Calibration strategies for FTIR and other IRIS instruments for accurate $\delta^{13}C$ and $\delta^{18}O$ measurements of CO_2 in air

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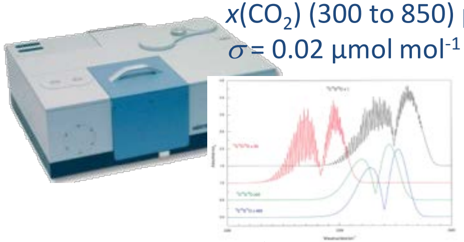
Bureau
International des
Poids et
Mesures

Measuring accurate CO_2 mole fraction for CCQM-K120

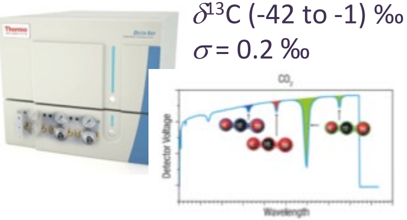
International comparison CCQM-K120 (2017)
Coordinated by BIPM
Using **GC-FID** and **FTIR** to compare
$x(CO_2)$ in participants' standards

FTIR
$x(CO_2)$ (300 to 850) µmol mol^{-1}
σ = 0.02 µmol mol^{-1}

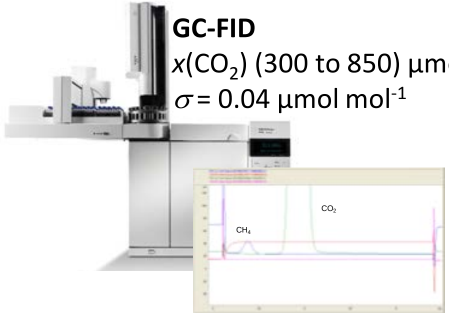


Correction of bias due to different isotopic compositions

IRIS
$\delta^{13}C$ (-42 to -1) ‰ (VPDB scale)
σ = 0.2 ‰



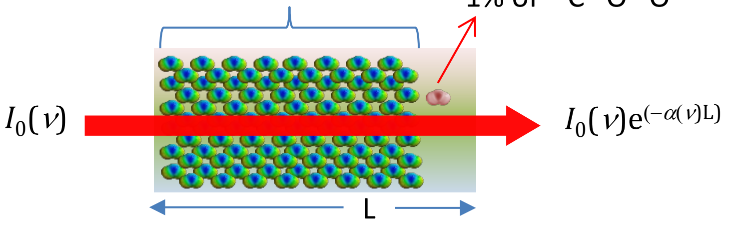
GC-FID
$x(CO_2)$ (300 to 850) µmol mol^{-1}
σ = 0.04 µmol mol^{-1}



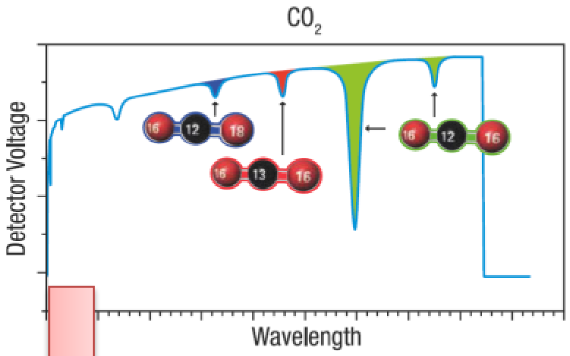
Measurements completed. Results to come end 2017.

Measuring CO_2 isotopes by Infrared Spectroscopy

Simplified view of absorption spectroscopy of CO_2 in air samples



Typical transmittance spectrum



Measurement provides mole fractions

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

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

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

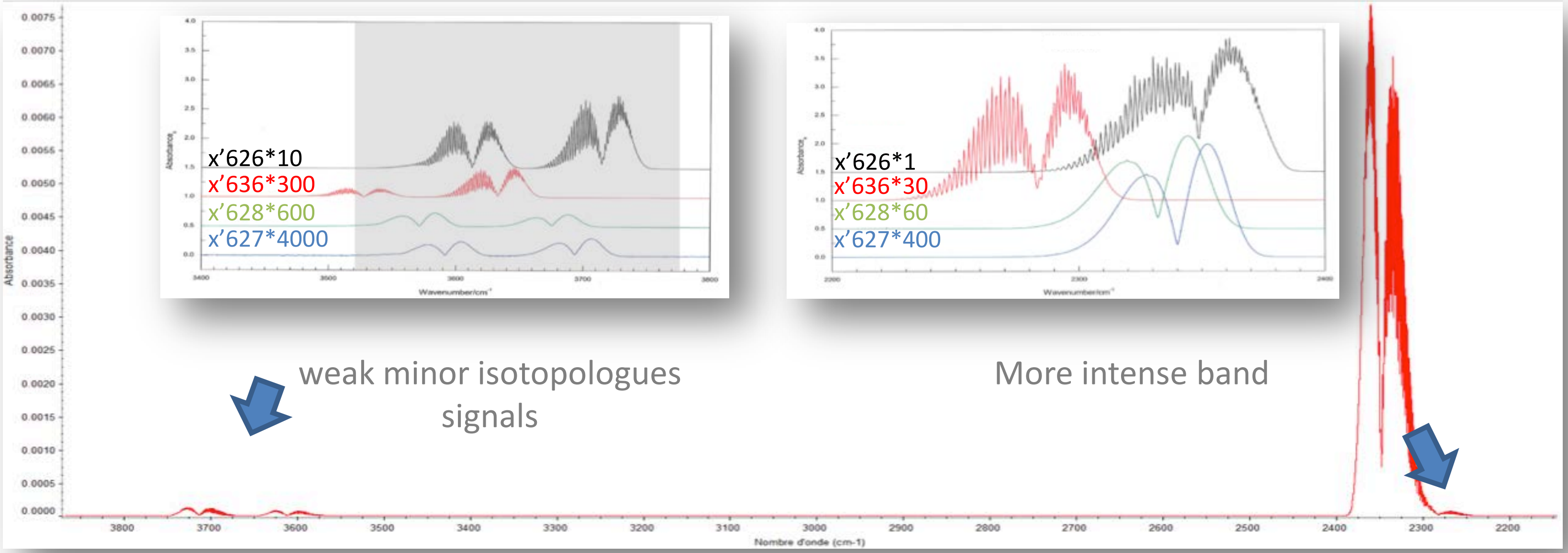
Requires standards of known isotopic composition

$$\delta^{13}C = \left(\frac{R^{13}}{R^{13}_{VPDB}} - 1\right)10^3$$

$$\delta^{18}O = \left(\frac{R^{18}}{R^{18}_{VPDB}} - 1\right)10^3$$

Measuring CO_2 isotopes by FTIR

FTIR spectra cover larger wavelength bands

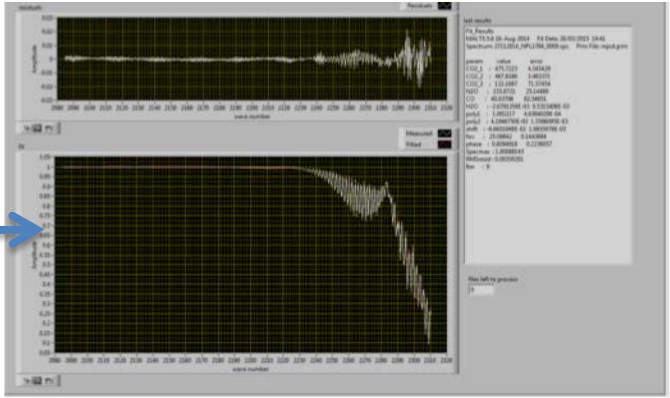


Preferred region for 626

Preferred region for 636 and 628

FTIR spectrometer & measurement process

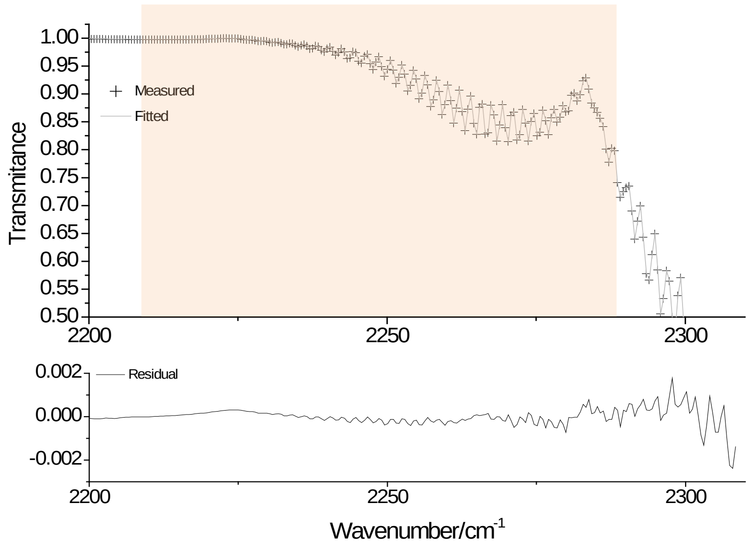
- Vertex 70v (vacuum inside the box) with InSb detector
- White-type cell of 10.01 ± 0.41 m (volume of ~750 mL)
- Sample flow 400 mL min^{-1}
- 360 scans recorded in about 320 seconds to provide one single beam spectrum of a sample;
- 35 min flush to obtain 99.99999% fresh sample before measurement



- Acquisition controled by Labview
- Quantification with MALT

Quantification of isotopologues

Fit of spectra within a band with MALT



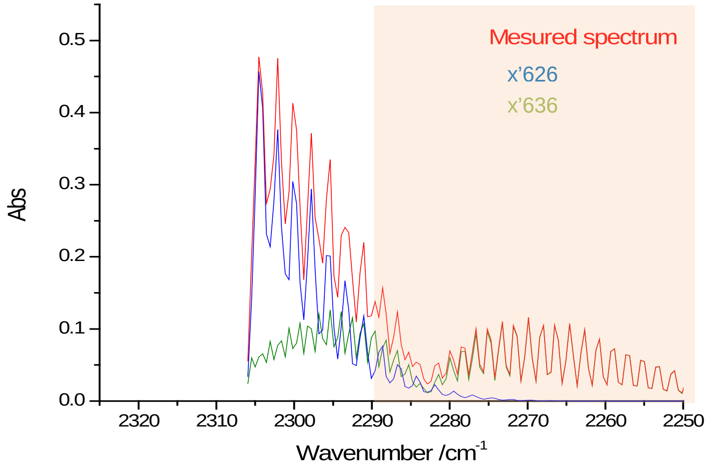
Output : (uncalibrated) mole fraction of each isotopologue (ppm)

Isotopologue	626	636	628
Mixture 1	367.41	3.94	1.47
Mixture 2	407.76	4.37	1.64

MALT = Multiple Atmospheric Layer Transmission[1]

Includes non-linear least-square fit of spectra using:

1) HITRAN lines positions and associated parameters
2) Spectrometer caracteristics influencing the lines shape



[1] Griffith, D. W. T. Appl. Spectrosc. 1996, 50 (1), 59−70.

Calibration strategy

Principle : independent two point calibrations of each isotopologue, using standards of same $\delta^{13}C$ but different mole fraction to bracket the target sample

Standard 1

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

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

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Sample

$x(CO_2)$	$\delta^{13}c$	$\delta^{18}O$
µmol/mol	‰ VPDB	‰ VPDB
393.97	-8.64	-1.44

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

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Standard 2

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

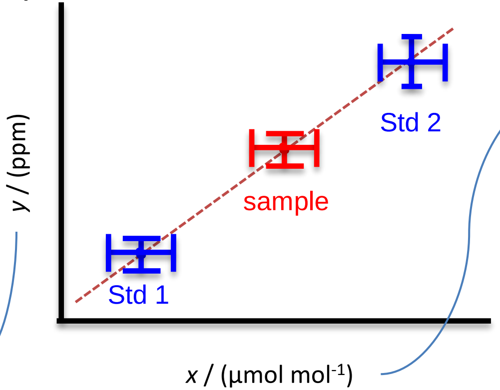
x_{626}	x_{636}	x_{628}
µmol/mol	µmol/mol	µmol/mol
413.96	4.46	1.67

Standard 1 and 2 : Scott Marin cylinders
Mole fraction certified by NIST
Delta values certified by MPI-Jena (IRMS)

Sample : NIST product, air like cylinder, certified in mole fraction
Delta value also certified by MPI-Jena

Uncertainties – example of 626 calibration

Two-points calibration of FTIR response, i.e. 626 signal in ppm



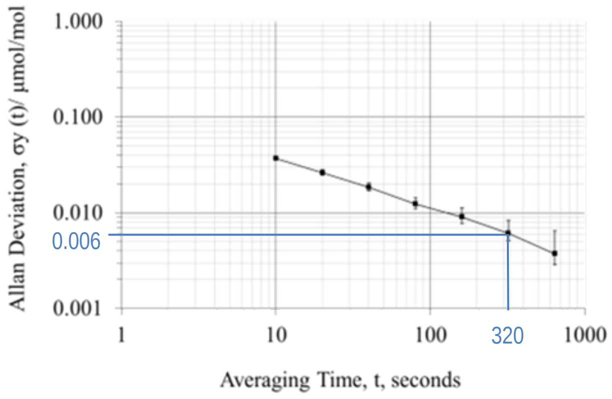
$$x_{626} = [X(^{12}\mathrm{C}) * X(^{16}\mathrm{O}) * X(^{16}\mathrm{O})] * x_{CO2}$$

Abundance includes delta values
Uncertainty = as measured by IRMS at MPI Jena
Repeatability $u(\delta^{13}C) = 0.015‰$

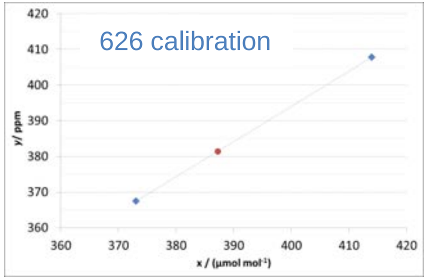
Mole fraction from gravimetric preparation
Uncertainty = provided by NIST
$u(x_{CO2}) \sim 0.05$ to 0.1 µmol mol^{-1}

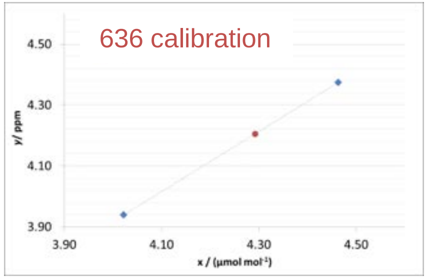
y axis is FTIR response
Uncertainty = noise as determined by Allan deviation

$u(y) = 0.006$ µmol mol^{-1} at 400 µmol mol^{-1}
(320 s integration time)



Uncertainties for all isotpologues





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

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

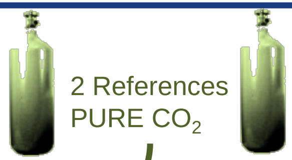
$$u(R^{13}) \sim 10^{-6}$$

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

δ^{13}C	$u(\delta^{13}$C)	δ^{18}O	$u(\delta^{18}$O)
‰ VPDB			
-8.610	0.092	-2.888	1.193

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

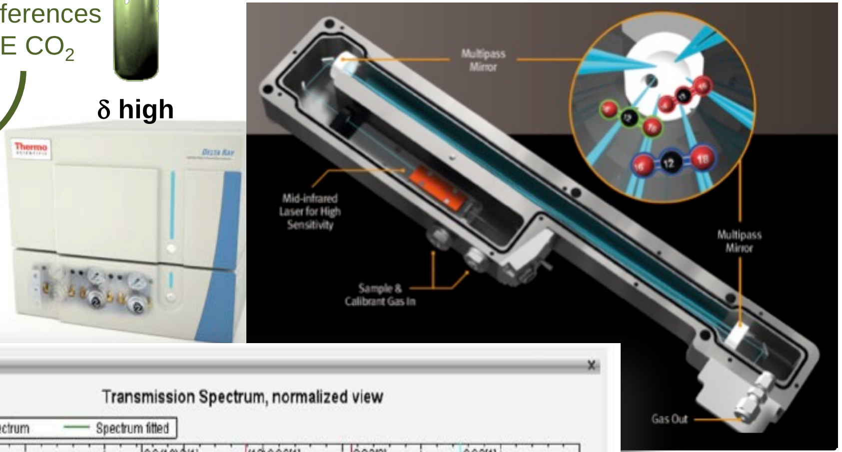
Calibration of the delta scale with the Delta Ray

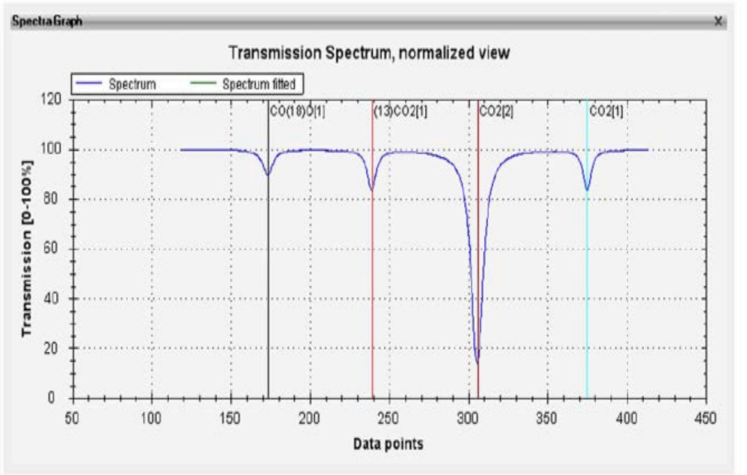


2 References
PURE CO_2

δ low

δ high



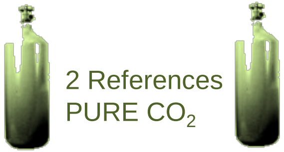


"Delta Ray uses a tunable diode laser that scans over a small spectral region in which the $^{12}CO_2$ and $^{13}CO_2$ isotopologues have absorption lines, fits the two corresponding peaks, determines their areas and calculate the ratio between both to provide δ-values".

Output are delta values. Calibrated with pure CO_2 references, anchored to VPDB.

$$\delta^{13}C = \left(\frac{R^{13}}{R^{13}_{VPDB}} - 1\right)10^3$$

$$\delta^{18}O = \left(\frac{R^{18}}{R^{18}_{VPDB}} - 1\right)10^3$$



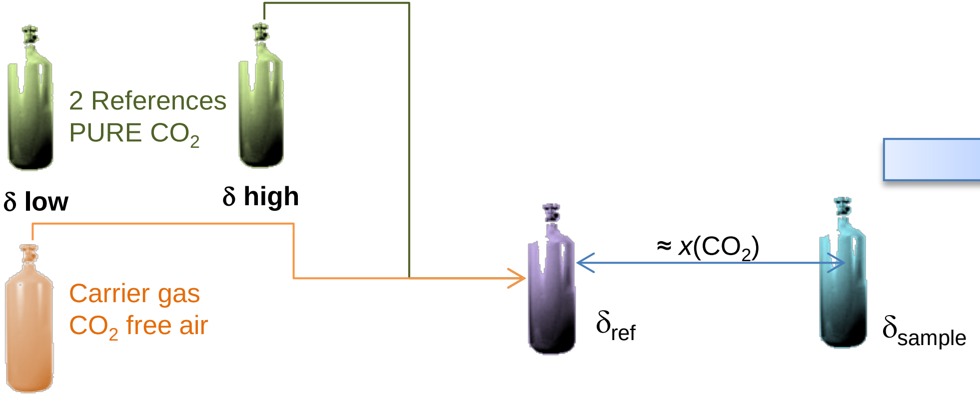
2 References
PURE CO_2

δ low

δ high

Finding appropriate standards

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

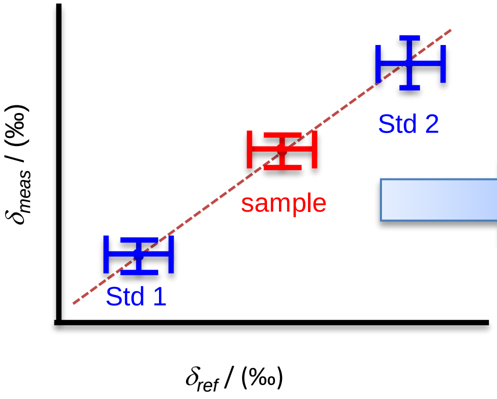


Bias > uncertainty

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

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

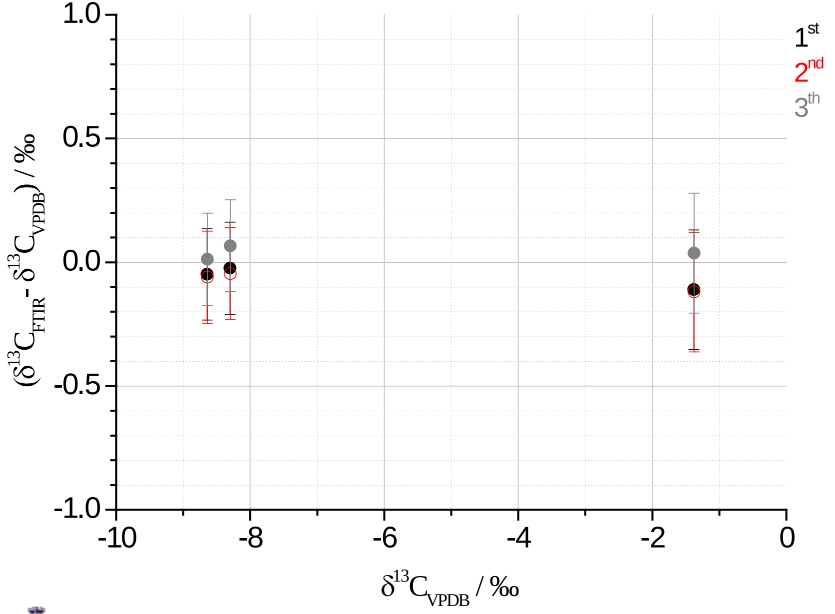
Sample Air Ref 2.
380 µmol mol^{-1}
$\delta^{13}C$ = -1.384 ‰
$\delta^{18}O$ = -7.148 ‰



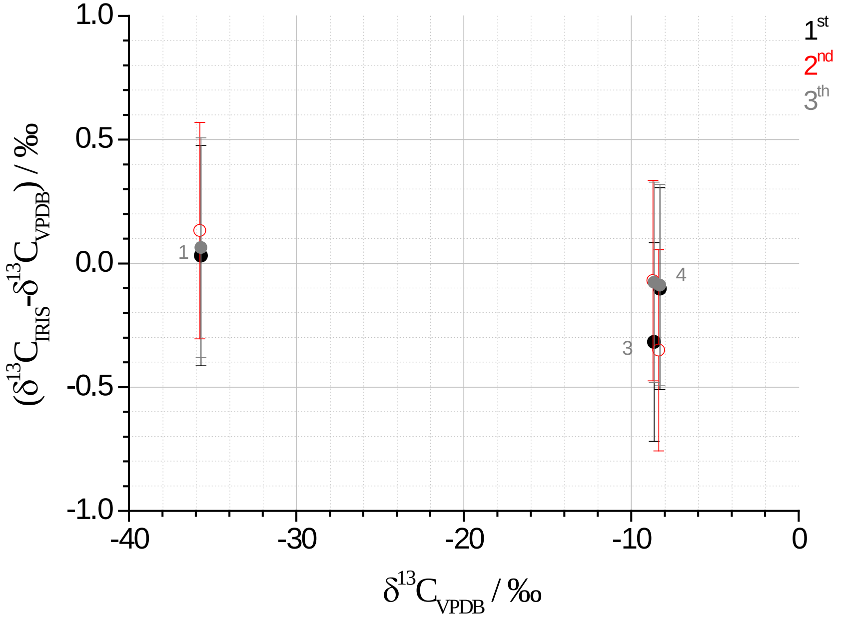
$\delta^{13}C$ ± 0.18 ‰
$\delta^{18}O$ ± 0.48 ‰

Validation by comparison with value assigned by IRMS

FTIR measurements on 3 samples :



IRIS (delta ray) 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‰

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 ‰

Conclusions

- Spectroscopic instruments have high potential to directly measure CO_2 isotopes in air samples
- Their principle (light absorption) results in isotopologues mole fractions as first output, from which delta values are **calculated**
- A calibration strategy using standards of CO_2 in air of **known isotopic composition** AND **mole fraction** was proposed and validated
- The measurement uncertainty is dominated by the mole fraction, as the delta scale in pure CO_2 has negligible uncertainty

Thank you!

Flores E., Viallon J., Moussay P., Griffith D.W.T., Wielgosz R.I., Calibration strategies for FT-IR and other isotope ratio infrared spectrometer instruments for accurate $\delta^{13}C$ and $\delta^{18}O$ measurements of CO_2 in air, *Anal. Chem.*, 2017, 89(6), 3648-3655