Carbon Monoxide in the Atmosphere Measurement Techniques

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GAWTEC webinar, 04 November 2021

GAW
Global Atmosphere Watch
QA / SAC Switzerland

Empa
Materials Science and Technology

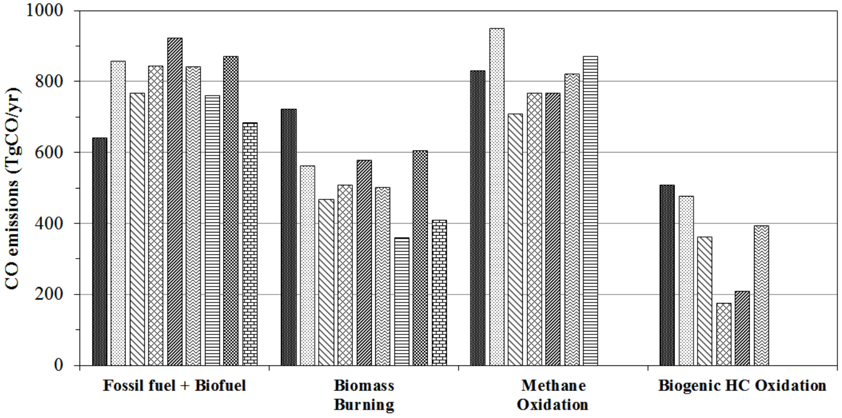
About me

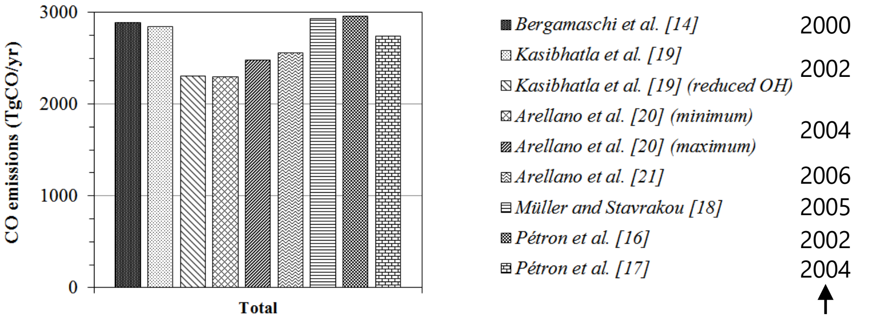
- meteorologist (University of Frankfurt, Germany)
- 2001 – 2004 PhD Fellow at the Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen, Switzerland
- 2004: PhD in Atmospheric Chemistry at ETH in Zurich, Switzerland
- since 2004: Scientist at Laboratory for Air Pollution / Environmental Technology, Empa, Duebendorf, Switzerland
  - principal operator of the air quality observations within the Swiss National Air Pollution Monitoring Network at the GAW site Jungfraujoch
  - manager of WMO/GAW Quality Assurance/Science Activity Centre Switzerland (supported by Schweizerische Eidgenossenschaft Confédération suisse Confederazione Svizzera Confederaziun svizra Federal Office of Meteorology and Climatology MeteoSwiss)
  - chair of the Atmospheric Monitoring Station Assembly of the Integrated Carbon Observation System
  - teaching at GAWTEC courses since 2008

Sources and Sinks of Atmospheric Carbon Monoxide

<u>Sources</u> [10^3 Tg CO/y] (Zheng et al., 2019)

anthropogenic (mainly combustion of fossil fuels and biofuels)	0.7
biomass burning	0.5
oceanic	0.02
biogenic	0.2
oxidation of methane	0.9
oxidation of hydrocarbons	0.3
total	**2.6**





Park et al., 2015

year of publication

Sources and Sinks of Atmospheric Carbon Monoxide

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Sinks (approx.)	
oxidation by OH	78%
soil uptake	17%
stratosphere	4%

Atmospheric Lifetime: months

CO plays an important role in atmospheric chemistry, the carbon cycle, and the Earth's radiative budget

CO oxidation by OH

$CO + OH \rightarrow CO_2 + H$

$H + O_2 \rightarrow HO_2$

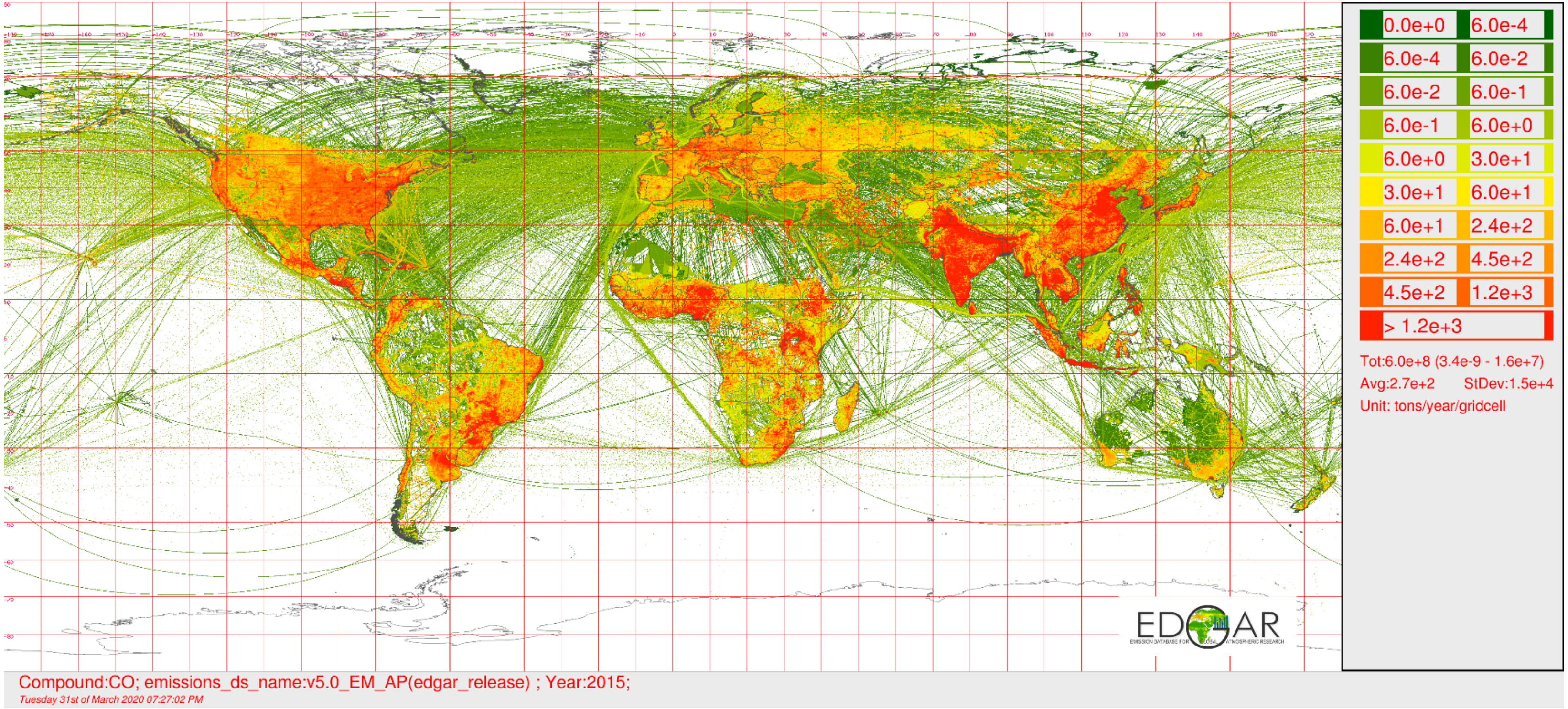
$HO_2 + NO \rightarrow OH + NO_2$

$NO_2 + h\nu \rightarrow NO + O$

$\underline{O + O_2 \rightarrow O_3}$

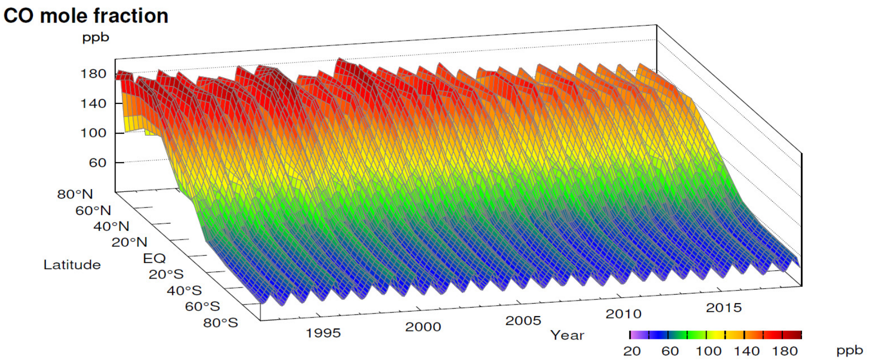
Net: $CO + 2O_2 \rightarrow CO_2 + O_3$

Global Distribution of Carbon Monoxide Sources

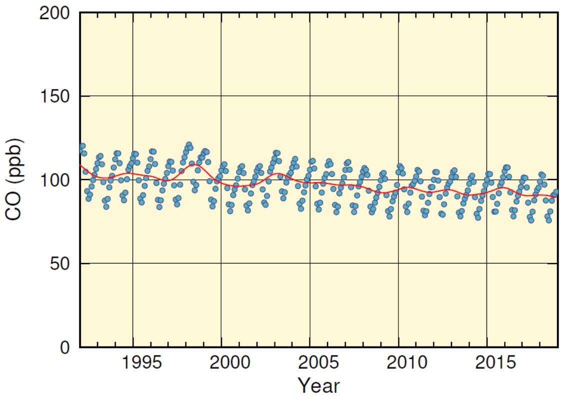


EDGAR - Emissions Database for Global Atmospheric Research, https://edgar.jrc.ec.europa.eu/

Carbon Monoxide Levels in the Atmosphere



WDCGG Data Summary #44, 2020



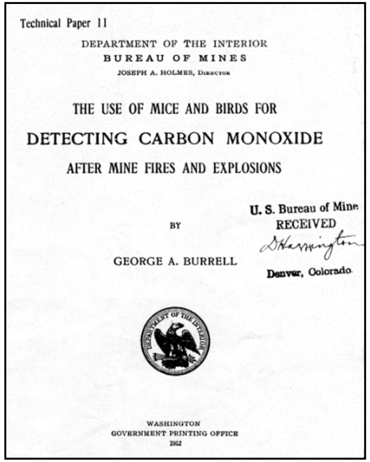
typical carbon monoxide mole fractions in various environments:

0.04 to 0.2 ppm	natural background atmosphere level [1]
0.3 to 0.4 ppm	yearly average at a kerbside station in CH [2]
0.5 to 5 ppm	average background level in homes [3]
6.9 ppm	Air Quality Limit in CH (24h-average)
5 to 15 ppm	near properly adjusted gas stoves in homes [3]
9 ppm	US 8-hour Air Quality Standard [3]
up to 16 ppm	levels in a highway tunnel [4]
30 ppm	threshold limit values at workplaces in Germany
> 30 ppm	in homes near poorly adjusted stoves [3]
up to ~ 4’000 ppm	undiluted car exhaust [5]
16’000 – 37’000 ppm	cigarette smoke [6]

[1] World Data Centre for Greenhouse Gases, https://gaw.kishou.go.jp
[2] Swiss National Air Pollution Monitoring Network, https://www.empa.ch/nabel
[3] https://www.epa.gov/indoor-air-quality-iaq/what-average-level-carbon-monoxide-homes
[4] Vollmer et al., 2007
[5] Bond et al., 2010
[6] Jaffe & Chavasse, 1999

Rationale for CO Measurements in the Atmosphere

- CO is a good tracer for anthropogenic pollution and biomass burning
- CO sources are known well => relative emission of other anthropogenic pollutants can be estimated
- CO is an intermediate product of the VOC degradation on the way to CO_2
- CO causes adverse health effects under highly polluted conditions


Technical Paper 11

DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

JOSEPH A. HOLMES, DIRECTOR

THE USE OF MICE AND BIRDS FOR

DETECTING CARBON MONOXIDE

AFTER MINE FIRES AND EXPLOSIONS

BY

GEORGE A. BURRELL

U. S. Bureau of Mines

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Denver, Colorado

WASHINGTON

GOVERNMENT PRINTING OFFICE

1912

http://books.google.com/books?id=RCCWMcWoZtIC

Techniques for Ambient Air in-situ CO Measurements

- Manometric Technique (e.g. Brenninkmeijer, 1993)
- Gas Chromatography (GC), followed by
  - flame ionization detection (GC-FID) (e.g. Rasmussen & Khalil, 1981)
  - HgO Reduction Detection (GC-RGD) (e.g. Novelli et al., 1998; Gros et al., 1999)
- Tunable Diode Laser Spectrometry (TDLAS) (e.g. Sachse et al., 1987)
- Non-Dispersive Infrared Spectrometry (NDIR) (e.g. Parrish et al., 1994)
- Vacuum Ultraviolet (UV) Fluorescence (e.g. Gerbig et al., 1999)
- Quantum Cascade Laser Absorption Spectroscopy (QCL) (Baer et al., 2002; McManus et al., 2015)
- Fourier-Transform Infrared Spectrometry (FTIR) (e.g. Griffith et al., 2012)
- Cavity Ringdown Spectroscopy (CRDS) (e.g. Chen et al., 2013)

Discontinuous techniques

Manometric Technique

An air sample is first passed through a series of chromatographic columns and cryogenic traps to remove CO_2, nitrogen oxides, water, and hydrocarbons. Flow over Schütze reagent (I_2O_5 on silica gel) quantitatively converts CO to CO_2, which is collected cryogenically.

The amount of CO-derived CO_2 is determined manometrically.

This sample preparation procedure provides an absolute manometric technique for determination of CO concentrations.

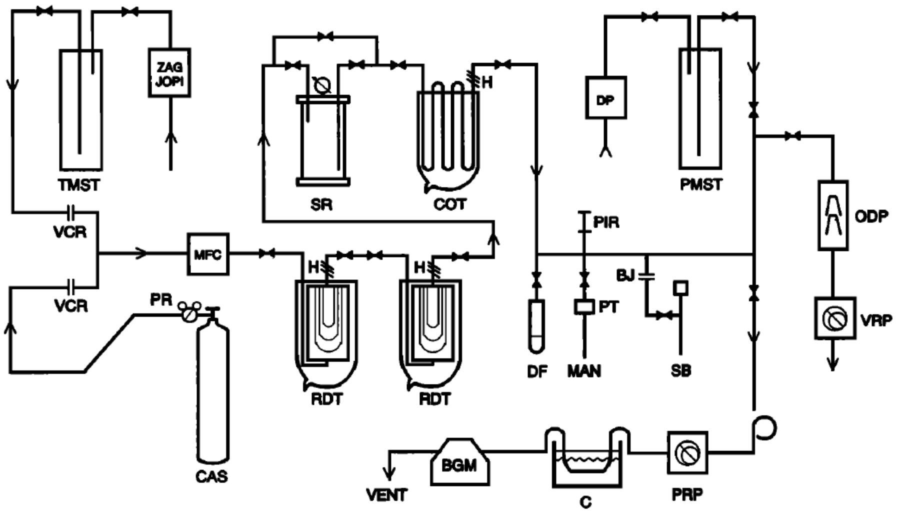


Fig. 2. The laboratory system for conversion and extraction of CO. MFC is a thermal sensor mass flow controller. ZAG is a generator of zero air, i.e., CO free air, consisting of a heated catalyst in the form of platinum on an aluminium oxide carrier or Hopcalite. TMST is a molecular sieve trap (13X) used in combination with the zero air generator. RDT's are Russian doll traps. SR is the Schütze reactor. COT is the six loop glass CO_2 collection trap, later replaced with a Russian doll trap. DF is a small drying finger containing a fraction of a gram of P_2O_5. PT is a piezoresistive absolute pressure transducer (Philips KP100A), with a resolution of 100 Pa. MAN is the manometer using a 5-mm Vacutap. PIR is a Pirani vacuum gauge. SB is the sample collection bottle. PMST is the purge molecular sieve trap, containing 9 k of 13X molecular sieve to strip laboratory air of its H_2O and CO_2 content. DP is a diaphragm pump providing the purge air-flow rate of 0.5 to 1.0 L min^{-1}. ODP is an air- cooled oil diffusion pump. VRP is a two-stage rotary vacuum pump. PRP is the air processing rotary pump. C is a bath for bringing the air at ambient temperatures. BGM is a domestic bellows type gas meter. Couplings used are Cajon Ultratorr fittings and Viton glass ball-cup connectors. For connecting air cylinders, Cajon VCR fittings are used. All valves are Viton o-ring valves (Young and Glass Expansion) and a 5-mm Vacutap [*Brenninkmeijer and Louwers*, 1985] for the small volume (0.95 cm^3) manometer. All liquid nitrogen traps are fitted with thermocouple based heater elements [*Brenninkmeijer and Hemmingsen*, 1988] to prevent hardening of the downstream Viton seals and to prevent lowering of the temperature of the Schütze reagent.

Brenninkmeijer et al., 1993

Gas Chromatography

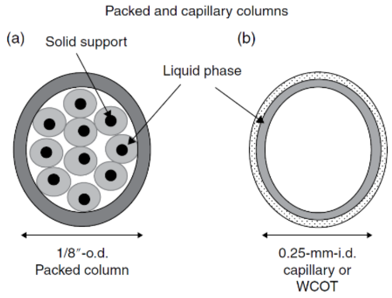
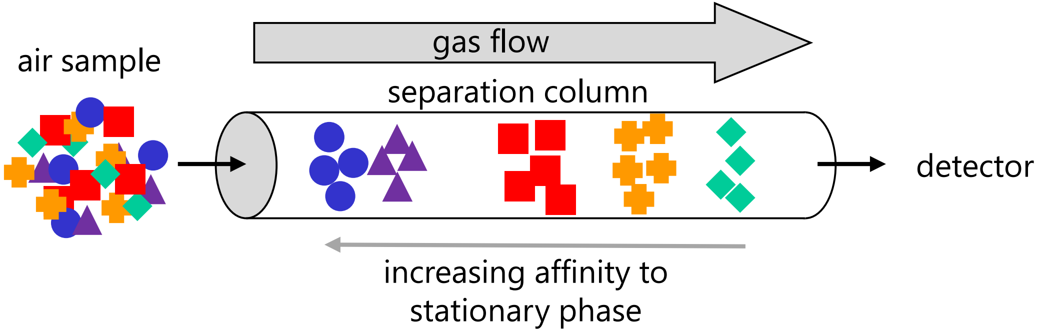
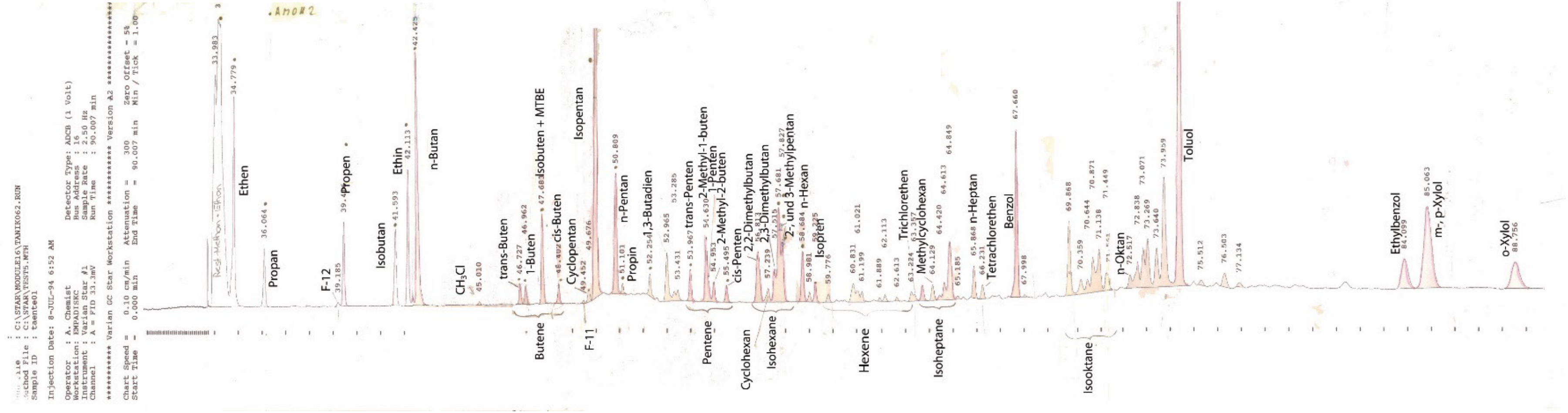


Figure 1.10. Schematic representation of (a) packed column and (b) capillary or open tubular column.

McNair et al., Basics Gas Chromatography, 2019



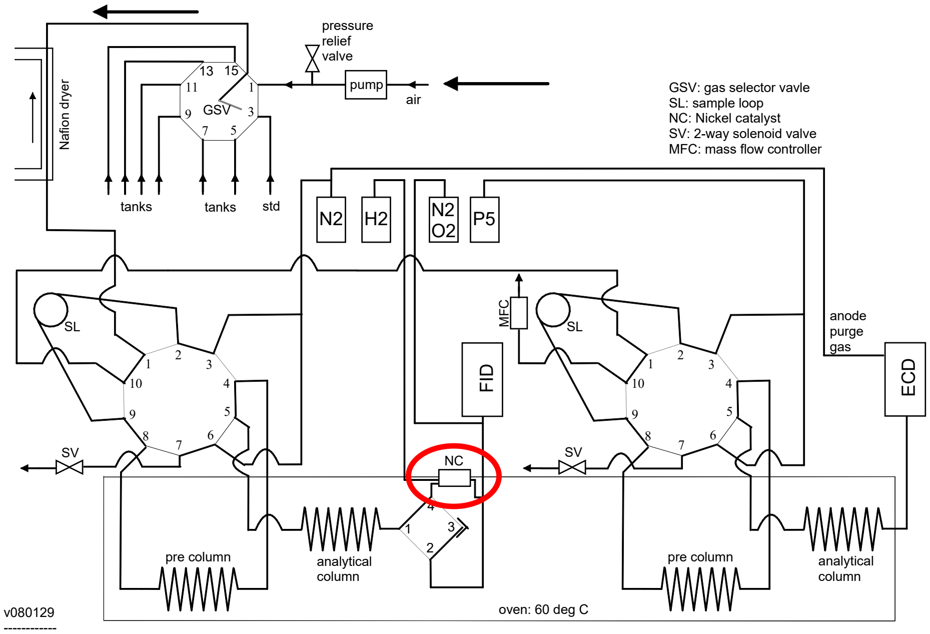
sample chromatogram for volatile organic compounds in Switzerland



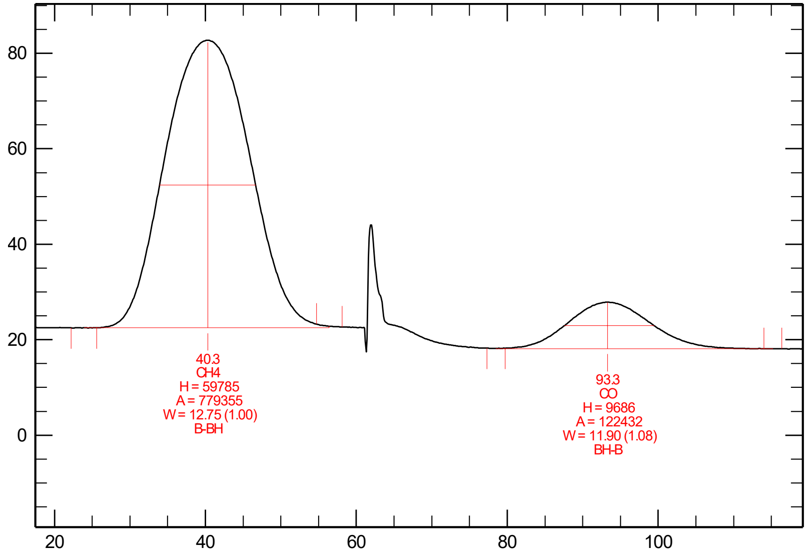
Gas Chromatography, cont'd

- CH_4 and CO, measured by flame ionization detection (FID)
- FID is best suited for compounds with C-H and C-C bonds
- Therefore, it requires that CO is first converted to CH_4. A hydrogen-rich oxygenated carrier gas over a hot nickel catalyst (NC) is typically used.

setup at Jungfraujoch



sample chromatogram for CH_4 and CO at Jungfraujoch



Continuous techniques

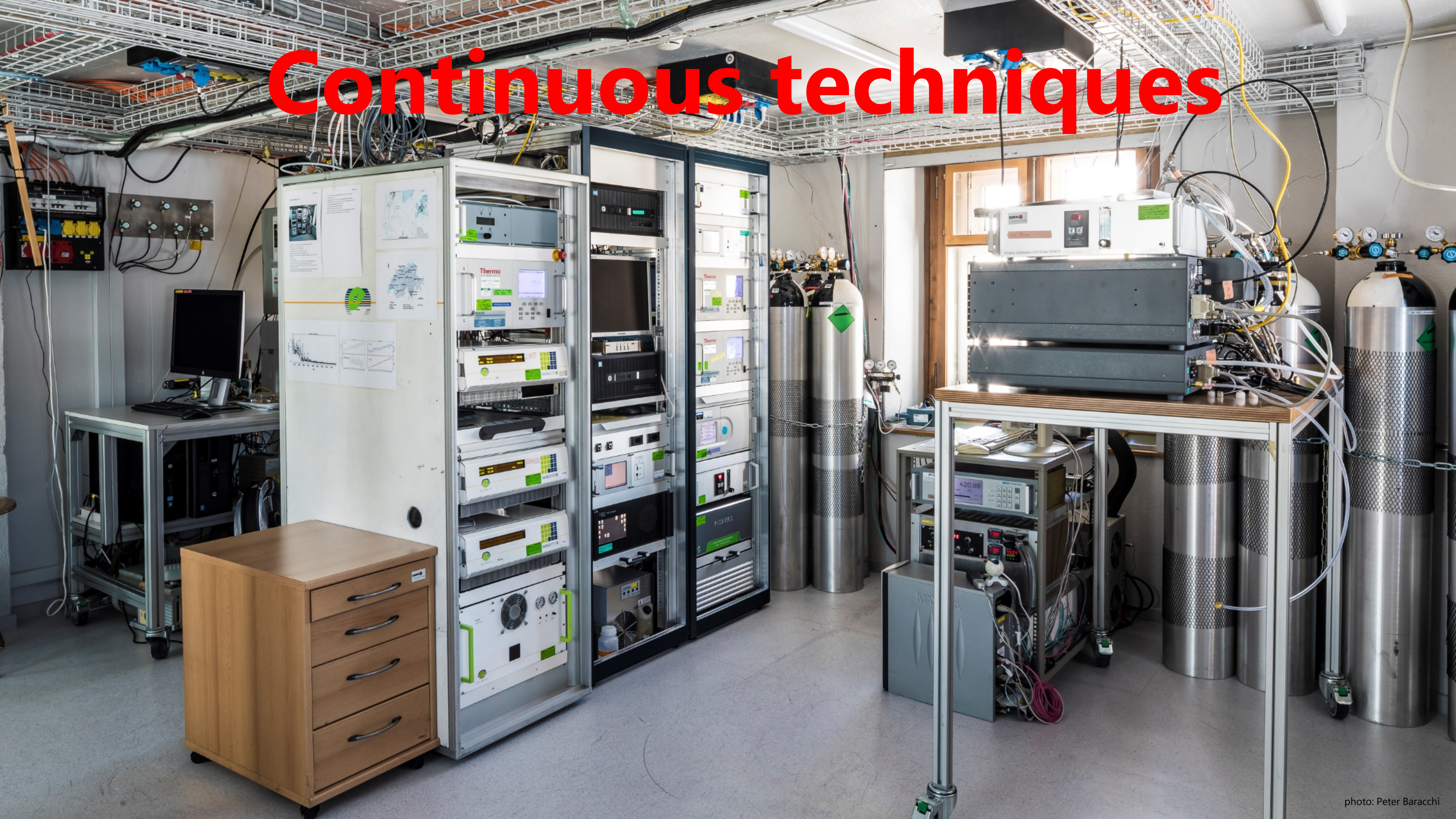
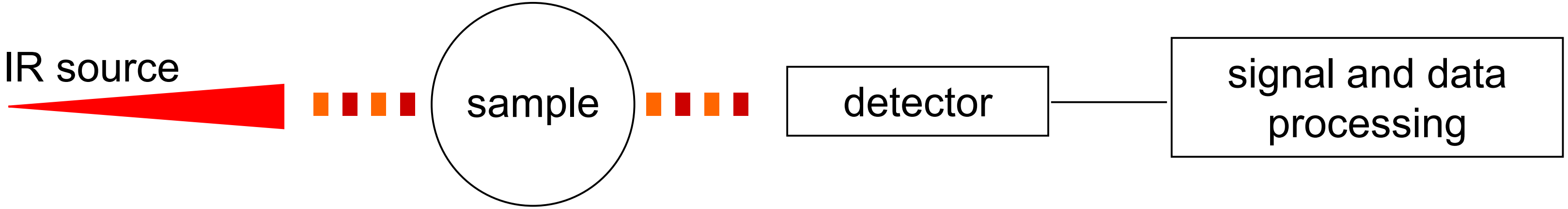


photo: Peter Baracchi

NDIR (Non-Dispersive Infrared Spectrometry)

- Infrared (IR) radiation from a stable source is first filtered and focused before passing through an optical cell containing the sample. IR absorption is detected.



- A reference signal is needed to compensate for matrix effects. This can be realized by means of Gas Filter Correlation (GFC) or by selective removal of CO with a catalyst.

Advantage: inexpensive continuous measurements, moderate requirements in terms of operation and maintenance.

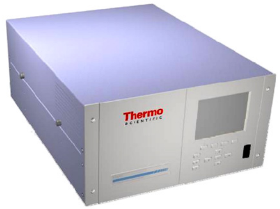
Disadvantage: rather high instrumental noise, rather high detection limit (a few tens of ppb), potential instrument drift.

➢ NDIR is most suitable for sites with elevated CO concentrations and less so at remote sites.

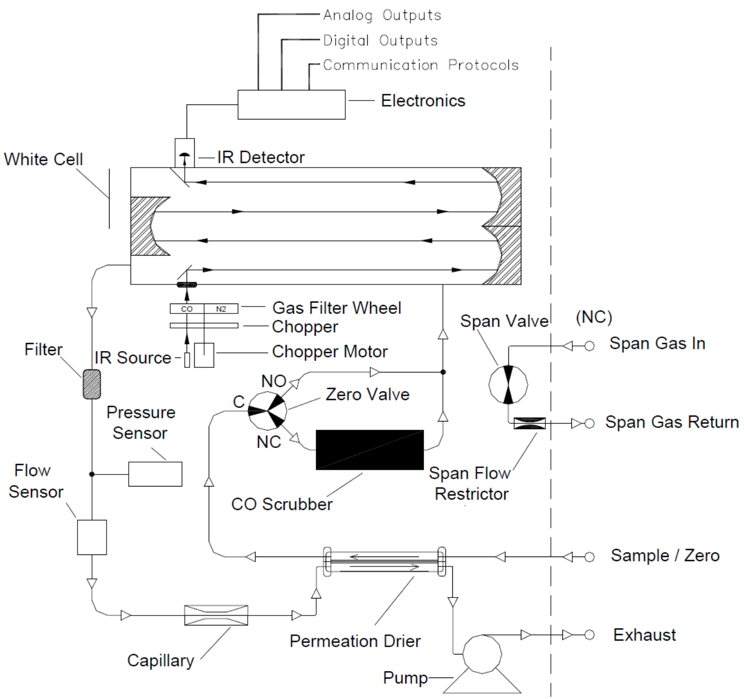
NDIR (Non-Dispersive Infrared Spectrometry)

Gas Filter Correlation

- radiation from IR source passes through a gas filter altering between CO and N_2
- CO gas filter produces a reference beam, N_2 gas filter produces a measure beam



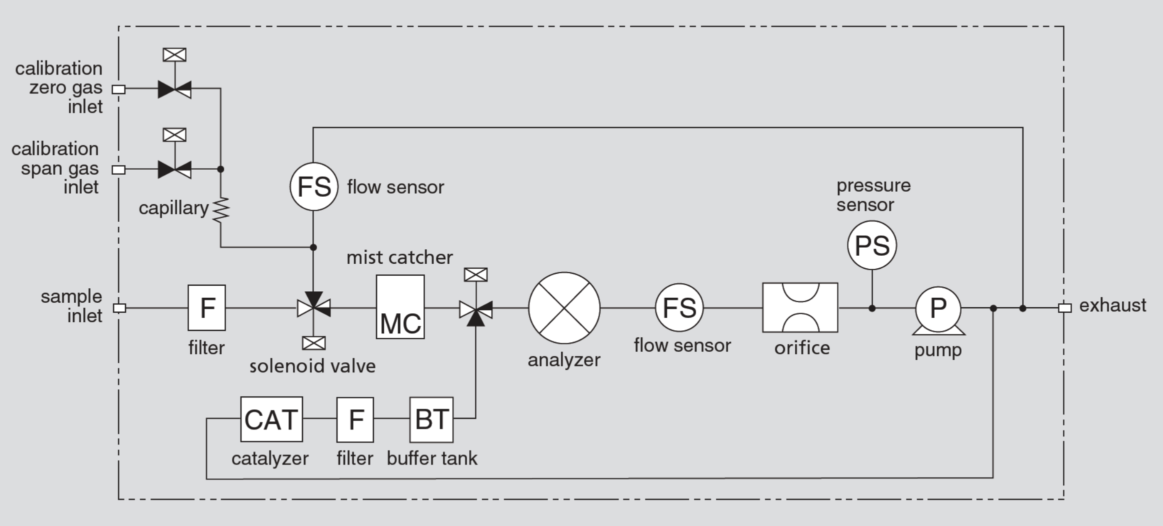
commercially e.g. available through Thermo Fisher Scientific Inc., USA
https://www.thermofisher.com/



Schematic of Thermo Scientific, model 48i

NDIR (Non-Dispersive Infrared Spectrometry)

Cross Flow Modulation



Schematic of Horiba, APMA-370

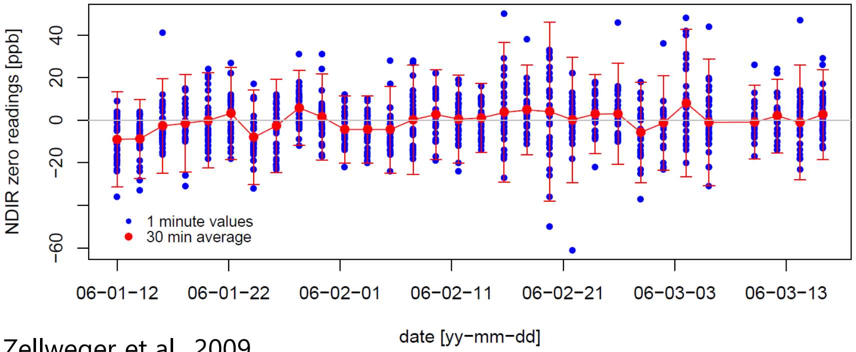
- air flow toggles between sample and reference
- the reference is sample air with only CO removed by a catalyst

commercially e.g. available through Horiba Ltd, Japan
https://www.horiba.com/

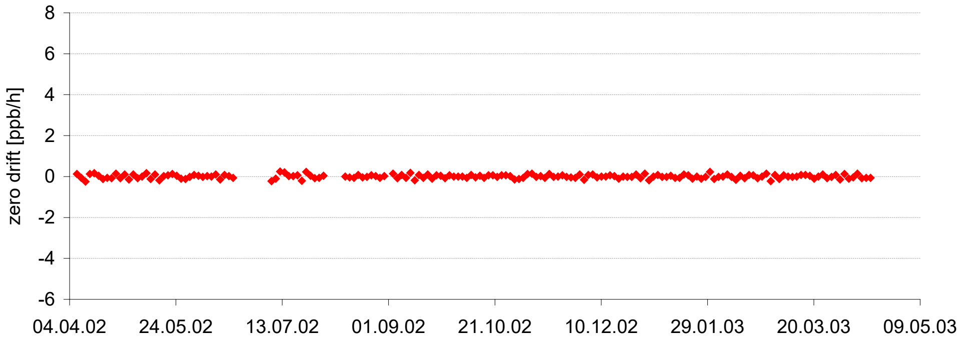
➢ both NDIR systems respond specifically to CO (theoretically)

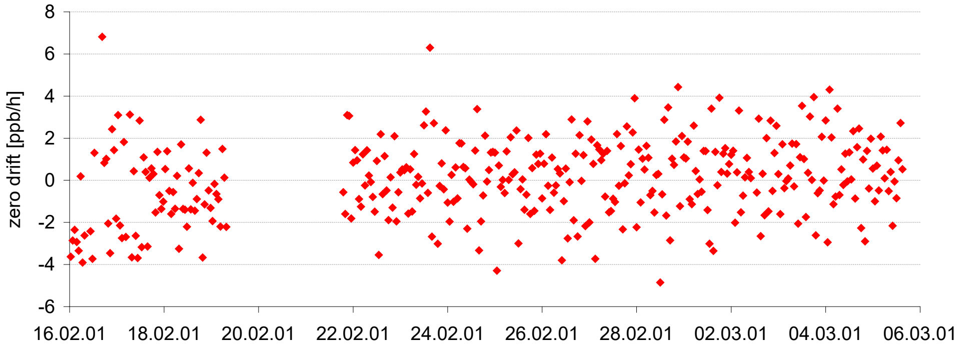
NDIR (Non-Dispersive Infrared Spectrometry)

- commercial NDIR instruments may show a significant zero drift of several ppb per hour
- as a consequence, frequent zeroing is needed to correct the data



Zellweger et al., 2009





➢ depending on instrument and laboratory conditions, zeroing needs to be performed every few hours

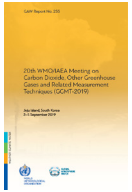
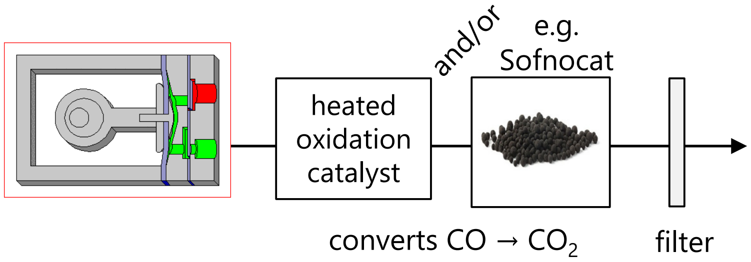
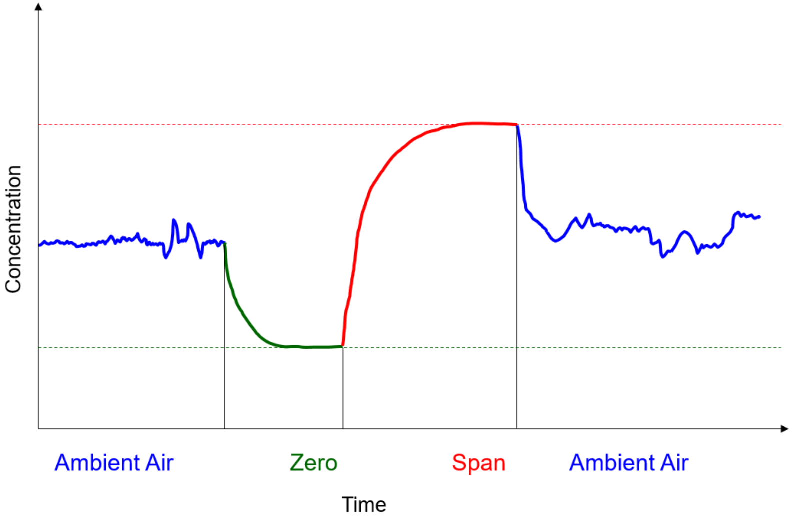


Table 1. Recommended network compatibility of measurements within the scope of WMO/GAW

Component	Network compatibility goal[1]	Extended network compatibility goal[2]	Range in unpolluted troposphere (approx. range for 2019)	Range covered by the WMO scale
CO_2	0.1 ppm (NH) 0.05 ppm (SH)	0.2 ppm	380 - 450 ppm	250 – 520[3] 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

Generation of CO-free air





- caution: commercially available zero air generators are often not optimized for CO removal

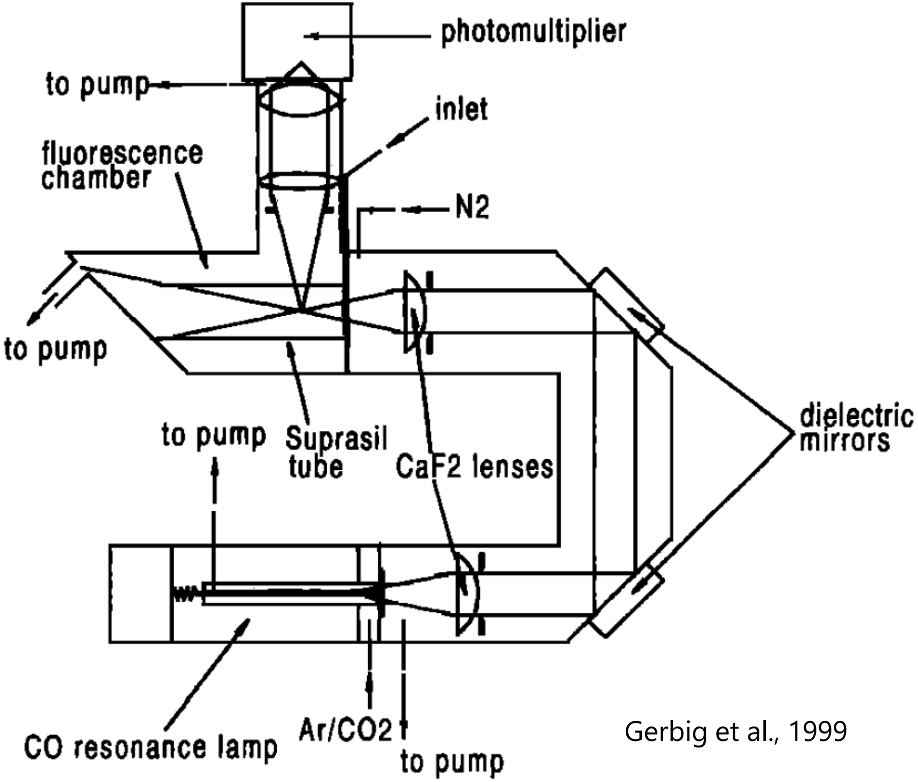
Vacuum UV Resonance Fluorescence (VURF)

CO shows resonance fluorescence (160-190 nm) when excited with UV (150 nm)

Advantage: fast (1s), precise, linear

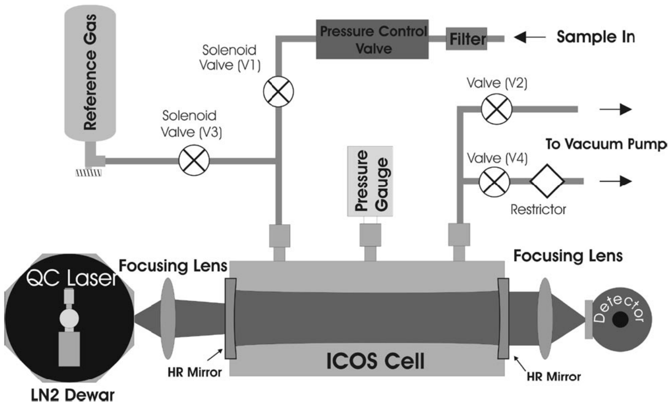
Disadvantage: expensive, delicate optics, maintenance intensive

commercially available through Aero-Laser GmbH, Germany
https://www.aero-laser.de

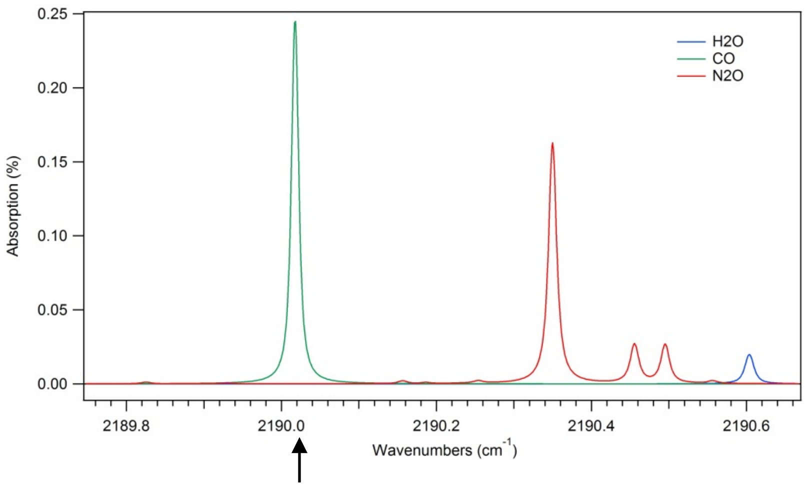


Gerbig et al., 1999

Laser Absorption Spectroscopy



Provencal et al., 2005



wavelength ~ 4.5 µm

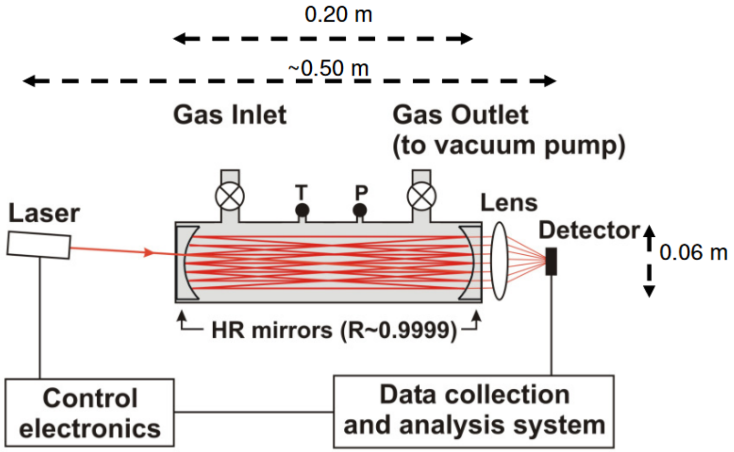
CO is detected in the near to mid-infrared region

Initially, laser had to be cooled with liquid nitrogen, which is unsuitable for long-term monitoring

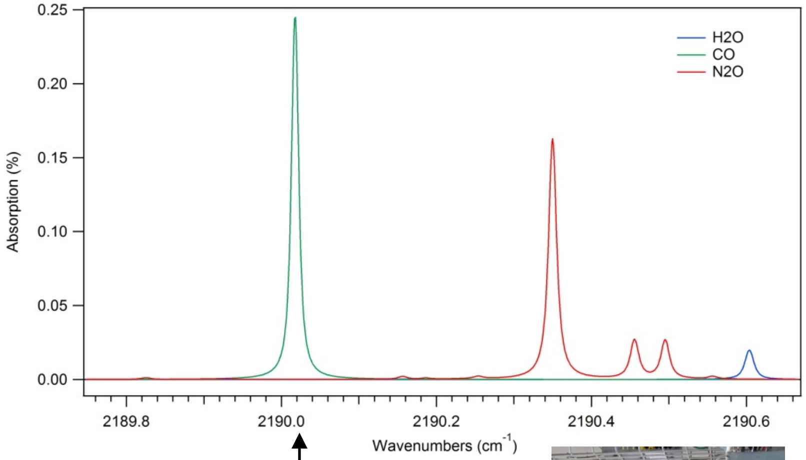
Empa Materials Science and Technology

Cavity-Enhanced Laser Absorption Spectroscopy

Off-axis integrated cavity output spectroscopy



Hendriks et al., 2008



wavelength ~ 4.5 µm

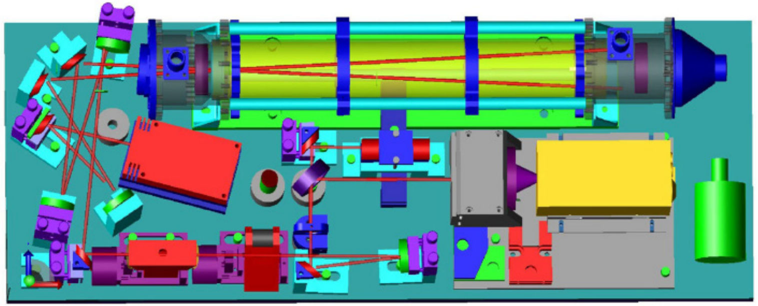
- simultaneous, rapid measurements of several trace gases with absorption features in the same wavelength range
- cryogenic free, measurement in the mid-infrared

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

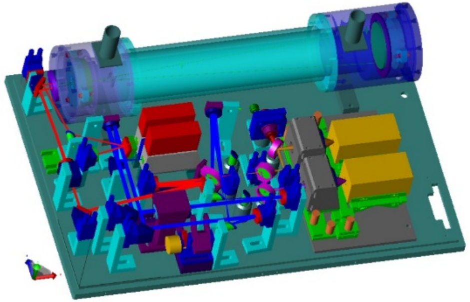
Cavity-Enhanced Laser Absorption Spectroscopy

Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS)

Mini Laser Trace Gas Monitor



Dual Laser Trace Gas Monitor

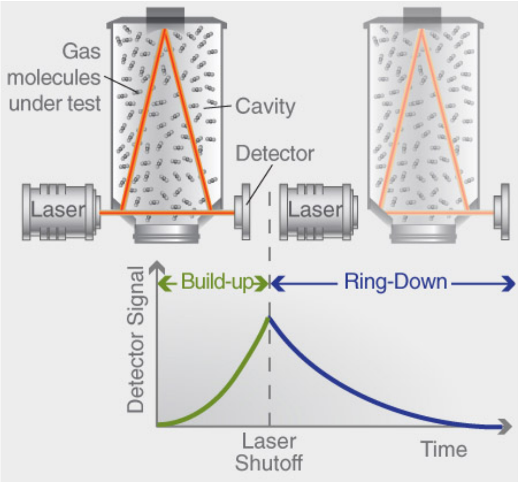


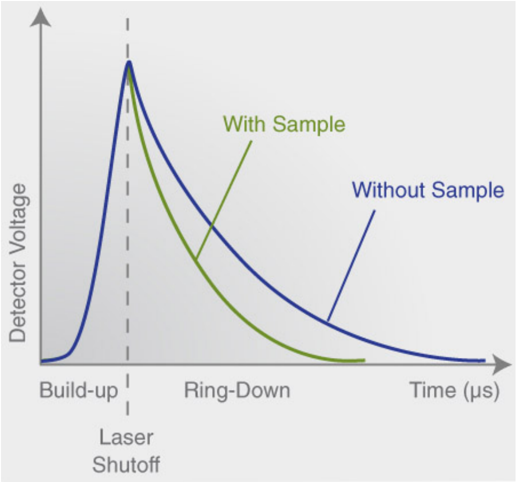
- simultaneous, rapid measurements of several trace gases with absorption features in the same wavelength range
- cryogenic free, measurement in the mid-infrared
- also produces and sells Dual QCL trace gas monitors which allow for the simultaneous measurement of multiple species, including NO, N2O, 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/

Cavity-Enhanced Laser Absorption Spectroscopy

Cavity Ringdown Spectroscopy

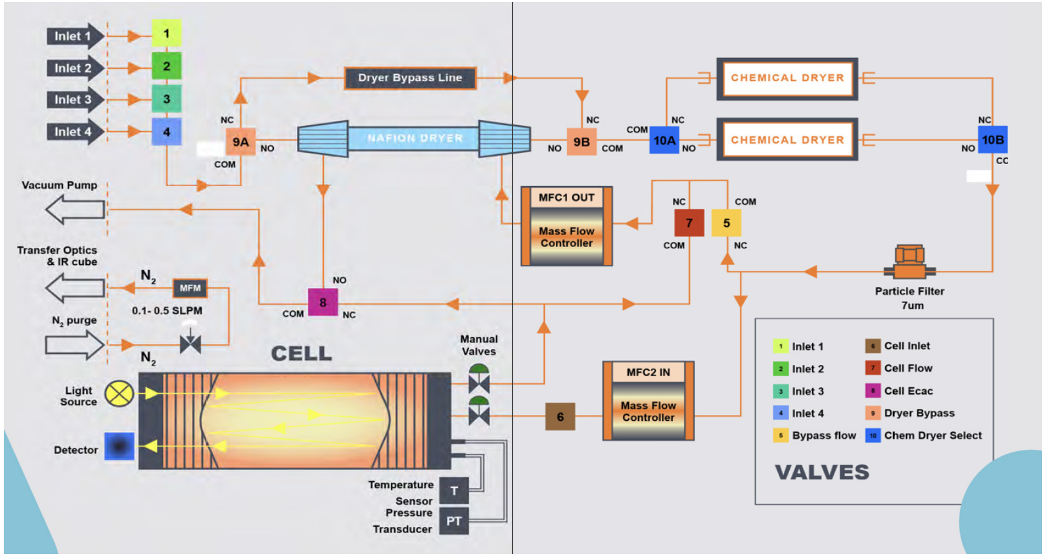




- simultaneous, rapid measurements of several trace gases with absorption features in the same wavelength range
- cryogenic free, measurement in the near-infrared
- laser is shut off, the intensity of light reaching the detector decreases or “rings down”

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

Fourier Transform Infrared (FTIR) Spectroscopy



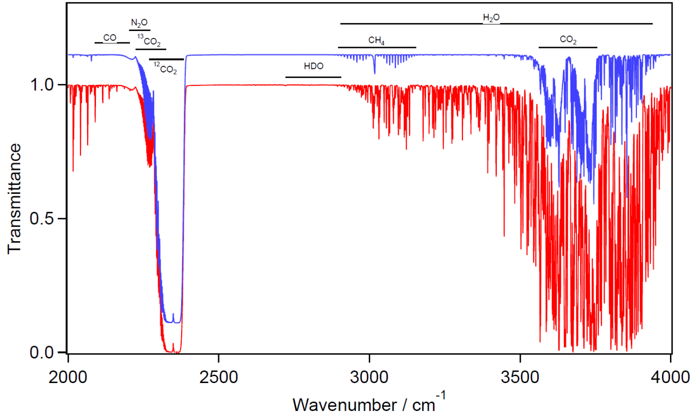


Fig. 1. The mid-infrared absorption spectrum of clean air in a 24 m cell. Red: undried air, blue: dried air. Positions of main absorption

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/

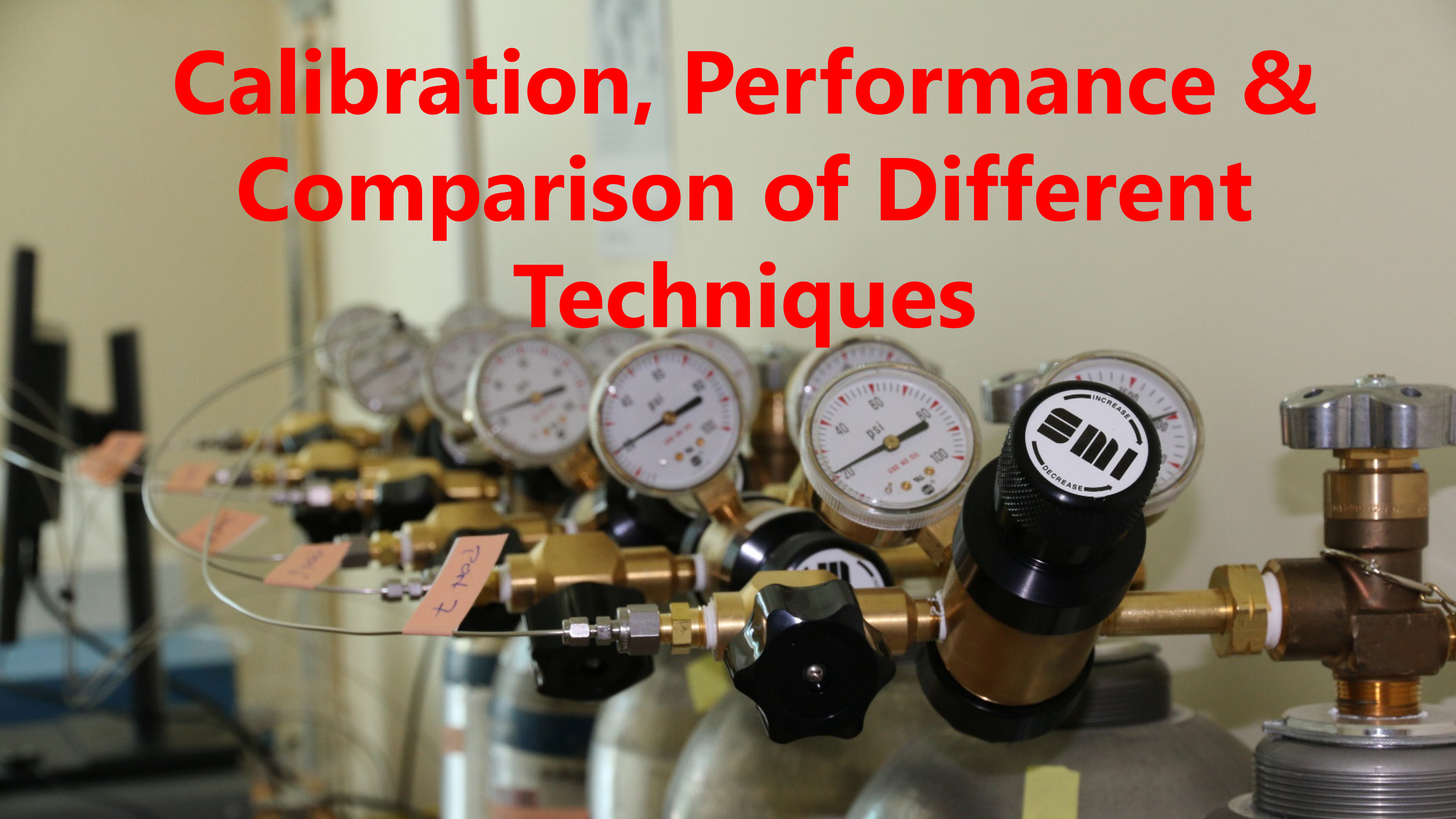
Thermo Scientific – Mid-IR Absorption Spectroscopy; https://www.thermofisher.com/

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

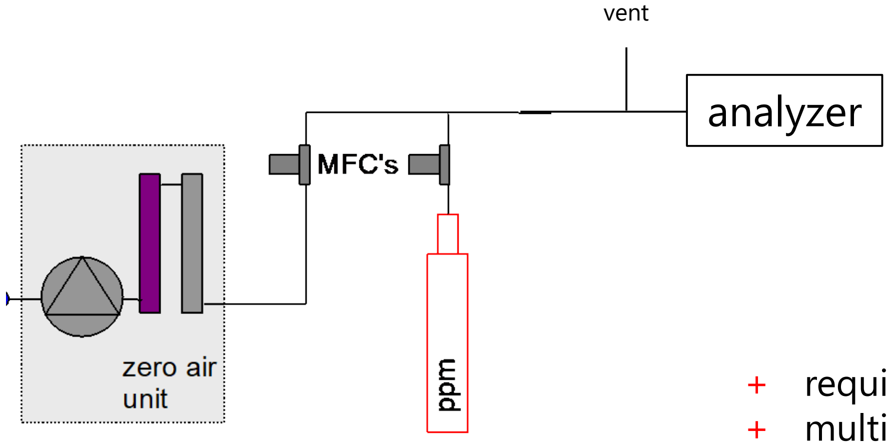
Aeris Technologies – Long-path Tunable Diode Laser Spectrometry; https://aerissensors.com

…

Calibration, Performance & Comparison of Different Techniques



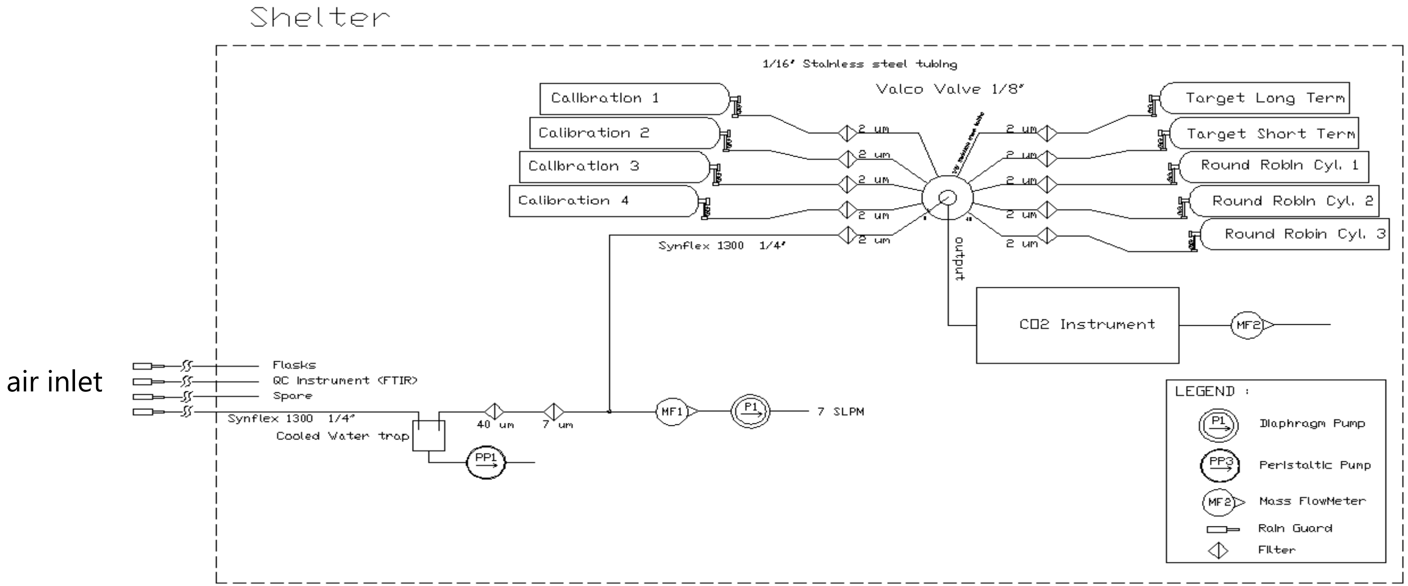
Calibration with Zero Air and ppm-level Reference Gas



+ requires only one cylinder
+ multi-point calibration is possible
+ consumption of reference gas is small
+ ppm-level standards are less prone to drifts

- difficult to achieve very good accuracy / to reach GAW compatibility goals
- direct traceability to GAW reference scale is not given

Calibration with a Suite of Ambient Level Reference Gases



ICOS RI, 2020

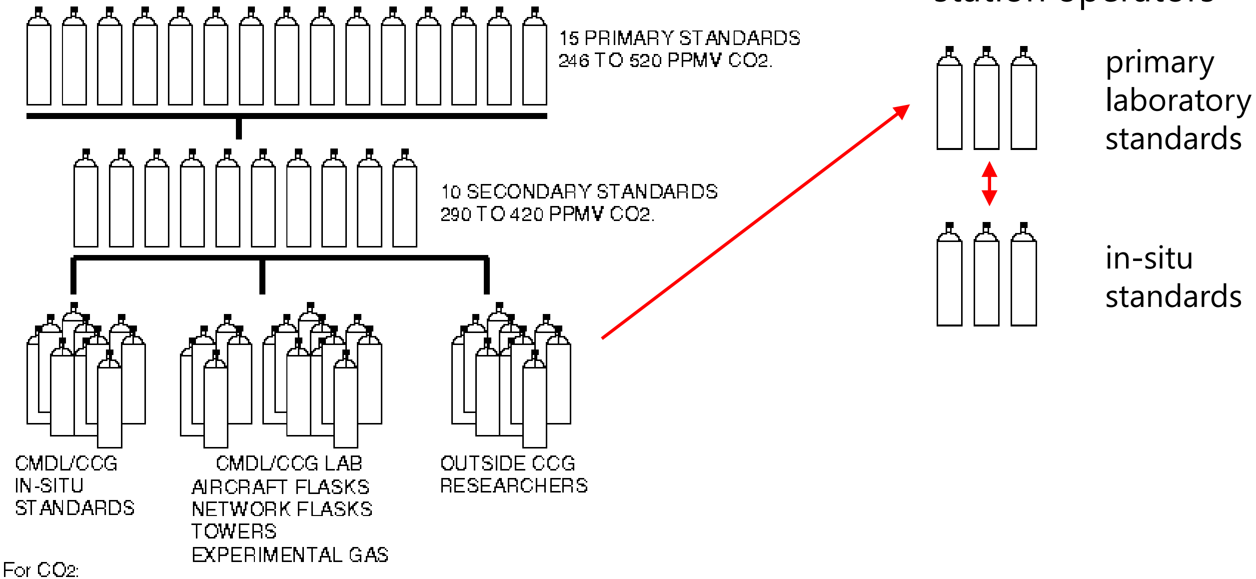
- \+ allows direct traceability to GAW reference scale
- \+ maximum accuracy and compatibility with other stations
- \+ setup can usually also accommodate other tanks for quality control

- \- consumption of reference gas is higher
- \- ppb-level standards are prone to drifts

Propagation of the GAW Reference Scale

NOAA ESRL is the GAW Central Calibration Laboratory (CCL) for CO2, CH4, CO, …

station operators



For CO2:

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

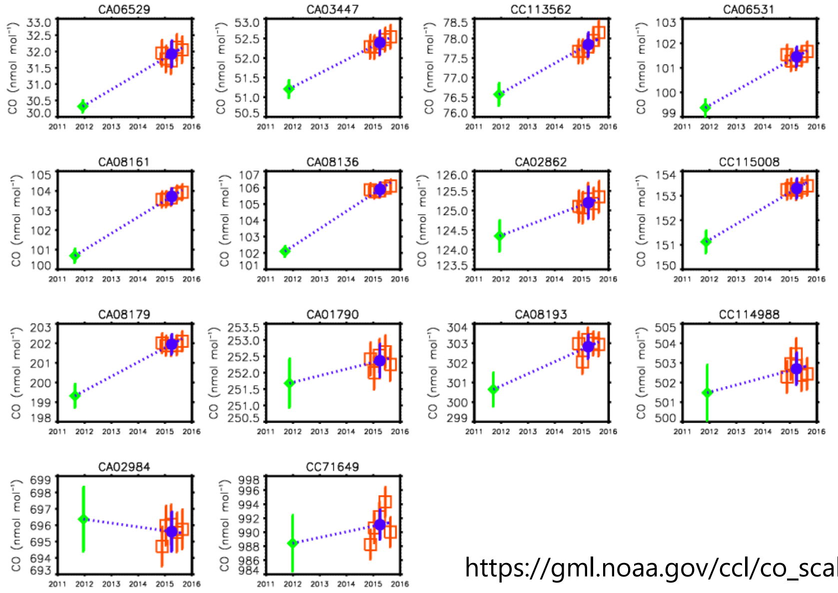
Absolute Uncertainty; 0.1 µmol/mol
Internal consistency [325-425 µmol/mol]; 0.04 µmol/mol [2 sigma] [< 2 years]

https://gml.noaa.gov/ccl/airstandard.html

Drifts in ppb-level CO reference standards

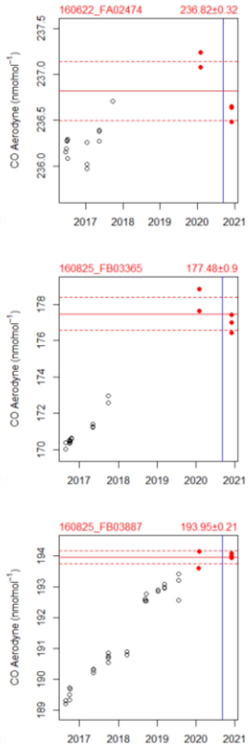
CO is high pressure cylinders is often subject to drift

Drifts in primary standards at CCL



https://gml.noaa.gov/ccl/co_scale.html

Drifts in travelling standards at the World Calibration Centre for CO (WCC-Empa)

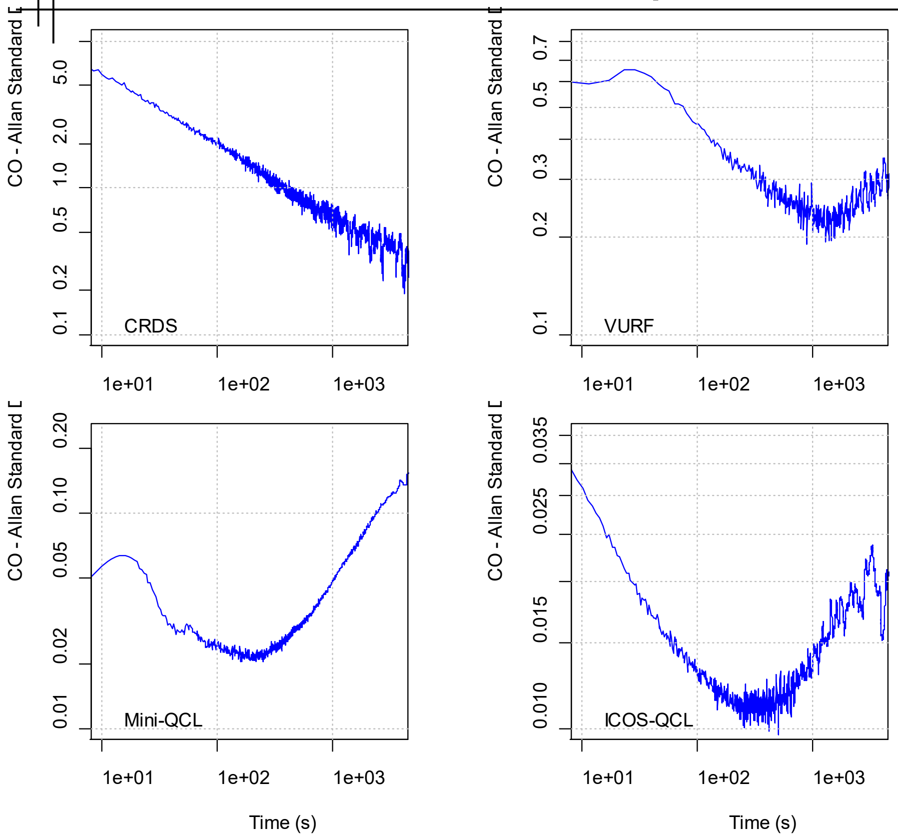


WMO, 2021

➢ drift needs to be tracked and to be accounted for

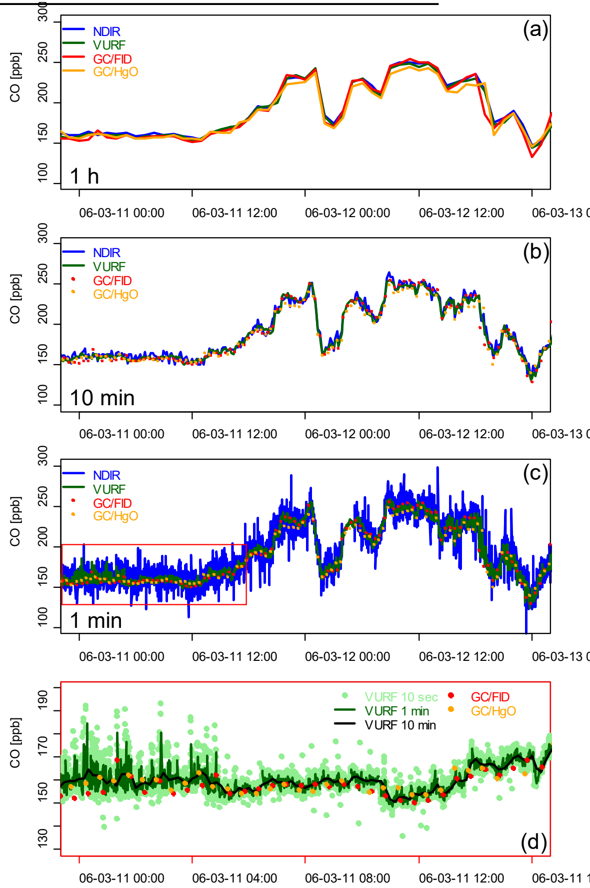
Empa Materials Science and Technology

Performance & Comparison of Different Techniques



Zellweger et al., 2012

Zellweger et al., 2009



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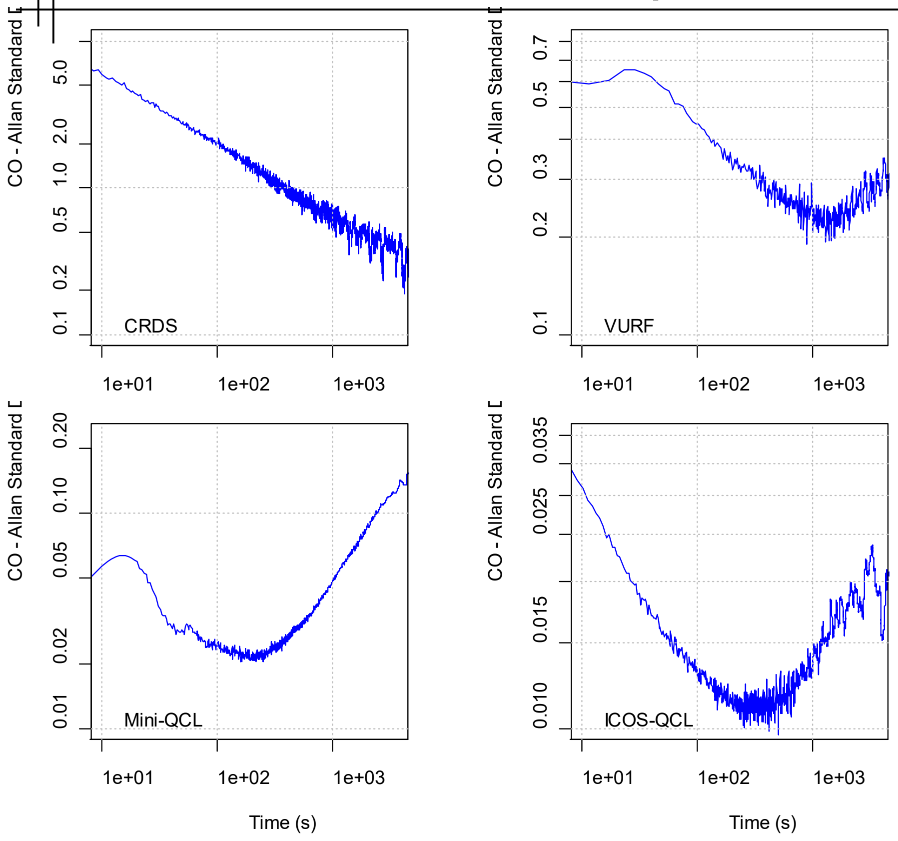
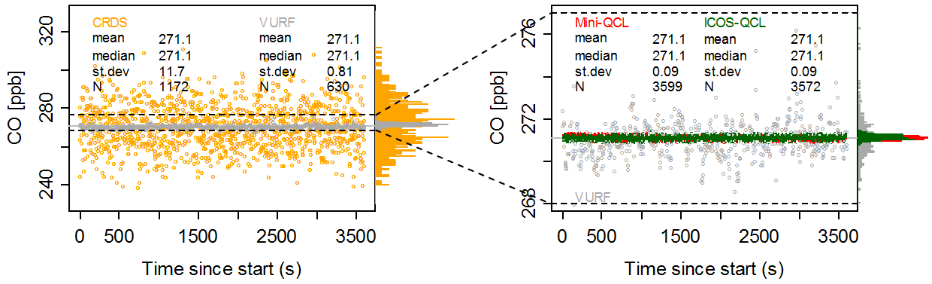
Performance & Comparison of Different Techniques

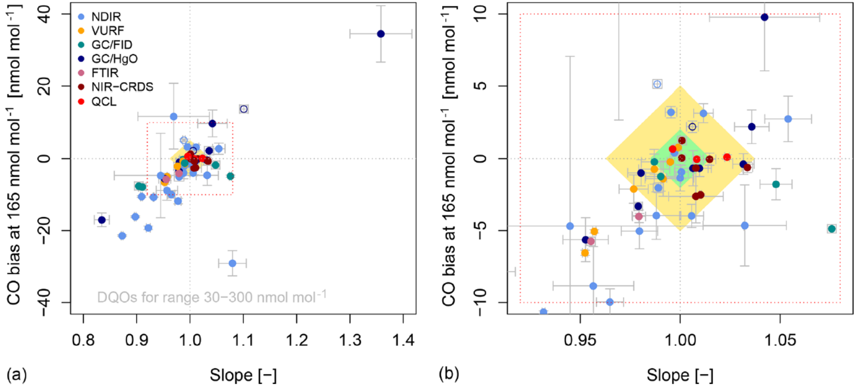


Zellweger et al., 2012



Zellweger et al., 2012

Summary of WCC-Audit Results



Zellweger et al., 2019

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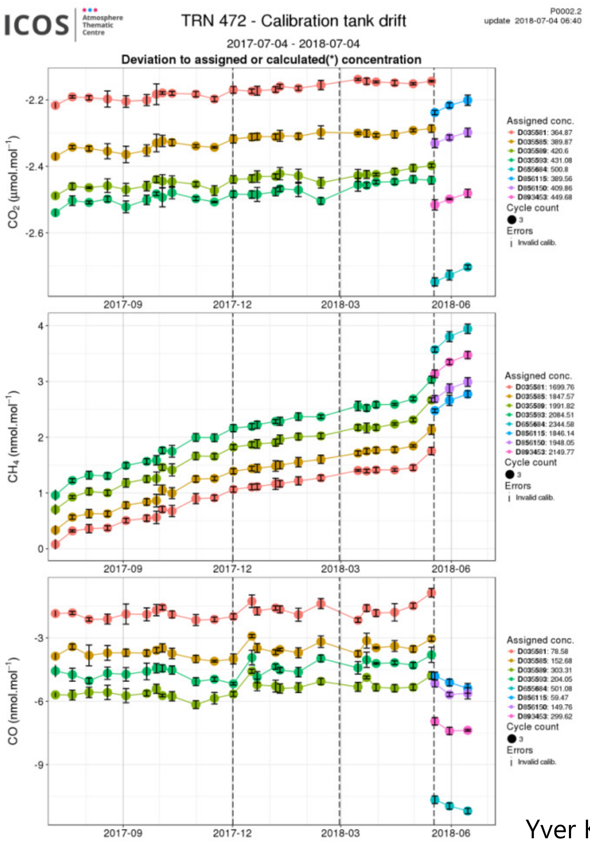
Performance & Comparison of Different Techniques



CRDS

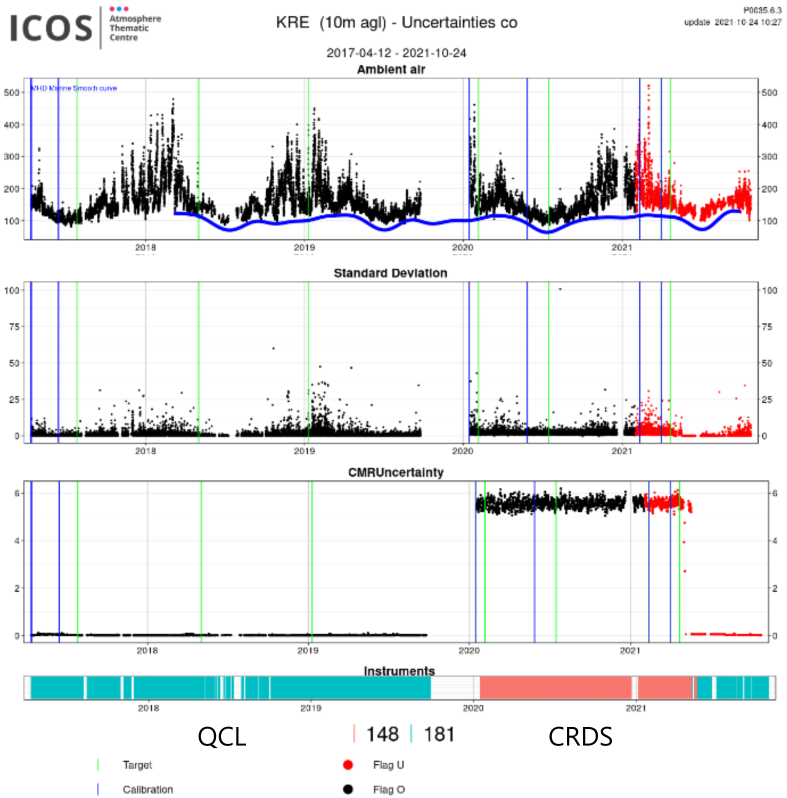
Results of 2-weekly calibrations

Yver Kwok et al., 2021

atmospheric mole fractions

atmospheric standard deviation

continuous measurement repeatability



QCL | 148 | 181 CRDS

https://icos-atc.lsce.ipsl.fr/dp

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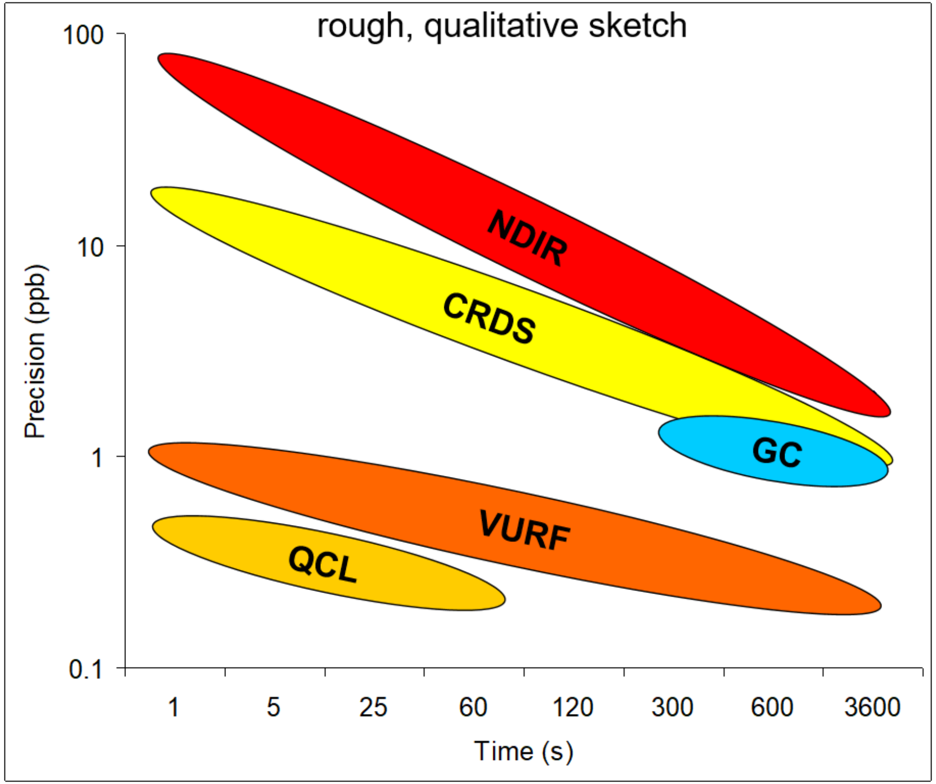
Graphical summary



values are estimates and can vary depending on instrument

Conclusions

- several analytical techniques are available for CO measurements in ambient air
- selection of measurement technique (and manufacturer) strongly relies on
  - the (scientific) rationale of the measurements (also: duration of the observations (long-term vs. campaign-like measurements), long-term stability vs. short-term, precision))
  - expected concentrations and its variability,
  - capacities for operation and maintenance,
  - available sample,
  - availability/accessibility of reference gases,
  - skills and expertise,
  - available space,
  - financial resources,
  - …

ask your colleagues and peers,
consult the literature

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Thank you for your attention !