

Interactive comment on “N₂O isotopocule measurements using laser spectroscopy: analyzer characterization and intercomparison” by Stephen J. Harris et al.

Anonymous Referee #2

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General comments:

The paper reports the results of a detailed intercomparison study on the performance of commercially available isotopic N₂O analyzers based on laser spectroscopic methods. Such analyzers allow for continuous measurement of absolute trace gas concentrations (here N₂O) and isotope ratios (here, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$) under field conditions. Isotopic analysis of N₂O is challenging, but is of high interest for source and sink identification in the biogeochemical community.

The extensive study was very well planned and conducted and produced large amount of data. As a result, a very extensive paper has been compiled by the authors. The

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paper is clearly structured and well-written. However, in order to limit the length of the paper to a bearable level, I suggest to shorten the main part by moving part of the Figure content and some Tables into the Supplement.

The presented results underline the necessity to carefully check analyzer performance, even for such sophisticated instruments as the ones used in this study. Although absorption based techniques should be essentially calibration-free (as they are simply based on Beer-Lambert law), the measurement of isotope ratios is prone to even smallest inaccuracies of the analyzers. This becomes quite obvious in case of the presented large uncertainties in the Keeling type experiments for source identification.

The paper ends with a clear conclusion and recommendation for the use of laser-based isotopic N₂O analyzers in practical applications. This is very useful and helps to design reasonable calibration strategies for future experiments. The paper is very technical, and not too much effort was spent to elaborate physical/spectroscopic explanations for the worked-out gas matrix effects and cross sensitivity issues. This may be well considered outside the scope of this paper, however, at least some brief statements about possible explanations are desirable.

However, overall this very good-excellent paper is a pleasure to read and for sure it is very well suited for publication in AMT, subject to changes (sorry for the long list – but it is a long paper. . .) as outlined in the following:

Specific Comments:

P4L16: There is no principle reason why laser spectroscopy should be limited to the MIR spectral range. Of course, isotope specific measurements can also be performed in the NIR, albeit the used instruments are based on strong rovibrational transitions of the asymmetric stretch vibrational band of N₂O. Detection in the NIR range, due to the fact that overtone or combination bands with lower line strengths must be probed, will be less sensitive, however, due to lower spectral congestion, interference issues may be less dramatic.

P5L18: Whereas items (1), (2), and (4) seem to be clear to me, this is not the case for item (3). Is it possible to include a short explanation why changes in the total N₂O mole fraction also affect the determined delta values? Is this directly related to the “delta calibration approach” (what is this?)?

P5L21: While pressure broadening changes the absorption line shape of a specific rovibrational transition, the integral absorption should not be affected. As such, I would expect that instruments like the Picarro-CRDS that presumably measures peak absorption (at least this is the case for the corresponding isotopic CO₂ instrument) are more prone to gas matrix effects than instruments that are based on integral absorption (I think this is the case for the Los Gatos-OA-ICOS, for example). This should be explained at some point in the manuscript.

Table1: From a spectroscopic point of view, it would be interesting to include the rotational quantum number and term energy (i.e. the energy of the lower state) of the probed transitions. On the one hand, pressure broadening and with it the gas matrix effect is known to sensitively depend on the rotational excitation of the probed molecules. On the other hand, the term energy largely determines the population of the lower state and with it is an important quantity to rationalize a potential temperature sensitivity of the instruments. According values can be taken from the HITRAN database.

Table 6 and Figure 3: How often these experiments have been repeated? How reproducible was the drift behavior of the QCLAS analyzers?

Figure 4: I wonder how the cell temperatures have been measured? In the middle of the cell? one or two pint measurements? Is anything known about possible T-gradients across the measurement cells? It seems that the experiment has only been conducted once. Do the authors believe that the measured trends in the signals are robust? Actually, for practical applications it would also have been interesting to perform an experiment at static (but different) temperatures.

Section 3.2: Please give some more information about possible reasons for the ob-

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served temperature effects. P33L20: Again, the reason for the N₂O mole fraction dependence is not fully clear to me without further explanation. I am sure that this is explained in some detail in the cited Griffith et al. papers, however, is it possible to roughly outline the main reason for this in 1-2 sentences?

Figure 6: Actually, I am surprised to see the strong effect of O₂ content for the integrating OA-ICOS experiment as well, in particular for the total N₂O data (see also my comment above). Do the authors have a physical/spectroscopic explanation for this effect?

P35L6: The authors state that minor gas matrix effects have been observed for Ar (in comparison with O₂). Well, as the Ar content has been changed by only 1% in comparison to 21% for O₂. Therefore, I think, this statement is not fully valid. Overall, the effect (on a mole fraction basis) is not very much different. May be the authors allude to the maximum effect expected for real-world measurement conditions.

Although the depicted trends seem to be instrument-specific in some cases (e.g., the different slopes of the gas matrix effects for variable N₂O content, which cannot be explained by a simple pressure broadening effect), I would appreciate to elaborate a little bit more on physical/spectroscopic reasons that may (at least partly) explain some of the observations.

In most Figures, the complete datasets for N₂O, delta 15N_{alpha}, delta15N_{beta} and deltaN₁₈O are given for all five instruments. Even though it is interesting to see all these results, keeping in mind the length of the paper, the authors may consider to somewhat lower the total number of subplots in each Figure by showing only selected trends. This would also allow one to somewhat increase the font size of the captions that are often hard to read anyway. Of course, the complete dataset should be included in the Supplement.

I agree with the anonymous referee 1 that a summary table highlighting the particular advantages and limitations of each instrument would be very helpful. Such a Table

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should also include an item about the versatility of an instrument (how many parameters can be set/changed by the user to fit a particular experimental requirement) or the disclosure of details of the used data evaluation algorithms (for black box instruments, it may be hard to figure out the physical reason for a specific instrumental behavior).

Comment: I think, some of the reported interferences and shortcomings of the instruments could be (at least partly) overcome by multi-line analysis. So far, laser spectroscopic instruments typically use only one selected absorption line for analysis of one species. In particular cross-sensitivity issues could be identified easier and also be less pronounced for multi-line instruments.

Technical Corrections:

P5L5: Please add an original reference for CRDS as well. P9L2&P9L19: I think that referring to the manufacturer website is OK. However, in addition an appropriate original reference should be included that explains details of the OA-ICOS and CRDS techniques. P8-P11: Next to the manufacturing date, the serial number of the used instruments should be included for future reference. P14L3-6: The (more detailed) synthesis procedure could be moved to the Supplement. P18L15: The Picarro-CRDS analyzer really does not report any absolute numbers for the individual mole fractions? May be they are provided in some of the log files? P19L16: While the meaning of the index “true” is clear in this context, I would prefer the index “reference” instead of “true”. P21L15: Please refer the reader to Fig 4 , because the actual T versus t trend is given there. P26L21: Replace “greatest” by “best”? Figure 5: The text labels are too small to be readable. I suggest to leave out the residual plots to free some space. P39L25: Weird sentence. Table 9+10: These Tables could be moved to the Supplement.

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