Atmos. Meas. Tech. Discuss., 7, C562–C564, 2014
www.atmos-meas-tech-discuss.net/7/C562/2014/

Atmospheric Measurement Techniques Discussions

Interactive comment on "Online technique for isotope and mixing ratios of CH_4, N_2O, Xe and mixing ratios of organic trace gases on a single ice core sample" *by* J. Schmitt et al.

Anonymous Referee #3

Received and published: 16 April 2014

This manuscript presents an exciting new technique for simultaneous analysis of several gas mixing ratios and gas isotope ratios in ice core and small air samples by CF-IRMS. This method represents an important advance in ice core analyses because it allows for simultaneous measurement of an impressively diverse number of species and reduces ice sample size requirement considerably while maintaining or even improving the external precision of the analyses. The method is very thoroughly described. Testing of almost all aspects of the method is very thorough and very well documented in the tables and figures in the manuscript. Overall, the manuscript is well written and organized. The scope of the work is a very good fit for AMT. The work

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presented does have one weakness, however, that I consider to be important. My recommendation is that this weakness (having to do with procedural blank determination) is addressed before the manuscript is accepted in its final form for publication in AMT.

Major comment: While the authors conducted routine procedural blank determinations with this new system, the blank tests are not fully representative of the handling of the real ice core samples. With the actual sample analyses, the air is liberated by melting the sample. However, ice melting is not included as part of the blank tests. Instead, the blank is assessed from a "dry" extraction where a reference gas is introduced over the ice sample and allowed to stay in the vessel for a representative amount of time, but without melting the sample. This kind of approach captures many aspects of the blank, but it would not detect procedural effects that arise from the presence of liquid water. For example, Xe and N2O are gases with relatively high solubilities in water. It is conceivable that dissolution effects would affect the measured isotopic ratios. Further, for the hydrocarbons, the presence of liquid water could potentially result in increased outgassing / production of the compounds in the ice core extraction vessel. The authors state that "gas free ice" that is available to them is not completely free of the measured components, which precludes them from using such ice in their tests. My recommendation is that some additional work is carried out to produce ice that is in fact sufficiently free of the components of interest, and additional procedural blank tests be done with this ice.

Minor and textual comments / suggestions:

p. 2019, line 17. CO is a ppb, not a ppt level gas in the atmosphere

p. 2022, line 9. "...extract gases with high solubilities in water..."

p. 2022, line 28. "We thereby expel..."

p. 2024, line 17. I am confused as to what the authors mean by "re-oxidize" here. "Boulder" is not yet defined at this stage in the manuscript (it is defined later)

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p. 2028, line 15 “need to be at a slight over-pressure”

Section 2.1.1 The bypass for running air while bypassing the ice core vessel is not shown in the diagram – seems like it should be included for clarity

Section 3.1.2 I would suggest that another table is added that summarizes the calibration values of all reference gases, for improved clarity

p. 2034, line 3. This sentence is confusing – I do not understand what exactly represents 0.15% of air volume of the ice sample

Section 4.1 I am confused about what the authors exactly mean by “blank air”. At first it seemed that this refers to the reference gases that are used in the procedural blank tests, but this doesn’t seem to be the case based on this section. This should be clarified.

p. 2035, line 9. This sentence is confusing and should be clarified

Section 5. For completeness, I would recommend that at least a brief discussion of precision for ppt-level gases is included here.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 2017, 2014.