Accuracy requirements for interchangeability of gas standards for greenhouse gas and precursor atmospheric monitoring

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Bureau
International des
Poids et
Mesures

Bureau International des Poids et Mesures (BIPM)

The International Bureau of Weights and Measures

- Intergovernmental organization with 56 Member States and 41 Associate States/economies, Established in 1875 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.***

5 scientific departments:

- **Chemistry**
- Electricity
- Ionizing Radiation
- Mass
- Time

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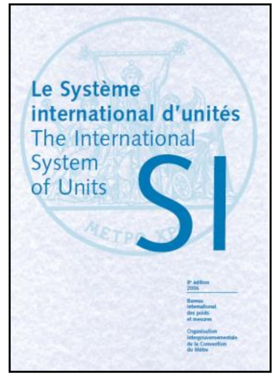
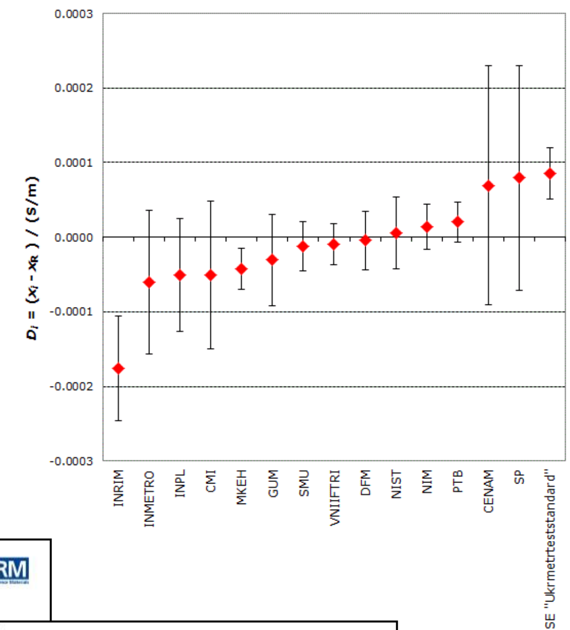
CIPM Mutual Recognition Arrangement

Definition

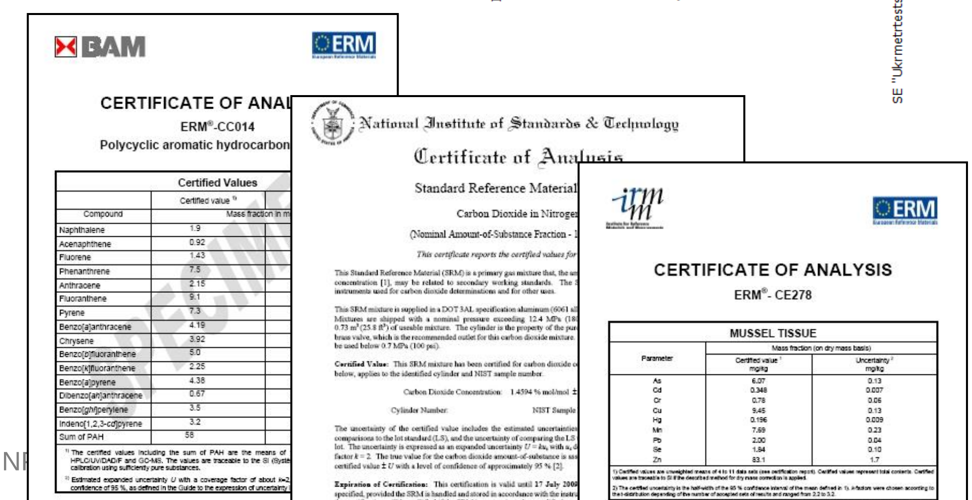


Realization

Comparisons



Dissemination



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International Gas Standard Comparisons coordinated by the BIPM Chemistry Department

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	2015
CCQM-K120.b	Carbon dioxide	380 µmol/mol – 800 µmol/mol	2015
CCQM-K68.2018	Nitrous oxide	350 nmol/mol	2018

Essential Climate Variables

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GCOS
GLOBAL CLIMATE OBSERVING SYSTEM

WMO IOC UNEP ICSU

: **Essential Climate Variables that are both currently feasible for global implementation and have a high impact on UNFCCC requirements**

Domain		Essential Climate Variables
Atmospheric (over land, sea and ice)	**Surface:**[8]	Air temperature, Wind speed and direction, Water vapour, Pressure, Precipitation, Surface radiation budget.
	Upper-air:[9]	Temperature, Wind speed and direction, Water vapour, Cloud properties, Earth radiation budget (including solar irradiance).
	Composition:	Carbon dioxide, Methane, and other long-lived greenhouse gases[10], Ozone and Aerosol, supported by their precursors[11]
Oceanic	**Surface:**[12]	Sea-surface temperature, Sea-surface salinity, Sea level, Sea state, Sea ice, Surface current, Ocean colour, Carbon dioxide partial pressure, Ocean acidity, Phytoplankton.
	Sub-surface:	Temperature, Salinity, Current, Nutrients, Carbon dioxide partial pressure, Ocean acidity, Oxygen, Tracers.
Terrestrial		River discharge, Water use, Groundwater, Lakes, Snow cover, Glaciers and ice caps, Ice sheets, Permafrost, Albedo, Land cover (including vegetation type), Fraction of absorbed photosynthetically active radiation (FAPAR), Leaf area index (LAI), Above-ground biomass, Soil carbon, Fire disturbance, Soil moisture.

8 Including measurements at standardized, but globally varying heights in close proximity to the surface.
9 Up to the stratopause.
10 Including $N_2$0, CFCs, HCFCs, HFCs, SF_6 and PFCs.
11 In particular NO_2, SO_2, HCHO and CO.
12 Including measurements within the surface mixed layer, usually within the upper 15 m.

Target uncertainties for primary standards

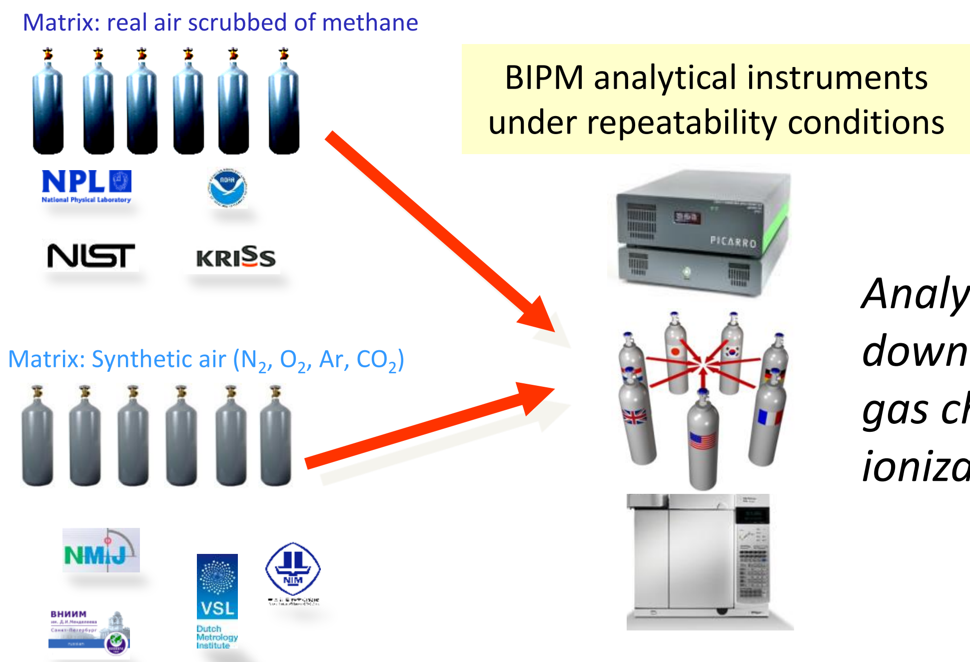
Component	Nominal Mole fraction	Primary Standard: target standard uncertainty
CO_2	400 µmol/mol	0.025 µmol/mol
CH_4	2000 nmol/mol	0.5 nmol/mol
N_2O	350 nmol/mol	0.025 nmol/mol

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

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

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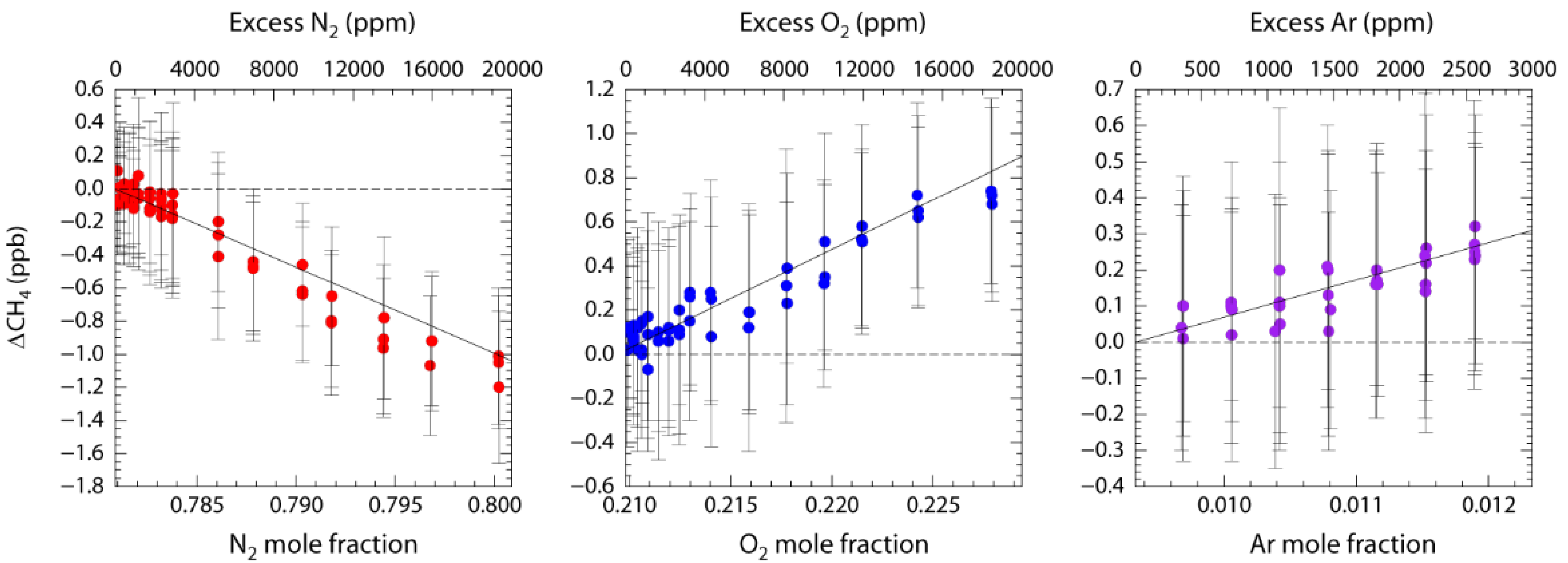
Accounting for potential biases in CRDS measurements

Uncertainty component included in BIPM measurement Results

Pressure broadening:

H. Nara; Tanimoto, H.; Tohjima, Y.; Mukai, H.; Nojiri, Y.; Katsumata, K.; Rella, C. W. "Effect of air composition (N_2, O_2, Ar, and H_2O) on CO_2 and CH_4 measurement by wavelength-scanned cavity ring-down spectroscopy: calibration and measurement strategy".Atmos. Meas. Tech. 2012. 5. 2689-2701.



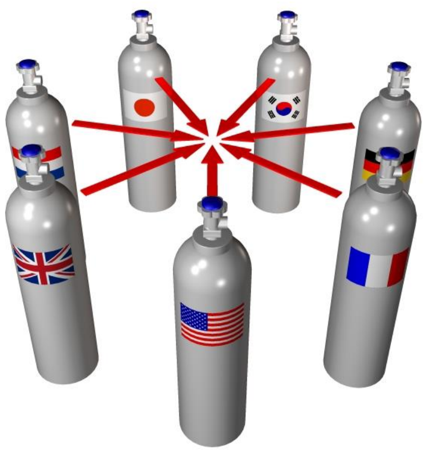
CRDS measurements and matrix gas composition

Target mole fractions:

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

Matrix composition

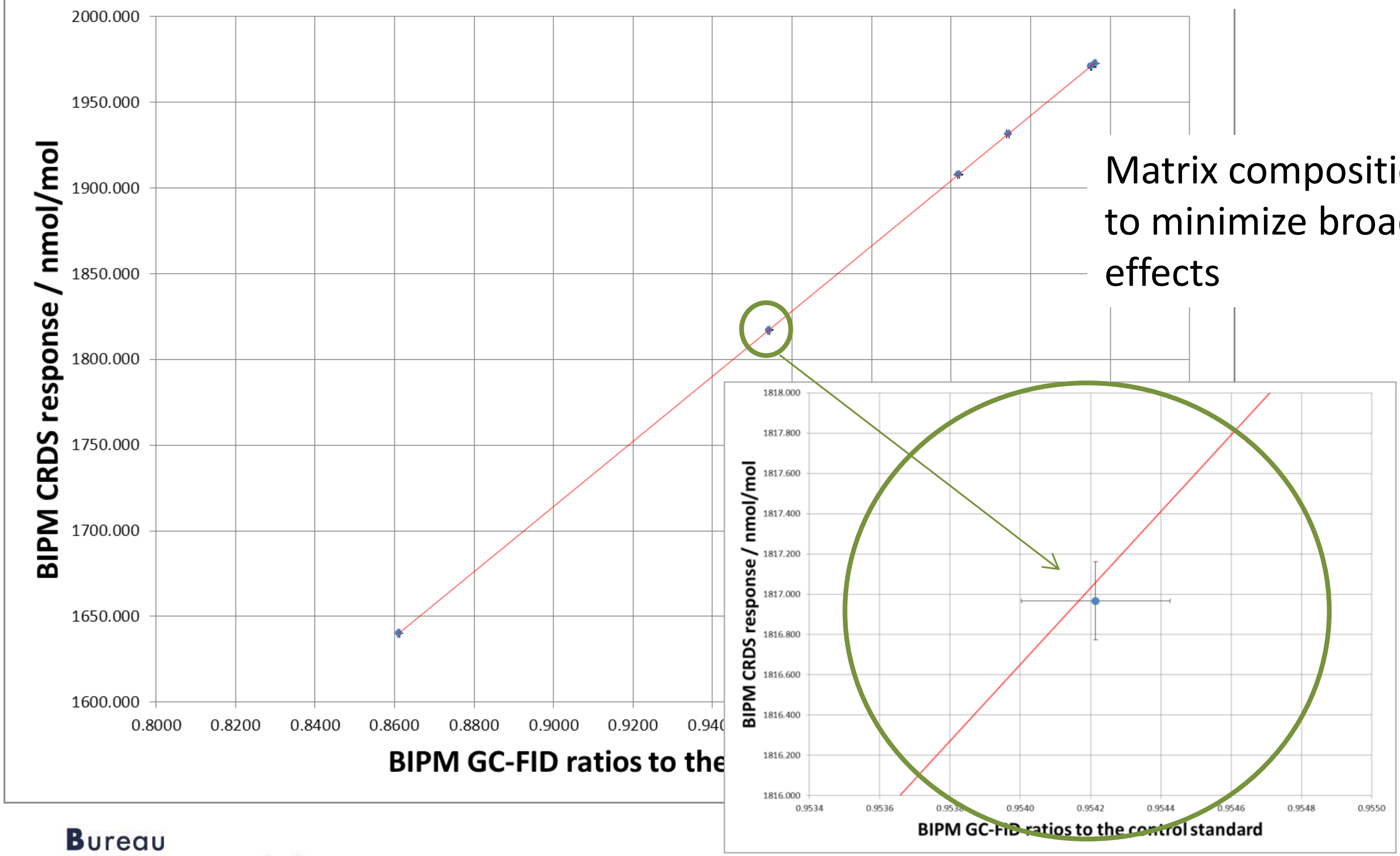
To minimize pressure broadening effects



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

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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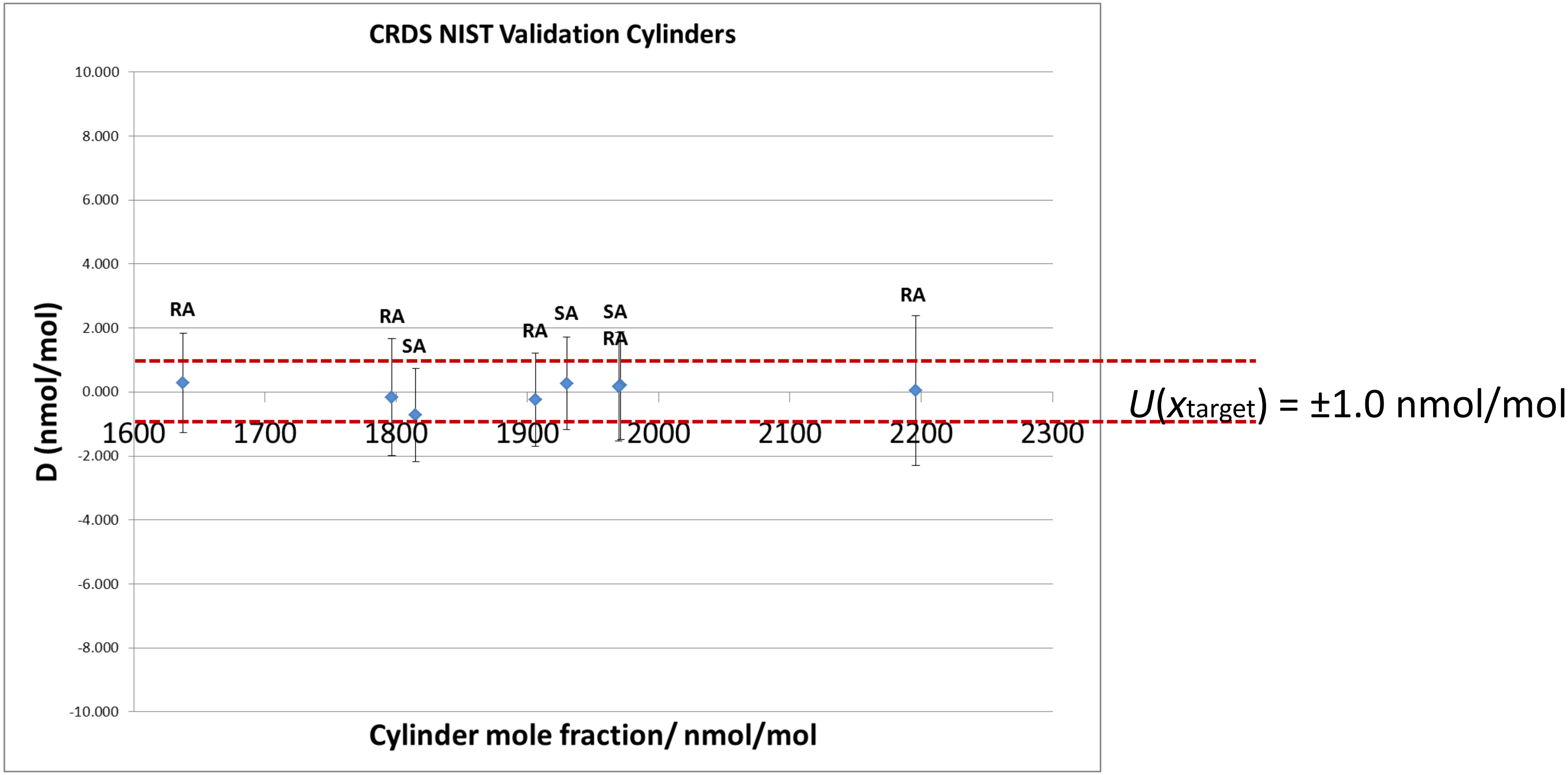
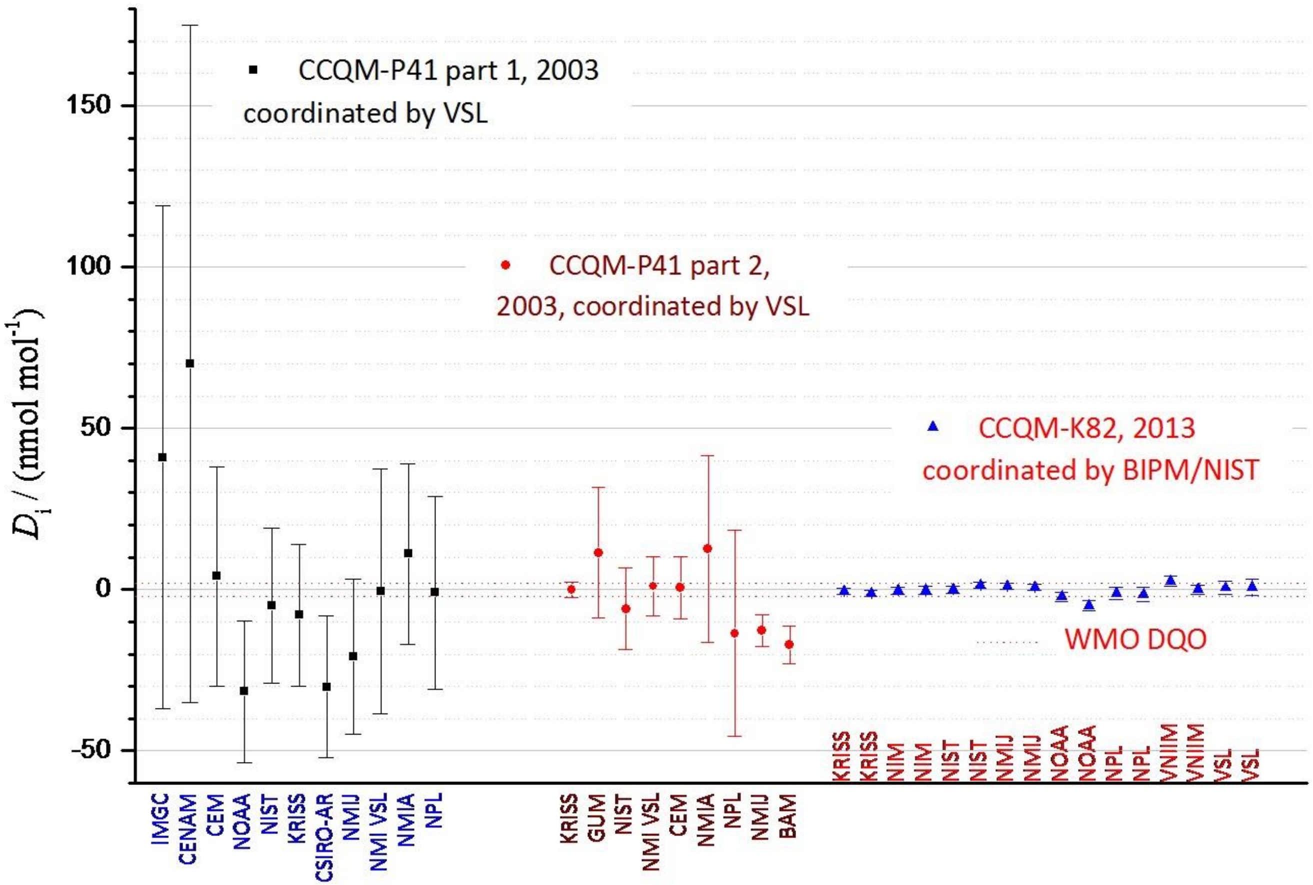
Validation of BIPM's Measurements facility with NIST standards



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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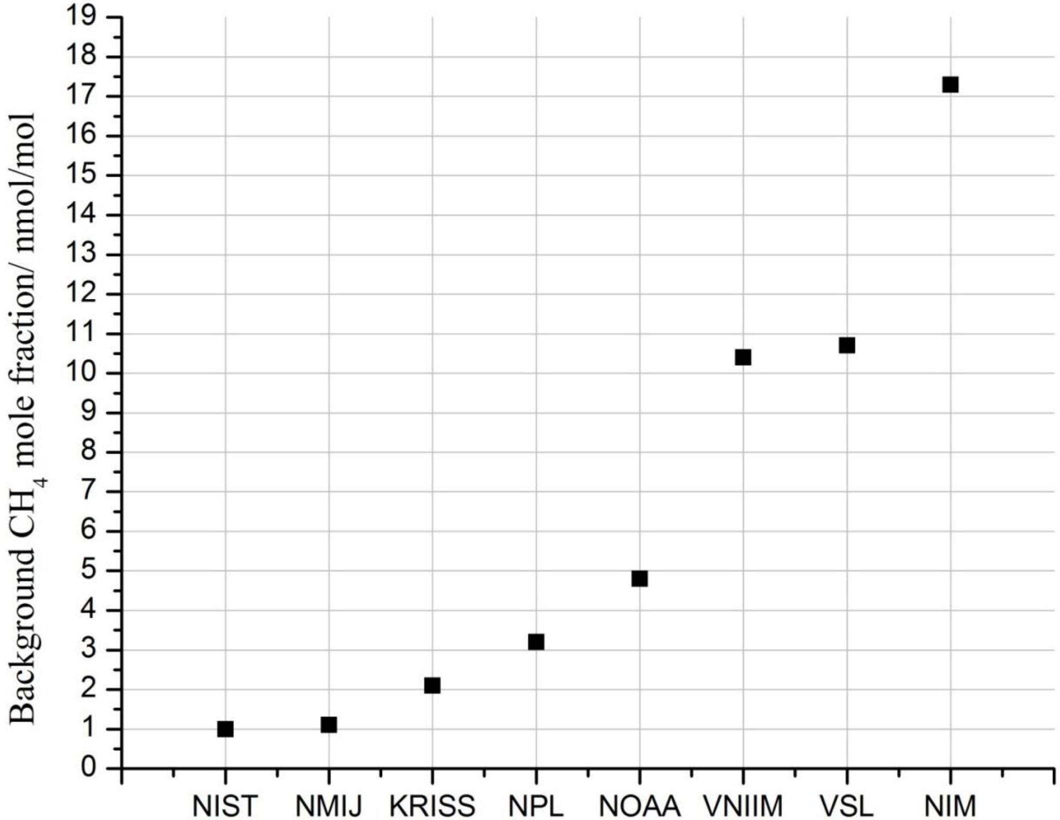
Development for future improvements in CH_4 in air standards



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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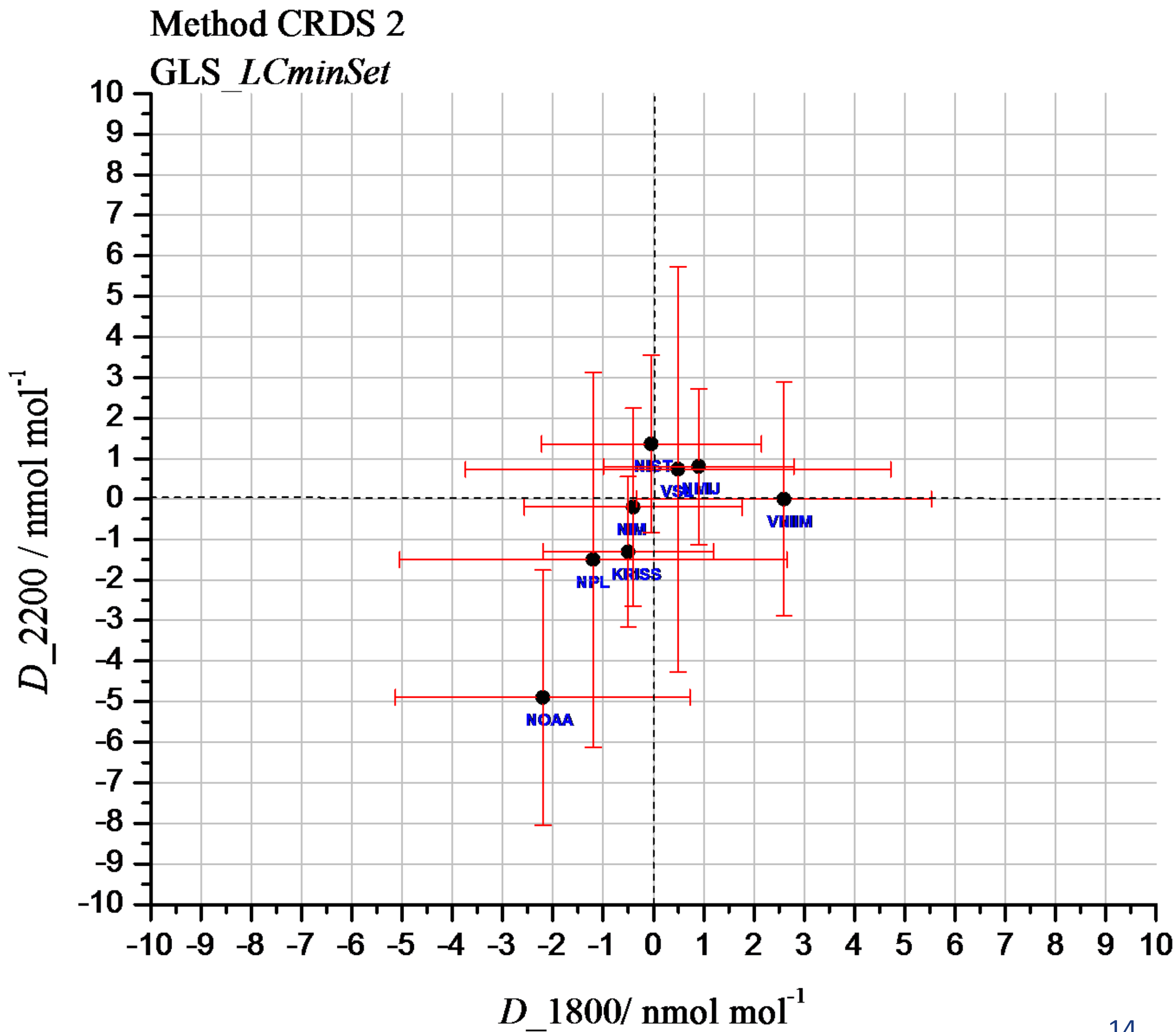
CCQM-K82 results accounting potential isotope ratio variation in CH_4



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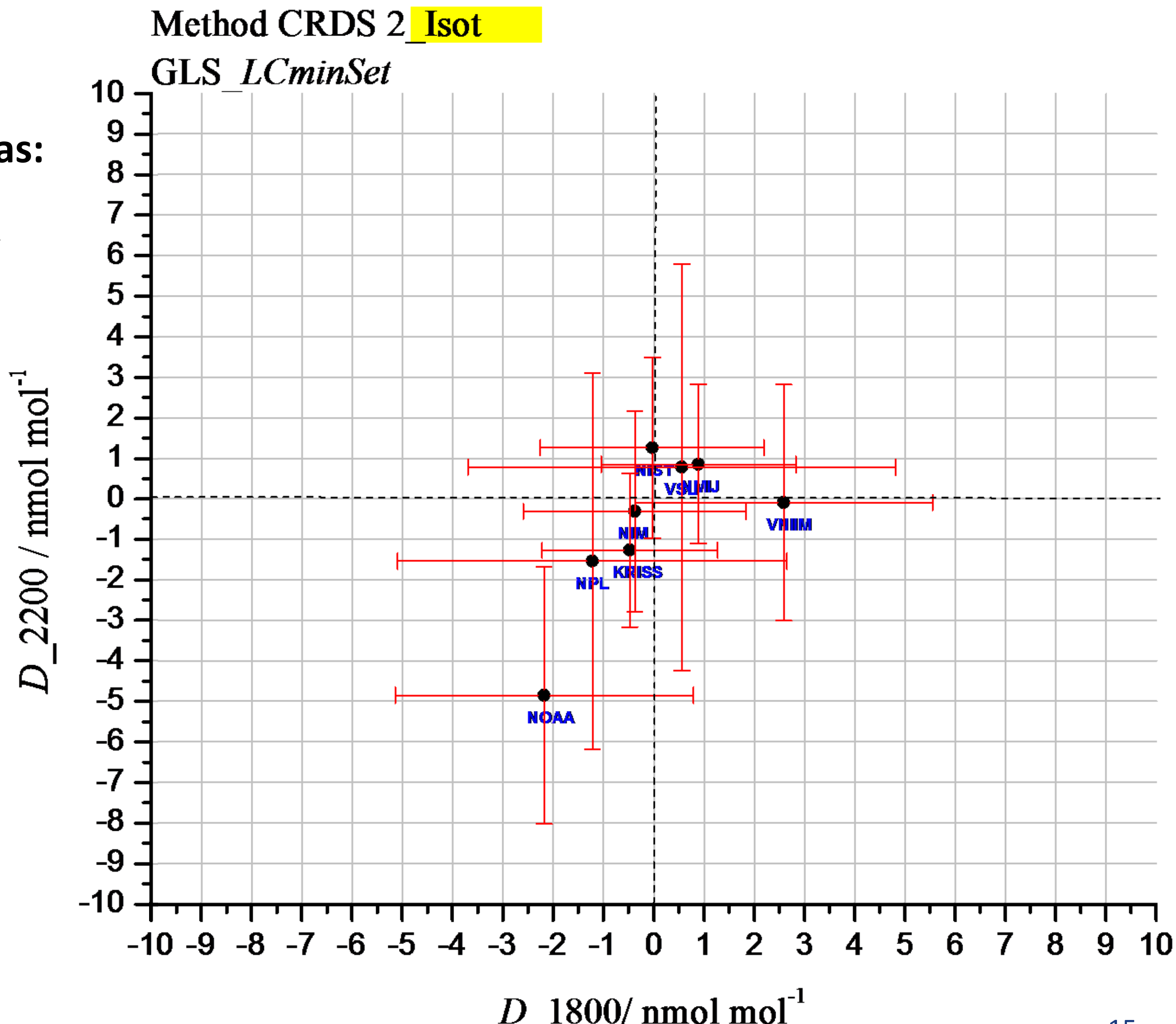
CCQM-K82 results including uncertainty component for potential isotope ratio variation in CH_4

Pure methane from natural gas:
–(43±7) ‰ for δ^{13}C (VPDB);
–(185±20) ‰ for δD (VSMOW

Bias in the CRDS:
+0.34 nmol/mol and
-0.38 nmol/mol;

Uncertainty component
u_δ =0.21 nmol/mol



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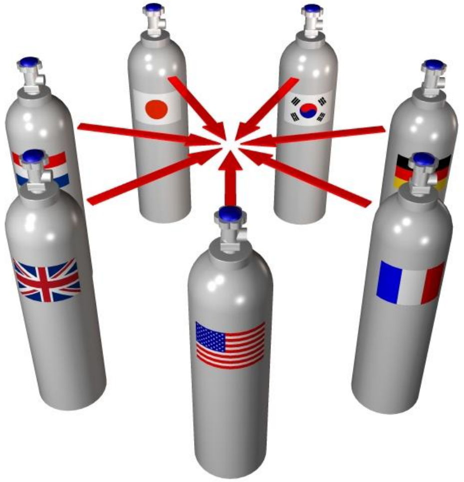
Preparing for the repeat ambient CO_2 in air key comparison (2015)

Preparation for CCQM-K120 (2015)

Coordinated by: BIPM/NIST



Agreed comparison (November 2013):

Comparison of NMI capabilities

CCQM-K120.a

CO_2 in air (380 µmol/mol to 480 µmol/mol)

Matrix : Scrubbed real air within 0.1% of atmospheric balance gases

CCQM-K120.b

CO_2 in air (380 µmol/mol to 800 µmol/mol)

Matrix : Air composition within 1% of atmospheric balance gases

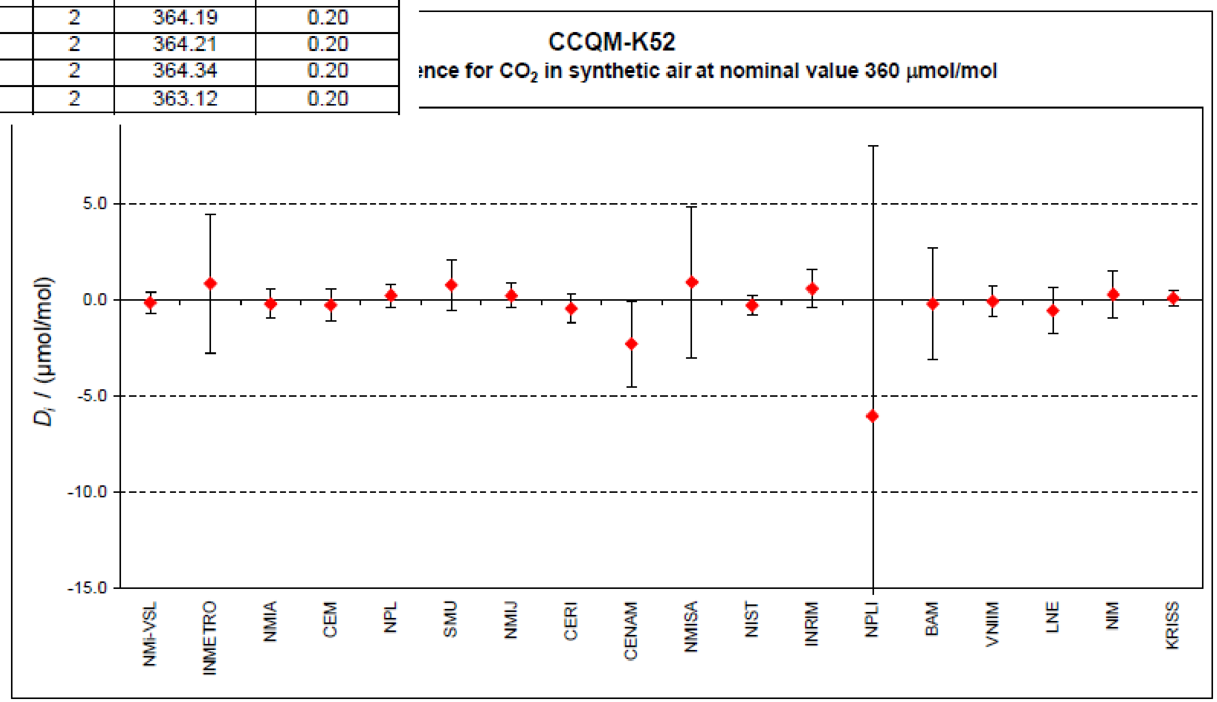
Preparing for the repeat ambient CO_2 in air key comparison (2015)

Previous comparison: CCQM-K52 (2006)   **Coordinated by: VSL**

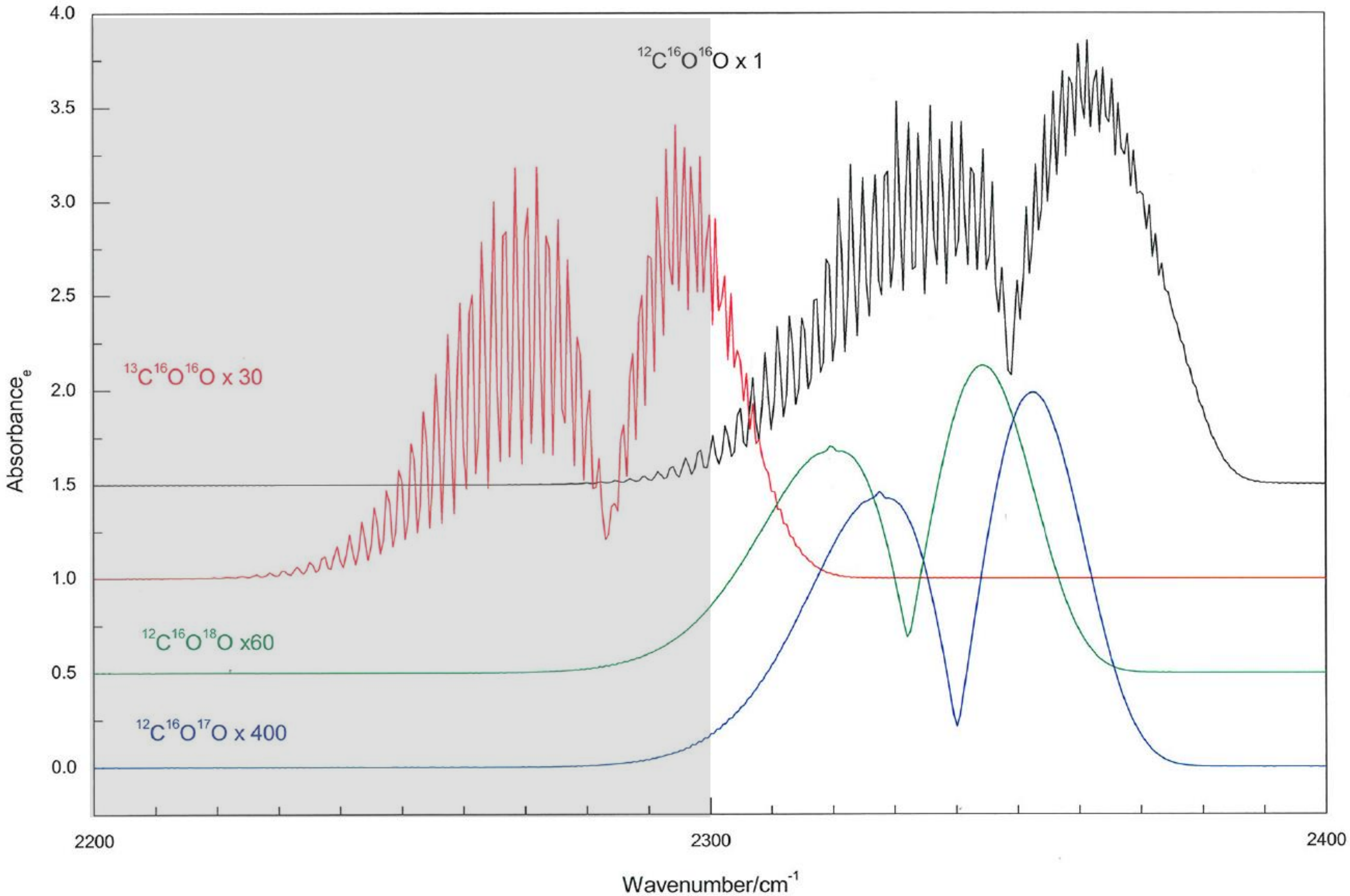
Lab *i*	Cylinder	x_i / (µmol/mol)	$U_{Lab\,i}$ / (µmol/mol)	k_i	$x_{i\,ref}$ / (µmol/mol)	$u_{i\,ref}$ / (µmol/mol)
NMi-VSL	D240036	364.13	0.36	2	364.30	0.20
INMETRO	D752038	364.0	3.6	2	363.18	0.20
NMIA	D751922	363.09	0.70	2.18	363.31	0.20
CEM	D751928	363.38	0.73	2	363.67	0.20
NPL	D751947	364.36	0.44	2	364.15	0.20
SMU	D751961	364.6	1.2	2	363.86	0.20
NMIJ	D751944	364.08	0.48	2	363.88	0.20
CERI	D751923	363.42	0.61	2	363.89	0.20
CENAM	D751924	361.6	2.2	2	363.91	0.20
NMISA	D751918	364.9	3.883	2	364.00	0.20
NIST	D751954	363.72	0.34	2	364.03	0.20
INRIM	D751935	364.62	0.90	2	364.05	0.20
NPLI	D751950	358.1	13.6	2	364.14	0.20
BAM	D751942	363.5	2.9	2	363.72	0.20
VNIIM	D751937	364.1	0.7	2	364.19	0.20
LNE	D750235	363.63	1.15	2	364.21	0.20
NIM	D751943	364.6	1.1	2	364.34	0.20
KRISS*	D751977	363.20	0.06	2	363.12	0.20

Results show good agreement, but…

Uncertainties on all standards > DQO for ambient monitoring community



Measuring mole fractions of CO_2 isotopologues



Target relative standard uncertainty *u(x) < 0.01%*

1 ‰ $\delta^{13}C$ = 4 ppb
1 ‰ $\delta^{18}O$ = 2 ppb

Region: 2085-2300 cm^{-1}

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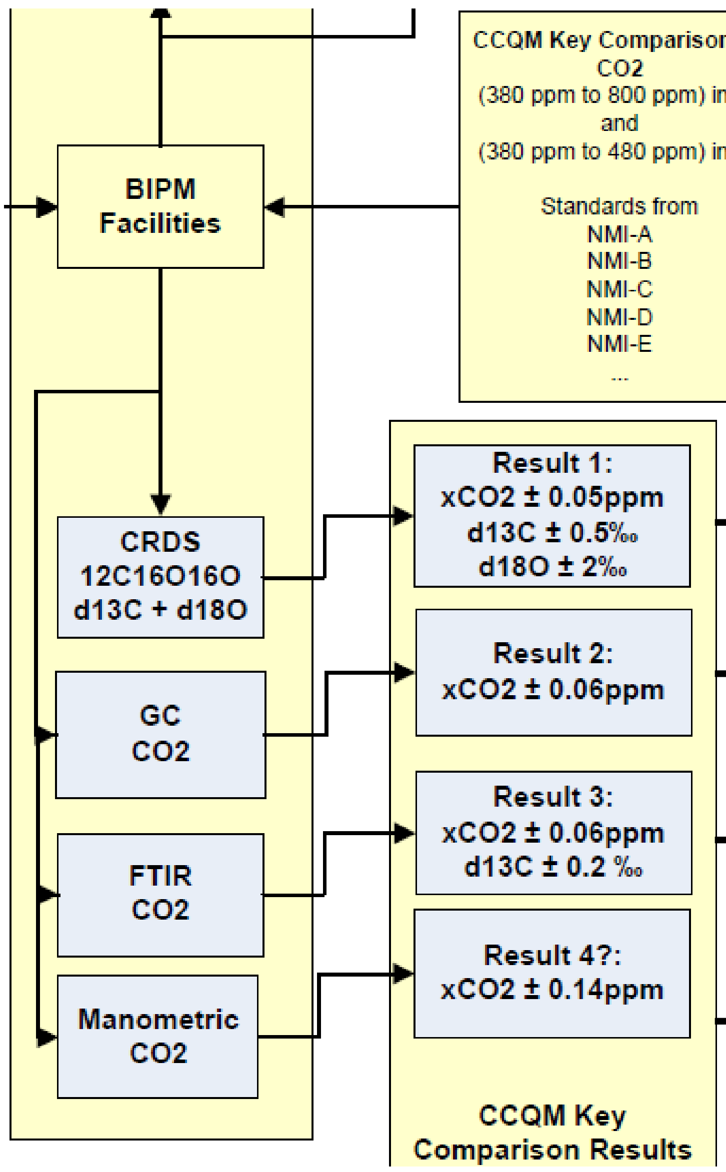
Preparing for the repeat ambient CO_2 in air key comparison (2015)

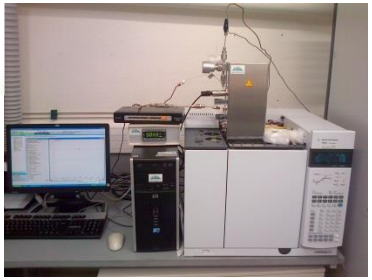


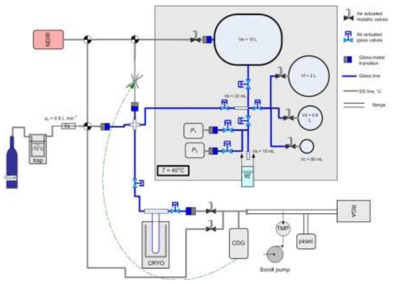
Preparation for CCQM-K120 (2015)

Coordinated by: BIPM/NIST

BIPM comparison facilities

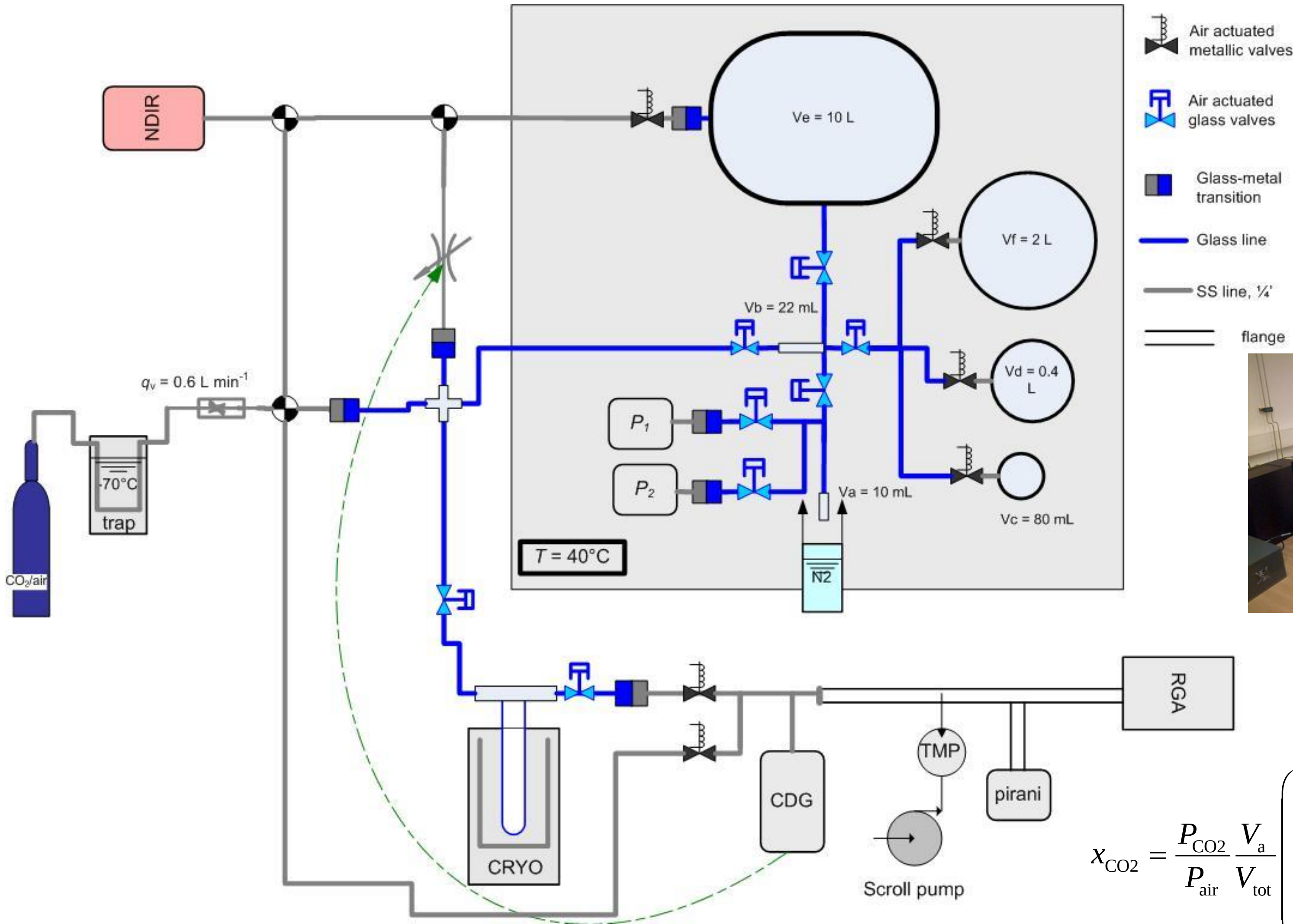
Isotope ratio measurements for corrections to CO_2 concentration measurements required at the ± 1 ‰ level





Preparing for the repeat ambient CO_2 in air key comparison (2015)

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



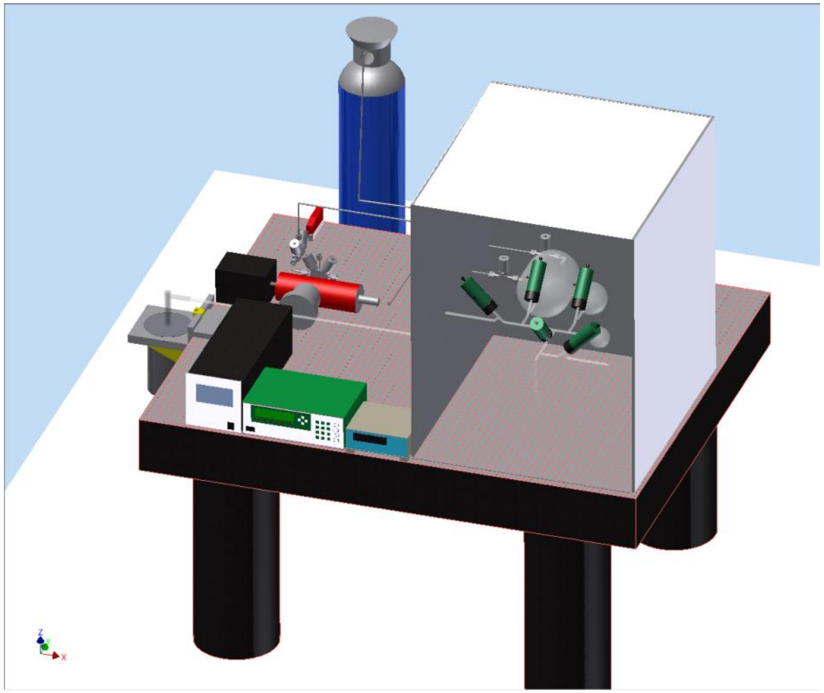
$$x_{CO2} = \frac{P_{CO2}}{P_{air}} \frac{V_a}{V_{tot}} \left(\frac{T_{air}}{T_{CO2}} \frac{1+\dfrac{B_{air}\left(T_{air}\right)P_{air}}{RT_{air}}}{1+\dfrac{B_{CO2}\left(T_{CO2}\right)P_{CO2}}{RT_{CO2}}} \right)$$

Preparing for the repeat ambient CO_2 in air key comparison (2015)

Preparation for CCQM-K120 (2015)
BIPM comparison facilities

Coordinated by: BIPM/NIST

Manometric System for CO_2



Volume ratio in system
1:1000
Mole fraction ratios (CO_2: air)
1:2500 to 1:1000

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

Preparing for the repeat ambient CO_2 in air key comparison (2015)

Preparation of Validation Standards (Mole fraction)

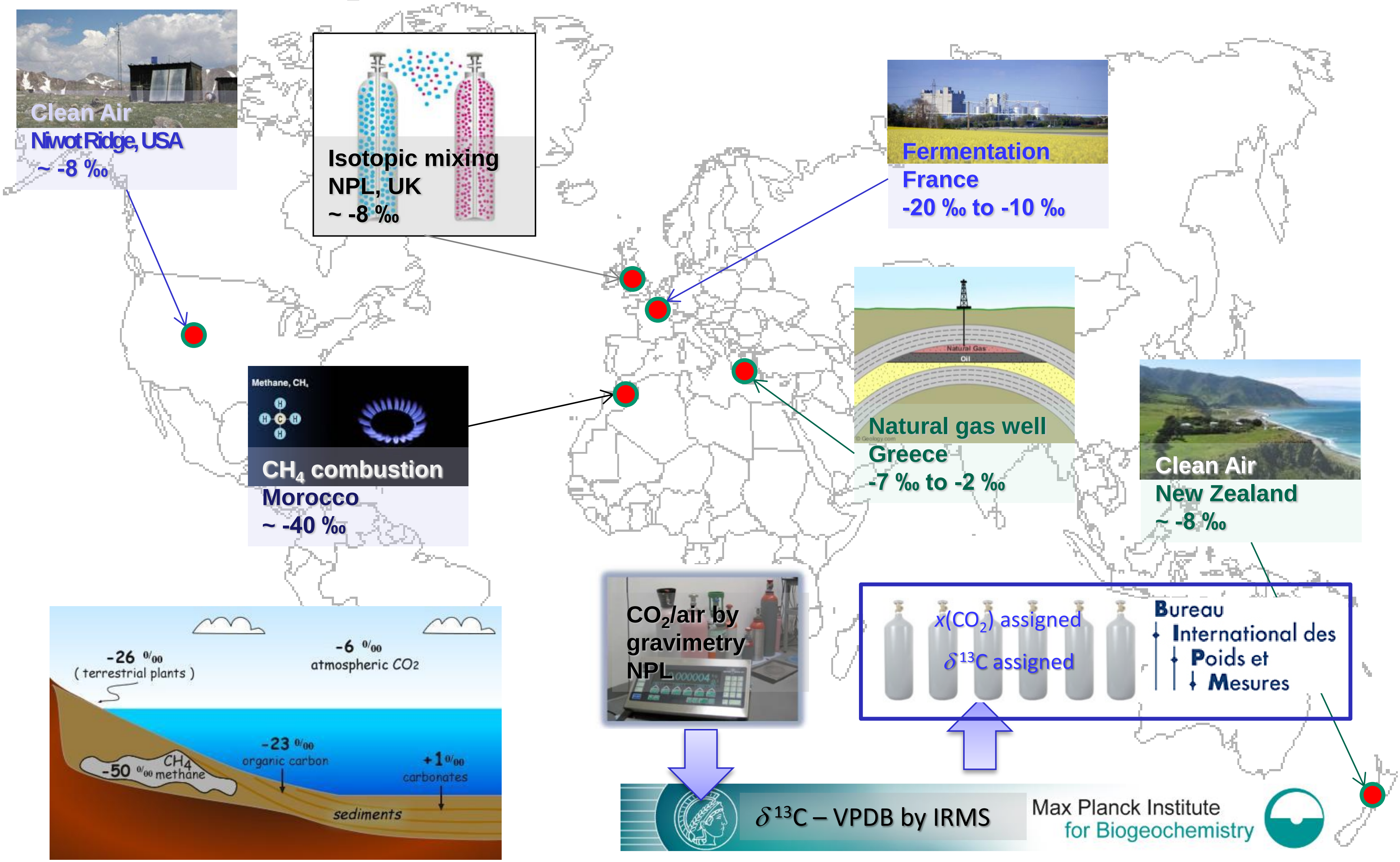
CO_2 Mole Fraction	CH_4 Mole fraction	N_2O mole fraction	Balance Gas*
380 ppm	1850 ppb	< 1ppb	Cryogenic Ultra-Pure Air
400 ppm	1850 ppb	< 1ppb	Cryogenic Ultra-Pure Air
425 ppm	1850 ppb	< 1ppb	Cryogenic Ultra-Pure Air
450 ppm	1850 ppb	< 1ppb	Cryogenic Ultra-Pure Air
500 ppm	1850 ppb	< 1ppb	Cryogenic Ultra-Pure Air
650 ppm	1850 ppb	< 1ppb	Cryogenic Ultra-Pure Air
800 ppm	1850 ppb	< 1ppb	Cryogenic Ultra-Pure Air
380 ppm	1850 ppb	325 ppb	Cryogenic Ultra-Pure Air
400 ppm	1850 ppb	325 ppb	Cryogenic Ultra-Pure Air
425 ppm	1850 ppb	325 ppb	Cryogenic Ultra-Pure Air

Standards prepared: October 2013; Value assigned by NIST July 2014;

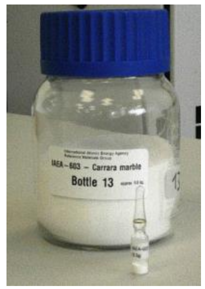
Subset sent to MPI BGC JENA for isotope ratio measurement (August 2014)

Validation standards with a range of isotopic compositions

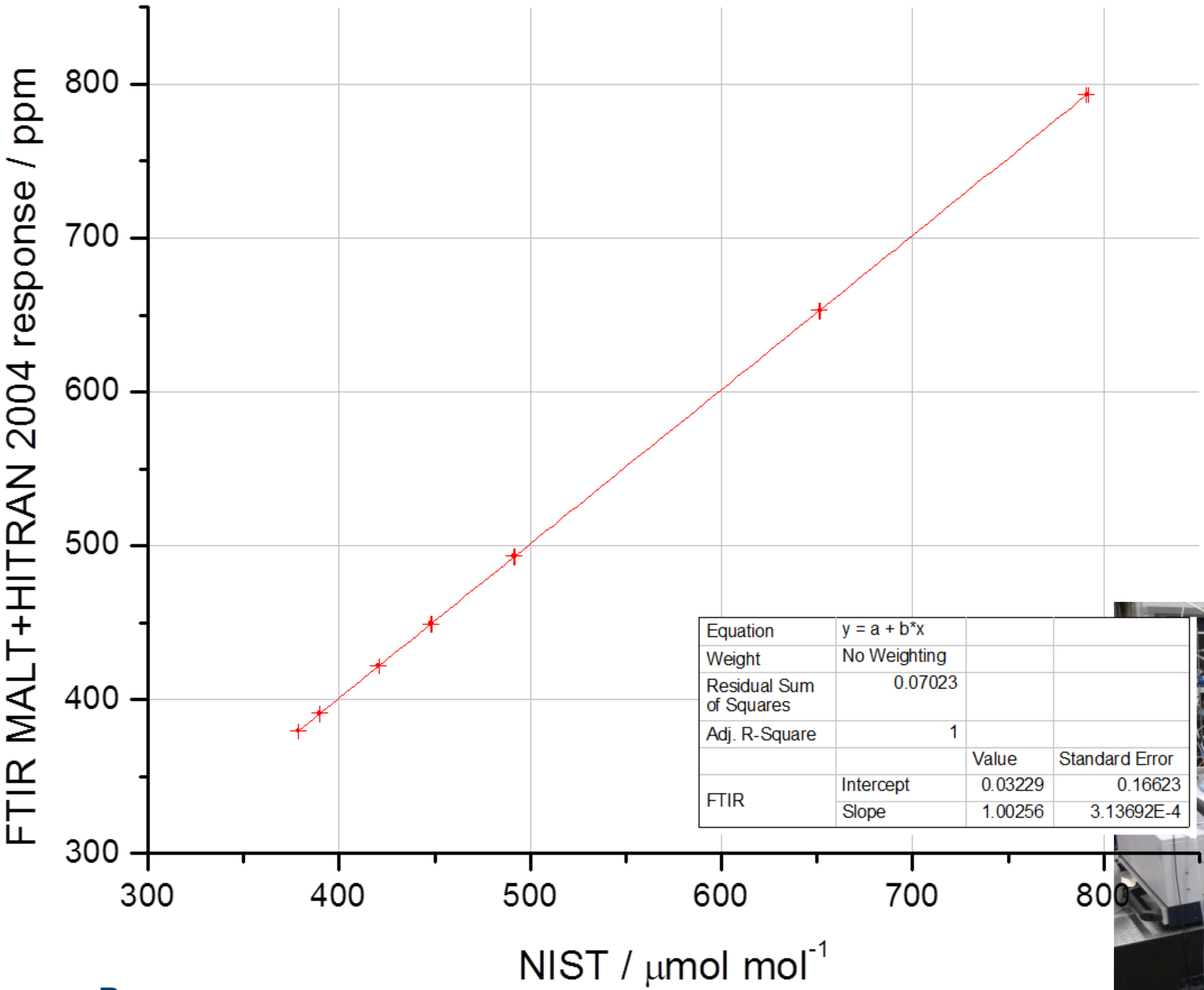
Selected pure CO_2 sources to span $\delta^{13}C$ in set of gravimetric standards



IAEA-BIPM Collaboration
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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W. Brand (MPI-JENA)