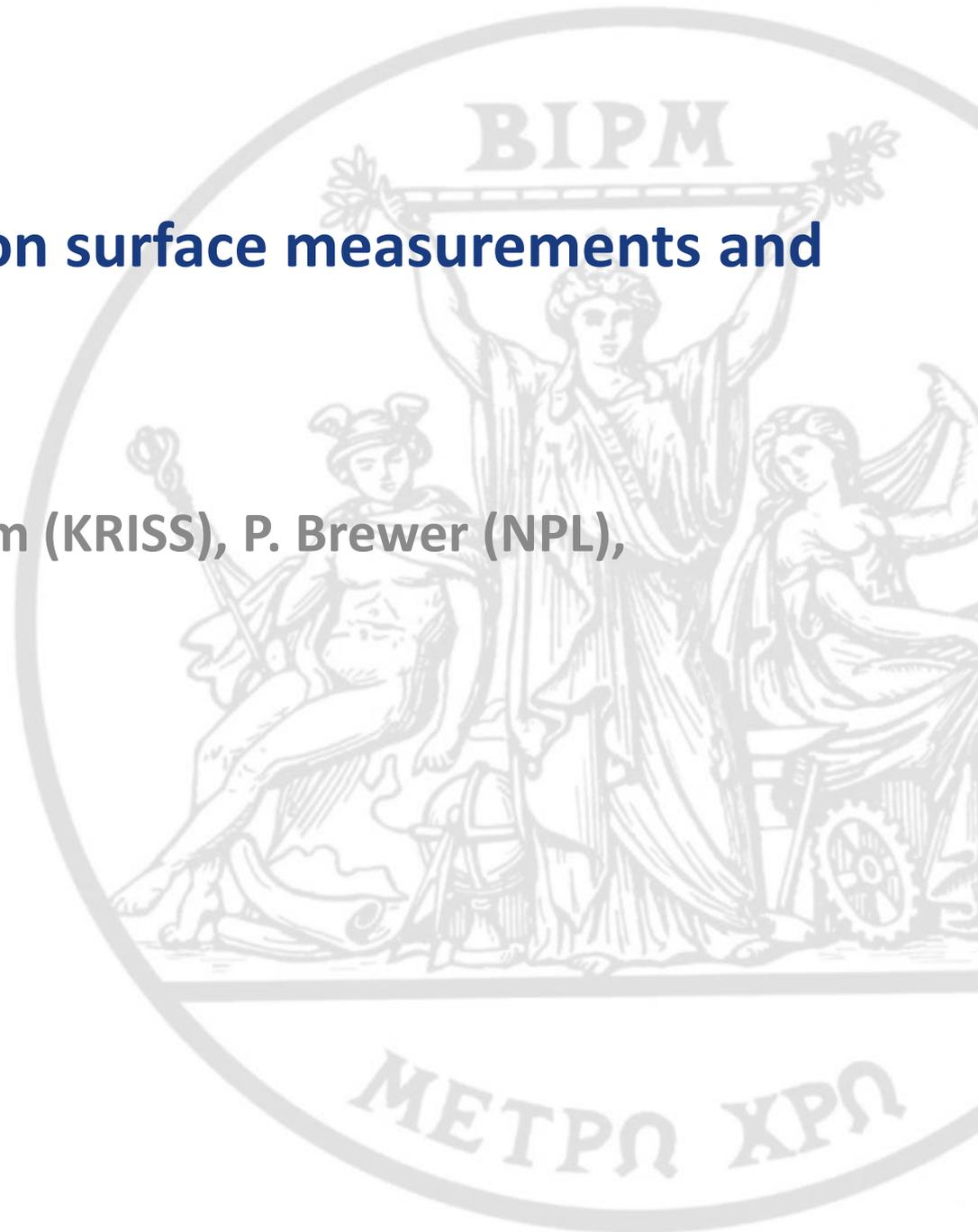


Gas metrology for carbon surface measurements and other related ECVs

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



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 CO₂
standards and
comparisons



Conclusions

CIPM Mutual Recognition Arrangement: CCQM GAWG Activities

Definition →



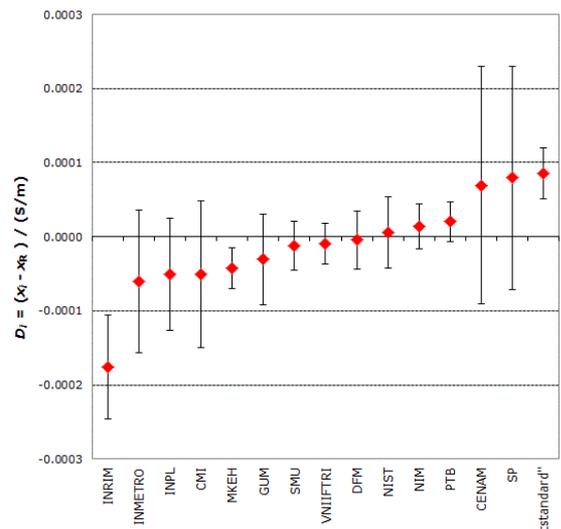
Realization



Comparisons →



Dissemination →



BAM **ERM**

CERTIFICATE OF ANALYSIS
ERM[®]-CC014
Polycyclic aromatic hydrocarbon

Certified Values	
Compound	Certified value ¹⁾
Naphthalene	1.9
Acenaphthene	0.92
Fluorene	1.23
Phenanthrene	7.5
Anthracene	2.15
Fluoranthene	9.1
Pyrene	7.3
Benzo[a]anthracene	4.19
Chrysene	3.92
Benzo[fluoranthene]	3.0
Benzo[a]fluoranthene	2.23
Benzo[b]fluoranthene	4.35
Dibenz[a,h]anthracene	0.57
Benzo[ghi]perylene	3.5
Indeno[1,2,3-cd]pyrene	3.2
Sum of PAH	58

¹⁾ The certified values including the sum of PAH are the means of individual GAWG and GOWE. The values are rounded to the 0.1 digit calibration using sufficiently pure substances.
²⁾ Estimated expanded uncertainty U with a coverage factor of about 1.95, confidence of 95 %, as defined in the GUM to the expression of uncertainty.

National Institute of Standards & Technology

Certificate of Analysis
Standard Reference Material
Carbon Dioxide in Nitrogen
(Nominal Amount-of-Substance Fraction = 0.01)

This certificate reports the certified values for:

This Standard Reference Material (SRM) is a primary gas mixture that, at the concentration [1], may be related to necessary working standards. The instruments used for carbon dioxide determination and for other uses.

This SRM mixture is supplied in a DOT 3AL specification aluminum (0041) 44 Mixtures are shipped with a nominal pressure according to 2.4 MPa (34.7 or 0.71 m³ (25.1 ft³) of usable mixture. This cylinder is the property of the purchaser and is to be used for the recommended use for this carbon dioxide mixture to be used before 07/2020 (100 yrs).

Certified Value: This SRM mixture has been certified for carbon dioxide as below, applies to the identified cylinder and NIST sample number.

Carbon Dioxide Concentration: 1.4394 % method 1

Cylinder Number: NIST Sample

The uncertainty of the certified value includes the estimated uncertainties comparable to the list standard (1,2), and the uncertainty of comparing the L3 list. The uncertainty is expressed as an expanded uncertainty U¹⁾ with a coverage factor k = 2. The true value for the carbon dioxide amount-of-substance is not certified value ± U¹⁾ with a level of confidence of approximately 95 % (2).

Expiration of Certification: This certification is valid until 31 July 2006 specified, provided the SRM is handled and stored in accordance with the rules, the certificate will be nullified if the SRM is contaminated or modified.

ERM

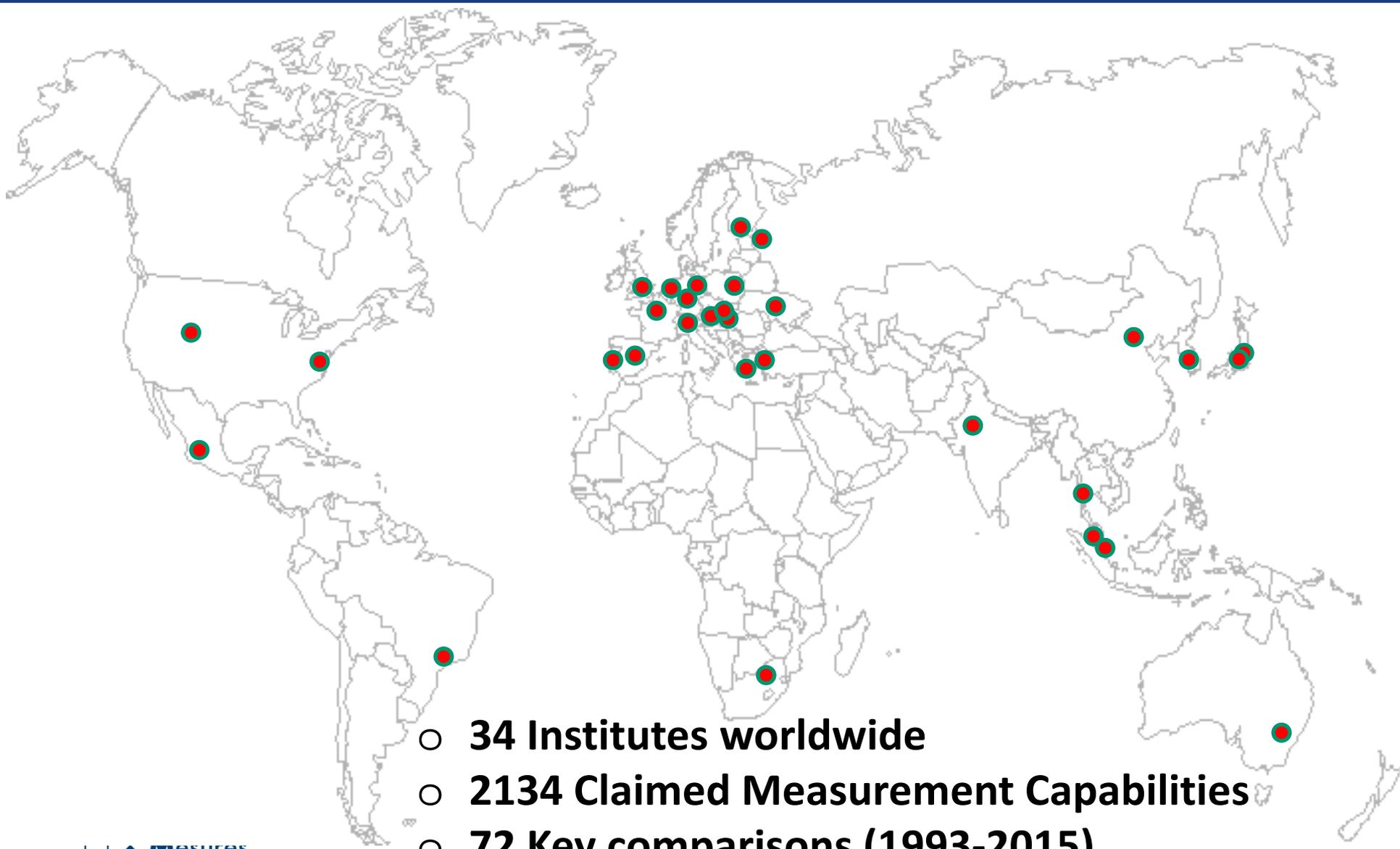
CERTIFICATE OF ANALYSIS
ERM[®]-CE278

MUSSEL TISSUE
Mass fraction (on dry mass basis)

Parameter	Mass fraction (on dry mass basis)	
	Certified value ¹⁾ mg/kg	Uncertainty ¹⁾ mg/kg
As	6.27	0.13
Cd	0.348	0.007
Cr	0.76	0.06
Cu	9.45	0.13
Pb	0.196	0.009
Mn	7.69	0.23
Hg	2.00	0.04
Se	1.94	0.10
Zn	83.1	0.7

¹⁾ Certified values are completed results of 111 data sets (see certification report). Certified values represent true contents. Certified values are based on 10 the number of certified and un-certified samples.
²⁾ The certified uncertainty is the half-width of the 95 % confidence interval of the mean, defined as U, a feature was chosen according to the GUM, depending on the number of certified and un-certified samples from 20 to 100.
This certificate is valid until 4/2007. Its validity may be extended as further evidence of stability becomes available.

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 μ mol/mol	2006
BIPM.QM-K1	Ozone (ground-level)	80 nmol/mol; 400 nmol/mol	2007
CCQM-K74	Nitrogen Dioxide	10 μ mol/mol	2009
CCQM-P110.B1 CCQM-P110.B2	Nitrogen Dioxide : Spectroscopic Studies	10 μ mol/mol	2009
CCQM-K82 [†]	Methane	2000 nmol/mol	2012
CCQM-K90	Formaldehyde	2000 nmol/mol	2014
CCQM-K120.a [†]	Carbon dioxide	380 μ mol/mol – 480 μ mol/mol	2016
CCQM-K120.b [†]	Carbon dioxide	480 μ mol/mol – 800 μ mol/mol	2016
CCQM-K68.2018 [‡]	Nitrous oxide	330 nmol/mol	2018

[†] with **NIST**

[‡] with **KRISS**

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



WMO has signed the CIPM-MRA

BIPM.QM-K1, O₃ in air,
ambient levels



CCQM-K82, CH₄ in air
CCQM-K120, CO₂ in air
CCQM-K68.2018, N₂O 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 ₂ O	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 CO₂ and N₂O) and

< 0.025 % (for CH₄)

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, CH₄ in air**)

Matrix: real air scrubbed of methane



NPL
National Physical Laboratory



NIST

KRIS

Matrix: Synthetic air (N₂, O₂, Ar, CO₂)



NMIJ



VSL

Dutch Metrology Institute



BIPM analytical instruments
under repeatability conditions



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

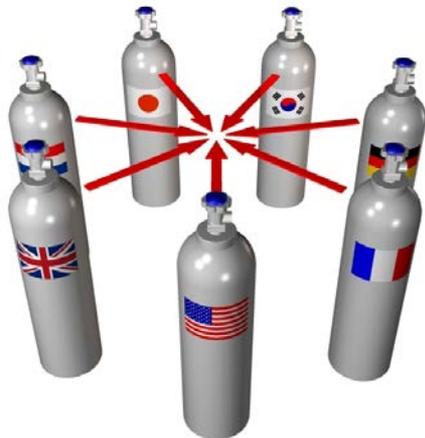
CRDS measurements and matrix gas composition

Target mole fractions:

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

Matrix composition

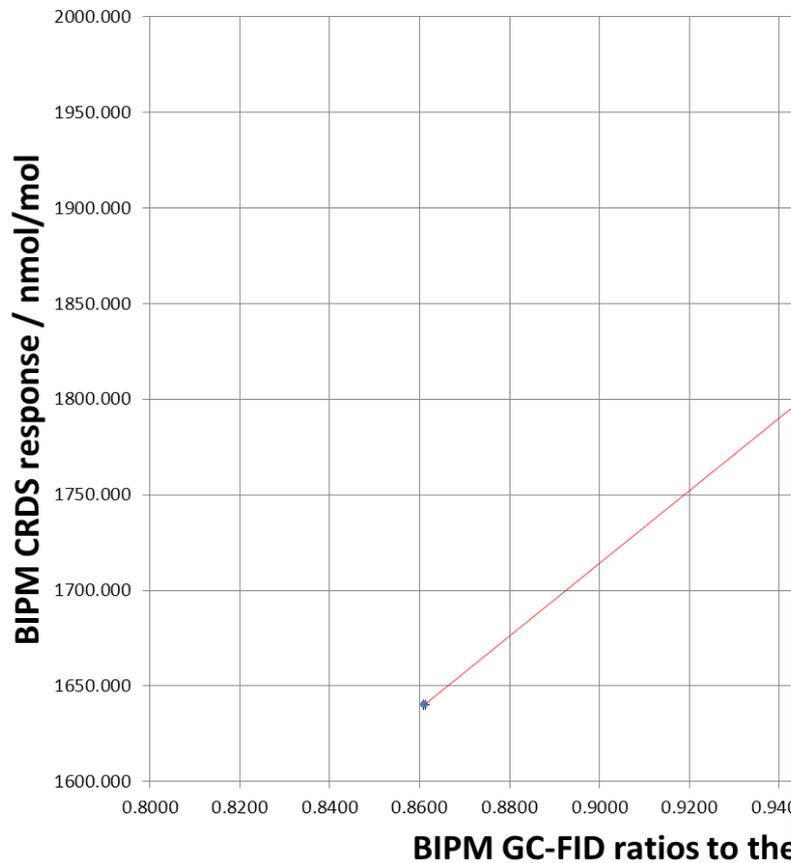
To minimize pressure broadening effects



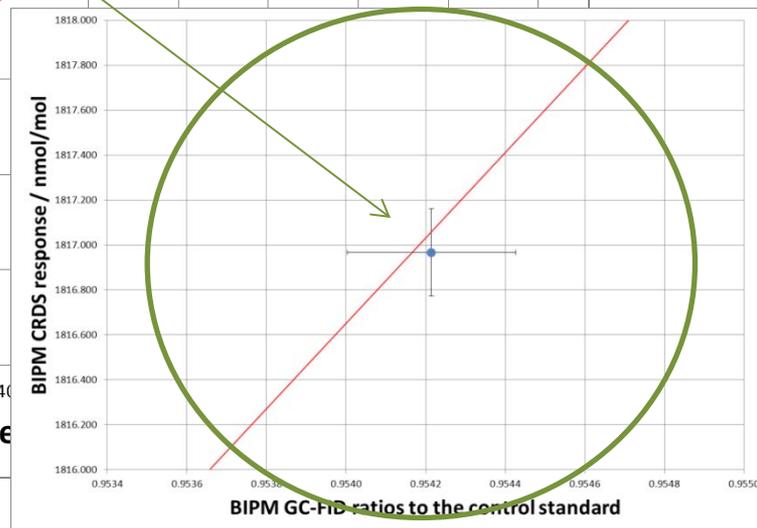
Component in Air	Minimum mole fraction permitted within submitted cylinder	Maximum mole fraction permitted within submitted cylinder
Nitrogen	0.77849 mol/mol	0.78317 mol/mol
Oxygen	0.20776 mol/mol	0.21111 mol/mol
Argon	8.865 mmol/mol	9.799 mmol/mol
Carbon Dioxide	360 μ mol/mol	400 μ mol/mol

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

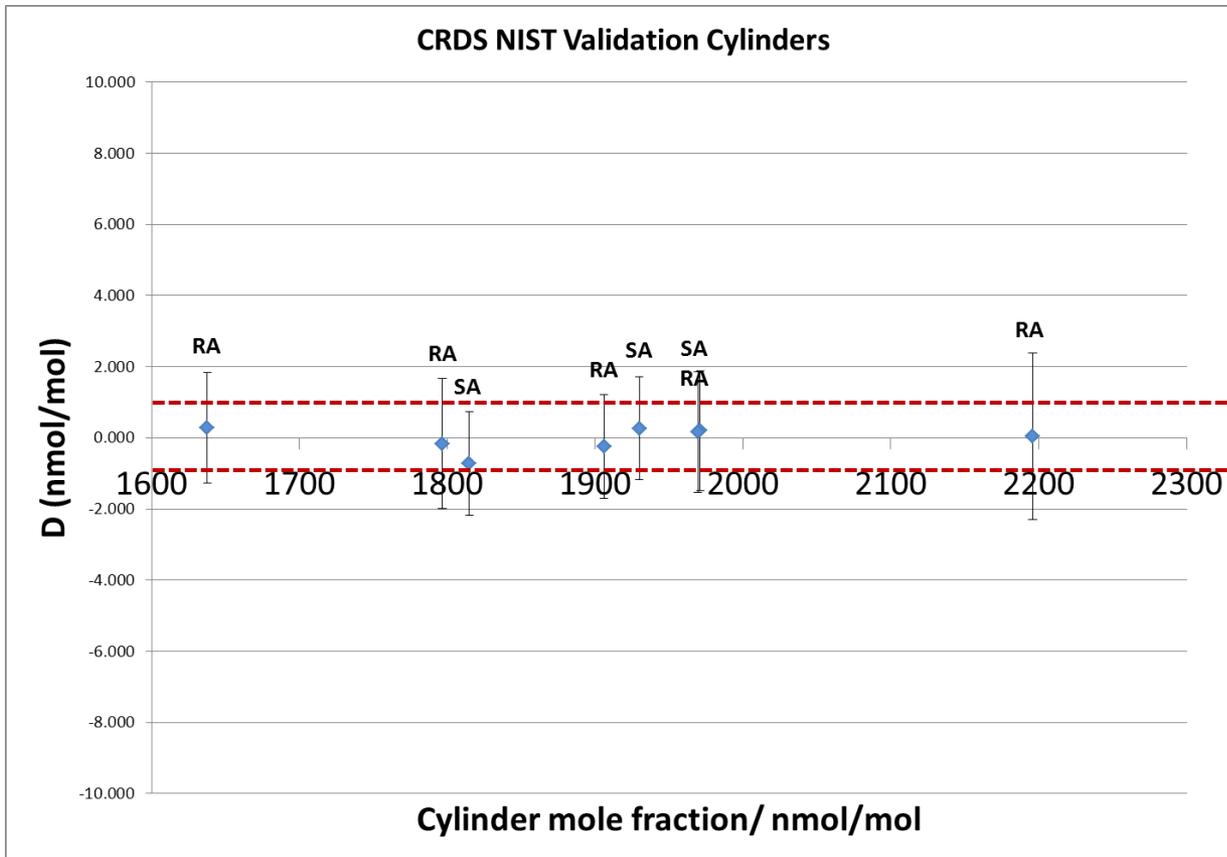
Validation of method using NIST real air and synthetic air standards



Matrix composition adapted to minimize broadening effects



Validation of BIPM's Measurements facility with NIST standards

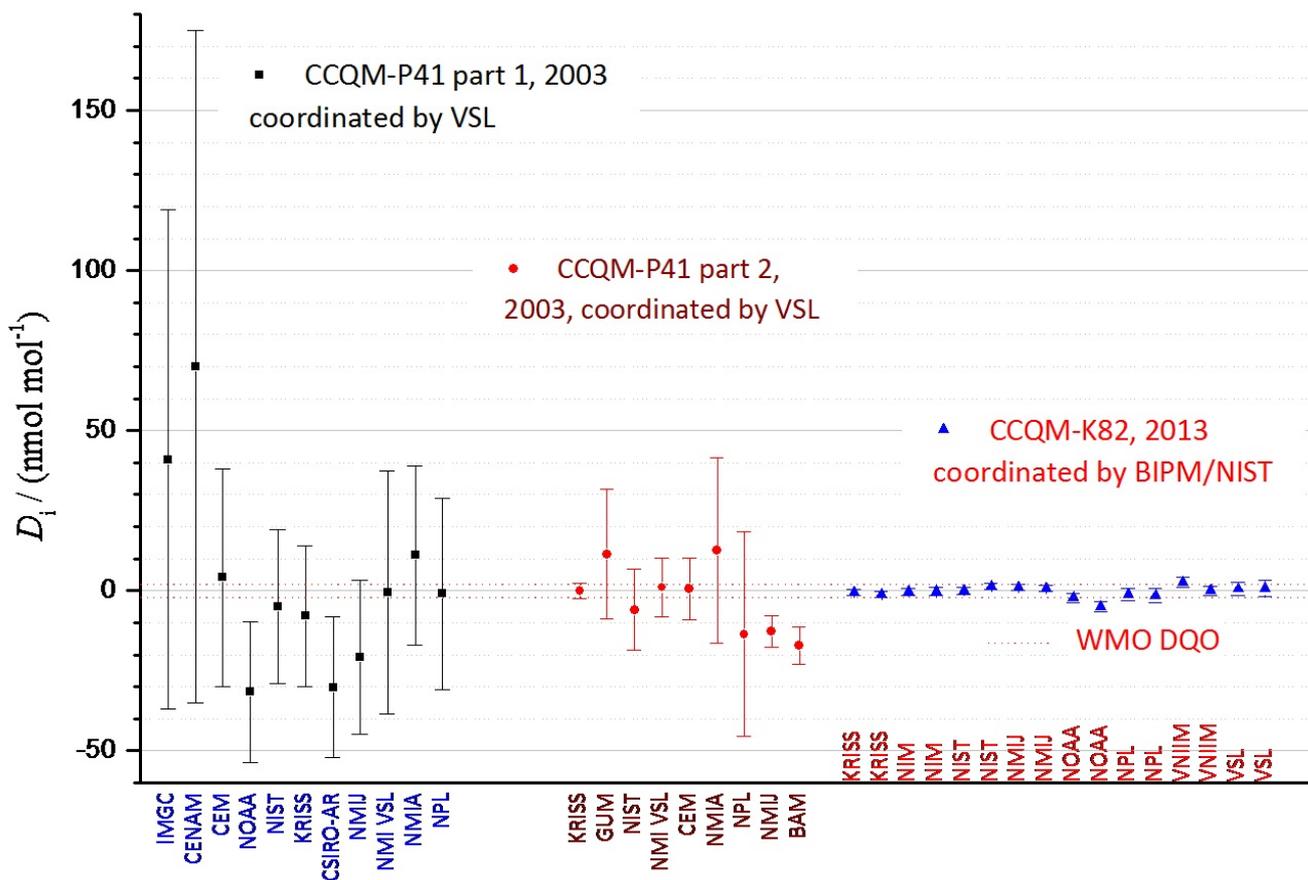


$$U(x_{\text{target}}) = \pm 1.0 \text{ nmol/mol}$$

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

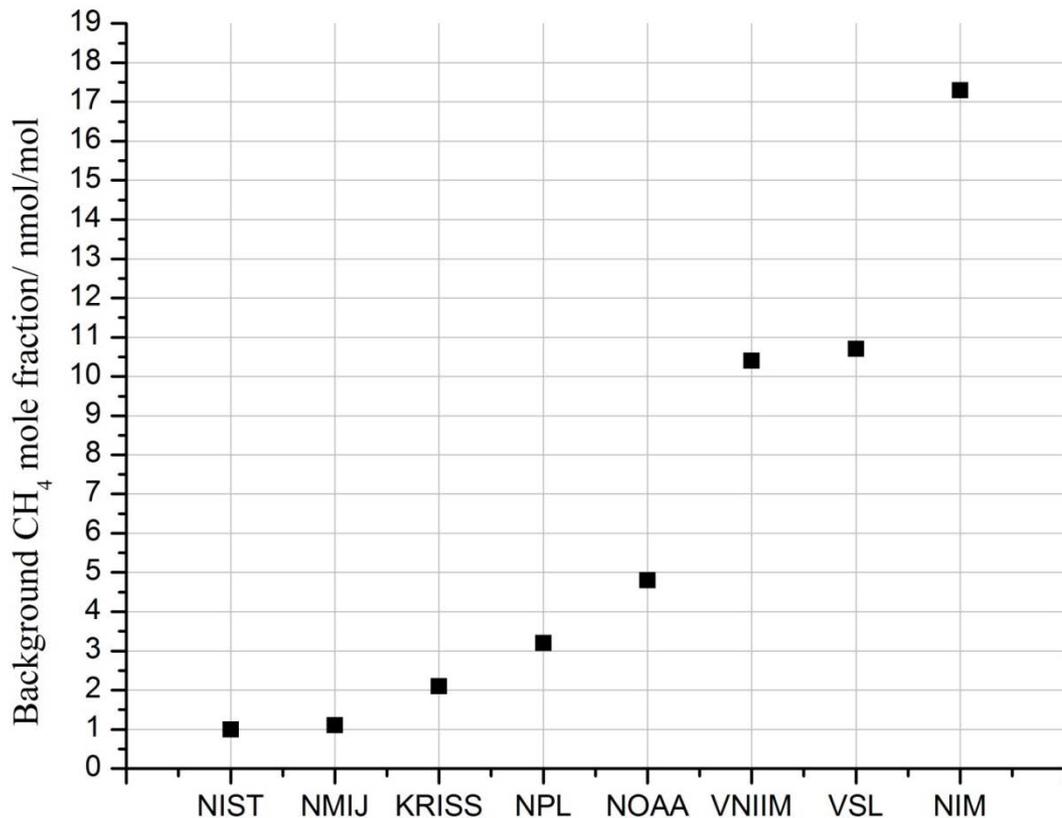
$\sigma_{(CCQM-K82)} = 1.17$ nmol/mol

Negligible impact of standards when:

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

$u(x), \sigma_{(CCQM-Kxx)} \leq 0.5$ nmol/mol

Development for future improvements in CH₄ in air standards



Accurate measurements of CH₄ in balance gas at 1 nmol/mol levels with $u(x) < 0.1$ nmol/mol required

Trace CH₄ mole fractions in balance gas as reported by participating laboratories in CCQM-K82

Measurement Challenges for CO₂ Standards and Comparisons



Comparison method

Matrix Composition/ Purity

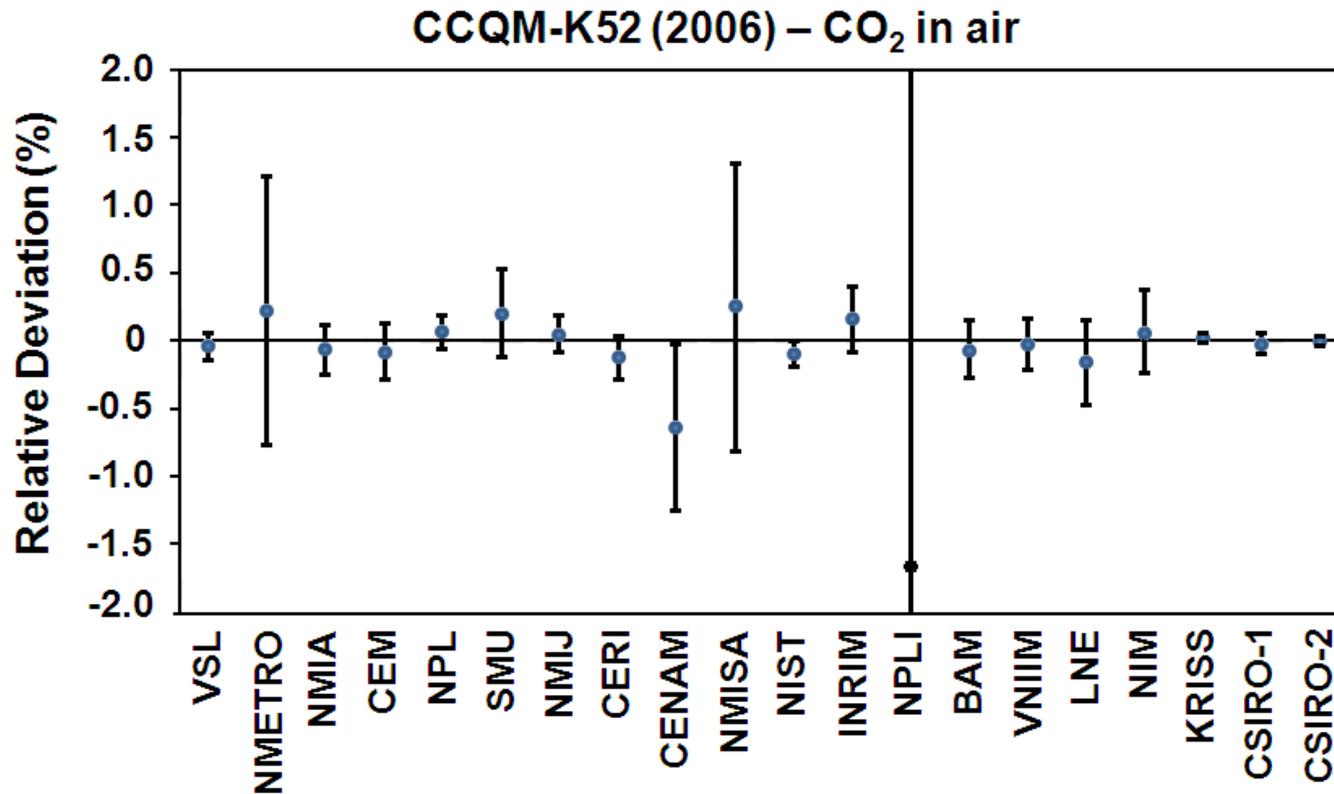
Isotopic Composition

Stability/Storage

**Target relative standard
uncertainty
< 0.007 %**



Preparing for the repeat CO₂ in air comparison (2016)



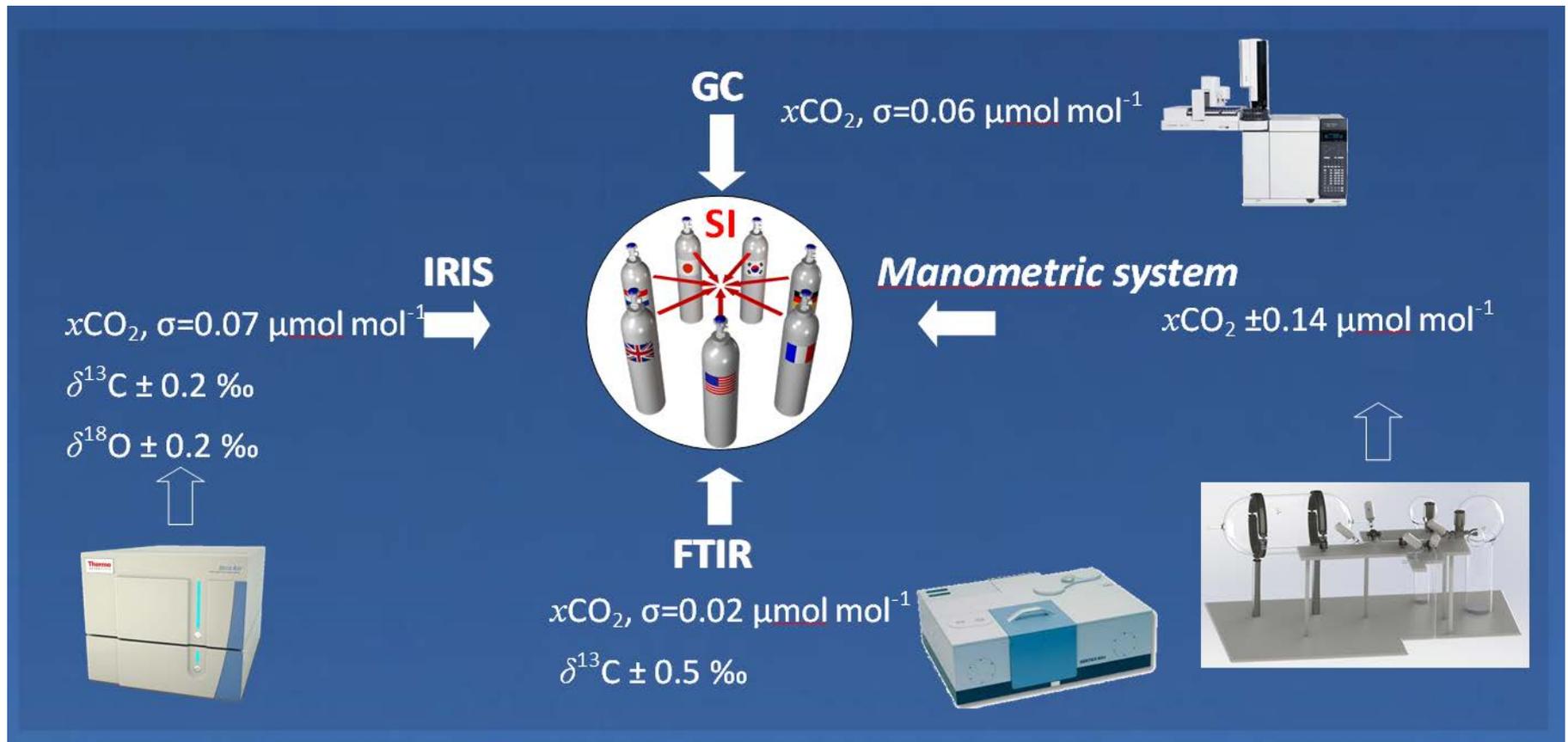
Uncertainties on standards >> DQOs for ambient monitoring community

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

Bureau
 International des
 Poids et
 Mesures

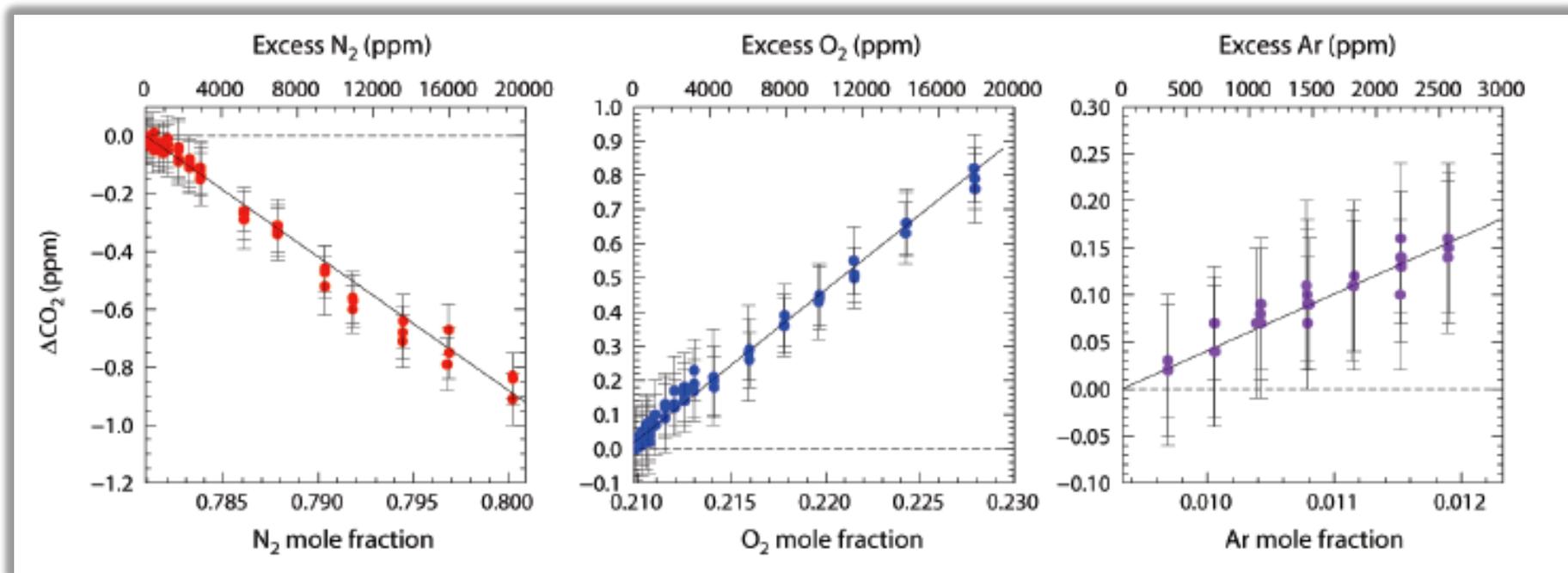
Preparing for the repeat CO₂ in air comparison (2016)

International comparison CCQM-K120 (2016): ambient level CO₂



Potential biases due to matrix composition

- Influence of the matrix composition on the spectroscopy
- More pronounced for CO₂
- For synthetic air standards this can be a major source of bias

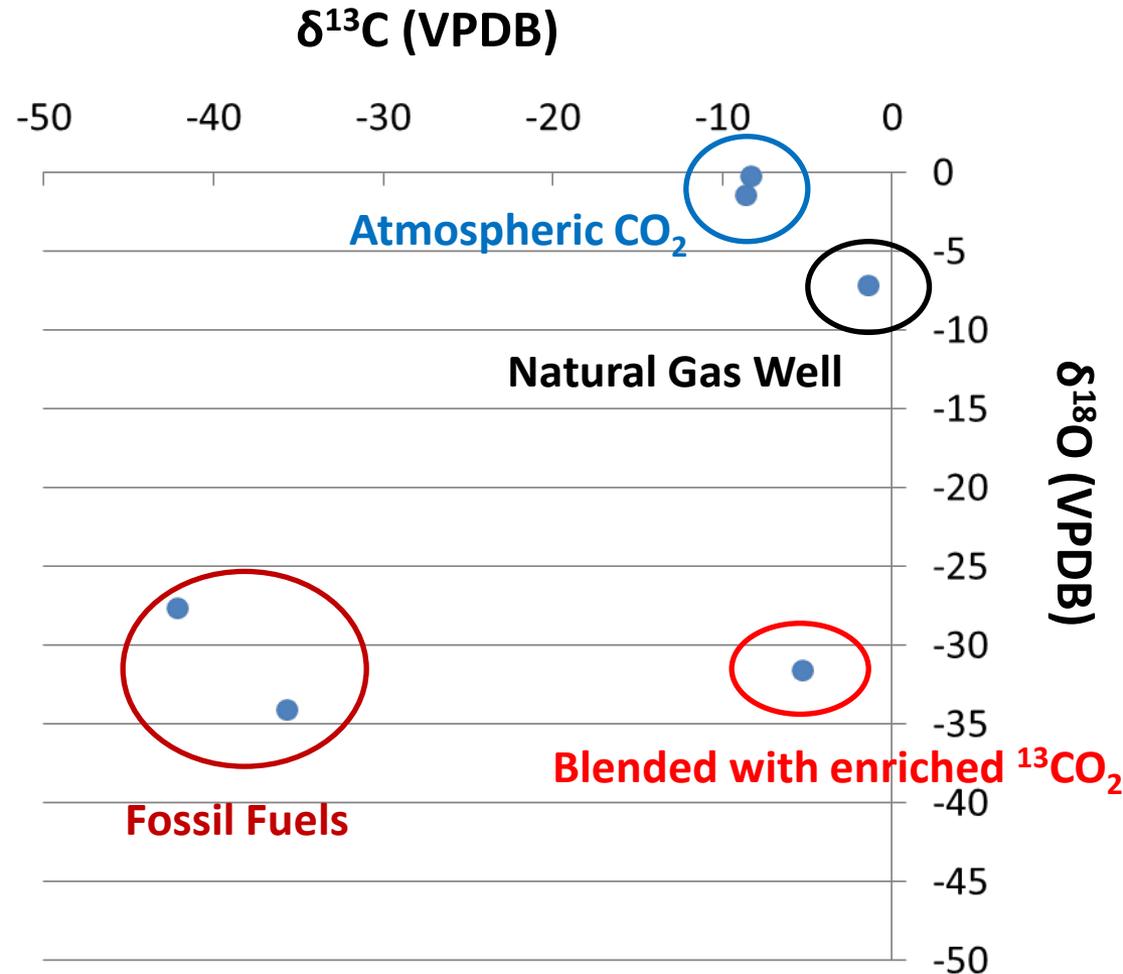


Consistency with atmospheric air composition (major components) to 0.5 mmol/mol

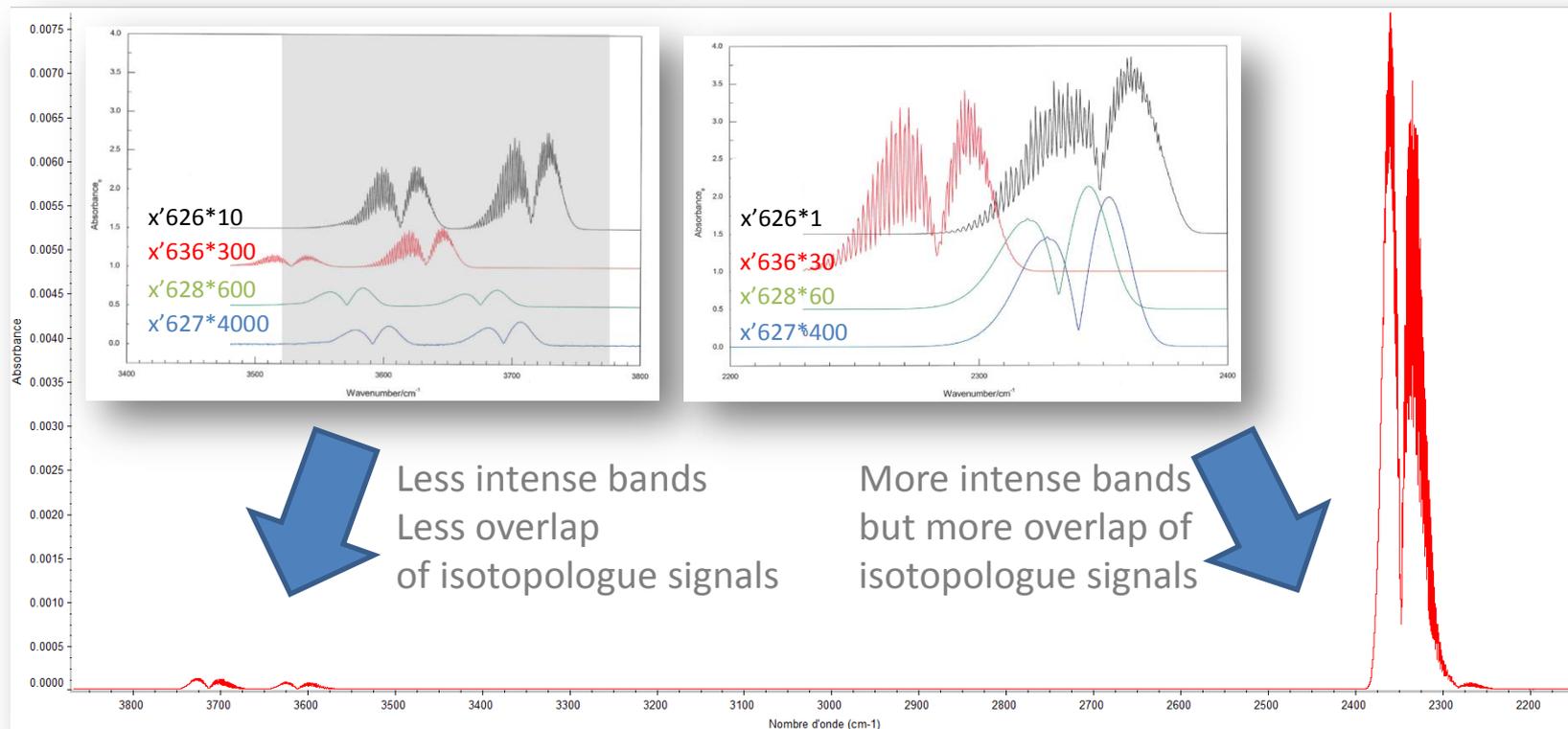
Accurate measurement of CO₂ (and CO₂ isotopologues)

Isotopes of CO₂

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



Accurate measurement of CO₂ (and CO₂ isotopologues) (by FTIR)



Validation standards with a range of compositions



Clean Air
Nivot Ridge, USA
~ -8 ‰



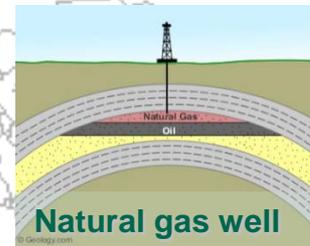
Isotopic mixing
NPL, UK
~ -8 ‰



Fermentation
France
-20 ‰ to -10 ‰



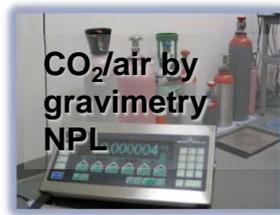
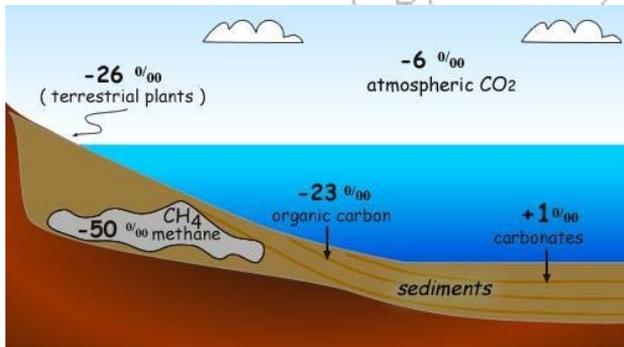
Methane, CH₄
CH₄ combustion
Morocco
~ -40 ‰



Natural gas well
Greece
-7 ‰ to -2 ‰



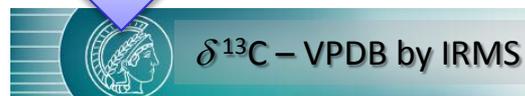
Clean Air
New Zealand
~ -8 ‰



CO₂/air by gravimetry
NPL



x(CO₂) assigned
δ¹³C assigned
Bureau International des Poids et Mesures



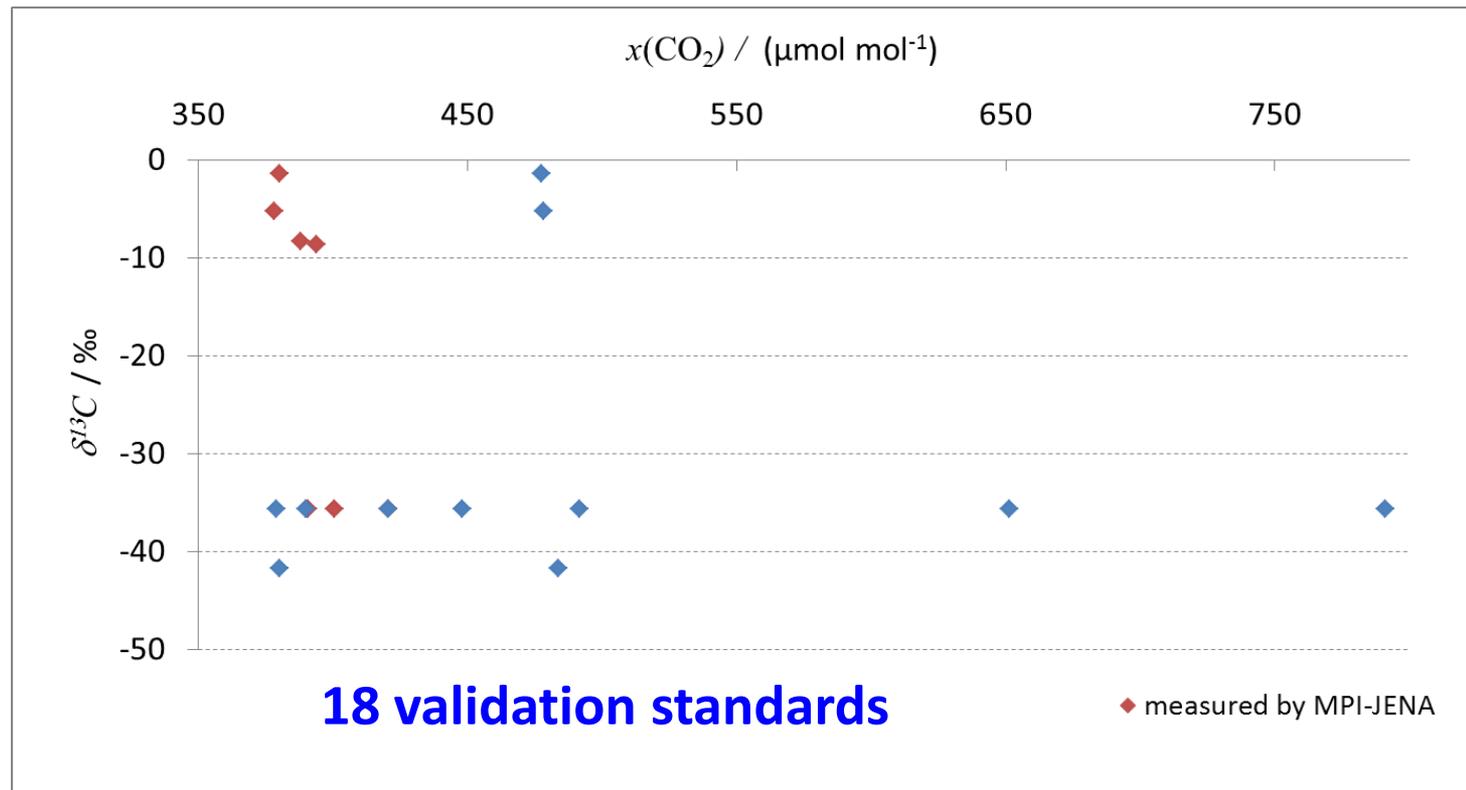
δ¹³C – VPDB by IRMS

Max Planck Institute
for Biogeochemistry



CO₂ 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



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

Bureau International des Poids et Mesures

Traceability of stable isotope standard measurements

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

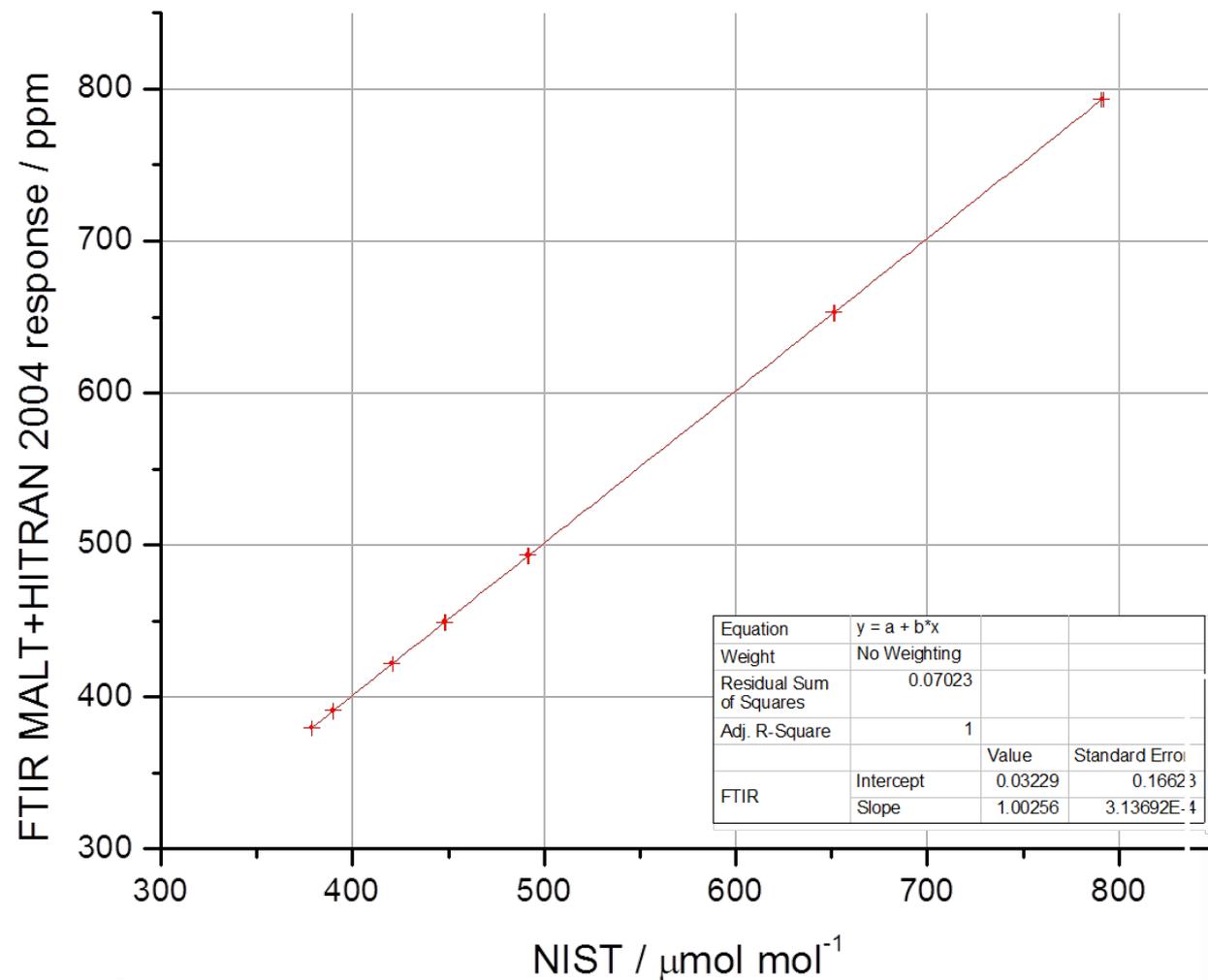
Organization

Quantity and types of standard

Calibrated/Measurement Instrument

 <p>International Atomic Energy Agency</p>	<p>$\delta^{13}\text{C}$ $\delta^{18}\text{O}$</p>  <p>Carbonates</p>	 <p>Pure CO_2</p>	 <p>Mass Spec.</p>
<p>Max Planck Institute for Biogeochemistry</p> 	<p>$\delta^{13}\text{C}$ $\delta^{18}\text{O}$</p>  <p>CO_2 from carbonates in real air</p>	 <p>Mass Spec.</p>	
<p>Bureau International des Poids et Mesures</p>	<p>CO_2 mole fraction ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) CCQM-K120</p>  <p>CO_2 in real/synthetic air</p>	<p>Optical Spectroscopic methods</p> 	

Comparisons of CO₂ standards with FTIR

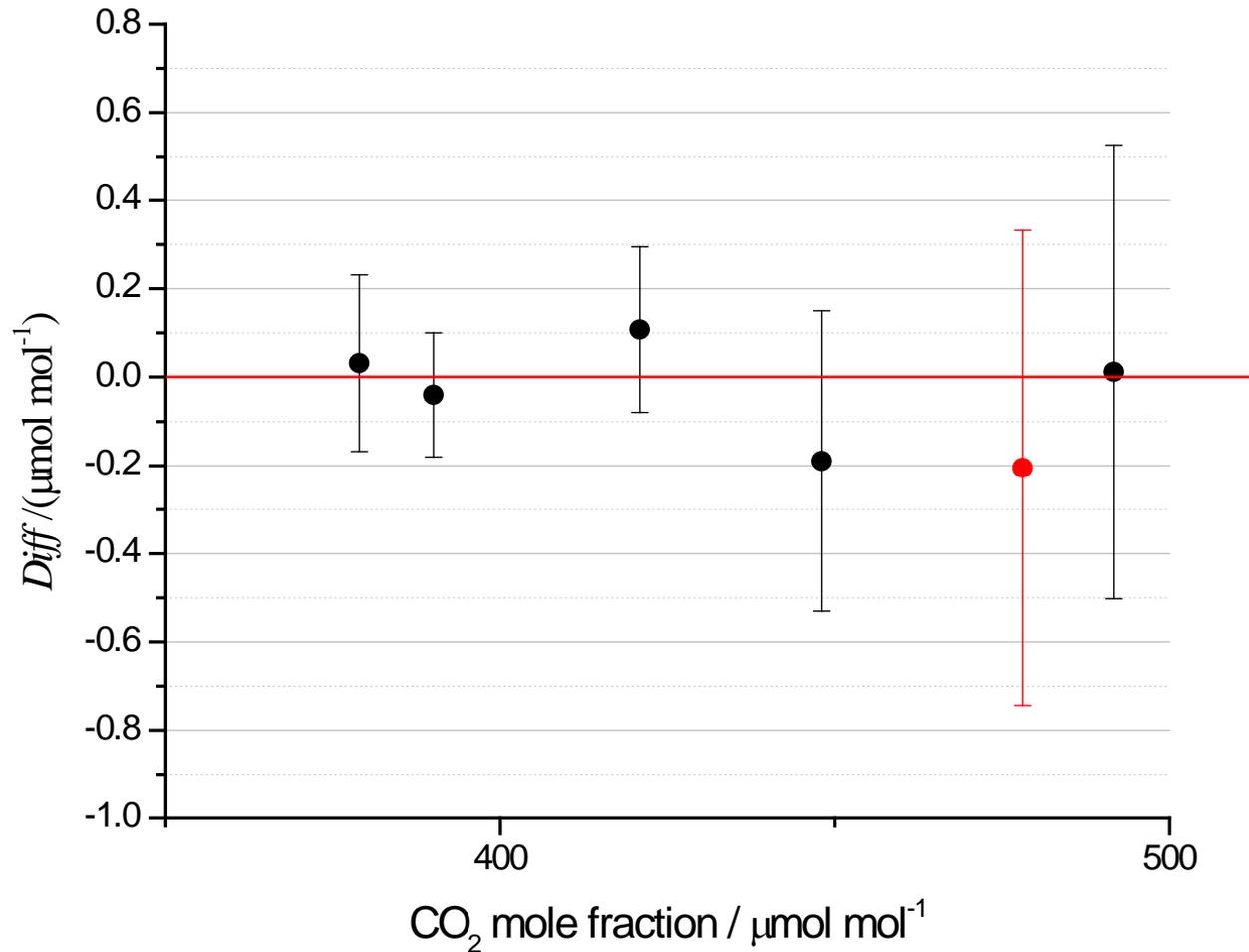


Under repeatability conditions with
 $u(x_{\text{FTIR}}) = 0.015 \mu\text{mol/mol}$



Non corrected FTIR response for isotopic effects

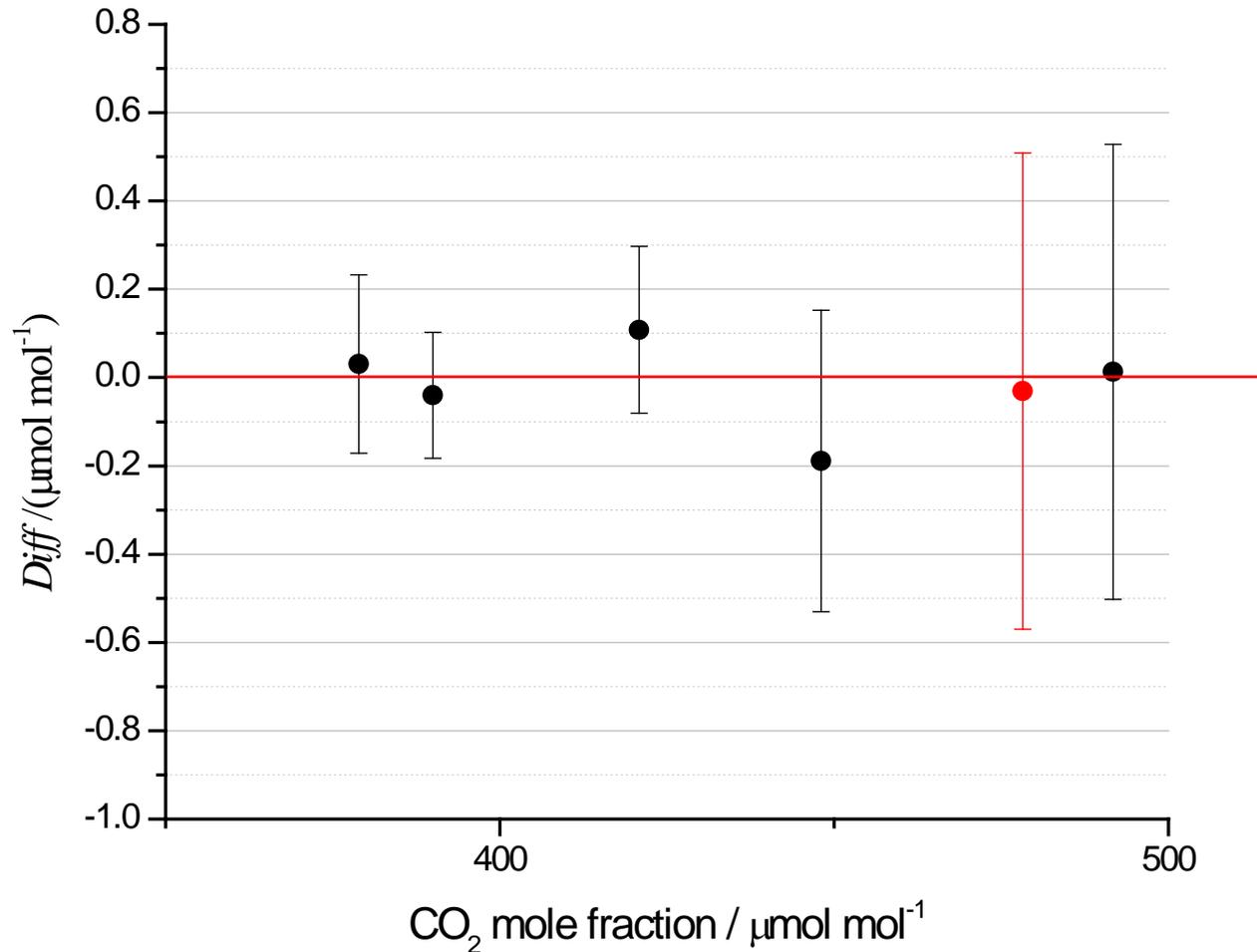
	$\delta^{13}\text{C}$ (VPDB) ‰	$\delta^{18}\text{O}$ (VPDB) ‰
STD A	-35.685	-34.478
STD B	-5.2494	-31.640



Corrected FTIR response for isotopic effects

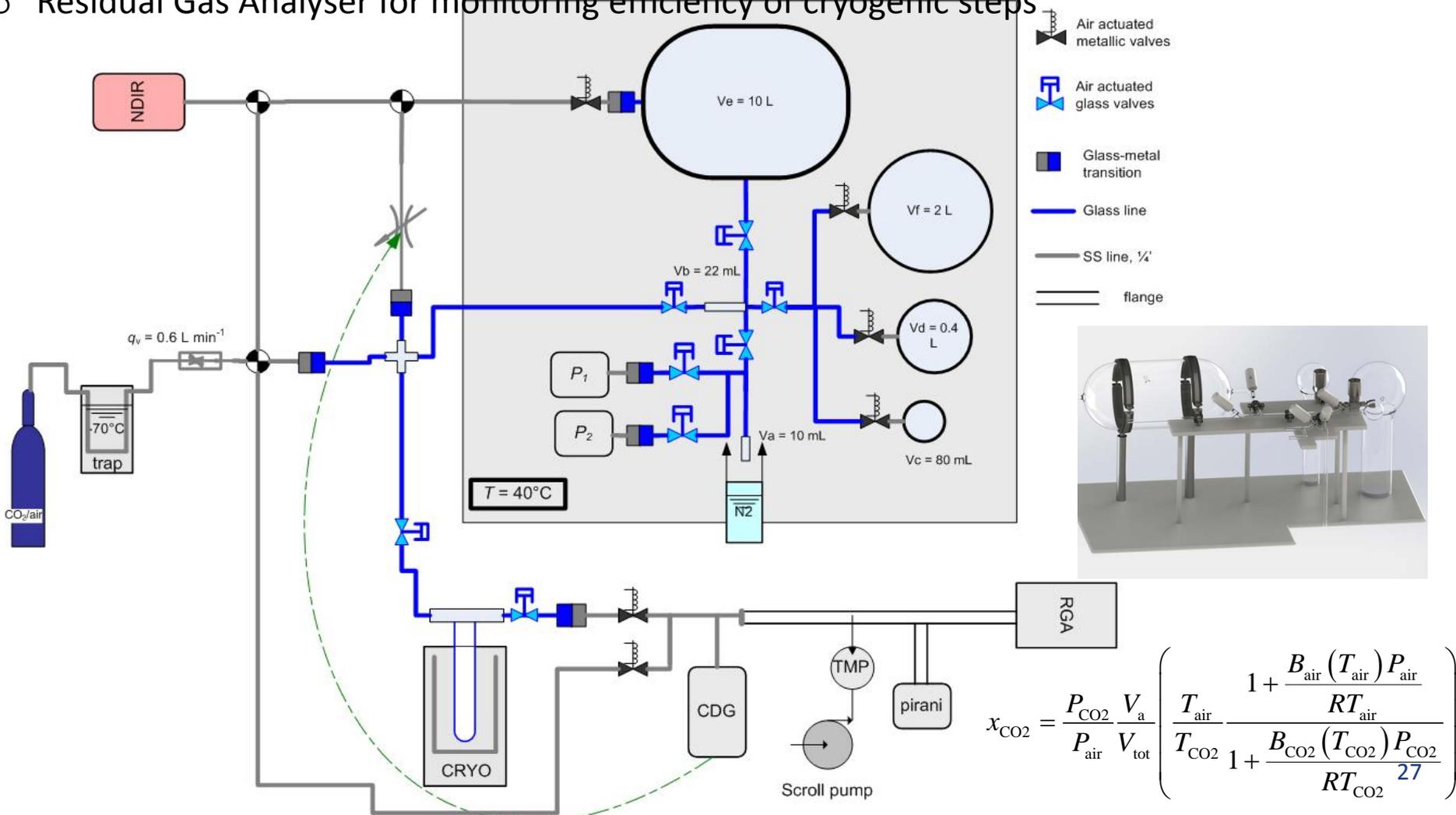
	$\delta^{13}\text{C}$ (VPDB) ‰	$\delta^{18}\text{O}$ (VPDB) ‰
STD A	-35.685	-34.478
STD B	-5.2494	-31.640

The correction is
 $\sim 0.170 \mu\text{mol mol}^{-1}$
Ten times the
measurement
repeatability
($0.015 \mu\text{mol mol}^{-1}$)

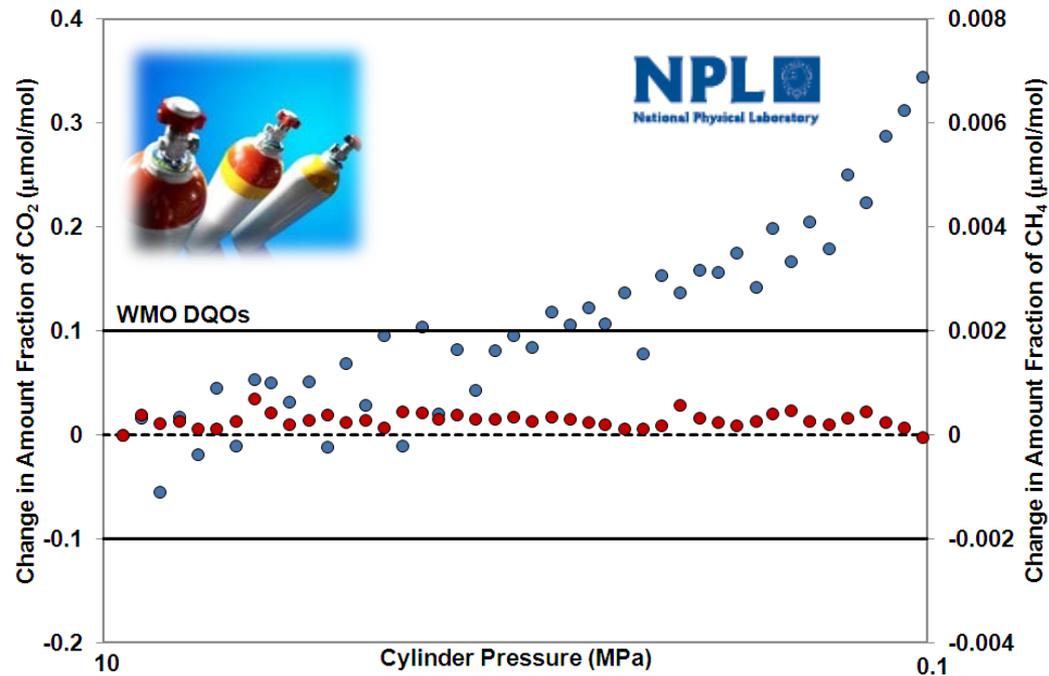


BIPM manometric facility for the CO₂ comparison (2016)

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

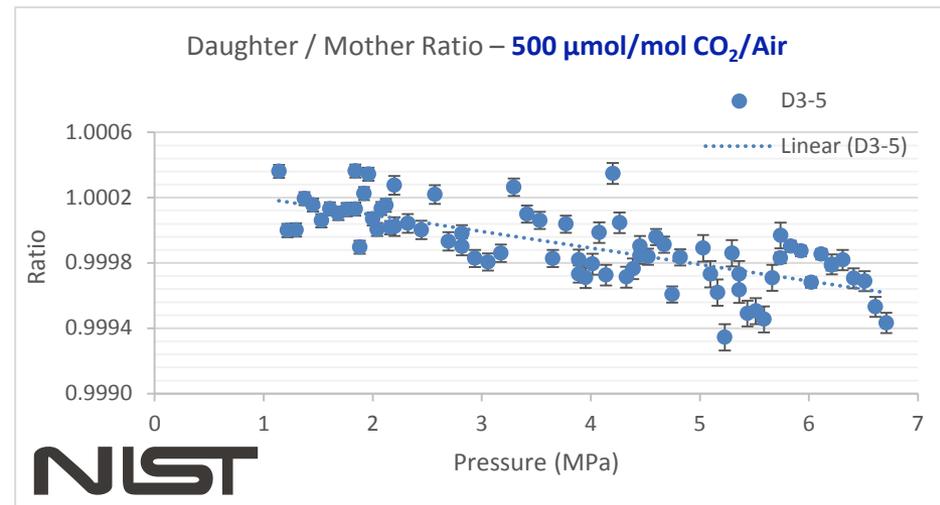


Stability of CO₂ standards



Pressure dependence of CO₂ in gas cylinders

As pressure drops in cylinder there is an increase in CO₂



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 CO₂ primary standards for both background and urban monitoring applications**

Acknowledgements

Co-authors: JS. Kim (KRISS), P. Brewer (NPL), G. Rhoderick (NIST)

CCQM-GAWG Members

J.Viallon, E. Flores, F. Idrees, P.Moussay (BIPM)

W. Miller, L. Gameson and F. Guenther (NIST)

M. Minarro (NPL)

S. Assonov and M. Groening (IAEA)

W. Brand (MPI-JENA)