N_2O isotope research: development of reference materials and metrological characterization of OIRS analyzers within the SIRS project

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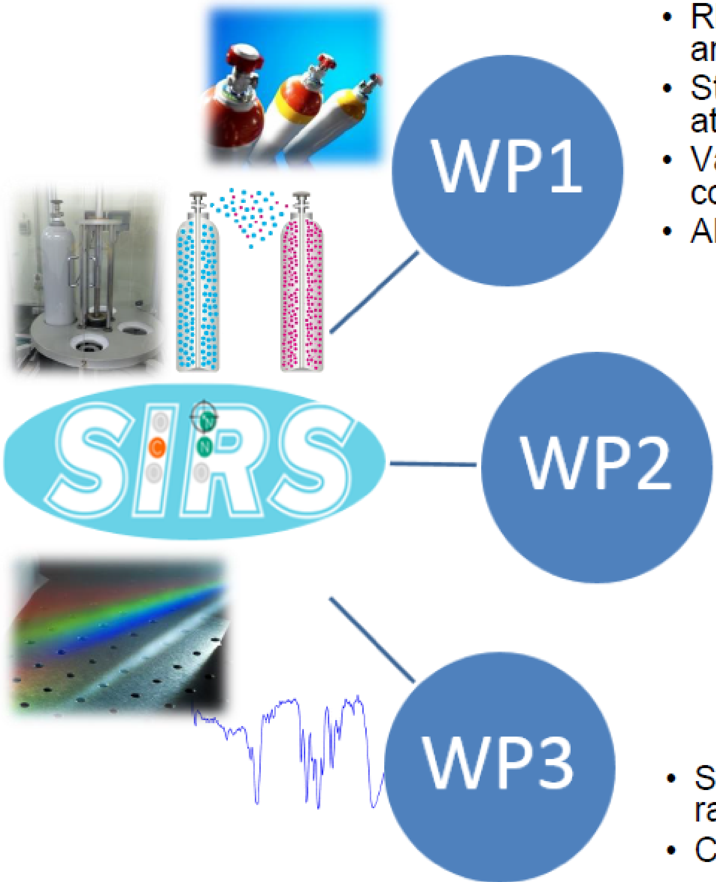
SIRS Metrology for stable isotope reference standards (PI P. Brewer, NPL)

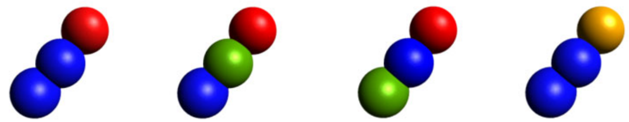


- RMs pure CO_2 for $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2
- Static and dynamic RMs of CO_2 at 400 µmol mol^{-1}
- Validation of RMs and comparisons (VPDB)
- Absolute measurements

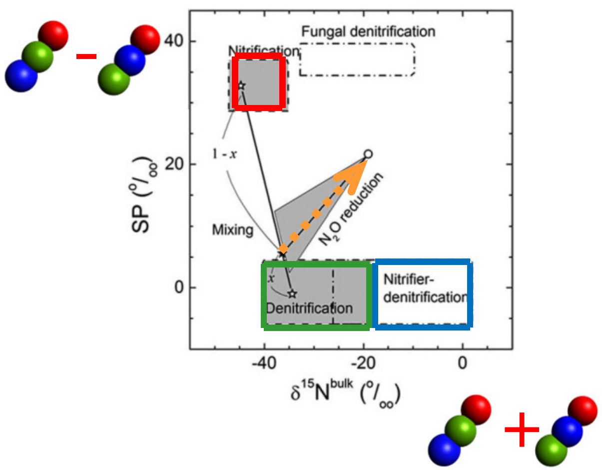
- Link $\delta^{15}N$, $\delta^{18}O$ and ^{15}N site preference in N_2O to the international stable isotope ratio scales
- RMs for $\delta^{15}N$, $\delta^{18}O$ and ^{15}N site preference in N_2O
- Static and dynamic mixtures at 300 to 1000 nmol mol^{-1} for instrument calibration

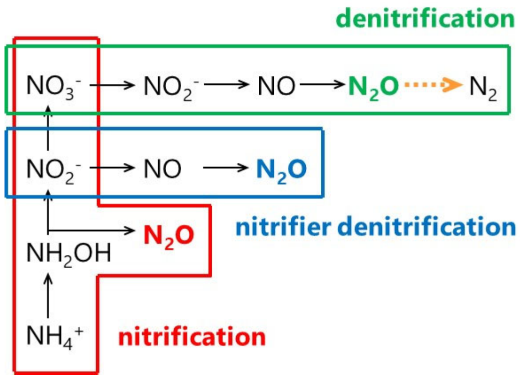
- Spectroscopic methods for isotope ratio measurements
- Comparison of methods

Motivation N_2O isotope research



$^{14}N^{14}N^{16}O$	$^{14}N^{15}N^{16}O$	$^{15}N^{14}N^{16}O$	$^{14}N^{14}N^{18}O$
446	456 (α)	546 (β)	448
9.903×10^{-1}	3.641×10^{-3}	3.641×10^{-3}	1.986×10^{-3}





Measurements of the four most abundant stable isotopocules of N_2O provides a valuable constraint on source attribution of atmospheric N_2O.

References:
S. Toyoda et al. (2017) DOI: 10.1002/mas.21459
T. Denk et al. (2017) DOI: 10.1016/j.soilbio.2016.11.015

N_2O isotopocules at natural abundance levels can be analyzed by isotope-ratio mass-spectrometry (IRMS) and more recently optical isotope ratio spectroscopy (OIRS).

References:
S. Toyoda et al. (1999) DOI: 10.1021/ac9904563
H. Wächter et al. (2008) DOI: 10.1364/OE.16.009239

Presentation overview

This presentation will highlight the recent progress, with respect to N_2O isotope research, achieved within the framework of the EMPIR project “Metrology for Stable Isotope Reference Standards (SIRS)”, namely:

Part 1: The **development of pure and diluted N_2O reference materials (RMs)**, covering the range of isotope values required by the scientific community. These gaseous standards will be available as pure N_2O or N_2O diluted in whole air. N_2O RMs were analyzed by an international group of laboratories for $\delta^{15}N$, $\delta^{18}O$ (MPI-BGC, Tokyo Institute of Technology, UEA), $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ (Empa, Tokyo Institute of Technology) and $\delta^{17}O$ (UEA) traceable to the existing isotope ratio scales.

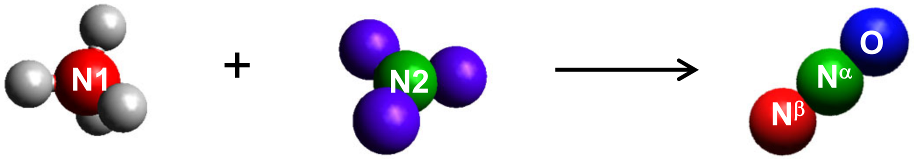
Part 2: The metrological **characterization of the three most common commercial N_2O isotope OIRS analyzers** (with/without precon QCLAS, OA-ICOS and CRDS) for gas matrix effects, spectral interferences of enhanced trace gas concentrations (CO_2, CH_4, CO, H_2O), short-term and long-term repeatability, drift and dependence of isotope deltas on N_2O concentrations.

Part 1: Development of N_2O RMs – Background

- N_2O isotope data are linked to the Air-N2 (for $^{15}N/^{14}N$) and VSMOW (for $^{18}O/^{16}O$) scales. First N_2O isotope RMs with provisional delta values were provided by USGS, but not suitable for 2-point calibration

Ostrom et al. (2018) DOI: 10.1002/rcm.8157

- Link between AIR-N2 and site specific N_2O isotopic composition provided by NH_4NO_3 thermal decomposition



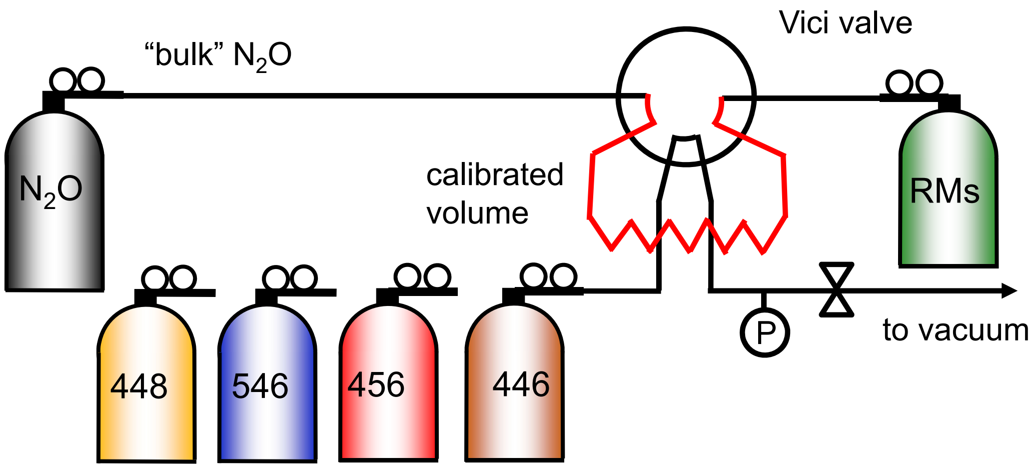
S. Toyoda & N. Yoshida (1999) DOI: 10.1021/ac9904563
M. Westley et al. (2007) DOI: 10.1002/rcm.2828
J. Mohn et al. (2016) DOI: 10.1002/rcm.7736

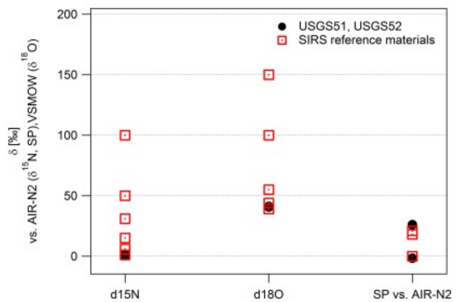
- Stakeholders, including the atmospheric monitoring community, encourage the release of RMs, pure-N_2O gas or N_2O in air with stated uncertainty, especially for $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$.

GGMT Report (2020) in preparation

Preparation of pure N_2O with different isotopic composition

- Different qualities of commercially available N_2O were analysed but offer only a limited span of $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$
- 6 RMs prepared by volumetric doping of commercial N_2O with isotopic pure $^{15}N^{14}NO$, $^{14}N^{15}NO$, ^{18}O-enriched N_2O and $^{15}N^{\beta}$-depleted N_2O





Optimisation of NH_4NO_3 thermal equilibration technique

- NH_4NO_3 salts (S1-S6) prepared by gravimetric doping with $^{15}NH_4NO_3$, $NH_4{}^{15}NO_3$, δ^{15}N-NH_4 depleted NH_4NO_3, δ^{15}N-NO_3-depleted NH_4NO_3 covering the δ^{15}N range of N_2O gases. Homegeneity of δ^{15}N in salts confirmed by IRMS at MPI-BGC.

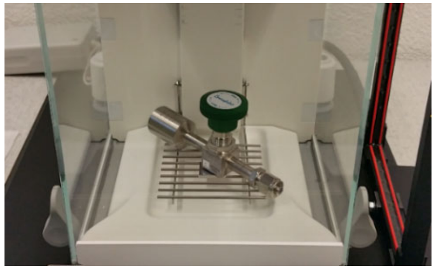
- δ^{15}N-NH_4, δ^{15}N-NO_3 and δ^{15}N-NH_4NO_3 in S1-S6 analysed at different laboratories / techniques: MPI-BGC, University of Eastern Finland, Tokyo Tech, University Vienna, University Ghent, University Pittsburg, UC Davis and Hydroisotope.

- Yield of thermal decomposition of NH_4NO_3 optimized in two variants: 1) NH_4NO_3 only, 2) NH_4NO_3 with $(NH_4)_2SO_4$ / NH_4HSO_4 novel technique achieves high yield of 92-96% (for 1) and 94-97% (for 2)

Szabo et al. (1985) DOI:10.1524/zpch.1985.144.144.187

- S1-S6 decomposed to N_2O, purified and purity confirmed by FTIR

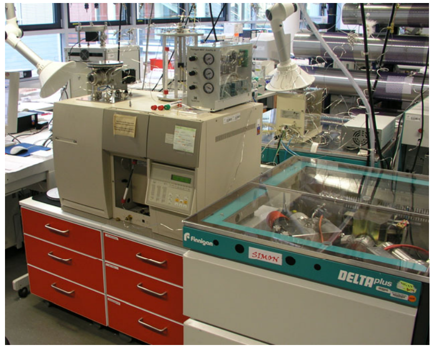
Glass bulbs with NH_4NO_3 used for thermal decomposition



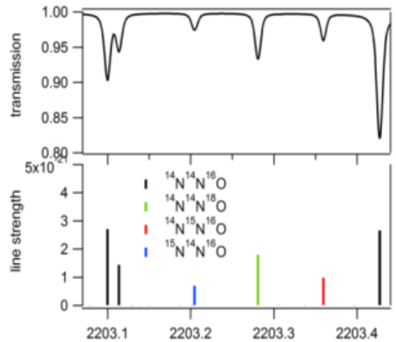
Gravimetric determination of N_2O yield

Analysis of N_2O RMs by IRMS and laser spectroscopy

- MPI-BGC analysed the prepared N_2O RMs for $\delta^{15}N$ and $\delta^{18}O$ using dual inlet IRMS (DI-IRMS).
- Tokyo Institute of Technology analysed RMs for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ by DI-IRMS.
- University of East Anglia analysed RMs for $\delta^{15}N$, $\delta^{18}O$ and $\delta^{17}O$ with/without decomposition in a heated gold tube by IRMS
- Empa analysed the N_2O RMs for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ by laser spectroscopy against Tokyo Tech standards and is currently performing analysis against own standards produced by NH_4NO_3 thermal decomposition.
- Summer / Fall 2020: Manuscript to report isotopic composition of pure N_2O RMs submitted and release of gases



IRMS analysis at MPI-BGC



Spectra of the laser spectrometer used for N_2O isotope analysis at Empa

Part 2: Characterization of the three most common commercial N_2O isotope OIRS analyzers

- What is the precision and repeatability of instruments?
- Do changes in N_2O concentration affect isotope measurements (non-linearities)?
  330 – 1250 ppb N_2O
- Do changes in the gas matrix affect delta values (pressure broadening)? i.e. incubation experiments
- Does the presence of other trace gases affect delta values (spectral interferences – "overlapping peaks")?
  CO_2, CH_4, CO

https://doi.org/10.5194/amt-2019-451
Preprint. Discussion started: 5 December 2019

Atmospheric Measurement Techniques Discussions

N_2O isotopocule measurements using laser spectroscopy: analyzer characterization and intercomparison

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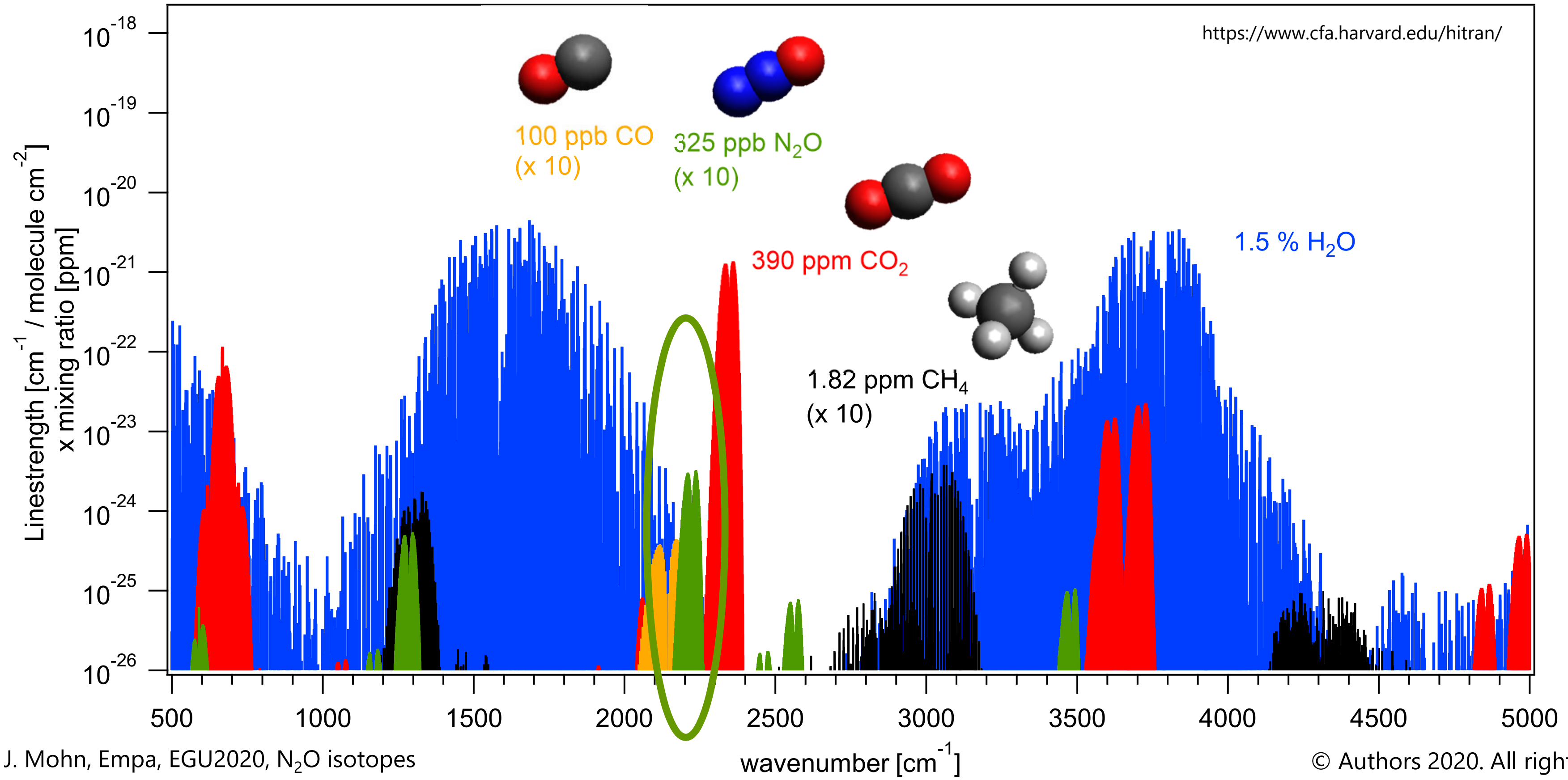
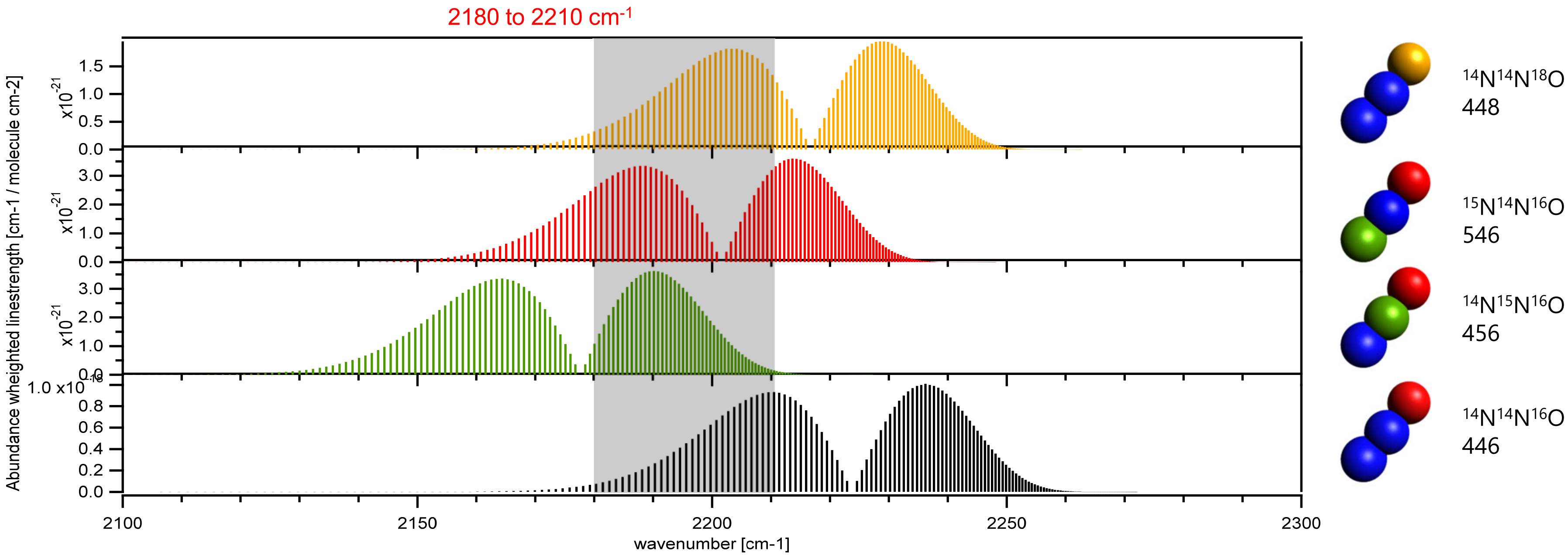
Paper selected as Highlight

For details please see:
S. Harris et al. (2020) DOI: 10.5194/amt-2019-451

MIR Laser spectroscopy



MIR Laser spectroscopy – “zoom in”



J. Mohn, Empa, EGU2020, N_2O isotopes

Commercial laser spectrometer

Direct absorption spectroscopy (QCLAS)

Dual / Mini Laser Trace Gas Monitor
2187.7–2188.2cm^{-1}, 2203.1–2203.4cm^{-1}

Dual QCLAS (2012, 2014, 2016)
$\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$

TREX-mini QCLAS (2013)
$\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$

Cavity ring-down spectroscopy (CRDS)

G5101-I 2187.7–2188.2cm^{-1}
G5131-I 2195.7–2196.3cm^{-1}

G5131-I (2014)
$\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$

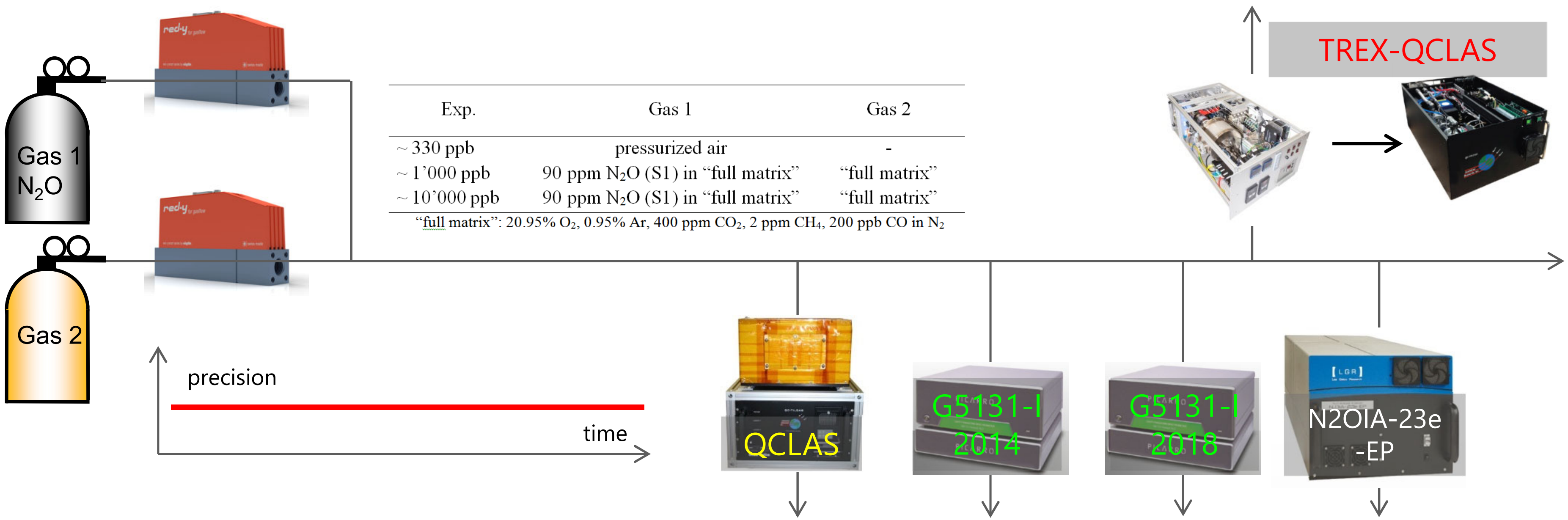
G5131-I (2018)
$\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$

Off-axis integrated cavity output Spectroscopy (OA-ICOS)

N2OIA-30e-EP
914-0027 2192.1–2192.5cm^{-1}
914-0022, 914-0060

914-0027 (2014)
$\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$

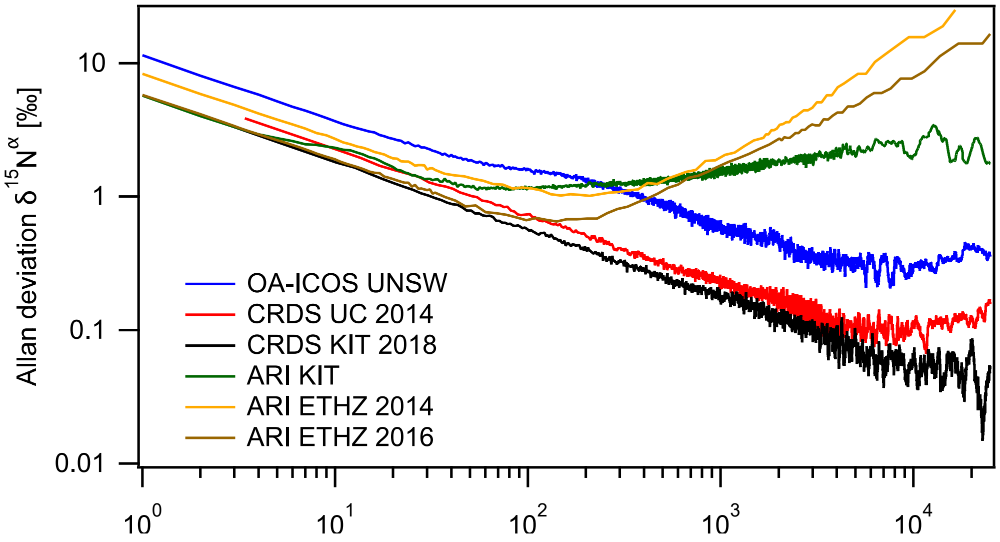
Precision experiments



Exp.	Gas 1	Gas 2
~ 330 ppb	pressurized air	-
~ 1'000 ppb	90 ppm N_2O (S1) in "full matrix"	"full matrix"
~ 10'000 ppb	90 ppm N_2O (S1) in "full matrix"	"full matrix"

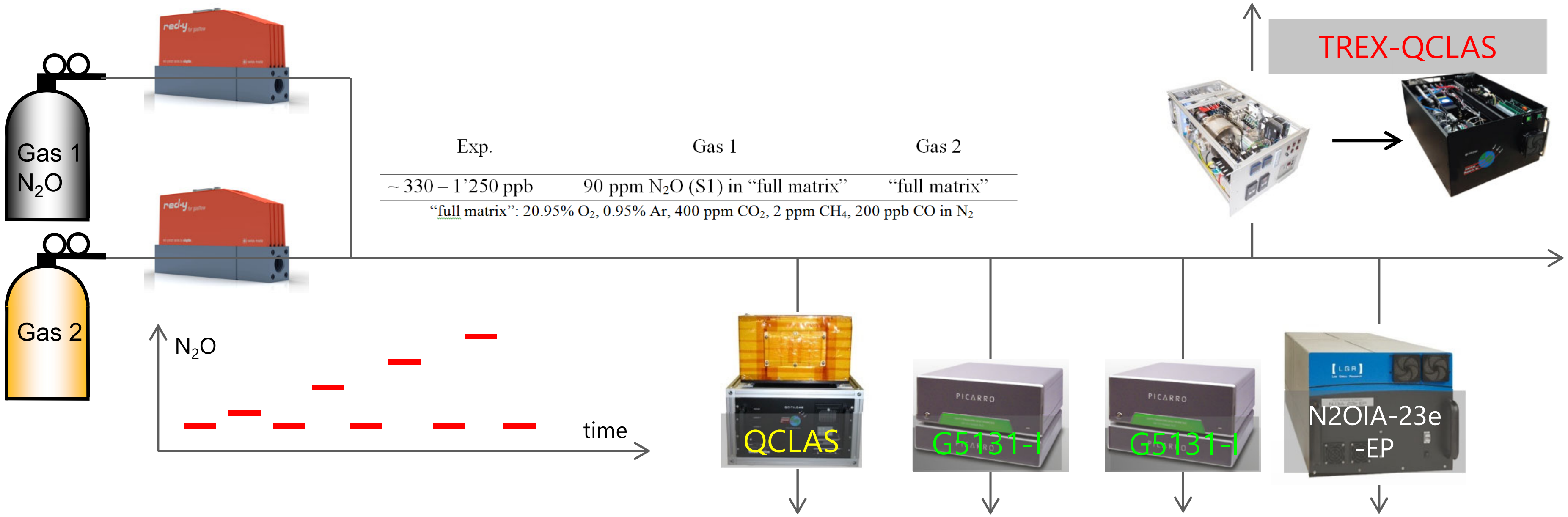
"full matrix": 20.95% O_2, 0.95% Ar, 400 ppm CO_2, 2 ppm CH_4, 200 ppb CO in N_2

Allan precision



Exemplary Allan deviation (square root of Allan Variance) plots for the OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green), QCLAS II (purple) and QCLAS III (brown) at 326.5 ppb N_2O mole fractions.

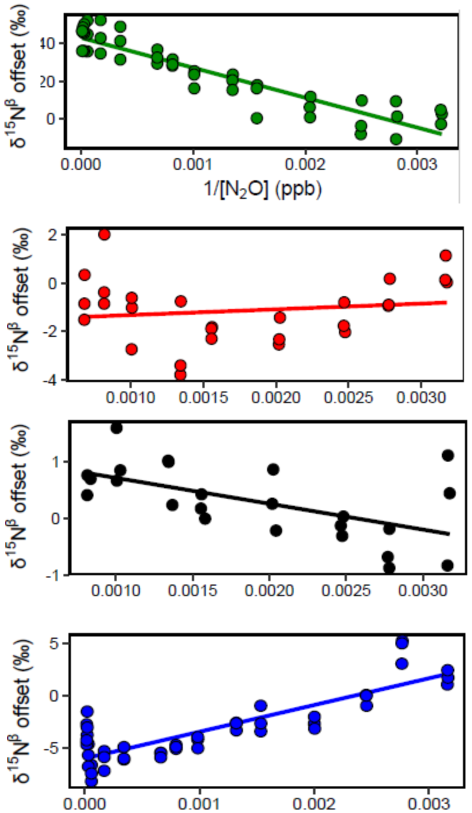
N_2O concentration effects on delta values



Exp.	Gas 1	Gas 2
~ 330 – 1'250 ppb	90 ppm N_2O (S1) in "full matrix"	"full matrix"

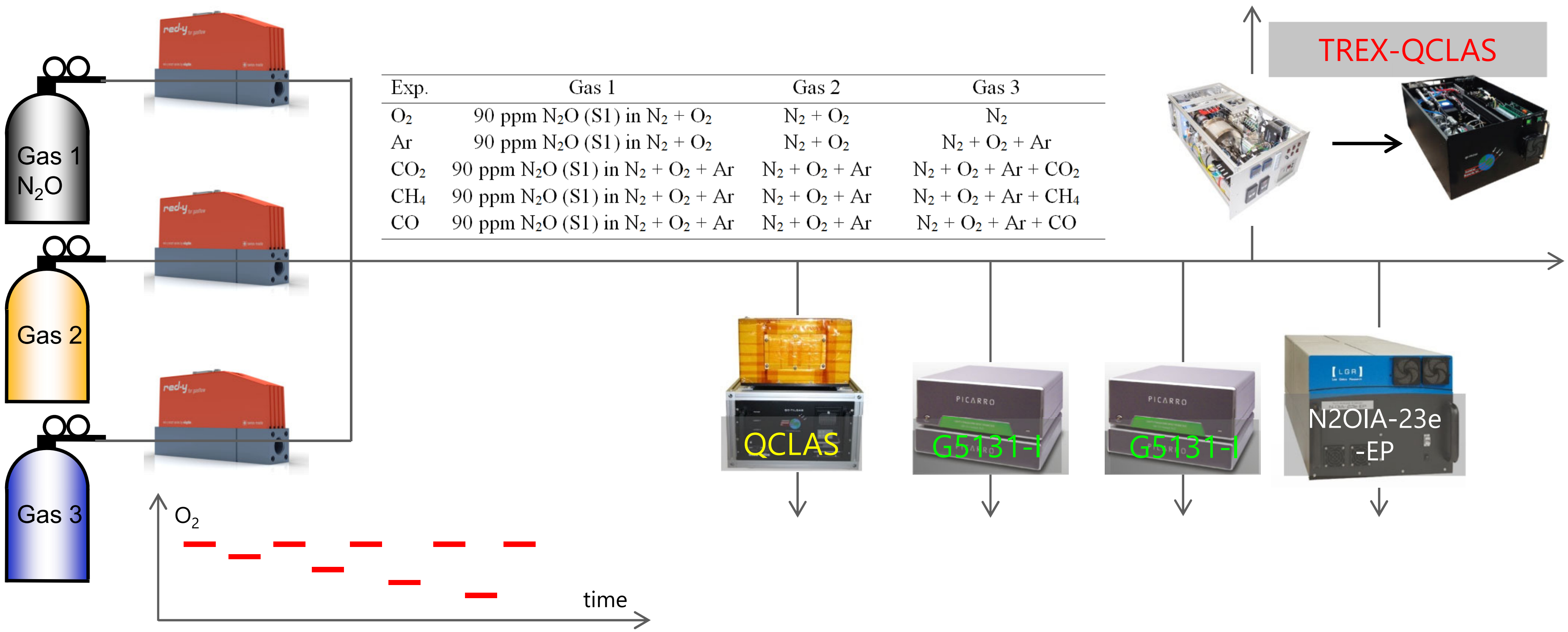
"full matrix": 20.95% O_2, 0.95% Ar, 400 ppm CO_2, 2 ppm CH_4, 200 ppb CO in N_2

N_2O concentration effects on delta values



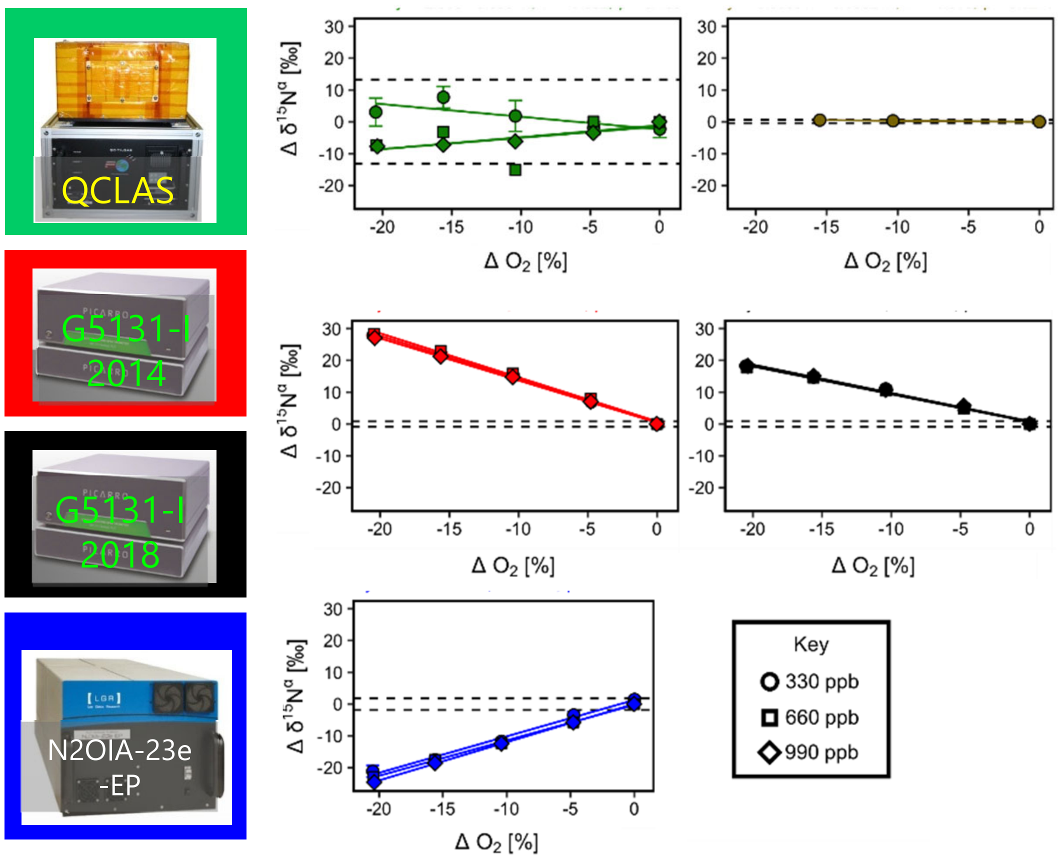
Deviations of the measured $\delta^{15}N^{\beta}$, values according to $1/[N_2O]$ for the OA-ICOS I (blue), CRDS I (red), CRDS II (black) and QCLAS I (green). Measurements span the manufacturer-specified operational ranges of the analyzers. A linear regression is indicated by the solid line.

Gas matrix and trace gas experiments



Exp.	Gas 1	Gas 2	Gas 3
O_2	90 ppm N_2O (S1) in $N_2 + O_2$	$N_2 + O_2$	N_2
Ar	90 ppm N_2O (S1) in $N_2 + O_2$	$N_2 + O_2$	$N_2 + O_2 + Ar$
CO_2	90 ppm N_2O (S1) in $N_2 + O_2 + Ar$	$N_2 + O_2 + Ar$	$N_2 + O_2 + Ar + CO_2$
CH_4	90 ppm N_2O (S1) in $N_2 + O_2 + Ar$	$N_2 + O_2 + Ar$	$N_2 + O_2 + Ar + CH_4$
CO	90 ppm N_2O (S1) in $N_2 + O_2 + Ar$	$N_2 + O_2 + Ar$	$N_2 + O_2 + Ar + CO$

Results gas matrix - Oxygen



Deviations of the measured $\delta^{15}N^{\beta}$ values according to O_2 (%) at 330, 660, 990 ppb N_2O for the OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green) and TREX-QCLAS I (brown). The standard deviation of the Anchor gas (±1σ) is indicated by dashed lines. Data points represent the mean and standard deviation (1σ) of triplicate measurements. Dependencies are best-described using linear regression, which are indicated by a solid line.

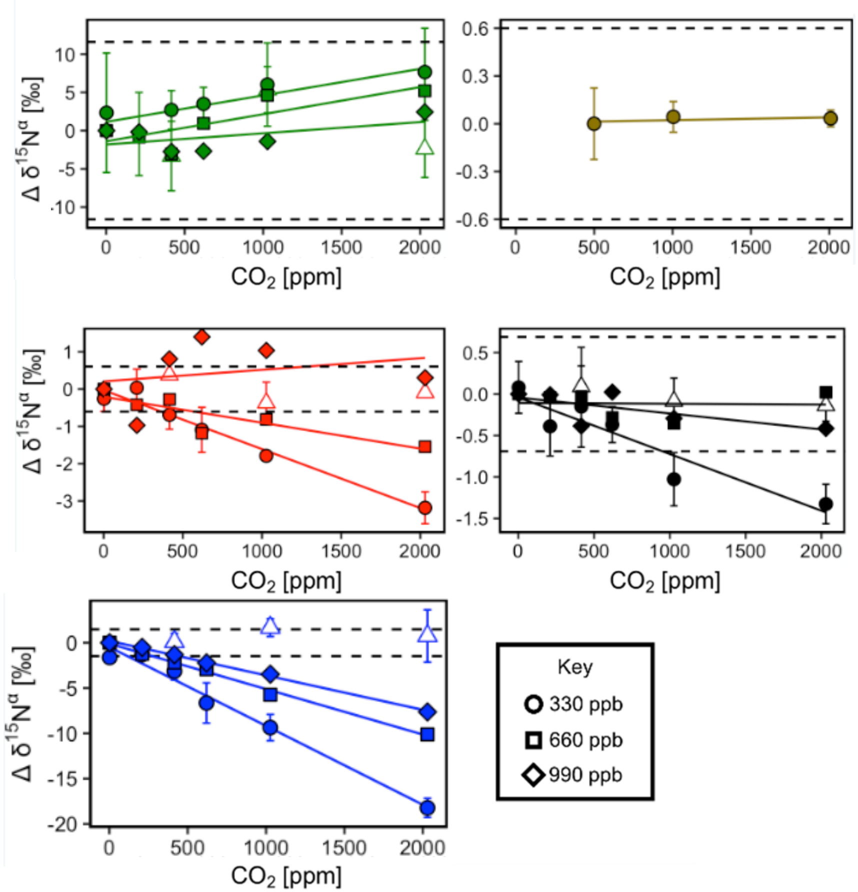
empirical corrections (O_2):

$$\Delta N_2O = (a_1\ [N_2O]^2 + b_1[N_2O])[O_2]$$

$$\Delta\delta = (a_2\ [N_2O]^2 + b_2[N_2O] + c_2)[O_2]$$

But complex interplay of $[O_2]$ and $[N_2O]$

Results trace gases – CO_2



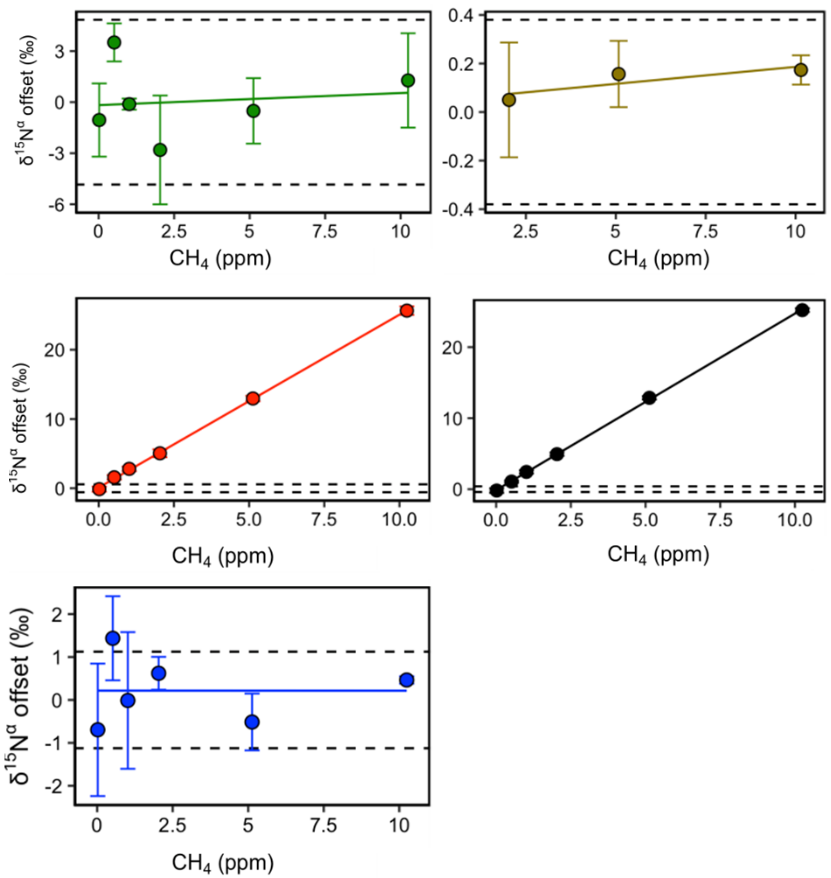
Deviations of the measured $\delta^{15}N^{\alpha}$ values according to CO_2 (ppm) at different N_2O mole fractions (330, 660 and 990 ppb) for the OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green) and TREX-QCLAS I (brown). The standard deviation of the Anchor gas (±1σ) is indicated by dashed lines. Data points represent the mean and standard deviation (1σ) of triplicate measurements. Dependencies are best-described by linear fits, which are indicated by solid lines.

empirical corrections (CO_2, N_2O):

$$\Delta N_2O = (a_1 \times [N_2O] + b_1)[CO_2]$$

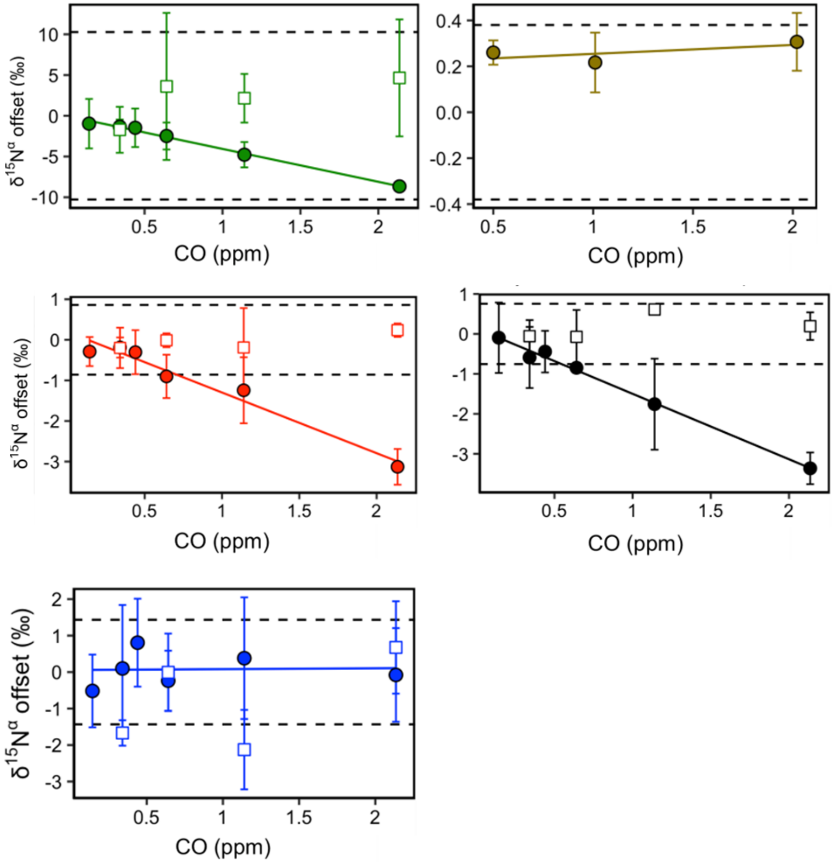
$$\Delta\delta = \left(\frac{a_2}{[N_2O]} + b_2\right)[CO_2]$$

Results trace gases – CH_4



Deviations of the measured $\delta^{15}N^{\alpha}$ values according to CH_4 (ppm) at 330 ppb N_2O for the OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green) and TREX-QCLAS I (brown). Data points represent the mean and standard deviation (1s) of triplicate measurements. Dependencies are best-described by linear fits, which are indicated by solid lines.

Results trace gases – CO



Deviations of the measured $\delta^{15}N^{\alpha}$ values according to CO (ppm) at 330 ppb N_2O for OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green) and TREX-QCLAS I (brown). The standard deviation of the Anchor gas (±1σ) is indicated by dashed lines. Data points represent the mean and standard deviation (1σ) of triplicate measurements. Dependencies are best-described by linear fits, which are indicated by solid lines.

Workflow

Pre-Measurement

What is the expected [N_2O], desired precision and sample gas volume?

Can temperature stability be achieved and maintained?

Will sample gas CO_2, CO and/or H_2O deviate from reference gases?

Will sample gas CO_2, CO and/or H_2O interfere with the measurements of the chosen analyser?

Implement Ascarite, Sofnocat and/or H_2O traps

Will sample gas CH_4 deviate from reference gases?

Will sample gas CH_4 interfere with the measurements of the chosen analyser?

Derive interference equations for analyzer and co-measure CH_4. For co-varying N_2O and CH_4 more sophisticated correction schemes must be applied.

Will sample gas O_2 and/or Ar deviate from those of the reference gases?

Derive interference equations for analyzer and co-measure O_2 and/or Ar. For co-varying N_2O and O_2 / Ar more sophisticated correction schemes must be applied.

Measurement

Systematically measure a reference gas to account for drift.

Measure reference gases with identical isotopic composition but with at least 3 different mole fractions that span the expected [N_2O] range of the sample gases. This may be achieved via dynamic dilution (this study) or static mixtures.

Measure a minimum of two reference gases with identical N_2O mole fractions but different isotopic composition spanning the expected isotopic range of the sample gases.

Measure the sample gases

Post-Measurement

If applicable apply analyzer specific O_2, Ar and CH_4 correction equations.

Apply N_2O mole fraction correction.

Correct for drift.

Standardize corrected δ values to international scales.

No

Yes

For details see S. Harris et al. (2020)
DOI: 10.5194/amt-2019-451

Summary

- N_2O isotope reference gases with different deltas needed (and will get available within SIRS)
- Field-deployable and precise laser instruments for N_2O isotopes on the market
- For accurate results a number of uncertainty terms have to be reduced / corrected:
  T fluctuations, $[N_2O]$ changes, $[O_2]/[Ar]$ (gas matrix) changes, $[CO_2]/[CH_4]/[CO]/\ldots$ (spectral interference) changes
- Preconcentration can solve some problems but with the price of additional effort
- Workflow suggested on how to perform accurate isotope measurements by laser spectroscopy

Thank you for your interest! If you have questions please contact me:
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