Physikalisch-Technische Bundesanstalt
Braunschweig and Berlin
National Metrology Institute

Advancing optical isotope ratio spectroscopy for carbon dioxide and methane

EMPIR 19ENV05 ‘STELLAR’ Work Package 3

Stakeholder meeting, 2021-02-26

J. Braden-Behrens, J. Nwaboh, O. Werhahn (PTB)
K. Zeyer, J. Mohn (Empa), F. Steur (RUG), F. Rolle (INRIM)

WP3 team

NPL National Physical Laboratory

PTB Physikalisch-Technische Bundesanstalt Braunschweig und Berlin

DFM Danish National Metrology Institute

Empa Materials Science and Technology

INRiM Istituto Nazionale di Ricerca Metrologica

VTT MIKES METROLOGY

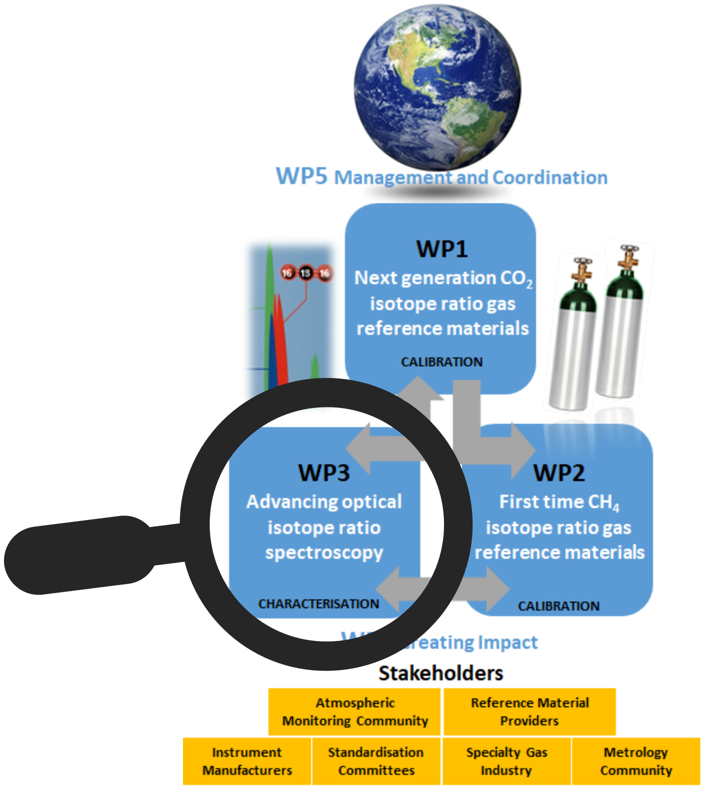
VSL

UNIVERSITY OF EASTERN FINLAND

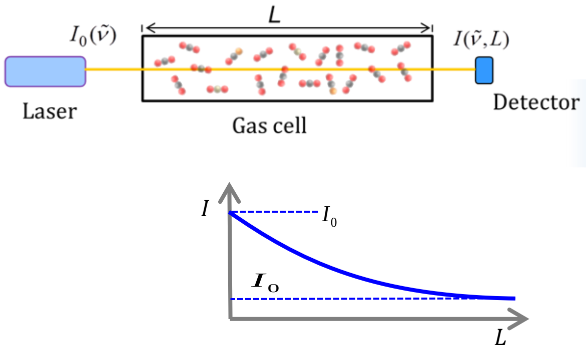
university of groningen

Max-Planck-Institut für Biogeochemie

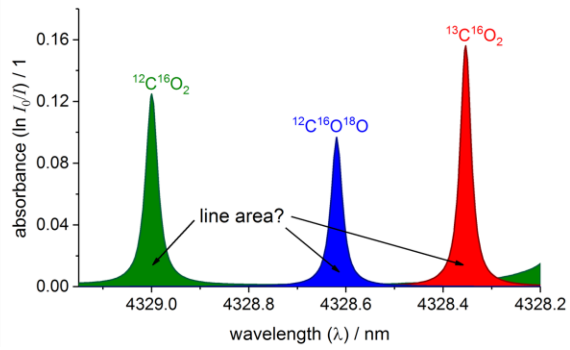
Relations within STELLAR



Optical isotope ratio spectroscopy (OIRS)



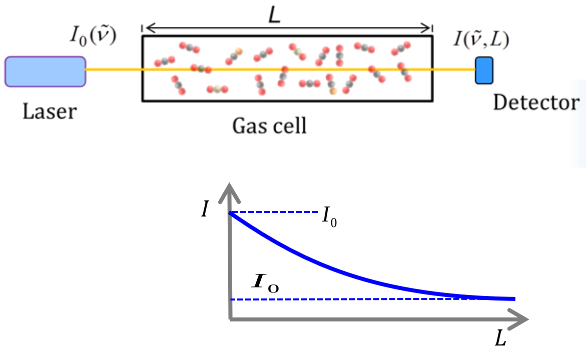
direct laser absorption experiment



high resolution laser absorption spectrum (example – CO_2 at 2.3 μm)

$$\frac{\text{line area isotope 1}}{\text{line area isotope 2}}\Big|\text{sample/reference} \Rightarrow \begin{cases} \delta\text{−value (calibration vs. reference)} \\ \text{absolute ratio (from spectroscopic measurements)} \end{cases}$$

Optical isotope ratio spectroscopy (OIRS)



direct laser absorption experiment

Optional spectroscopy techniques available:

1. TDLAS /QCLAS (EMPA, VSL, RUG, PTB, VTT, DFM, NPL)
2. CRDS (VSL, PTB)
3. FTIR (INRIM, VSL, PTB)

$$\frac{\text{line area isotope 1}}{\text{line area isotope 2}}\Big|\text{sample/reference} \Rightarrow \begin{cases} \delta\text{−value (calibration vs. reference)} \\ \text{absolute ratio (from spectroscopic measurements)} \end{cases}$$

Objectives of WP3

By bringing together experts from gas metrology, spectroscopy, and isotope ratio measurements, we want to:

Develop, characterize and improve field-deployable spectroscopic methods and calibration approaches for measurements of

- **$\delta^{13}C\text{-}CO_2$ and $\delta^{18}O\text{-}CO_2$ - target precision: 0.05 ‰**
- **$\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$ - target precisions: 0.2 ‰ and 1 ‰**

Characterize methods and evaluate calibration approaches

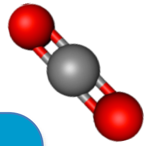
Quantify and control sources of uncertainty

Link OIRS results (isotopologue amount fractions) and δ scales

Develop practical recommendations for the user community

Tasks of WP3

$\delta^{13}C$ and $\delta^{18}O$ in CO_2



Task 3.1

Improvement of OIRS for CO_2

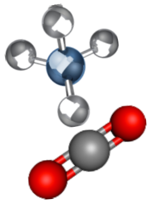
$\delta^{13}C$ and $\delta^{2}H$ in CH_4

Task 3.2

Development of OIRS for CH_4

Task 3.3

Field deployment of OIRS and demonstration of compatibility



PTB

Expected output

STELLAR

Tasks 3.1 and 3.2

Good practice guides for CO_2 and CH_4 OIRS:
- sample handling
- analytical procedures
- traceability
- uncertainty assessments

Tasks 3.3

Good practice guides OIRS for monitoring stations and close-to-source applications
- gas handling
- in-field compatibility (OIRS and IRMS)

All tasks

Input to WP4 'Creating impact':

- OIRS papers,
- conf. contr.
- input to standardisation committees (ISO, CCQM-IRWG, WMO, etc.)

Expected output

Tasks 3.1 and 3.2

Good practice guides for CO_2 and CH_4 OIRS:
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Tasks 3.3

Good practice guides OIRS for monitoring stations and close-to-source applications
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- in-field compatibility (OIRS and IRMS)

All tasks

Input to WP4 ‘Creating impact’:

- OIRS papers,
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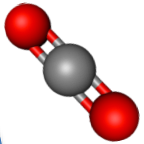
Current activities: Task 3.1

Improved OIRS for CO_2



Develop and improve measurement strategy

Improve protocols for metrological characterizations of OIRS instruments

Ongoing Activity

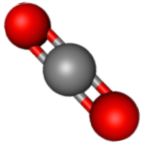
Identified potential improvements

1. Calibration routine
   - gases / cylinders
   - mathematics
   - procedures (e.g. continuous drift correction and gas handling)
2. Instrument improvement
   - line shapes
   - spectral line data
   - assessment of wavenumber axis
   - matrix effects
3. Gas sample conditions
   - *T*, *p*, flow rate

Current activities: Task 3.1

Improved OIRS for CO_2

Ongoing Activity



Develop and improve measurement strategy: Drift correction

Continuous drift correction by alternation of sample measurements by working gas measurement:

All st. dev. in ‰	n=5		n=10	
	uncor	cor	uncor	cor
r636	0.04	0.020	0.06	0.025
r628	0.05	0.021	0.10	0.029
r627	0.06	0.018	0.18	0.03

Standard deviations of 5 and 10 sample aliquot measurements, without (uncor) and with (cor) drift correction.

CO2 analyzer at RUG (F. Steur)

Current activities: Task 3.1

Improved OIRS for CO_2

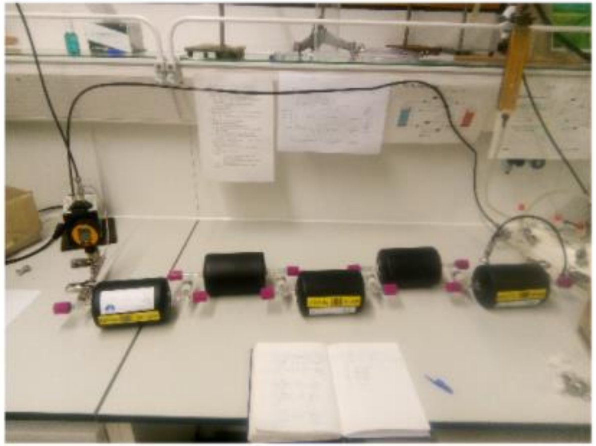
Improved protocol for metrological characterization of OIRS

Ongoing Activity
IRMS comparison
(F. Steur)

First steps are made towards a comparison of IRMS and OIRS measurements:

3 CO_2-in-air mixtures (provided by NPL and INRIM) will be measured by RUG (OIRS) and MPI-BGC (IRMS)

To exclude deviations due to sampling methods, flasks are filled with the reference gas ('sausage method'), first measured at RUG, then sent to MPI-BGC for measurement of the same flasks.



Filling flasks with the reference gas using the sausage method: flasks are connected and flushed with the reference gas

Current activities: Task 3.2

19ENV05 – STELLAR 2020-12-4

Report on key factors limiting the precision and accuracy of OIRS analyzers for $\delta^{13}C\text{-}CH_4$ and $\delta D\text{-}CH_4$

A3.2.1 (Deadline M3-30th Nov 2020) Version 10th Dec 2020

Authors: Joachim Mohn (Empa), Chris Rennick (NPL), Tim Arnold (NPL), Stefan Persijn (VSL), Javis Nwaboh (PTB), Olav Werhahn (PTB), Thomas Hausmaninger (VTT)

Empa, PTB, DFM and NPL will identify (from literature and their existing knowledge) and report on key factors, e.g. matrix effects, spectral interferences, measurement sequence and calibration procedure, limiting the precision and accuracy of existing OIRS analysers for $\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$. This activity will provide input to A3.2.2, A3.2.7 and A3.2.8.

document status: confidential 1/13

Improved OIRS for CH_4

Identify key factors that limit precision and uncertainty

EMPA (J. Mohn K. Zeyer)

Current activities: Task 3.2

19ENV05 – STELLAR 2020-12-4

Report on key factors limiting the precision and accuracy of OIRS analyzers for $\delta^{13}C$-CH_4 and δD-CH_4

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document status: confidential 1/13

	Hardware	Factors	Experiment	References
Precision	Spectrometer	Baseline / fringe changes Temperature, pressure changes Stability laser source / electronics Stability power supply etc.	Allan Werle variance	(Werle *et al.*, 1993; Werle, 2011)
Uncertainty	Scale	Link to primary reference materials defining the scale Uncertainty of the scale propagation to working standards	Publication / Certificate Error propagation	
	Spectrometer	Repeatability Gas matrix effects (O_2, N_2, Ar, H_2O etc.) Spectral interferences (CO_2, N_2O, CO, etc.) CH_4 concentration changes	Experiment Different gas matrixes Different spectral interferences Different concentrations	(Eyer *et al.*, 2016)
	Data collection + processing	Measurement protocol Data processing algorithm	Reproducibility experiment	
	Preconcentration (if applied)	Isotopic fractionation Gas matrix changes	Identical Treatment (IT) experiment	(I 2

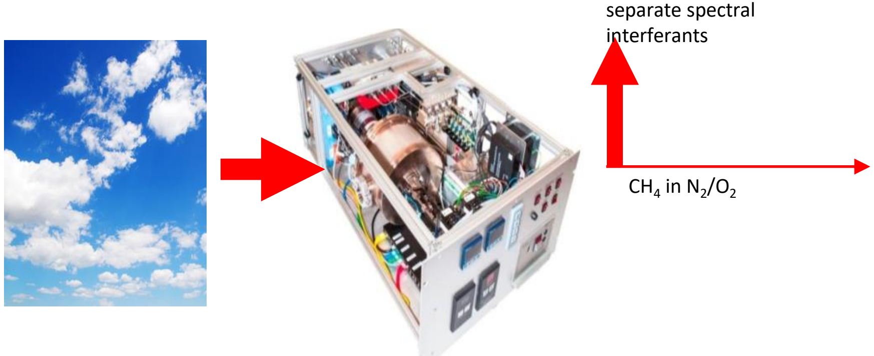
EMPA (J. Mohn K. Zeyer)

Current activities: Task 3.2

Improved OIRS for CH_4

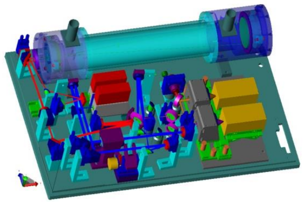
Ongoing Activity
CH_4 analyzer at EMPA
(J. Mohn, K. Zeyer)

Implement modifications to existing analyzers



- Currently upgrade of OIRS at Aerodyne Research for better *T* control.
- **Foreseen experiments:**
  Test, improve precision
  Test spectral interferences (N_2O) and gas matrix effects (O_2) using mixtures prepared in WP2

- Currently set-up phase, integration of second cryofocusing trap to better separate O_2.
- **Foreseen experiments:**
  Improve removal of interfering trace gases (N_2O, CO_2)
  Reduce changes in gas matrix (O_2)



Current activities: Task 3.3

Ongoing activity

Identify target applications

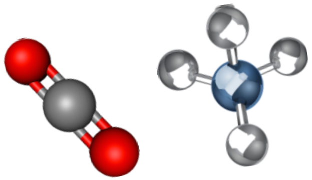


Table 1: Target applications of OIRS for CO_2 detection.

Application category	Target application	Possible Collaborators (main responsible Institute)	Suitable Instruments
Ambient	Monitoring station	• ICOS Finland network (VTT)	• VTT CO2 OIRS (A3.1.6)
Source	Forest sources and sinks	• Bioclimatology, Göttingen University	• PTB CO2 OIRS

Table 2: Target applications of OIRS for CH_4 detection.

Application category	Target application	Possible Collaborators (main responsible Institute)	Suitable Instruments
Source	Methane source monitoring	• Outokumpu Deep Drilling Project (VTT)	• VTT CH4 OIRS

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

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δ^2H
$\delta^{13}C$
STELLAR

Willkommen
Welcome
Bienvenue

Joachim Mohn Kerstin Zeyer
joachim.mohn@empa.ch

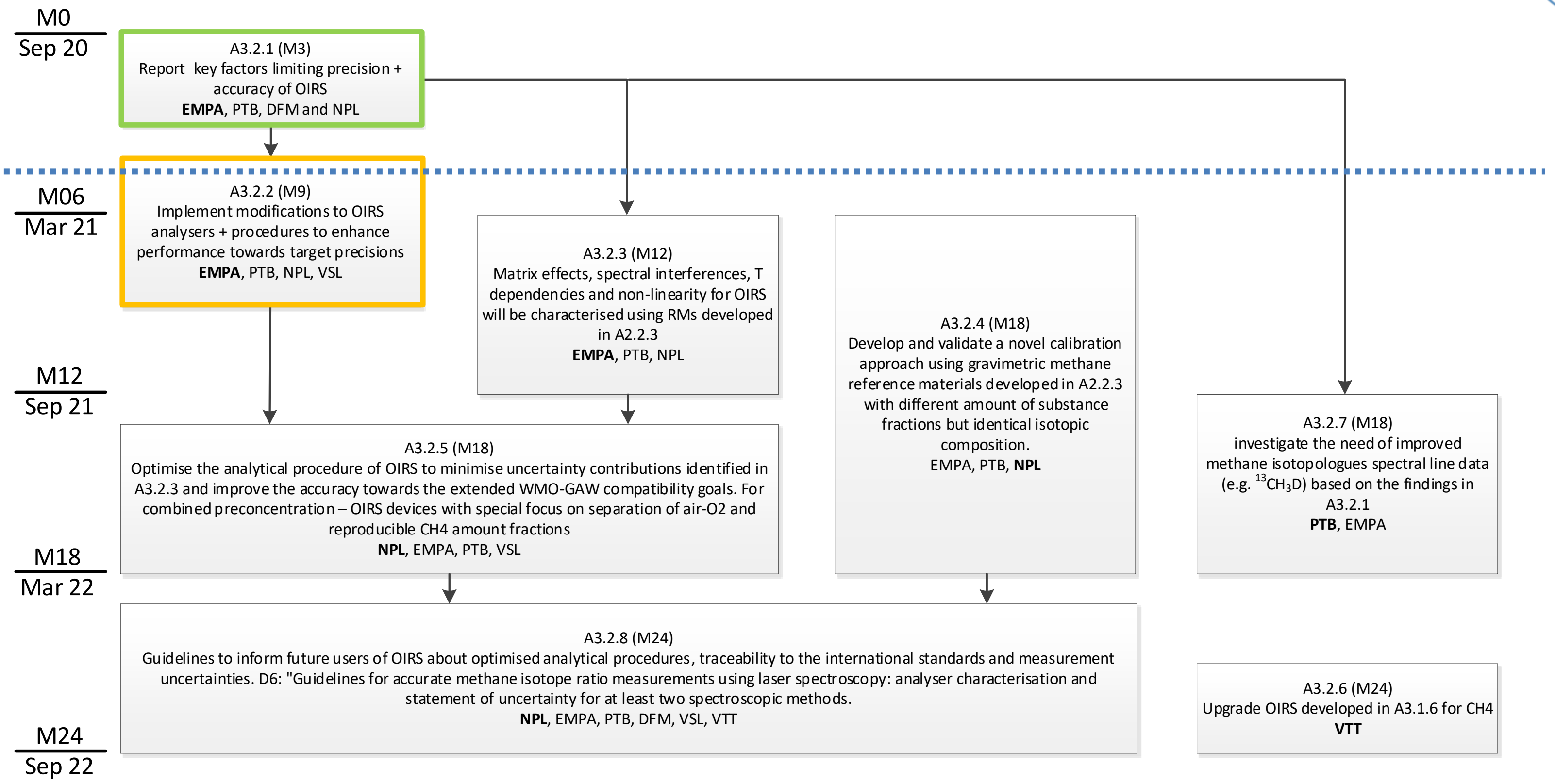
Empa
Materials Science and Technology

Task 3.2: Development of OIRS for methane isotopologues EMPA, PTB, VSL, NPL, VTT, DFM

The aim of this task is to advance and metrologically characterise spectroscopic methods for isotope ratio measurements of methane.

- Work towards a target precision of 0.2‰ for $\delta^{13}C\text{-}CH_4$ and 1‰ for $\delta^{2}H\text{-}CH_4$
- Qualify available spectroscopic isotope-specific line data
- Develop novel approach for calibrating OIRS for individual isotopologues
- Identify main uncertainty contributions, assess an uncertainty budget and publish guideline

Activities Task 3.2

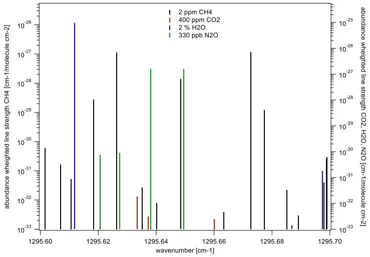


A3.2.1 Key factors limiting precision / accuracy of OIRS_1

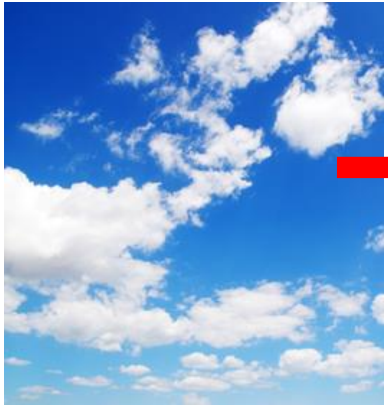
	Hardware	Factors	Experiment	References
Precision	Spectrometer	Baseline / fringe changes Temperature, pressure changes Stability laser source / electronics Stability power supply etc.	Allan Werle variance	(Werle *et al.*, 1993; Werle, 2011)
Uncertainty	Scale	Link to primary reference materials defining the scale Uncertainty of the scale propagation to working standards	Publication / Certificate Error propagation	
	Spectrometer	Repeatability Gas matrix effects (O_2, N_2, Ar, H_2O etc.) Spectral interferences (CO_2, N_2O, CO, etc.) CH_4 concentration changes	Experiment Different gas matrixes Different spectral interferences Different concentrations	(Eyer *et al.*, 2016)
	Data collection + processing	Measurement protocol Data processing algorithm	Reproducibility experiment	
	Preconcentration (if applied)	Isotopic fractionation Gas matrix changes	Identical Treatment (IT) experiment	(Eyer *et al.*, 2016)

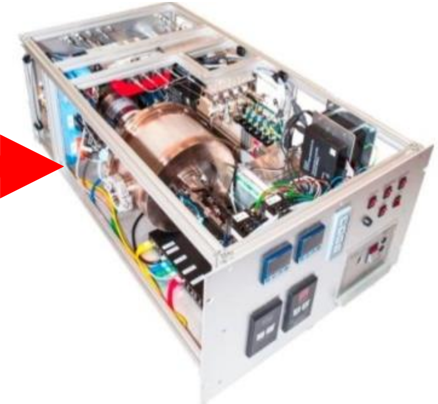
A3.2.1 Key factors limiting precision / accuracy of OIRS_2

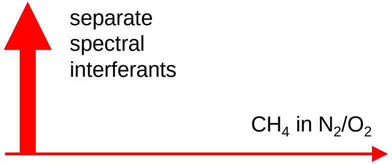
Instrument (Institute)	Wavenumber [cm^{-1}]	Isotopic species	Line positions [cm^{-1}] / abundance-weighted line strength [cm^{-1}/ (molecule cm^{-2})]	Reference
Aerodyne (Empa)	1295.6 – 1295.7	211	1295.673 / 5.811x10^{-22}	(Eyer *et al.*, 2016)
			1295.649 / 6.050x10^{-23}	
		311	1295.626 / 5.654x10^{-22}	
	1306.9 – 1307.05	211	1306.948 / 9.273x10^{-23}	
		212	1307.040 / 2.229x10^{-23}	
		N_2O	1306.929 / 1.040x10^{-19}	
Aerodyne (NPL)	1293.702 – 1293.814	211	1293.781 / 4.482×10^{-22}	
		311	1293.716 / 4.129×10^{-22}	
	1306.885-1307.082	212	1307.04 cm^{-1} / 2.22×10^{-23}	
		N_2O	1306.929 cm^{-1} / 1.04×10^{-19}	
		H_2O	1307.019 cm^{-1} / 6.30×10^{-24}	
Picarro G2201-I (PTB)	6029 – 6057	211	6057.08 / 1.52×10^{-21}	(https://www.picarro.com/products/g2201i_isotopic_analyzer)
		311	6029.11 / 1.52×10^{-23}	
dTDLAS OIRS instrument (PTB)	to be determined	211		
		311		
CRDS (VSL)	2950.8-2951.4 (211 & 311)	211	2950.863 / 1.447x10^{-24}	Hitran: 2951.35955 cm-1 and 2951.35983 cm-1 with same S
		311	2951.3057 / 1.233x10^{-22}	
			2950.851 / 2.734x10^{-23}	
			2951.360 / 1.884x10^{-24}	
	3067.4-3069.0 (211, 311 & 212)	212	3068.95048 / 4.409x10^{-23}	
TDLAS (VTT)	3060.25 – 3060.45	311	3060.320 / 7.20×10^{-24}	(Kääriäinen *et al.*, 2018)
		211	3060.363 / 1.38×10^{-23}	
		311	3060.377 / 5.10×10^{-24}	
		211	3060.408 / 1.20×10^{-24}	
	3061.38 – 3061.53	212	3061.414 / 5.08 e^{-23}	
		211	3061.494 / 9.64 e^{-23}	

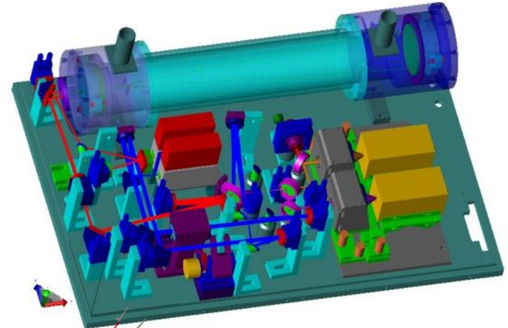


A3.2.2 (M9) – Empa Status









- Currently set-up phase, integration of second cryofocusing trap to better separate O_2.
- Foreseen experiments:
  Improve removal of interfering trace gases (N_2O, CO_2)
  Reduce changes in gas matrix (O_2)

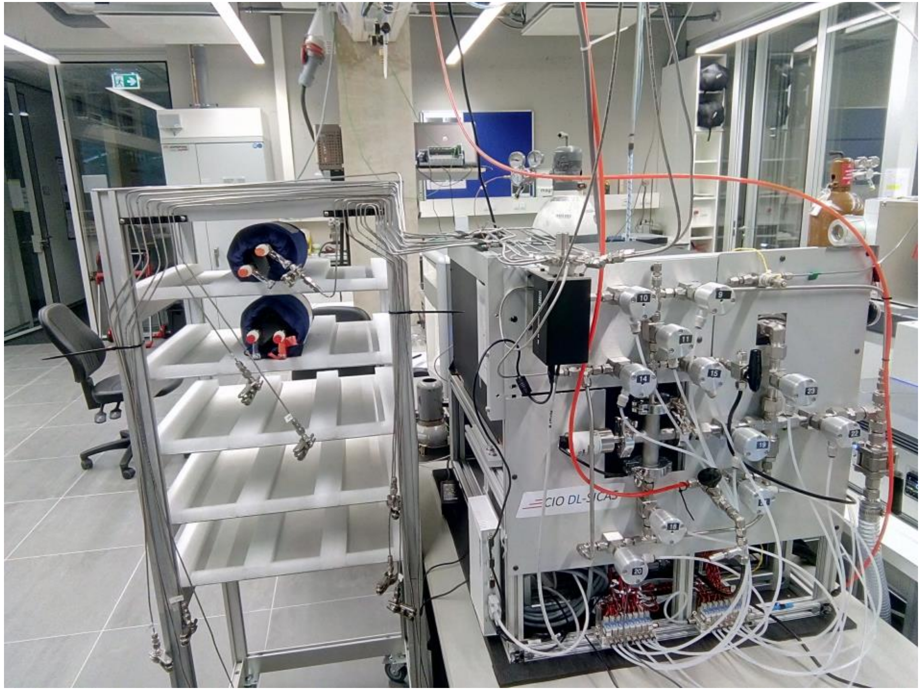
- Currently upgrade of OIRS at Aerodyne Research for better T control.
- Foreseen experiments:
  Test, improve precision
  Test spectral interferences (N_2O) and gas matrix effects (O_2) using mixtures prepared in A2.2.3.

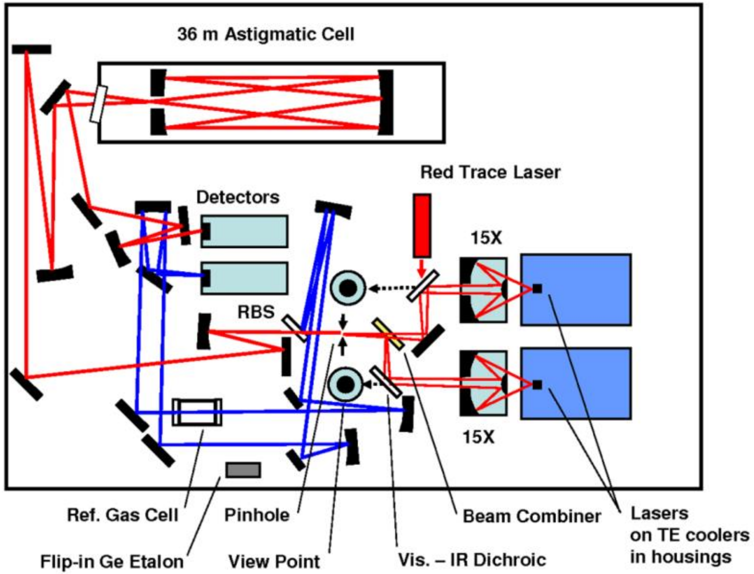
Aerodyne dual laser optical spectrometer (CW-IC-TILDAS-D)

Measures discrete air samples (flasks) in static mode

Species: 626, 636, 628 and 627

RUG – F. Steur





A3.1.1 – develop strategies to measure $\delta^{13}C$ and $\delta^{18}O$ with target precisions of 0.05‰

Continuous drift correction by alternation of sample measurements by working gas measurement:

All st. dev. in ‰	n=5		n=10	
	uncor	cor	uncor	cor
r636	0.04	0.020	0.06	0.025
r628	0.05	0.021	0.10	0.029
r627	0.06	0.018	0.18	0.03

Standard deviations of 5 and 10 sample aliquot measurements, without (uncor) and with (cor) drift correction.

Drift correction as applied in measurement procedure:

$$M_{sample(t)drift\ corrected} = \frac{M_{sample(t)}}{M_{working\ gas(t)}}$$

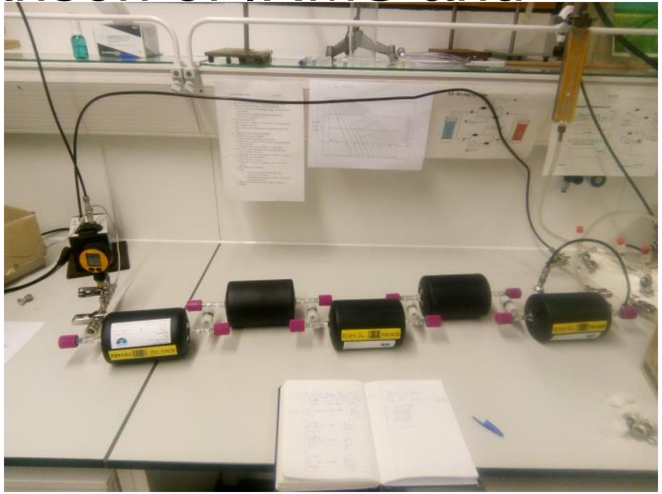
$M_{working\ gas(t)}$ is the working gas measurement at time t derived from the time-dependent linear regression of working gas measurements bracketing the sample measurement.

A3.1.2 – compatibility IRMS and OIRS

First steps are made towards a comparison of IRMS and OIRS measurements:

3 CO_2-in-air mixtures (provided by NPL and INRIM) will be measured by RUG (OIRS) and MPI-BGC (IRMS)

To exclude deviations due to sampling methods, flasks are filled with the reference gas (‘sausage method’), first measured at RUG, then sent to MPI-BGC for measurement of the same flasks.



Filling flasks with the reference gas using the sausage method: flasks are connected and flushed with the reference gas

Stable isotope metrology to enable climate action and regulation

Stefan Persijn

EMPIR 2019 Environment

Partnering meeting, London (UK)
26 and 27June 2019

VSL's track record

- Provide gas standards for CO_2 and CH_4
- Good connections to industry and standardisation (ISO/TC158 & CEN/TC 264)
- Laser spectroscopic measurements of isotopes and purity analysis

References

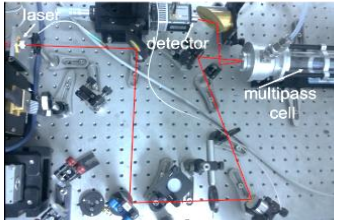
1. Kiseleva, M, Mandon, J, Persijn, S, & Harren, F. (2018). Line strength measurements and relative isotopic ratio $^{13}C/^{12}C$ measurements in carbon dioxide using cavity ring down spectroscopy. *JQSRT*, *204*, 152-158.
2. Dueck, T, De Visser, R, Poorter, H., Persijn, S., ... (2007). No evidence for substantial aerobic methane emission by terrestrial plants: a ^{13}C-labelling approach. *New Phyt. 175*(1), 29-35.
3. Nieuwenkamp, G., van der Veen, A. (2006). Discrepancy in infrared measurement results of carbon monoxide in nitrogen mixtures due to variations of the $^{13}C/^{12}C$ isotope ratio. Accredit Qual Assur, *10*(9), 506-509.

VSL facilities

- Static (ISO 6142) and dynamic (ISO 6145) gravimetric gas mixture preparation

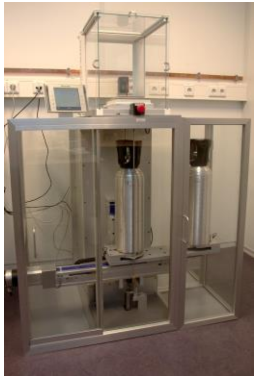
- Bruker Vertex 70v FTIR spectrometer

- Mid-IR CRDS spectrometer (2.4-5.1 µm)
- TDLAS (QCL, ICL and DFB mid-IR lasers in range 2.4 to 9.6 µm) with various cells (up to 76 m)



VSL's offer (1)

- Prepare static isotopic gas mixtures for CO_2 (obj. 1)
- To develop traceable measurement methods for absolute isotope ratio measurements of CO_2 (obj. 3)
- Line strength measurements of CO_2 isotopes in the mid-IR wavelength region (obj. 4)
- Impact: Disseminate results in ISO/TC 158 and CEN/TC 264 (obj. 5)



Finances

- Labour ~ 190 k€ (~20 MM)
- Costs ~ 40 k€
  - Publication fees
  - Gas cylinders
  - Gases
  - Travel and subsistence

F. Rolle

FTIR Set-up at INRIM (I)

- Thermo Scientific Nicolet iS50
- Detector DLaTGS
- 10 m 'White type' gas cell (Thermo Scientific)
- Glove box for pure N_2 flushing

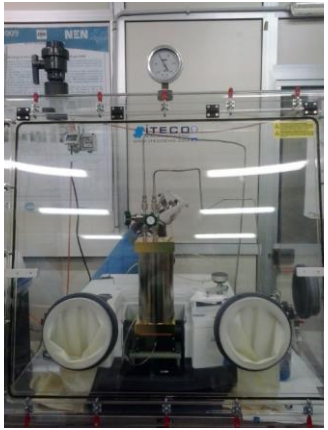


Fig. 1: FTIR set-up at INRIM

- Use for δ^{13}C measurements in CO_2/synthetic air mixtures at 400 µmol mol^{-1} within the SIRS and STELLAR projects
- Use of MALT and B-FOS software
- B-FOS software, developed by the *Bureau International des Poids et Mesures* (BIPM), interfaces the FTIR software and MALT to fit the spectra and quantify the analytes
- Uncertainty evaluation

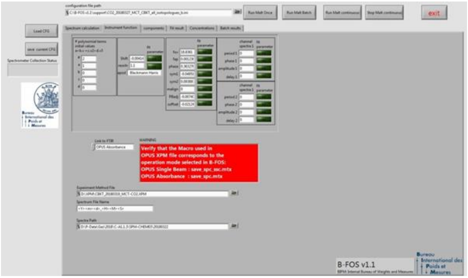


Fig. 2: B-FOS interface

FTIR Set-up at INRIM (II)

- CALIBRATION OF FTIR:
  - Two CO_2 standards of different mole fraction but similar isotopic values
  - Bracketing of unknown samples
  - Measurement of isotopologues 626 and 636
  - Spectroscopic regions 2200-2310 cm^{-1} and 3500-3800 cm^{-1}

Fig. 3: gravimetric mixtures prepared at INRIM

FURTHER STEPS:

- Production of gravimetric mixtures using different pure CO_2 reference materials from the SIRS project and their verification by FTIR
- Preparation of mixtures of CO_2/SA at 400 µmol/mol by dynamic dilution by means of the dilution system developed at INRIM within the SIRS project for FTIR calibration
- Improvement of the FTIR system for $\delta^{18}O$ measurements

Fig. 4: Mixing chamber of the dilution system developed at INRIM

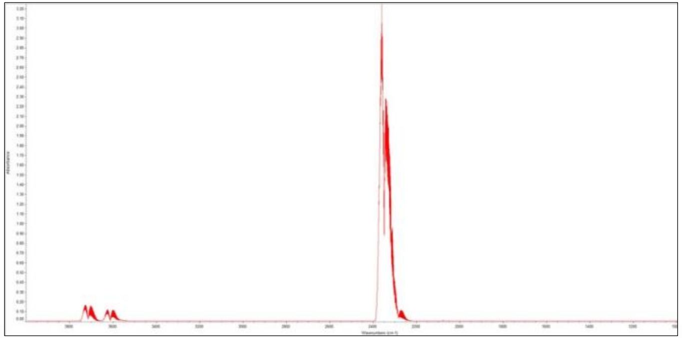


Fig. 5: CO_2/SA mixture at 400 µmol mol^{-1} spectrum