

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

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HIGHGAS Stakeholder Workshop,
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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

CIPM Mutual Recognition Arrangement

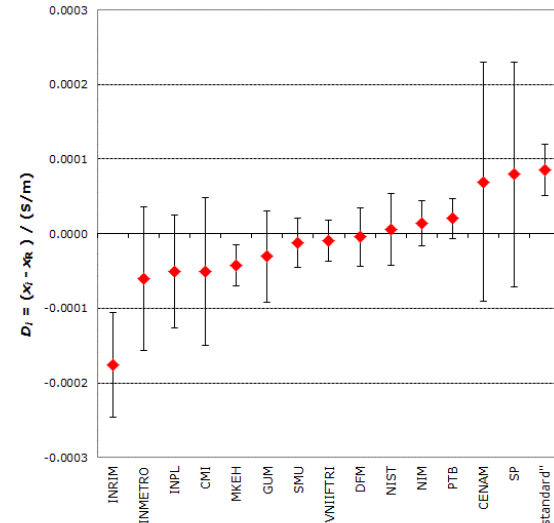
Definition



Realization



Comparisons



Dissemination



BAM **ERM**

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

Certified Values	
Compound	Certified value ¹⁾
Mass fraction in %	
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[b]fluoranthene	3.6
Benzo[k]fluoranthene	2.25
Benzo[e]pyrene	4.35
Dibenz[a,h]anthracene	0.67
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 triplicate (and/or quadruplicate) measurements. The values are traceable to the SI through calibration using sufficiently pure substances.

²⁾ Estimated expanded uncertainty U with a coverage factor of about 1.96 (confidence of 95 %), as defined in the GUM to the expression of uncertainty in measurement.

National Institute of Standards & Technology

Certificate of Analysis
Standard Reference Material
Carbon Dioxide in Nitrogen
(Nominal Amount-of-Substance Fraction = 1)

This certificate reports the certified values for Carbon Dioxide in Nitrogen.

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

This SRM mixture is supplied in a DOT 3AL specification aluminum (0041) 40 L cylinder with a nominal pressure according to 2.4 MPa (34.7 psia) (25.8 MPa) of usable mixture. The cylinder is the property of the purchaser and is to be returned to NIST in accordance with the terms of the purchase order.

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

Carbon Dioxide Concentration: 1.4594 to method ± 0.0001 (100 %)

Cylinder Number: NIST Sample

The uncertainty of the certified value includes the estimated uncertainties associated with the lot standard (1.2), and the uncertainty of comparing the lot standard to the SRM (1.1). The values are traceable to the SI through calibration using sufficiently pure substances.

Expiration of Certification: This certification is valid until 31 July 2009, provided the SRM is handled and stored in accordance with the terms of the certificate. This certification will be nullified if the SRM is contaminated or modified.

CERTIFICATE OF ANALYSIS
ERM[®]-CE278

MUSSEL TISSUE
Mass fraction (on dry mass basis)

Parameter	Mass fraction (on dry mass basis)	
	Certified value ¹⁾	Uncertainty ¹⁾
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	7.89	0.23
Hg	2.00	0.04
Se	1.94	0.10
Zn	83.1	1.7

¹⁾ Certified values are calculated means of 10 to 15 test sets (one multiplier report). Certified values represent data corrected. Certified values are traceable to SI through calibration using sufficiently pure substances.

²⁾ The certified uncertainty is the half-width of the 95% confidence interval; the mass defined in % is a fraction value chosen according to the definition of the parameter. The number of test sets of which are reported from 10 to 15.

This certificate is valid until 4/2007. This validity may be extended as further evidence of stability becomes available.

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

Essential Climate Variables



: 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 N₂O, CFCs, HCFCs, HFCs, SF₆ and PFCs.

¹¹ In particular NO₂, SO₂, 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 ₂ O	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, CH₄ in air**)

Matrix: real air scrubbed of methane



NPL
National Physical Laboratory



NIST

KRIS

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



NMIJ

ВНИИМ
Федеральное государственное учреждение
"ВНИИМ им. А.А. Бабкинского
Федерального государственного метрологического научно-исследовательского центра"

VSL
Dutch
Metrology
Institute



BIPM analytical instruments
under repeatability conditions



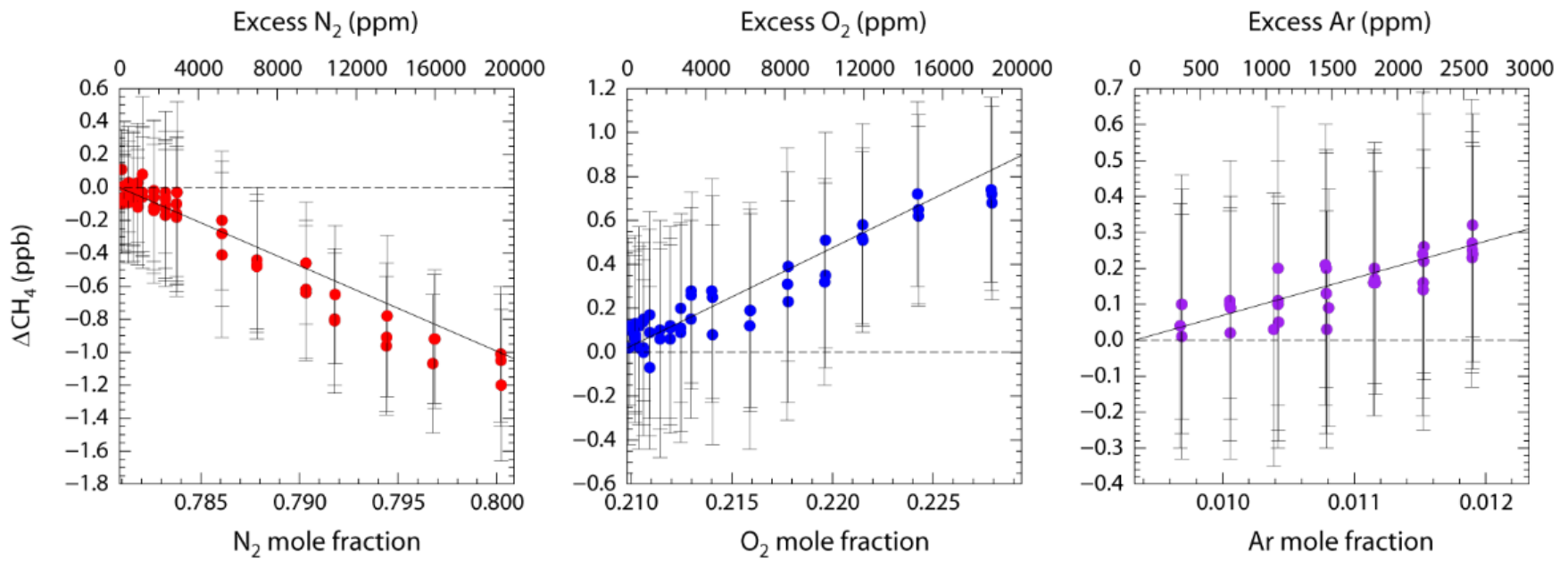
*Analysis made by cavity ring
down spectroscopy and
gas chromatography-flame
ionization detector*

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.



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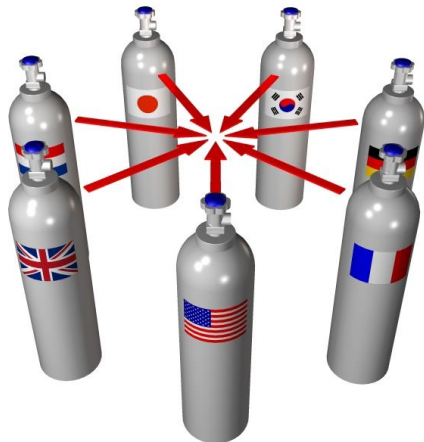
CRDS measurements and matrix gas composition

Target mole fractions:

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

Matrix composition

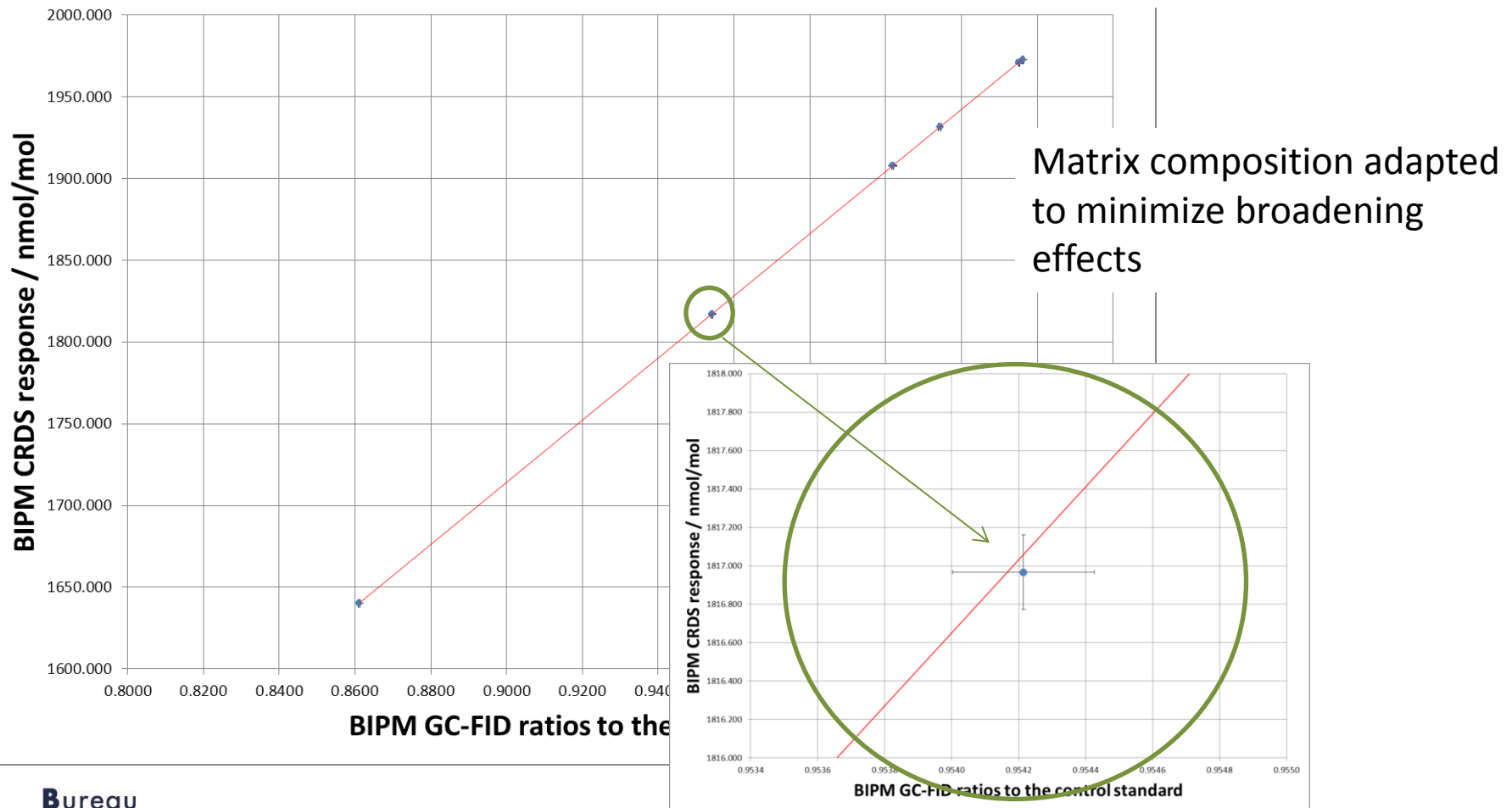
To minimize pressure broadening effects



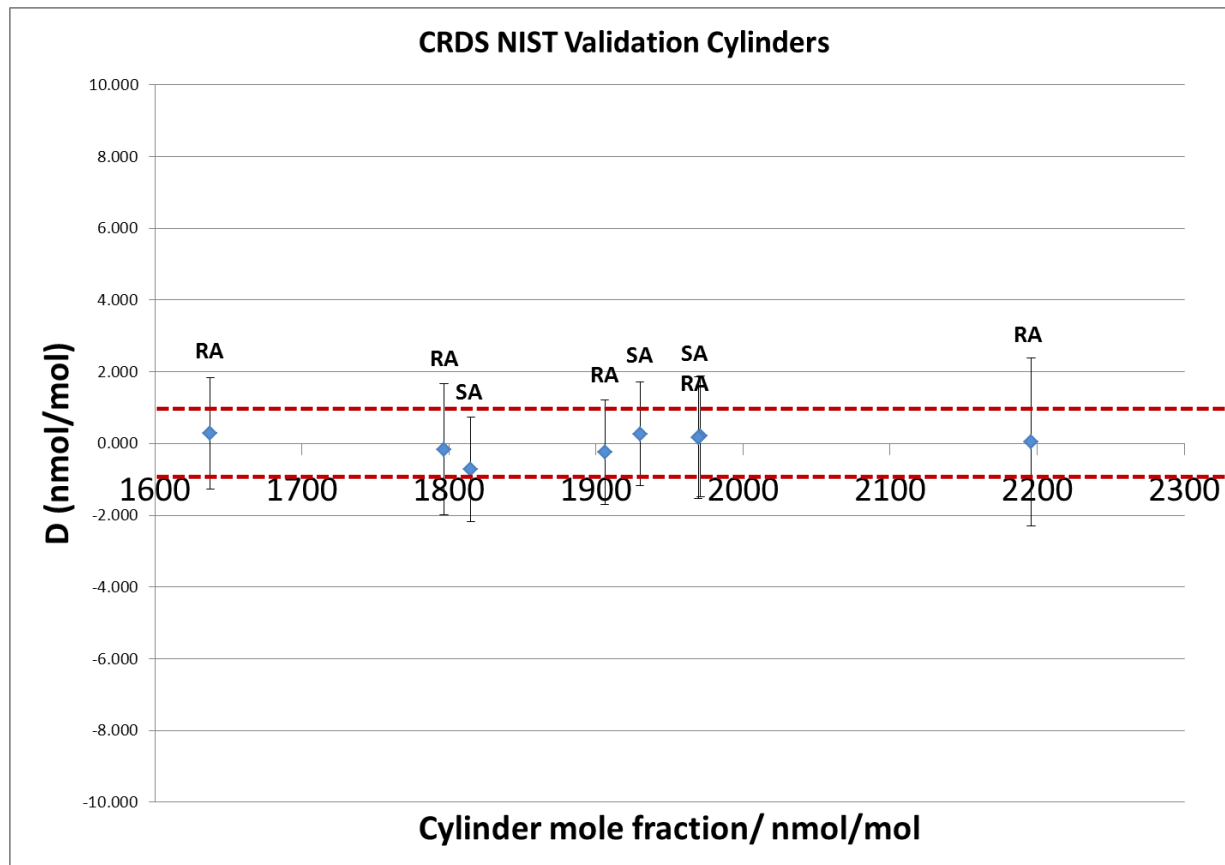
Component in Air	Minimum mole fraction permitted within submitted cylinder	Maximum mole fraction permitted within submitted cylinder
Nitrogen	0.77849 mol/mol	0.78317 mol/mol
Oxygen	0.20776 mol/mol	0.21111 mol/mol
Argon	8.865 mmol/mol	9.799 mmol/mol
Carbon Dioxide	360 μ mol/mol	400 μ mol/mol

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

Validation of method using NIST real air and synthetic air standards

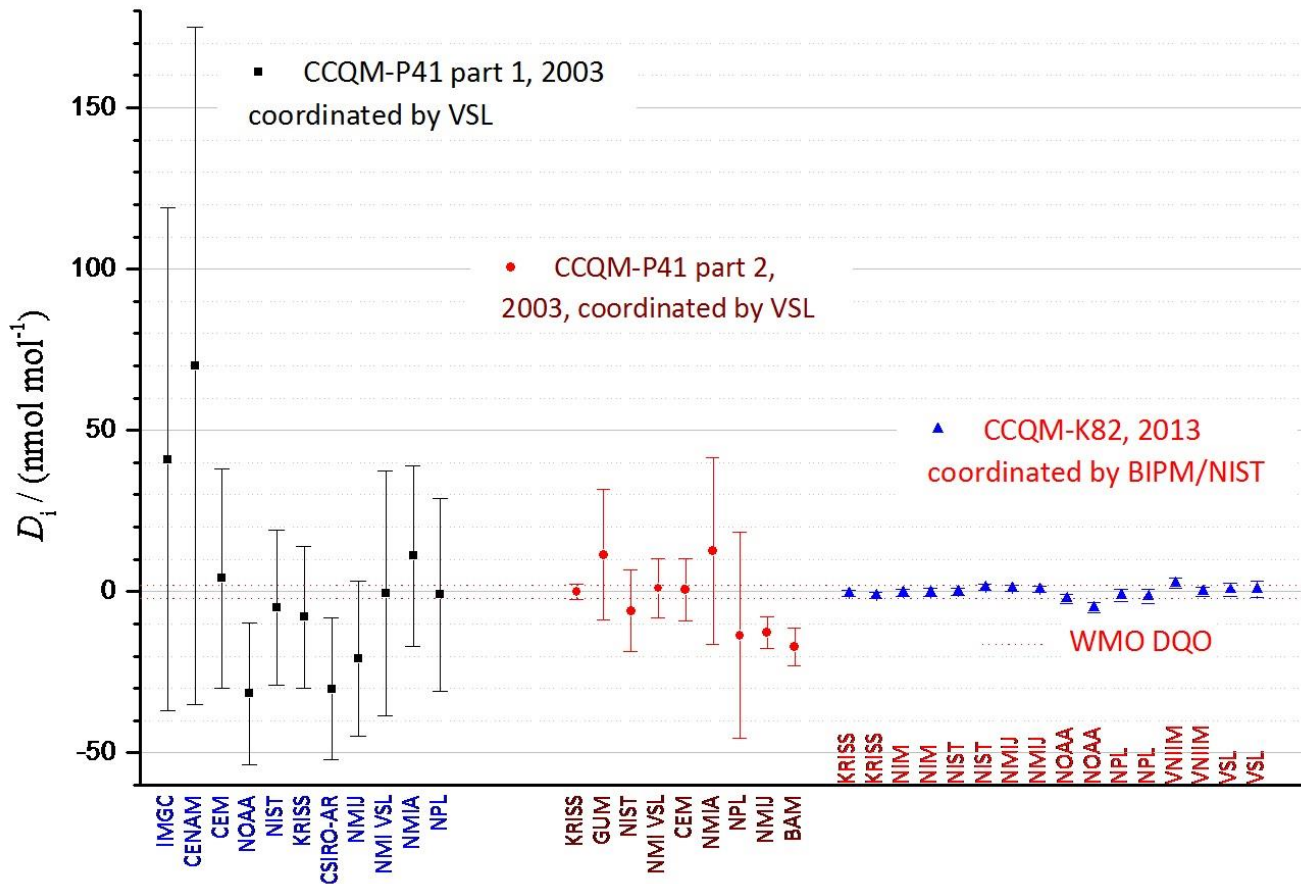


Validation of BIPM's Measurements facility with NIST standards



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

Improvements in global compatibility of methane in air standards



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Comparison results vs. Data Compatibility Goals

DQO = ± 2 nmol/mol

For CCQM-K82:

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

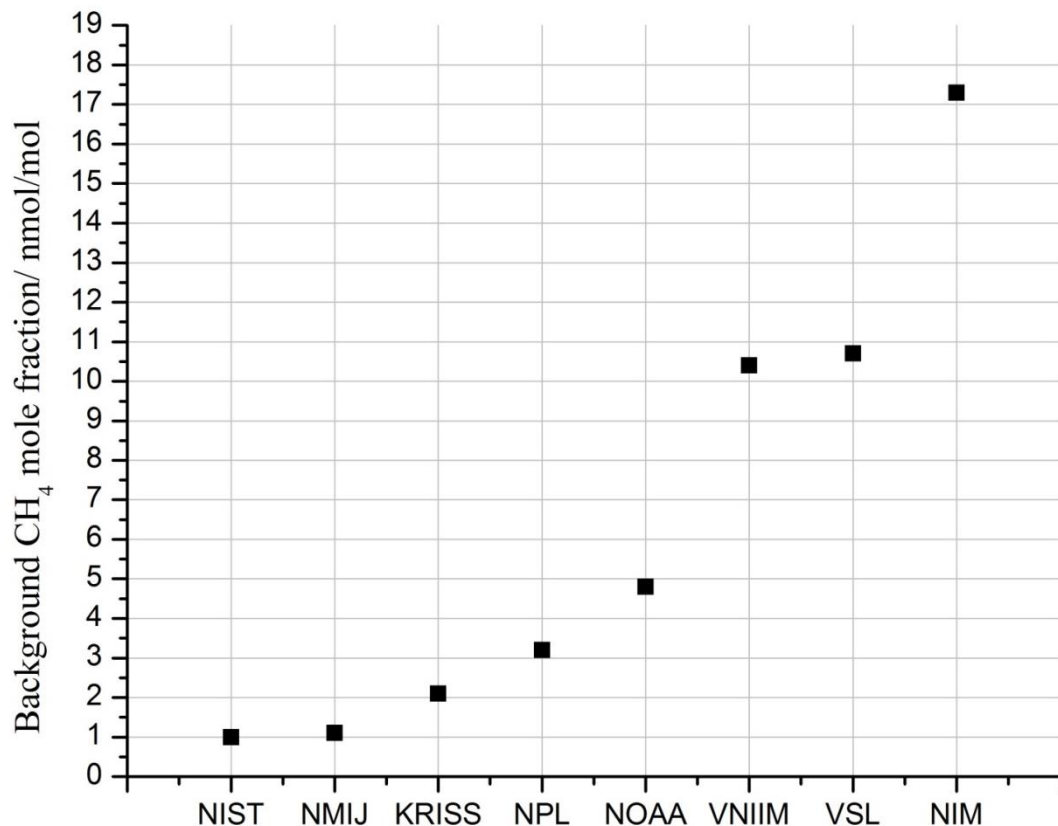
$\sigma_{(\text{CCQM-K82})} = 1.17$ nmol/mol

Negligible impact of standards when:

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

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

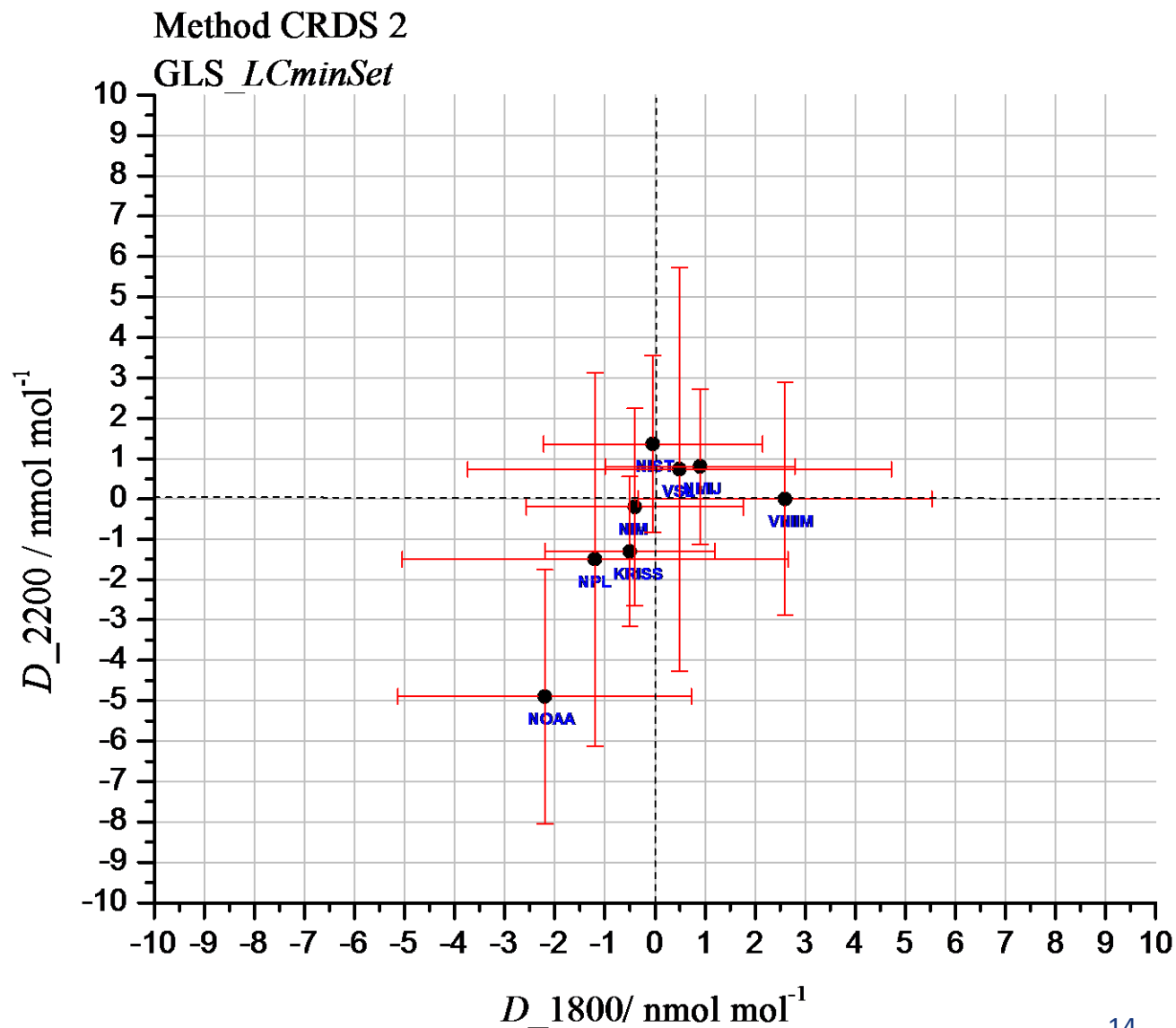
Development for future improvements in CH₄ in air standards



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

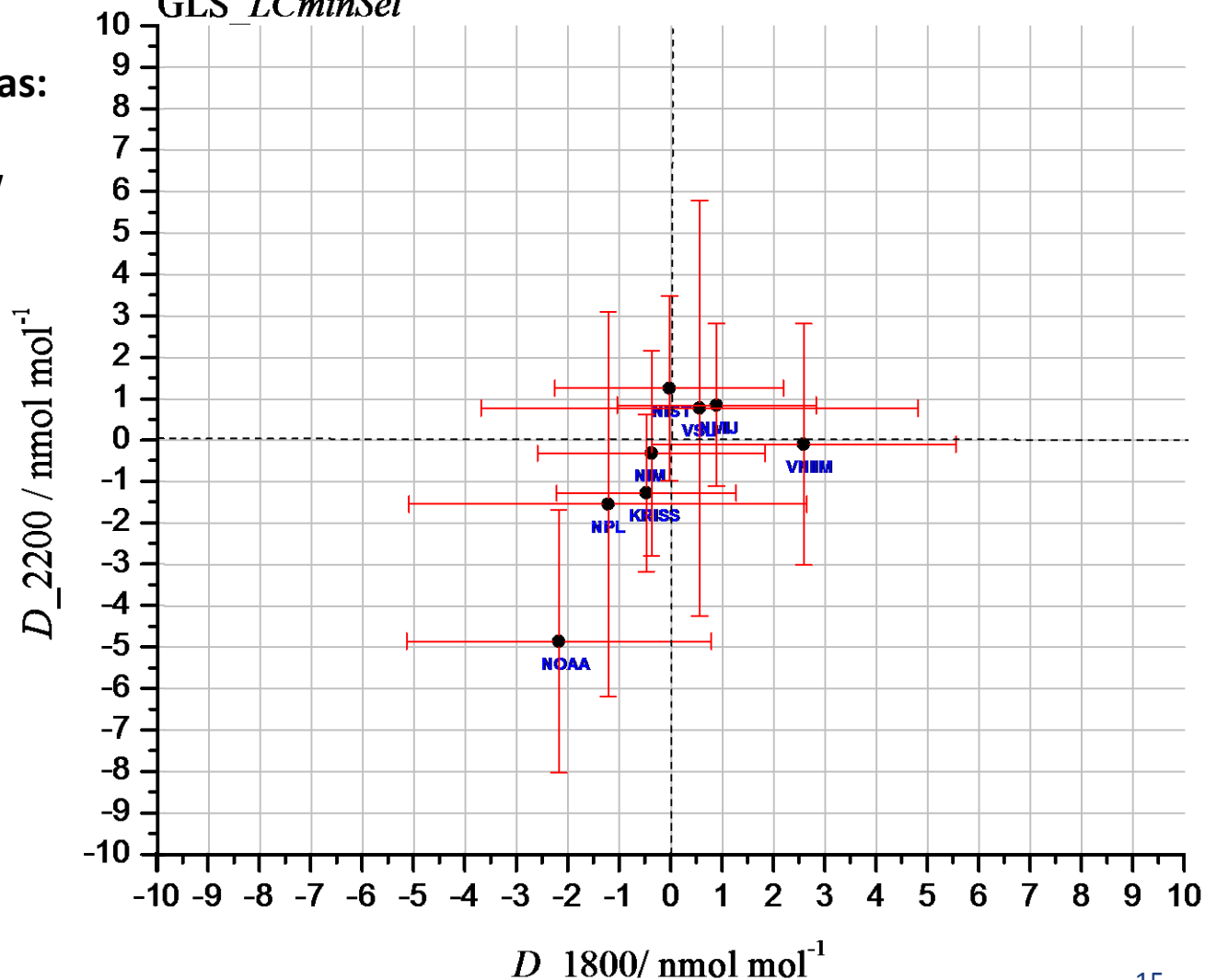
CCQM-K82 results accounting potential isotope ratio variation in CH₄



CCQM-K82 results including uncertainty component for potential isotope ratio variation in CH₄

Method CRDS 2 **Isot**

GLS *LCminSet*



Pure methane from natural gas:

$-(43 \pm 7) \text{‰}$ for $\delta^{13}\text{C}$ (VPDB);

$-(185 \pm 20) \text{‰}$ for δD (VSMOW)

Bias in the CRDS:

+0.34 nmol/mol and

-0.38 nmol/mol;

Uncertainty component

$u_{\delta} = 0.21 \text{ nmol/mol}$

Preparing for the repeat ambient CO₂ 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

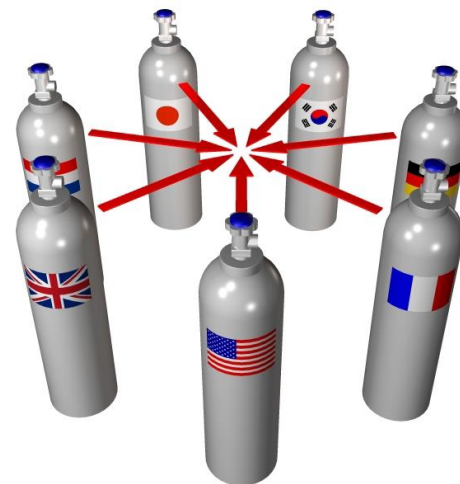
CO₂ in air (380 μmol/mol to 480 μmol/mol)

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

CCQM-K120.b

CO₂ in air (380 μmol/mol to 800 μmol/mol)

Matrix : Air composition within 1% of atmospheric balance gases



Preparing for the repeat ambient CO₂ in air key comparison (2015)

Previous comparison: CCQM-K52 (2006)

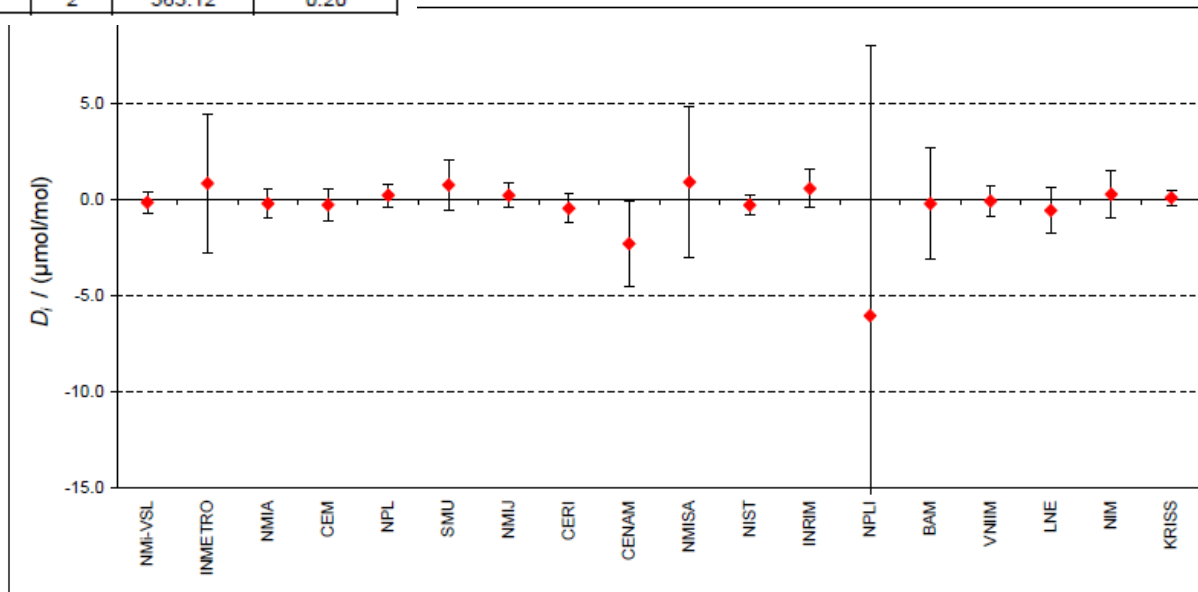
Coordinated by: VSL

Lab <i>i</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

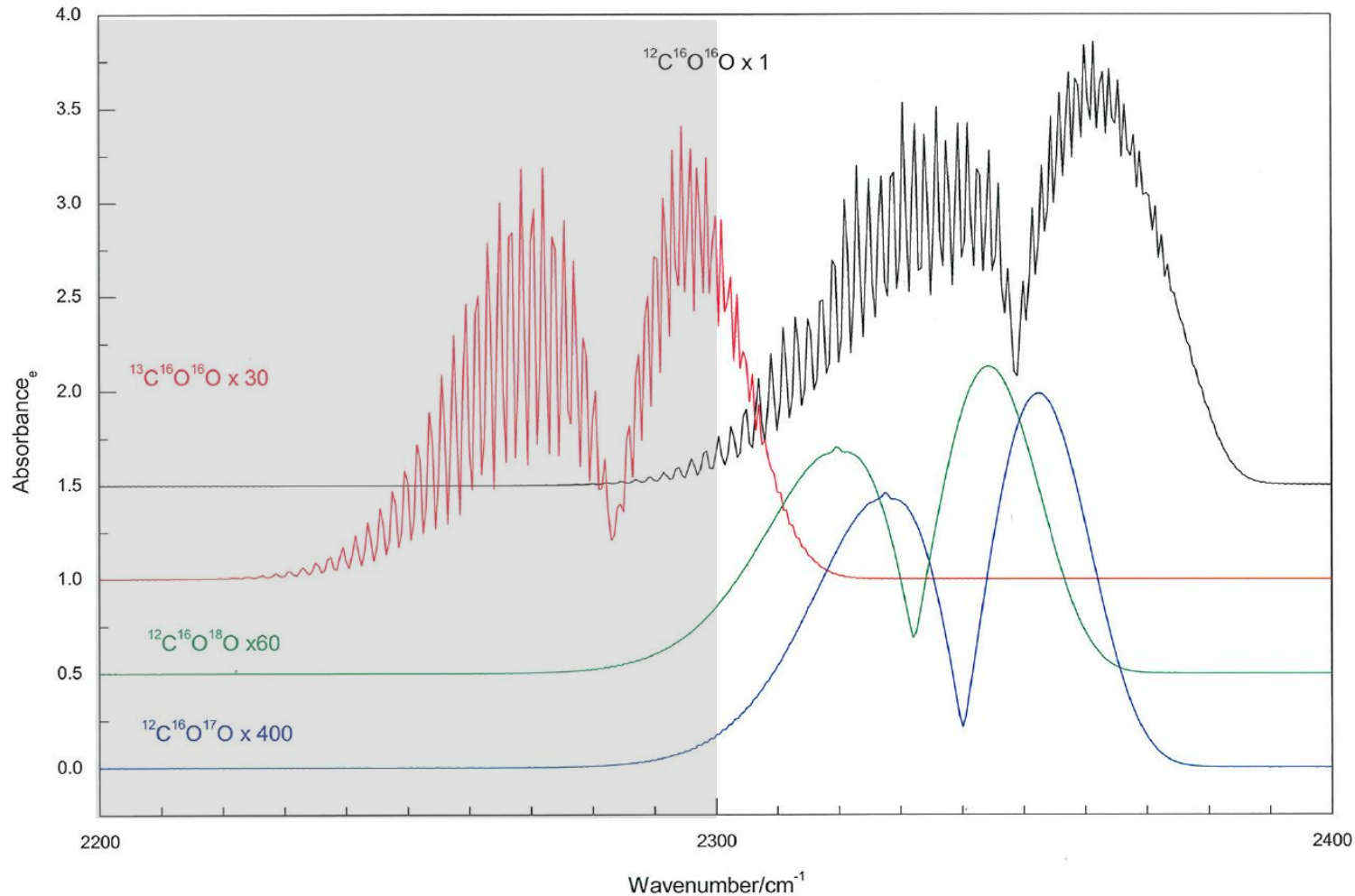
Results show good agreement, but...

Uncertainties on all standards > DQO for ambient monitoring community

CCQM-K52
Reference for CO₂ in synthetic air at nominal value 360 μmol/mol



Measuring mole fractions of CO₂ isotopologues



Target relative
standard
uncertainty
 $u(x) < 0.01\%$

1 ‰ $\delta^{13}\text{C}$ = 4 ppb

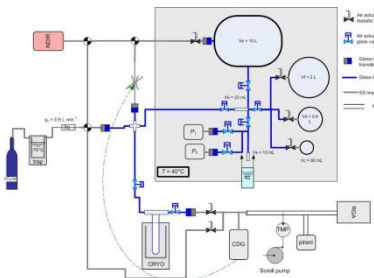
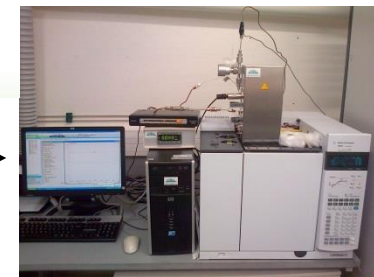
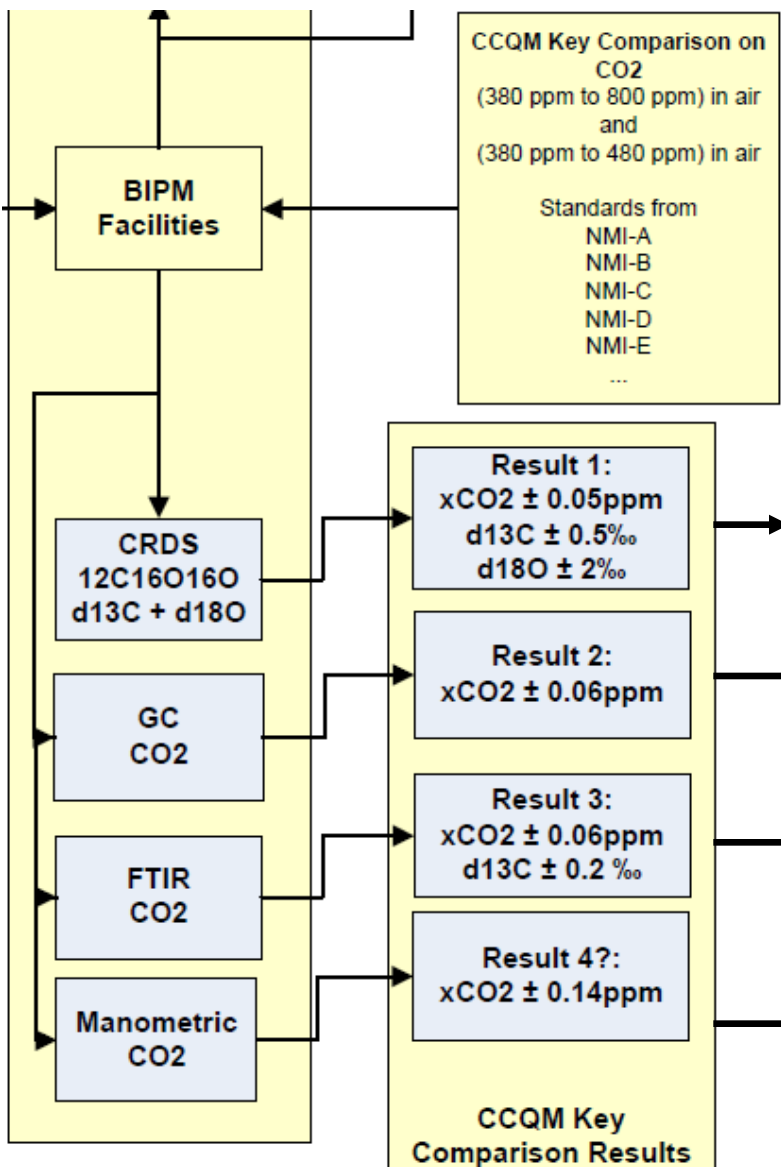
1 ‰ $\delta^{18}\text{O}$ = 2 ppb

Preparing for the repeat ambient CO₂ in air key comparison (2015)

Preparation for CCQM-K120 (2015)

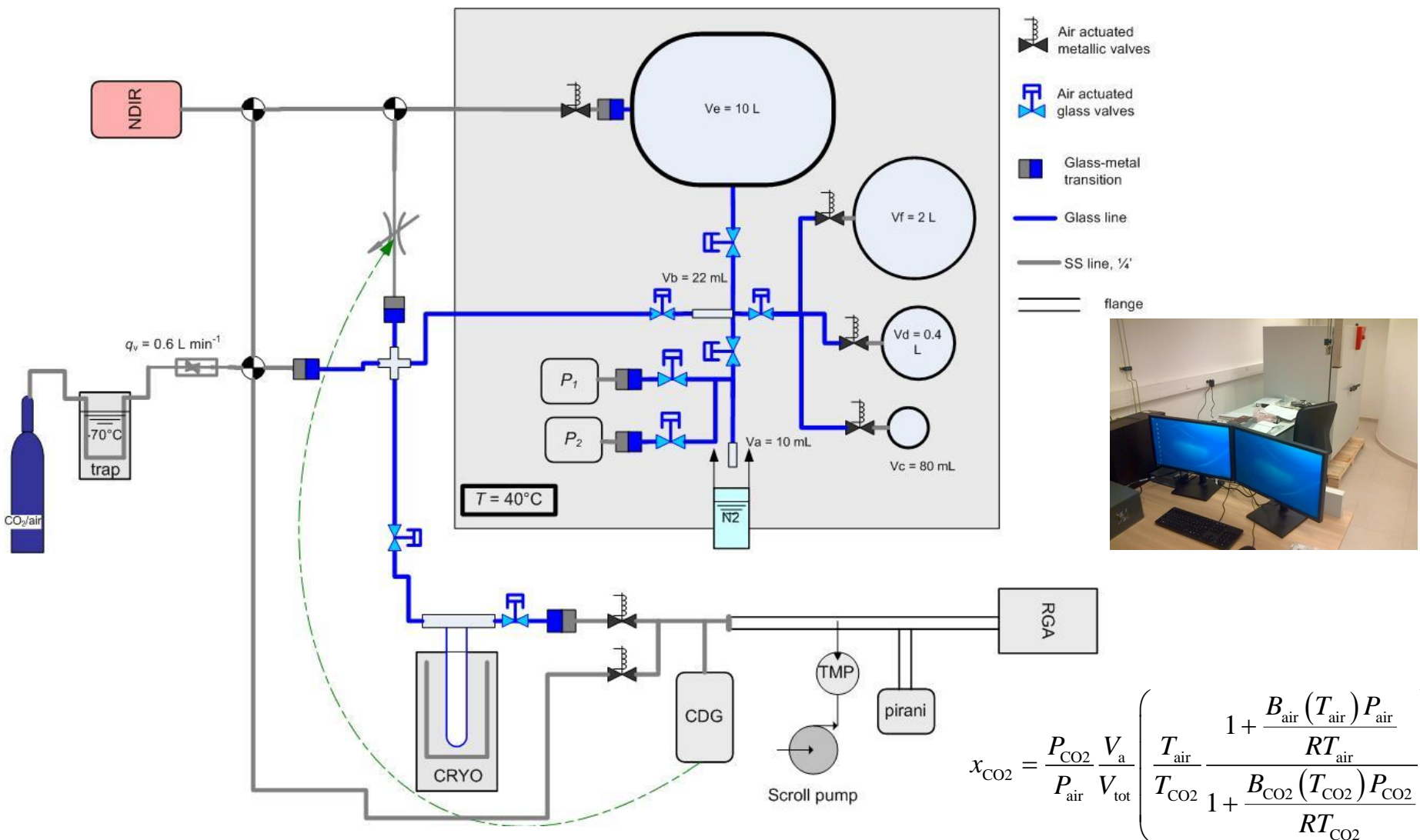
Coordinated by: BIPM/NIST
BIPM comparison facilities

Isotope ratio measurements for corrections to CO₂ concentration measurements required at the ± 1 ‰ level



Preparing for the repeat ambient CO₂ in air key comparison (2015)

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



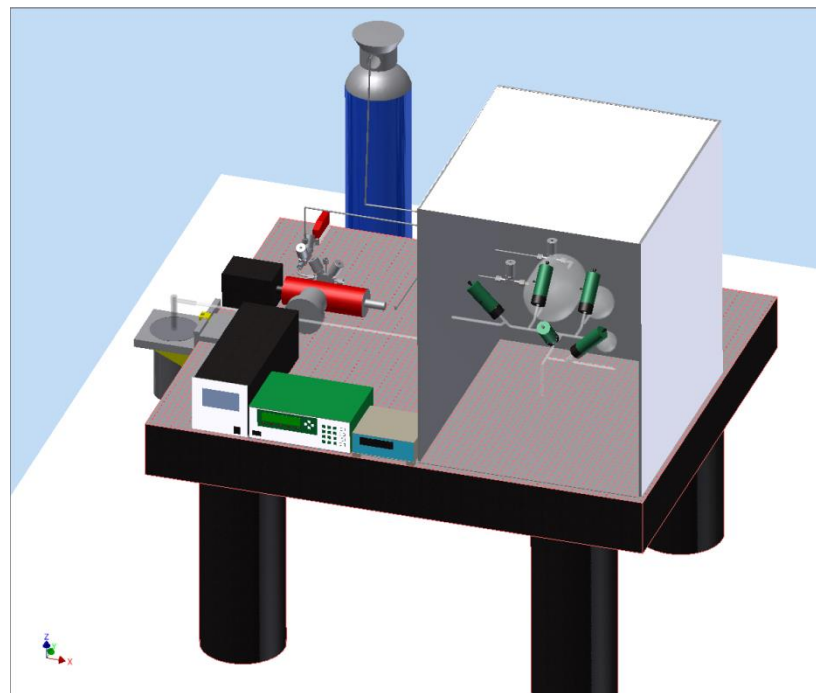
$$x_{\text{CO}_2} = \frac{P_{\text{CO}_2}}{P_{\text{air}}} \frac{V_a}{V_{\text{tot}}} \left(\frac{T_{\text{air}}}{T_{\text{CO}_2}} \frac{1 + \frac{B_{\text{air}}(T_{\text{air}})P_{\text{air}}}{RT_{\text{air}}}}{1 + \frac{B_{\text{CO}_2}(T_{\text{CO}_2})P_{\text{CO}_2}}{RT_{\text{CO}_2}}} \right)$$

Preparing for the repeat ambient CO₂ in air key comparison (2015)

**Preparation for CCQM-K120 (2015)
BIPM comparison facilities**

Coordinated by: BIPM/NIST

Manometric System for CO₂



Volume ratio in system

1:1000

Mole fraction ratios (CO₂: air)

1:2500 to 1:1000

$$x_{\text{CO}_2} = \frac{P_{\text{CO}_2}}{P_{\text{air}}} \frac{V_a}{V_{\text{tot}}} \left(\frac{T_{\text{air}}}{T_{\text{CO}_2}} \frac{1 + \frac{B_{\text{air}}(T_{\text{air}})P_{\text{air}}}{RT_{\text{air}}}}{1 + \frac{B_{\text{CO}_2}(T_{\text{CO}_2})P_{\text{CO}_2}}{RT_{\text{CO}_2}}} \right)$$

Preparing for the repeat ambient CO₂ in air key comparison (2015)

Preparation of Validation Standards (Mole fraction)

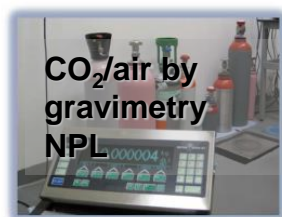
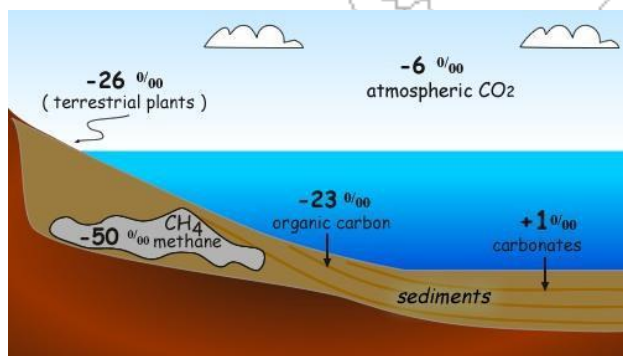
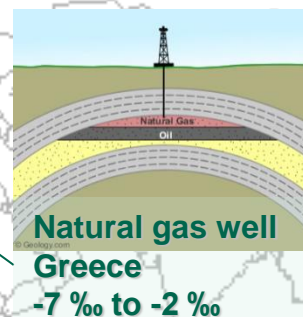
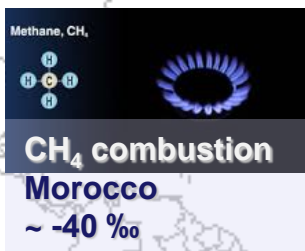
CO ₂ Mole Fraction	CH ₄ Mole fraction	N ₂ O mole fraction	Balance Gas*
380 ppm	1850 ppb	< 1ppb	Cryogenic Ultra-Pure Air
400 ppm	1850 ppb	< 1ppb	Cryogenic Ultra-Pure Air
425 ppm	1850 ppb	< 1ppb	Cryogenic Ultra-Pure Air
450 ppm	1850 ppb	< 1ppb	Cryogenic Ultra-Pure Air
500 ppm	1850 ppb	< 1ppb	Cryogenic 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 CO₂ sources to span $\delta^{13}\text{C}$ in set of gravimetric standards



$\delta^{13}\text{C}$ – VPDB by IRMS

Max Planck Institute
for Biogeochemistry



IAEA-BIPM Collaboration

IAEA Workshop on Stable Isotopes (3-5 Sept 2014)

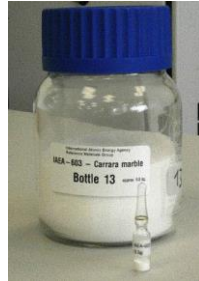
Organization

Quantity and types of standard

Calibrated/Measurement Instrument



$\delta^{13}\text{C}$
 $\delta^{18}\text{O}$



Carbonates



Pure CO₂



Mass Spec.

Max Planck Institute
for Biogeochemistry



$\delta^{13}\text{C}$
 $\delta^{18}\text{O}$



CO₂ from carbonates in real air



Mass Spec.

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CO₂ mole fraction
($\delta^{13}\text{C}$, $\delta^{18}\text{O}$)
CCQM-K120

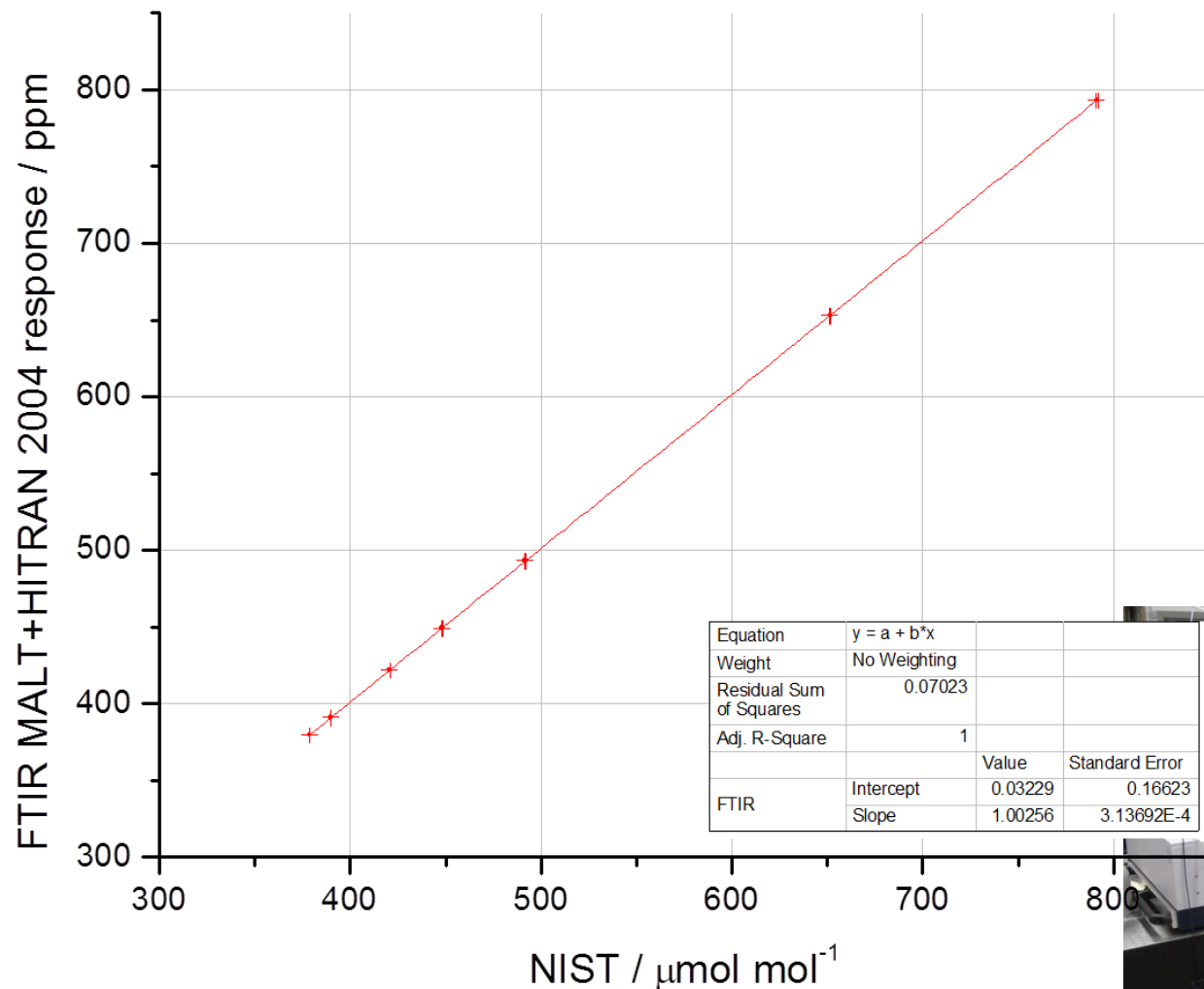


CO₂ in real/synthetic air

Optical Spectroscopic methods



Comparisons of CO₂ standards with FTIR



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



Acknowledgements

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W. Brand (MPI-JENA)