Schweizerische Eidgenossenschaft
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Federal Office of Meteorology and Climatology MeteoSwiss

WMO OMM

GLOBAL ATMOSPHERE WATCH

Empa
Materials Science and Technology

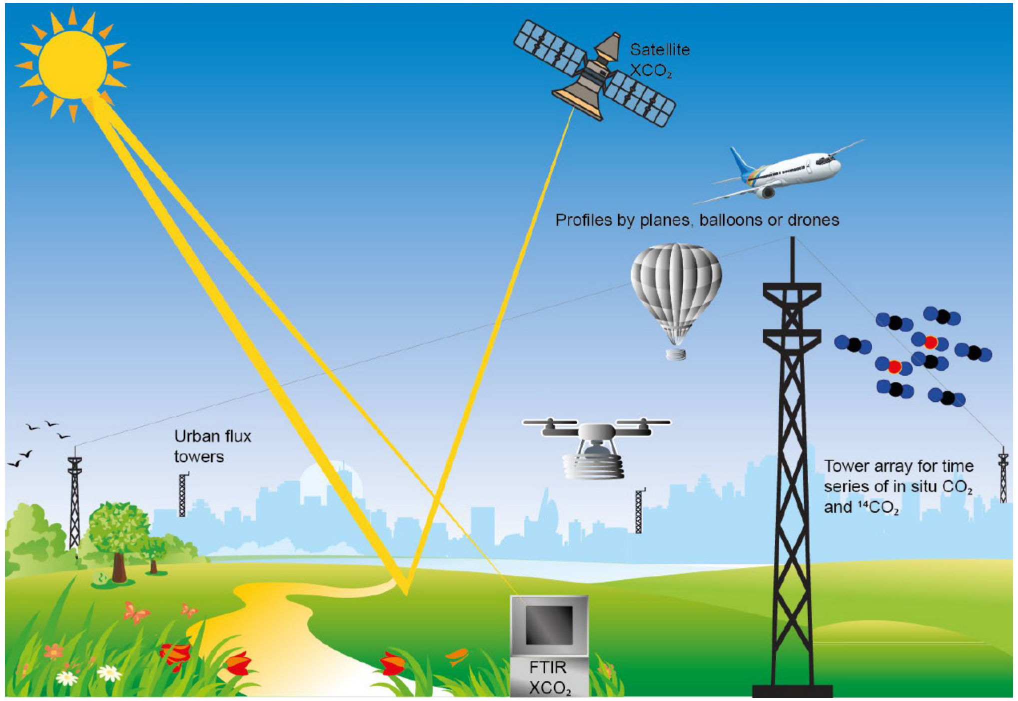
Greenhouse Gas Observations with Laser Spectroscopy

Martin Steinbacher
martin.steinbacher@empa.ch

6th WCC-SF6 Training and Education Course, 02 November 2022

Planning of ambient air measurements

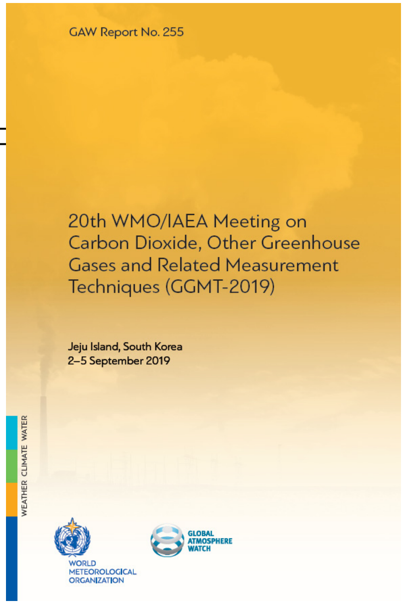
- Why do I want/need to measure?
- Which compounds are of interest?
  (gaseous compounds, particulates, deposition, meteorological parameters)
- Where are measurements reasonable?
  (e.g., representativeness of the sample, avoid influence of undesirable sources)
- What kind of data series are needed?
  (continuous, discrete, time resolution, concentration range, spatial resolution, stationary vs. mobile, etc.)
- What are the requirements in terms of traceability, accuracy and precision?



here: focus on ground-based in-situ observations

Instrumentation – which technique to use

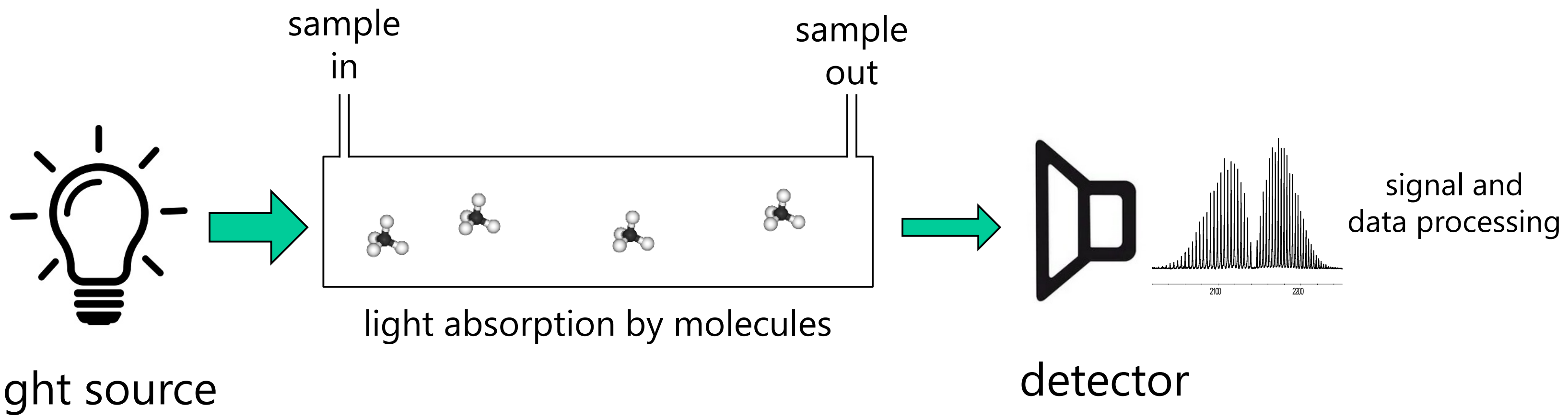
"… To achieve the required levels of network compatibility […] it is important to understand and carefully consider the design of the whole analysis system including instrument, gas handling, calibration and data management. No single instrument type is recommended. Many can be used with equal success and none are fool proof when poor choices are made with gas handling or data management. A trade-off in instrument stability and complexity versus cost must often be balanced according to the needs, resources and challenges of the measurement programme. …"

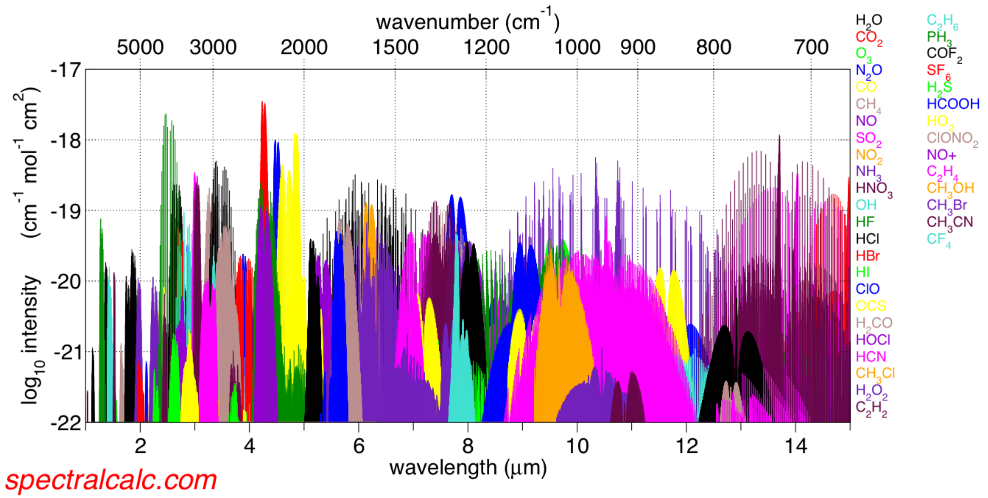


GGMT-2019 Report, GAW Report Nr. 255, 2020

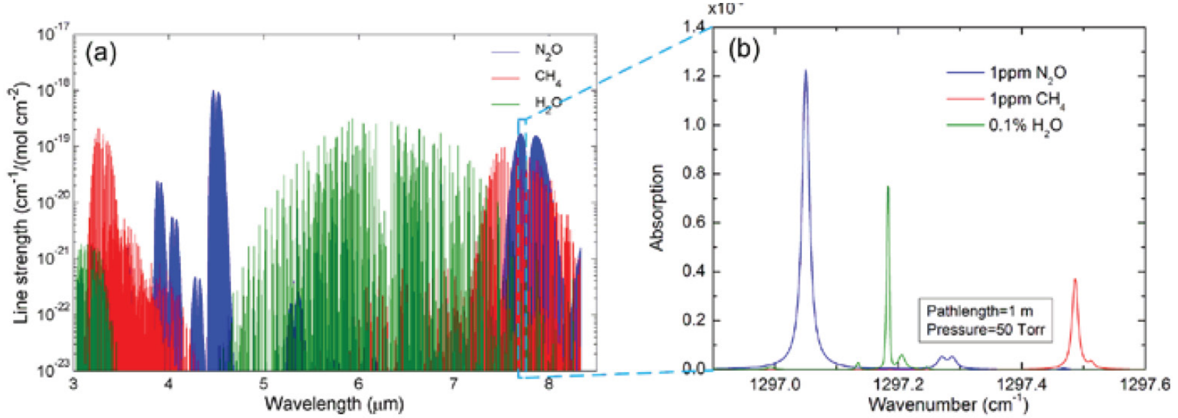
martin.steinbacher@empa.ch, Laboratory for Air Pollution/Environmental Technology

Fundamentals of (laser) spectroscopy





https://commons.wikimedia.org/wiki/File:Spectralcalc_infrared_bands.png



Dong et al., 2015

- ➢ choosing the right wavelength is key
- ➢ pay special attention to water vapour

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H2O levels in the atmosphere can be high … and highly variable

location	datetime	T [C]	rel hum [%]	atm. pressure [hPa]	E_H2O [hPa]	e_H2O [hPa]	vol mix ratio [%]	vol mix ratio [ppm]	mass mix ratio [g/kg]
American Samoa	01.01.2005 14:00	27.3	94	998	36.34	34.16	3.4%	34229	21.3
BEO Moussala (summer)	17.08.2009 14:00	6.5	94.4	719.5	9.69	9.15	1.3%	12711	7.9
BEO Moussala (winter)	07.01.2009 16:00	-10.6	25.4	706.8	2.72	0.69	0.1%	977	0.6
Cape Point (summer)	04.01.2008 19:00	24	70.6	983.2	29.89	21.10	2.1%	21460	13.3
Cape Point (winter)	01.07.2010 19:00	6.1	58.2	983.6	9.42	5.48	0.6%	5576	3.5
Mount Kenya	02.01.2006 17:00	15.1	83.1	659.5	17.19	14.28	2.2%	21659	13.5
Zugspitze	18.10.2010 14:00	-7.6	77	705	3.44	2.65	0.4%	3761	2.3

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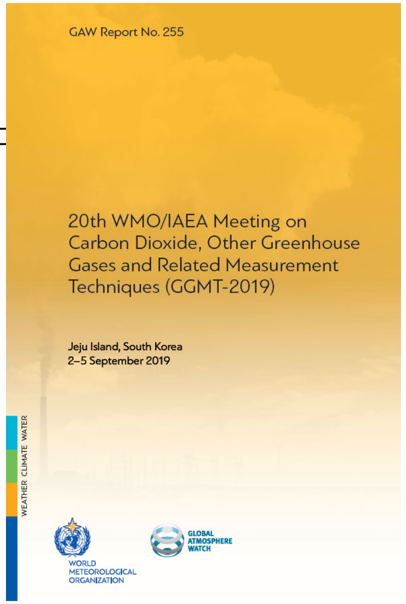
Sample drying


GAW Report No. 255

20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2019)

Jeju Island, South Korea
2–5 September 2019

GGMT-2019 Report,
GAW Report Nr. 255, 2020

- *water and water vapour should be removed from the sample gas stream*
- *or, understanding its influence on the mole fraction determination must be carefully quantified*
- *water vapour effects influencing accurate mole fraction determination include dilution, transient surface effects from wetting and drying tubing walls, and instrument specific spectroscopic interference*

- *both calibration standards and sample air should pass through the same drying vessel immediately prior to analysis*
- *the preferred method of drying is cryogenic, typically via a 'cold trap' immersed in an ethanol bath*
- *most chemical drying agents can absorb CO_2 and are unsuitable*
- *magnesium perchlorate ($Mg(ClO_4)_2$) can be used, but only under conditions of constant flow and pressure*
- *Nafion® membrane dryers may be used, but also only under conditions of constant flow, pressure and humidity*

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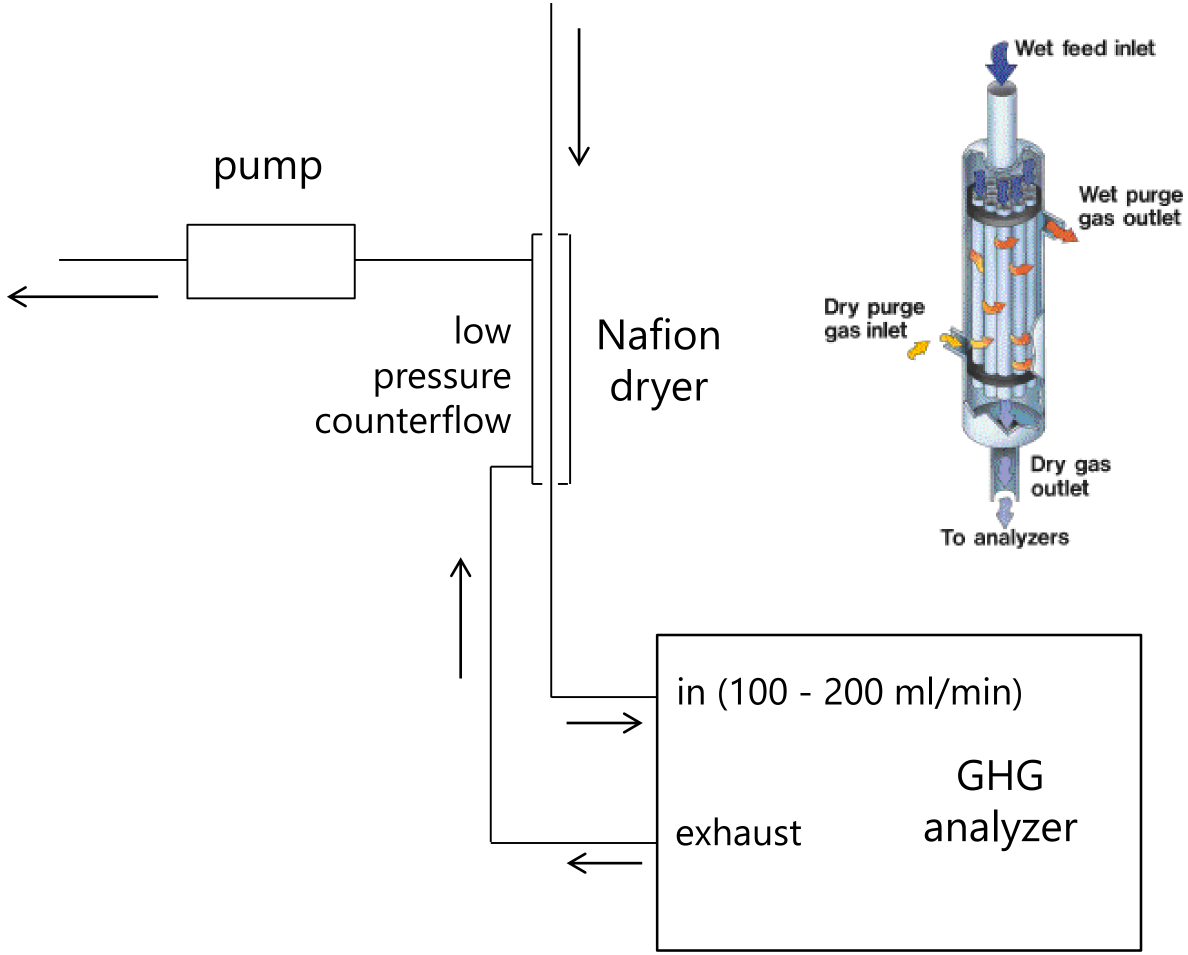
Sample drying, simplified scheme with Nafion dryer (reflux method)



http://www.permapure.com

dew point of ~ - 35 degC can be achieved

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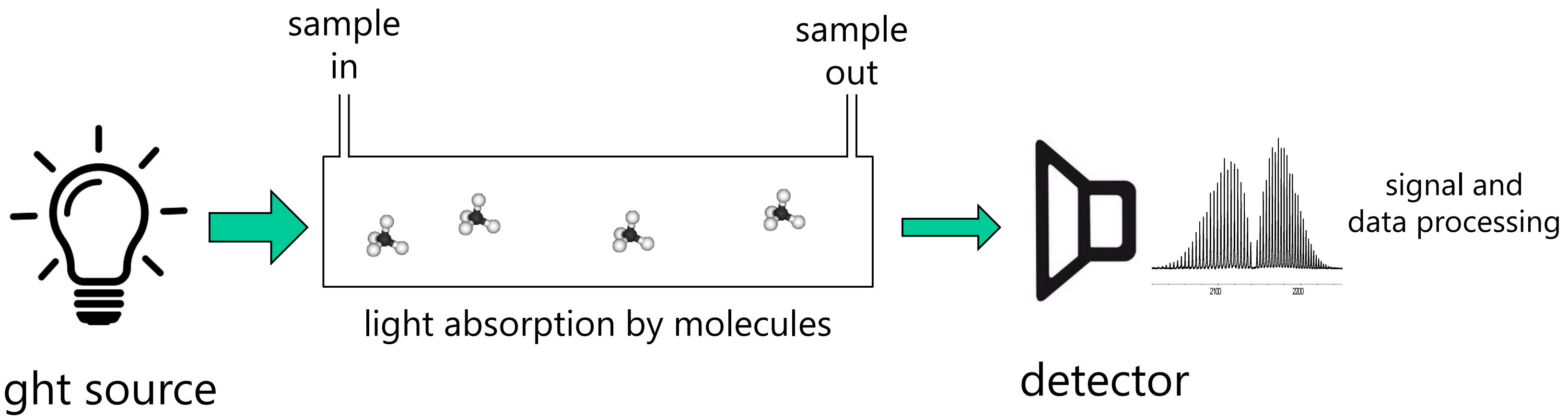
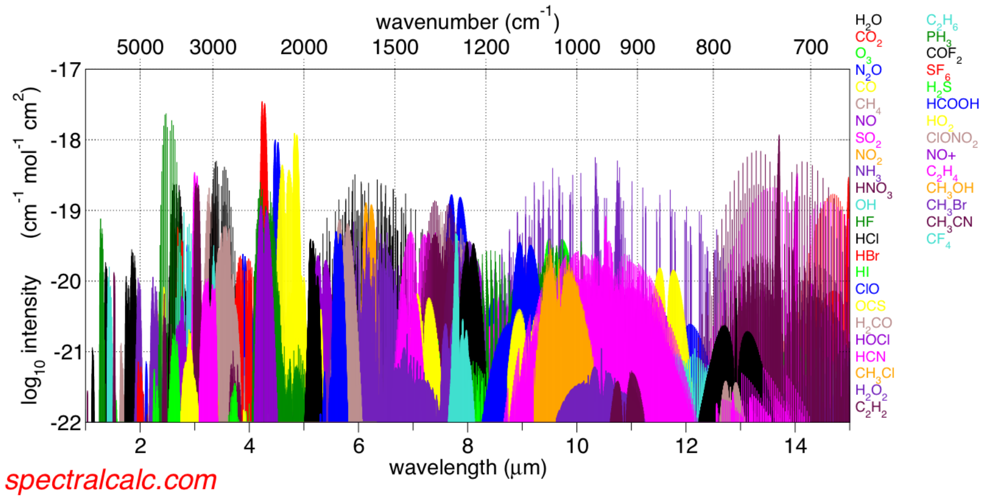
Fundamentals of (laser) spectroscopy





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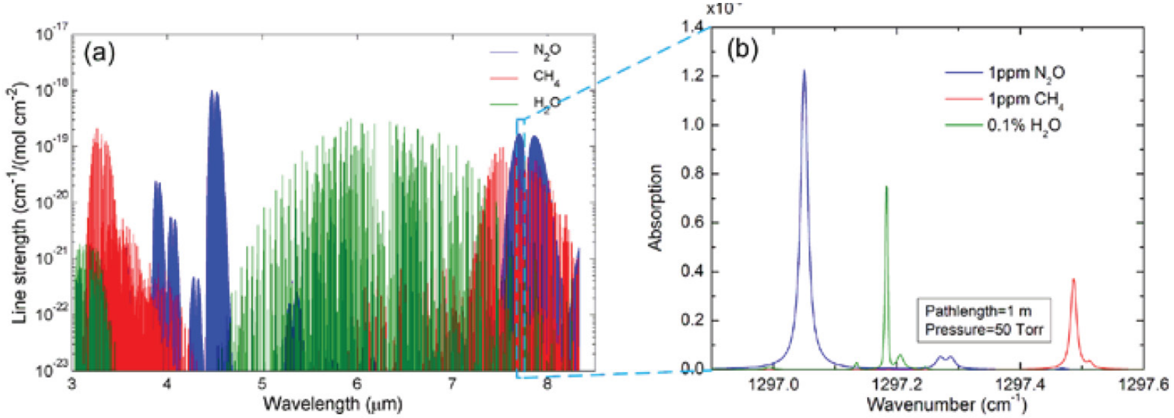

Dong et al., 2015

- choosing the right wavelength is key
- pay special attention to water vapour

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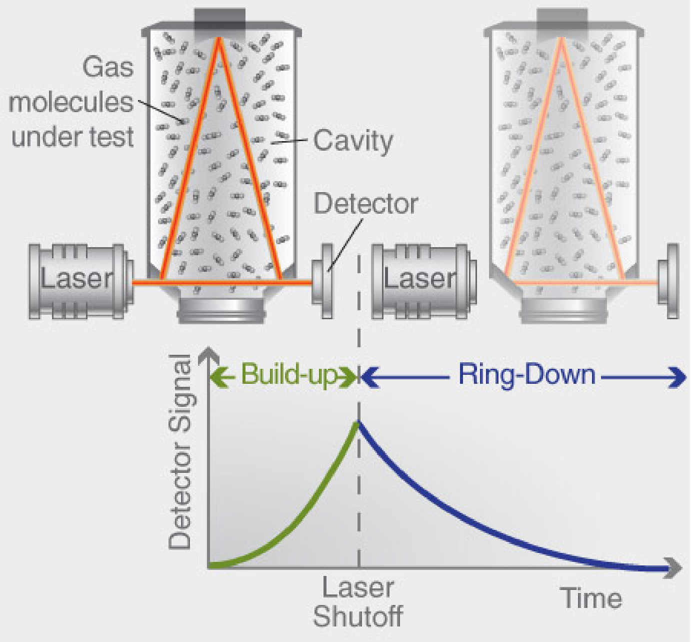
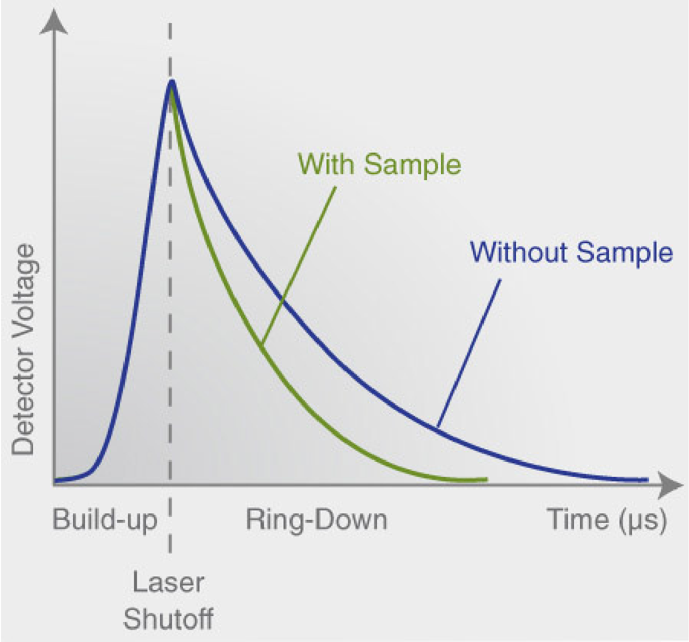
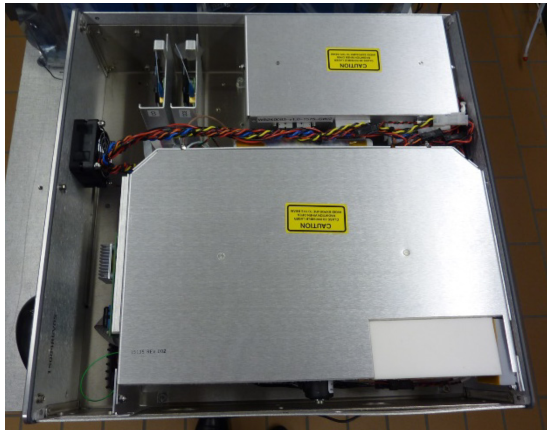
Laser Absorption Spectroscopy

Cavity Ringdown Spectroscopy







- simultaneous, rapid measurements of several trace gases with absorption features in the same wavelength range
- cryogenic free, measurement in the near-infrared
- laser is shut off, the intensity of light reaching the detector decreases or “rings down”

commercially available through Picarro, Inc., USA
https://www.picarro.com/

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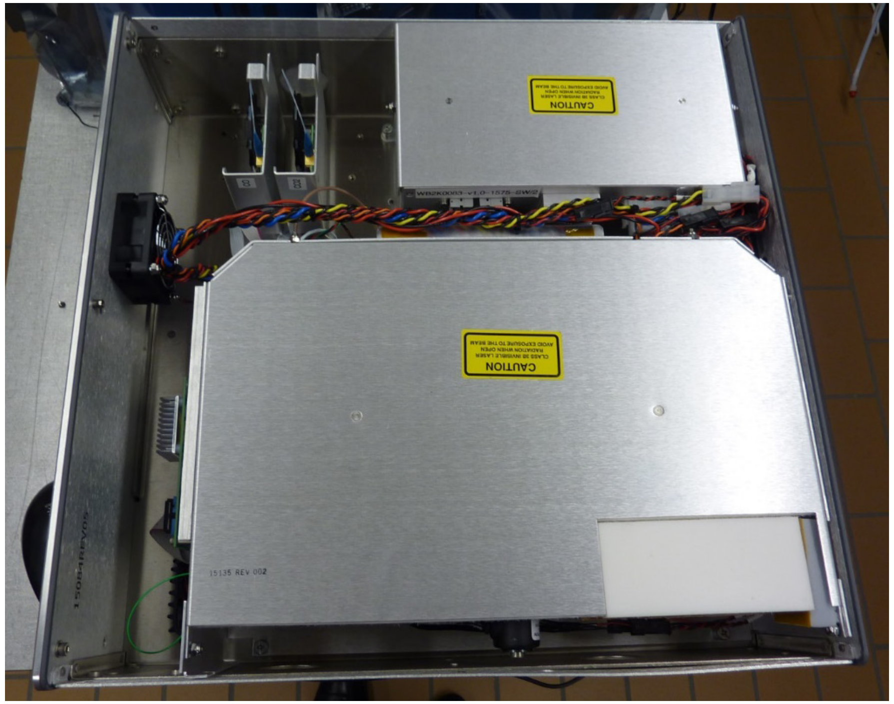
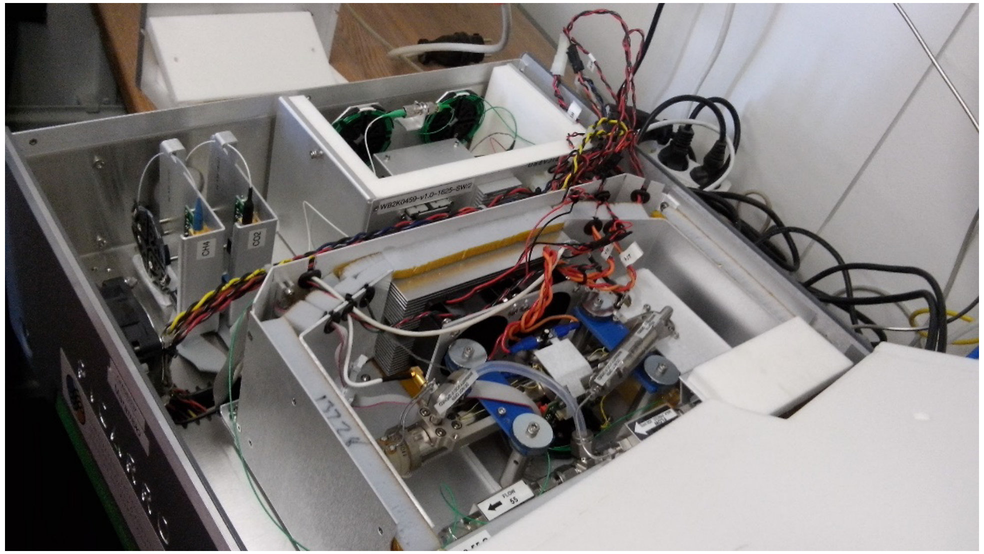
Laser Absorption Spectroscopy

Cavity Ringdown Spectroscopy





commercially available through Picarro, Inc., USA
https://www.picarro.com/

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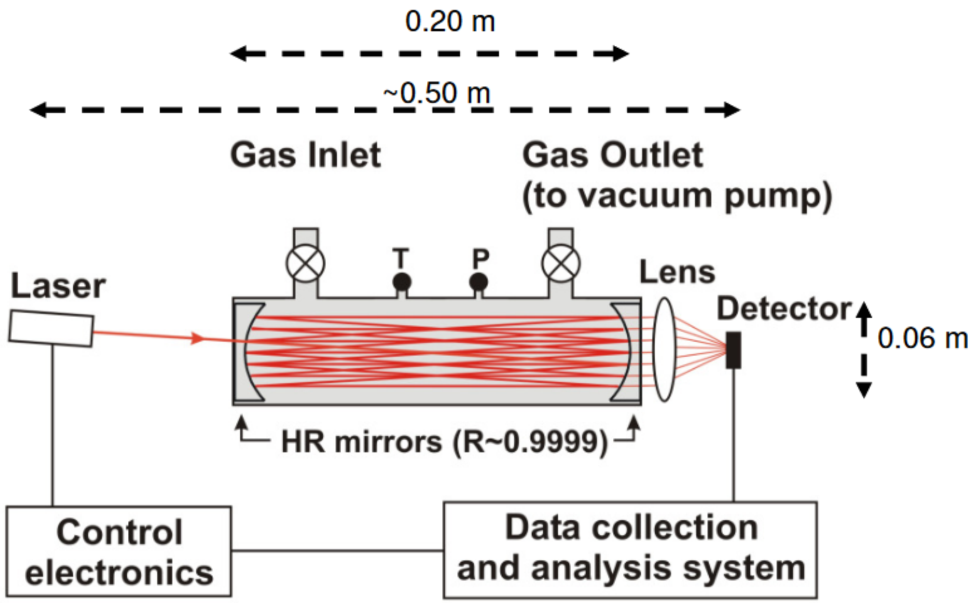
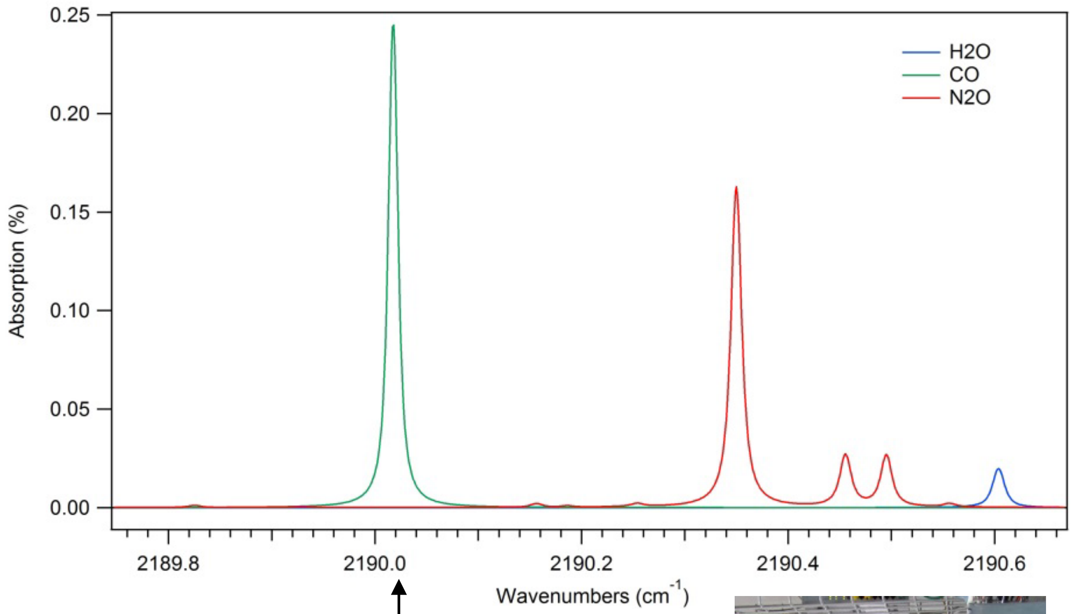
Laser Absorption Spectroscopy

Off-axis integrated cavity output spectroscopy



Hendriks et al., 2008



wavelength ~ 4.5 µm

- simultaneous, rapid measurements of several trace gases with absorption features in the same wavelength range
- cryogenic free, measurement in the mid-infrared

commercially available through ABB-Los Gatos Research, USA
http://www.lgrinc.com/

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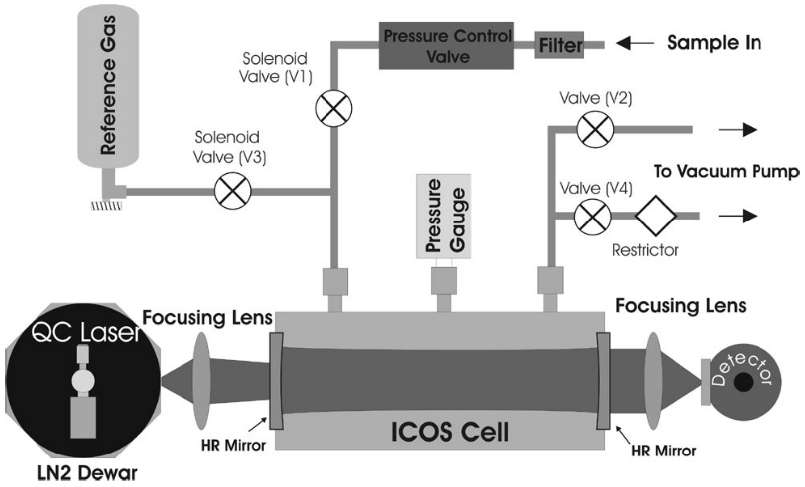
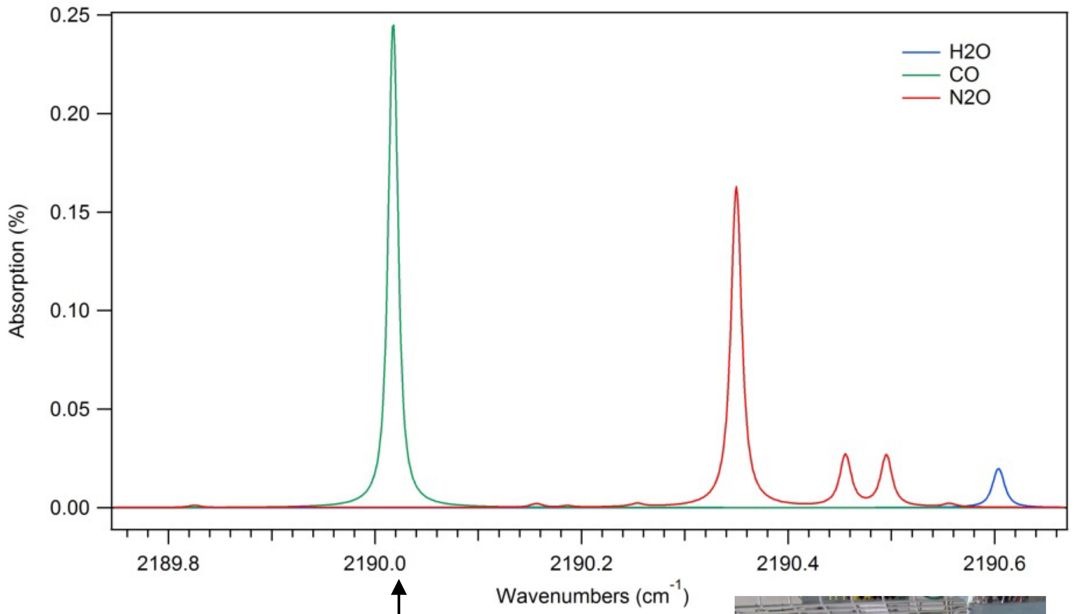
Laser Absorption Spectroscopy

Off-axis integrated cavity output spectroscopy



Provencal et al., 2005

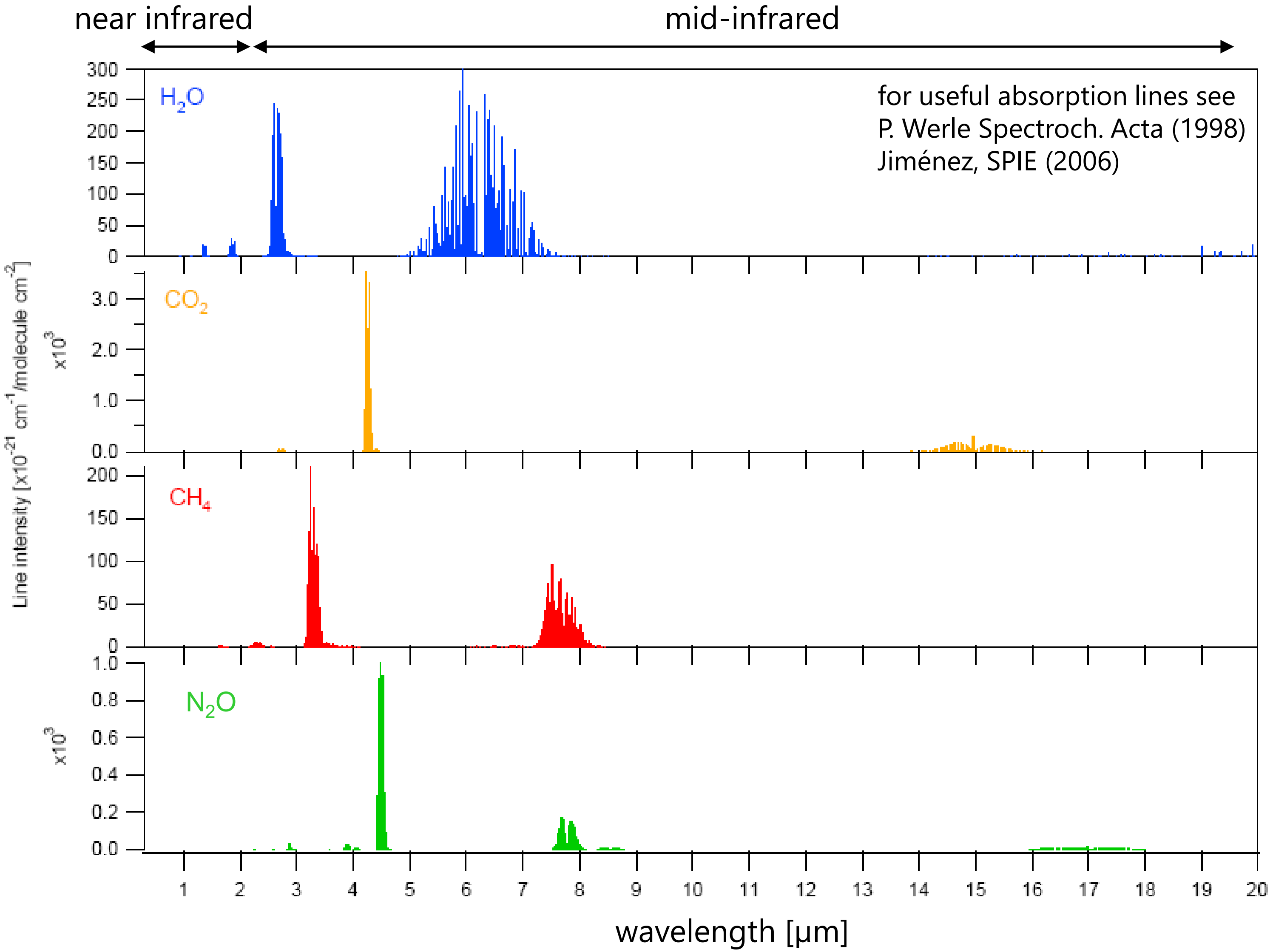


wavelength ~ 4.5 µm

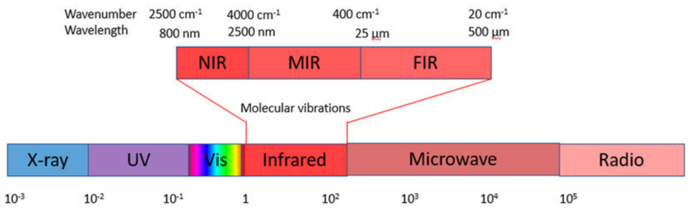
- an earlier version of the measurement setup (in the mid-infrared), still requiring liquid nitrogen, shows a bit more of the neighbouring plumbing

commercially available through ABB-Los Gatos Research, USA
http://www.lgrinc.com/

Line intensities in the infrared range



for useful absorption lines see
P. Werle Spectroch. Acta (1998)
Jiménez, SPIE (2006)



Fox, 2020

stronger absorption features require less long path lengths in the measurement cell

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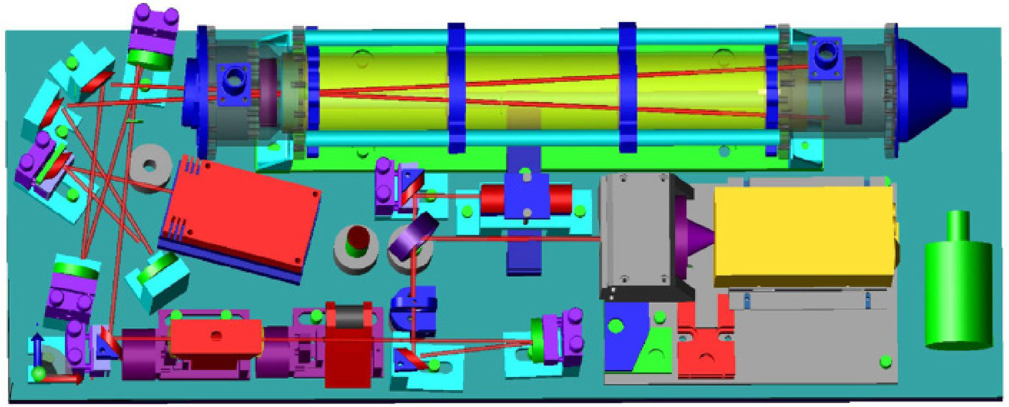
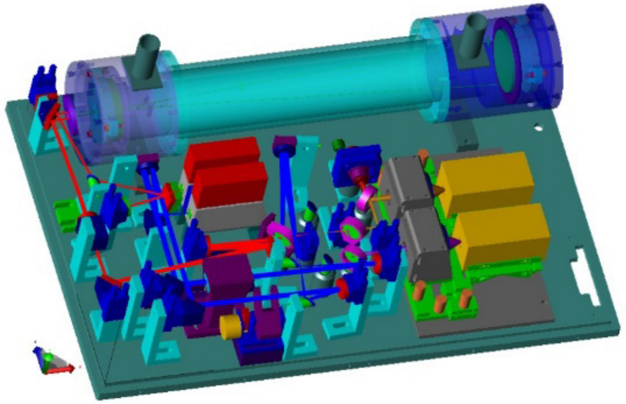
Laser Absorption Spectroscopy

Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS)

Mini Laser Trace Gas Monitor



Dual Laser Trace Gas Monitor



- simultaneous, rapid measurements of several trace gases with absorption features in the same wavelength range
- cryogenic free, measurement in the mid-infrared
- also produces and sells Dual QCL trace gas monitors which allow for the simultaneous measurement of multiple species, including NO, N2O, NO2, NH3, HONO, HNO3, CO, CH4, C2H4, HCHO, CHOOH, SO2, COS, O3, HOOH and others

commercially available through Aerodyne Research Inc., USA
https://www.aerodyne.com/

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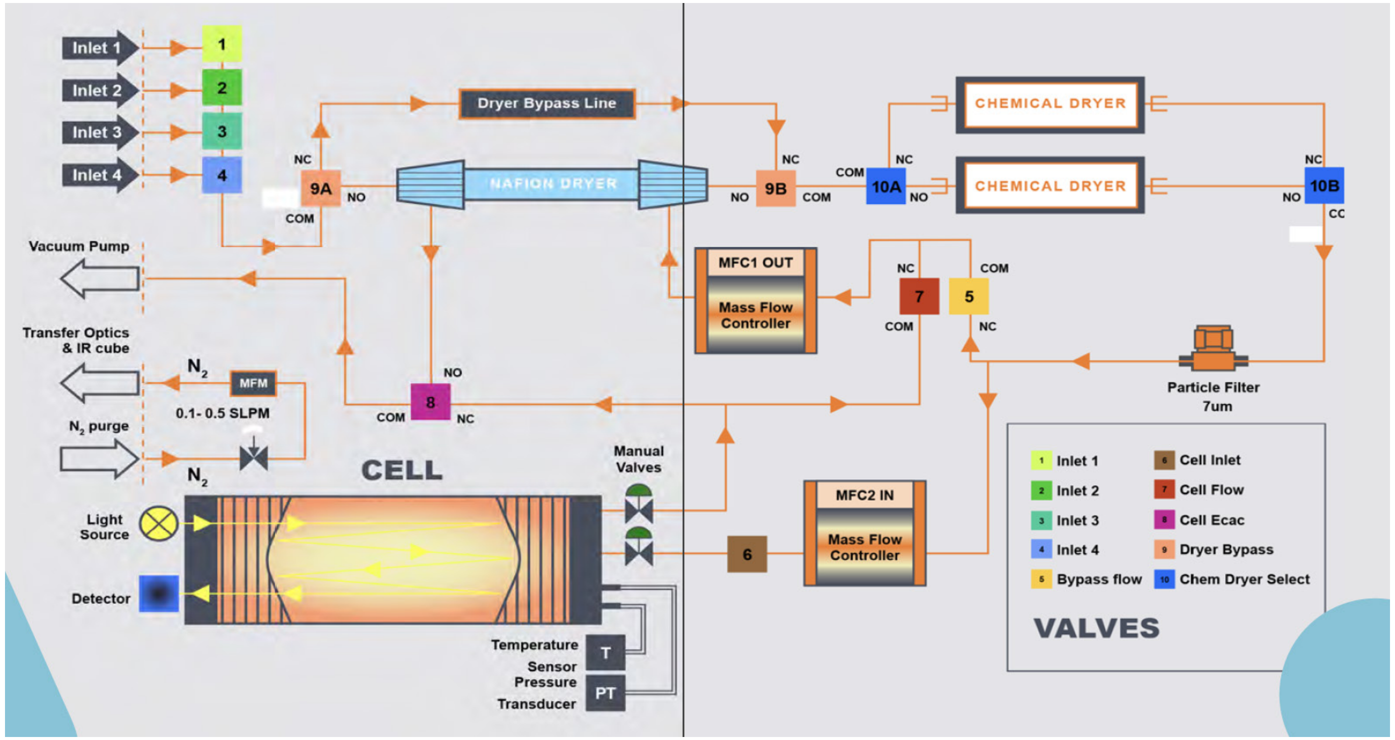
Empa

Fourier Transform Infrared (FTIR) Spectroscopy



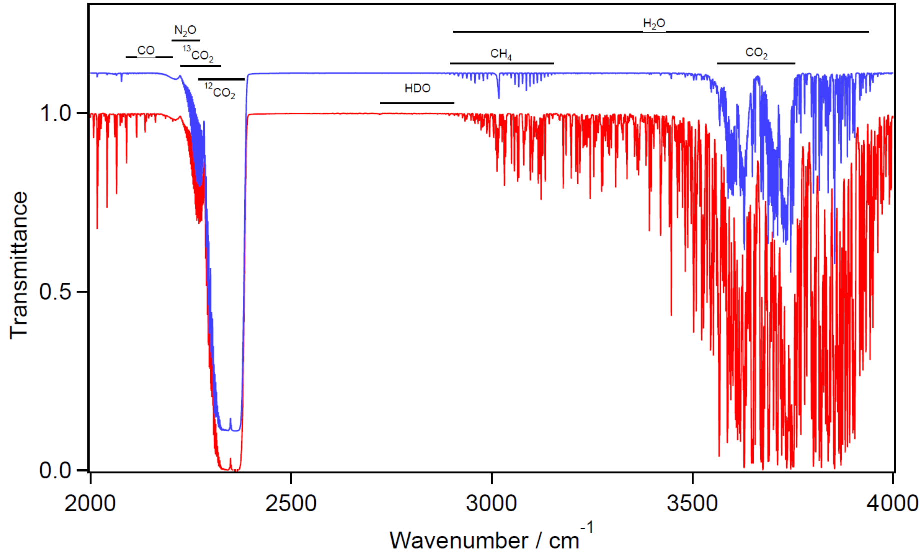


Fig. 1. The mid-infrared absorption spectrum of clean air in a 24 m cell. Red: undried air, blue: dried air. Positions of main absorption

Griffith et al., 2012

- FTIR measures over a broad wavelength range in the infrared region.
- simultaneous measurements of several trace gases with absorption features in the IR range.
- requires nitrogen as purge gas

commercially available through Acoem Ecotech, Australia
https://www.ecotech.com/

Other Manufacturers …

e.g.

Miro Analytical; Direct laser absorption spectroscopy; https://miro-analytical.com/

Thermo Scientific; Mid-IR Absorption Spectroscopy; https://www.thermofisher.com/

Tiger Optics; Cavity Ringdown Spectroscopy; https://www.tigeroptics.com/

Aeris Technologies; Long-path Tunable Diode Laser Spectrometry; https://aerissensors.com/

LI-COR; Optical Feedback – Cavity Enhanced Absorption Spectroscopy; https://www.licor.com

…

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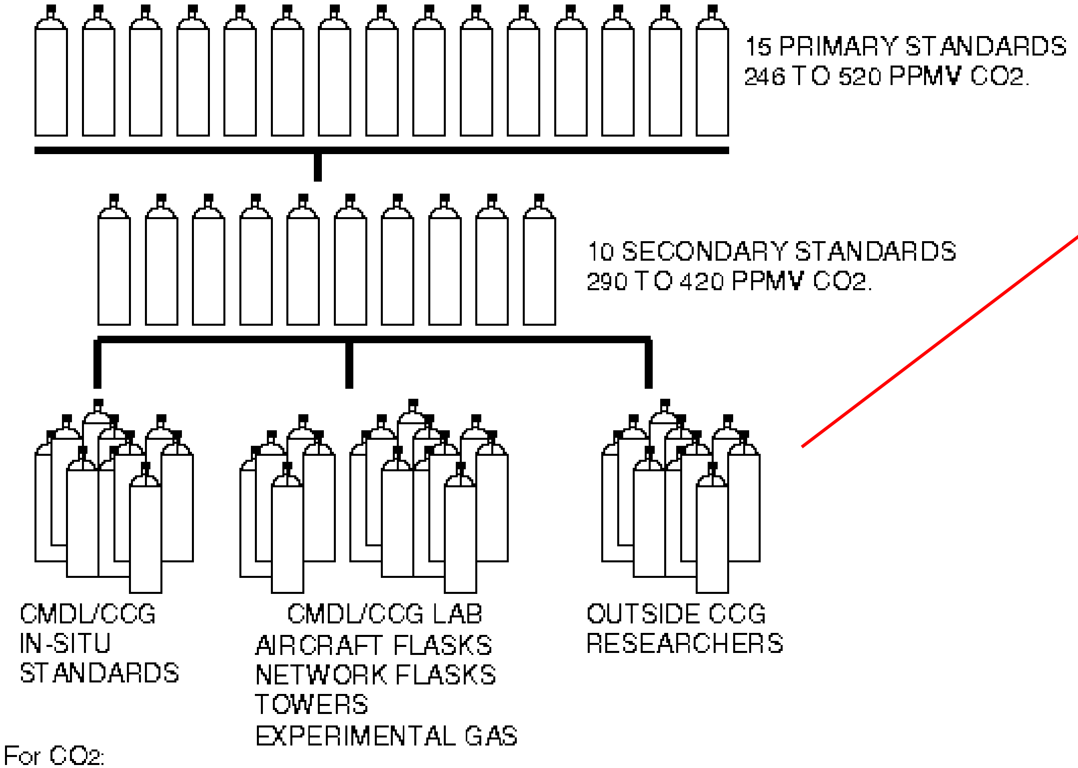
Quality Assurance / Quality Control

Traceability and calibration

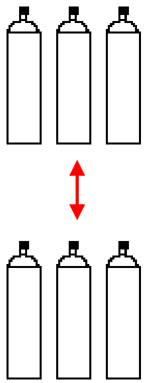


For CO_2:
CALIBRATION PRECISION; 0.014 µmol/mol [1 sd of calibrations < 6 months apart].
precision for < 325 approx. 0.1
precision for > 425 approx. 0.25

Absolute Uncertainty; 0.1 µmol/mol
Internal consistency [325-425 µmol/mol]; 0.04 µmol/mol [2 sigma] [< 2 years]

https://www.esrl.noaa.gov/gmd/ccl/airstandard.html

station operators



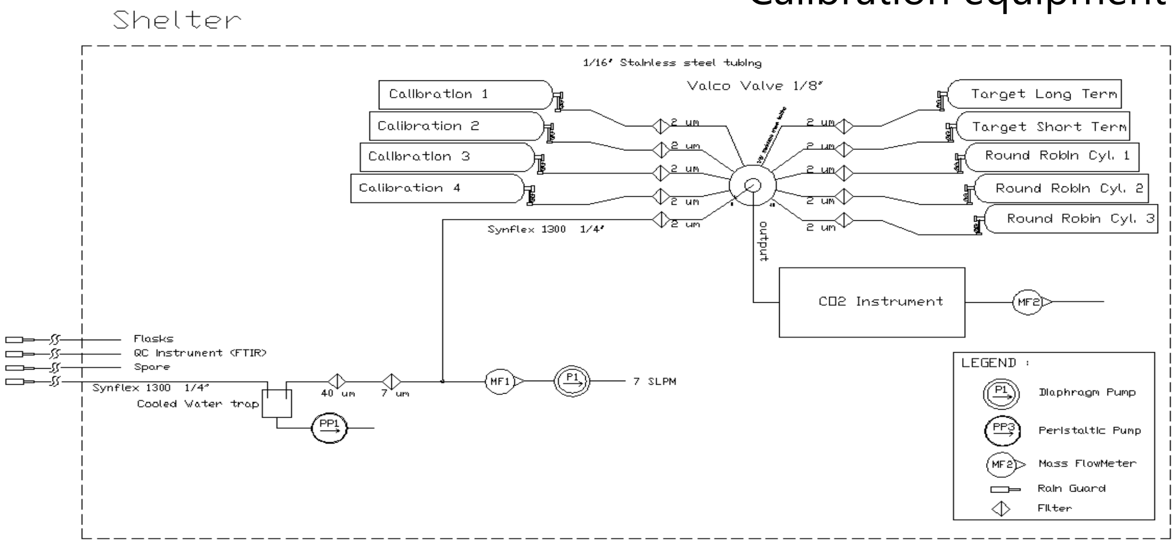
primary
laboratory
standards

working
standards
(in-situ)

recalibration every x years !

Calibration equipment

air
inlet(s)



ICOS RI, 2020

Traceability and calibration, documentation

- make sure that you know your traceability chain
- add this information to your data / metadata

File | Contact | Observation | Reference(s) | Gallery

Organization

NO	17
Acronym	DMC
Name	Direccion Meteorologica de Chile
Address 1	
Address 2	Dirección Meteorológica de Chile
Address 3	Av. Portales 3450, Estación Central - Santiago
Country/Territory	Chile
Website	http://www.meteochile.gob.cl/

Data header

```
# intake_height_total_listed : 1
# intake_height_1 : 5
# intake_height_1_units : m
# intake_height_1_start_date : 2012-12-31T00:00:00Z
# intake_height_1_end_date : 2020-12-31T00:00:00Z
# instrument_total_listed : 1
# instrument_1 : Picarro Inc., G2401, S/N CFKADS203:
# instrument_1_measurement_method_type_code : 18
# instrument_1_measurement_method_name : CRDS
# instrument_1_start_date : 2012-12-31T00:00:00Z
# instrument_1_end_date : 2020-12-31T00:00:00Z
# scale_total_listed : 1
# scale_1_code : 3
# scale_1_name : WMO CH4 X2004A
# scale_1_start_date : 2013-01-01T00:00:00Z
# scale_1_end_date : 2020-12-31T00:00:00Z
# observation_status_code : 1
# observation_status : Operational/Reporting
# measurement_calibration : Four calibration tanks a
# measurement_calibration : All assigned mole fract:
# sampling_frequency_code : 12
# sampling_frequency : 1 second
#
```

CH4 _ TLL _ surface - insitu _ DMC _ data1

File | Contact | Observation | DOI/Reference(s) | Gallery

Search by a keyword: (start typing)

Collaborator(s)	NO: 23 Acronym: Empa Name: Swiss Federal Laboratories for Materials Science and Technology
Aim of Observation	Background observation
Data Time zone	UTC
Unit	ppb
Calibration Scale	9999-12-31 00:00:00 - 9999-12-31 23:59:59: WMO CH4 X2004A
Instrument(s)	2012-12-31 00:00:00 - 9999-12-31 23:59:59: Picarro Inc., G2401, S/N CFKADS2031(CRDS)
Intake Height above ground level	2012-12-31 00:00:00 - 9999-12-31 23:59:59: 5 (m)
Sampling Frequency	1 second
Measurement Calibration	Four calibration tanks are measured automatically every 2 to 9 days. Three of them are tanks purchased from the GAW Central Calibration Laboratory (NOAA ESRL), the mole fractions of the fourth tank are determined by the GAW World Calibration Centre for CH4, CO2, CO and surface O3 (WCC-Empa). WCC-Empa also assigned the mole fractions of an additional target cylinder that is measured every second day for quality control. All assigned mole fractions were initially reported on the WMO CH4 X2004 scale. In July 2021, all data were reprocessed and (re-)submitted and, since then, the whole time series is traceable to the WMO CH4 X2004A scale. Data 2020 and onwards were directly processed using the X2004A assignments of the reference gases, earlier data were converted using the equation X2004A = 0.99351 x X2004 - 11.69558. Parameters were retrieved based on the assignments of the GAW Central Calibration Laboratory for CH4 (NOAA GML) reported on the X2004 and the X2004A scales. Data 2020 and onwards were processed with updated nominal CH4 mole fractions traceable to WMO X2004A. The quality of the calibration is verified with a fifth reference gas (target cylinder).
Data Processing	Quality assurance procedures involve time series plots, target tank (i.e. cylinders containing natural air with assigned trace gas mole fractions that are treated as (unknown) sample in a sequence of analyses) measurements, and consistency checks.
Processing for averaging	[Hourly] high-resolution data are aggregated to 1min averages before hourly averages are calculated. Thus, ND (the number of detections) refers to the number of available 1min averages within the respective hour. Minimum requirement is availability of 20 1-min data within one hour. [Daily] hourly averages are aggregated to daily means. Thus, ND (the number of detections) refers to the number of available hourly averages within the respective day. Minimum requirement is availability of 8 hourly averages within on day. [Monthly] daily data are aggregated to monthly means. Thus, ND (the number of detections) refers to the number of available daily averages within the respective month. Minimum requirement is availability of 10 daily averages within one month.

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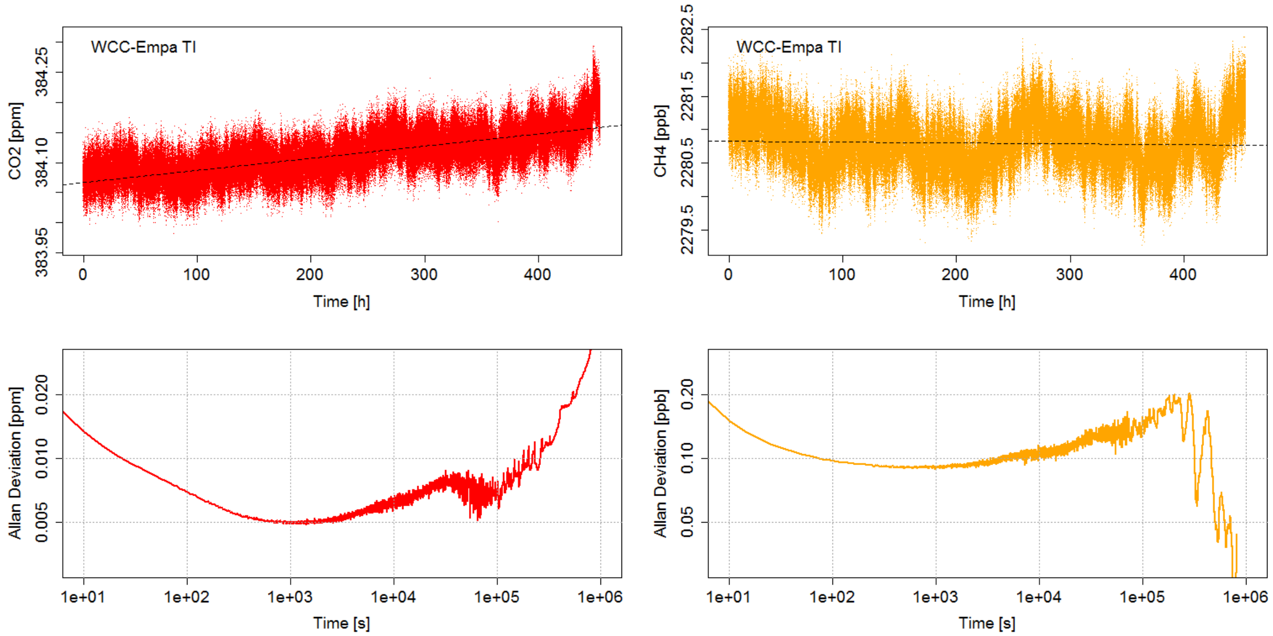
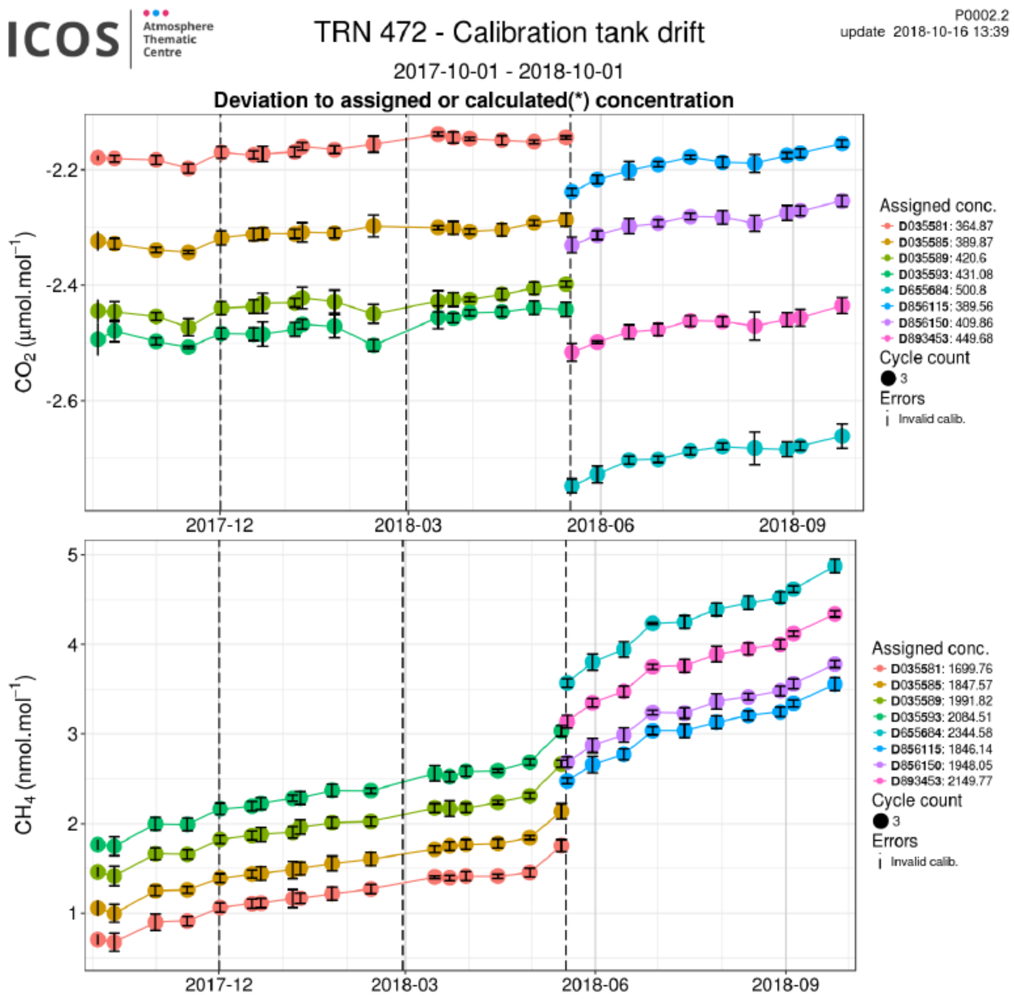
Frequency of calibration and QA/QC

laboratory tests



Zellweger et al., 2016

(long-term) field tests



"… A thorough analysis of the CO_2 and CH_4 stability of [this type of cavity enhanced laser spectrometer] indicates that the optimal calibration frequency is approximately 30 h. …"

Yver-Kwok et al., 2020

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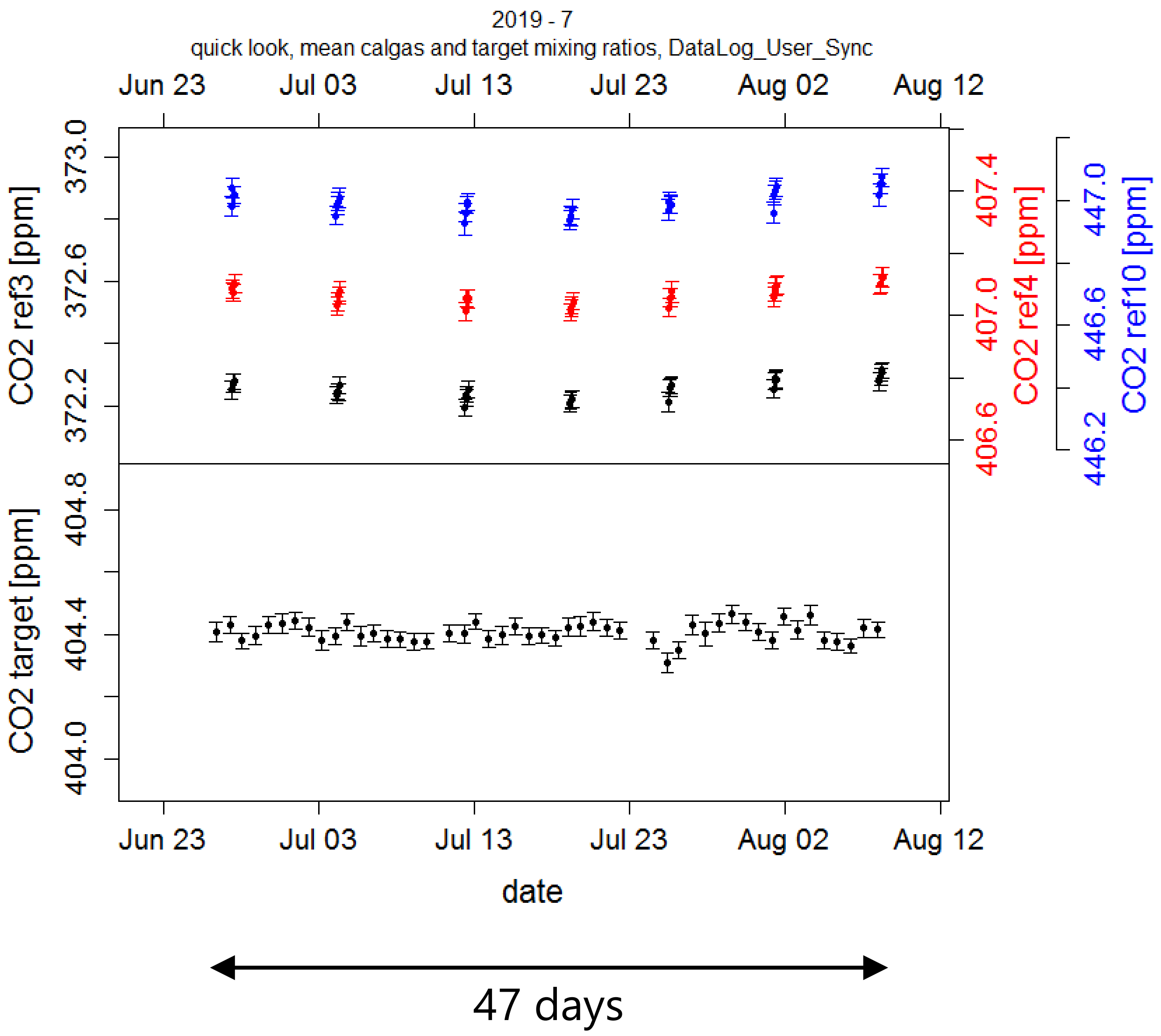
Use of target gases for QA/QC

Target reference is a known sample which is considered to be unknown and is treated like an ambient air sample. Target references do not need to be of the highermost hierarchy, thus, are usually less expensive and can be used up faster. Therefore, more frequent analysis is possible, which will in turn allow fast detection of instrumental artefacts.

Appropriate processing software needs to be available.



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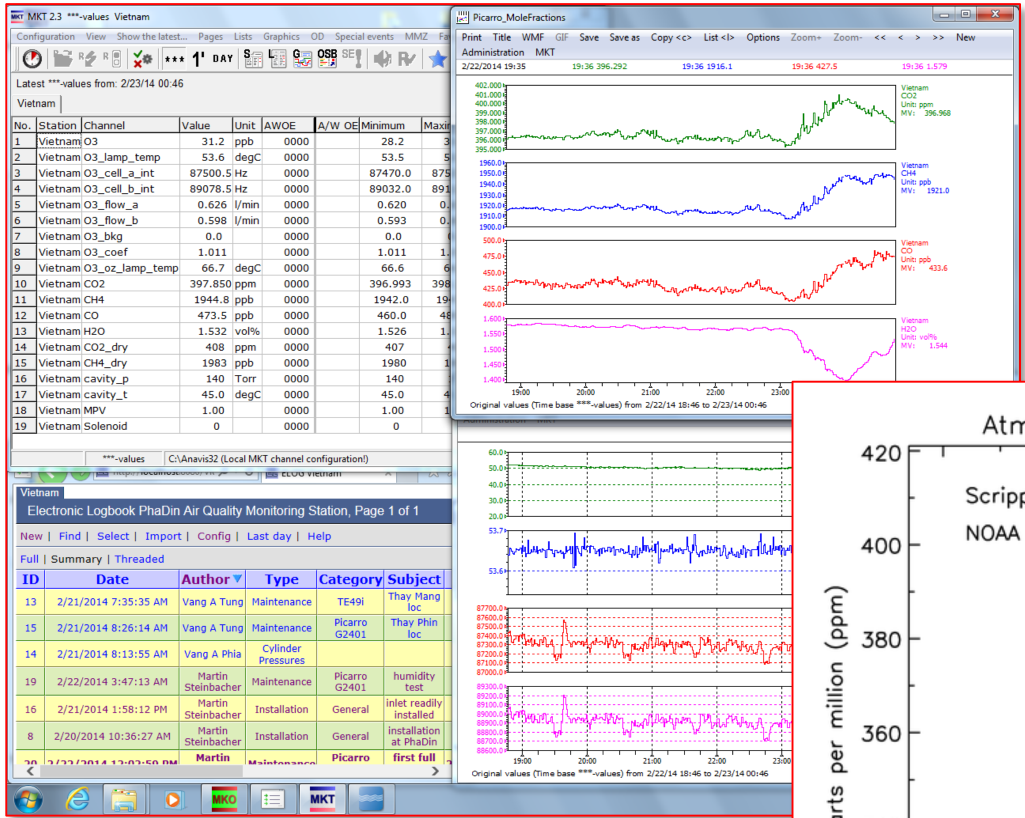
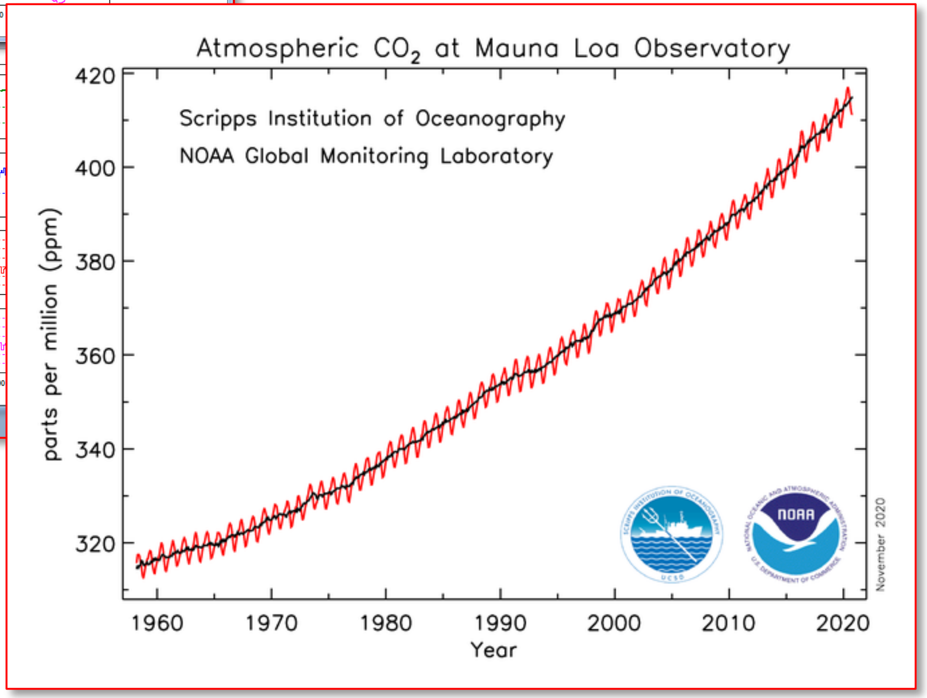
Empa

Data management & data processing

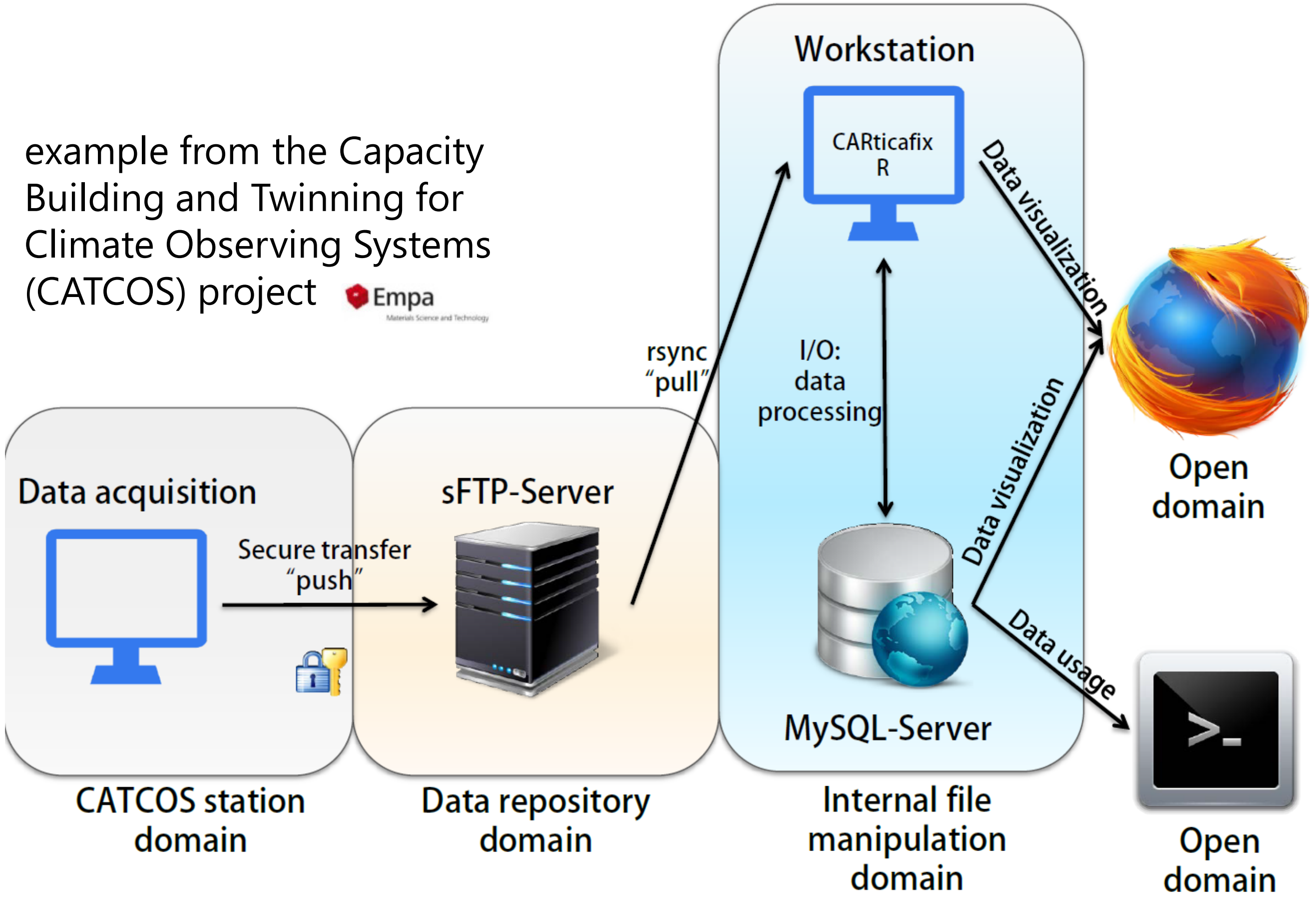




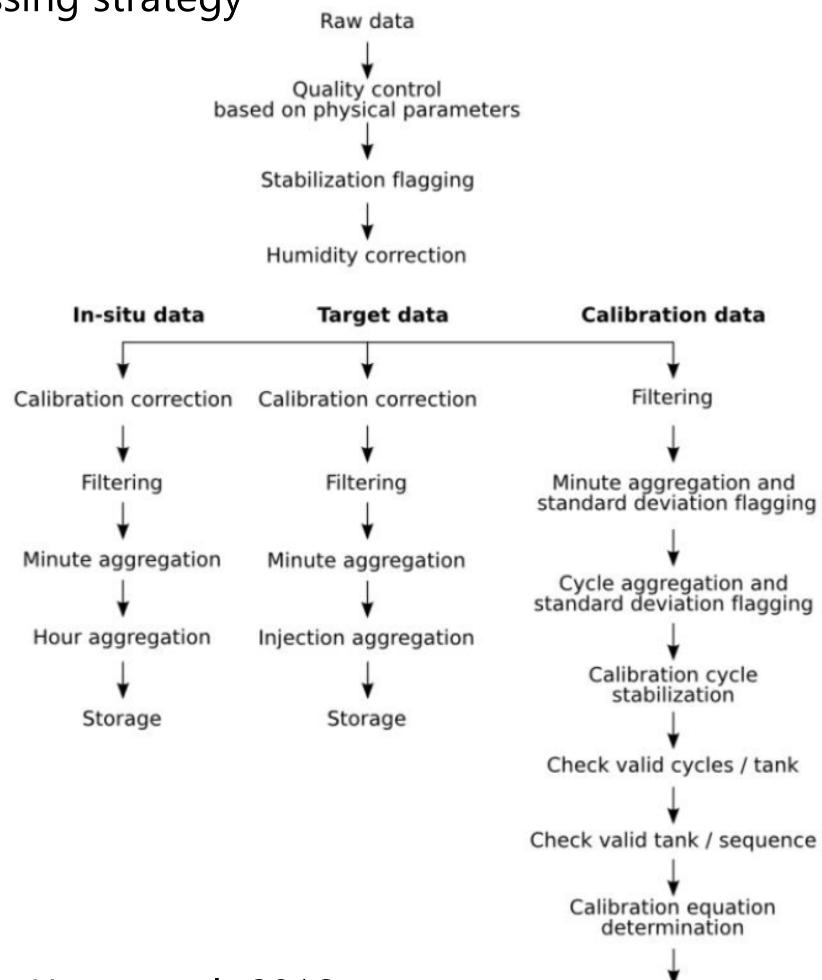
Data management

overall concept

example from the Capacity Building and Twinning for Climate Observing Systems (CATCOS) project Empa



data processing strategy



Hazan et al., 2016

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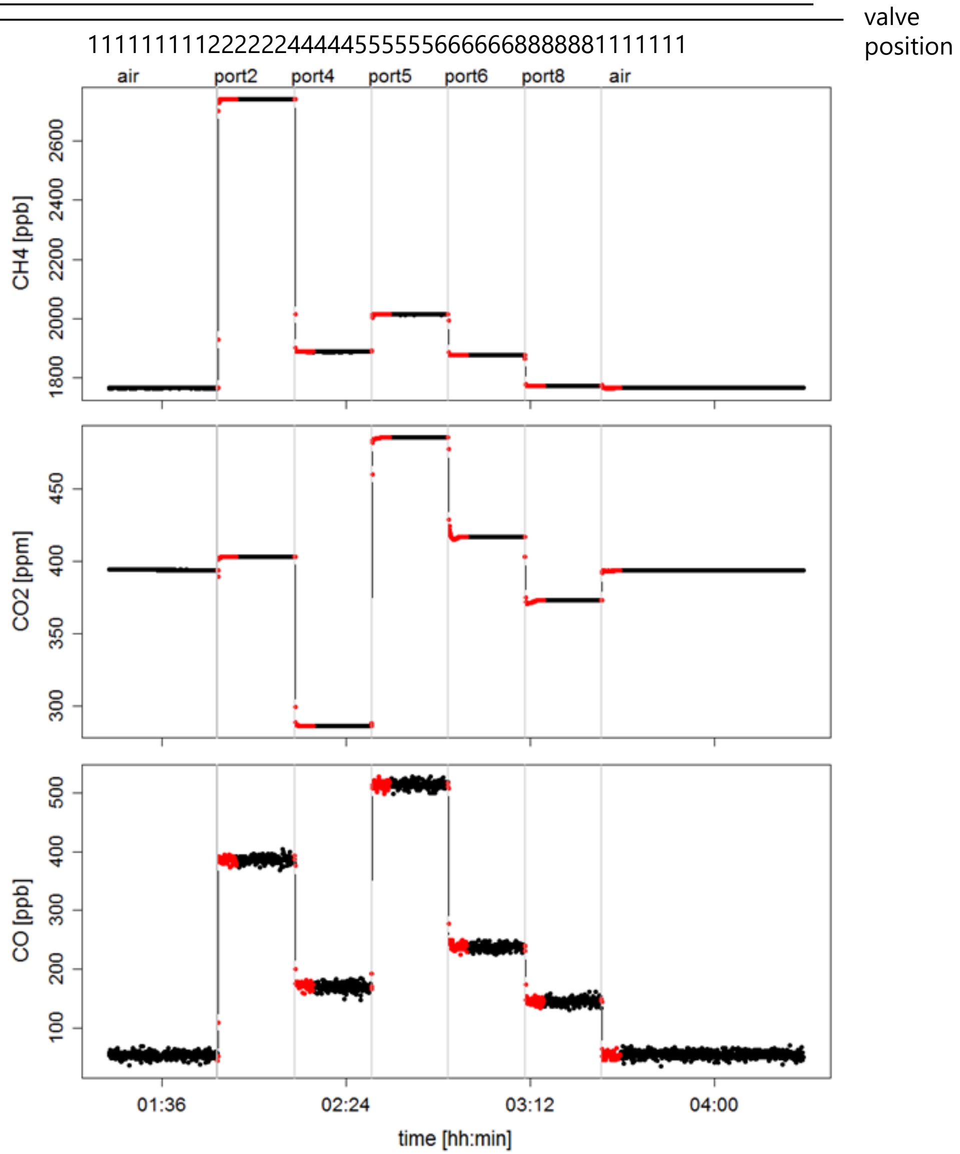
Data management

When changing from ambient air to calibration gas, or from one calibration gas to another, do exclude the first data after the change to account for the transition time until a stable signal is reached.



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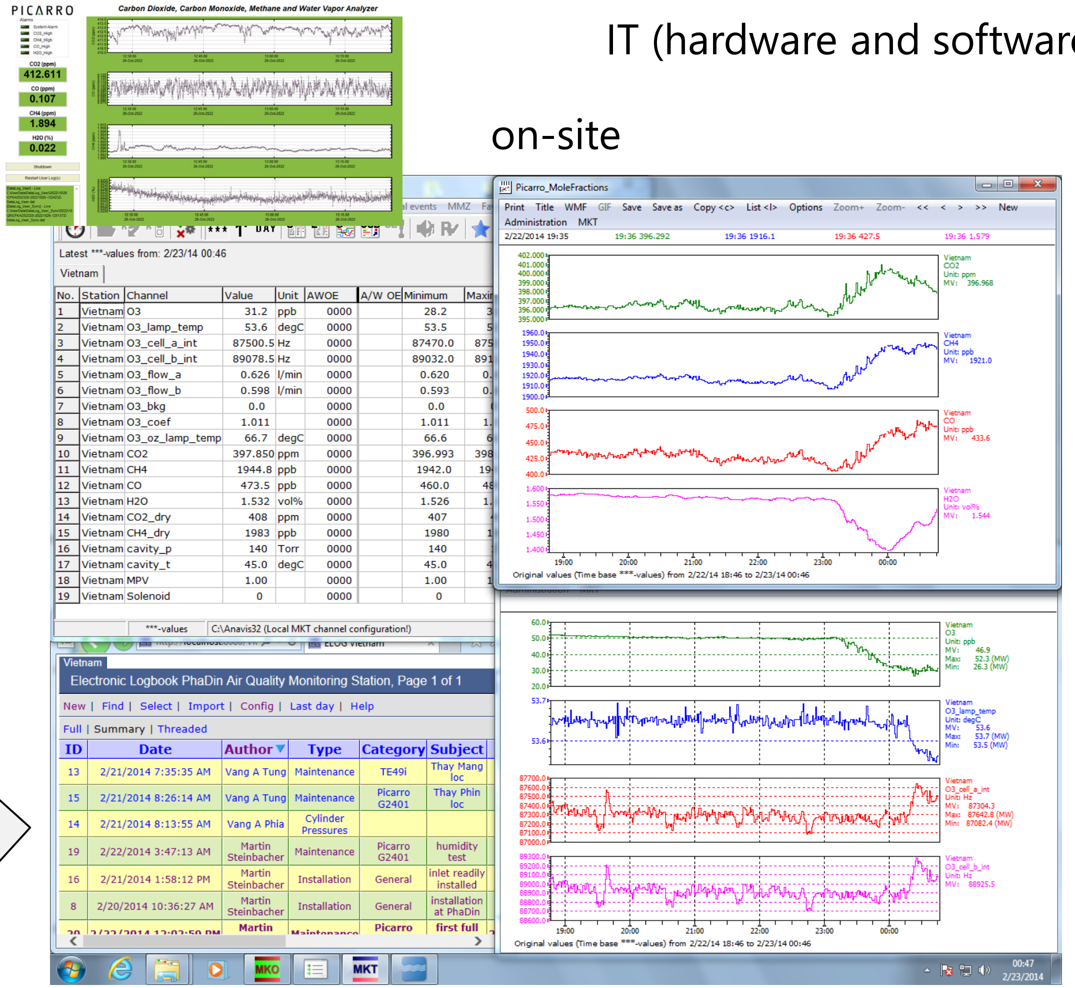
Data management

IT (hardware and software) resources are needed

on-site

central data processing unit



log book (meta data management) !

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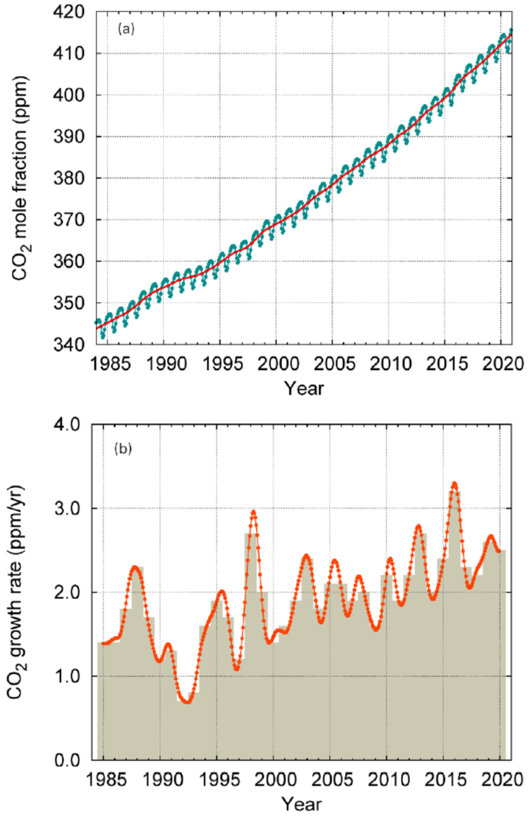
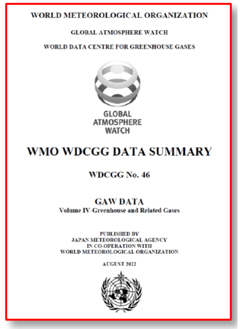
Empa

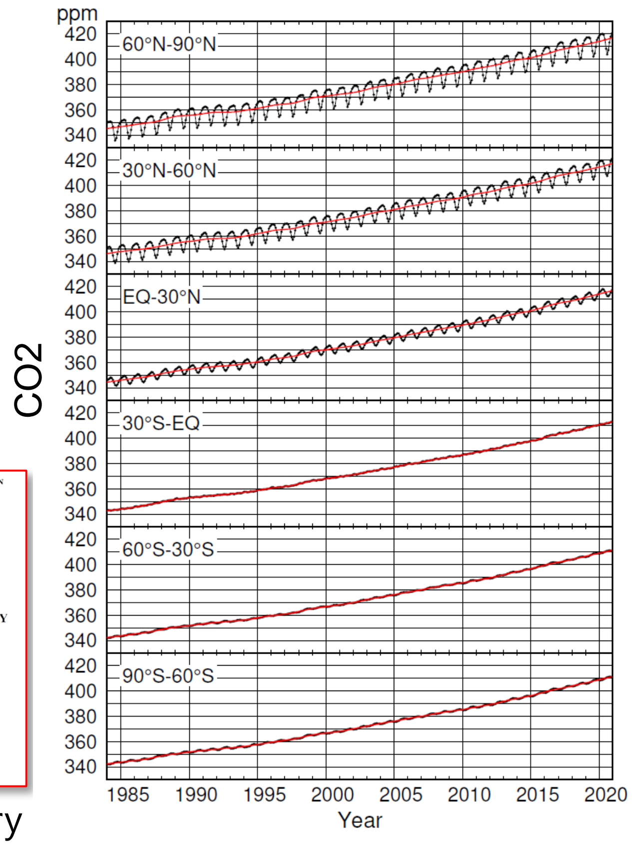
Additional quality control – comparison with other data

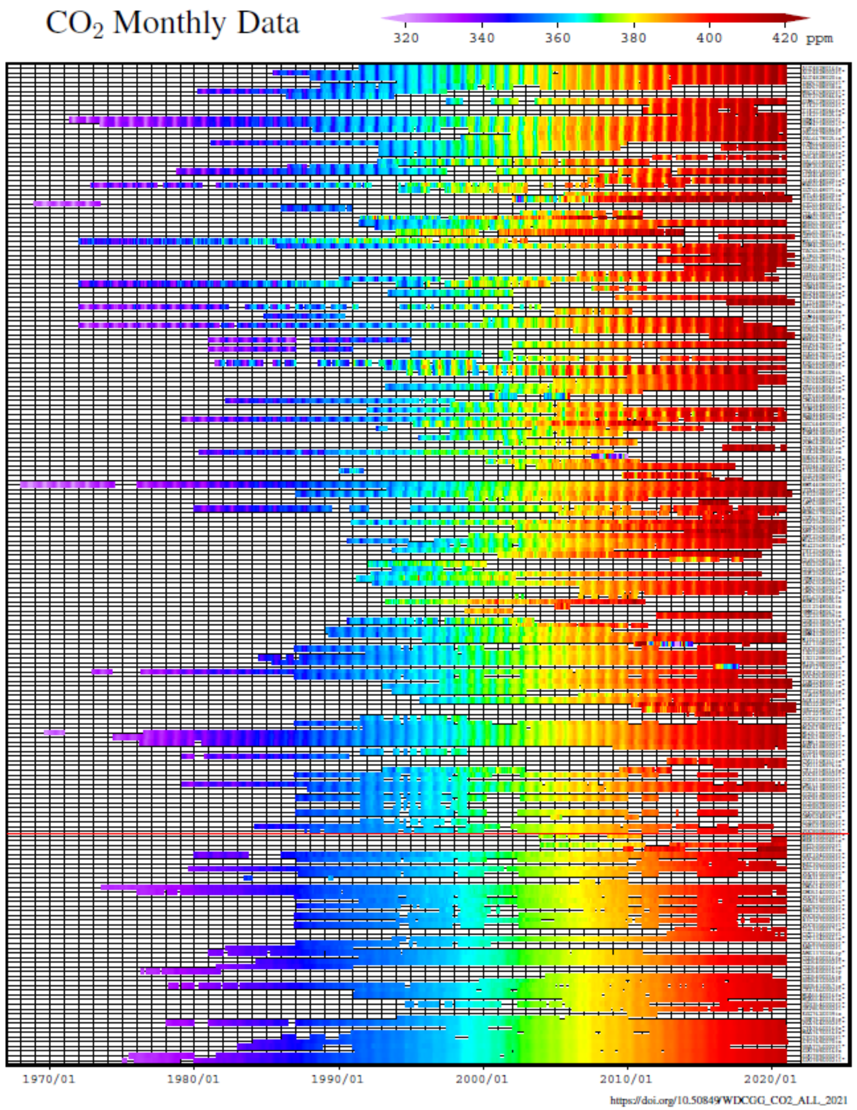
- participation in comparison (e.g. round robin) exercises
- comparison of data with data from «similar» stations





WDCGG Data Summary Report #46, 2022





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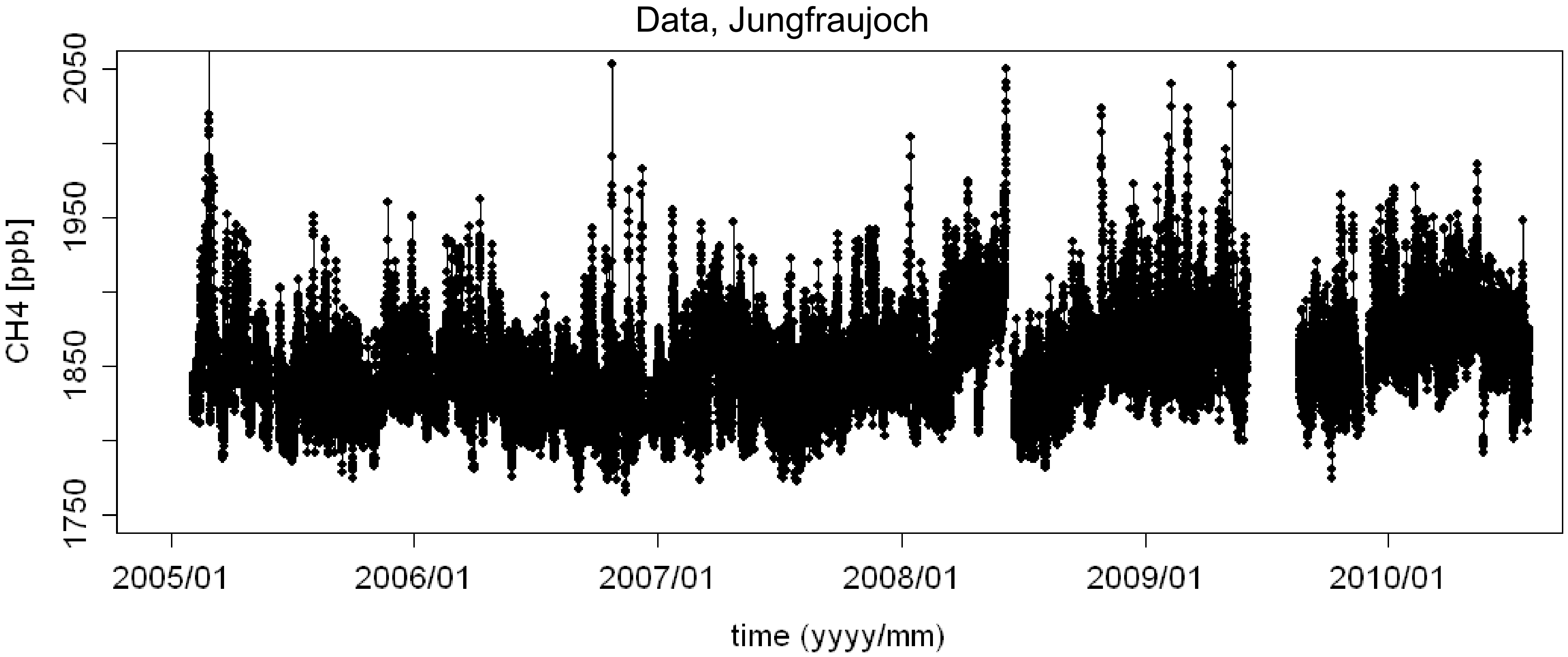
Additional quality control – comparison with other data



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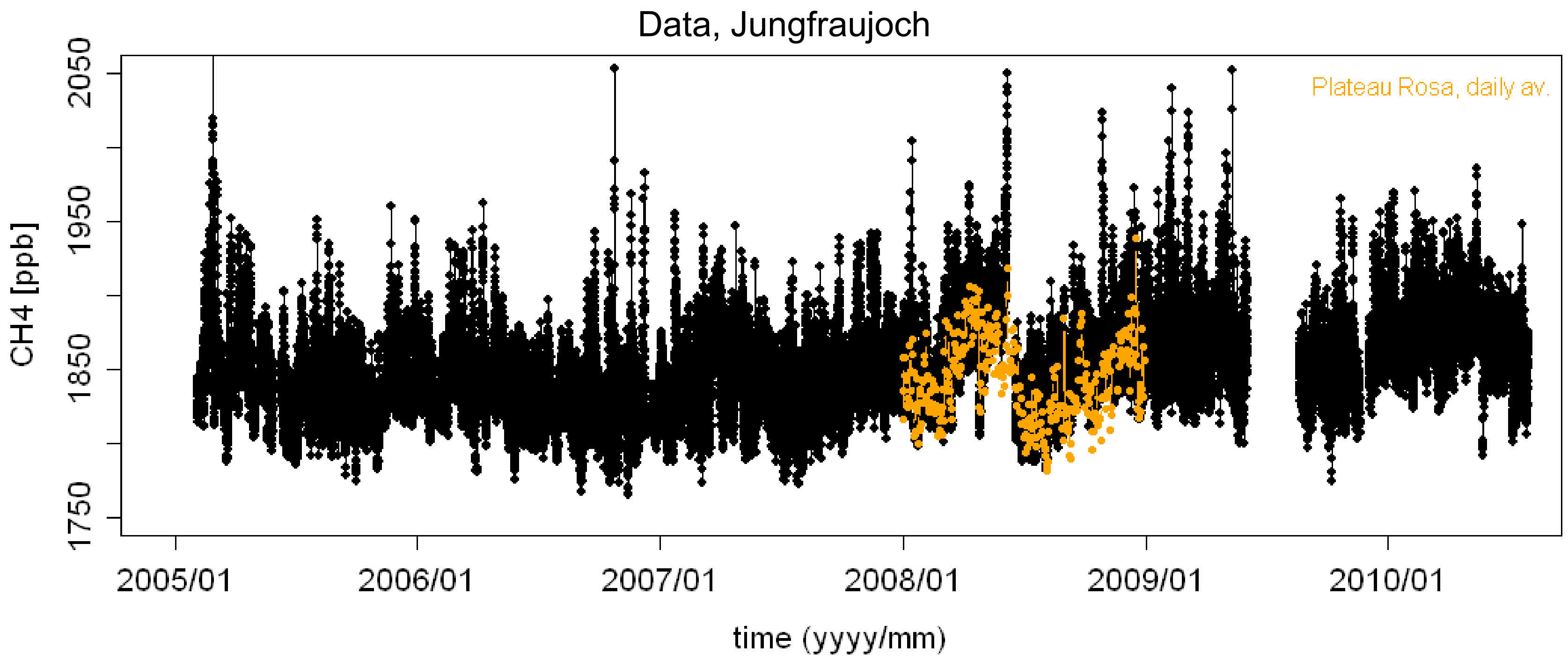
Additional quality control – comparison with other data



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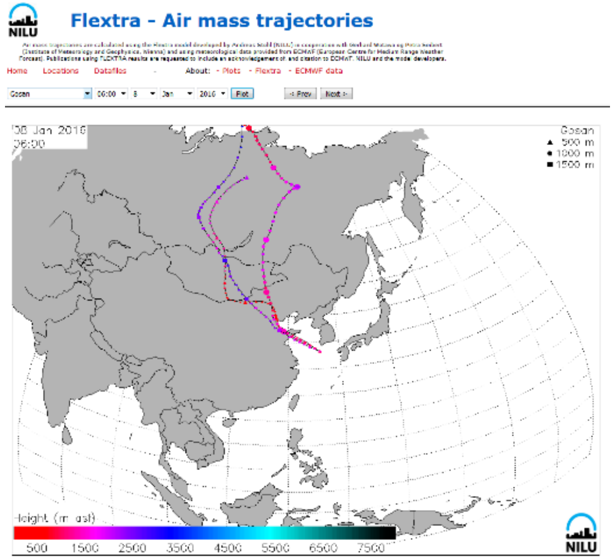
Additional quality control

- participation in comparison (e.g. round robin) exercises
- comparison of data with data from «similar» stations
- use available online tools for trajectory calculations, e.g.



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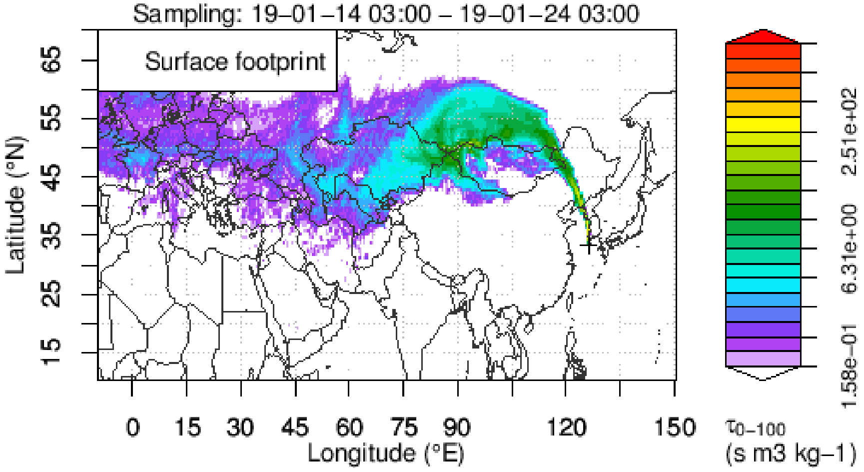

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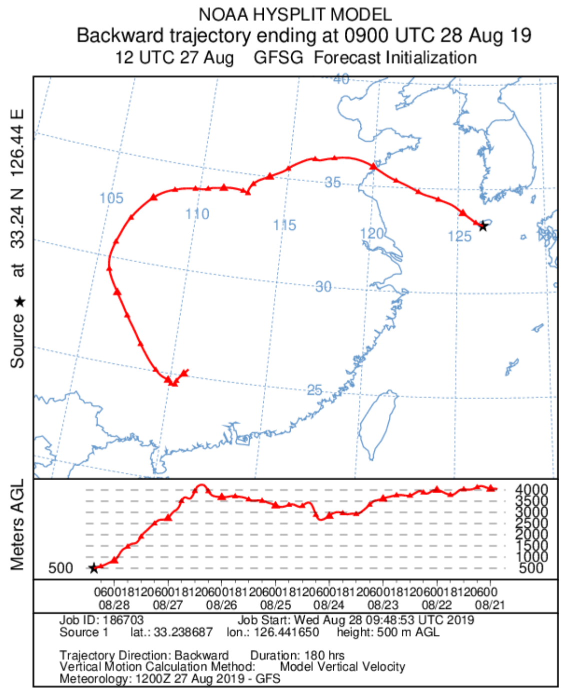

https://ready.arl.noaa.gov/hypub-bin/trajtype.pl

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Empa

Take-home Messages

"… To achieve the required levels of network compatibility […] it is important to understand and carefully consider the design of the whole analysis system including instrument, gas handling, calibration and data management. No single instrument type is recommended. Many can be used with equal success and none are fool proof when poor choices are made with gas handling or data management. A trade-off in instrument stability and complexity versus cost must often be balanced according to the needs, resources and challenges of the measurement programme. …"

What you need:

- adequate GHG analyzer
- periphery for automatic calibration
- reference gases (cals, targets)
- pressure reducers
- plumbing (additional pumps, tubing, connectors, inlet hat, drying unit, …)
- documentation tools
- data logger / data visualization
- consumables, spare parts, backup instruments, …

What else to think about:

- be clear about your traceability
- maintain a hierarchy of standards to ensure the best possible continuity & to allow for drift detection
- use target gases for quality control
- use (automated) scripts for data processing
- consult the literature, talk to your peers

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