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Atmospheric
Measurement
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Discussions

Interactive comment on "Continuous-flow isotope ratio mass spectrometry method for carbon and hydrogen isotope measurements on atmospheric methane" *by* M. Brass and T. Röckmann

Anonymous Referee #2

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In their manuscript, Continuous-flow isotope ratio mass spectrometry method for carbon and hydrogen isotope measurements on atmospheric methane, M. Brass and T. Rockmann detail the development and evaluation of their analytical system for high-precision measurements of atmospheric methane isotopologues.

Overall, their work is methodical and careful and their manuscript is detailed and well presented. This manuscript would be of particular value to those interested in constructing a similar analytical system or automating an existing system. As a result, I recommend it for publication in AMT.

That said, this is not the first study to use and document this approach. In addition to the work cited by the authors in section 2, there are also two additional papers that I am aware of: K. Yamada et al., Atmospheric Environment 37 (2003) 1975–1982 J. Potter and M. Siemann, Rapid Commun. Mass Spectrom. 2004; 18: 175–18 . . . and potentially others. As a result the approach can no longer said to be ”novel” at this point and the bar for publication should be somewhat higher.

On balance, I think authors have overcome this hurdle by adding substantively in a couple of areas. First, authors found that the D/H measurements lacked precision and linearity when using the commercial Thermo Scientific Isodat software. They spent considerable time and effort developing their own more accurate corrections using custom software. They have documented this effort in the manuscript which I know IRMS users will find helpful in their own efforts. This could have been a brief publication of its own right in RCM, but authors chose to include it here. Second, authors did considerable work automating their analytical system. This is a non-trivial task given the low temperatures of the preconcentration traps and the complexity of the system. Though authors clearly drew upon the work of Miller et al (2002) who developed and automated the CH4 GC-IRMS system for the NOAA ESRL laboratory, their methods are carefully laid out and would be quite easy to follow.

Though the study was well conducted and all needed data are presented, there are a few weaknesses in the manuscript that should be addressed prior to publication in AMT. I list the most critical aspects first followed by a few topical comments or questions later.

Some of the manuscript suffers from reading less like a scientific paper and more like a user-manual. As the authors want to impart their experience into this paper, I appreciate the detailed information presented. However, in several cases there are passages that contain information that is not backed up by data presented in the manuscript. For example: Lines 265-267 discuss the impact of that H2O and other compounds can have on isotope ratio measurements. While I do not disagree with the authors comment, no data is shown to support this nor is any citation provided. Lines 309-321 are excessive in terms of description of heating and cooling rates while providing very little actual information on procedure. Lines 536-542 mentions change in instrument linearity with time. Again, I don't disagree with the authors remarks, there is simply no data provided in the manuscript to support the statements or references given. One might de-emphasize the points and state them in a short single sentence.

Section 3. The reprocessing of hydrogen (D/H) isodat data is well presented in both rationale and procedure. However, it is unclear to this reviewer why the carbon isotopic composition does not suffer from the same problems. Why would applying such a correction would not also improve the 13C/12C ratio measurements? If it did not, why not?

Section 2.9 and Section 4. In a typical run sequence the value of a sample is determined from the difference between it and the reference gas (SiL). As I read the manuscript, this means that δD(SiL)meas. varies somewhat from sequence to sequence. What is the variability of this value (δD(SiL)meas.) – is it close to the precision of measurement in which case it may be correcting noise; or is it well outside this limit and cannot be controlled with instrument parameters? Also is the uncertainty in SiL propagated to the measurement precision of a sample?

Minor points

Line 58. I suggest changing the sentence to read "Figure 1.1 is a schematic of the experimental setup…" for clarity

Section 2.2.2 What style vacuum pump is used to evacuate the sample loop? What is the approximate vacuum attained?

Line 128. Is this one year OR permanently? It cannot be both.

Line 130. I believe "Figure 4a and b" are referring to Figure 3

Lines 184-186. What is the length of column used in the cryofocus?

Lines 244-246. What is the “break down” referring to here? Is this a loss in peak amplitude? I find this passage confusing.

Line 258. I believe “Figure 3” should be “Figure 4”

Section 3. I believe Fig. 5 is not referred to in the discussion

Line 361. What would constitute a “perfect” choice of background. This point is confusing.

Line 371. “SPI allows to” is missing a subject

Lines 376-378. This sentence is confusing. Please clarify what is being optimized here. Is the constant background value from 1. Adjusted by an arbitrary constant until linearity is minimized?

Line 387. Remove the word “get” from the sentence

Section 3.1.2 How is reproducibility defined here? Is it the difference between a measurement and a known value? 1 sigma?

Line 462. I believe the third dDcal should be cal3 (?)

Section 4.2.1 Is there any known or suspected reason that the CH4-He mixtures yield a different value from CH4-air?

Line 489. Change “As 17O. . .” to “For the 17O. . .” Line 500. Remove the work “excellently”

Section 4.4 Title. Change to “linearity” as the word “issues” adds little and is confusing.

Section 4.4 lines 518-522. It is a little late in the discussion to define linearity here as it has been discussed in several previous sections. I think a definition is useful here, but it should be moved to section 3.

Section 4.3 A table providing the calibration of the suite of isotope standards (DCX) measured at the 3 institutions would be useful here for clarity. Also useful in the table would be the number of measurements the assigned value is based on.

Figure 4. Is of quite poor quality in the version I have. The top two figures look like screenshots from Isodat which do not reproduce well for a journal. Authors might consider exporting the raw data and representing the chromatogram using different software. The bottom figure (which looks much better) has symbols related to mass 2 and 3 traces, but no color traces (both are black and white). Finally, what are the two poorly shaped peaks that elute after CH4 on the bottom figure?

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 2433, 2010.

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