Laser spectroscopic analysis of N_2O isotopes: How to get trustworthy data?

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In recent years, various mid-IR laser spectrometers for N_2O isotope analysis have become commercially available, applying different detection schemes, such as direct absorption spectroscopy (DAS, Aerodyne Research Inc., MIRO Analytical AG), cavity ring-down spectroscopy (CRDS, Picarro Inc.) and off-axis integrated cavity output spectroscopy (OA-ICOS, LGR-ABB). While optical techniques offer advantages in terms of high temporal resolution, site-selectivity for ^{15}N substitution (^{15}NNO vs. $N^{15}NO$) and no or minimal sample treatment, variability in gas composition also poses significant challenges for data quality [1].

We will showcase several application examples, ranging from pure microbial cultures, wastewater treatment, and agricultural soils to atmospheric monitoring, where we applied DAS, CRDS, and OA-ICOS analyzers to resolve temporal trends in N_2O isotopes. We notice that N_2O isotope laser spectrometer performance is governed by an interplay between instrumental precision, drift (e.g. temperature driven), and spectral artifacts, caused by changes in gas matrix (N_2, O_2, argon), spectral interferences and non-linearity.

We suggest two strategies to preserve trustworthy, i.e. accurate, data: 1) to minimize differences in composition between sample and reference gases by proving appropriate reference gases or by removing variable inference gases from the sample; where this is not feasible or wanted, 2) to post-correct deviations between sample and reference using predefined, analyser-specific correction functions. We developed and validated a mathematical framework along with a Matlab code that outlines the necessary corrections and suggests their logical order. Finally, we demonstrate potential of exemplary N_2O isotope data to interpret production / destruction processes.

Our suggested approach for data processing is well-aligned with a recent guideline targeting CH_4 isotope analysis by CRDS [2], so is broadly applicable for different isotopic species and laser spectroscopic detection schemes.

References

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