Comparison of isotope ratio measurement capabilities for CO_2: Sample preparation and characterization by Isotope Ratio Infrared Spectroscopy

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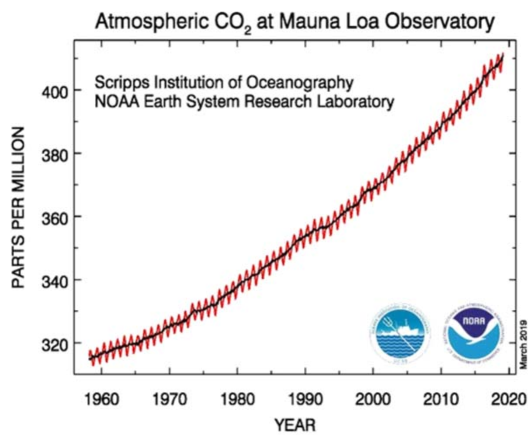
Alert (82N, 62 W, 200 masl)

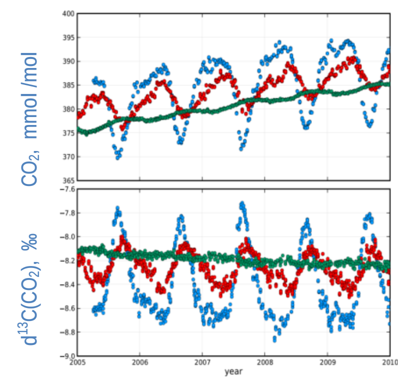
Mauna Loa (19N, 155W, 3397 masl)

South Pole (89S, 24 W, 2810 masl)

CO_2

- **2.87 µmol mol^{-1} increase in 2018** (NOAA's Mauna Loa Observatory)
- 4th largest increase in 60 years of record-keeping.
- Jan. 2018: 407.05 µmol mol^{-1},
- Jan. 2019: 409.92 µmol mol^{-1}.





CO_2

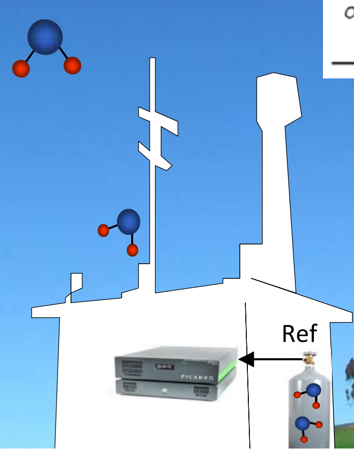
- Stable isotope ratios are used as tracers in many scientific fields such as geochemistry, medicine, forensics etc.
- Strong need for improved understanding of global carbon cycle: sources and sinks of greenhouse gases in atmosphere
- CO_2 exists in 12 stable isotopometric forms
- More than 99.9% of CO_2 is accounted for by the four most abundant species $^{12}C^{16}O^{16}O$ (98.42%), $^{13}C^{16}O^{16}O$ (1.09%), $^{12}C^{16}O^{18}O$ (0.40%)

CO_2

WMO-GAW Network Data Quality Objectives (Compatibility)

Table 1. Recommended compatibility of measurements within the scope of GGMT

Component	Compatibility goal 1-sigma	Extended compatibility goal[1]	Range in unpolluted troposphere (approx. range for 2015)	Range covered by the WMO scale
CO_2	± 0.1 ppm (North.Hem.) ± 0.05 ppm (So.Hemisph)	± 0.2 ppm	380 - 450 ppm	250 – 520 ppm
CH_4	± 2 ppb	± 5 ppb	1750 – 2100 ppb	300 – 5900 ppb
CO	± 2 ppb	± 5 ppb	30 – 300 ppb	30 -500 ppb
N_2O	± 0.1 ppb	± 0.3 ppb	325 – 335 ppb	260 – 370 ppb
SF_6	± 0.02 ppt	± 0.05 ppt	8 – 10 ppt	2.0 – 20 ppt
H_2	± 2 ppb	± 5 ppb	400 – 600 ppb	140 –1200 ppb
$\delta^{13}C\text{-}CO_2$	± 0.01‰	± 0.1‰	-9.5 to -7.5‰ (VPDB)	
$\delta^{18}O\text{-}CO_2$	± 0.05‰	± 0.1‰	-2 to +2‰ (VPDB-CO_2)	
$\Delta^{14}C\text{-}CO_2$	± 0.5‰	± 3‰	-50 to 50‰	
$\Delta^{14}C\text{-}CH_4$	± 0.5‰		50-350‰	
$\Delta^{14}C\text{-}CO$	± 2 molecules cm^{-3}		0-25 molecules cm^{-3}	
$\delta^{13}C\text{-}CH_4$	± 0.02‰	± 0.2‰		
$\delta D\text{-}CH_4$	± 1‰	± 5‰		
O_2/N_2	± 2 per meg	± 10 per meg	-900 to -400 per meg (vs. SIO scale)	



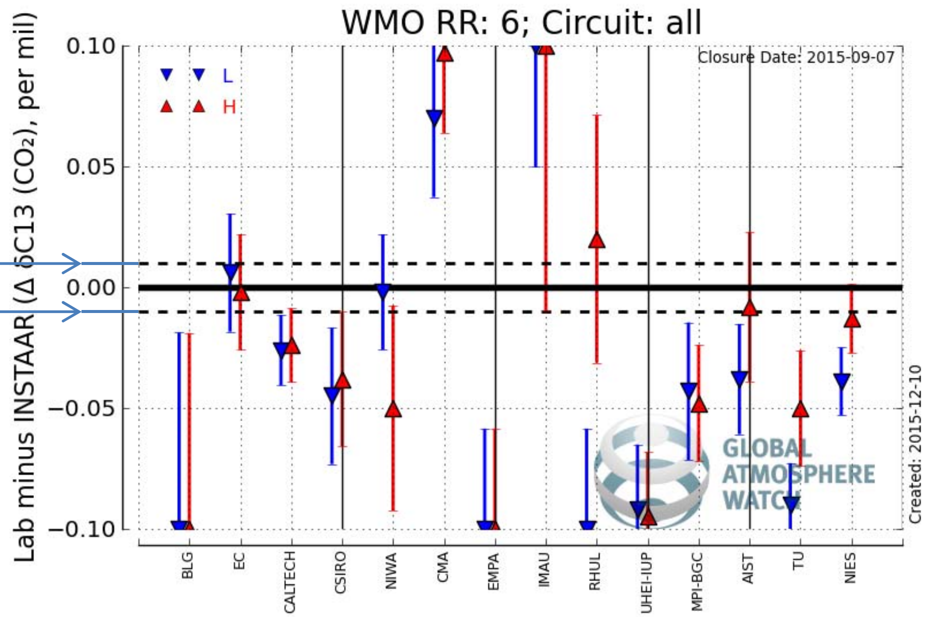
18th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2015)

Challenges with $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 measurements in air

Agreed network compatibility goal at GGMT-2017

Component	Compatibility goal
CO_2	± 0.1 ppm (Northern hemisphere) ± 0.05 ppm (South. hemisphere)
CH_4	± 2 ppb
CO	± 2 ppb
N_2O	± 0.1 ppb
SF_6	± 0.02 ppt
H_2	± 2 ppb
$\delta^{13}C$-CO_2	± 0.01‰
$\delta^{18}O$-CO_2	± 0.05‰
$\Delta^{14}C$-CO_2	± 0.5‰
$\Delta^{14}C$-CH_4	± 0.5‰
$\Delta^{14}C$-CO $\delta^{13}C$-CH_4	± 2 molecules cm^{-3} ± 0.02‰
δD-CH_4	± 1‰
O_2/N_2	± 2 per meg

2015 Round robin result for $\delta^{13}C$-CO_2



https://www.esrl.noaa.gov/gmd/ccgg/wmorr/wmorr_results.php?rr=rr6&param=co2c13&option=results

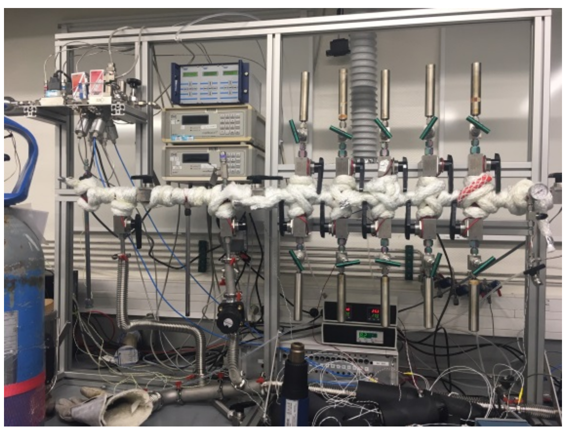
SIRM-Gen

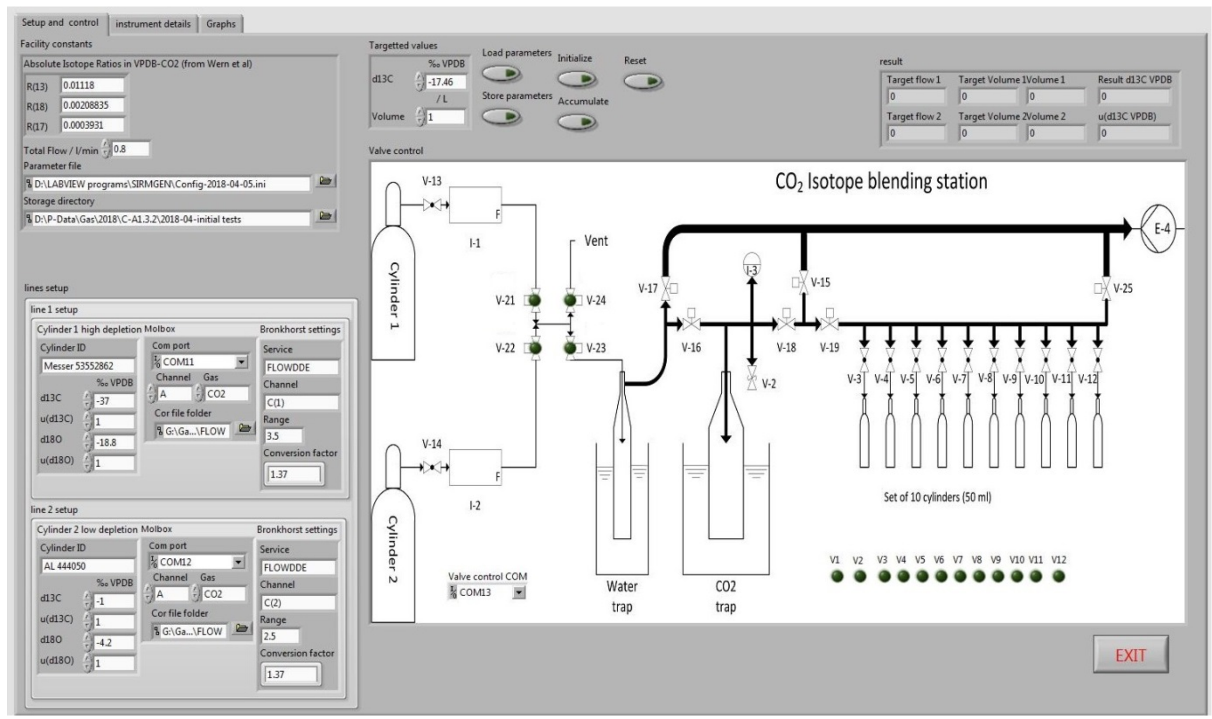
SIRM-Gen is a Stable Isotope Ratio Mixture Generator

The SIRM-Gen facility is used for the preparation of CO_2 reference mixtures. The standards will be used for CCQM-P204 “CO_2 Isotope Ratios” comparison.

SIRM-Gen facility

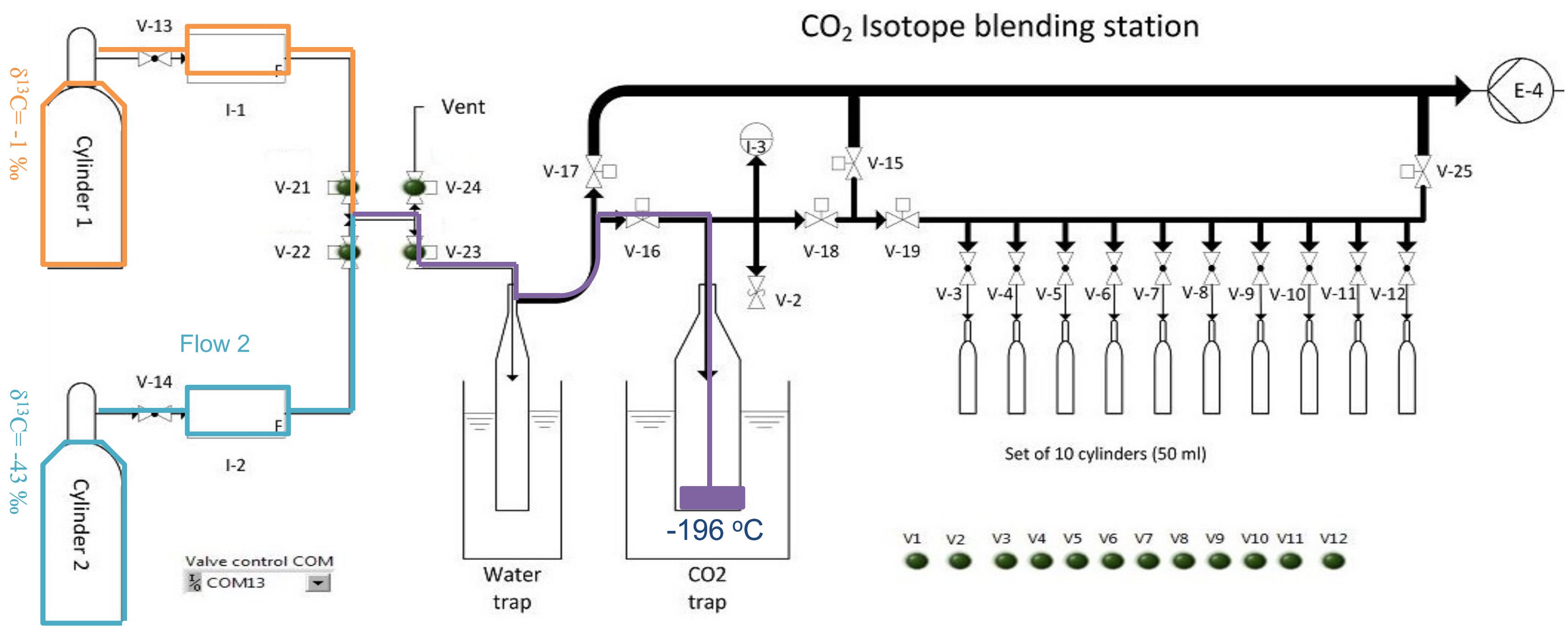
This facility allows filling up to ten aliquots of 50 mL at a pressure of 2 bar with the same gas. The aliquots are made in 316 stainless steel and closed by stainless steel bellows-sealed valves



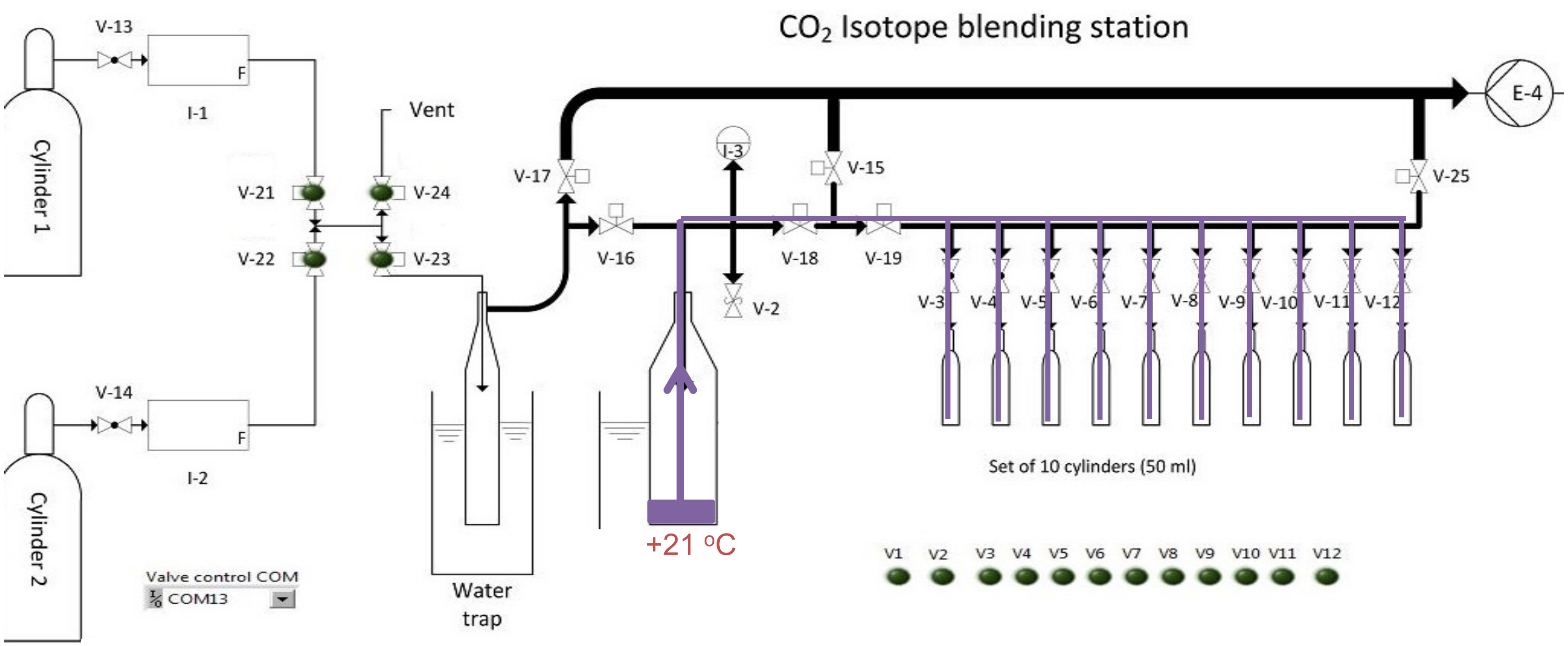


LabVIEW interface for the blending of two pure CO_2 gases

SIRM-Gen facility



SIRM-Gen facility



Homogeneity assessment of BIPM CO_2 gases in new gas containers

Samples produced at BIPM by the SIRM-Gen

Nominal values of $\delta^{13}C$ vs. VPDB :

-1 ‰ | -35‰ | -42‰

Sampling System for **pure CO_2** aliquots

Stability and homogeneity measured at BIPM
((1σ) $\delta^{13}C = 0.02$ ‰ (1σ) $\delta^{18}O = 0.02$ ‰)

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Homogeneity measured
((1σ) $\delta^{13}C > 0.0125$ ‰
(1σ) $\delta^{18}O > 0.025$‰

CO2 generated from the primary RM IAEA-603 by the carbonate-H3PO4

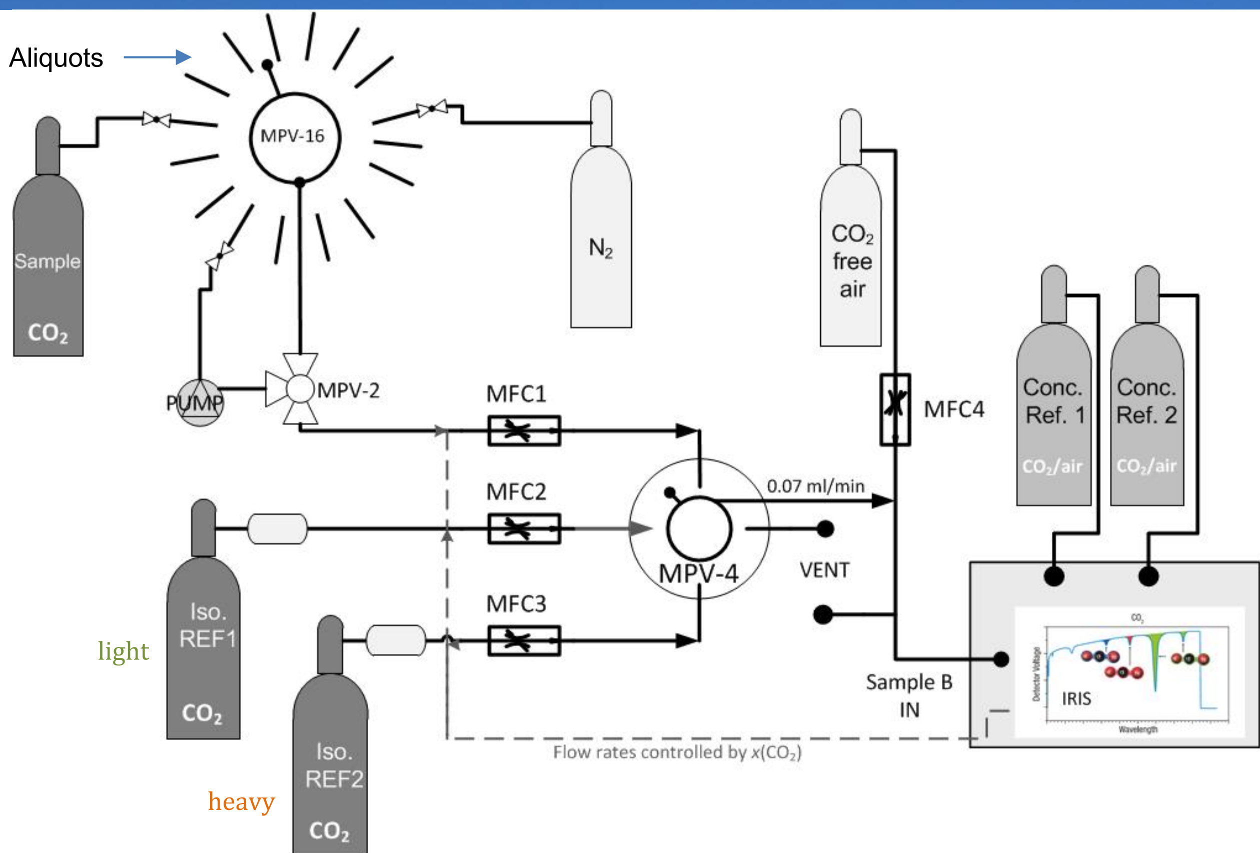
Sampling System for pure CO_2 aliquots

Sampling System for **pure CO_2** aliquots

The system

- The samples are connected to a 16 positions valve.
- Two pure CO_2 references (Iso. REF1 and REF2) are used to calibrate the measurements, chosen to span a large range of the ^{13}C isotopic ratio. The values of the isotopic ratios in both of them were estimated from IRMS measurements performed by MPI-BGC.
- CO_2 free air is used as the carrier gas to dilute the reference and sample gases, so as to obtain the optimal mole fraction of CO_2 in the gas cell of the IRIS analyser.
- Conc. Ref.1 and 2 denote two mixtures of CO_2 in air with known mole fractions required by the IRIS analyser during the starting phase (GET READY process). The values of the CO_2 mole fraction was measured by the NIST for previous work.

Sampling System for **pure CO_2** aliquots



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

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

Sampling System for **pure CO_2** aliquots

The sampling 1/2

- Designed for identical treatment of the sample and the reference gases (as much as possible), while allowing automated sampling of a minimum of fourteen pure CO_2 samples (VICI 16−position dead−end valve (MPV−16) with a micro electric actuator was chosen)

- Not use of the XPand box

- The sample and reference diluted with a carrier gas and a vent introduced just before the analyser to allow flushing of tubing just after MPV−4 between two measurements of different gases (references and sample). After the vent the flow of CO_2/air is similar to what would be used for measurements of samples of dry ambient air and it was connected to sample B port, which is the default port the analyser always returns to when a measurement sequence is completed. This avoids sampling room air which could introduce moisture inside the tubing. In addition, the Nafion dryer was by−passed as all samples were already dry.

- Of the 16 available ports, one was connected to a dry nitrogen cylinder at a pressure of 2 bar, which was used outside of measurement periods to prevent contamination of the lines by room air.

- A second port was connected to a diaphragm vacuum pump (Vacuubrand MV 2) that allowed pressure reduction in the lines down to 0.5×10^{-3} bar when needed. The output of the valve was also connected to the pump via a two−position valve (MPV−2) with pneumatic actuator, in order to evacuate all 16 ports after connection of the samples.

Sampling System for **pure CO_2** aliquots

The sampling 2/2

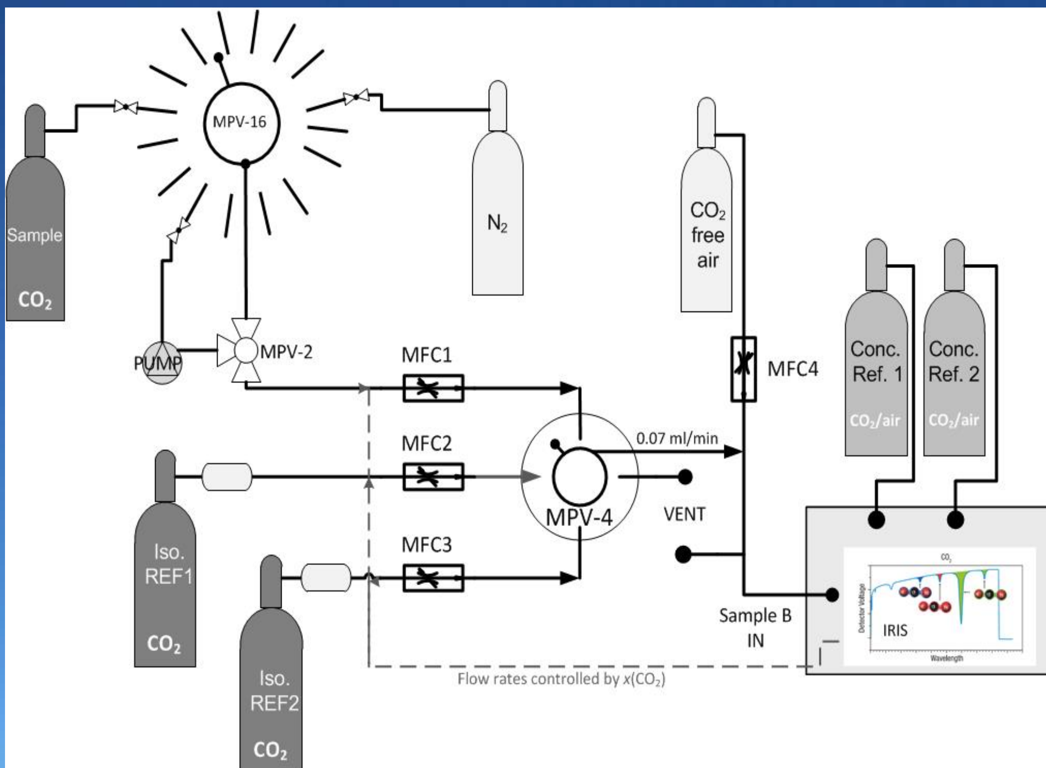
- Mass flow controllers (Bronkhorst, MFC1, 2 and 3) were used to control the flow rate of the sample, reference 1 and reference 2 gases accordingly. They allowed flows to be controlled from 0.06 ml/min to 0.7 ml/min with an accuracy of ±0.5 % of reading plus ±0.1 % of full scale. A VICI 4−position flow through valve (MPV−4) allowed switching between sample, reference 1 and reference 2. All exit ports of the valve were connected to the exhaust in order to let all three gases to flow at the same rate during the analysis, either to the analyser or the exhaust.

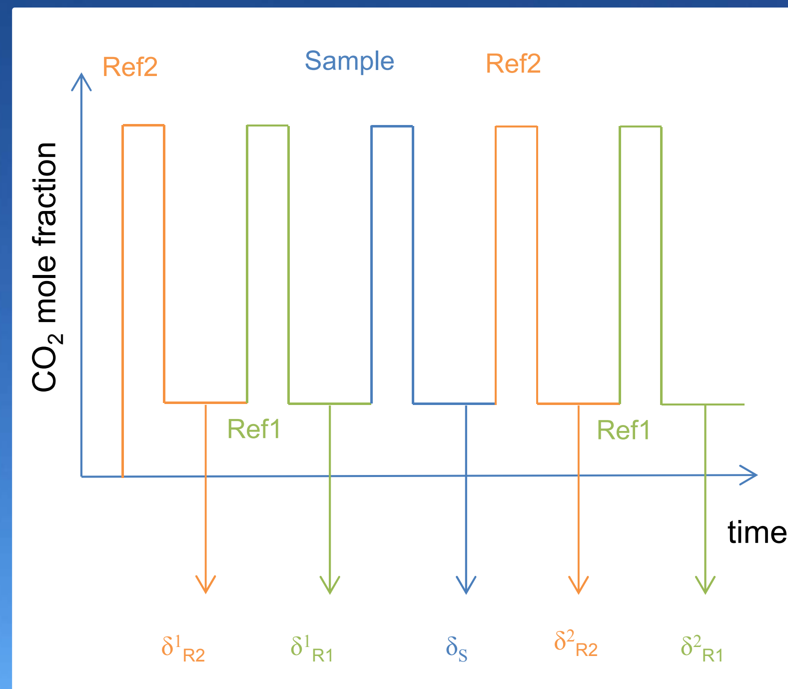
- After MPV−4 the pure CO_2 gas was diluted by the carrier gas (AIR). The air flow rate was controlled by a Red-y (Vögtlin) mass flow controller (MFC−4) at a nominal rate of 95 mL min^{-1}. The flow of CO_2 in air was connected with a tee to the analyser port B and to an exhaust to evacuate the excess of gas not being used by the analyser.

- All lines were made of 1/16 inches tubing in 316 stainless steel coated with SilcoNert 2000®. Valves and pressure reducers were in 316 stainless steel.

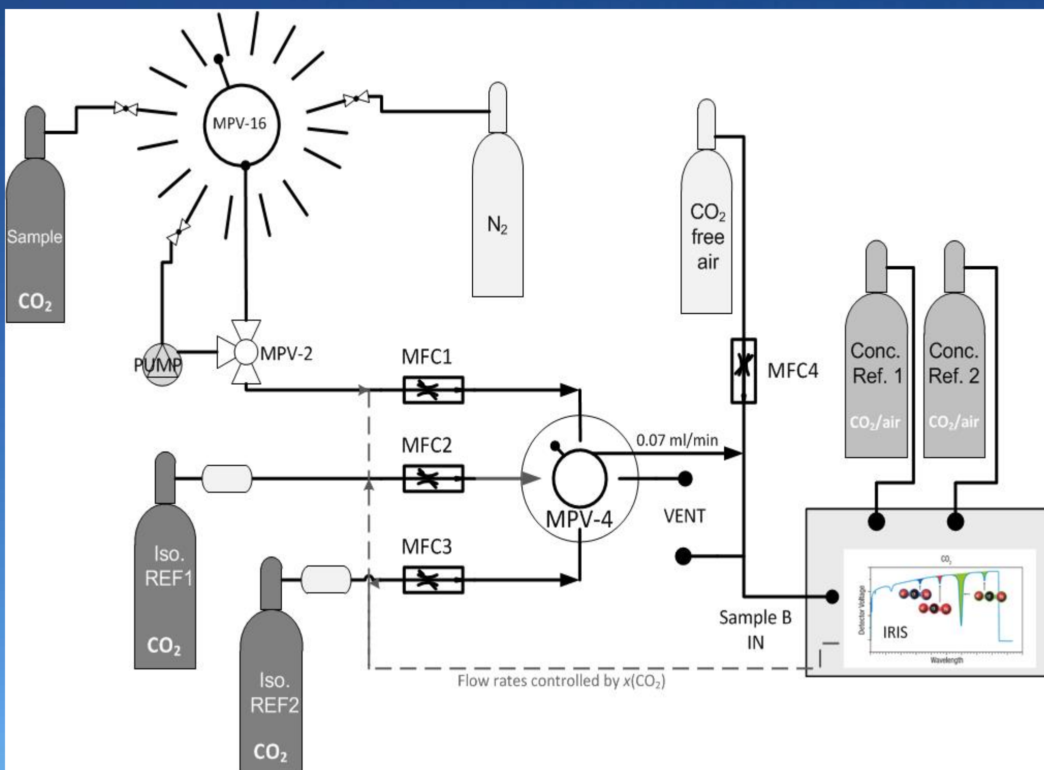
- With this system, the path of samples and reference gases is identical from MPV−4 up to the analyser gas cell. Results presented in this paper do not reveal observable impact of the path difference introduced before MPV−4

Measurement procedure





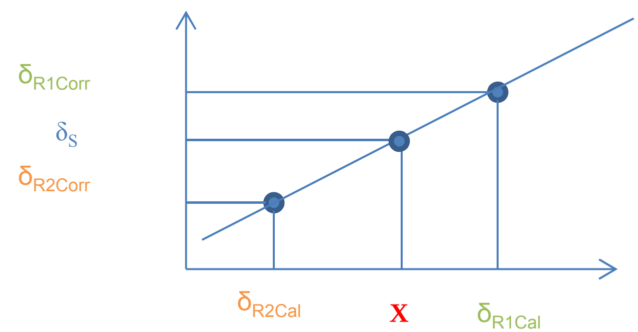
Measurement procedure



-Drift correction

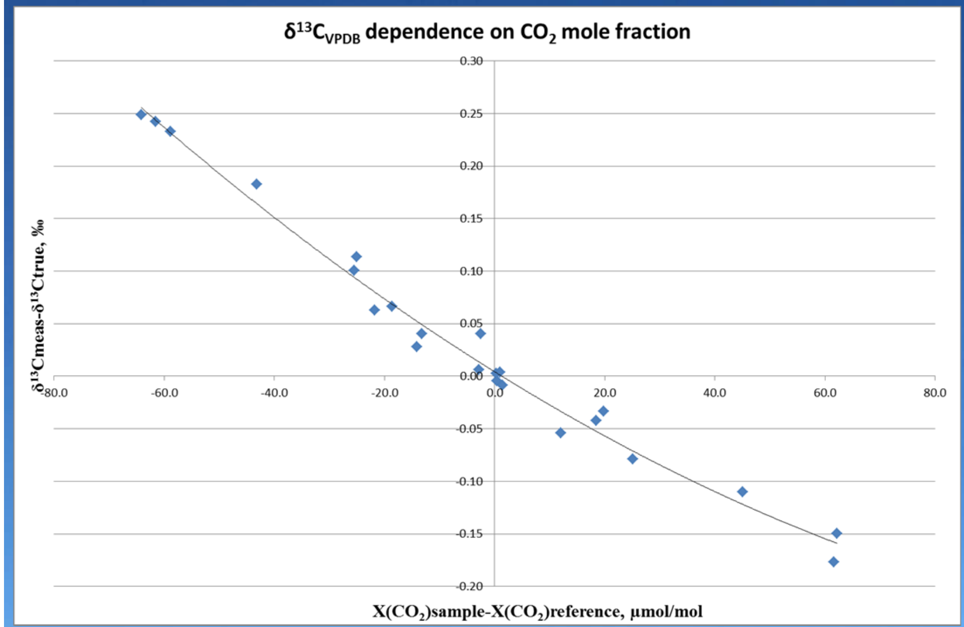
$$\delta_{R2Corr}=\delta^1_{R2}+(\delta^2_{R2}-\delta^1_{R2})*1/3$$
$$\delta_{R1Corr}=\delta^1_{R1}+(\delta^2_{R1}-\delta^1_{R1})*1/3$$

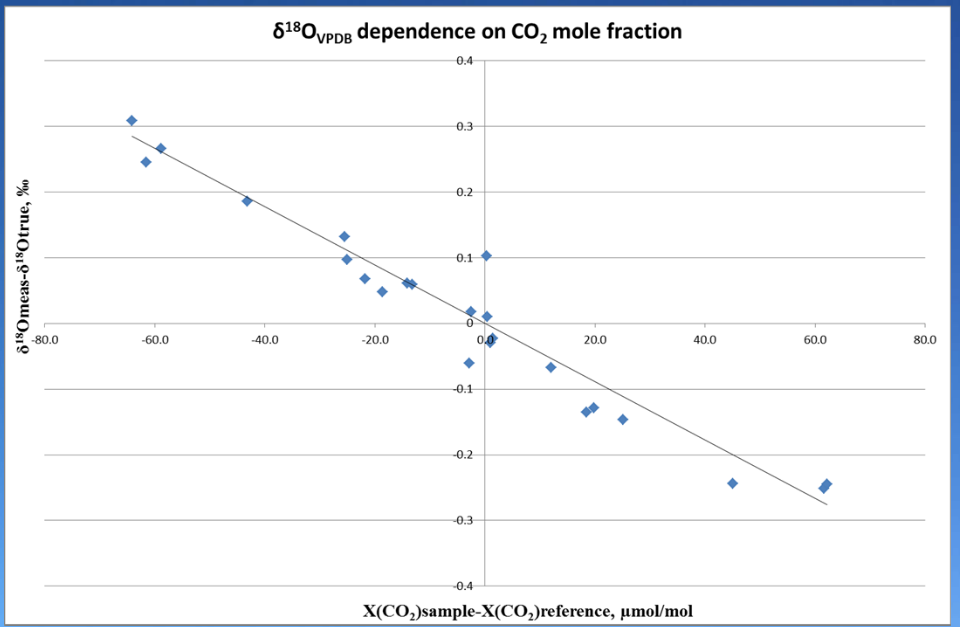
-Two points post calibration



Optimising performances: CO_2 mole fraction control

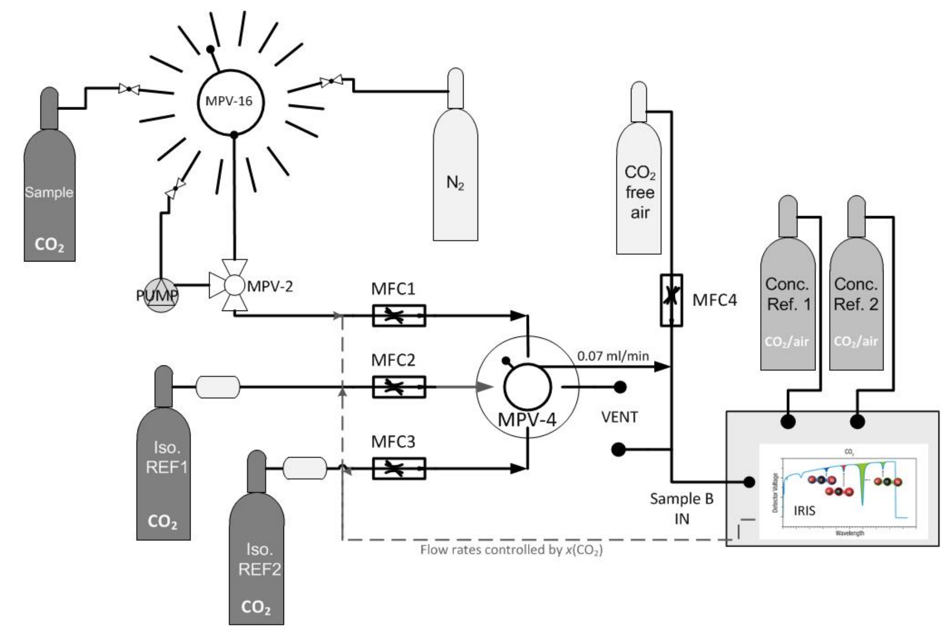
Variations of $x(CO_2)$ in the instrument's gas cell induce variations of isotope ratios





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

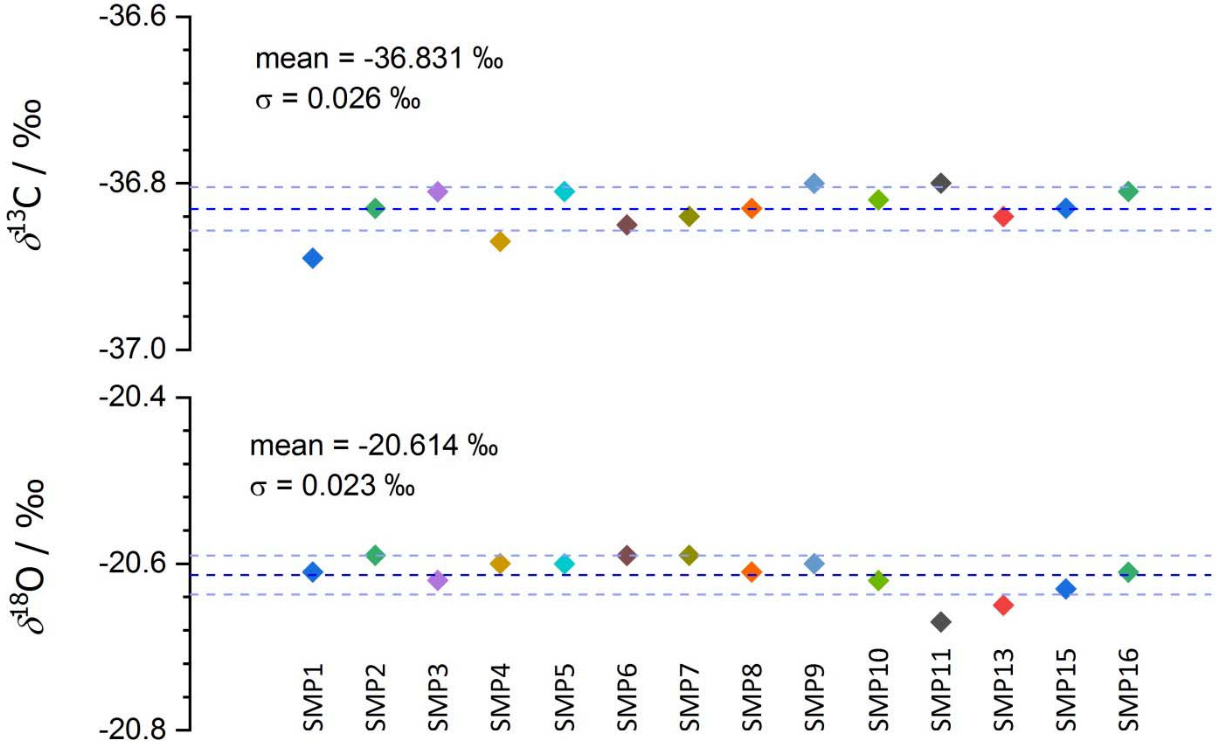
↓

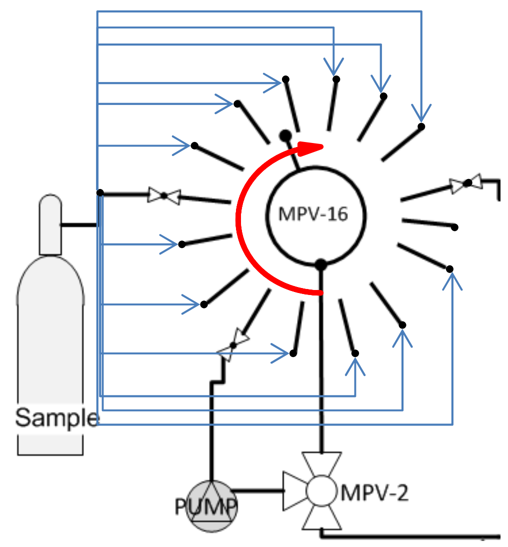
Correction of the flows

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

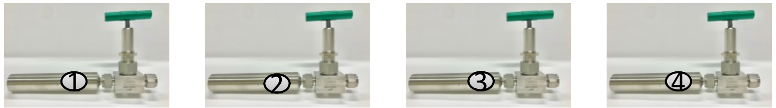




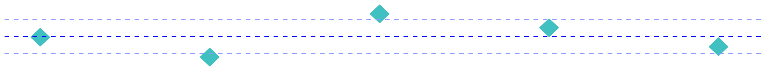
Repeatability & homogeneity over the range

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

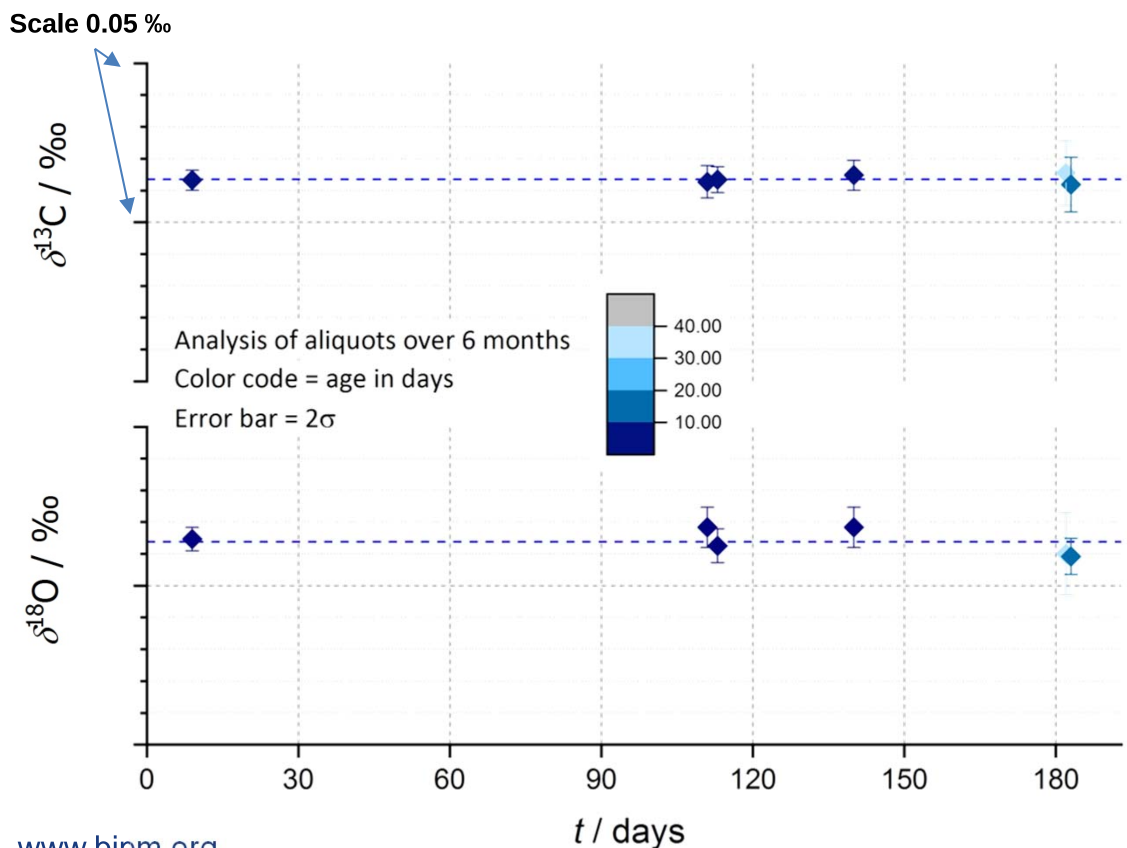
N_s = number of samples



N_m = number of measurements



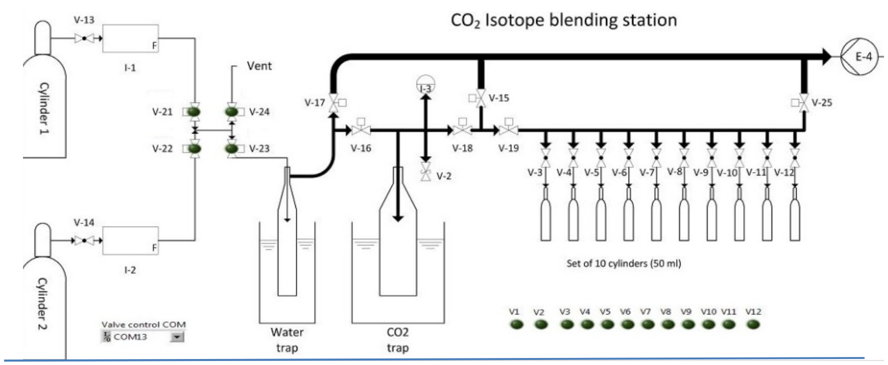
Stability of aliquots is being assessed over 6 months



- Reproducible preparations
- Up to 36 days stability

Aliquots sent to IAEA

Homogeneity assessment of BIPM CO_2 gases in new gas containers



- 1‰ - 35‰ - 42‰

Samples produced at BIPM by the SIRM-Gen

Nominal values of $\delta^{13}C$ vs. VPDB

-1 ‰ -35‰ -42‰

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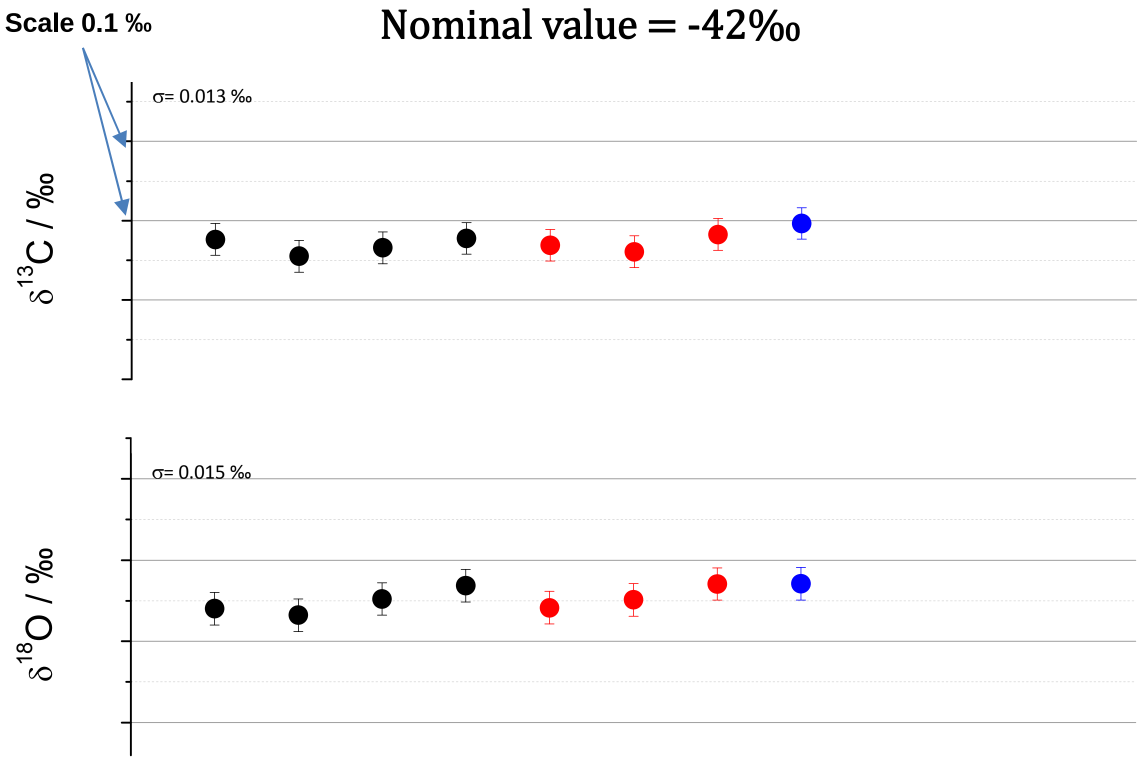
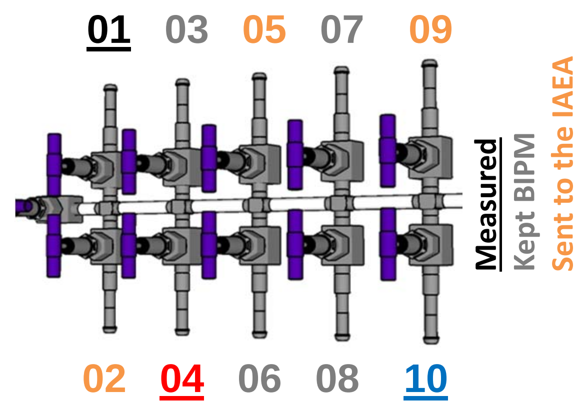
BIPM measurements on batch with samples sent to IAEA

Nominal value = -42‰





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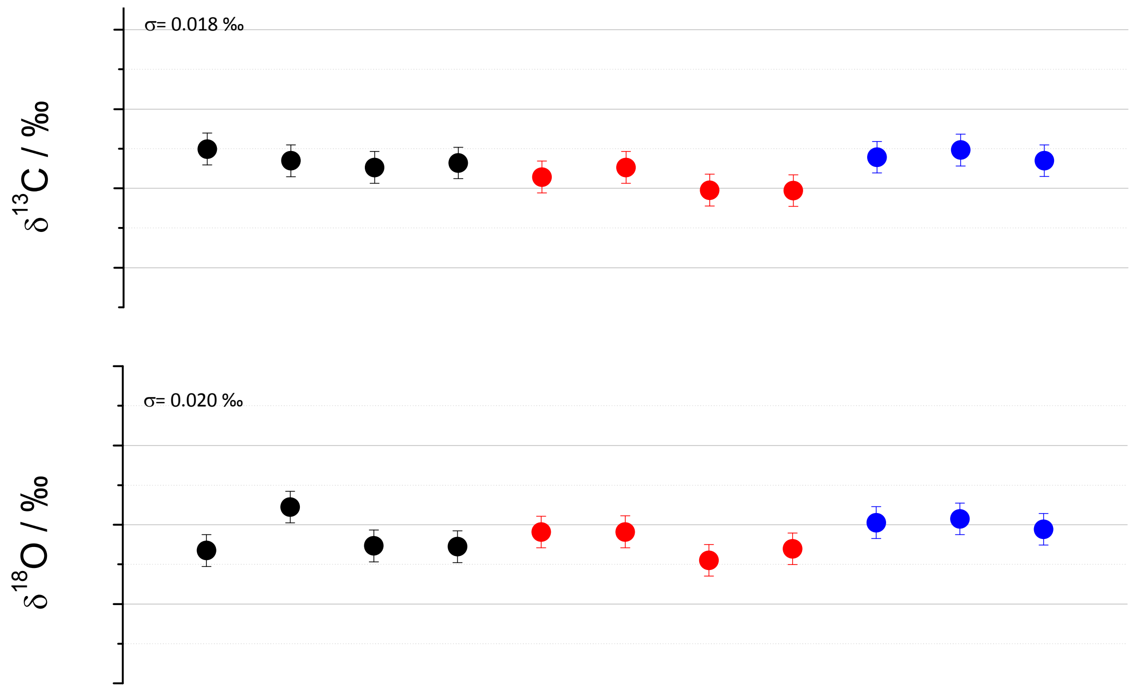
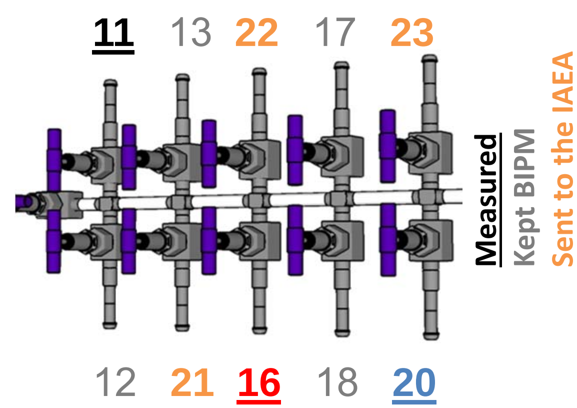
BIPM measurements on batch with samples sent to IAEA

Scale 0.1 ‰

Nominal value = -1 ‰





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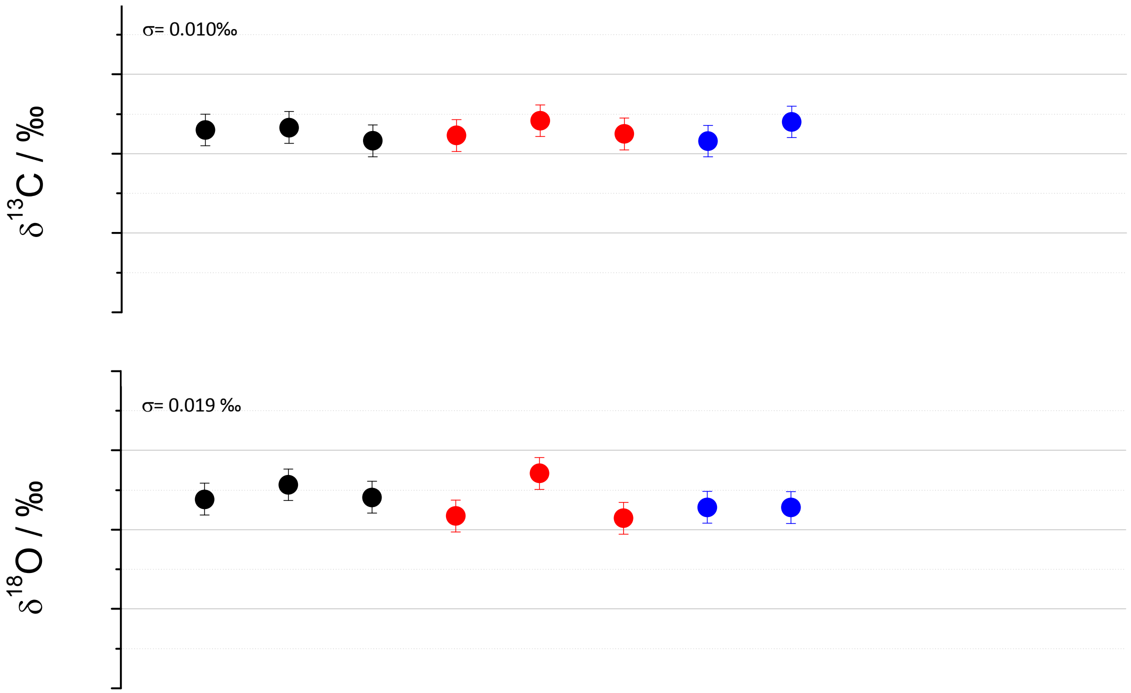
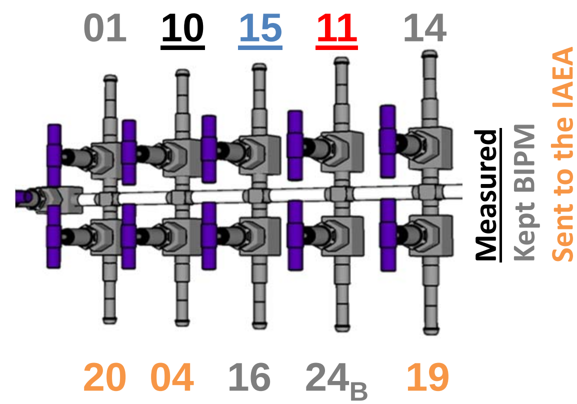
BIPM measurements on batch with samples sent to IAEA

Scale 0.1 ‰

Nominal value = -35 ‰





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Conclusions

- The reproducibility of the isotope ratio measurements $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ was significantly improved
- Stable Isotope Ratio Mixture Generation facility was validated
- Measurements on samples at IAEA confirm excellent within batch homogeneity (full report to be given by S.Assonov)
- Traceability to IAEA primary standards can be established through transfer standards

Special thanks to Visiting Scientist from NMIs

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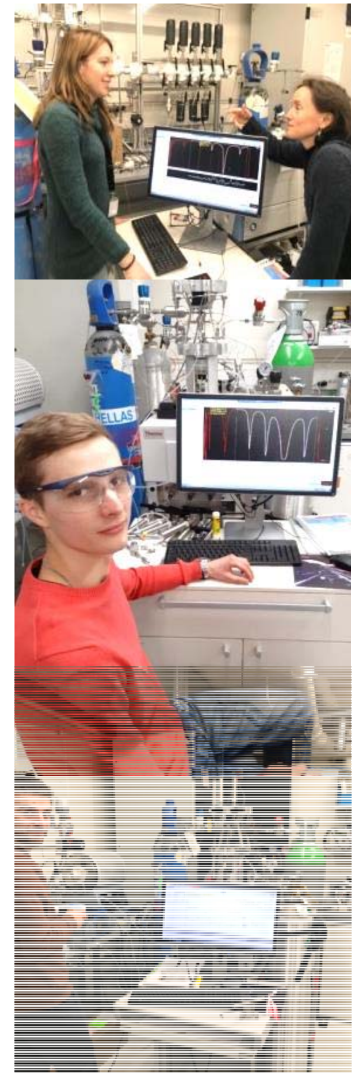
Yan Chubchenko	**VNIIM** (Russia)	Oct 2018-March 2019
Eric Mussell Webber	**NPL** (UK)	April 2019 - June 2019



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