Long-term field intercomparison of \( \text{N}_2\text{O} \) observations with GC-ECD and Cavity Enhanced Absorption Spectroscopy at Jungfraujoch

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Jungfraujoch (JFJ)

3580 m asl, 7° 59' E, 46° 32' N

- part of the Swiss National Air Monitoring Pollution Network
- one of the 29 Global GAW sites

well suited for
- monitoring the free troposphere
- source allocations in Central Europe

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Nitrous Oxide Measurements @ JFJ

GC-ECD

Agilent 6890N
with
FID (CH₄, CO) and
ECD (N₂O, SF₆) detector

since February 2005

- length of run: 12min
- each ambient air sample is bracketed with calibration runs
- standards are traced back to SIO-98 (till April 2012) and NOAA-2006A (after April 2012) scale
- target gas measurements three times a week (3 subsequent analysis)
- samples are dried with a Nafion dryer
- precision based on recurrent working standard analyses: ~ 0.07% for N₂O
N2O time series at Jungfraujoch

trend (2005 – 2012): 1.0 ppb yr$^{-1}$

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N2O time series at Jungfraujoch

- observation of distinct events is rare
- a seasonal cycle can be seen when considering all data

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LGR-23r N2O/CO with enhanced performance

- analysis based on off-axis integrated cavity output spectroscopy
- detection in the mid-IR using a quantum-cascade laser
- 42 cm (width) x 50 cm (height) x 80 cm (depth), 70kg
- enhanced performance, i.e. active temperature stabilization

model N₂O/CO-23r with enhanced performance configuration

model N₂O/CO-23d

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Los Gatos LGR-23r N2O/CO monitor

N₂O precision:
0.11 ppb for 1 Hz
0.02 ppb for 1-min data)

for comparison:
results of 12 injections of a reference gas, measured with GC-ECD
(required time ~ 4 ½ h)
Allan Variance Plot

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Allan Variance Plot

**N2O/CO 23d**

**N2O/CO 23r EP**

**achieved precisions:**

<table>
<thead>
<tr>
<th>Precision [ppb]</th>
<th>Averaging Time [min]</th>
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<tbody>
<tr>
<td>~ 0.01</td>
<td>2</td>
</tr>
<tr>
<td>~ 0.005</td>
<td>10</td>
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</tbody>
</table>

EP version is slightly superior compared to version w/o enhanced performance

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LGR-23r at Jungfraujoch

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MIU before and after modification

Disadvantages:
no overflow option, teflon tubing and teflon bulkhead unions, dead volumes
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Modifications:
additional solenoid valve to allow measuring pressurized air under ambient pressure conditions, dekabon tubing, stainless steel bulkhead unions, use of only 8 ports
flows for each port can be individually set with needle valves
Calibration results

March till mid-April 2013

- 3 calibration gases every 47 hours, one target cylinder every 15 hours

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Calibration results, cont’d

several sudden significant sensitivity losses, accompanied by huge \( \text{H}_2\text{O} \) signals

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Ambient air data – N2O, hourly averages

i.e. average of 2 to 3 discrete injections (ECD) and full coverage hourly averages (LGR)

- small bias (cross-calibration of the calibration gases is still pending)
- short-term structure seen with LGR isn’t always resolved with ECD

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Ambient air data – CO

comparison of LGR’s CO data with other available CO record at Jungferaujoch

- rather good agreement, all features are recorded with both techniques

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Ambient are data – N2O, CH4 & CO

does the N\textsubscript{2}O variability correlate with variations of other trace gases?

- some events are seen in all trace gases while others (especially with low N\textsubscript{2}O) are not reflected in the CH\textsubscript{4} and CO data record

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Conclusions

- laboratory tests of the off-axis ICOS from LGR showed very satisfactory and promising results
- modifications were required to use the LGR Multi Inlet Unit according to our needs
- in the field, calibrations every 2 days revealed the need for frequent sensitivity checks
- severe sensitivity losses were observed 3 times in 6 months, always accompanied with events of very high H$_2$O readings
- agreement for N$_2$O with GC-ECD is poor
- agreement for CO with another laser spectrometer is satisfactory
- comparison of the N$_2$O, CH$_4$ and CO time series at Jungfraujoch identifies some common features
- the origin of some patterns in the N$_2$O record measured with the LGR analyzer (atmospheric variability, artifacts ?) are subject to further investigations
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Thank you for your attention!

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