

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 $\delta^{13}\text{C}$ - CH_4 in synthetic air” by P. Sperlich et al.

Anonymous Referee #3
June 18, 2012

General comments

This manuscript is addressing an important issue in atmospheric CH_4 measurements, i.e., establishing a traceable approach for air- CH_4 isotope standards. This is particularly critical for detecting the changes of CH_4 sources and sinks in the atmosphere with time via using its isotope measurements ($\delta^{13}\text{C}$ and δD). The methods and procedures are carefully described and presentation is well constructed. This effort may advance the field of atmospheric CH_4 isotope measurements in a big step, which will be appreciated by the community.

The specific comments

(1) P3502 Section 2.1: a short review is helpful for readers to understand the following sections. It would be even better to have a flow chat for visualizing the components (e.g., purification of biogenic CH_4 , making pure GIS_p , MIS_p , calibration of pure CH_4 and producing and measuring GIS and MIS etc.) and the relationship among the components. Those critical values (e.g., 280 μL , 1L, 6L, etc. and the various temperatures) and numbers should be indicated on the chat. Figure 1 may be part of the chat (by its own is not enough).

(2) P3503 line 2: Is CO_2 40 339 a referenced pure CO_2 gas? What does it mean “ CO_2 N48” in Table 1? It is suggested to have a Table for all the relevant standards (see below) listing their isotopic compositions and indicating the respective traceability path to the primary scales (i.e., VPDB- CO_2 in $\delta^{13}\text{C}$, VSMOW-2 and VSLAP-2 in $\delta^{18}\text{O}$ and δD respectively). Those should include the follows:

- RM-8563
- CO_2 - 40 339
- DC'02
- NM'09
- -15

(3) P3503 lines 24 – 26: it is stated that two quartz glass tubes are routed through one tube furnace. I am wondering how to control the different temperature at each individual quartz tubes as shown in Fig 2a (850°C vs. 600°C).

(4) P3504 lines 5-8: the 250mL should be marked on the figure (Fig 2a). Is the tear shaped bottle be able to be disconnected from the system for pipetting the sample into a vial? If yes, why is it not shown on Fig.2a?

(5) P3504 line 19: It is suggested replacing “1l” with “1L” and throughout the whole text.

(6) P3505 lines 2-4: It is suggested to mark the pathway for the cryo-transfer in Fig.2. Should H₂O-trap be merged first or CO₂ –trap be merged first? How to prevent H₂O from being trapped in CO₂-trap (at -198°C) during the alternations of submerging? Again, a clear flow chat suggested in (1) will clarify those questions.

(7) P3505 line 9-10: The verification of the quantitative combustion of CH₄ should be described and discussed in more details. Fig 3 and its caption are not well understood. It seems that three scans of mass abundances were overlapped in Fg.3A, which is not clearly mentioned in the caption. How long does it take for one cryo-transfer cycle?

(8) P3506 line 1: how to transfer the H₂O from the tear shaped bottle into the 1ml glass vial ?

(9) P3506 lines 23-24: it is suggested to re-phrase the sentence as “ we mix the fossil CH₄ with the Biogenic CH₄ and barometrically controlled the mixing ratio between the two.”

(10) P3507 lines 1-14: it is suggested including the procedure of making CH₄ free air (N₂/O₂), as a component, in the flow chat suggested in (1).

(11) P3507 line 18: It is suggested replacing “6l” with “6L” and throughout the whole text.

(12) P3507 line 21: I am wondering why at a pressure of 1 bar, the CH₄-free air flow was re-routed through the aliquot instead of at the vacuum pressure from the beginning.

(13) P 3507 line 27: I am wondering what the maximum pressure is after the filling.

(14) P3509 lines 11-19: The offset implies that the isotopic fractionation in mixing (with N₂/O₂) procedure could not be totally ruled out, as other procedures you mentioned. It is suggested to list GIS and MIS values (i.e., the means and the corresponding standard deviations) measured by GC-IRMS, which are the data before offset corrections, then to derive a relative difference between GIS and MIS, which should be equal to the corresponding relative difference between GIS_p and MIS_p measured by off-line if the whole approach introduces the same degree of isotopic fractionation for both GIS and MIS. Otherwise, the method

may not provide with you a consistent air-CH₄ isotope reference for a period of long time (e.g., decadal time), which is required by serving the WMO-GAW atmospheric measurement network. I am wondering how many 6L flasks of GIS and MIS were prepared in total for this work. You should derive an uncertainty of GIS and MIS from those independently prepared flasks, including both preparing and measuring processes. It is likely that the current errors listed in Table 2 are only measurement errors from the GC-IRMS.

(15) P3514 line1 in Table 1: what is N45?

(16) P3518 Fig 3b: What is the definition of the normalized $\delta^{13}\text{CH}_4$ offset? The legends in Fig. 3 are not clear. It is suggested to replace black line with red line.