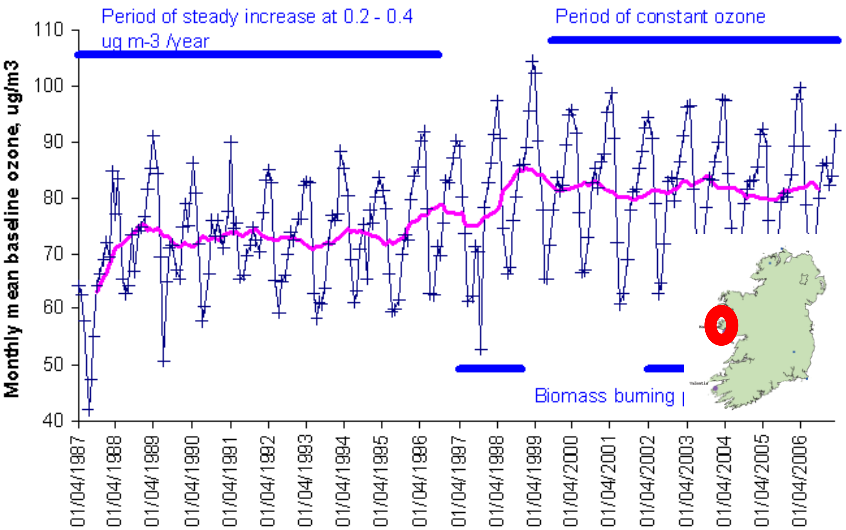
GAW CCL for CH_4 and CO_2 to participate in BIPM comparisons

Establishing Traceability for Atmospheric Ozone Measurements

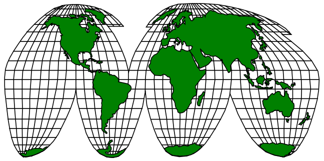


Surface Ozone Measurements



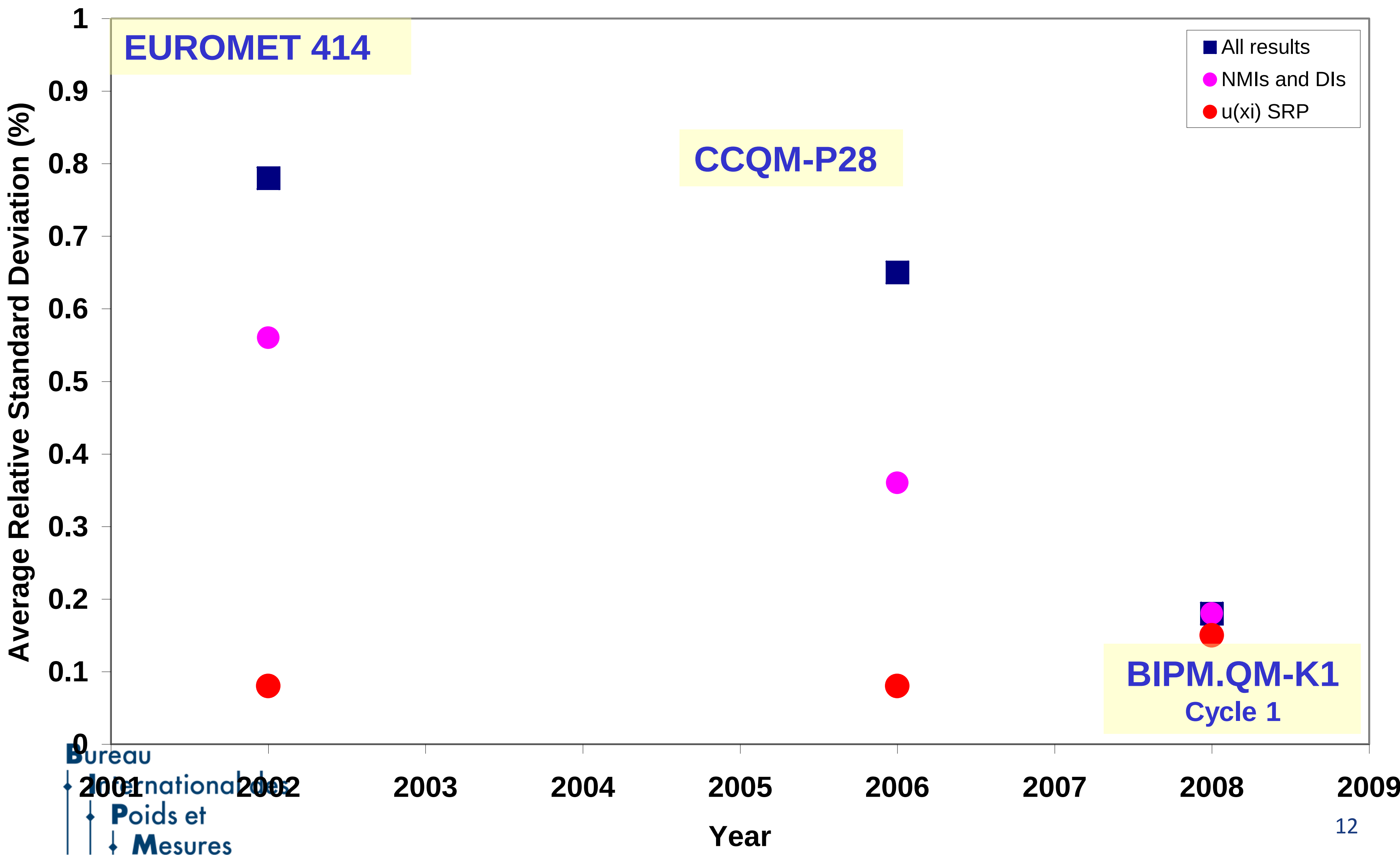


BIPM-NIST programme to maintain the comparability of the worldwide network of ozone reference standards



NIST BIPM

Improvements in demonstrated performance of Ozone Standards



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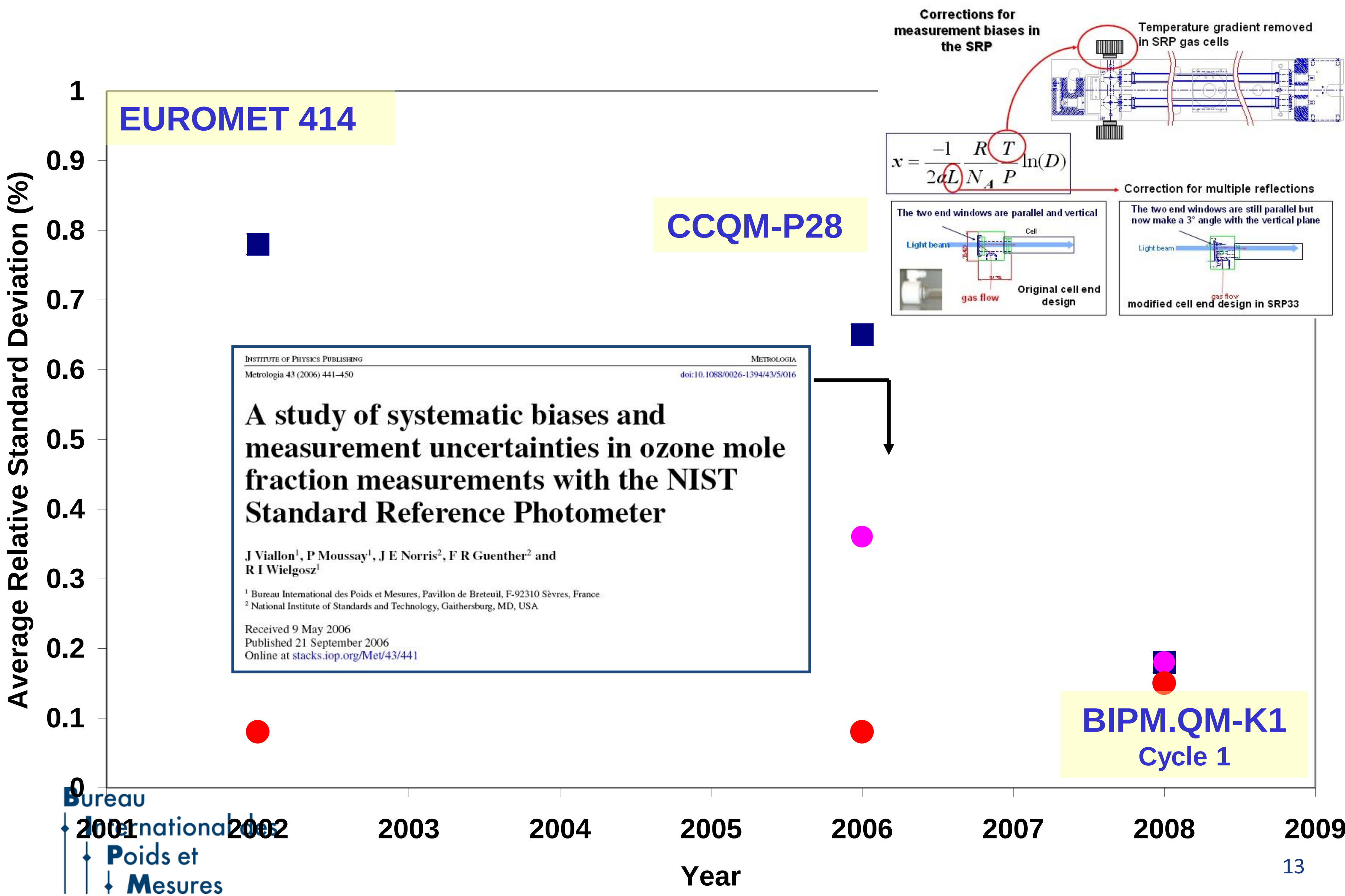
Improvements in demonstrated performance of Ozone Standards



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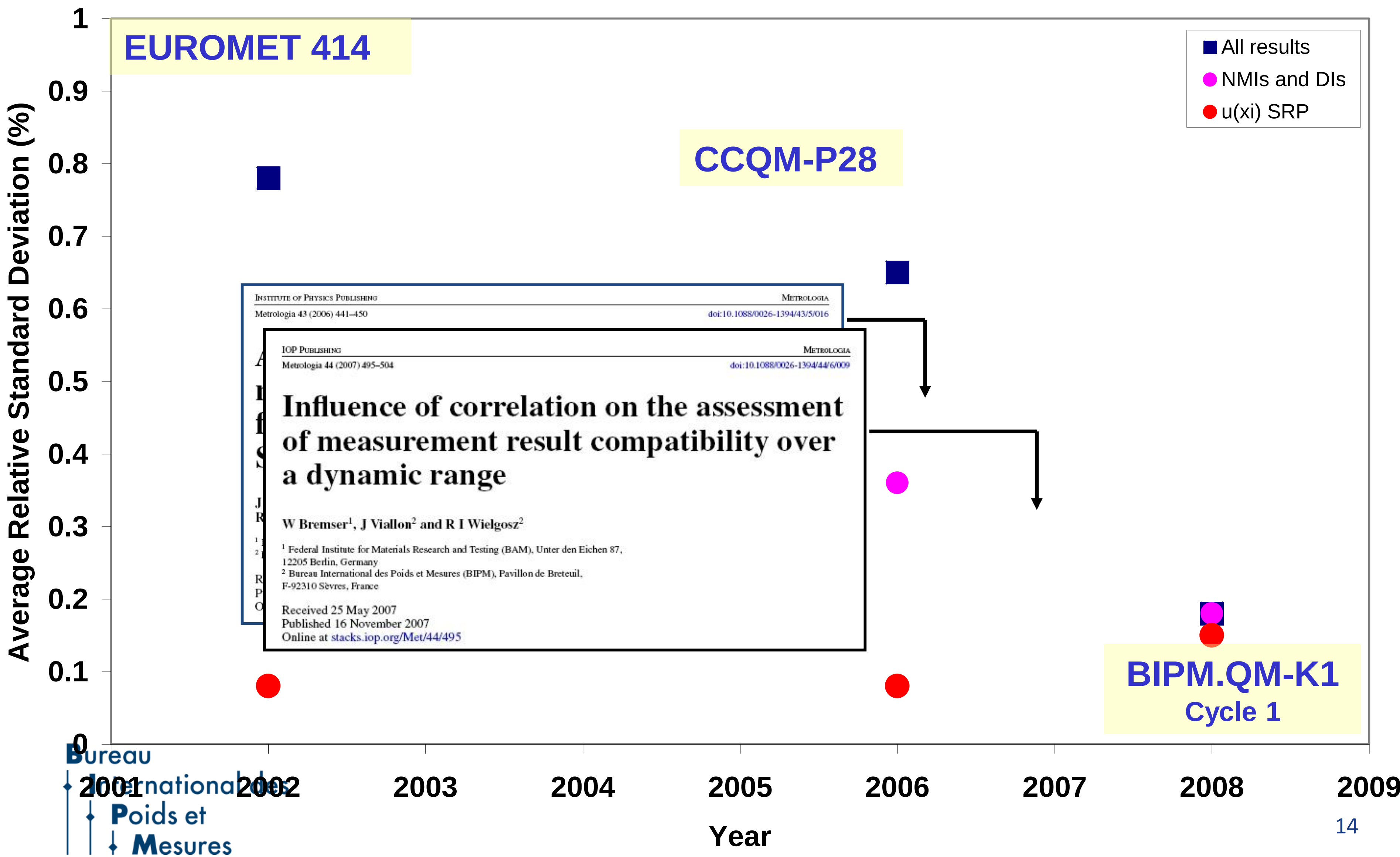
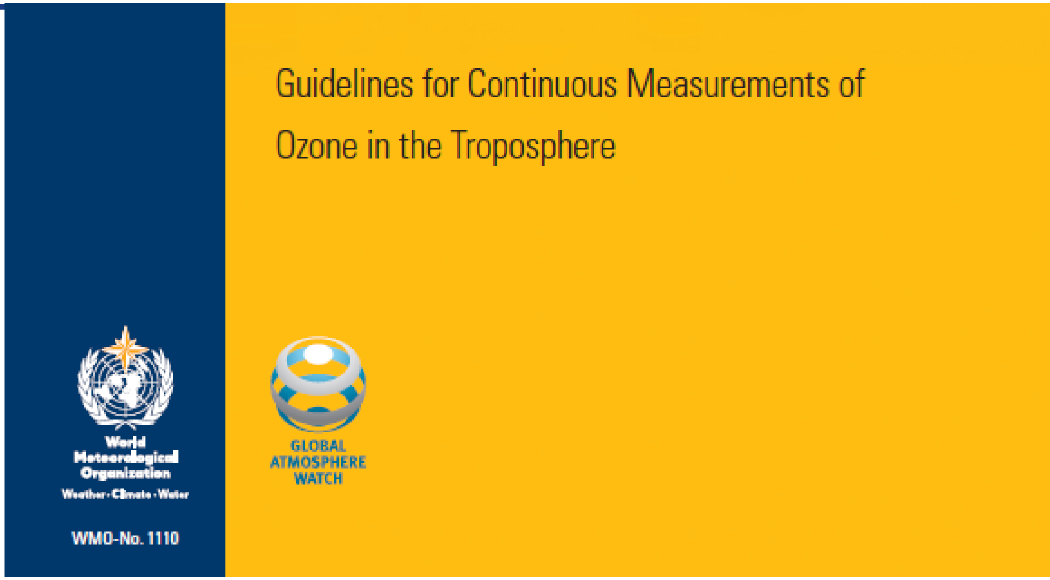
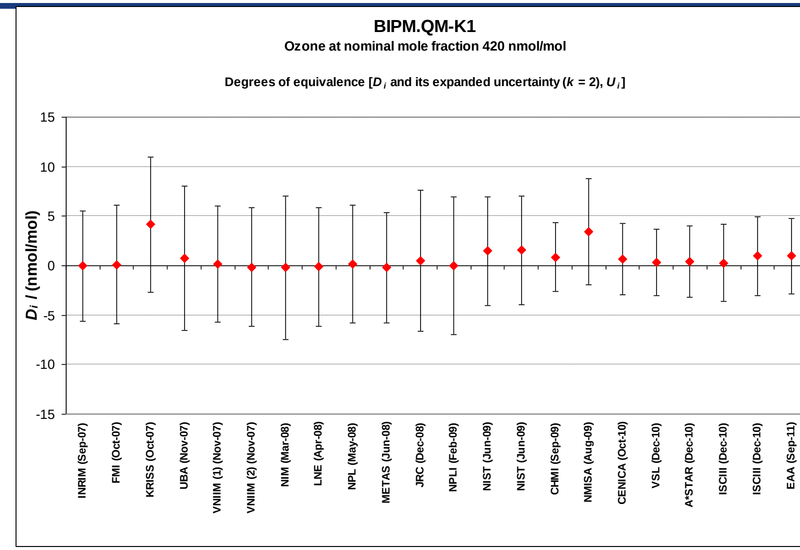
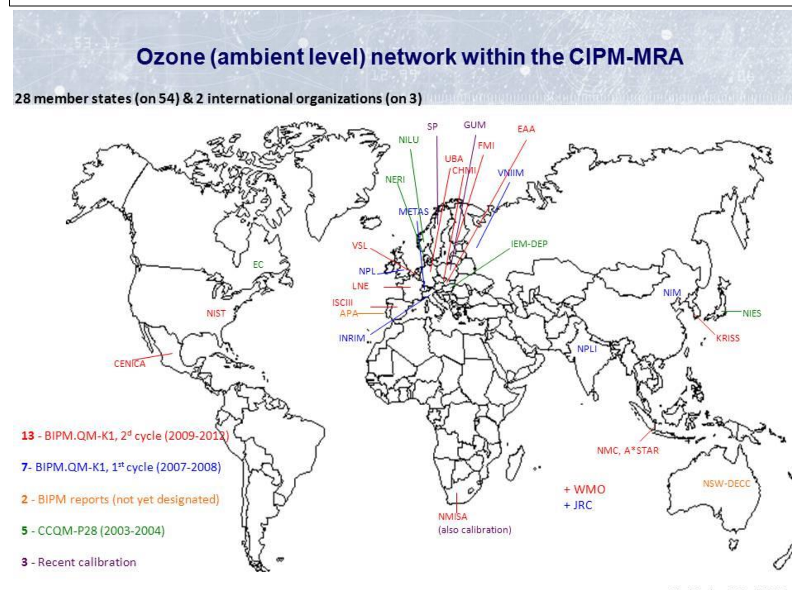
Improvements in demonstrated performance of Ozone Standards



New guidelines for surface ozone measurements







Galbally I.E., Schultz M.G., Buchmann B., Gilge S., Guenther F., Koide H., Ottmans S., Patrick L., Scheel H.-E., Smit H., Steinbacher M., Steinbrecht W., Tarasova O., Viallon J., Volz-Thomas A., Weber M., Wielgosz R., Zellweger C., Guidelines for continuous measurements of ozone in the troposphere, **GAW Report No. 209, 2013, 76 pp**

Norris J.E., Choquette S.J., Viallon J., Moussay P., Wielgosz R., Guenther F.R., Temperature measurement and optical path-length bias improvement modifications to National Institute of Standards and Technology ozone reference standards, **J. Air & Waste Manage. Assoc., 2013, 63(5), 565-574**

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Differences in Reference Methods for Ozone

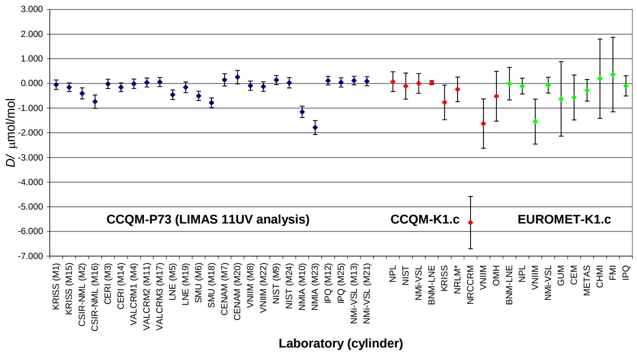
Gas Phase Titration

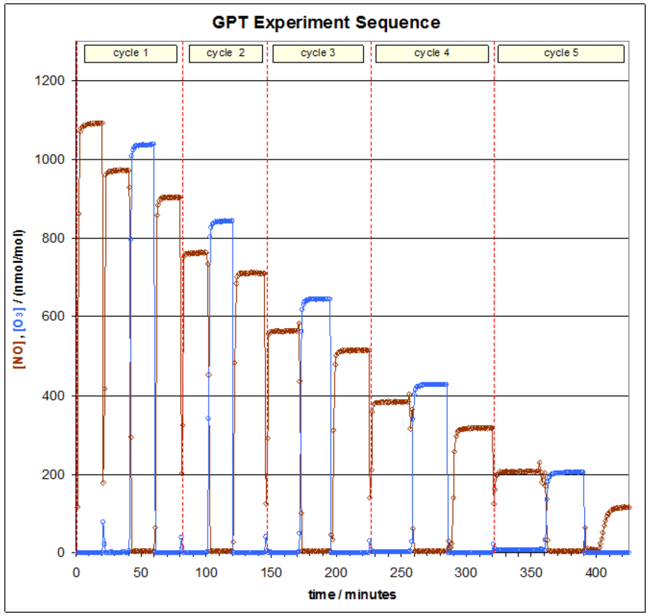
$NO + O_3 \rightarrow NO_2 + O_2$

Nitrogen Monoxide Comparison

CCQM-P73

NO (30-70) µmol/mol

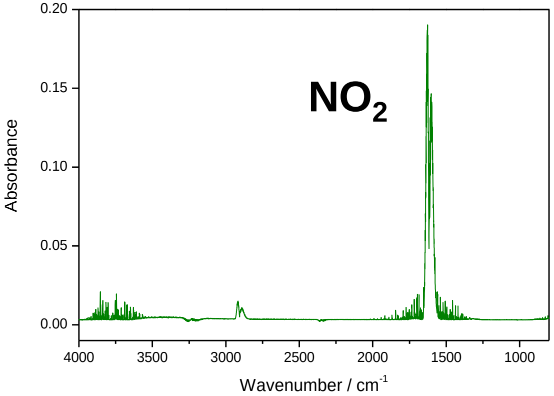




NO_2 primary facility (dynamic preparation)

CCQM-K74

(including validation of spectroscopic methods)



Ozone reference standard comparison facility

CCQM-P28

BIPM.QM-K1

Ozone (2-1000) nmol/mol

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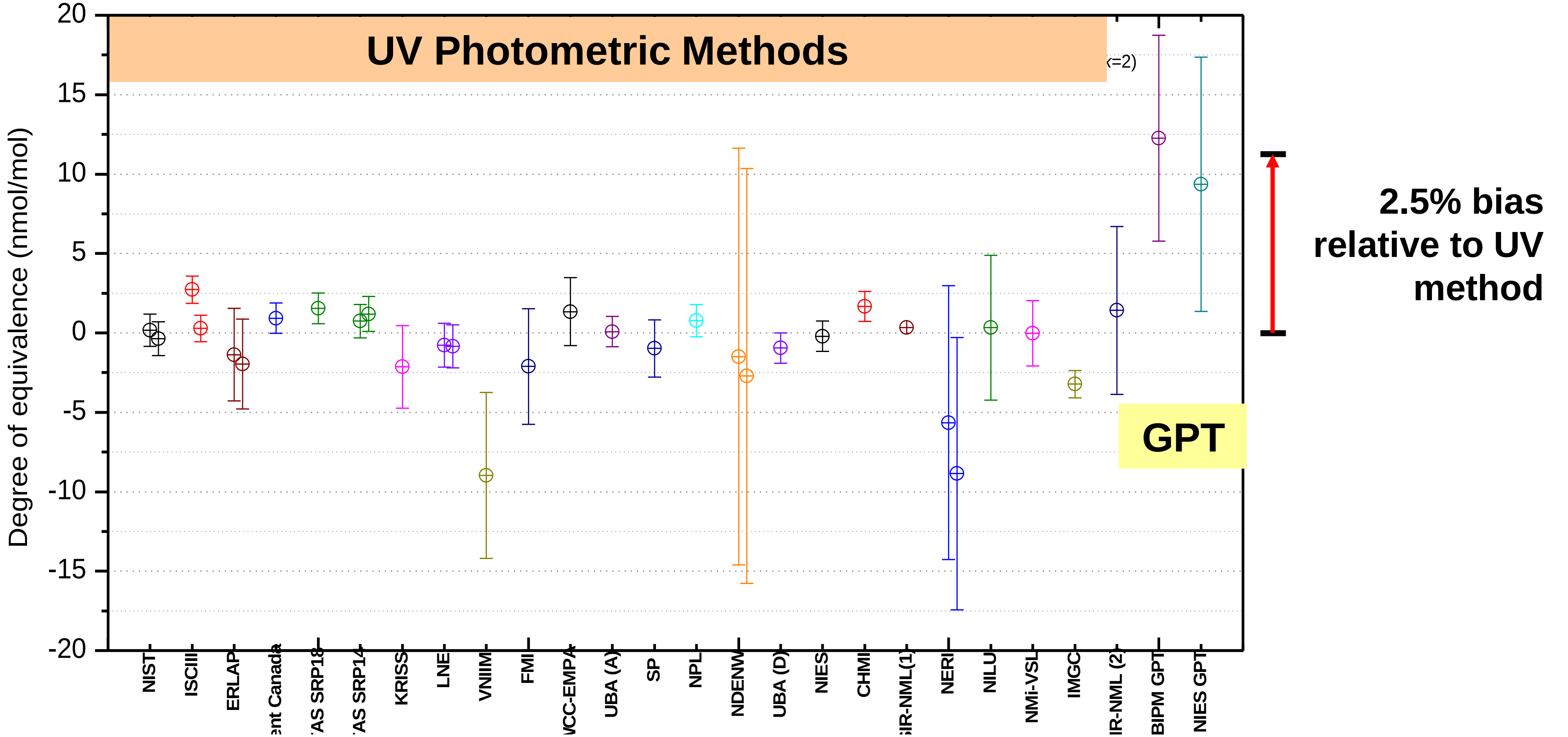
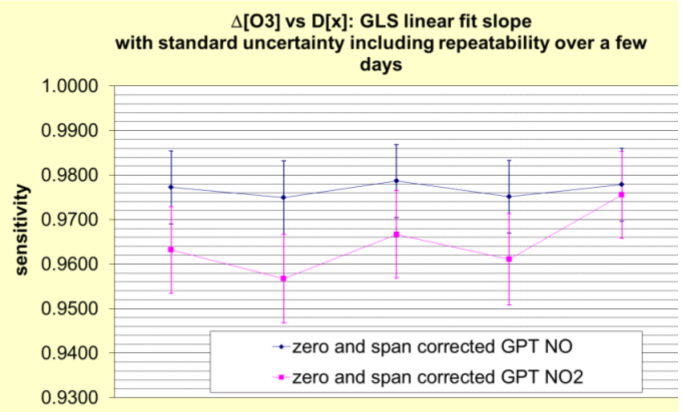
CCQM-P28 Degrees of Equivalence, Ozone mole fraction:420nmol/mol





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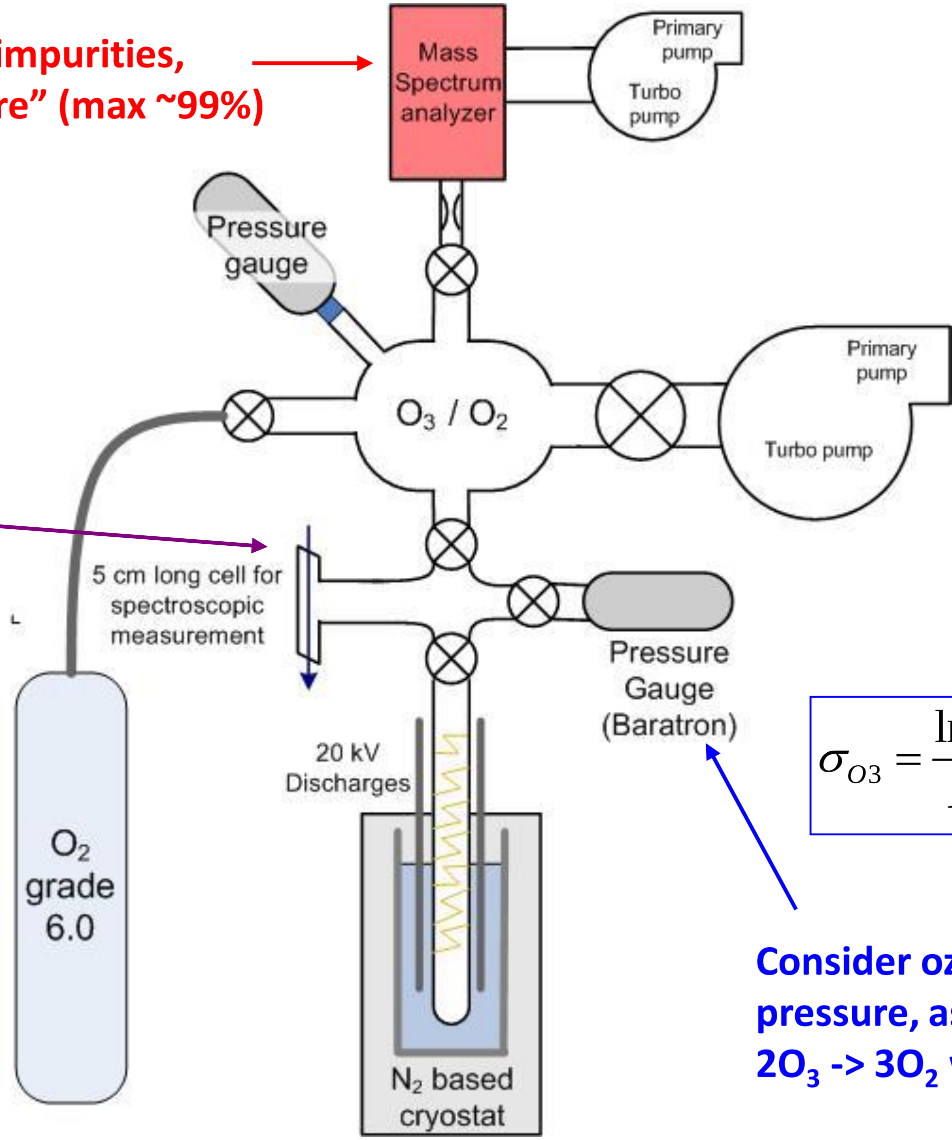
Ozone cross-section a measurement challenge

Measure O_2 and other impurities, as O_3 will never be "pure" (max ~99%)

***L_{opt}* to be measured by interferometry**



$$\sigma_{O3} = \frac{\ln(\tau)}{L_{opt}} \frac{T}{2(P_i - P_T)} \frac{R}{Na}$$

Consider ozone partial pressure, as decomposition $2O_3 \rightarrow 3O_2$ will rapidly occur

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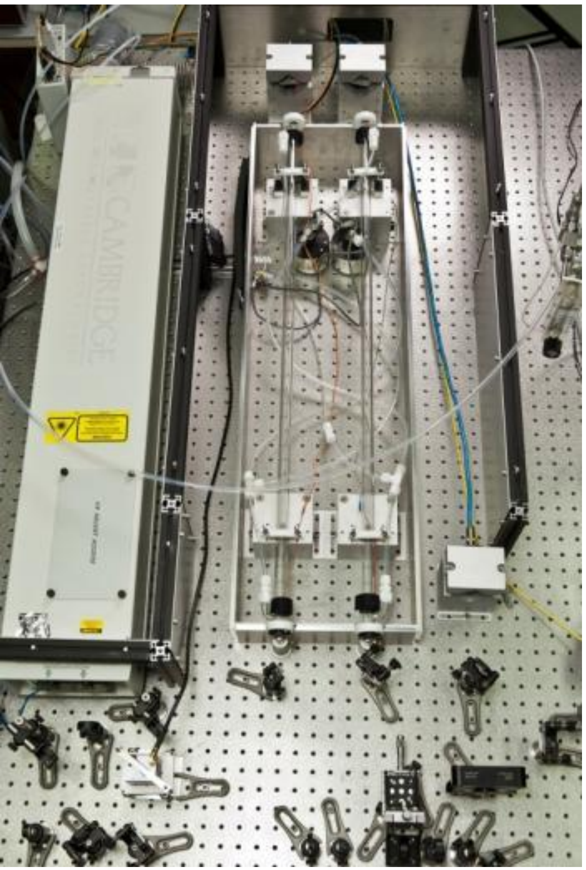
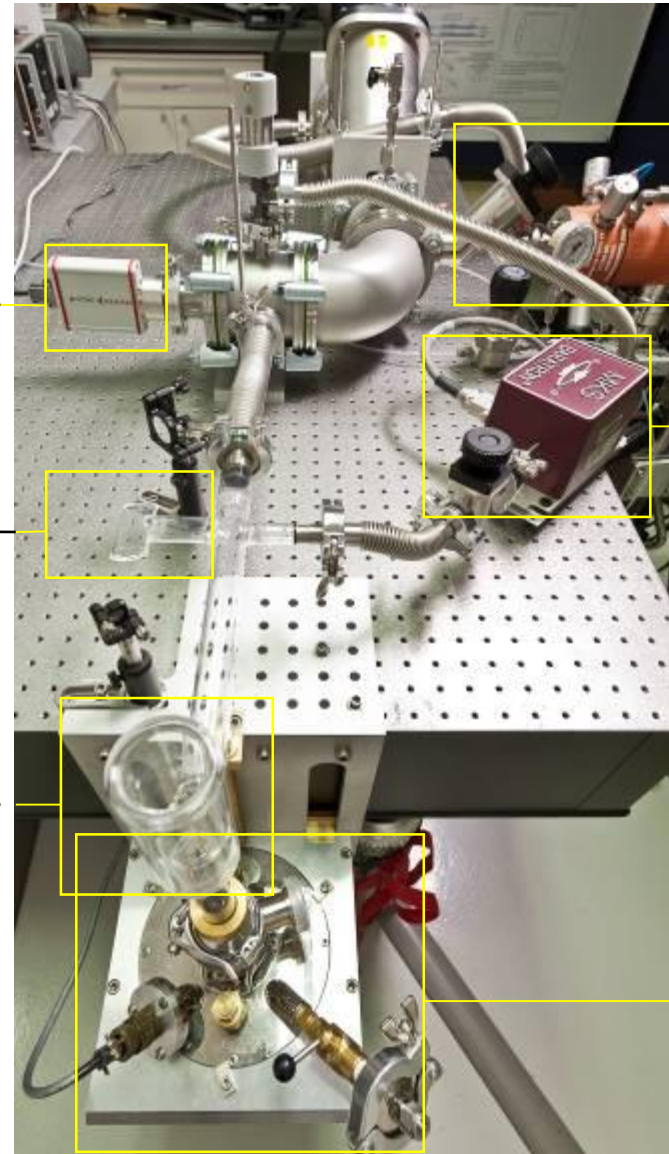
BIPM facility for ozone cross section measurements

Frequency doubled argon-ion laser with intensity stabilisation





Large range pressure gauge

5 cm absorption cell

Ozone generator (high voltage discharges)

Mass spectrometer

High accuracy pressure gauge (Baratron) for $P < 1$ mbar

Temperature controlled cryostat

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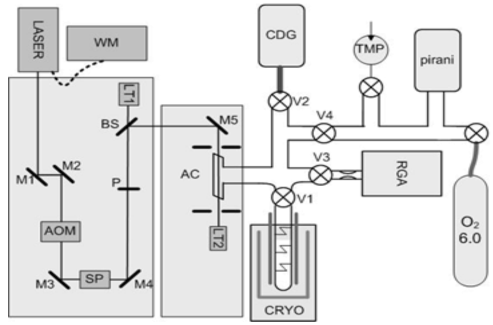
Ozone absorption cross-section measurements

Aims/Deliverables:

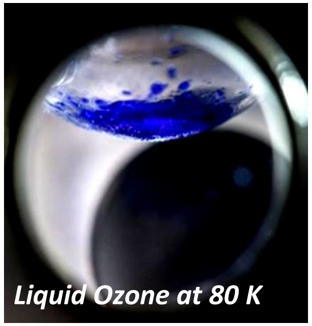
Resolve differences between reference methods

Status:

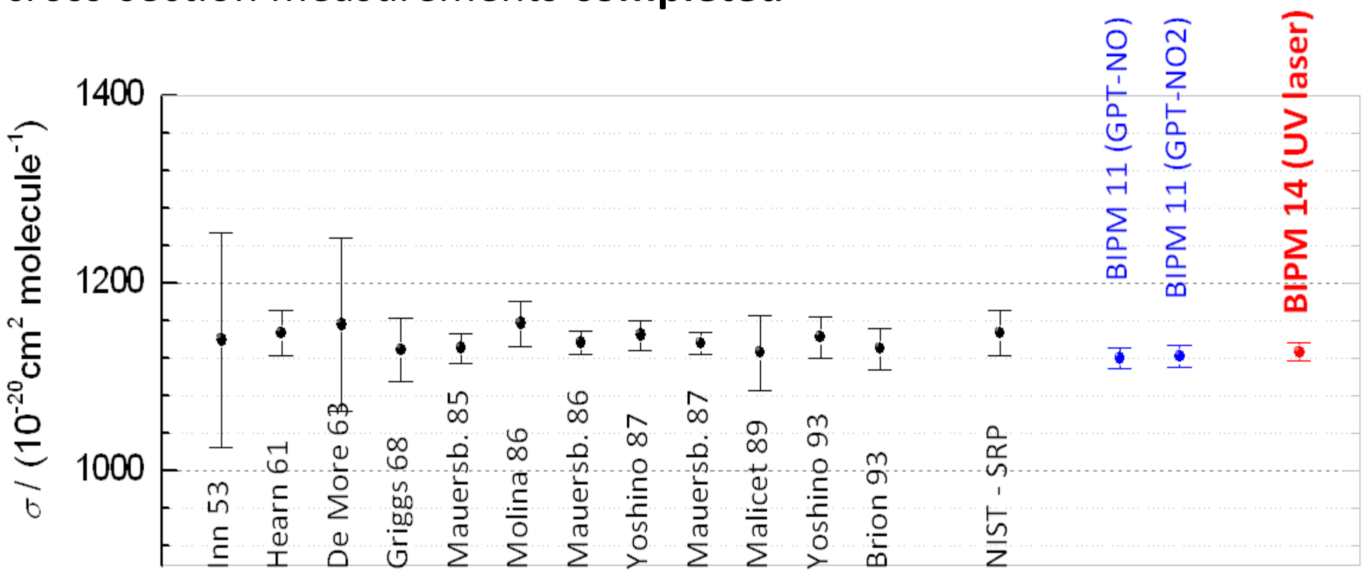
- **pure ozone generation system** purity > 98.1%
- **evaporation-condensation** cycle method
- cross-section measurements **completed**



Scheme of the ozone cross-section measurement setup



Liquid Ozone at 80 K



Secondments

Dr. S. Lee, KRISS, 2013

K. Tworek, GUM, 2012

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

Gas Standards for long term monitoring of nitrogen oxides

WMO/GAW Expert Workshop on Global Long-term Measurements of Nitrogen Oxides and Recommendations for GAW Nitrogen Oxides Network

(Hohenpeissenberg, Germany, 8-9 October 2009)

World Meteorological Organization
Weather • Climate • Water

WMO/TD - No. 1570

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

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

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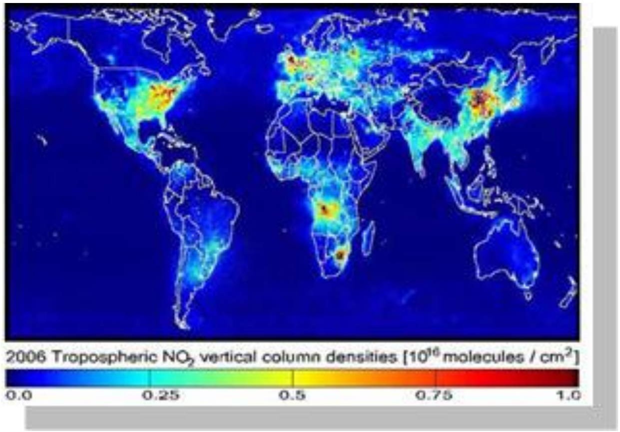
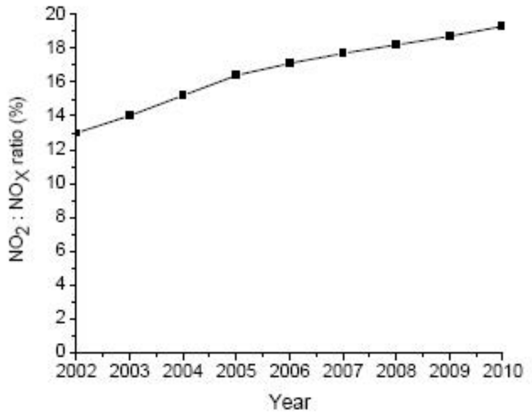
NO_2 standards and comparison (10ppm)

CCQM GAWG key comparison on NO_2 and Spectroscopic Measurements



BIPM dynamic gas standard facility for NO_2

Figure 2.12: The percentage composition of primary nitrogen dioxide in NO_x for all vehicle types in London.



The Air Quality Strategy for England, Scotland, Wales and Northern Ireland

Objectives (for 2020) for particulate matter (PM_{10}), nitrogen dioxide (NO_2), ozone (O_3), and polycyclic aromatic hydrocarbons (PAHs) are unlikely to be achieved, without further measures

BIPM facility for NO_2 Standards

Flow Control System for Rubotherm

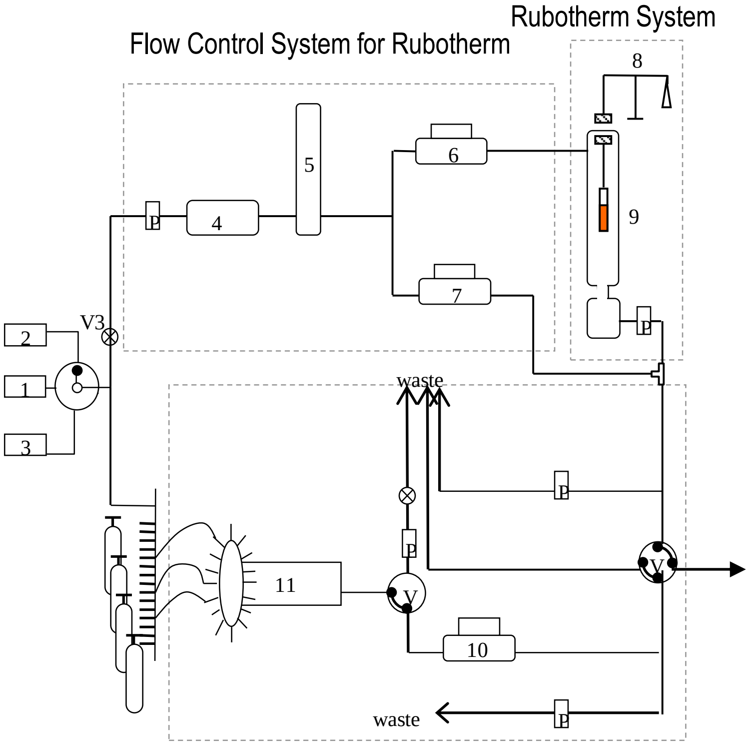
1. Zero air generator
2. Nitrogen Generator
3. Nitrogen Cylinders
4. molbloc (0-1000) mL/min
5. SAES Nitrogen purifier
6. Mass flow controller (0-100) mL/min
7. Mass flow controller (0-1000) mL/min

Rubotherm System (dynamic gas mixtures)

8. Magnetic suspension balance
9. NO_2 permeation tube

Flow Control System for NO_2 Gas Standards

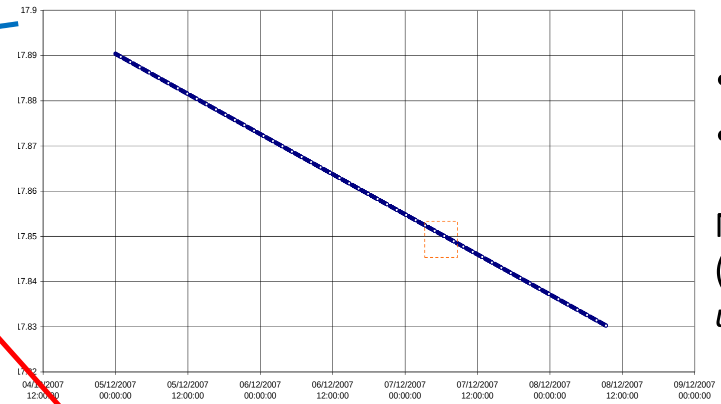
10. Mass flow controller (0-1000) mL/min
11. Multi position valve (16-ports)



Flow Control System for NO_2 Gas Standards

NO_2 Permeation Rate and Impurities

$$x_{NO_2} = \left(\frac{P \times V_m}{q_v \times M_{NO_2}} \right) - \left(\frac{M_{HNO_3} \times x_{HNO_3}}{M_{NO_2}} \right)$$



- Resolution: 2 µg;
- Stability,3 days: ~ 0.5 µg;

NO_2 permeation rate, *P*, (5000-10000) ng/min
$u \approx 2$ ng/min

x_{NO2} - NO_2 mole fraction;

P - NO_2 permeation rate;

Vm - molar volume of nitrogen;

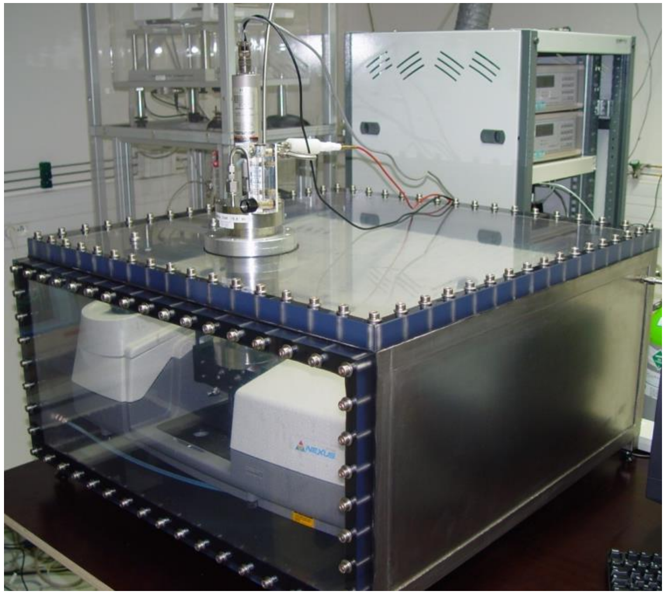
M_{NO2} - the molar mass of NO_2;

q_v - total flow of nitrogen;

M_{HNO3} - the molar mass of NO_3; and

x_{HNO3} - HNO_3 mole fraction measured by FTIR.

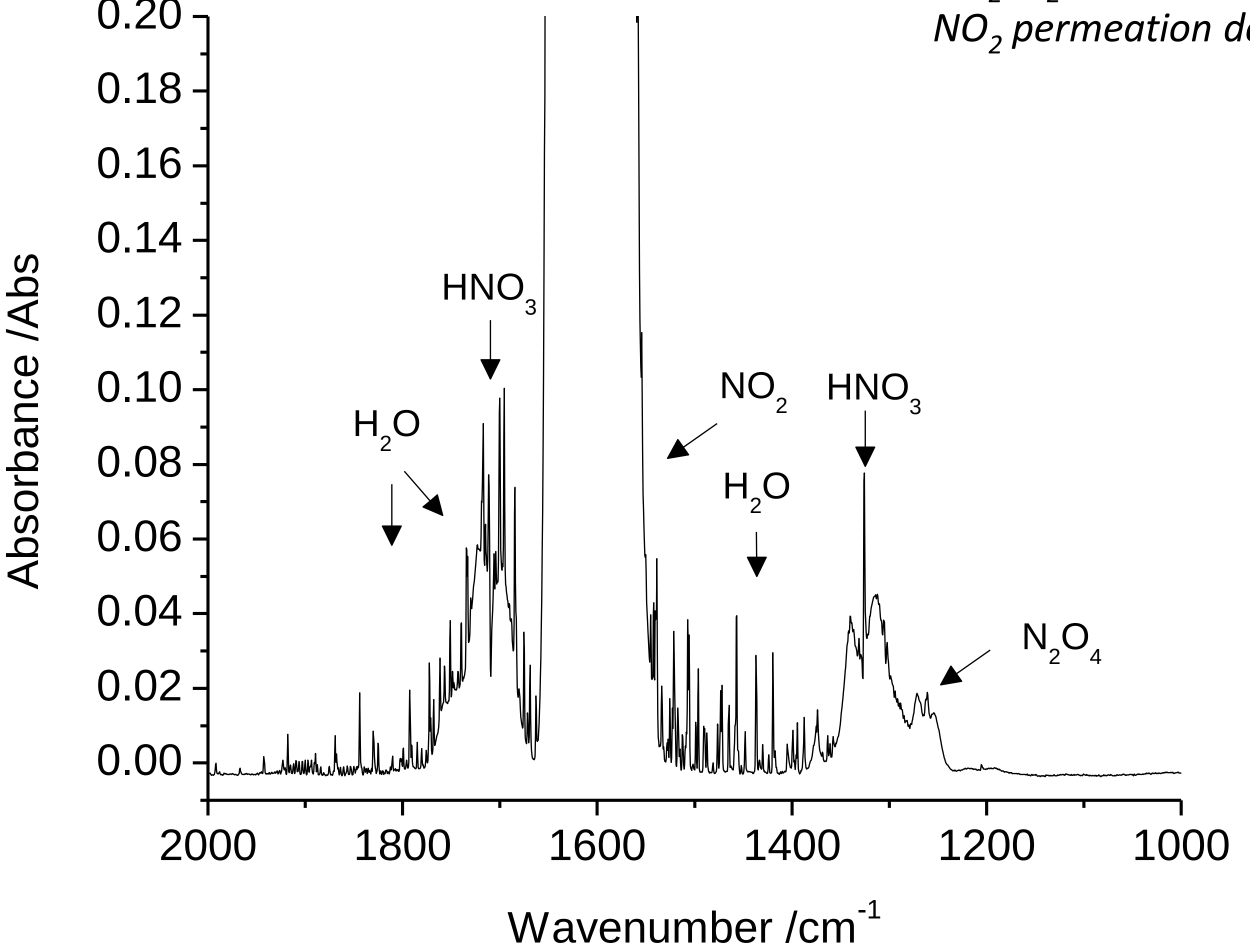
FTIR gas facility



Flores E., Idrees F., Moussay P., Viallon J., Wielgosz R., Highly Accurate Nitrogen Dioxide (NO_2) in Nitrogen Standards Based on Permeation, *Anal. Chem., 2012, 84(23), 10283-10290*

Purity and quantification of permeating gas: Analysis by FTIR

Infrared absorbance spectrum of a 150 µmol mol^{-1} NO_2/N_2 gas mixture generated using the small NO_2 permeation device



Quantification of HNO_3 without gas standards?

N_2O_4 negligible impurity at lower concentrations

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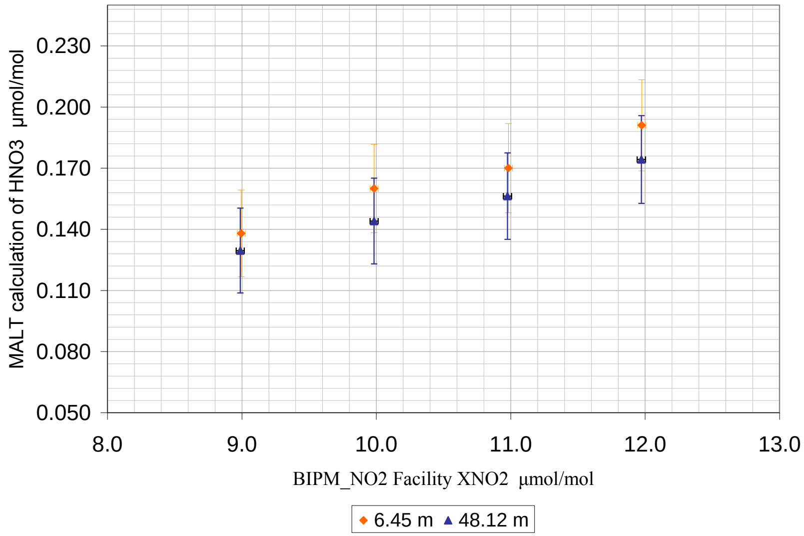
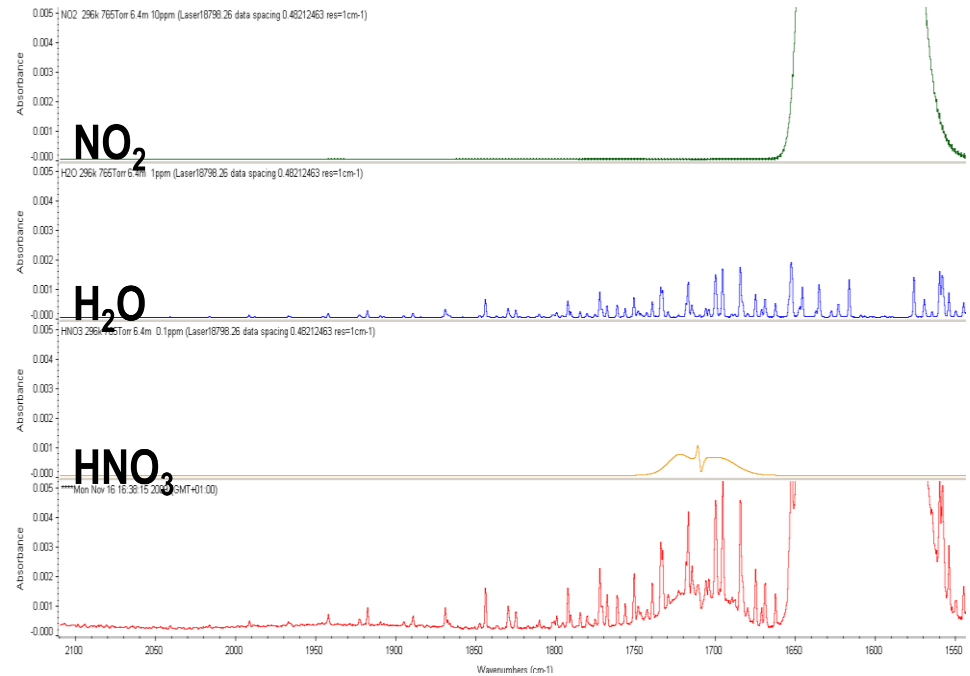
HNO_3 quantification using MALT





Uncertainty budget for the HNO_3 for mole fractions of (0.1-0.2) µmol/mol

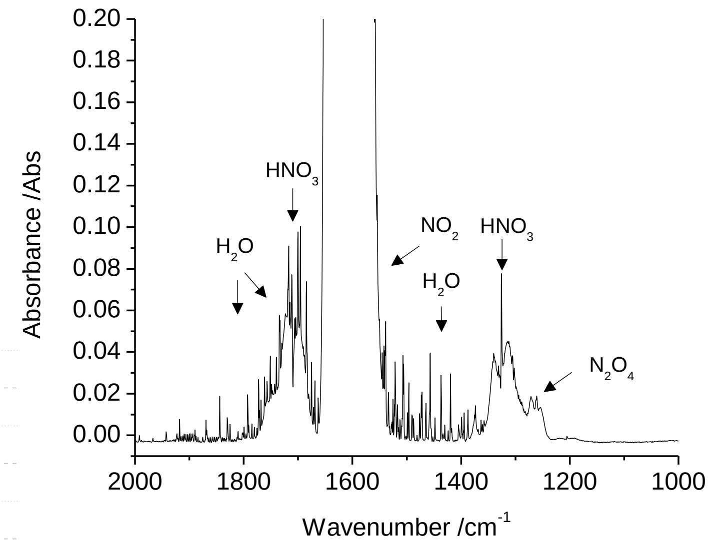
$$u(x_{\mathrm{HNO_3}}) = \sqrt{(0.020)^2 + \left(0.017 x_{\mathrm{HNO_3}}\right)^2 + \left(0.05 x_{\mathrm{HNO_3}}\right)^2}$$

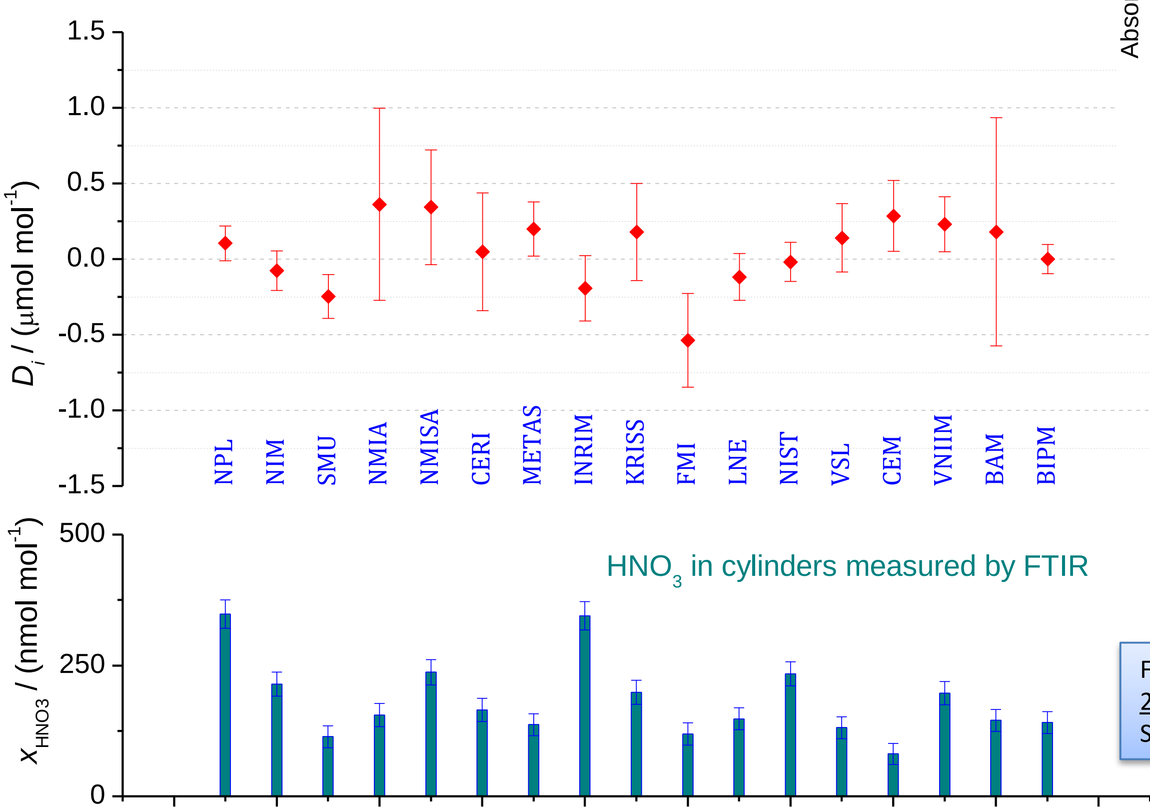
Signal stability — MALT-CLS — HITRAN database

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

CCQM-K74

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

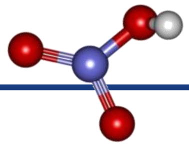




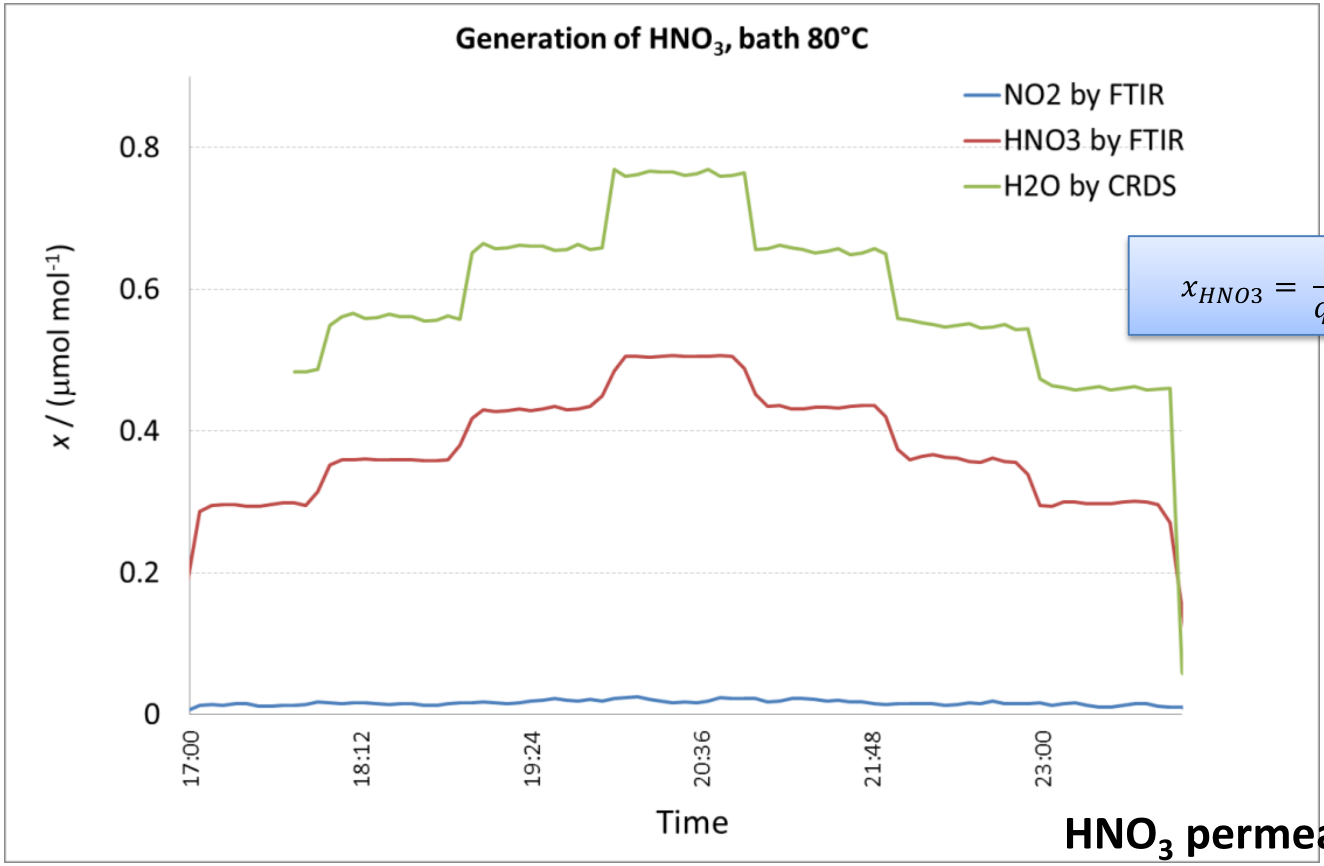
Key issue : HNO_3 in cylinders & in dynamic mixtures

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

Preparing for a repeat comparison **CCQM-K74.2017**



Generation of dynamic mixtures of HNO_3 in nitrogen by permeation



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

Secondment of C. Pascale (METAS) 2014

HNO_3 permeation [200-500] nmol mol^{-1}

Permeation rate ~ 30 % H_2O

H_2O accurate quantification is crucial

Preparing for a repeat comparison **CCQM-K74.2017**

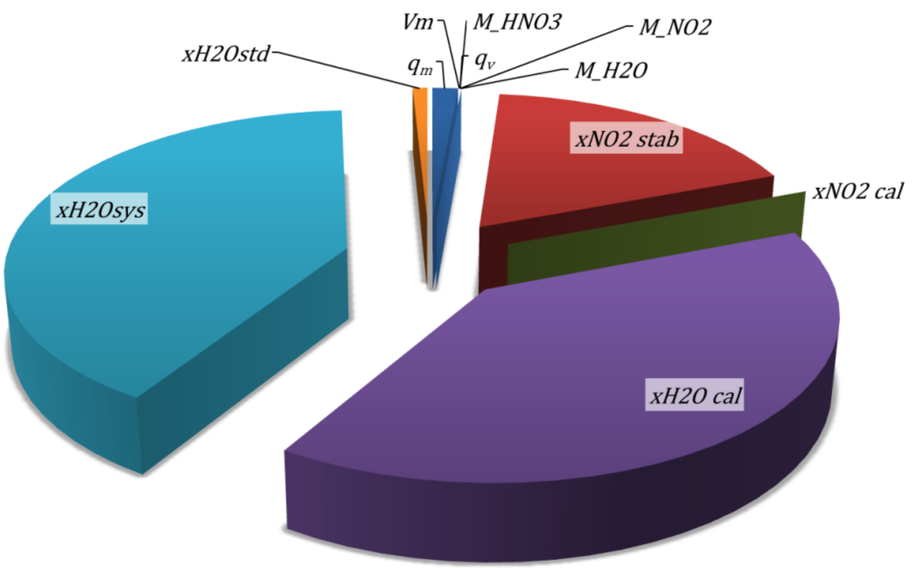
Generation of dynamic mixtures of HNO_3 in nitrogen by permeation

Quantity	Value	Standard Uncertainty
q_m	9104 ng min^{-1}	8.3 ng min^{-1}
V_m	22.40037 g mol^{-1}	340·10^{-6} g mol^{-1}
q_v	4.8 L min^{-1}	72.0·10^{-6} L min^{-1}
M_HNO_3	63.0130 g mol^{-1}	3.40·10^{-3} g mol^{-1}
M_NO_2	46.0055 g mol^{-1}	2.80·10^{-3} g mol^{-1}
M_H_2O	18.0147 g mol^{-1}	0.5·10^{-3} g mol^{-1}
x_{NO2} stability	0.0 ppb	3.00 ppb
x_{NO2} calibration	19.80 ppb	0.0396 ppb
x_{H2O} calibration	749.79 ppb	11.4 ppb
x_{H2O} system	50.0 ppb	11.5 ppb
x_{H2O} stability	0.0	1.64 ppb

Quantity	Value	Standard Uncertainty
$x(HNO_3)$	456.1 nmol mol^{-1}	5.2 nmol mol^{-1}

H_2O quantification:

- CRDS analysis calibrated by NPL
- Contribution from the matrix (system)



Greenhouse gases: target uncertainties for primary standards

Component	Nominal Mole fraction	Primary Standard: target standard uncertainty
CO_2	400 µmol/mol	0.025 µmol/mol
CH_4	2000 nmol/mol	0.5 nmol/mol
N_2O	330 nmol/mol	0.025 nmol/mol

Based on primary standard contributing to less than 5% of measurement uncertainty for monitoring, based on most stringent data compatibility requirements

This means relative standard uncertainties:

< 0.007 % (for CO_2 and N_2O) and

< 0.025 % (for CH_4)

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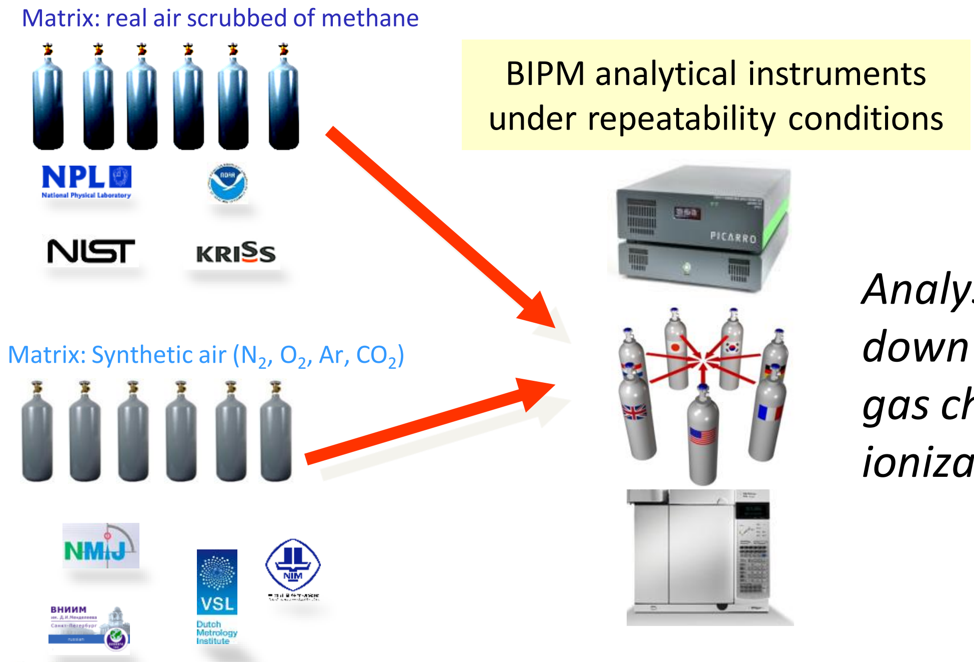
International comparison of methane in air standards (2012)

Aims/Deliverables:

Demonstrate the degree of equivalence of national methane in air gas standards in support of green house gas monitoring **(CCQM-K82, CH_4 in air)**



Analysis made by cavity ring down spectroscopy and gas chromatography-flame ionization detector

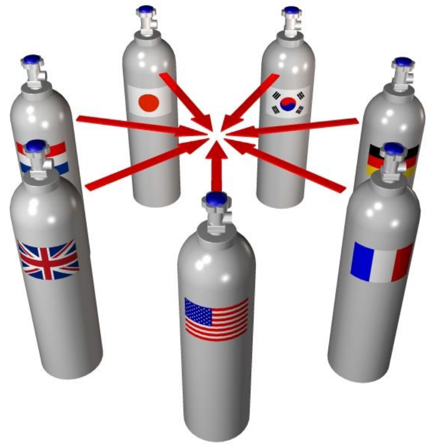
CRDS measurements and matrix gas composition

Target mole fractions:

1800±10 nmol/mol and 2200±10 nmol/mol.

Matrix composition

To minimize pressure broadening effects



Component in Air	Minimum mole fraction permitted within submitted cylinder	Maximum mole fraction permitted within submitted cylinder
Nitrogen	0.77849 mol/mol	0.78317 mol/mol
Oxygen	0.20776 mol/mol	0.21111 mol/mol
Argon	8.865 mmol/mol	9.799 mmol/mol
Carbon Dioxide	360 µmol/mol	400 µmol/mol

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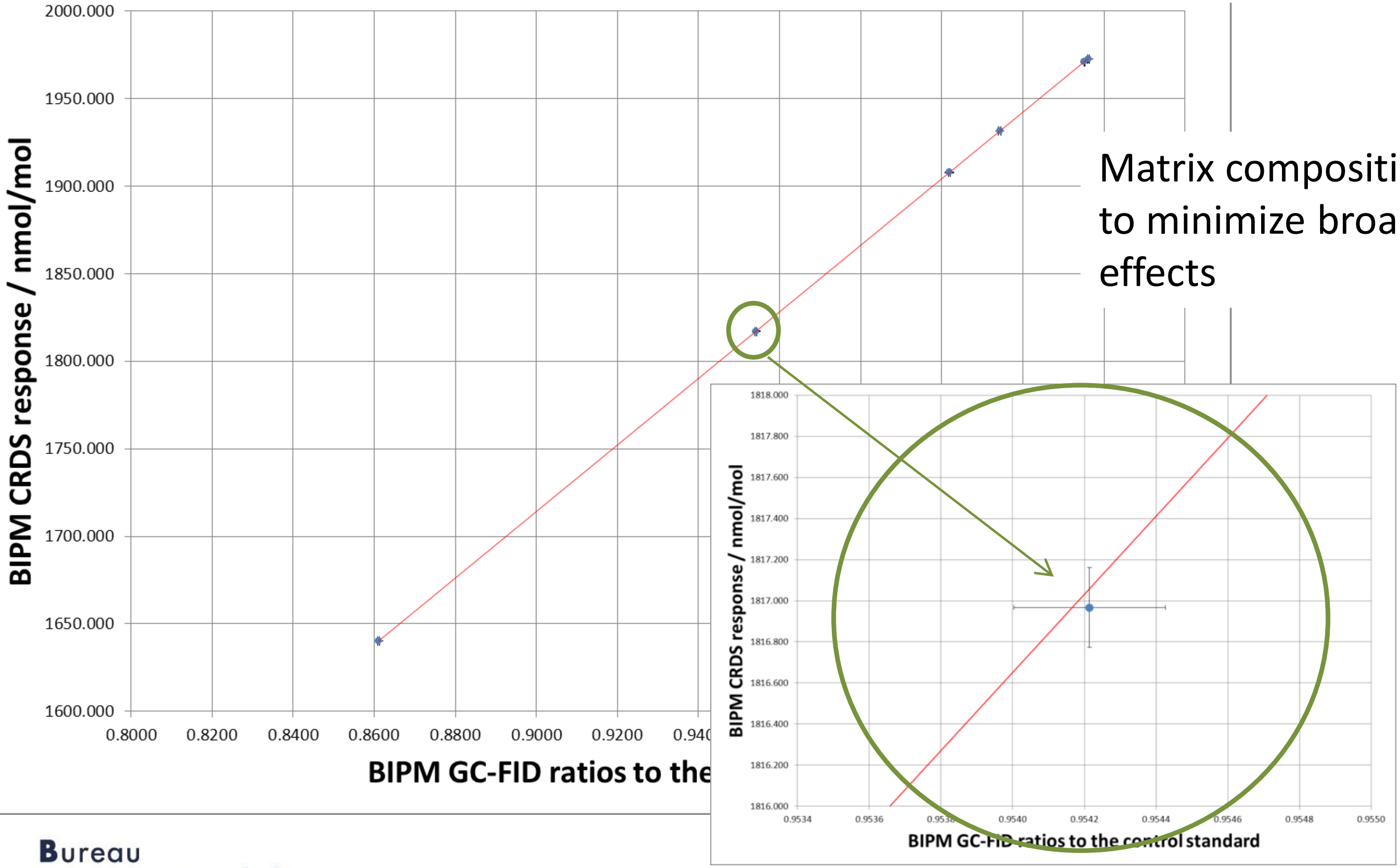
Comparison of GC-GID and CRDS methods for methane in air

Validation of method using NIST real air and synthetic air standards



Matrix composition adapted to minimize broadening effects

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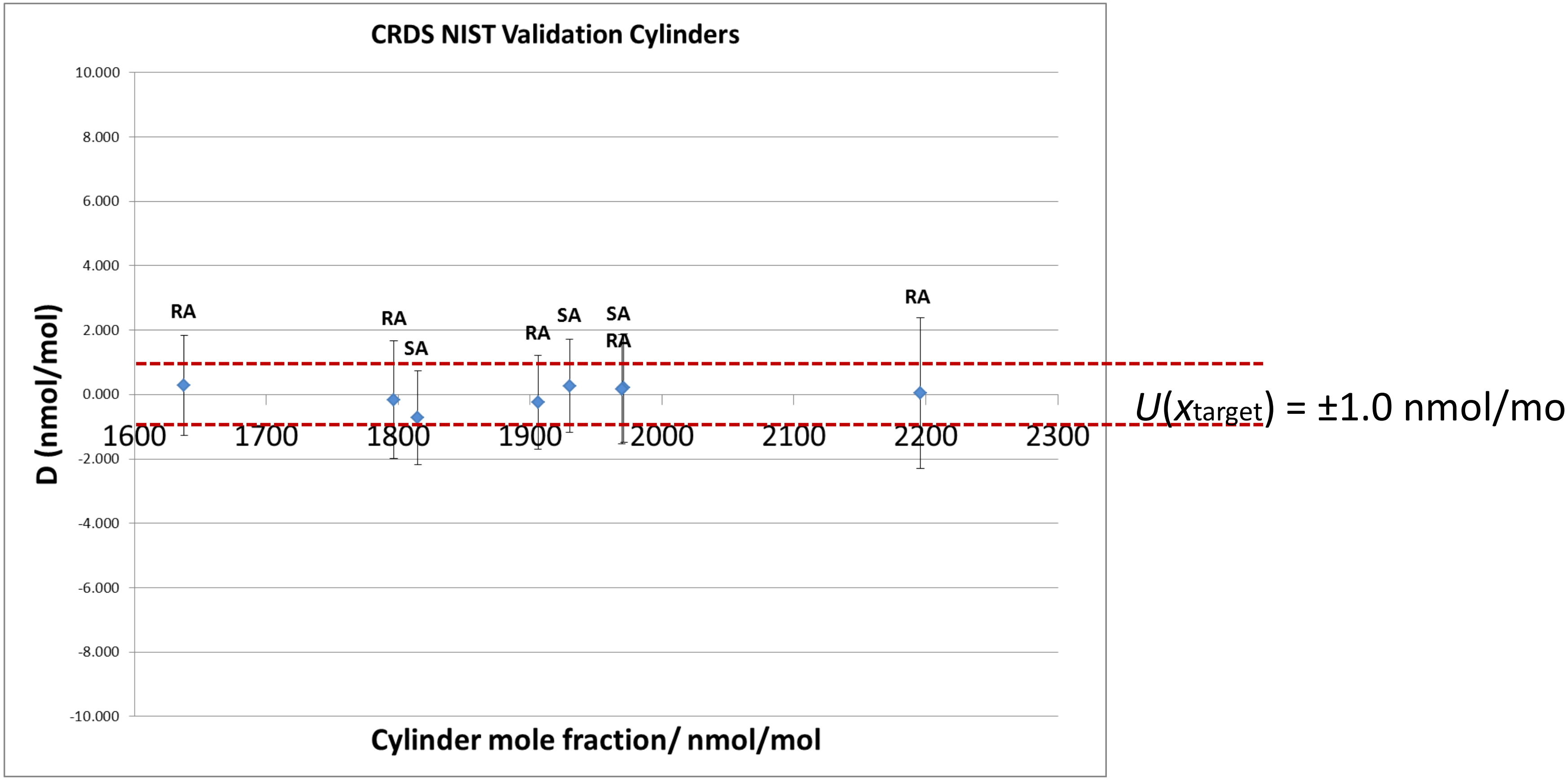
Validation of BIPM's Measurements facility with NIST standards



Methane standards made in whole and synthetic air compared by CRDS and GC-FID for atmospheric monitoring applications	*Analytical Chemistry, 2015, 87(6), 3272-3279*

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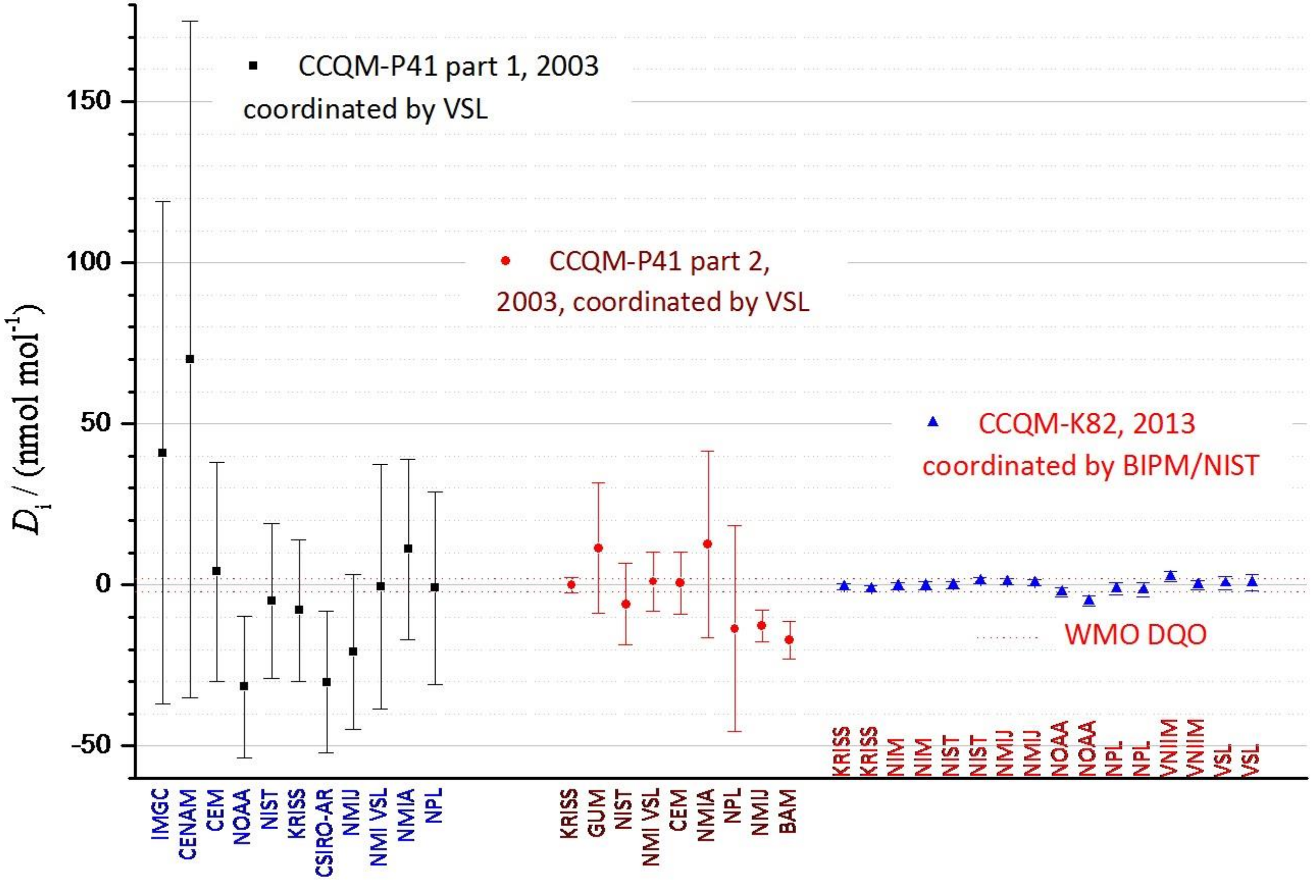
Improvements in global compatibility of methane in air standards



Comparison results vs. Data Compatibility Goals

DQO = ± 2 nmol/mol

For CCQM-K82:

Smallest *u*(*x*) = 0.5 nmol/mol

$\sigma_{(CCQM\text{-}K82)}$= 1.17 nmol/mol

Negligible impact of standards when:

u(x), $\sigma_{(CCQM\text{-}Kxx)}$ ≤ DQO/4

u(x), $\sigma_{(CCQM\text{-}Kxx)}$ ≤ 0. 5 nmol/mol

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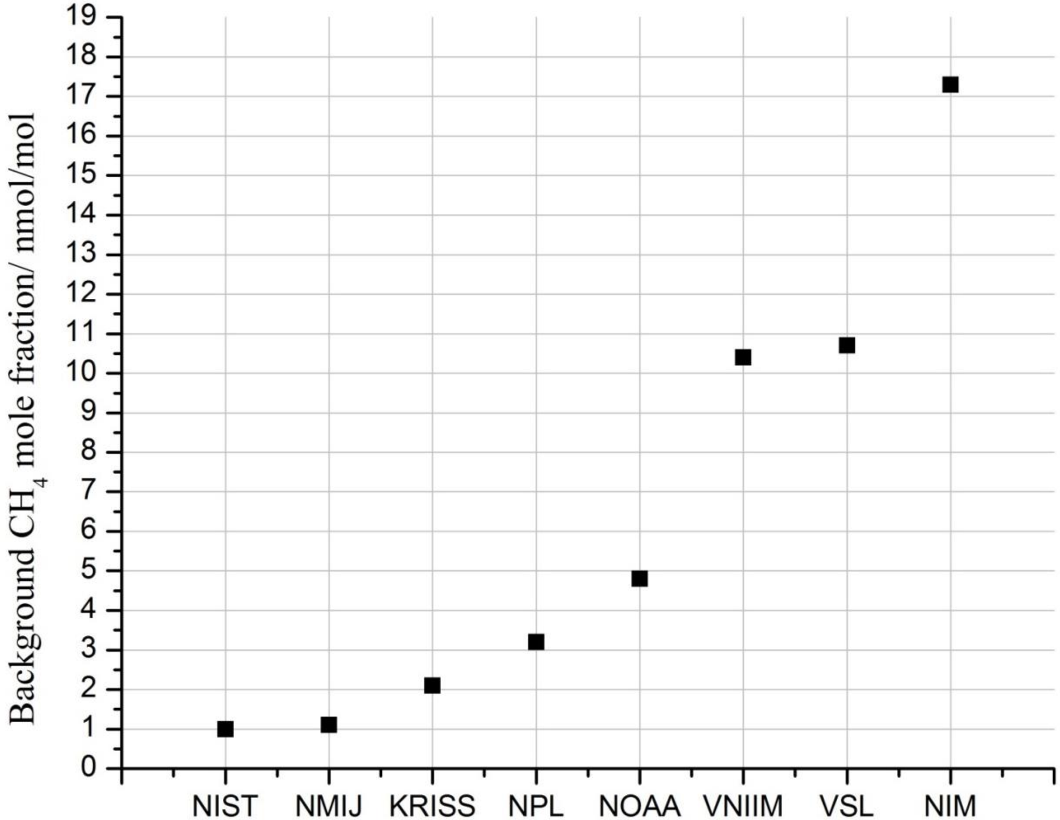
Development for future improvements in CH_4 in air standards



Trace CH_4 mole fractions in balance gas as reported by participating laboratories in CCQM-K82

Accurate measurements of CH_4 in balance gas at 1 nmol/mol levels with $u(x) < 0.1$ nmol/mol required

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Measurement Challenges for CO_2 Standards and Comparisons

Comparison method

Matrix Composition/ Purity

Isotopic Composition

Stability/Storage

Target relative standard uncertainty
< 0.007 %

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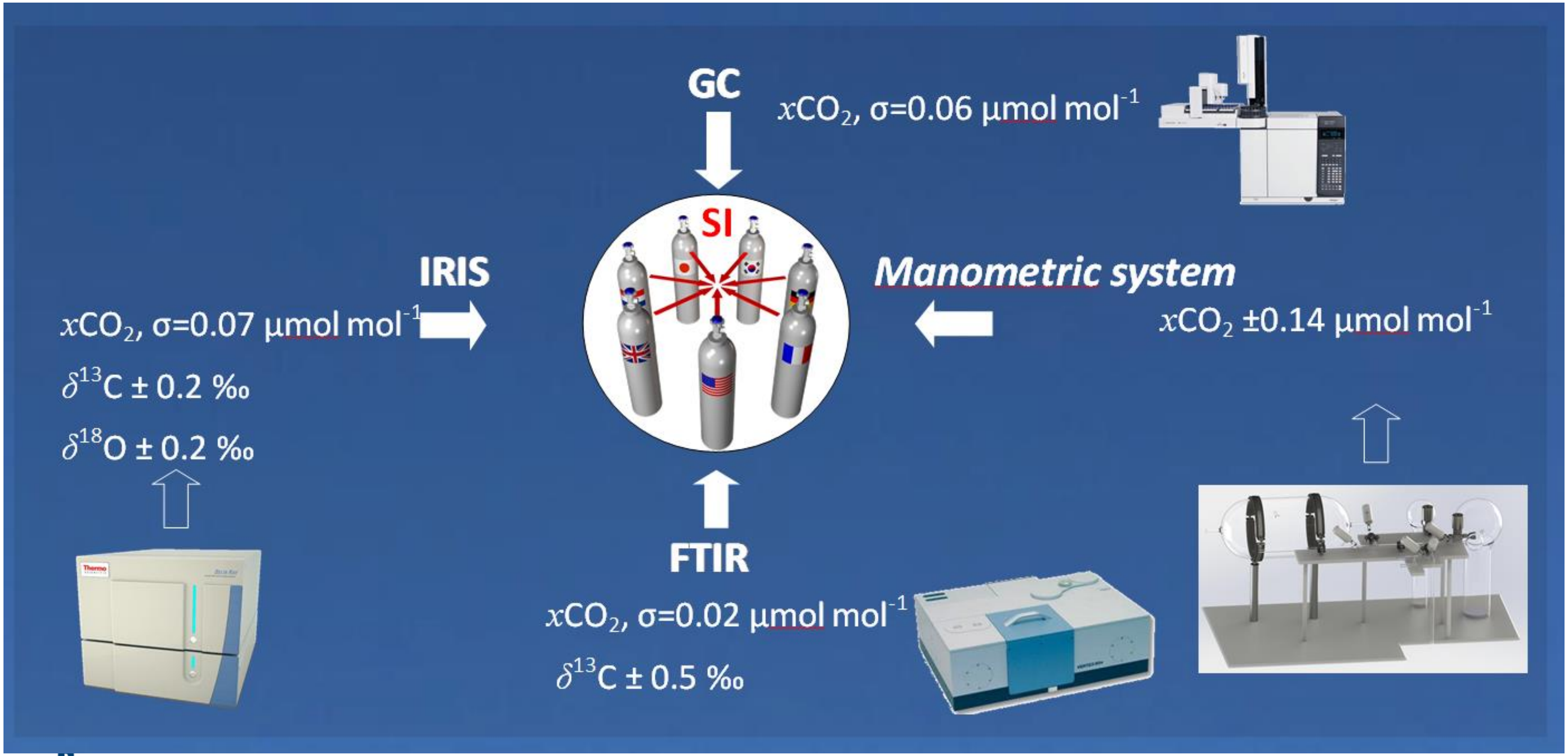
Preparing for the repeat CO_2 in air comparison (2016)

International comparison CCQM-K120 (2016): ambient level CO_2



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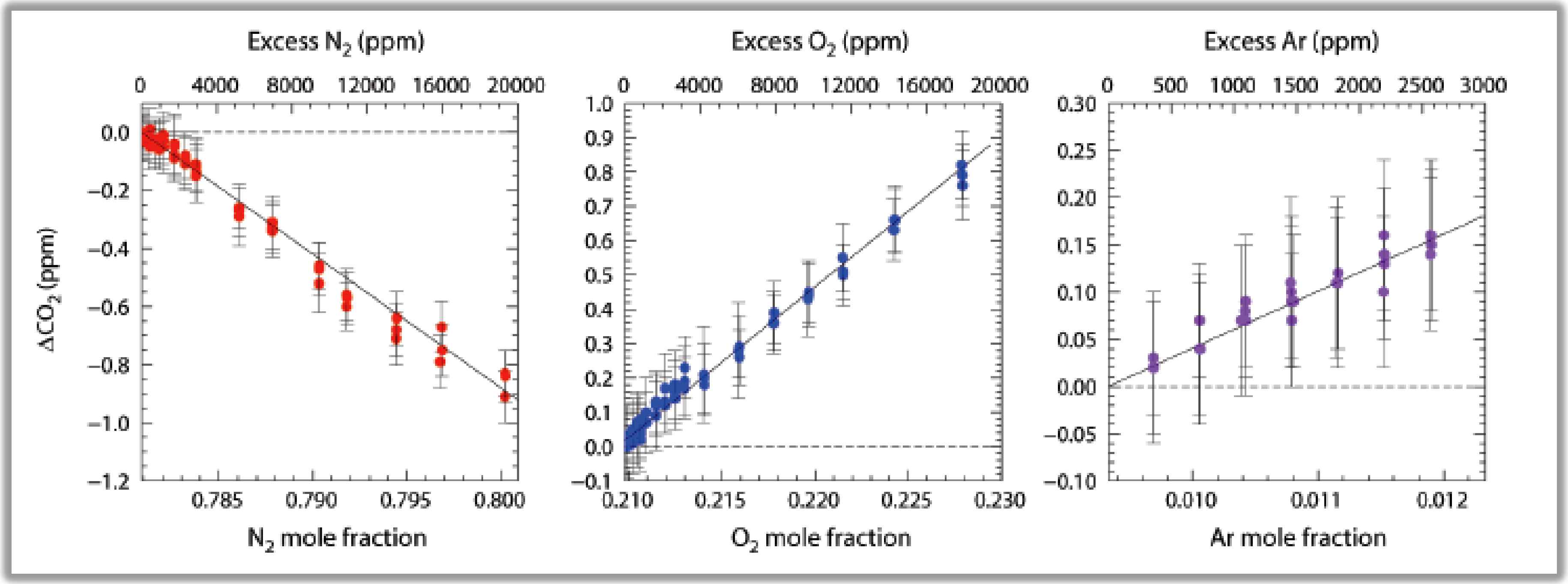
Potential biases due to matrix composition

- **Influence of the matrix composition on the spectroscopy**
- **More pronounced for CO_2**
- **For synthetic air standards this can be a major source of bias**



Consistency with atmospheric air composition (major components) to 0.5 mmol/mol

H. Nara, H. Tanimoto, Y. Tohjima, H. Mukai, Y. Nojiri, K. Katsumata and C. W. Rella, *Atmos. Meas. Tech.*, **5**, 2689–2701, (2012).

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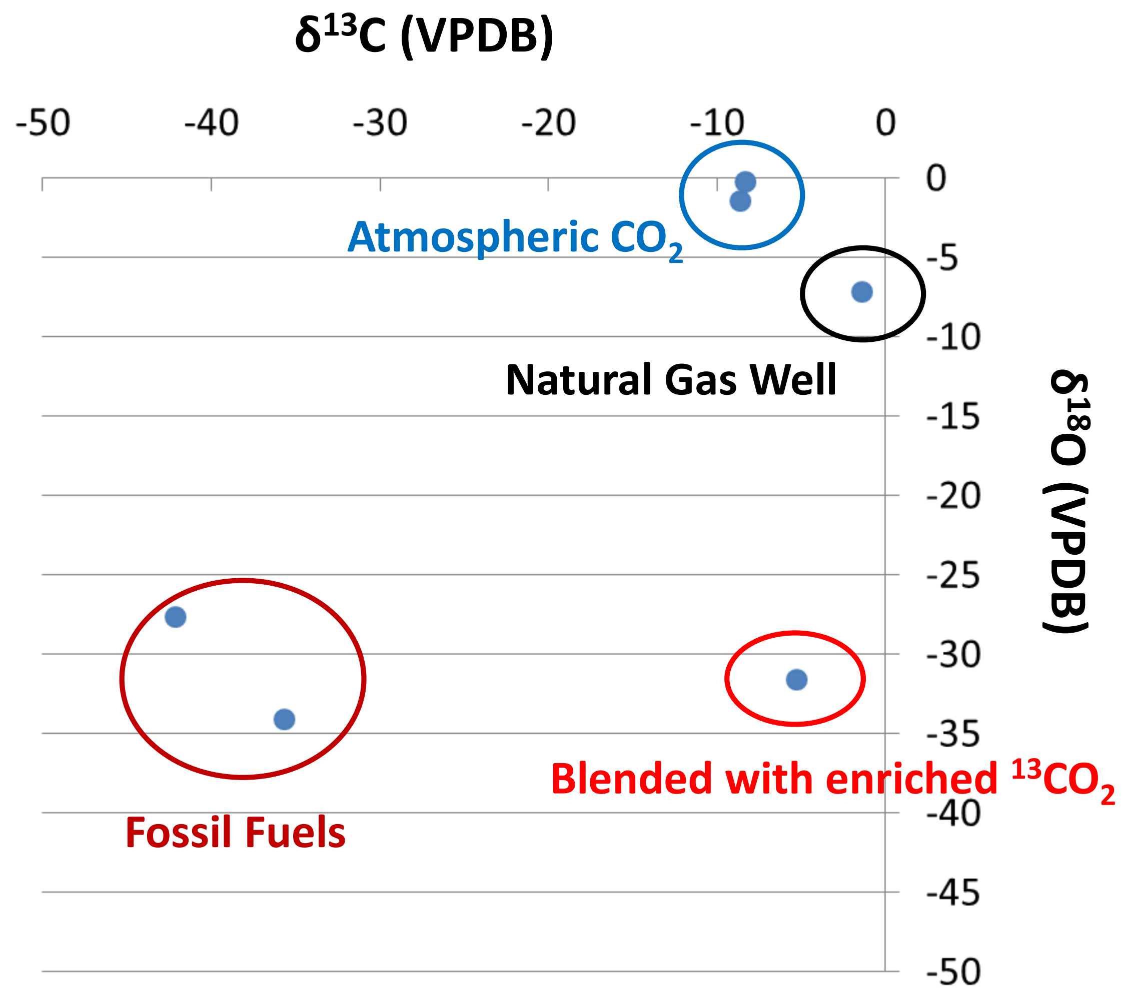
Accurate measurement of CO_2 (and CO_2 isotopologues)

Isotopes of CO_2

M/z	CO_2 Isotope
44	$^{12}C^{16}O_2$
45	$^{13}C^{16}O_2$, $^{12}C^{16}O^{17}O$
46	$^{12}C^{16}O^{18}O$, $^{13}C^{16}O^{17}O$, $^{12}C^{17}O_2$
47	$^{13}C^{16}O^{18}O$, $^{12}C^{17}O^{18}O$, $^{13}C^{17}O_2$
48	$^{13}C^{17}O^{18}O$, $^{12}C^{18}O_2$
49	$^{13}C^{18}O_2$



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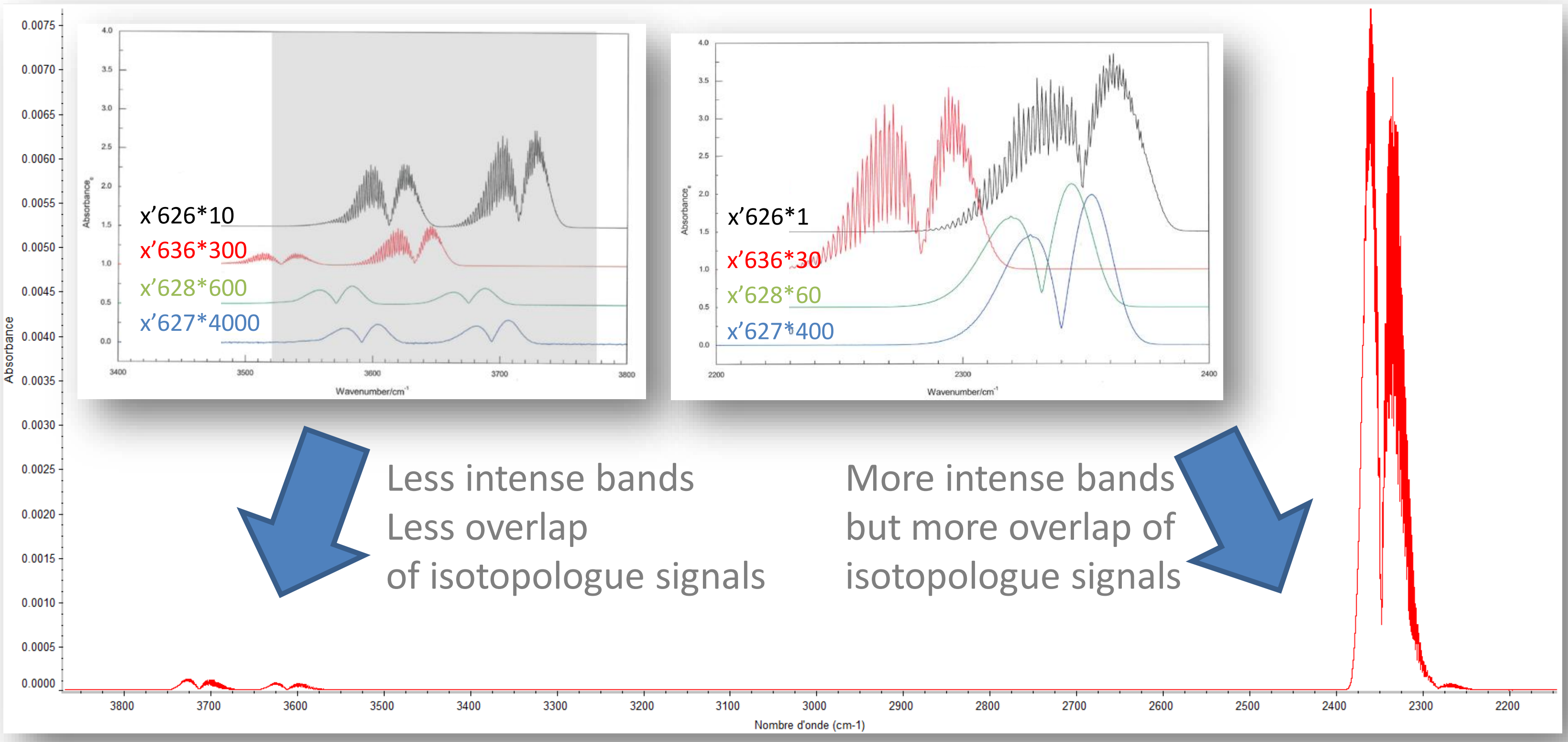
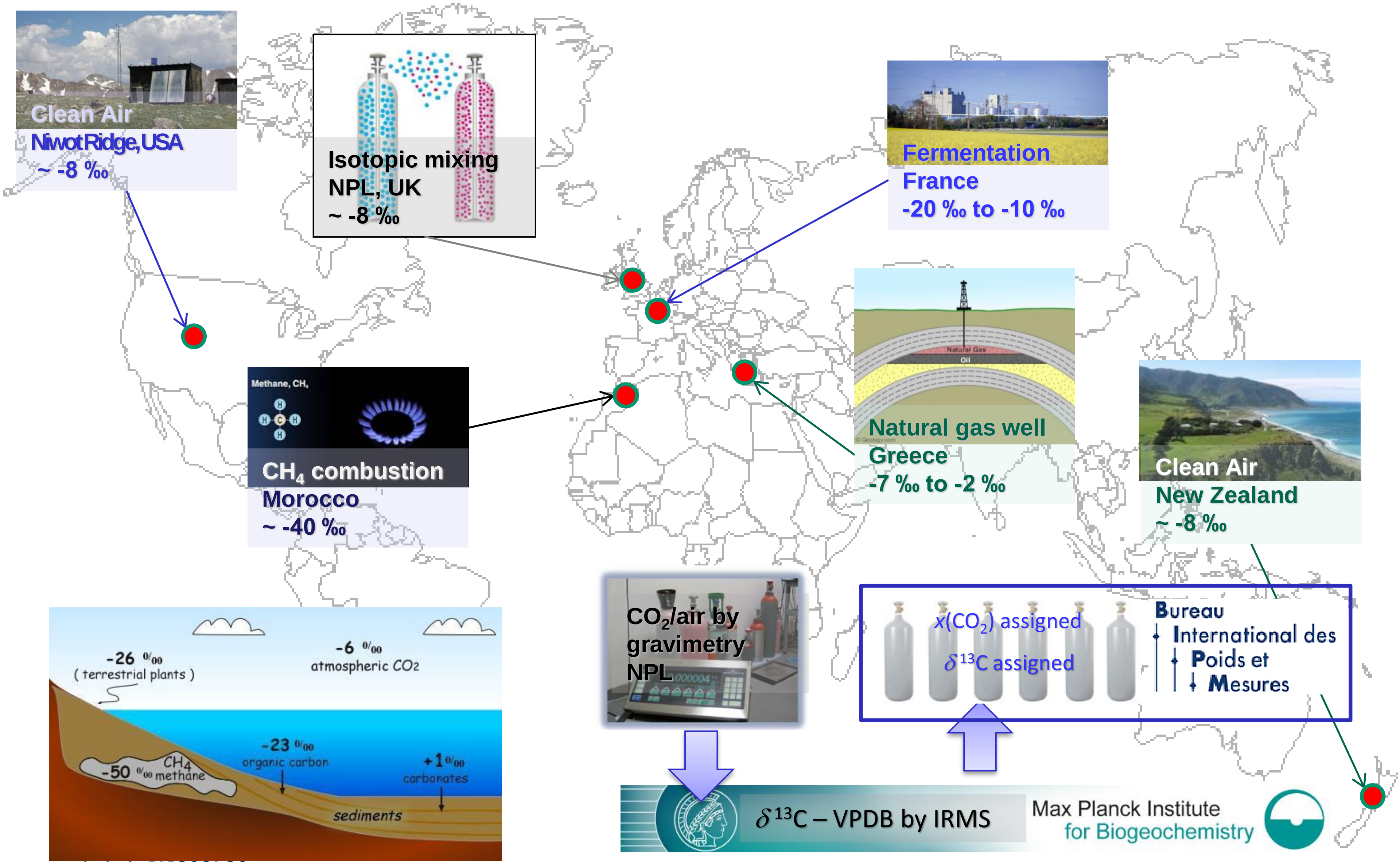
Isotope ratio measurements for corrections to CO_2 concentration measurements required at the ± 1 ‰ level

Accurate measurement of CO_2 (and CO_2 isotopologues) (by FTIR)



Validation standards with a range of compositions

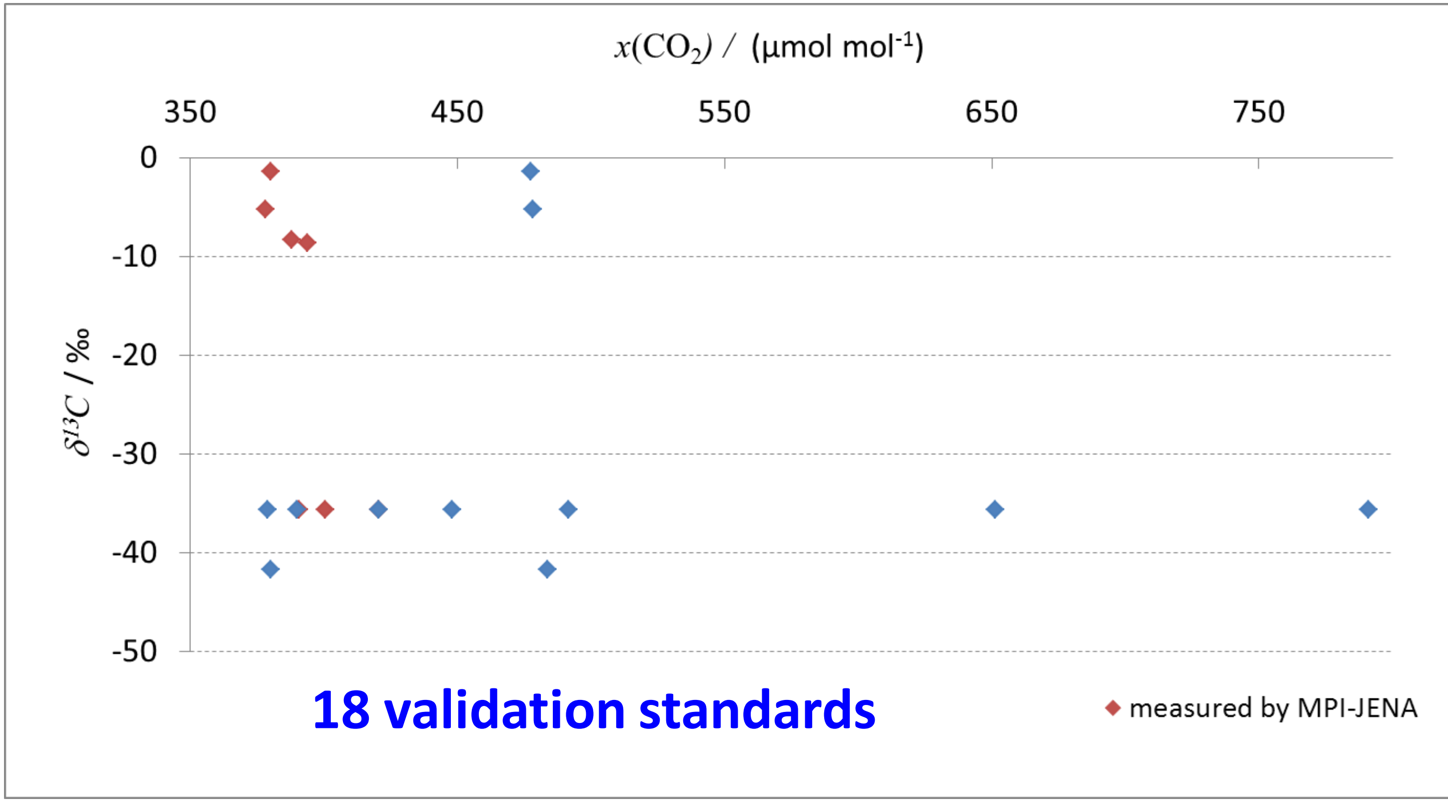


CO_2 validation standards

Traceability of mole fraction values to: NIST and NPL

Traceability of isotope ratio delta values to JRAS standards and VPDB scale

Max Planck Institute for Biogeochemistry



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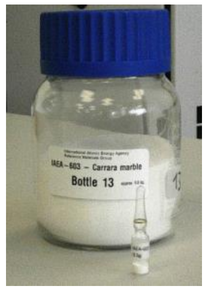
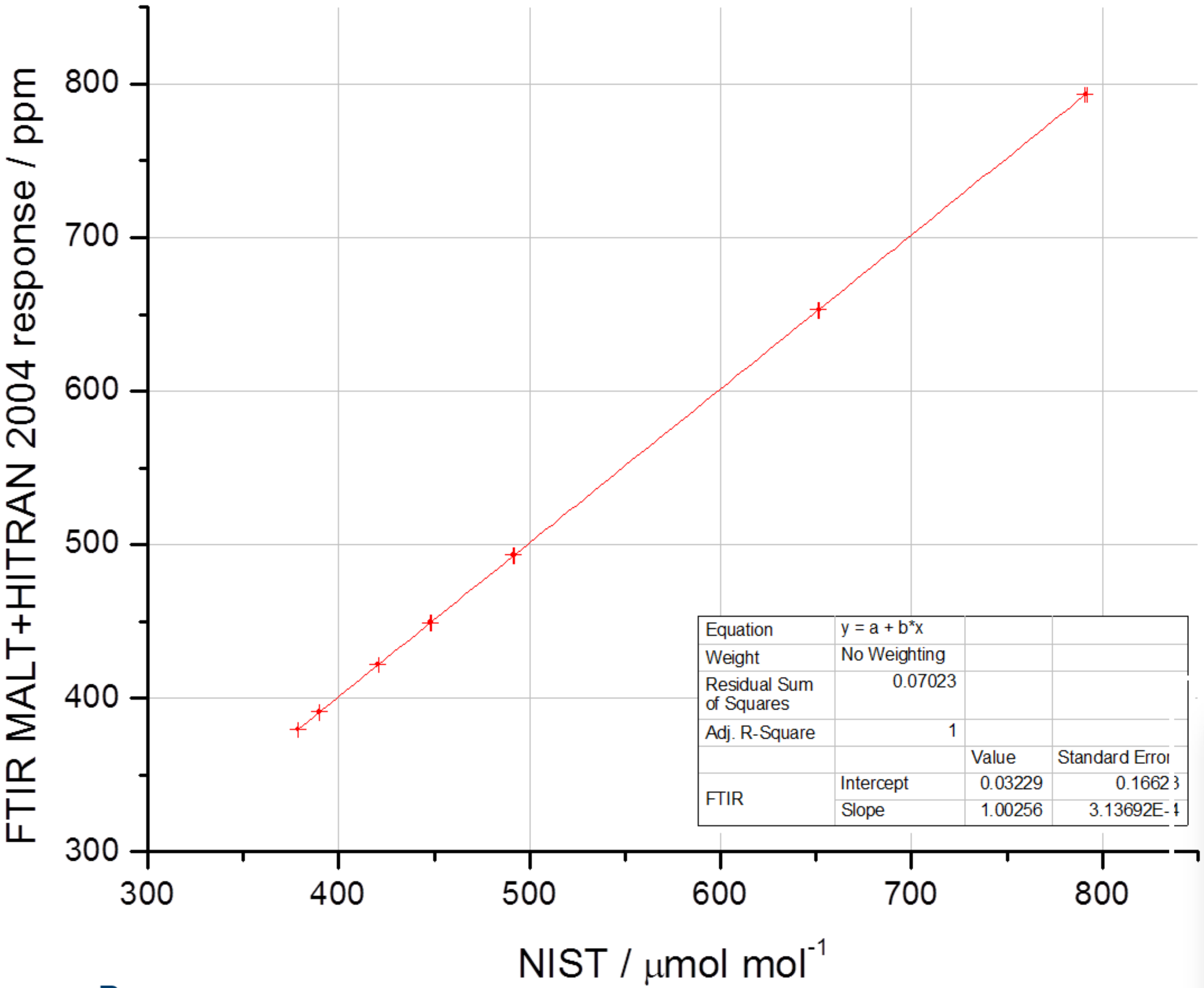
3 additional standards for the set to be provided by NOAA in 2015

Traceability of stable isotope standard measurements

BIPM-IAEA Symposium 4 June 2013; IAEA Workshop on Stable Isotopes (3-5 Sept 2014)

Organization	Quantity and types of standard	Calibrated/Measurement Instrument
IAEA International Atomic Energy Agency	$\delta^{13}C$ $\delta^{18}O$  Carbonates  Pure CO_2	 Mass Spec.
Max Planck Institute for Biogeochemistry	$\delta^{13}C$ $\delta^{18}O$  CO_2 from carbonates in real air	 Mass Spec.
Bureau International des Poids et Mesures	CO_2 mole fraction ($\delta^{13}C$, $\delta^{18}O$) CCQM-K120  CO_2 in real/synthetic air	Optical Spectroscopic methods    

Comparisons of CO_2 standards with FTIR



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.07023		
Adj. R-Square	1		
		Value	Standard Error
FTIR	Intercept	0.03229	0.16623
	Slope	1.00256	3.13692E-4

Under repeatability conditions with $u(x_{FTIR})$ = 0.015 µmol/mol

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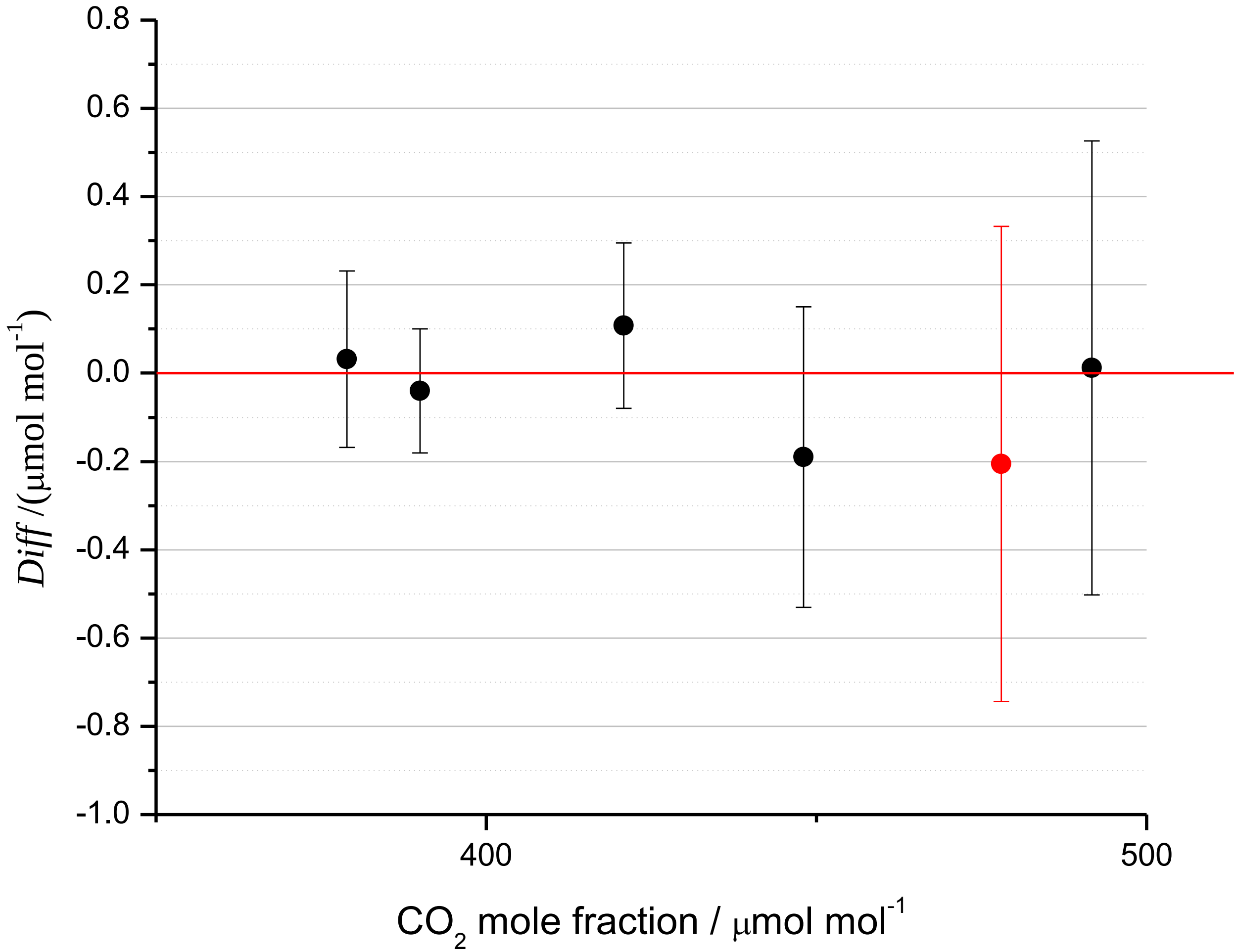
Non corrected FTIR response for isotopic effects

	$\delta^{13}C$ (VPDB) ‰	$\delta^{18}O$ (VPDB) ‰
STD A	-35.685	-34.478
STD B	-5.2494	-31.640



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Corrected FTIR response for isotopic effects

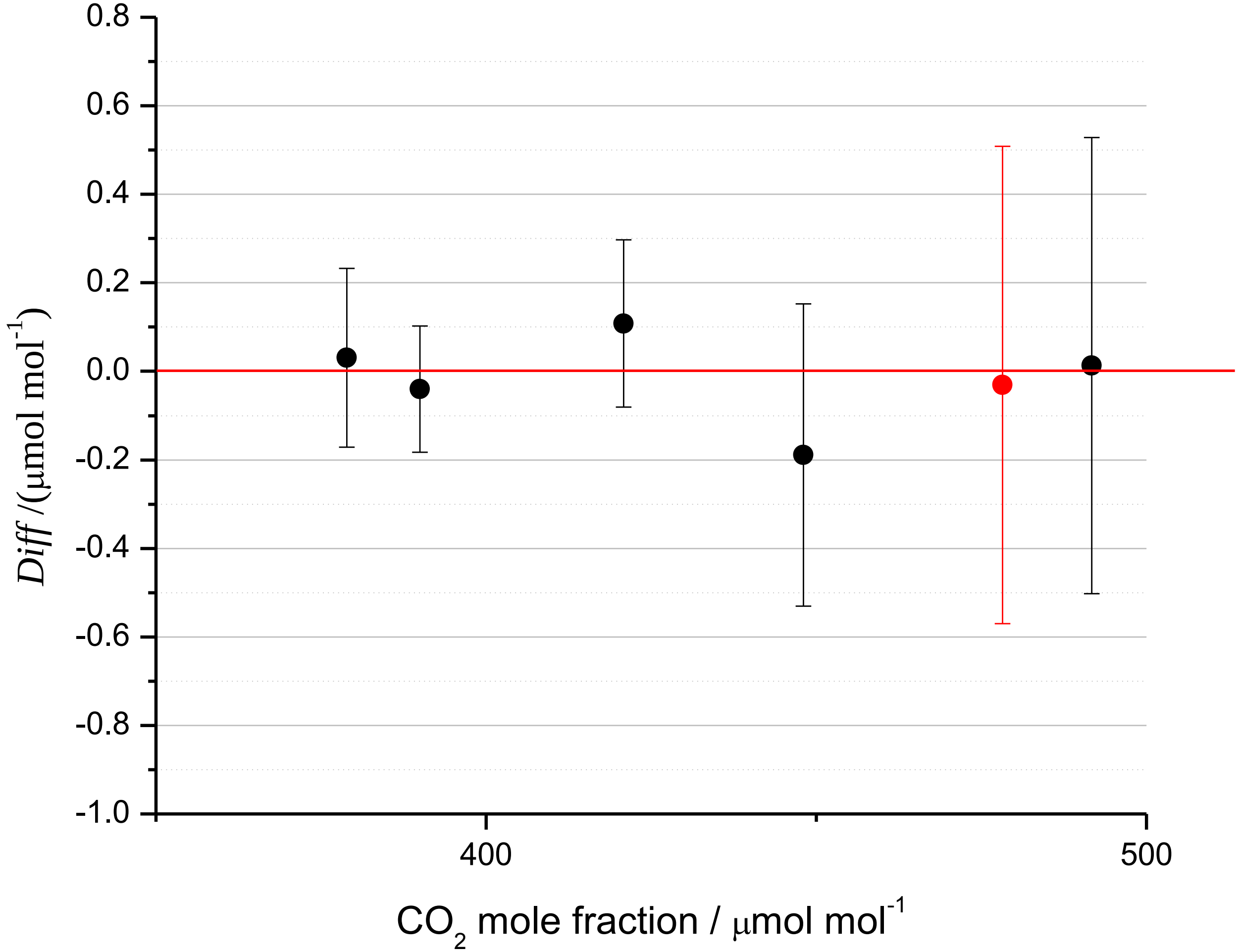
	$\delta^{13}C$ (VPDB) ‰	$\delta^{18}O$ (VPDB) ‰
STD A	-35.685	-34.478
STD B	-5.2494	-31.640

The correction is

~ 0.170 µmol mol^{-1}

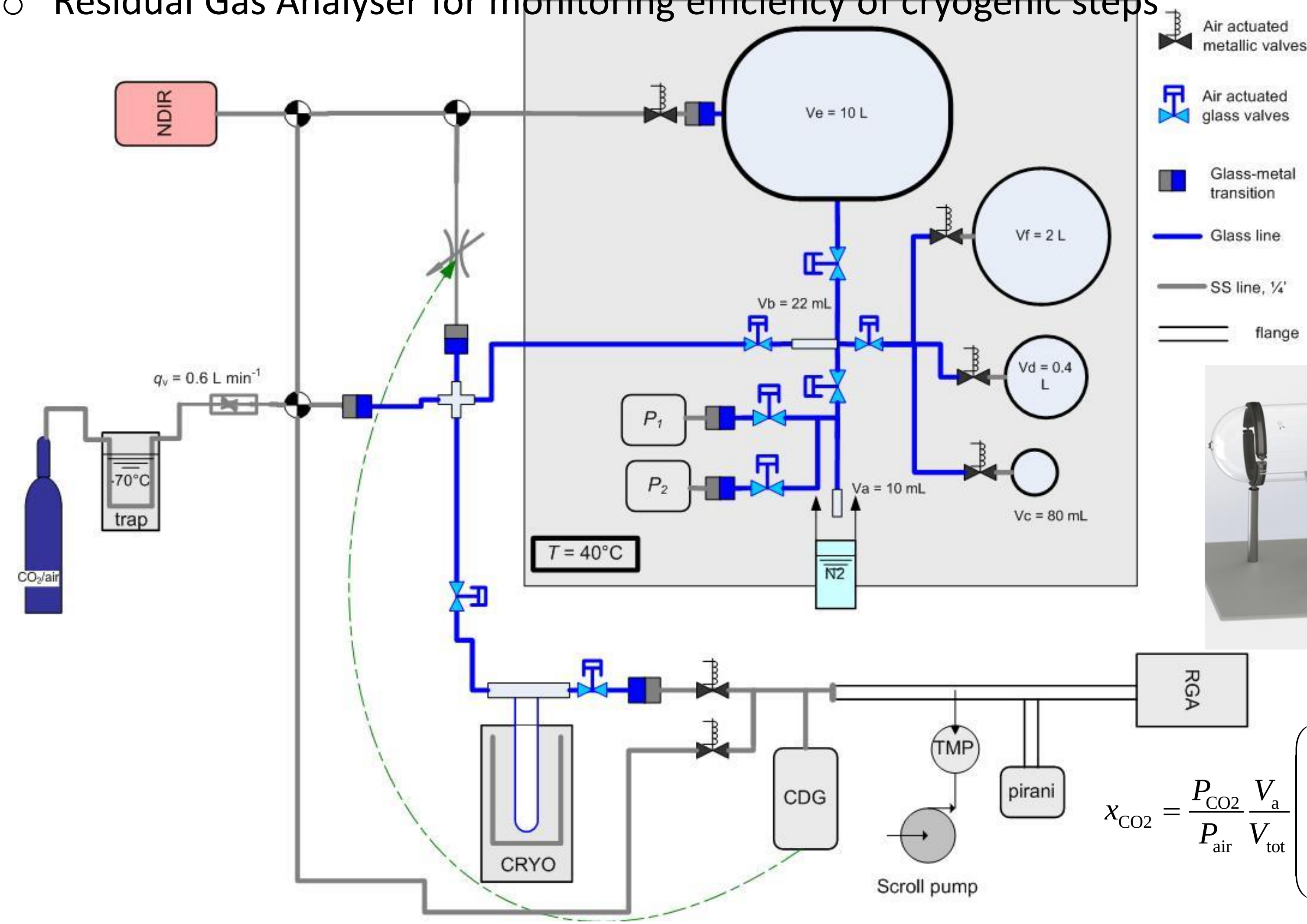
Ten times the measurement repeatability

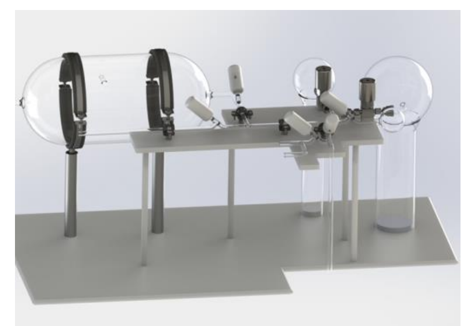
(0.015 µmol mol^{-1})



BIPM manometric facility for the CO_2 comparison (2016)

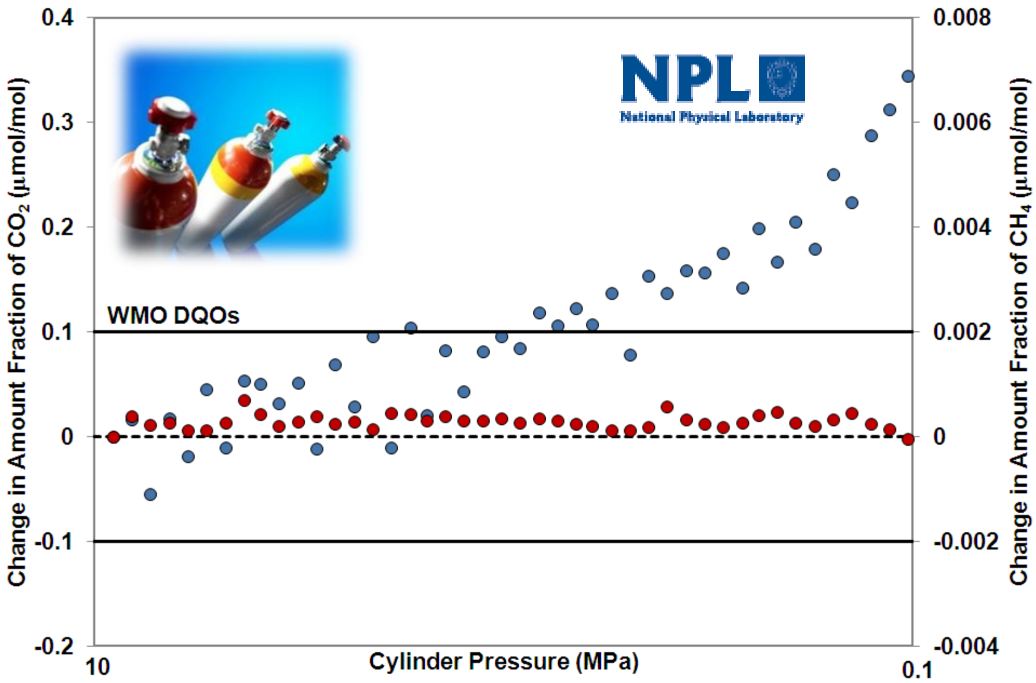
- Optimized volumes and wall thicknesses for pressure measurements
- Automated system for cryogens
- Residual Gas Analyser for monitoring efficiency of cryogenic steps





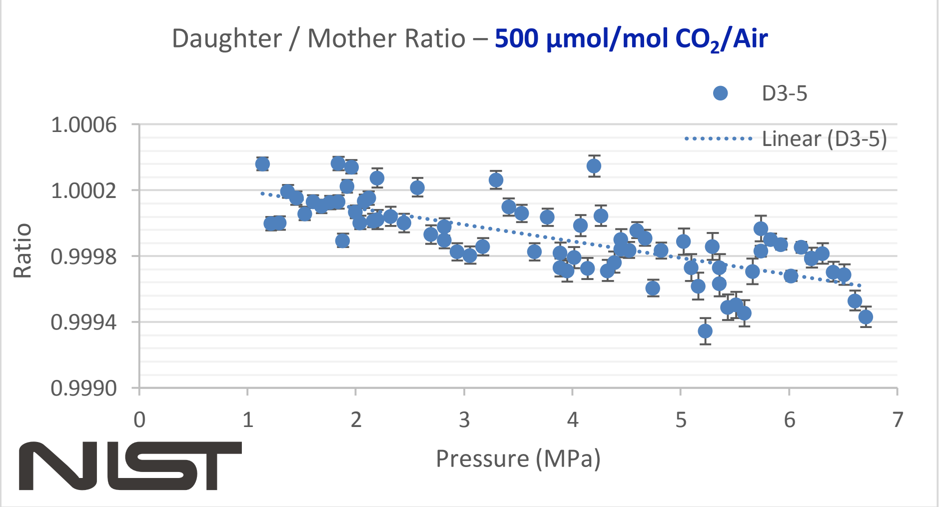
$$x_{CO2} = \frac{P_{CO2}}{P_{air}} \frac{V_a}{V_{tot}} \left(\frac{T_{air}}{T_{CO2}} \frac{1 + \frac{B_{air}(T_{air}) P_{air}}{R T_{air}}}{1 + \frac{B_{CO2}(T_{CO2}) P_{CO2}}{R T_{CO2}}} \right)$$

Stability of CO_2 standards



Pressure dependence of CO_2 in gas cylinders

As pressure drops in cylinder there is an increase in CO_2



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Conclusions

- SI traceable standards for long term atmospheric monitoring is a **challenging area**, but considerable progress has been made
- **Strong Collaboration** between BIPM, National Metrology Institutes, Designated Institutes, CCQM-GAWG, WMO, WMO-GAW, and more recently IAEA
- Leads to **innovation** and improved **international agreement** of standards at very low levels of uncertainty

Acknowledgements

- CCQM Gas Analysis Working Group (GAWG)
- J.Viallon, E. Flores, P. Moussay and F. Idrees (BIPM)
- NMI visiting scientists