Review for the manuscript "Continuous-flow isotope ratio mass spectrometry method for carbon and hydrogen isotope measurements on atmospheric methane " by M. Brass and T. Roeckmann

General comments

The paper describes a fully automated measurement system for both stable isotopes of CH4 (and mixing ratio) from atmospheric samples. I consider this contribution worthy of publication in AMT. It is analytically sound and concisely written. New are the cooling devices for the cryogenic traps including their temperature regulation. The data reduction routine developed for dD is not completely novel but seems to be an elegant tool. I feel that a more detailed description would be appropriate. In comparison to commercial tools the routine brings progress in terms of improved precision. The authors share valuable remarks on conditions in the high temperature furnaces.

Nevertheless, I recommend to address the following issues before publication in AMT.

Specific comments

Abstract

It might be worthy to mention typical values for precision and that the developed data reduction routine for dD is crucial.

Line 6: specify that "Trace amounts of interfering compounds **are** separated..." (in line with page 2436 line 8)

Line 7: delete "fully"

Line 9: Insert "," after "coolant".

Use ppb**v** instead of ppb (throughout the manuscript).

Section 1: Introduction

page 2435 line 9f: insert ‰ after numbers

line 10: close bracket after "mining"

line 18: You might also cite more recent papers:

- Mischler, J. A., T. A. Sowers, R. B. Alley, M. Battle, J. R. McConnell, L. Mitchell, T. Popp, E. Sofen, and M. K. Spencer. 2009. Carbon and hydrogen isotopic composition of methane over the last 1000 years, Global Biogeochem. Cycles, 23, GB4024, doi:10.1029/2009GB003460
- Sowers, T. Atmospheric methane isotope records covering the Holocene period, Quaternary Science Reviews, Climate of the Last Million Years: New Insights from EPICA and Other Records, 2010, 29, 213-221
- Bock, M.; Schmitt, J.; Moller, L.; Spahni, R.; Blunier, T. & Fischer, H. Hydrogen Isotopes Preclude Marine Hydrate CH4 Emissions at the Onset of Dansgaard-Oeschger Events, Science, 2010, 328, 1686-1689

line 22: delete "small", put 40 mL out of brackets: "… that uses sample amounts of 40 mL air."

line 24: Although the focus of this study is somewhat different (emphasizing the background detection), I am aware of the following papers that addressed peak integration issues:

- Ricci, M. P.; Merritt, D. A.; Freeman, K. H. & Hayes, J. Acquisition and processing of data for isotope-ratio-monitoring mass spectrometry Organic Geochemistry, Compound-Specific Isotope Analysis in Biogeochemistry and Petroleum Research, 1994, 21, 561-571
- Sessions, A. L.; Burgoyne, T. W. & Hayes, J. M. Correction of H3+ Contributions in Hydrogen Isotope Ratio Monitoring Mass Spectrometry Analytical Chemistry, American Chemical Society, 2001, 73, 192-199

- Sessions, A. L.; Burgoyne, T. W. & Hayes, J. M. Determination of the H3 Factor in Hydrogen Isotope Ratio Monitoring Mass Spectrometry Analytical Chemistry, American Chemical Society, 2001, 73, 200-207
- Bock, M.; Schmitt, J.; Behrens, M.; Möller, L.; Schneider, R.; Sapart, C. & Fischer, H. A gas chromatography/pyrolysis/isotope ratio mass spectrometry system for high-precision dD measurements of atmospheric methane extracted from ice cores Rapid Communications in Mass Spectrometry, 2010, 24, 621-633

Section 2: The analytical system

In this part you should mention which capillaries are used in which part of the system: materials, inner diameters, suppliers. Maybe this can be visualized in Fig. 1? Is it already the case for diameters?
page 2436 line 5: you may also cite:
Schäfer, H. & Whiticar, M. J., Measurement of stable carbon isotope ratios of methane in ice samples Organic Geochemistry, 2007, 38, 216-226
line 5+6: remove “isotope”: “A measurement is performed...”
line 7+8: replace “and” by “,i.e.”: “CH4 is pre-concentrated, i.e. separated...”
line 17f: tell us which MFCs are used (supplier, model).
The text is inconsistent with Fig. 1:

- in Fig 1. MFC2 is the high flow controller (while the text states MFC3), MFC3 is the multi purpose MFC in Fig. 1
- you only have to change MFC3 and 2 but as a reader I would find it pleasant to have it chronologically: MFC1 as the high flow controller, MFC2 for transporting the purified sample and MFC3 as multi purpose controller. (Then you also have to update Fig. 2)
- The flow rate of MFC1 is 0.4-1.2mL/min in the text but 1.2-3.5mL/min in Fig. 1. Which is correct?

Line 20: was “GC” introduced before?
Line 22: specify “it”: e.g.: the low flow operates...
line 26: specify “it”: e.g.: by default MFC x flow is set to...
Line 27: please give more information on the used Valco valves, they cannot be found using “A4xxWM”
page 2437 line 5: delete the word “combustions” as there is a pyrolysis oven. Also do not name it “combustion units” but maybe “conversion units” or “furnaces”
line 9: change mb to mbar
line 18: “usually” can be omitted
line 20: right now it is MFC2 in Fig.1, not MFC3
Page 2438 Line 5: replace “as usual” by “as for the HP.”
line 6: insert “,” after finished
line 7: which pressure sensor, range, supplier?
Line 11: remove “,” before “because”
Line 16: give the name of the HayeSep supplier
line 22: what about the unusual case? Omit “(usually)”
Line 25: in my view the HSD is a separation column
Line 26/27: mention “MFC number X” for the transfer to the cryofocus.
Line 28: right now it is MFC2 not MFC3 in Fig 1.
page 2439 line 11: only Teflon ferrules? I assume also nut and fitting?
page 2440 Line 12: insert °C after 70

page 2441 line 6: you defined IRMS as isotope ratio mass spectrometry in the abstract (not ...meter)
line 22-26: Is the cryofocus column experiencing a well defined temperature ramp? The description appears a bit coincidental: given is a 20°C range (and the remark about the cold spot). The presented traps offer narrow temperature windows and are a major advancement of this manuscript...
How quick is the cryofocus heated to +50°C (seconds?)
Page 2442: This page seems a bit ad hoc.
GC: Two (not very differing) columns are mentioned, could another one help to separate the troublesome substances that are trapped in the front trap? They eluate simultaneously with CH4.
Line 3: insert CO2 after “remaining traces”.
Line 6: “separation of oxygen from methane”
line 14: In principle it is possible to measure CH4 directly:
Jackson, S. M.; Morgan, G. H.; Morse, A. D.; Butterworth, A. L. & Pillinger, C. T. The use of static mass spectrometry to determine the combined stable isotopic composition of small samples of atmospheric methane Rapid Commun. Mass Spectrom., John Wiley & Sons, Ltd., 1999, 13, 1329-1333
One can also argue that section 2.6 could be left out.
line 20: What is the advantage of the new combustion procedure? Earlier descriptions (e.g. Merritt, Miller, Schäfer, Behrens,...) seem to work well. Copper is not a catalyst but the O2 donor. I think, the melt temperature given here is too low. Why is no Pt catalyst used?
line 15f: use mass/charge (m/z) instead of mass (whole manuscript)
line 25: it is MFC3 in Fig 1.
page 2443 line 9: replace “helpful” by “necessary” as this seems to be crucial.
line 14: mention supplier of the silica tube
line 15: “without catalyst” can be omitted
line 23: “the CH4 molecule is cracked” can be omitted
page 2444 Line 14: When is the front trap lowered? At the beginning of an dD acquisition or before a sample's CH4 peak? Is It cooled before/during/after the range in the chromatogram you use as background range? Is the background of major/minor beams visibly affected before the peak? (it is the case after the peak) This may lead to artifacts depending on how the H3+ contribution is determined and corrected for . Please see Session's papers mentioned above. The implementation of the H3+ factor should be explained (see below).
Why is the front trap not used for CO2 analysis?
line 22: How has the hydrogen yield been tested? Replace “slightly below....” by 97+/-2%
line 27: remove “,” before “because”
Page 2445 line 7: update MFC number?
Line 6: “sample capillary” should be the one inducing the sample into the mass spec. The one meant here should be the GC capillary. Please give the length and inner diameter of the sample and reference capillaries that go the into the mass spec and give the pressure of the MS.
Line 8f: Which flow rates are used?
Line 9: which Nafion inner diameter is used and at which counter flow rate? (also mention supplier)
Page 2446 line 1: omit “(simultaneous)”
line 11: mention what PID means.
Page 2447 line 14: “MS running gas” is more widely known as “working standard” or “reference gas”
Page 2448 line 4+5: mention what VSMOW and VPDB mean
line 12: Does ISODAT correct for the H3+ contribution on the basis of the raw data? How is the H3+ factor determined?

Section 3: Hydrogen peak integration

In this section I miss information on the H3+ issue for dD analysis. How is the H3+ factor determined (analytically, software)? How is the correction implemented in the SPI? Are differences between SPI and ISODAT partly due to the applied H3+ correction?
Is it maybe the case that the H3+ factor is not determined externally and no H3+ correction is applied explicitly in SPI? Do I understand correctly, that the H3+ correction is simply included in the overall linearity correction - the background level adjustment of m/z 3? This would be a valid approach and should be made clear. If ISODAT offers H3+ corrected time series (raw data files) this should be stated.
For both d13C and dD I miss information about time shift correction (which setting in ISODAT, how is it calculated in SPI?).
It is not obvious to the reader what is meant by “non-linearity” in this section. In section 4.4 this is explained nicely. You could move (parts of) section 4.4 here as an introductory section.

Page 2448 Line 18: insert “,” after “obvious that”
line 22/23: “… but showed non-linearity”: It cannot be decided at this point whether this is due to data processing or a real non-linearity of the physical system.

Page 2449 Line 5: “... if the choice of the background level is not perfect, a systematic error is introduced...”: I do not agree with this statement. You do not necessarily introduce a systematic error by the background level, which should be chosen by objective means in the first place. Put it the other way round: Your system introduces non-linearity which could be due to any part of the preconcentration system (sample loop, HSD, Cryofocus, GC, valve switching, pyrolysis, open split, MS,....) and which can be corrected. The presented procedure (adapting the background level to minimize non-linearity) is just an empirical correction that could also be done differently, e.g. on the basis of a fit to the peak data processed without adapting the background level. The results should be the same.
Nevertheless, the presented method of adapting the background level for a batch is ok, as long as the shift is identical for all standards and samples.

Line 16: Do you really define the range of the background for each peak individually? If so, this violates the Identical Treatment principle. Which facts are the basis for the automated and individual determination of the history? Is it also optimized to result in minimized non-linearity? I imagine you have 2 optimization loops, (1) for the background range and (2) for its level. Otherwise it should be explained that the background level is formidably stable not only during one chromatogram, but also over days and weeks. In Line 13 page 2449 it is stated the the background level is stable, and I assume that referencing from run to run is not biased. Assuming identical background histories throughout different chromatograms raises the question why SPI should find an individual background range for each peak. Did I miss something? Is there an issue connected to the front trap? As I understand, the background range could be easily defined as a constant range (and offset) before peak starts, without compromises in precision.

Page 2450 Line 11: The background linearity correction is based on the m/z 3 beam. This is perfectly OK, but I wonder why the minor beam is used for the concentration determination? It adds only minor information and is biased by your background level adjustment.

line 19f: Which traditional non-linearity corrections do you refer to? It is possible to correct for non-linearity effects without knowing the sample's concentration by using directly the different peak sizes of standard measurements. See e.g.:

Potter, J. & Siemann, M. G. A new method for determining δ13C and δD simultaneously for CH4 by gas chromatography/continuous-flow isotope-ratio mass spectrometry Rapid Commun. Mass Spectrom., John Wiley & Sons, Ltd., 2004, 18, 175-180

Page 2449 Line 13: insert “is” after “background”
Page 2450 Line 7: linearity test**s**
line 9: peak area**s**
page 2451 line 13: With the given information I find it impossible to understand this sentence. What is the issue with the H_3^+ -factor here?

Section 4: Data reduction and calibration
page 2452 line 21: According to the IT principle the lower hydrogen yield is also true for the standard, therefore this should cancel. How can you proof the combustion to be complete? This should be reworded.
Page 2453 line 20: maybe “dilute gas” is better than “bath gas”
line 26: yes, I agree. Another explanation could be that the CH4 free air has some impurity.
Page 2456 line 28: omit “has been”

Tables and figures

Table 2: It is “N” in the caption but “n” in the table. No units given.
Table 3: in line 2 of the table two standard deviations are missing, by accident?
Table 5: add ‰ for Δ(CAL-SiL)

Remove the underlining of the spell checker in all figures.
Fig. 1: naming of MFCs is inconsistent with the text.
Fig. 2: the “d” of “Lab Standard Air Cylinder” is not complete
Fig. 3: HayeSep D columns are showed as 1/16" in the figure. In the text they are 1/8".
Fig. 5: make the symbols bigger. Are the closed symbols from ISODAT or from SPI before the m/z 3 background optimization? What is represented by the error bars, standard deviation from x runs? This seems clear after having read the whole paper, but should be clarified in the caption.
Fig. 6: use “.” instead of “,” as decimal marker
make symbols bigger
add ‰ to y-axis
Fig. 7 & 8: make symbols bigger, the SPI diamonds do not appear open in my printout.
Fig 9: use “.” instead of “,” as decimal marker