Gas metrology for carbon surface measurements and other related ECVs

R.I. Wielgosz (BIPM), JS. Kim (KRISS), P. Brewer (NPL),
G. Rhoderick (NIST)

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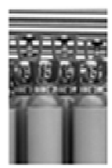
Outline

NMI activities in the CCQM Gas Analysis Working Group

Challenges of gas standards for GHG monitoring



Comparison of methane in air standards

Progress with CO_2 standards and comparisons

Conclusions

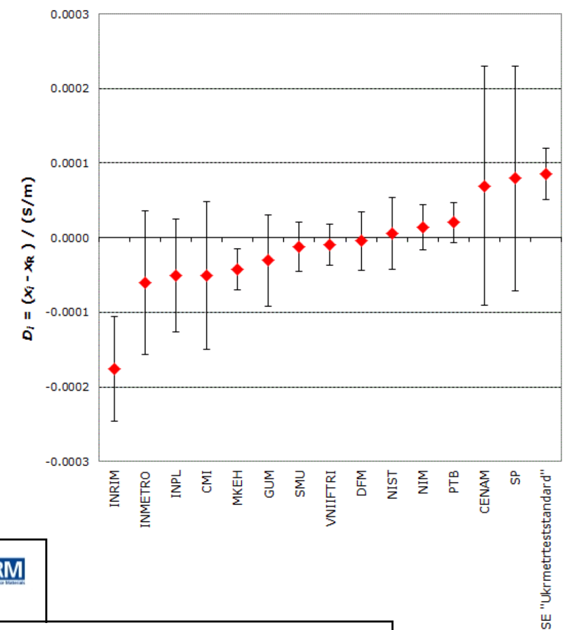
CIPM Mutual Recognition Arrangement: CCQM GAWG Activities

Definition → 

↓

Realization

↓

Comparisons → 

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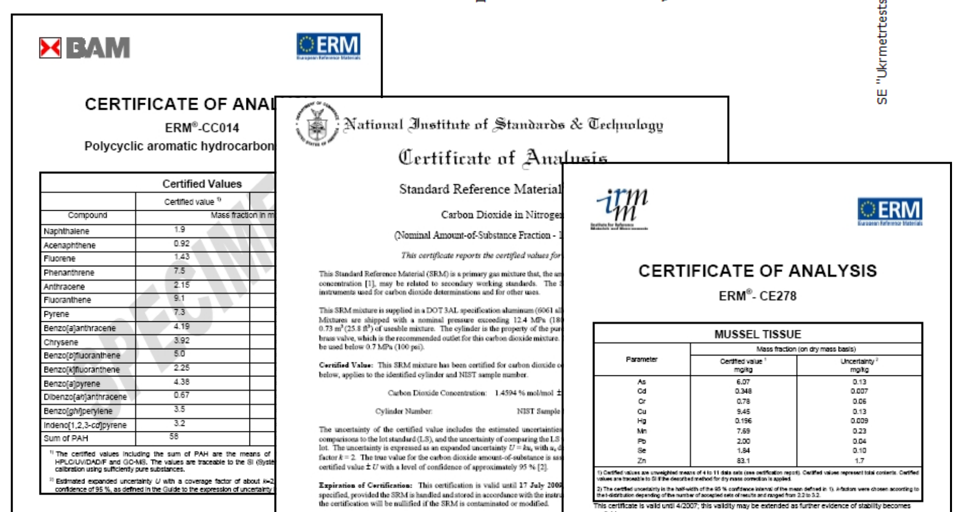
Dissemination → 

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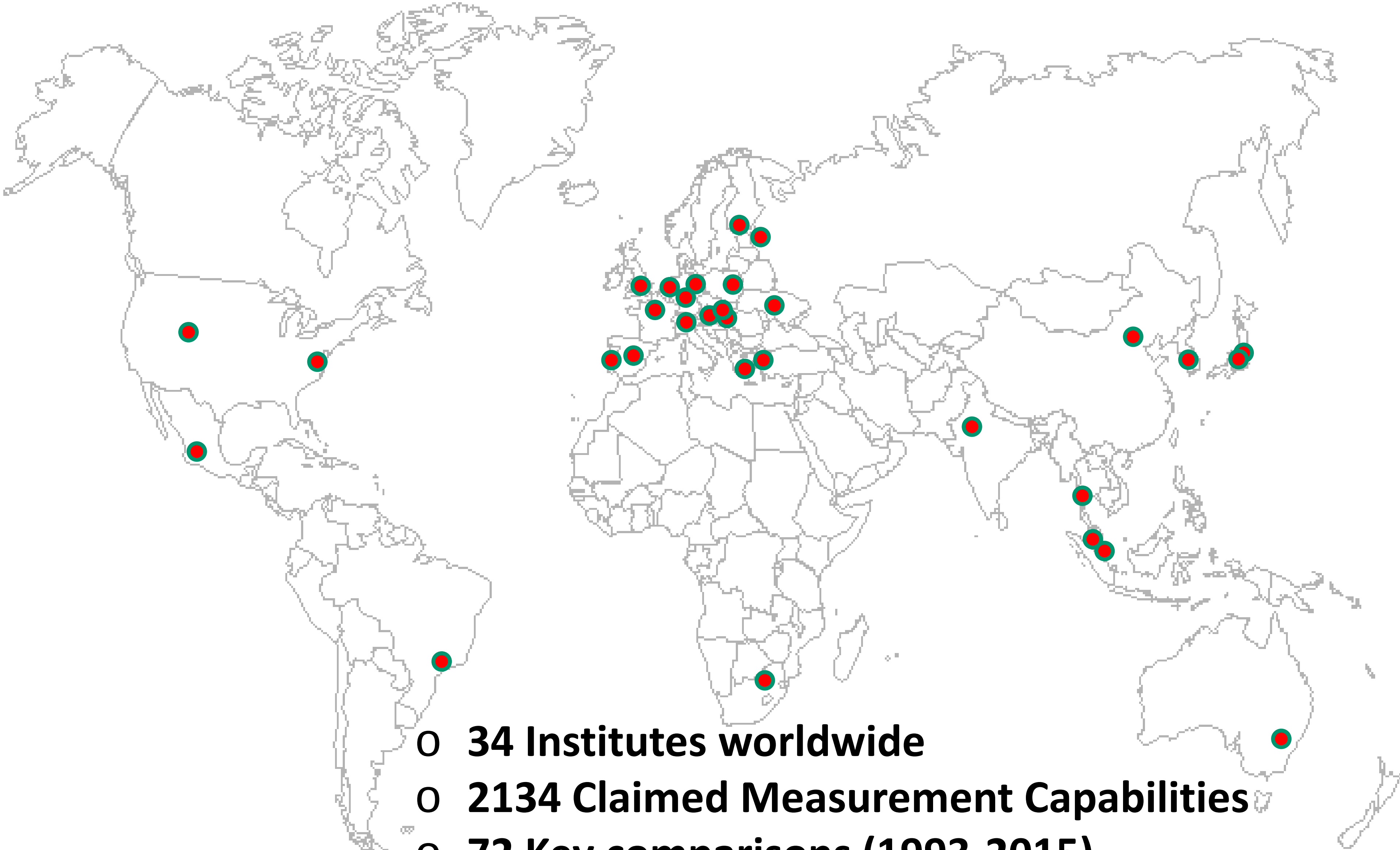
NMIs active in the CCQM Gas Analysis Working Group (GAWG)



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

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-K68.2018‡	Nitrous oxide	330 nmol/mol	2018

†with **NIST** ‡ with **KRISS**

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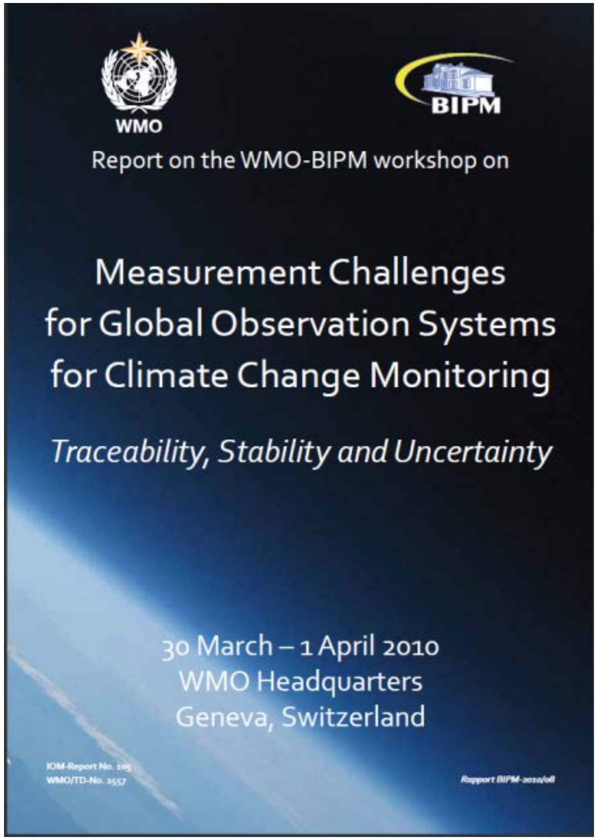
BIPM-WMO joint activities



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

BIPM-WMO joint activities

WMO-GAW an important stakeholder in **CCQM-GAWG programme**

GAW

WMO has signed the CIPM-MRA

BIPM.QM-K1, O_3 in air, *ambient levels*

EMPA

Swiss Federal Laboratories for Materials Testing and Research (EMPA)

CCQM-K82, CH_4 in air
CCQM-K120, CO_2 in air
CCQM-K68.2018, N_2O in air

WMO-GAW Laboratories:
NOAA ESRL and EMPA, participate directly in CCQM comparisons

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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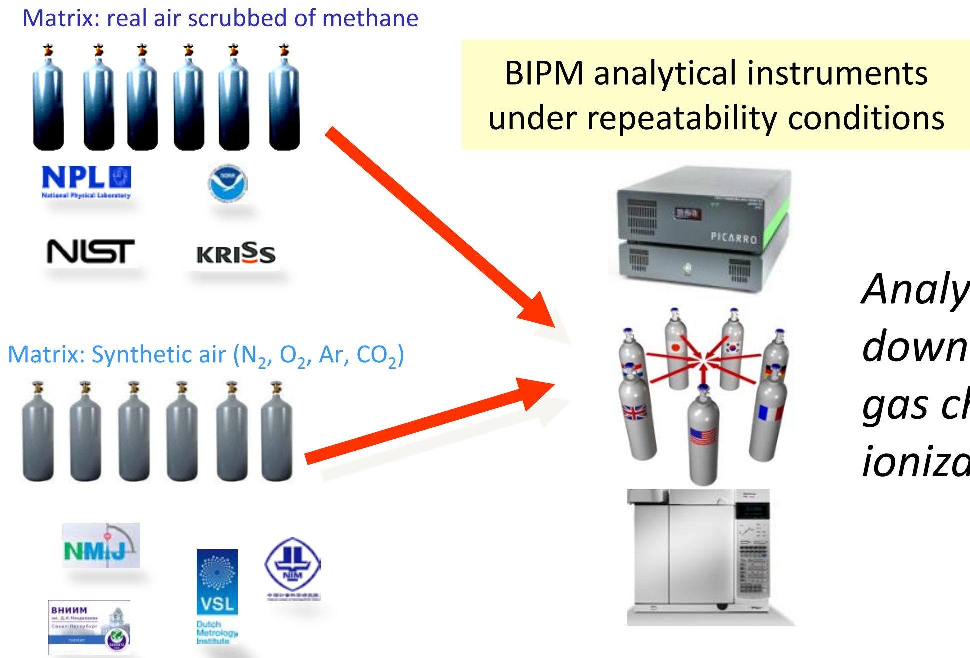
International comparison of methane in air standards (2012)

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

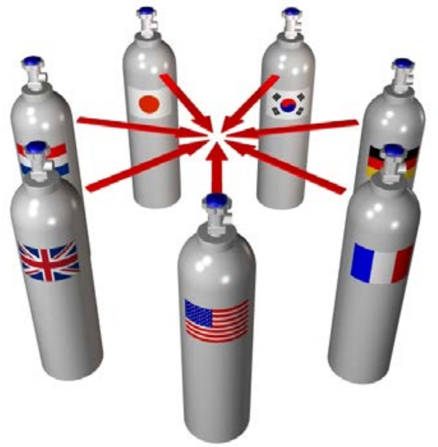
CRDS measurements and matrix gas composition

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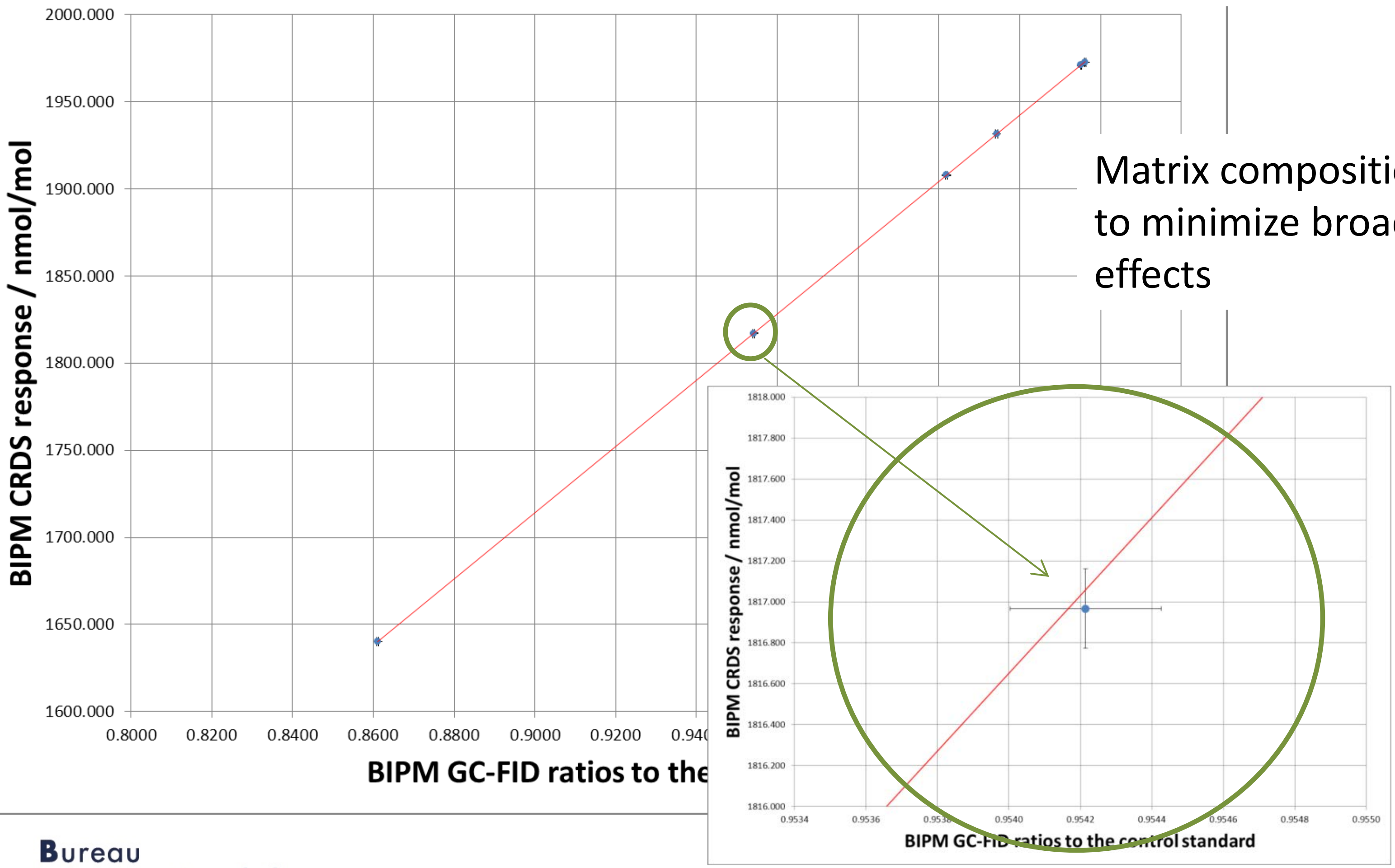
Comparison of GC-GID and CRDS methods for methane in air

Validation of method using NIST real air and synthetic air standards



Matrix composition adapted to minimize broadening effects

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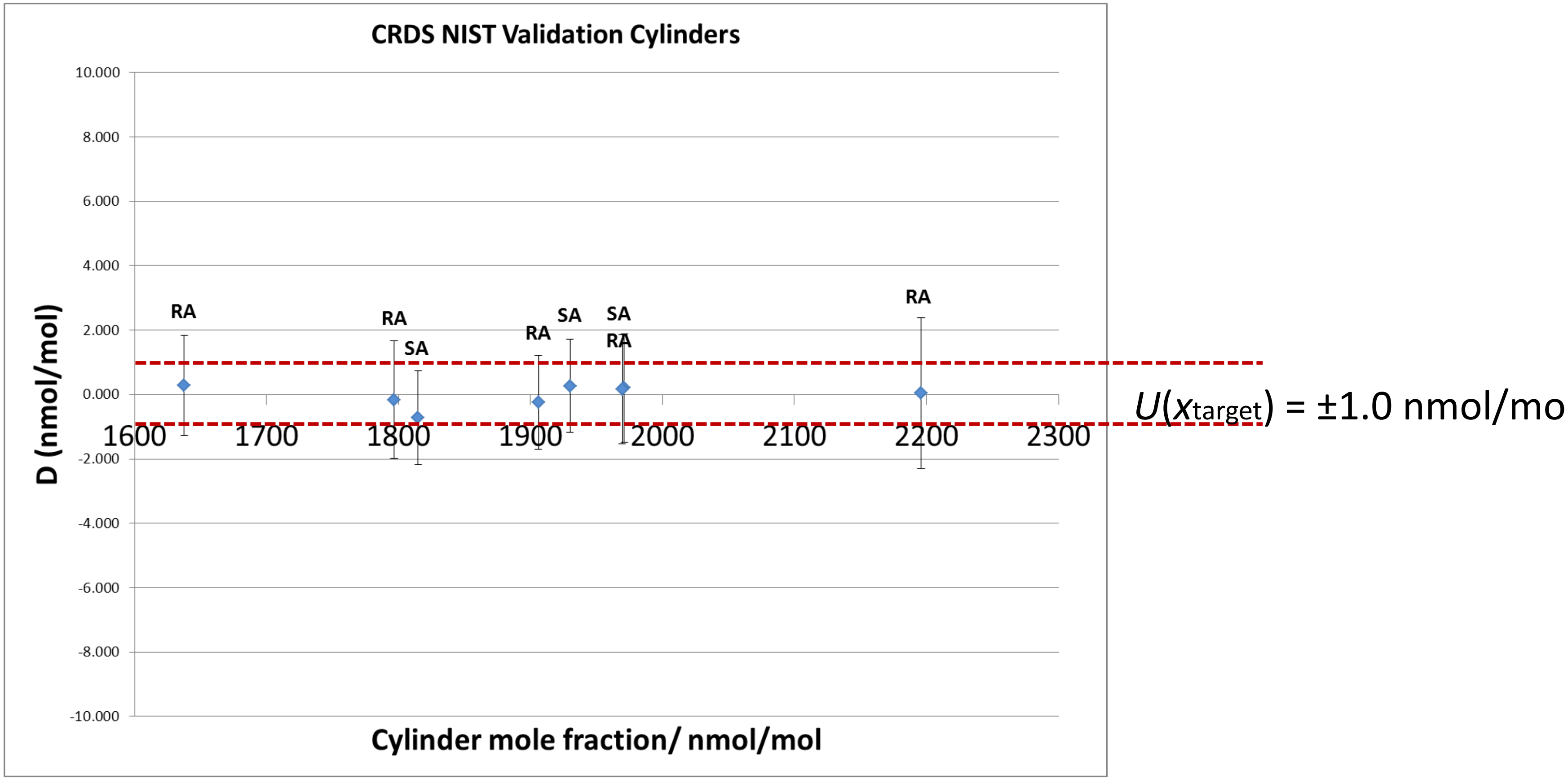
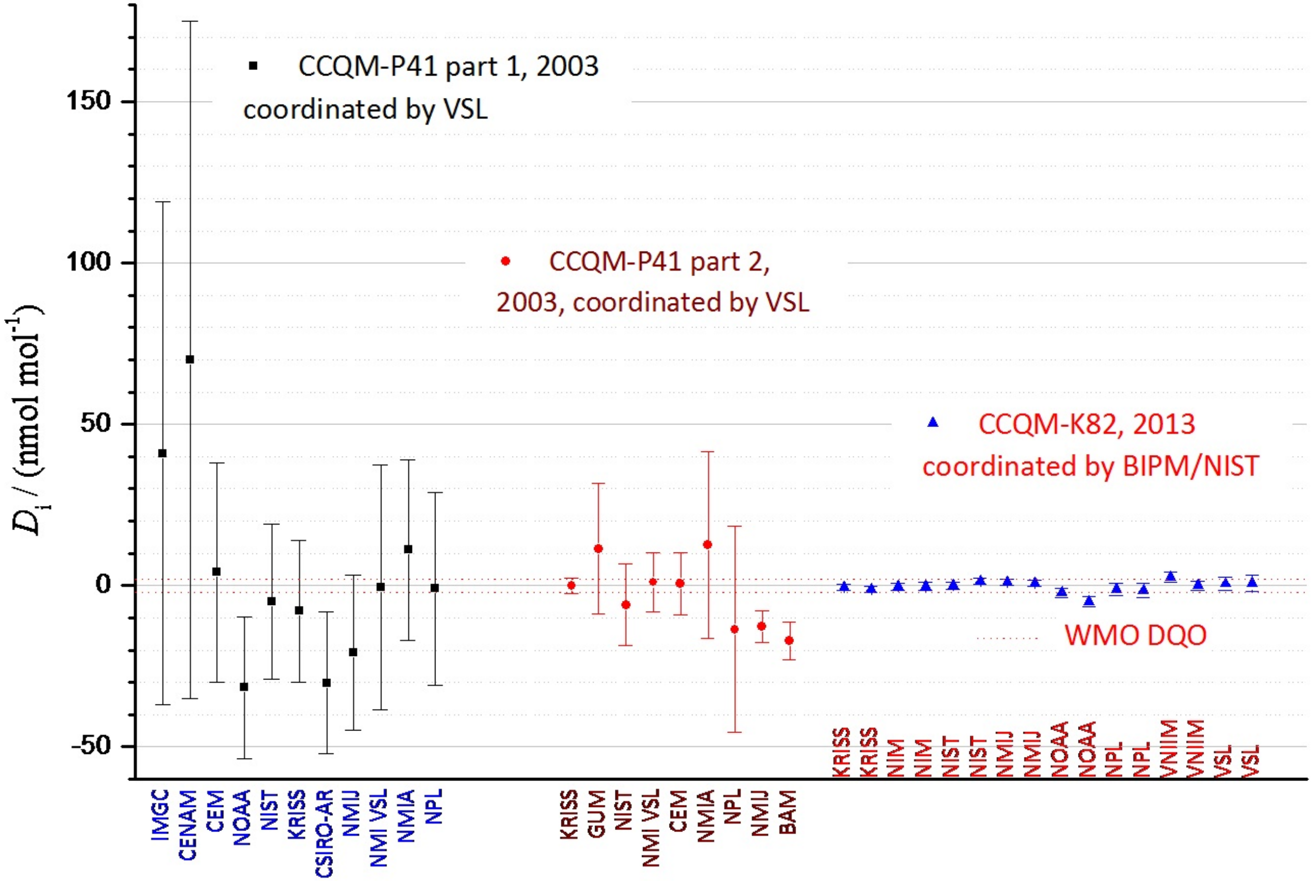
Validation of BIPM's Measurements facility with NIST standards



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]()

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), $\sigma_{(CCQM\text{-}Kxx)} \leq$ DQO/4

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

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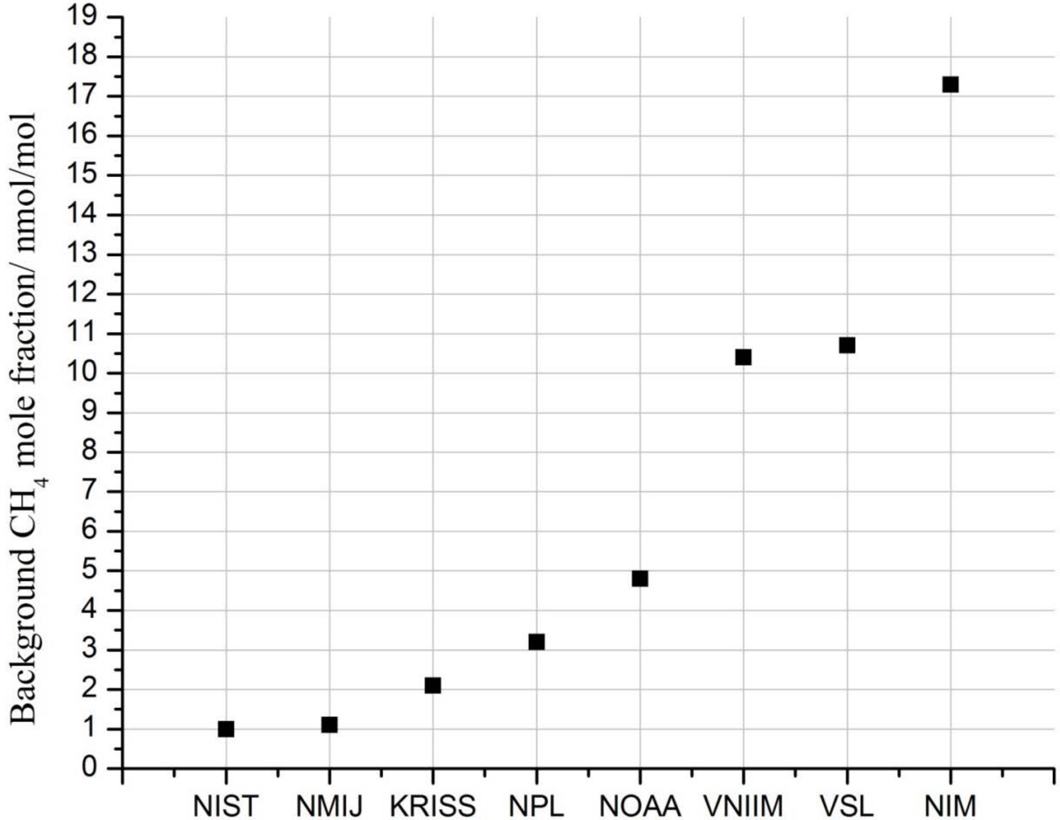
Development for future improvements in CH_4 in air standards



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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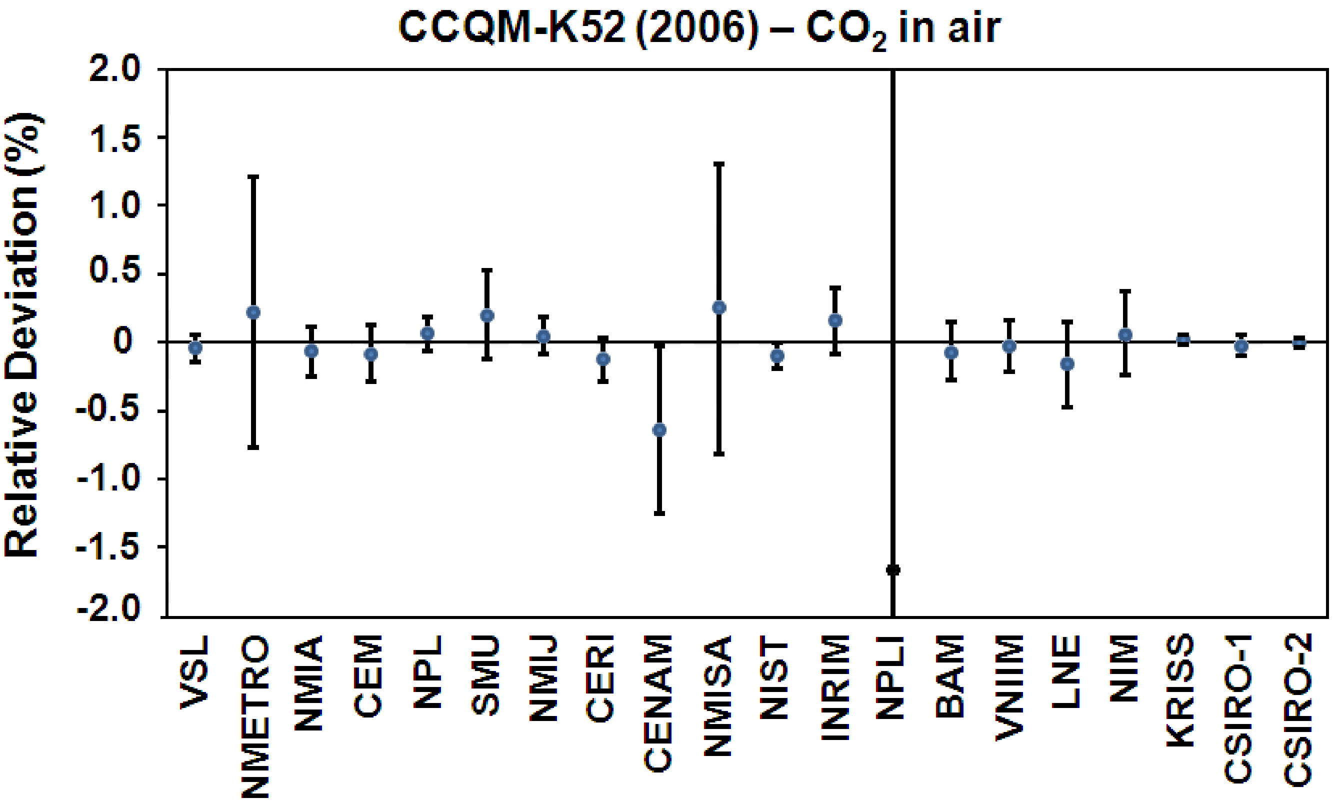
Preparing for the repeat CO_2 in air comparison (2016)



Uncertainties on standards >> DQOs for ambient monitoring community

- **Participation of WMO laboratory in Australia (in parallel pilot study)**
- **The WMO scale and the NMI values agree**

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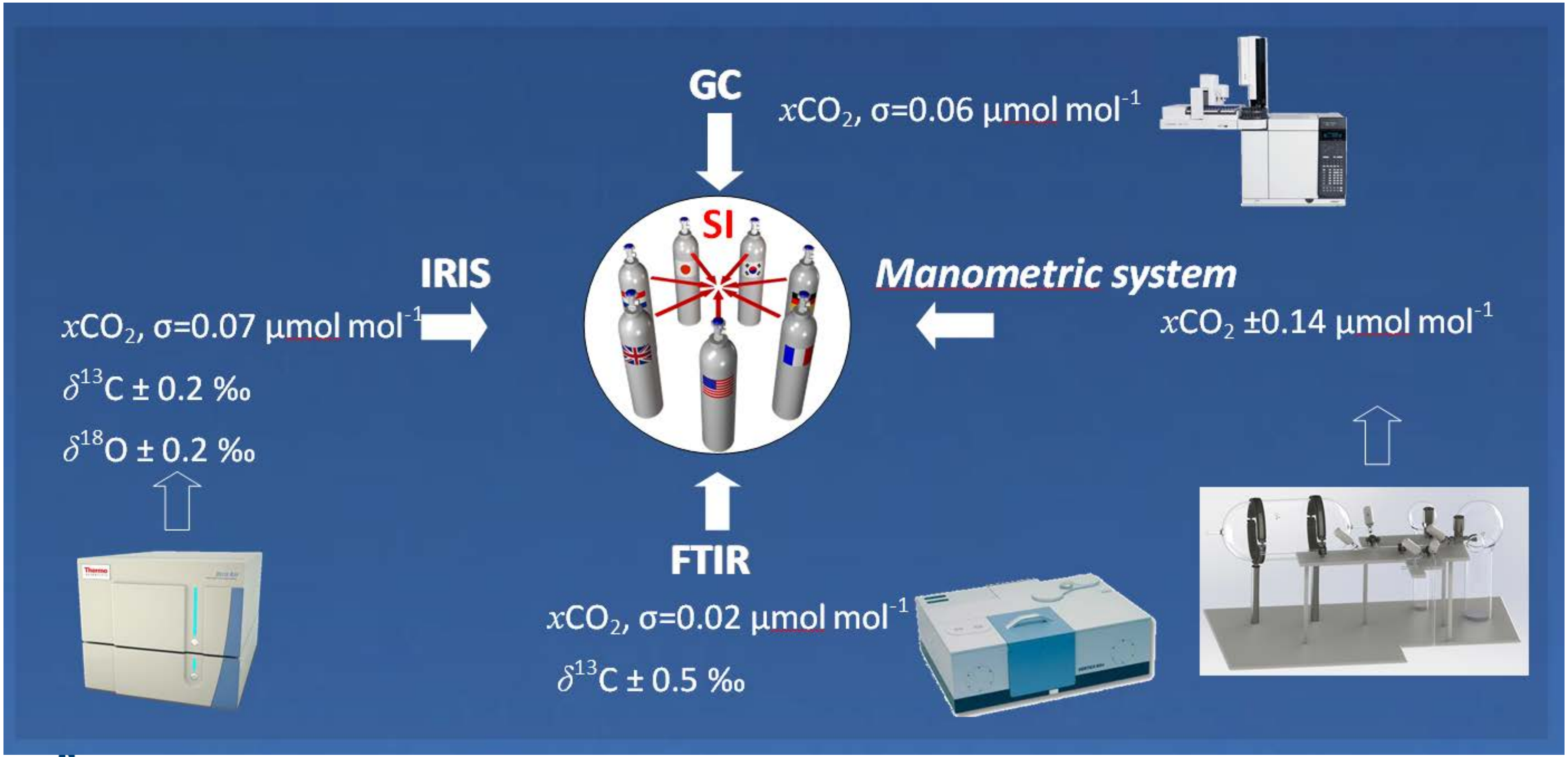
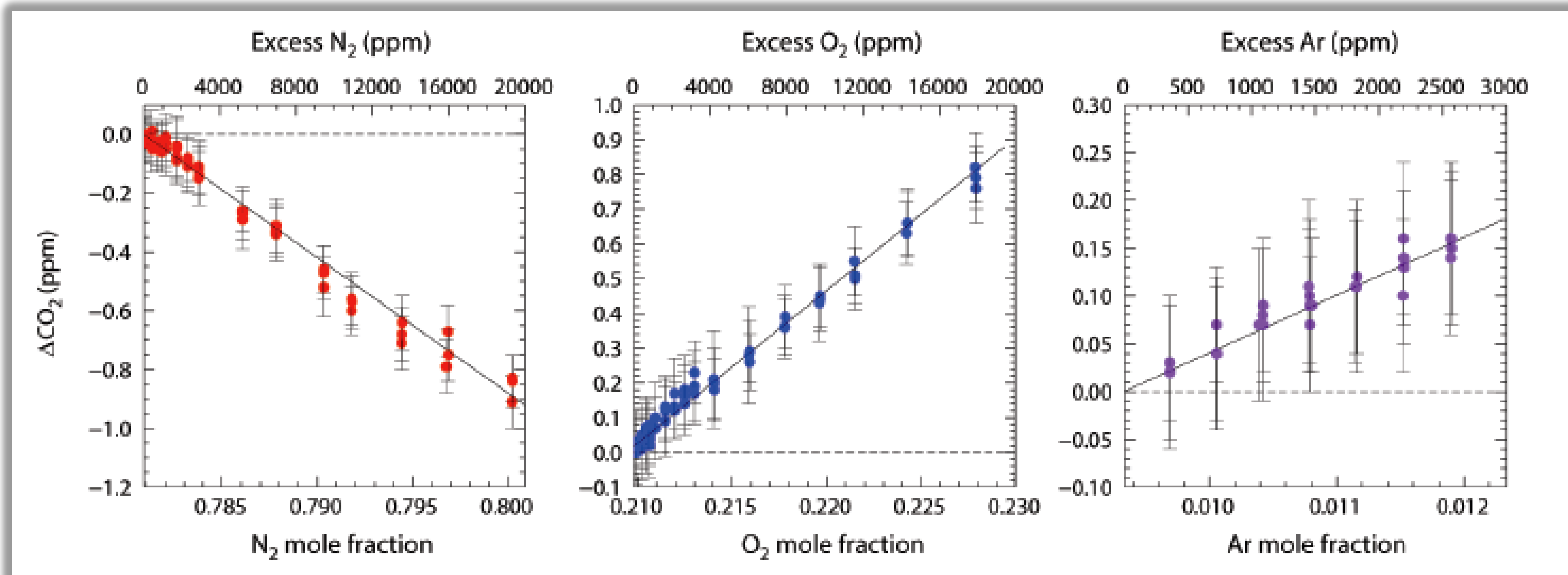
Preparing for the repeat CO_2 in air comparison (2016)

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



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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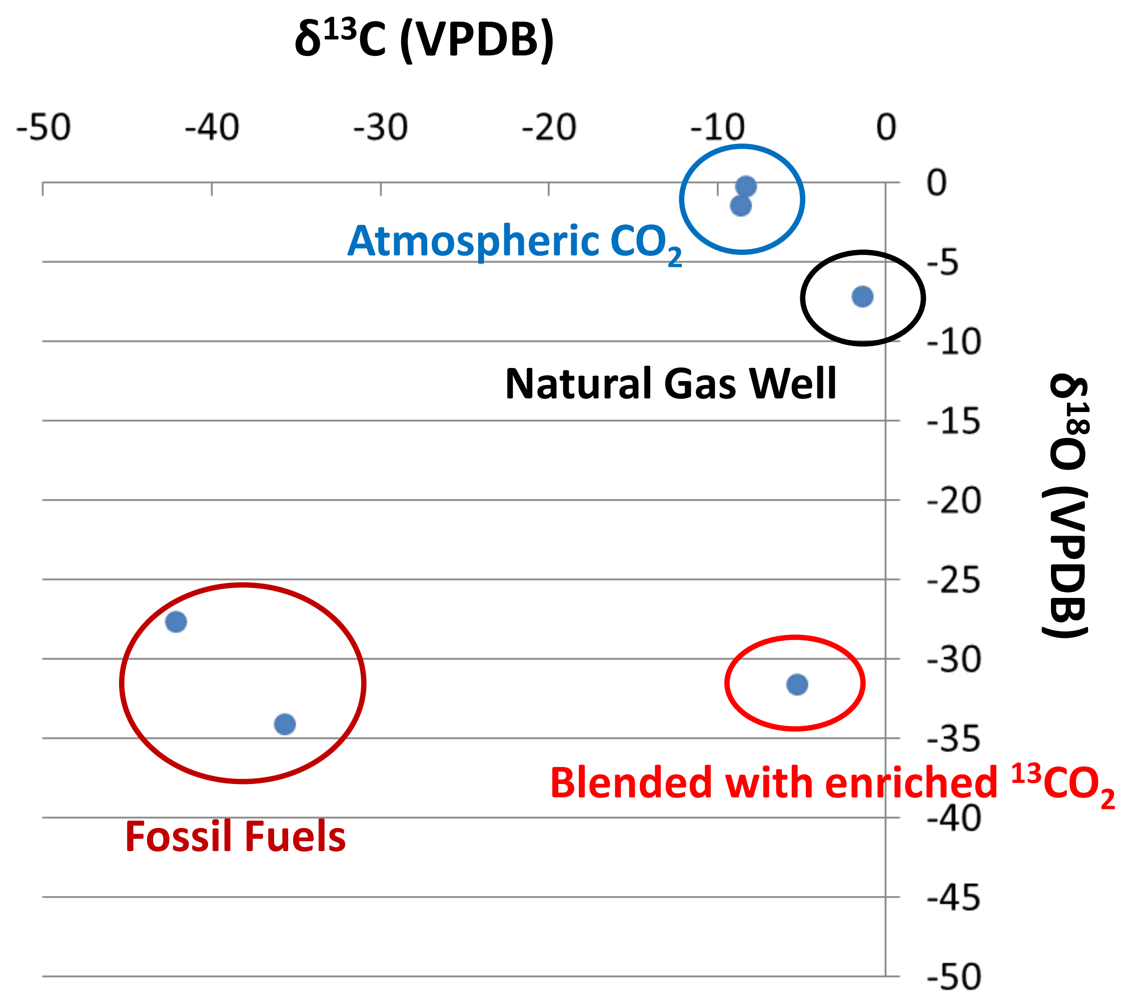
Accurate measurement of CO_2 (and CO_2 isotopologues)

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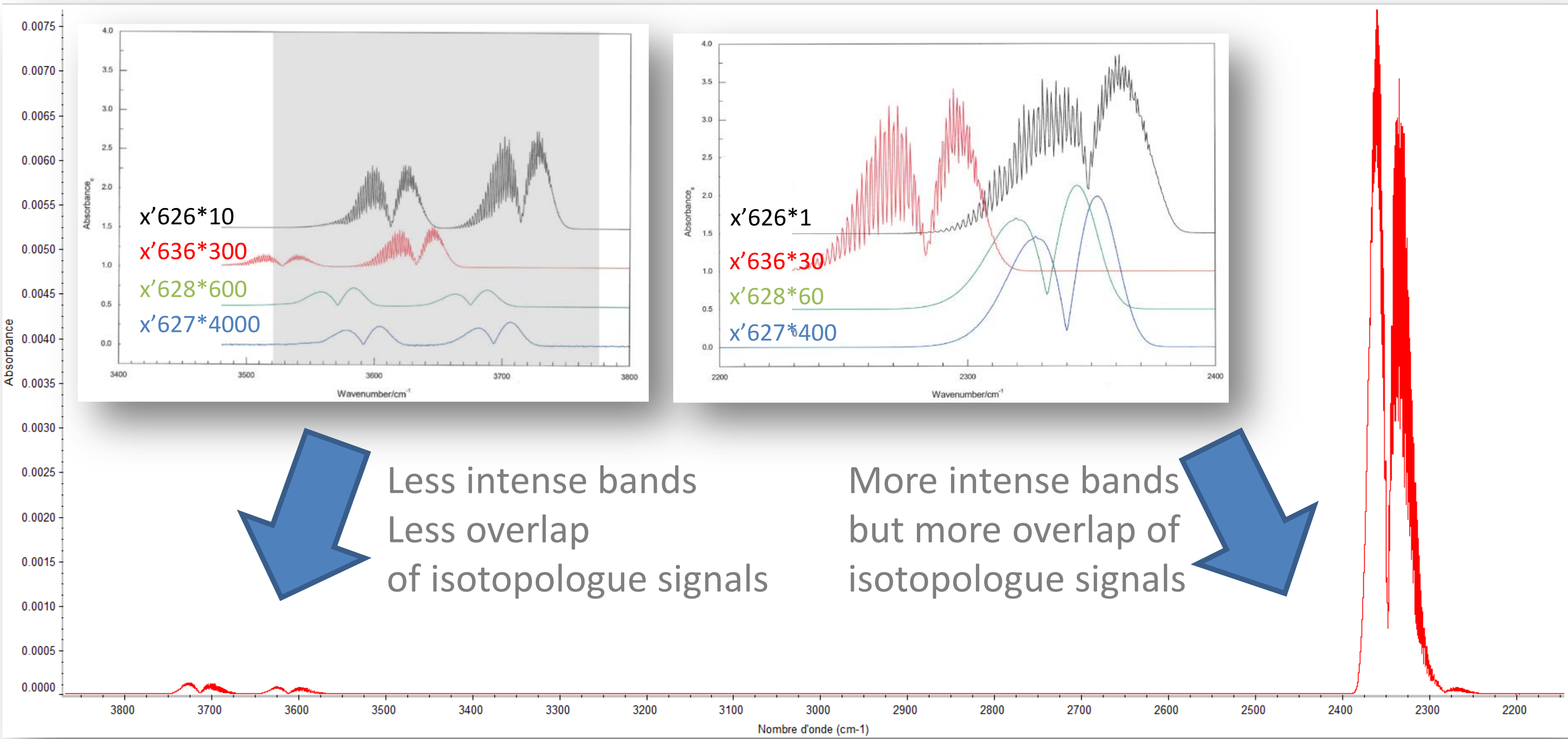
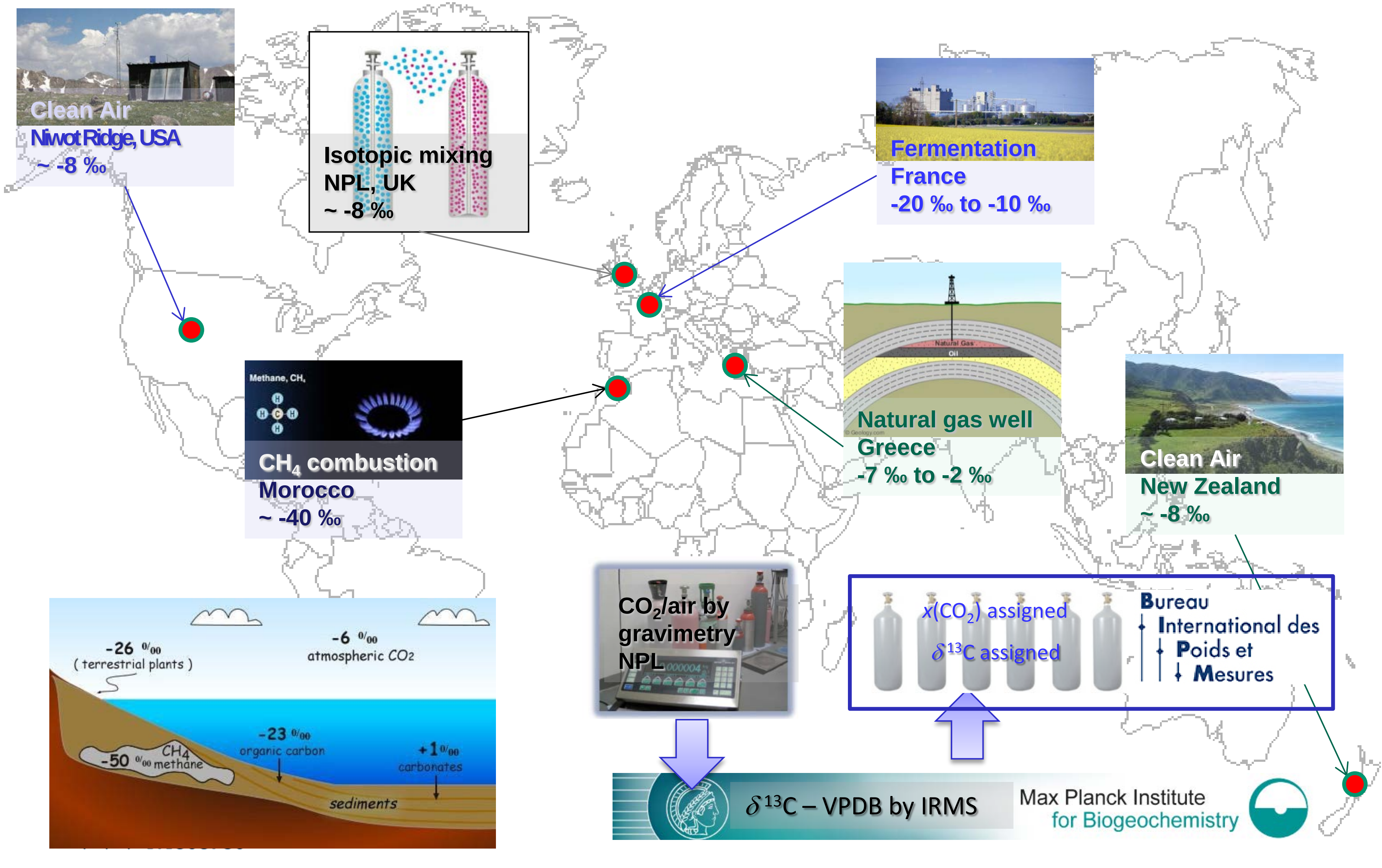
Isotope ratio measurements for corrections to CO_2 concentration measurements required at the ± 1 ‰ level

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



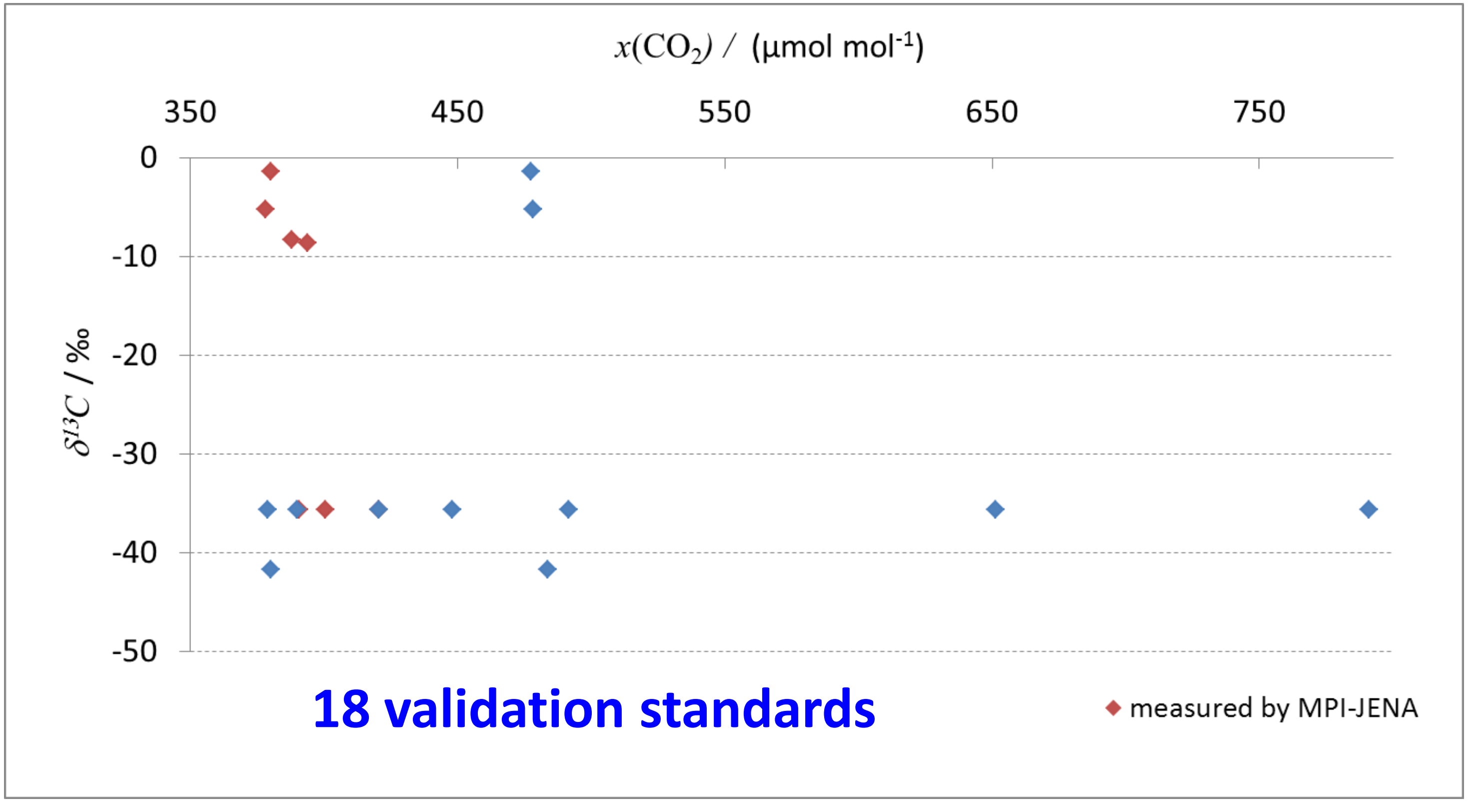
Validation standards with a range of compositions



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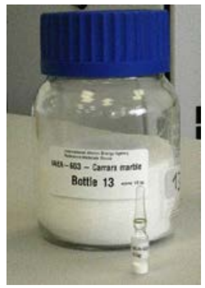
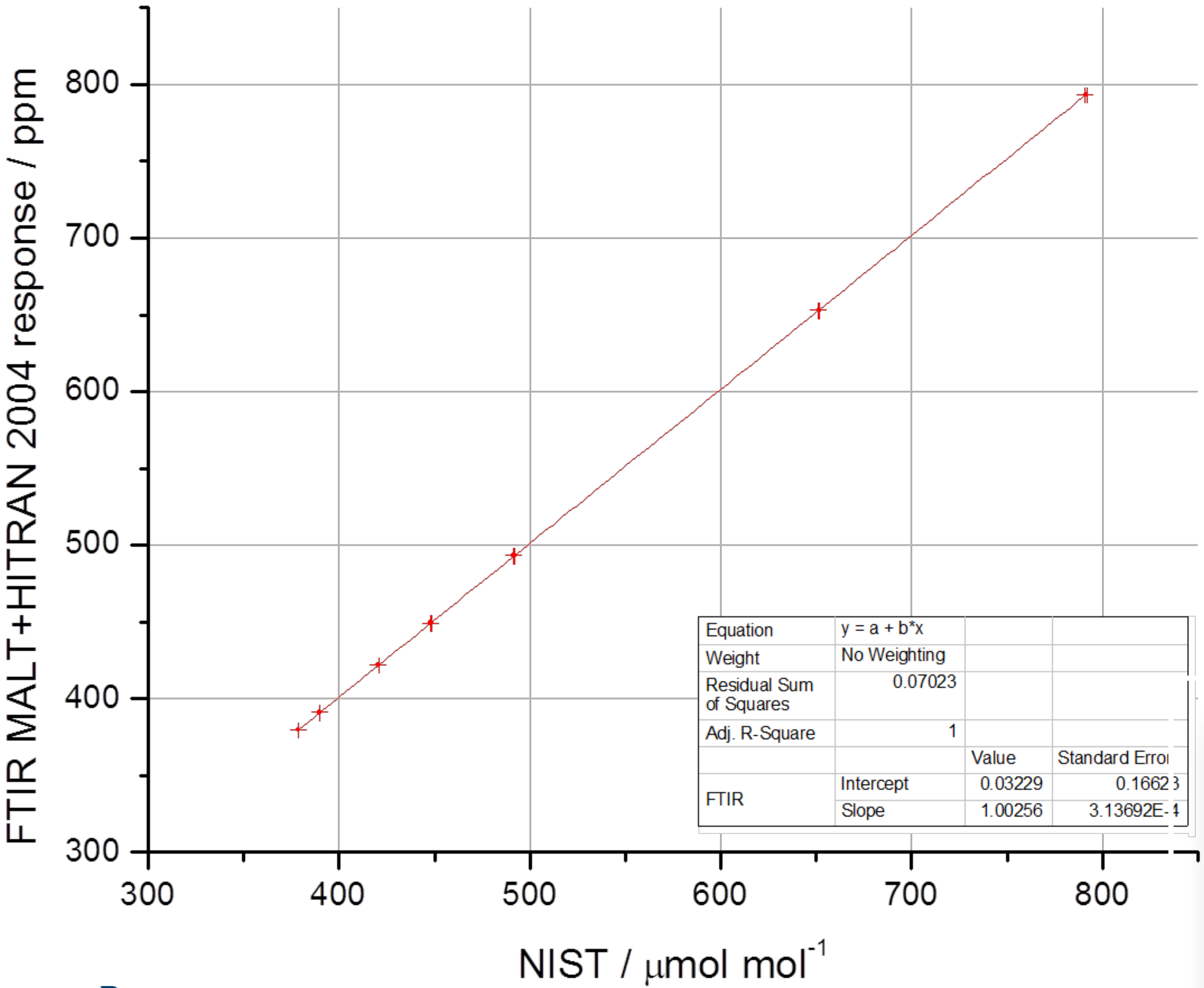
3 additional standards for the set to be provided by NOAA in 2015

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



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

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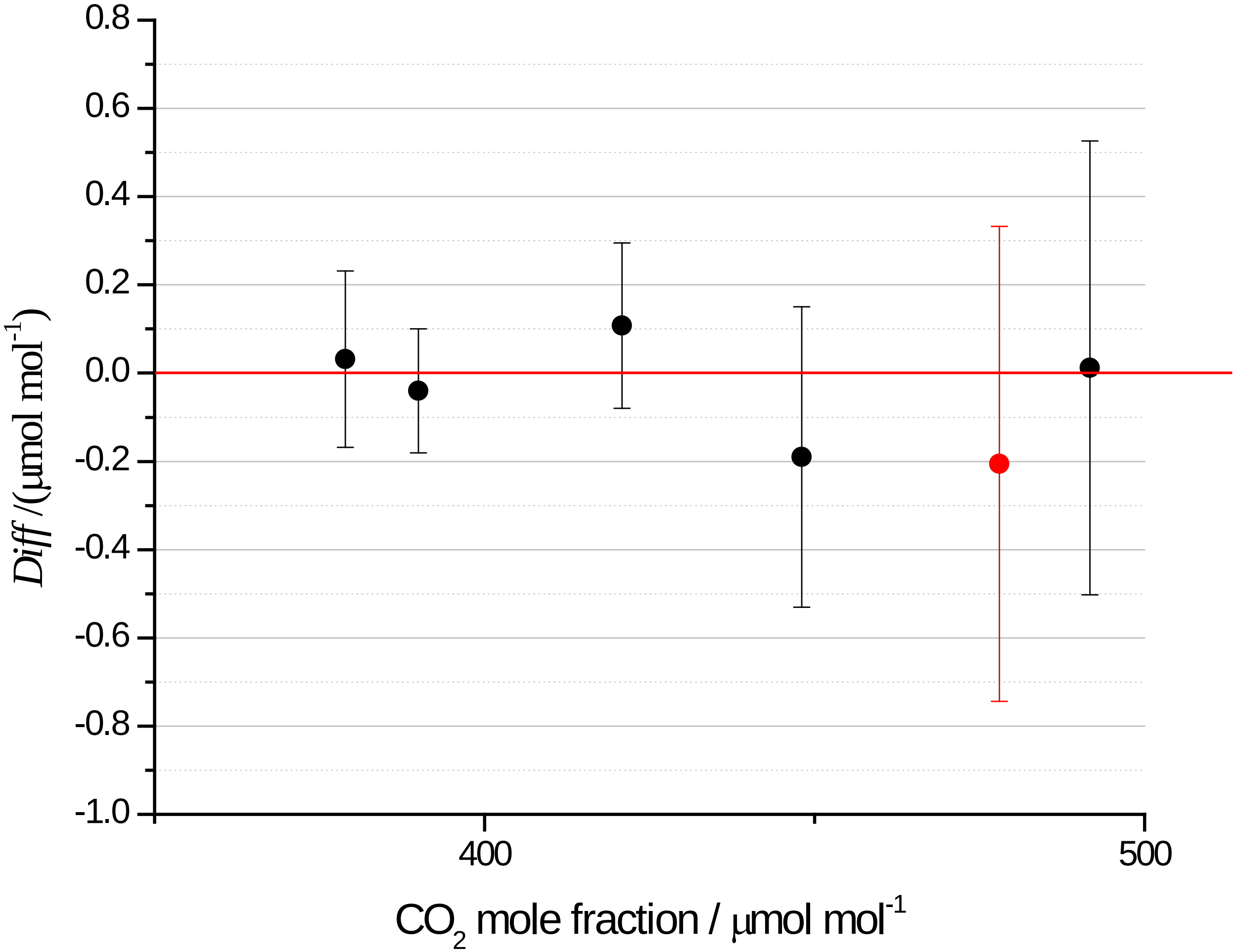
Non corrected FTIR response for isotopic effects

	$\delta^{13}C$ (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

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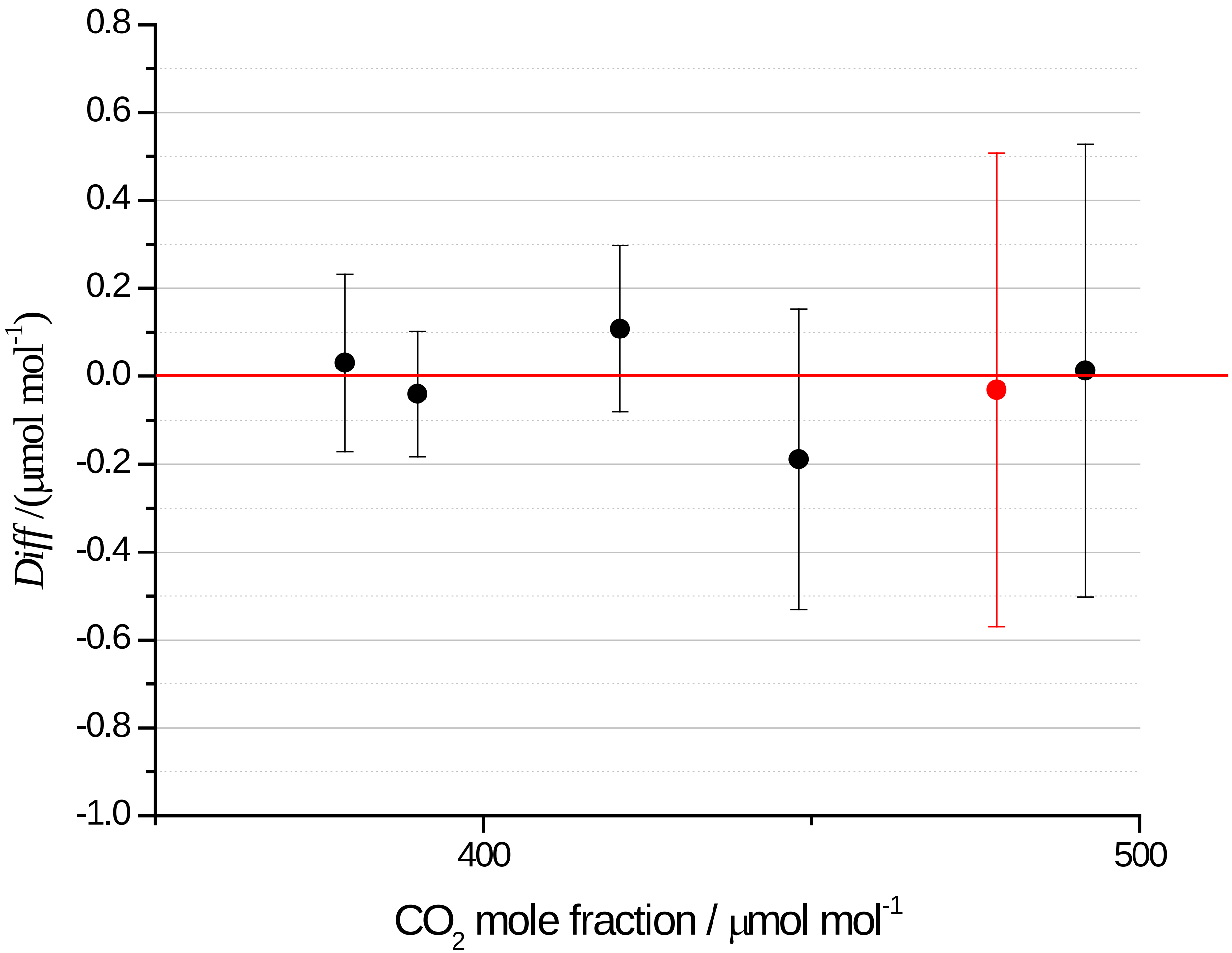


The correction is

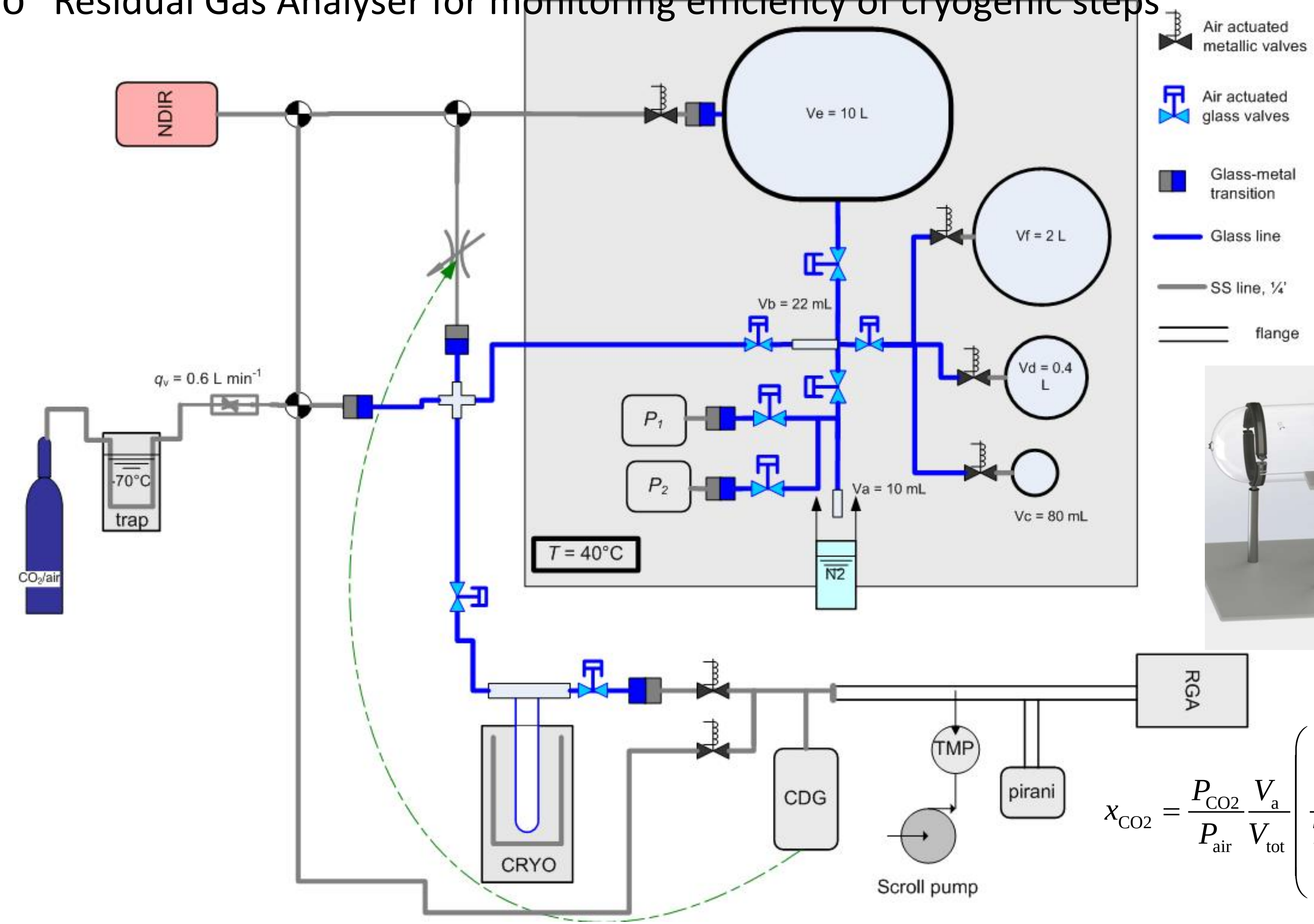
~ 0.170 µmol mol^{-1}

Ten times the measurement repeatability

(0.015 µmol mol^{-1})

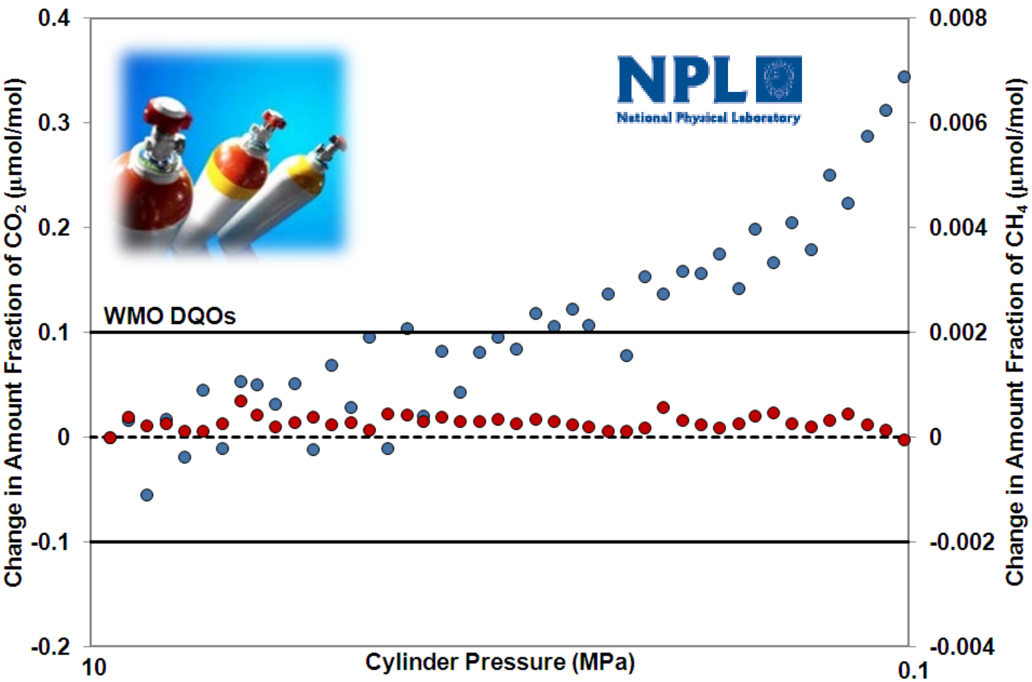
BIPM manometric facility for the CO_2 comparison (2016)

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



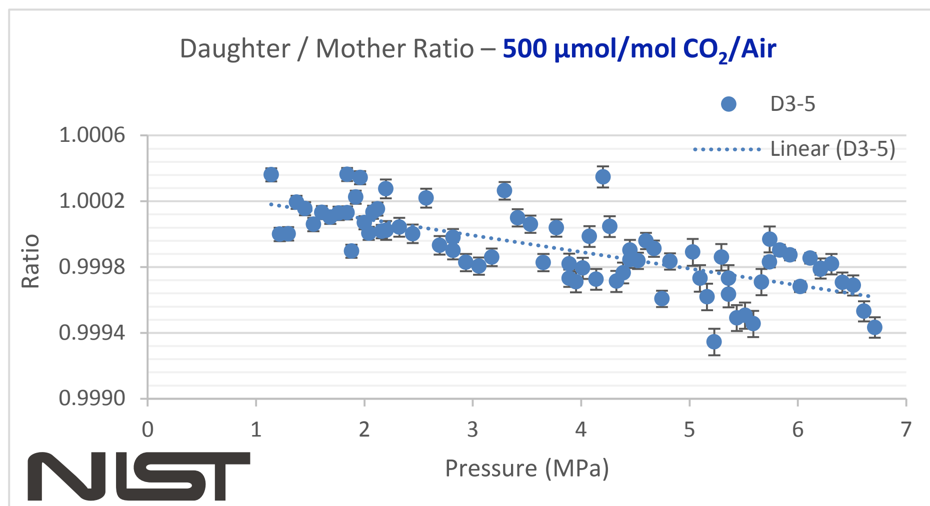
$$x_{CO2} = \frac{P_{CO2}}{P_{air}}\frac{V_a}{V_{tot}}\left(\frac{T_{air}}{T_{CO2}}\frac{1+\frac{B_{air}\left(T_{air}\right)P_{air}}{RT_{air}}}{1+\frac{B_{CO2}\left(T_{CO2}\right)P_{CO2}}{RT_{CO2}}}\right)$$

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

- DQOs result in very stringent requirements on target uncertainties for GHG standards
- Key comparison exercises have been successful in demonstrating needs for improvements and improvements in standards
- Behaviour of standards with different analytical methods is crucial (Commutability)
- Substantial improvement in demonstrable equivalence of methane in air standards over last 10 years
- Target uncertainties for methane in air standards are within reach
- 2016 key comparison will demonstrate degree of equivalence of CO_2 primary standards for both background and urban monitoring applications

Acknowledgements

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CCQM-GAWG Members

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