Calibration methods for IRIS instruments for high precision measurements of $\delta^{13}C$ and $\delta^{18}O$ in CO_2

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Developments in Isotope Ratio Measurements for Gas Analysis Workshop
METAS, Berne, Switzerland | 10 October 2019

Bureau International des Poids et Mesures

International comparison CCQM-K120 (2017)

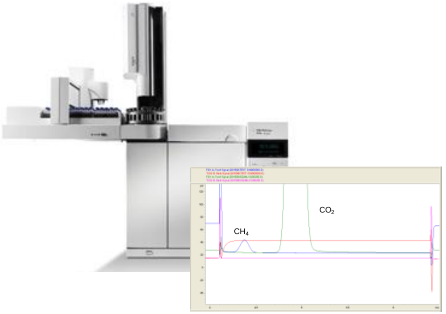
Measuring accurate CO_2 mole fraction for CCQM-K120

Coordinated by BIPM

GC-FID

$x(CO_2)$ (300 to 850) μmol mol^{-1}

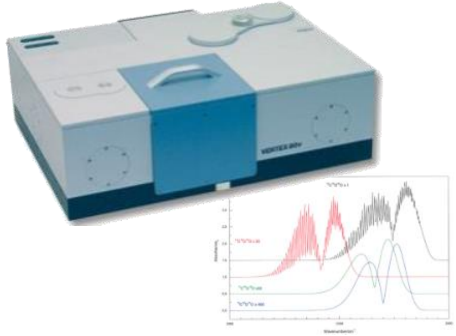
$\sigma = 0.04$ μmol mol^{-1}



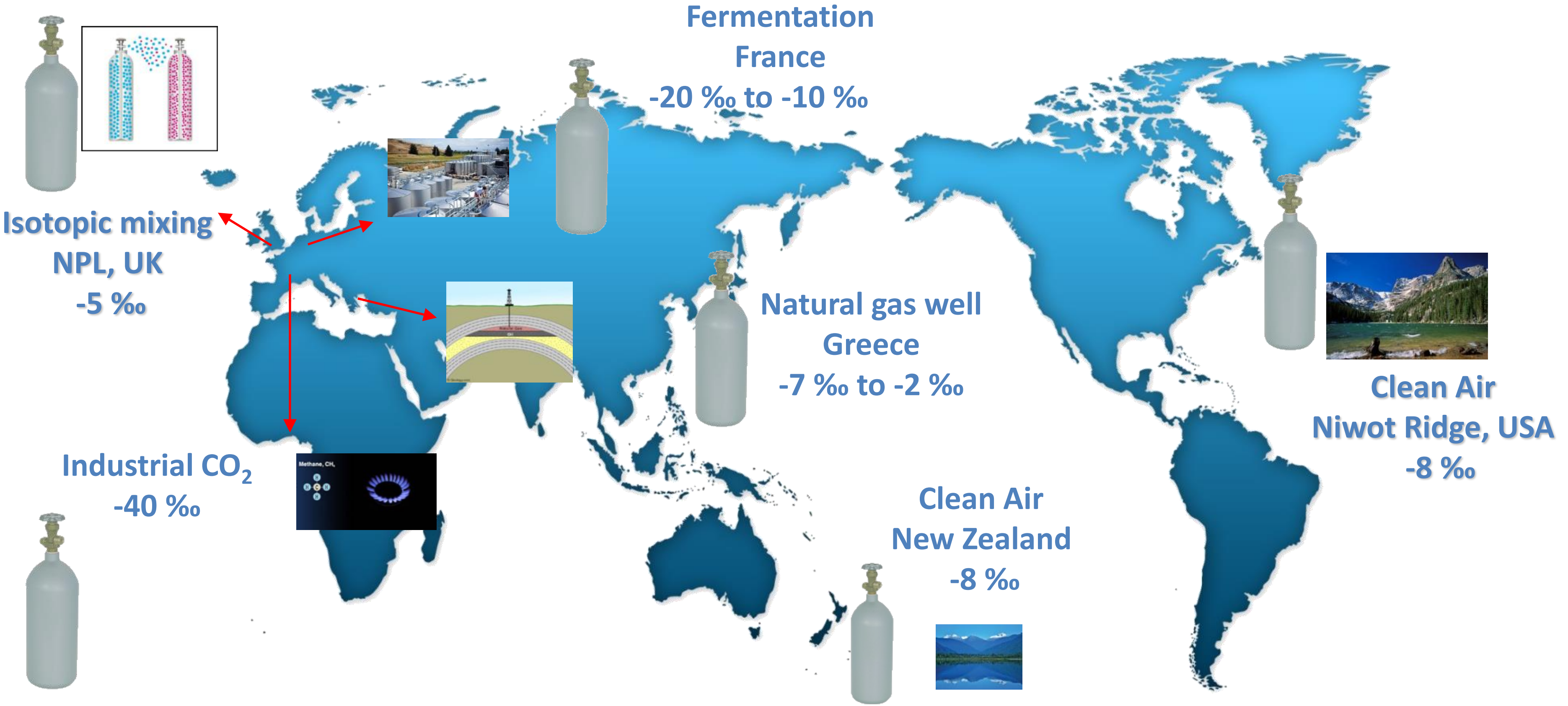
FTIR

$x(CO_2)$ (300 to 850) μmol mol^{-1}

$\sigma = 0.02$ μmol mol^{-1}

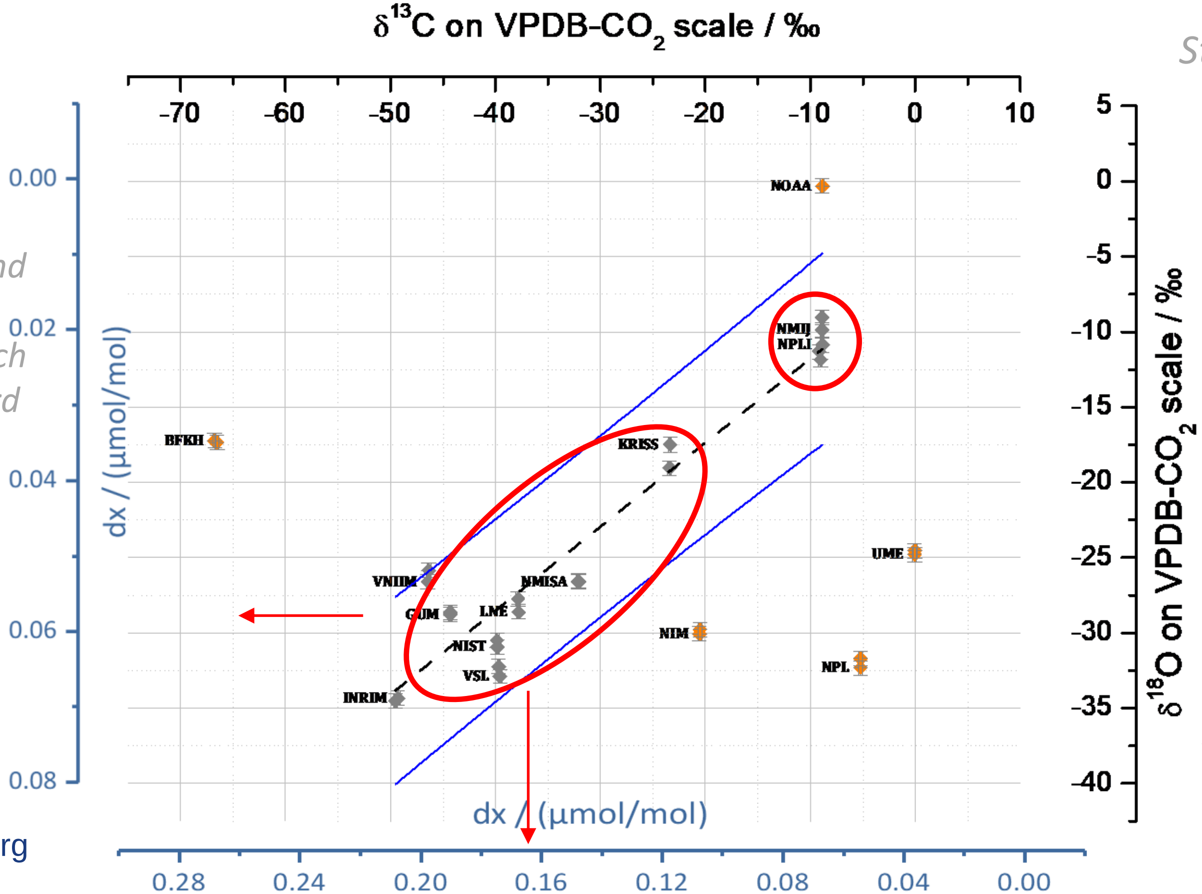


International comparison CCQM-K120 (2017)



Measured δ^{13}C and δ^{18}O in CCQM-K120 standards

Standards of 15 NMI's

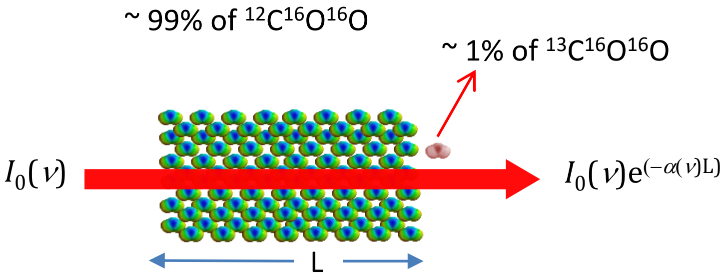


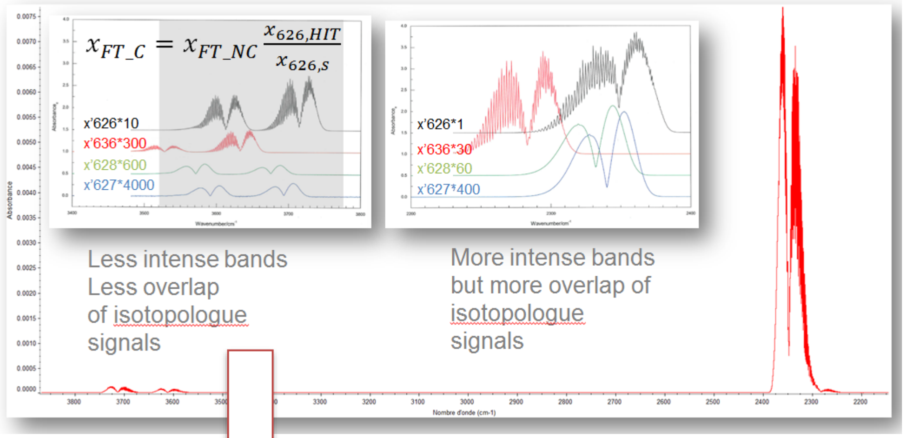
Measured δ^{13}C and δ^{18}O values, vs VPDB-CO_2, for each CO_2 in air standard studied. Blue: prediction bands from selected set of standards.

Isotope Ratio Infrared Spectroscopy - FTIR

CO_2 in air

Measuring CO_2 isotopes by Infrared Spectroscopy





$$R^{13} = \frac{x_{636}}{x_{626}}$$

$$R^{18} = \frac{x_{628}}{x_{626} * 2}$$

636 is $^{13}C^{16}O^{16}O$
626 is $^{12}C^{16}O^{16}O$
628 is $^{12}C^{18}O^{16}O$

Conversion to delta scale

$$\delta^{13}C = \left(\frac{R^{13}}{R^{13}_{VPDB-CO_2}} - 1\right)$$

$$\delta^{18}O = \left(\frac{R^{18}}{R^{18}_{VPDB-CO_2}} - 1\right)$$

Requires standards of known isotopic composition

Mole fractions, ratios and delta values

$$\delta^{13}C = \left(\frac{R^{13}}{R^{13}_{VPDB-CO_2}} - 1\right)$$

$$\delta^{18}O = \left(\frac{R^{18}}{R^{18}_{VPDB-CO_2}} - 1\right)$$

Delta values allow small differences in isotope ratios, and thereby mole fractions of isotopes to be readily expressed

Conventional values used for the isotope ratios in CO_2 gas produced from carbonate standard

$R^{13}_{VPDB-CO2}$ = 0.011180

$R^{17}_{VPDB-CO2}$ = 0.0003931

$R^{18}_{VPDB-CO2}$ = 0.00208835

Allows abundances and mole fraction of CO_2 isotopologues to be calculated

IAEA
International Atomic Energy Agency
Atoms for Peace

Max-Planck-Institut
für Biogeochemie

Brand Willi, A.; Assonov Sergey, S.; Coplen Tyler, B. In Pure Appl. Chem., 2010; Vol. 82, pp 1719.

Calibration strategy

Principle : independent two points calibrations of each isotopologue, using standards of same δ^{13}C but different mole fraction to <u>bracket the target sample</u>

$$R^{13} = \frac{x_{636}}{x_{626}}$$

$$R^{18} = \frac{x_{628}}{x_{626}}$$

Ref 1

Max-Planck-Institut für Biogeochemie

$x(CO_2)$ µmol/mol	δ^{13}c ‰ VPDB	δ^{18}O ‰ VPDB
378.90	-35.68	-34.48

x_{626} µmol/mol	x_{636} µmol/mol	x_{628} µmol/mol
373.07	4.02	1.50

Ref 2

Max-Planck-Institut für Biogeochemie

$x(CO_2)$ µmol/mol	δ^{13}c ‰ VPDB	δ^{18}O ‰ VPDB
420.43	-35.68	-34.12

x_{626} µmol/mol	x_{636} µmol/mol	x_{628} µmol/mol
413.96	4.46	1.67

$x(CO_2)$ µmol/mol
393.97

Calibration strategy

Principle : independent two points calibrations of each isotopologue, using standards of same δ^{13}C but different mole fraction to <u>bracket the target sample</u>

$$R^{13} = \frac{x_{636}}{x_{626}}$$

$$R^{18} = \frac{x_{628}}{x_{626}}$$

Ref 1

FTIR

x_{626} x_{636} x_{628}

x_{626} µmol/mol	x_{636} µmol/mol	x_{628} µmol/mol
373.07	4.02	1.50

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FTIR

x_{626} x_{636} x_{628}

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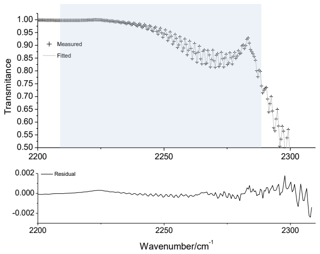
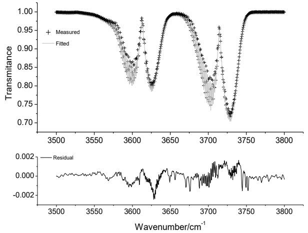
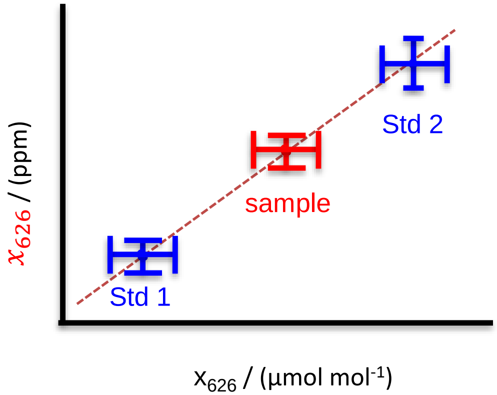






Calibration strategy

Principle : independent two points calibrations of each isotopologue, using standards of same δ^{13}C but different mole fraction to <u>bracket the target sample</u>

$$R^{13} = \frac{x_{636}}{x_{626}}$$

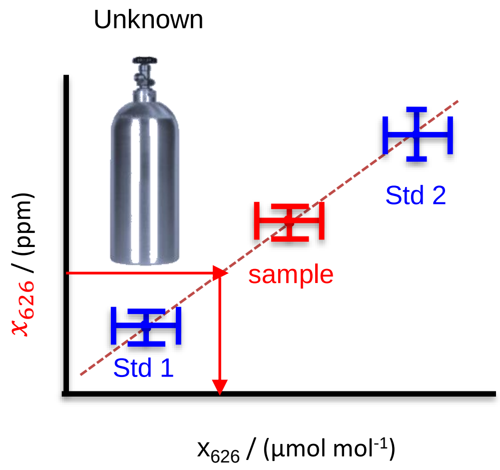
$$R^{18} = \frac{x_{628}}{x_{626}}$$

FTIR

x_{626} x_{636} x_{628}

Max-Planck-Institut für Biogeochemie

x_{626} µmol/mol	x_{636} µmol/mol	x_{628} µmol/mol
387.25	4.29	1.61



Uncertainty for FTIR $\delta^{13}C$ and $\delta^{18}O$ measurements

1. Standard Approach

Individual isotopologue mole fraction:

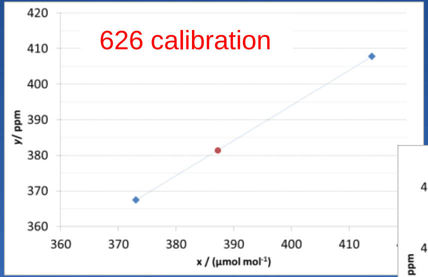
- two-point calibration process,
- model equation for each isotopologue deduced from the two calibration standards' reference values and FT-IR responses.

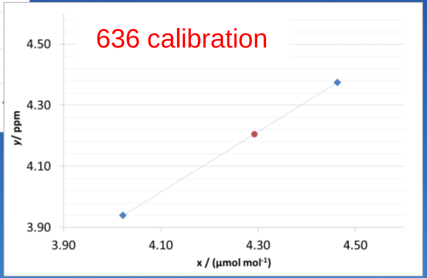
2. Sensitivity Study

Varying the calibration input parameters (GUM)

- parameter variation chosen according by its standard uncertainty $x_i - u(x_i)$ to $x_i + u(x_i)$.
- contribution to the total standard uncertainty was considered equal to half the variation (ΔY) observed in the delta values.

Uncertainty for FTIR $\delta^{13}C$ and $\delta^{18}O$ measurements





$$R^{13} = \frac{x_{636}}{x_{626}}$$

$$u(R^{13}) = R^{13}\sqrt{\left(\frac{u(x_{636})}{x_{636}}\right)^2 + \left(\frac{u(x_{626})}{x_{626}}\right)^2}$$

$$u(R^{13}) \sim 10^{-6}$$

Final uncertainties on delta values, for the « air like » sample:

$\delta^{13}C$	$u(\delta^{13}C)$	$\delta^{18}O$	$u(\delta^{18}O)$
‰ VPDB CO_2			
-8.61	0.09	-2.8	1.19

- Main component is the certified CO_2 mole fraction
- Uncertainty on delta value negligible (only repeatability, no uncertainty on VPDB)

Uncertainty for FTIR $\delta^{13}C$ and $\delta^{18}O$ measurements

2. Sensitivity Study

$\delta^{13}C$	$u(\delta^{13}C)$	$\delta^{18}O$	$u(\delta^{18}O)$
	‰ VPDB CO_2		
-8.61	0.09	-2.8	1.07

- Confirmed that for $\delta^{13}C$ the main uncertainty contributor comes from the uncertainty of the mole fraction of both CO_2/air mixtures used to calibrate the FTIR
- the $\delta^{18}O$ main uncertainty contributor is FT-IR response (93% of the index for the total uncertainty combining the measurements of cylinders 1, 2, and 3).

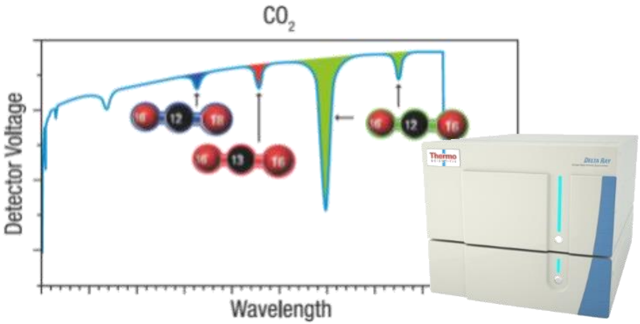
FTIR Method input parameter	Estimated value x_i	Standard uncertainty $u(x_i)$	$\delta^{13}C$ Measurand variation ΔY μmol mol^{-1}	$\delta^{13}C$ Index to uncertainty in %	$\delta^{18}O$ Measurand variation ΔY μmol mol^{-1}	$\delta^{18}O$ Index to uncertainty in %
x_{CO2_1}	378.9 μmol mol^{-1}	0.090 μmol mol^{-1}	0.14	49.88	0.15	0.46
$\delta^{13}C\_1$	-35.68 ‰	-0.015 ‰	0.0200	1.02	-0.0001	0.00
$\delta^{18}O\_1$	-34.48 ‰	-0.328 ‰	-0.0008	0.00	-0.2194	1.05
y_{626_1}	367.406 μmol mol^{-1}	0.006 μmol mol^{-1}	-0.0203	1.05	-0.0204	0.01
y_{636_1}	3.93919 μmol mol^{-1}	0.00007 μmol mol^{-1}	0.0127	0.41	0.00	0.00
y_{628_1}	1.4677 μmol mol^{-1}	0.0014 μmol mol^{-1}	0.00	0.00	0.57522	7.22
x_{CO2_2}	420.43 μmol mol^{-1}	0.10 μmol mol^{-1}	-0.13	40.14	-0.15	0.46
$\delta^{13}C\_1$	-35.68 ‰	-0.015 ‰	-0.02	0.97	0.0001	0.00
$\delta^{18}O\_1$	-34.12 ‰	-0.328 ‰	0.0008	0.00	-0.4579	4.57
y_{626_2}	407.758 μmol mol^{-1}	0.006 μmol mol^{-1}	-0.0108	0.30	-0.0109	0.00
y_{636_2}	4.37382 μmol mol^{-1}	0.00007 μmol mol^{-1}	0.0201	1.03	0.00	0.00
y_{628_2}	1.640481 μmol mol^{-1}	0.0014 μmol mol^{-1}	0.000	0.00	1.08860	25.84
y_{626_3}	381.403 μmol mol^{-1}	0.006 μmol mol^{-1}	0.0311	2.47	0.03	0.02
y_{636_3}	4.20550 μmol mol^{-1}	0.00007 μmol mol^{-1}	-0.0328	2.74	0.00	0.00
y_{628_3}	1.5807 μmol mol^{-1}	0.0014 μmol mol^{-1}	0.00	0.00	-1.66	60.36

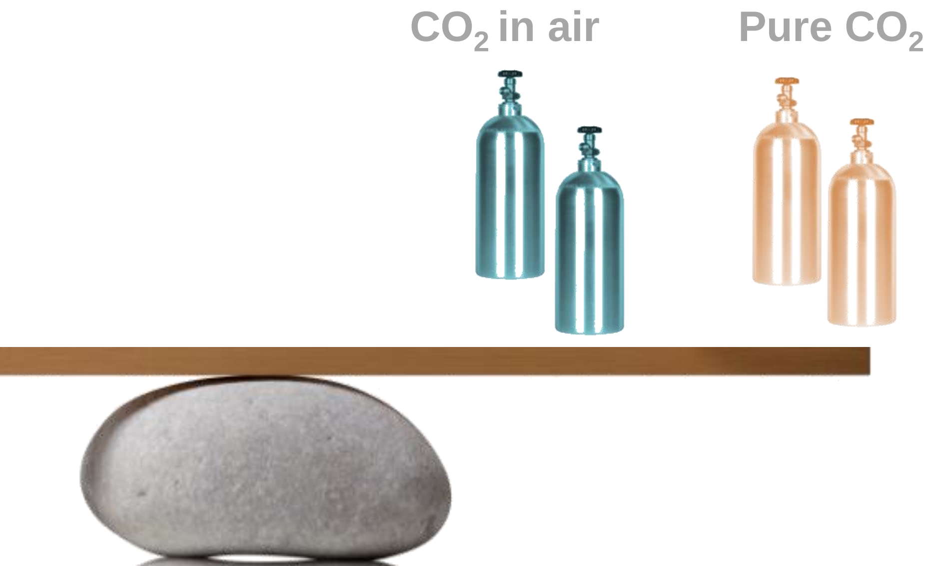
Isotope Ratio Infrared Spectroscopy – Laser spectroscopy

CO_2 in air

Isotope Ratio Infrared Spectroscopy

- Laser absorption at 4.3 µm
- Scanning over absorption peaks of 3 main CO_2 isotopologues
- Typical sample = CO_2 in air, ambient concentration (~ 400 µmol/mol)

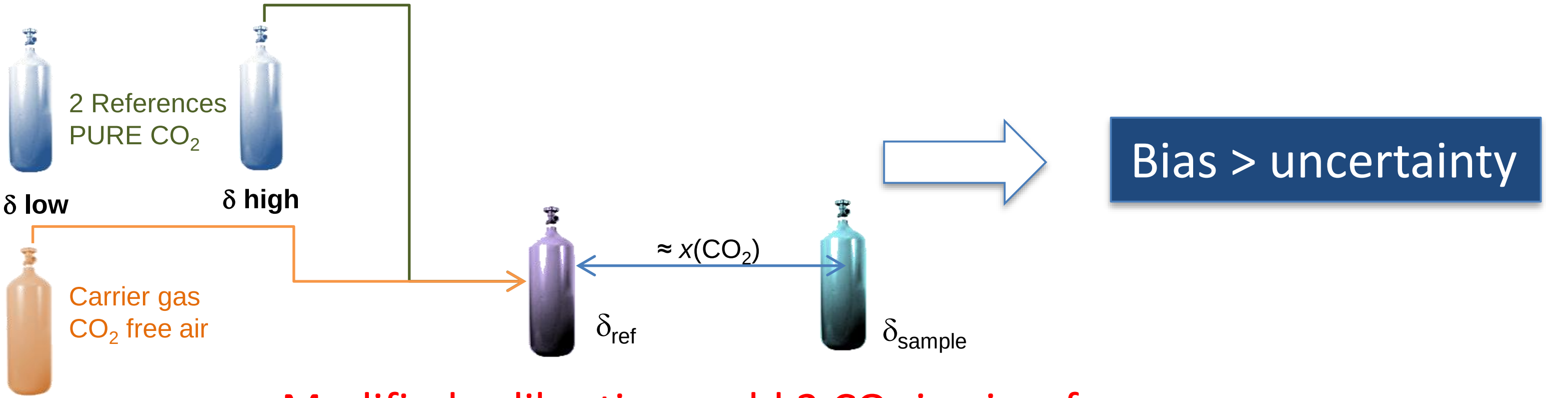




Delta Ray – Calibration Strategy

Get Ready procedure

Original idea : dilute the reference standards (pure CO_2) to match the sample



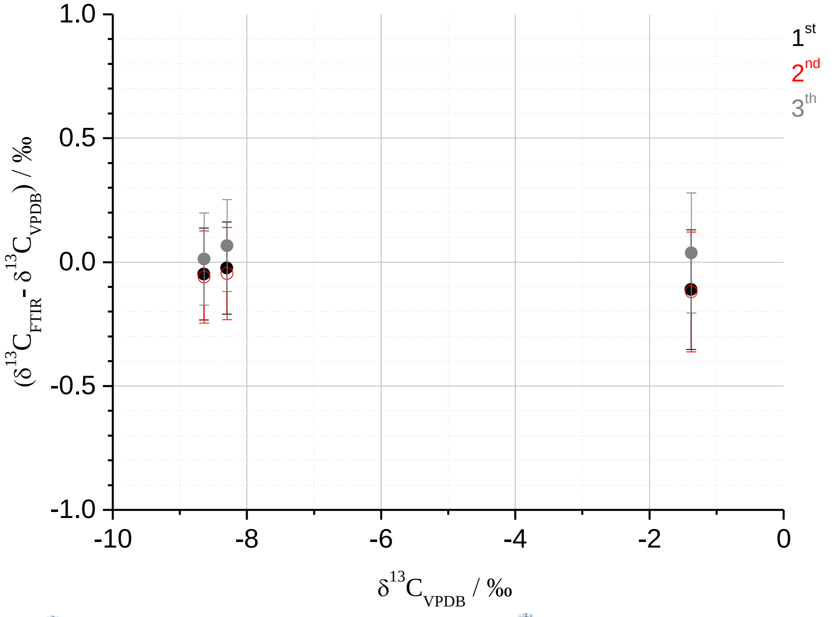
Modified calibration : add 2 CO_2 in air references and perform a 2 point calibration of δ values

Sample Air Ref 1.
420.43 µmol mol^{-1}
$\delta^{13}C$ = -35.682 ‰
$\delta^{18}O$ = -34.478 ‰

Sample Air Ref 2.
380 µmol mol^{-1}
$\delta^{13}C$ = -1.384 ‰
$\delta^{18}O$ = -7.148 ‰

Validation by comparison with value assigned by IRMS

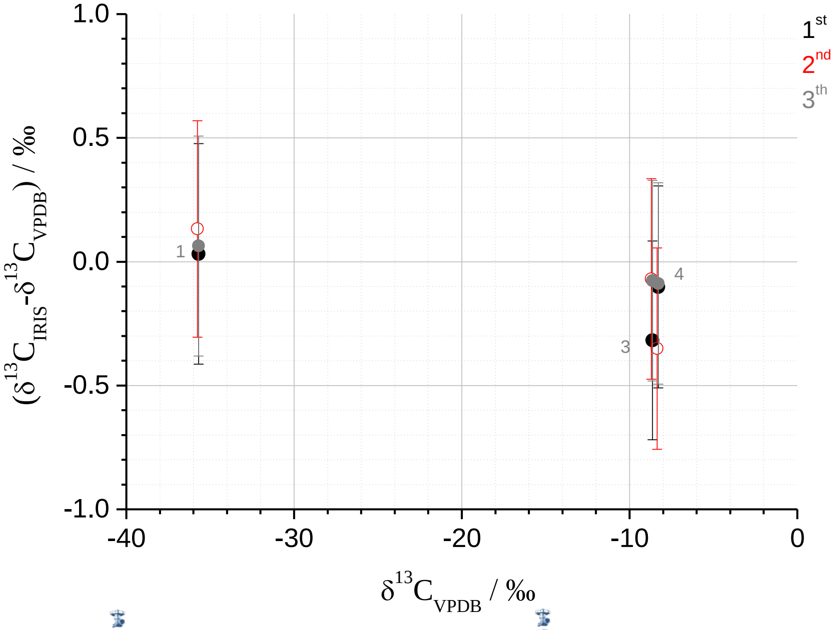
FTIR measurements on 3 samples :



Ref 1.
379.90 µmol mol^{-1}
$\delta^{13}C$ = -35.685 ‰
$\delta^{18}O$ = -34.478 ‰

Ref 2.
420.43 µmol mol^{-1}
$\delta^{13}C$ = -35.682 ‰
$\delta^{18}O$ = -34.115‰

IRIS (delta ray) measurements on 3 samples :



Sample Air Ref 1.
420.43 µmol mol^{-1}
$\delta^{13}C$ = -35.682 ‰
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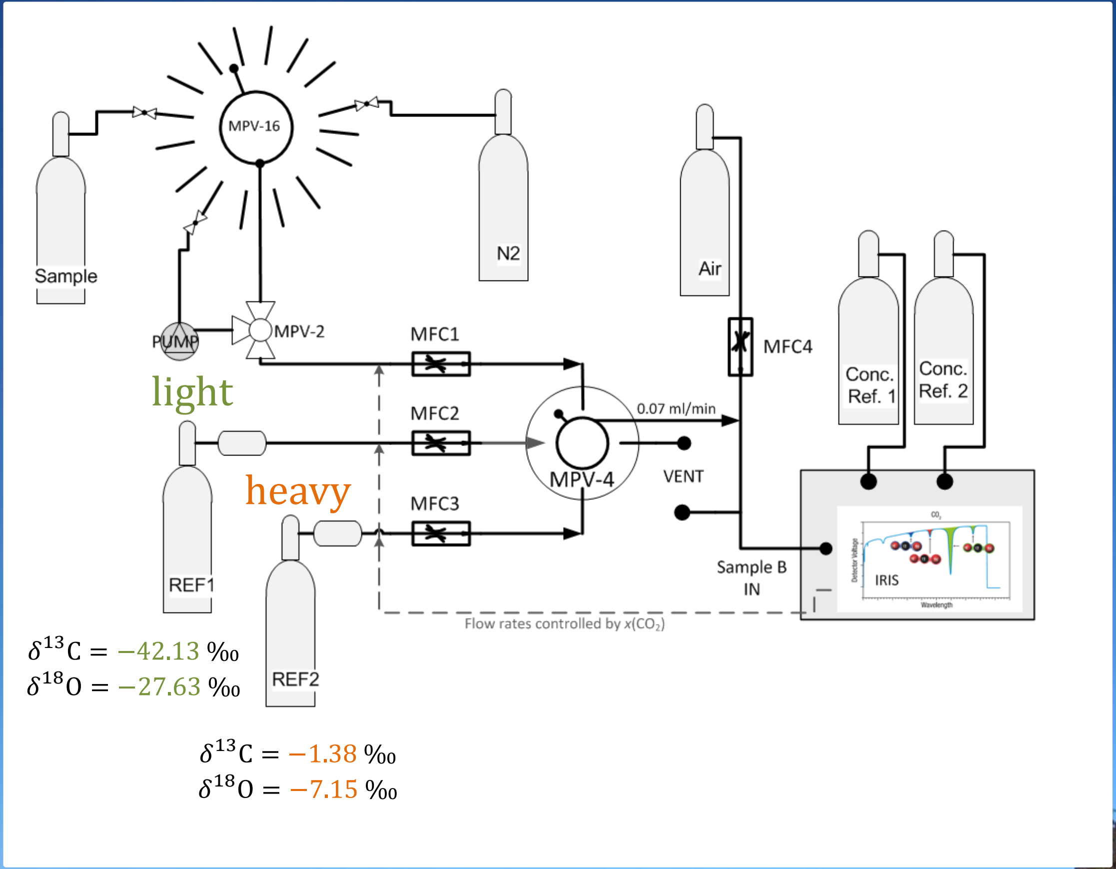
Sample Air Ref 2.
380 µmol mol^{-1}
$\delta^{13}C$ = -1.384 ‰
$\delta^{18}O$ = -7.148 ‰

Isotope **R**atio **I**nfrared **S**pectroscopy– Laser spectroscopy

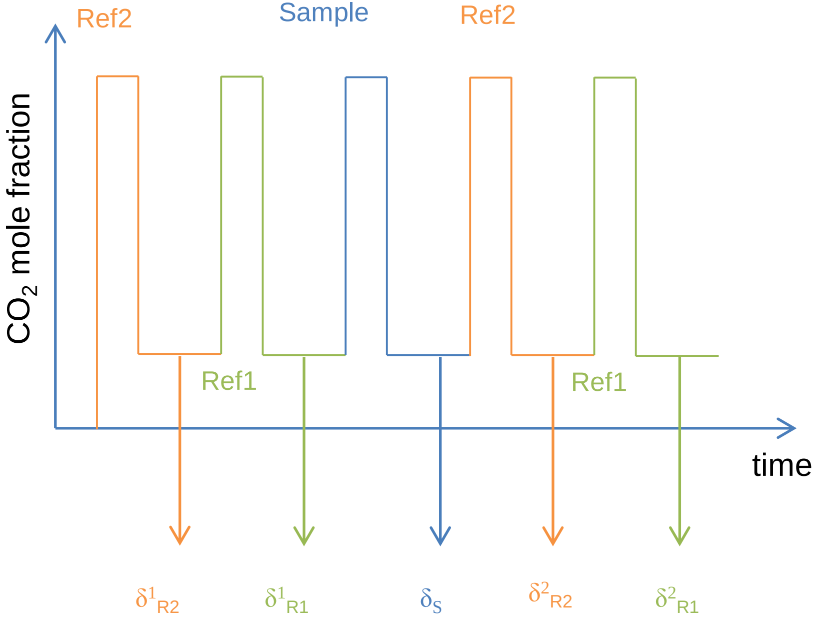
Pure CO_2

Sampling System for **pure CO_2** aliquots



- Controlled flow rates
- Automatic sequential analysis
- Up to **16 samples** analysis
- **Identical treatment** of samples and references

Measurement sequence with **calibration** & **drift correction**

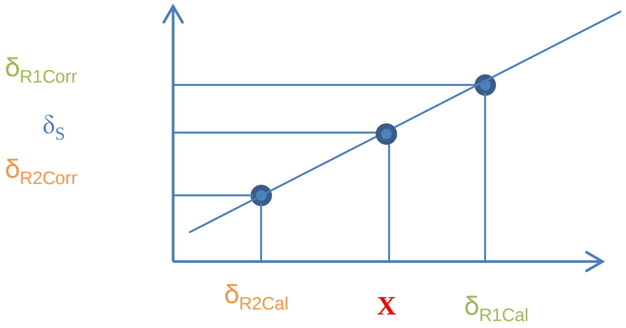


-Drift correction

$\delta_{R2Corr}=\delta^1_{R2}+(\delta^2_{R2}-\delta^1_{R2})*1/3$

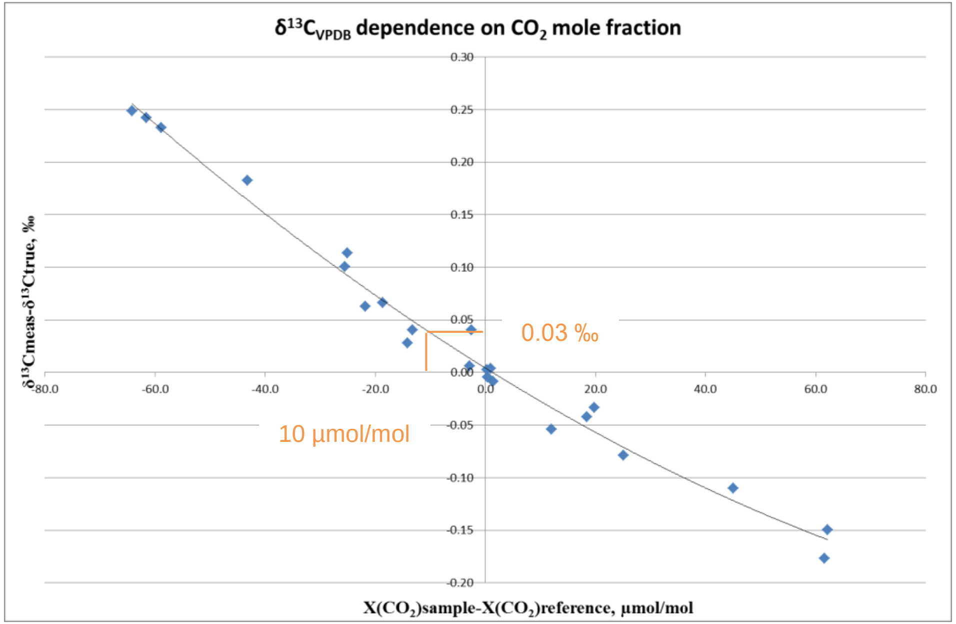
$\delta_{R1Corr}=\delta^1_{R1}+(\delta^2_{R1}-\delta^1_{R1})*1/3$

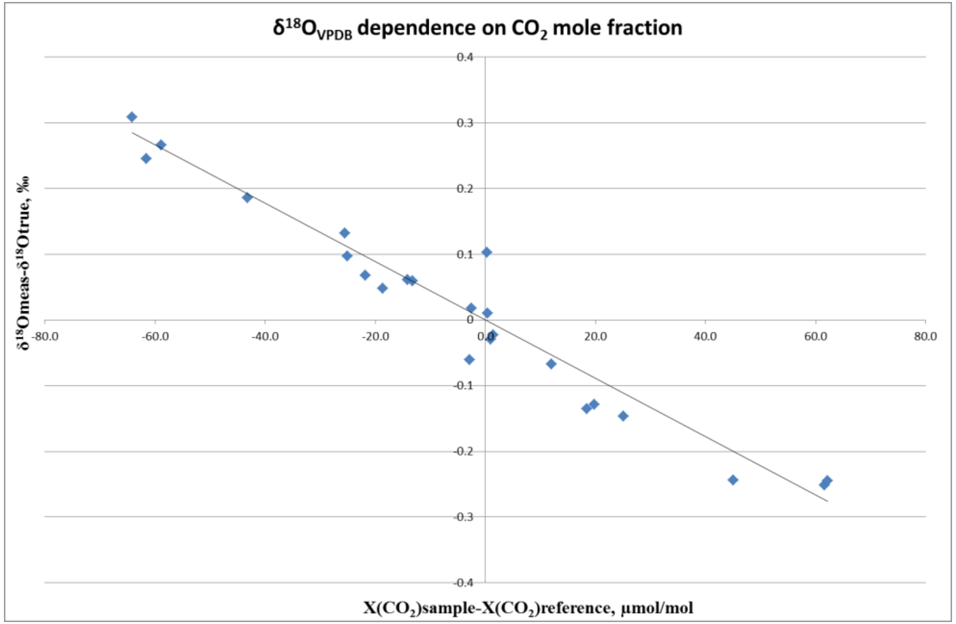
-Two points post calibration



Optimising performances: CO_2 mole fraction control

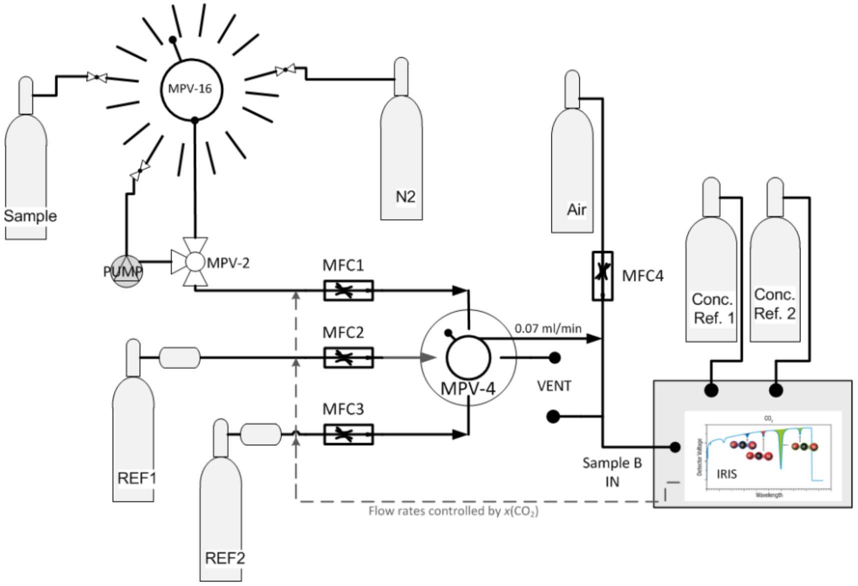
Variations of $x(CO_2)$ in the instrument's gas cell induce variations of isotope ratios





Optimising performances: CO_2 mole fraction control

Feedback loop implemented in control software to obtain ± 2 µmol/mol



Raw CO_2 data

→ Software to control the flows

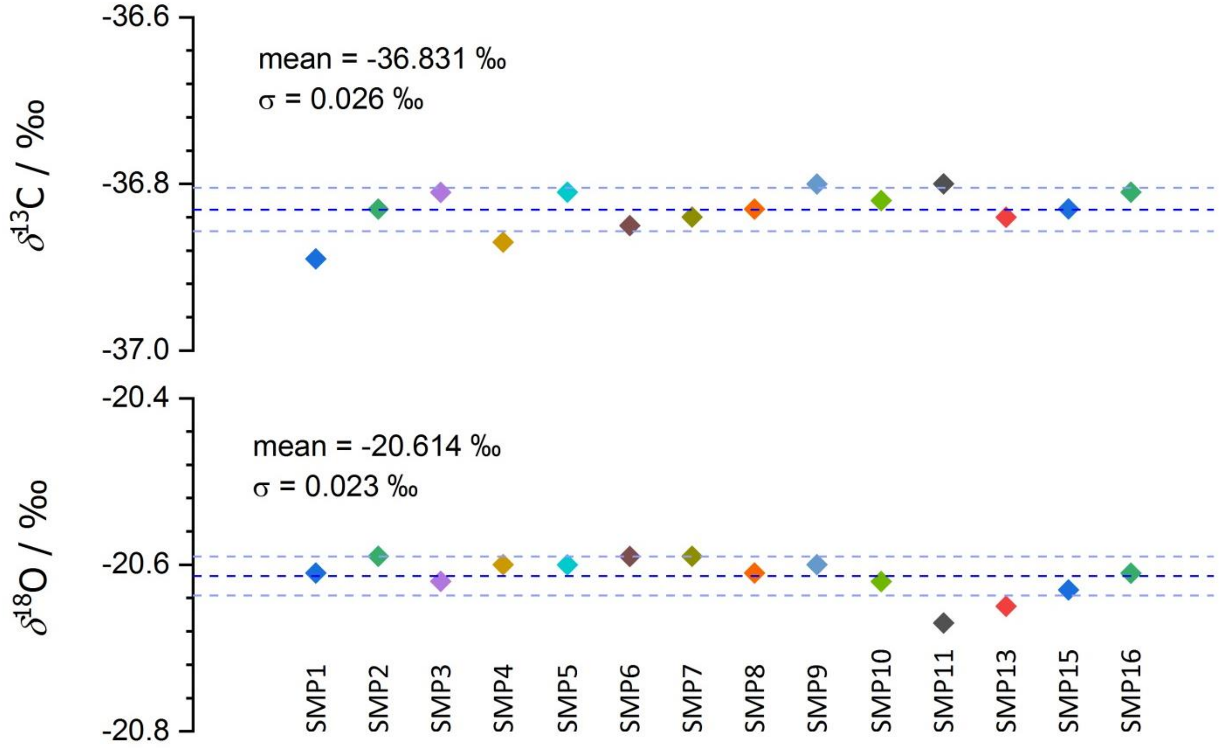
→ Calculation of the flow correction factor

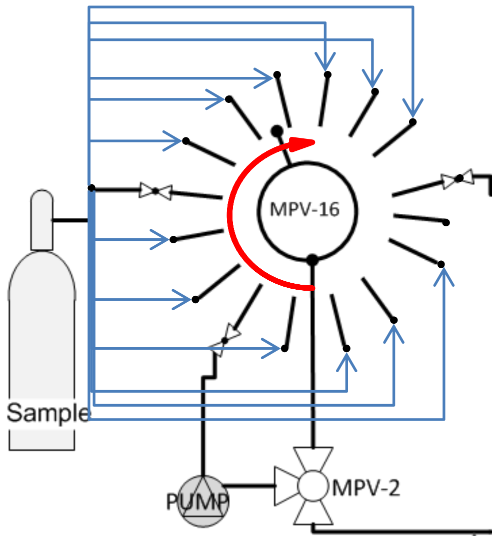
→ Correction of the flows

Maximum bias
0.007 ‰ on $\delta^{13}C_{VPDB}$
0.009 ‰ on $\delta^{18}O_{VPDB}$

Carousel ports variability

Switching over 16 carousel ports shows no port-variability



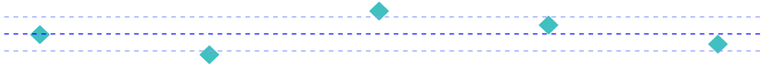


Repeatability & homogeneity over the range

N_m	N_s	$\delta^{13}C$ / ‰		$\delta^{18}O$ / ‰	
		Mean	σ	Mean	σ
6	1	-43.362	0.023	-35.350	0.021
12	8	-36.717	0.020	-20.400	0.052
12	3	-29.884	0.021	-27.341	0.020
10	3	-19.937	0.031	-21.216	0.027
12	3	-10.741	0.019	-15.225	0.023
9	3	-1.375	0.019	-9.290	0.020
	Average		0.022	0.027	

N_s = number of samples

N_m = number of measurements



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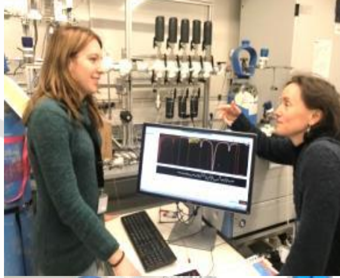
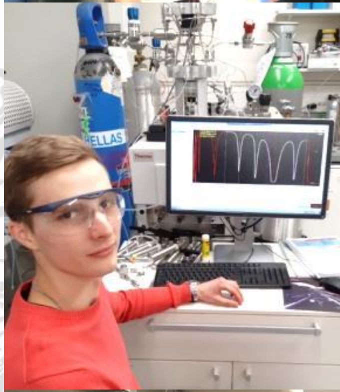
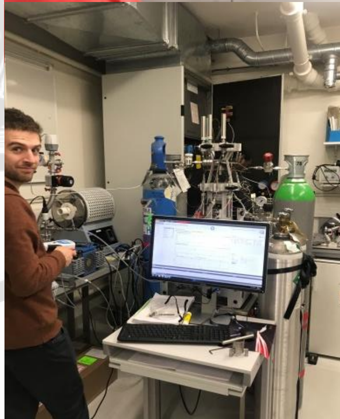
Francesca Rolle	**INRIM** (Italia)	Feb 2018-July 2018
Yan Chubchenko	**VNIIM** (Russia)	Oct 2018-March 2019
Eric Mussell Webber	**NPL** (UK)	April 2019 - June 2019







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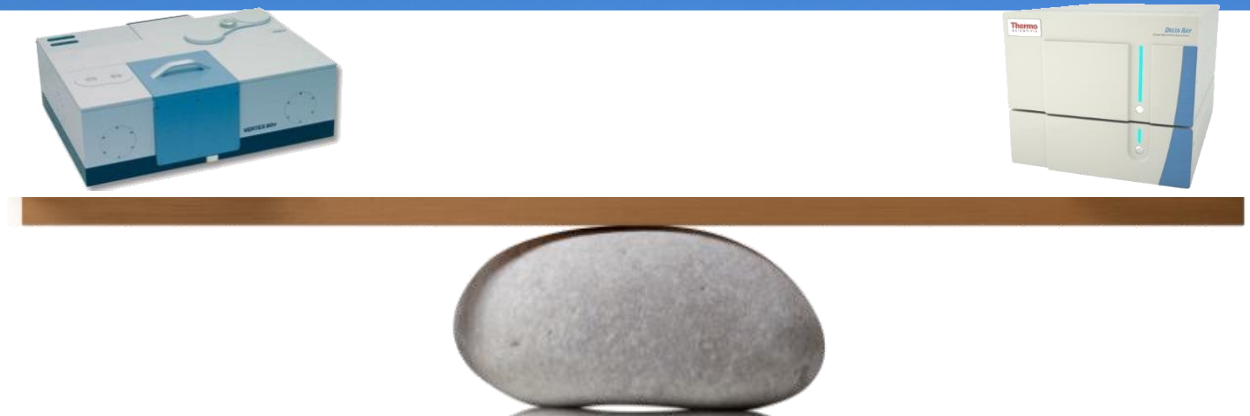
CONCLUSIONS

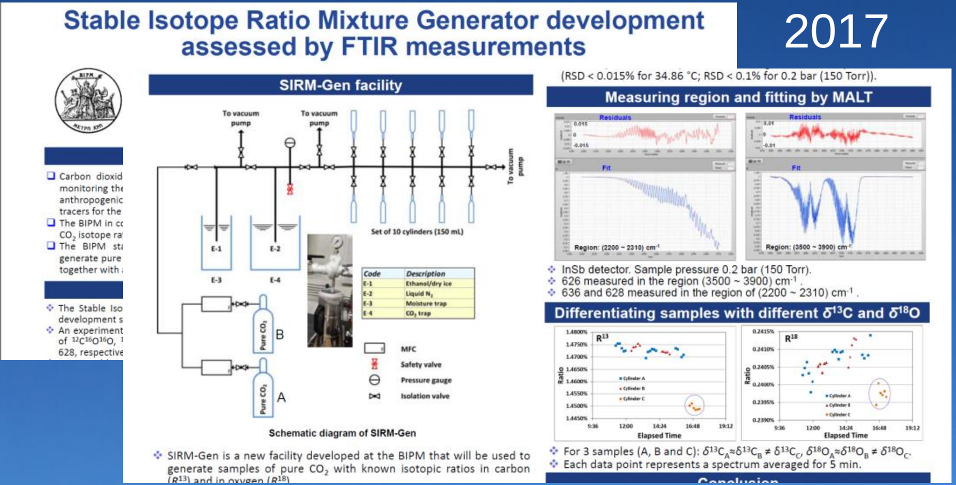


FTIR vs Delta Ray

FTIR: two cylinders with the same delta values and different mole fractions, bracketing the mole fractions to be measured, δ^{13}C and δ^{18}O values can be measured with uncertainties of $u_{\delta 13C\_FT}$ = 0.09 ‰ and $u_{\delta 18O\_FT}$ = 1.03 ‰

Delta Ray: a residual bias in the δ^{13}C and δ^{18}O measurements, which remained following the implementation of the manufacturer's calibration procedure, was removed by the application of an additional two point calibration (two CO_2 in air standards with known but differing isotopic composition). The resulting standard uncertainty of measurements achieved was $u_{\delta 13C\_DRT}$= 0.18 ‰ and $u_{\delta 18O\_DR}$= 0.48 ‰.

FTIR vs Delta Ray



2017

Delta Ray: a residual bias in the $\delta^{13}C$ and $\delta^{18}O$ measurements, which remained following the implementation of the manufacturer's calibration procedure, was removed by the application of an additional two point calibration (two CO_2 in air standards with known but differing isotopic composition). The resulting standard uncertainty of measurements achieved was $u_{\delta 13C\_DRT}$ = **0.02 ‰** and $u_{\delta 18O\_DR}$ = **0.02 ‰**.

2019

Pure CO_2 **Pure** CO_2

THANKS!