Continuous in-situ CO$_2$ and CH$_4$ observations at Jungfraujoch with Cavity Ringdown Spectroscopy – sample drying issues and long-term stability

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Picarro G1301 @ Jungfraujoch

- in operation since December 2009
- continuous operation; CH₄, CO₂ and H₂O data every 4 seconds
- equipped with a custom-built (drying and) calibration unit
- samples were dried with a Nafion dryer until August 2010

- calibration runs (2 standards) every 46 hours
- data are reported on the WMO X2007 (CO₂) and NOAA04 (CH₄) scale
- target gas measured every 15 hours
- mean standard deviations for 20 mins of working standard analyses:
  ~ 0.015% (~ 0.05 ppm) for CO₂
  < 0.02% (~ 0.3 ppb) for CH₄
Long-term stability of instrument sensitivity

CO2

CH4

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Drying setup – simplified scheme

- Pump
- Nafion dryer
- Needle valve
- Overflow (~ 20 ml/min)
- Exhaust
- Counterflow at ~ -0.5 barg

Dew point ~ -35°C

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Advantage of simultaneous H2O measurements

- water vapor correction instead of sample drying (= less maintenance, no potential interaction of the sample with the drying system)
- correction accounts for both dilution and spectroscopic effects
- water vapor measurements are available as an additional parameter!

\[
\frac{(CO_2)_{\text{wet}}}{(CO_2)_{\text{dry}}} = 1 + -0.01198 \cdot (H_{\text{rep}}) + -0.00026 \cdot (H_{\text{rep}})^2
\]

\[
\frac{(CH_4)_{\text{wet}}}{(CH_4)_{\text{dry}}} = 1 + -0.01022 \cdot (H_{\text{rep}}) + -0.00012 \cdot (H_{\text{rep}})^2
\]
Advantage of simultaneous H2O measurements

- water vapor correction instead of sample drying (= less maintenance, no potential interaction of the sample with the drying system)
- correction accounts for both dilution and spectroscopic effects
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**injection of water droplet**

![Graph showing CH4 and H2O concentrations over time](image)

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Nafion dryer effects

- non-negligible CO$_2$ losses in the drying system
- no bias in calibrated data if data processing accounts for losses
- drying system humidifies standards
- amount of humidification depends on ambient air humidity
Conclusions – Sample drying, pros & cons

Pro sample drying
- no humidity correction function to be determined
- accuracy of H₂O readings of no importance

Contra sample drying
- more simple setup
- setup less prone to failure / leaks
- no loss in data quality
- H₂O as an additional parameter
Long-term stability of instrument sensitivity

CO2

CH4

⇒ what is the optimum calibration frequency?

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Long-term stability of instrument sensitivity

CO2

April 2010

CH4

quick look, individual slopes and intercepts, CO2

quick look, individual slopes and intercepts, CH4

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Long-term stability of instrument sensitivity

CO2 April 2010 CH4

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Long-term stability of instrument sensitivity

CO2
April 2011

CH4

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Long-term stability of instrument sensitivity

CO2

Quick look, mean calgas and target mixing ratios

CO2 target [ppm]

CH4

Quick look, mean calgas and target mixing ratios

CH4 target [ppb]

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Long-term stability of instrument sensitivity

CO2

April 2010

monthly mean calibration applied

CH4

target mole fractions

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Long-term stability of instrument sensitivity

CO2
April 2010
CH4

only first cal of the month applied

target mole fractions

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Long-term stability of instrument sensitivity

**CO2**

**April 2010**

**CH4**

only last cal of the month applied

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Long-term stability of instrument sensitivity

April 2011

monthly mean calibration applied

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Long-term stability of instrument sensitivity

April 2011
only first cal of the month considered

CO2 [ppm]

CH4 [ppb]

target mole fractions

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Long-term stability of instrument sensitivity

April 2011
only last cal of the month considered

CO2 [ppm] target mole fractions

CH4 [ppb] target mole fractions
Long-term stability of instrument sensitivity

April 2011
Linear cal

CO2 [ppm] 425.8 425.9 426.0 426.1 426.2
2011/04

2011/04

Target mole fractions

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Conclusions – Calibration Frequency

- currently: analysis of 2 working standards every 46h
  1 target tank every 15h

- observed long-term stability of the CRDS analyzer allows longer intervals

- frequent target tank analysis recommended for rapid detection of instrumental failures

- results of several calibrations might be pooled, single calibrations are only a snapshot introducing random noise to the data