Comments on “Photochemical method for removing methane interference for improved gas analysis” by Merve Polat et al.

General comments:

This manuscript describes a photochemical scrubbing method, using Cl_2, for the removal of CH_4 in whole air samples. This described method is intended to enable accurate determination of the isotopic composition of N_2O ($\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, and $\delta^{18}O$) by minimizing the spectroscopic interference arising from CH_4 (among several others), which poses immense challenge. This method indeed shows potential as the removal of CH_4 through this photochemical scrubbing does not alter the matrix composition dramatically. In addition to the experimental work, the authors have also complemented their experimental results with predictions using a kinetic model studying all the dependencies. This method in general can be used for any application requiring removal of CH_4 (and other hydrocarbons/VOCs), and is not just limited to the measurements involving N_2O. And hence is an important development that the scientific community could benefit from.

Although the content of the manuscript is very interesting, consisting of appropriate method-development related experiments and complementing model prediction, the manuscript itself is difficult to follow at times due to: the use of too many abbreviations, and having to go back-and-forth between the main section of the manuscript and the supplementary section where part of the information is. Additionally, there are sections where the texts require rephrasing to make the content more understandable. Please see details in the specific comments section.

While this proof-of-concept method is aimed towards reducing the interferences of CH_4 during the measurements of the singly-substituted isotopologues of N_2O, the experiments and results shown to demonstrate the applicability is very limited. Since the removal efficiency of CH_4 achieved is never ~100%, discussion on its implication was not evaluated thoroughly. This is particularly concerning because one has to then always co-measure methane, which is partially scrubbed, in order to incorporate any possible CH_4-dependent correction. So does the method provide any benefit over performing a careful CH_4-dependent interference correction? Additional experiments showing the repeatability expected from this method using isotopically-calibrated N_2O samples was also missing.

The manuscript in its current form requires considerable rework and I would recommend publication after all concerns have been addressed.

Specific comments:

Line 74 and Table 2: How is tank A calibrated for [Cl_2]? Is this a commercial product?

Line 82: The chlorine detector is rated for 0-20 ppm, so how were chlorine concentrations determined in experiments done above 20 ppm, shown later in the manuscript?

Line 85: LED already stands for Light emitting diodes, so should be mentioned “LED” only and not “LED diodes”. Please correct this throughout the manuscript.

Line 93: Please provide supplier details/ part number for Krytox™.

Line 96: Magnesium perchlorate is $Mg(ClO_4)_2$.

Line 100: Please provide supplier details, part number, specification for the activated carbon trap used.

Line 103: "*A final set of experiments is conducted using a Picarro CRDS model G5131-i, capable of measuring N_2O mixing ratio and* its *isotopic abundance*."

Lines 150-152: Throughout the manuscript, the steps are referred to as S1, S2.... and not as in your example C5 (line 152), please check and revise accordingly to be consistent.

Line 155: "H5": please see my previous comment

Lines 159-162: This paragraph somehow feels very unlinked with the previous paragraph. Please explain the "issue" by pointing the reader to the graph, what exactly to look at? How does the build-up of H_2O happen? Why is the Cl_2 raw data not shown along with?

Figure 4: Typically, when you have units shown on the axis label, you don't have to show them on the tick labels, so the % signs on the ticks can be removed. And the abbreviation RE has not been introduced anywhere in the text, so please include this.

Line 187: What is d here? Please define your notation. Is it delta that you are referring to? If so, please describe how often you measure your reference/ calibration etc. Please check and change this throughout the manuscript.

Line 187-188: "*The results are from experiment L, where a sofnocat trap ~~had been~~* was *installed to remove the CO formed by the CH_4 oxidation.*"

Line 189: "…*it was found that the isotopic enrichments* …" Please introduce this to the reader why they should expect isotopic enrichment and not depletion in $\delta^{15}N^{\alpha}$ and $\delta^{18}O$.

Line 190: How stable is the oxidation process in a prolonged time period, e.g. during a continuous 10 hr measurement period, and in practice you would really turn it ON all the time during a measurement. How much of the variability in $[Cl_2]$ translates into your final measurement uncertainty?

Line 193-194: How is the variation in $[N_2O]$ due to variation in $[Cl_2]$, is it not due to dilution? And correct the spelling of variation in Line 194.

Section 3.1.1 (in general): Why was the method with the highest removal efficiency not used here?

Line 229: "… *that an increase in Cl_2 concentration~~s~~ increases the $[CCl_4]$ production* (*see Figures 7a, 7b and 7d.*)"

Figure 7 (caption): "The Removal efficiency of methane depletion (Black), …" should be "The removal efficiency of methane (Black), …"

Line 233-234: If you use NaOH to remove CO_2 from a sample, the matrix changes significantly. To what level of matrix alteration not a problem?

Lines 234-235: "*The NO_x concentration in our experiments is insignificant* and hence *these reactions have not been included in the model.*"

Line 252: What is the typical concentration range of Cl_2 produced by this method? Please elaborate this and describe the calibration and monitoring/ data recording method for Cl_2.

Line 285-286: Please rephrase.

Lines 331-336: Please avoid repeating texts already used in the main body of the manuscript (lines 89-93).

Figure B1: Abbreviations are typically introduced once, the first time they come up in the document. So please don't expand your abbreviations every time you describe a figure.

Line 354: How does CO interfere with N_2O, please elaborate this and remind the reader which isotopologues are specifically affected.

Figure C1: Why repeat a figure when you can refer to Figure 2?

Lines 407-410: Please rephrase this paragraph and elaborate on "This effect…". The explanation is not clear.

Table D4 (Caption): "… refeer to the three isotypes of N_2O." should be something like "… in ‰ refers to the three isotopologue measurements of N_2O."