

Interactive comment on “A combustion setup to precisely reference $\delta^{13}\text{C}$ and $\delta^2\text{H}$ isotope ratios of pure CH_4 to produce isotope reference gases of $\delta^{13}\text{C}\text{-CH}_4$ in synthetic air” by P. Sperlich et al.

Anonymous Referee #1

Received and published: 13 June 2012

The manuscript by Sperlich and coauthors presents results from a calibration effort for CH_4 in air isotopic measurements. The method is both, elegant and straightforward: CH_4 from two sources with different isotopic signatures is combusted for both, $\delta^{13}\text{C}$ and $\delta^2\text{H}$ analysis. The former is made by analyzing the resulting purified CO_2 gas against the light international reference CO_2 gas RM8563, which serves as the scale anchor to the VPDB scale. Hydrogen isotopes are determined by comparing the combustion-water with VSMOW-2 and SLAP-2 directly (reduction with uranium?). The quantitative combustion is ensured by sending the reactant gas over the hot reaction zone until the yield is quantitative. The two gases then are mixed with methane-free air

C1264

in different proportions in order to produce air-references with known isotopic composition in the desired range (at least for ^{13}C ; the methodology for the hydrogen isotopes is still in development). The paper is clear and describes most aspects of the experiments in a comprehensive fashion. Details of the automated GC-IRMS system are missing in the context, it may have been described somewhere else, but the reference is missing. Overall, the paper serves the purpose to address the problem of a missing common isotopic reference for methane in air. It is a big step forward towards making such gases available to the research community.

For the final version the following comments should be considered:

P 3501 L14: Replace “rare over the abundant isotope” by “heavy over the light isotope” (this is the IUPAC convention, see Coplen, RCM 2012)

P 3502 L7: Reference ‘Brand 2011’ missing

P 3503 L8: The abbreviation GISP is a bit unfortunate, can be mixed up with GISP

P 3503 L11: “..see Fig.1 and section 2.2”

P 3503 L19: “..the results for two external. . .”

P 3505 L9: Comment: So, the yield is the criterion for accuracy. Any other sources of error (eg increasing blank) detected?

P 3506 L17: Comment: this is not shown in Fig 2b

P 3506 L21: Comment: How did you measure the purity of the biogenic CH_4 ? Please provide a quantitative figure (Any residual organic compound would show up in the final delta value).

P 3508 L2: Comment: Both gases (MIS and GIS) do not have CO_2 or N_2O at atmospheric levels. This might become important during on-line trapping and separation when NEEM air is analyzed.

C1265

P 3508 L3: Comment: You either need to describe the analytical system in more detail, or provide a reference for further details.

P 3508 L7: This is certainly not compatible with the IT principle. The CO₂ square peaks go through a different history, including the capillary, and can serve only as a mediator between complete air aliquots used as samples used reference.

P 3508 L12: Comment: Please describe correction procedure. Moreover, the primary scale anchor seems to be NEEM, not MIS or GIS, right? But NEEM has not been calibrated independently by DI-IRMS. What is the anchor value? Please clarify.

P 3509 L2: Comment: What does this offset consist of? Laser system calib versus calibration using uranium reduction / ms measurements?

P 3509 L20: Comment: This is almost too good to be true. Do you expect this to be typical?

P 3510 L18: Comment: I think this should simply be a more 2-H enriched source gas? 'Heavily fractionated' implies a process for producing such gas, which is not the only option.

P 3514 Table 1: Please add the isotope reference values used for the respective materials in this study

P 3517 Fig. 2: cleaning equipment for bio-CH₄ missing

P 3518 Fig. 3: - The upper plot would be easier to digest as a 3-d plot (with 3 traces)
- Caption line 3: replace "CH₄ and CO₂ fractionate in the source, but" with "CH₄⁺ and CO₂⁺ decompose in the ion source; but..." (Comment: It is not correct to say that the gases fractionate in the source. They do, but the processes are much more complex when it comes to unimolecular decomposition of ions in the ion source following electron impact.) - Caption line 10: Why is the offset negative?

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 3499, 2012.

C1266