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Atmospheric Measurement Techniques Discussions



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

**Anonymous Referee #2**

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General Comment

This manuscript is a very welcome reminder of the calibration issues that still hamper the methane isotope community and the urgent need for easily available methane in air standards that cover a range of ambient air values. What isn't made clear though is how these standards will be made available to the wider community and in what quantity. Something similar to the NOAA-INSTAAR cylinders for CO2, CH4, d13C of CO2 is required and at quantities that will allow regular and long-term calibration. The mixtures in air also need a wider intercomparison with laboratories that measure d13C

/ dD of CH4 in modern ambient air before finalizing a values for the standards as some of these labs can achieve higher precision than reported here and NIWA, NZ, would be a good starting point for this.

Specific Comments

How long is the total time to prepare a CO2 and H2O for offline analysis?

P3505 – Lines 4-10. The concept of cryo-transfer cycles is not clear. How long is each cycle? Why are 25 needed to get 100 % yield. Does this not imply that the copper oxide combustion efficiency is low? Would the number of cycles required be lower if the combustion temperature was increased?

P3506 – Line 1 – What do you mean by a 1 ml glass vial? Is this a breakseal? P3506 – Line 2 – How long does re-oxidation take? P3506 – Line 6 – What are the instrument precisions? Are these the errors shown in Table 2?

P3507 – Line 8 – This should read 'two traps in series removed H2O from the air flow' P3507 – Line 25 – These errors suggest that MIS and GIS aliquots have to be prepared separately each time. Is it not possible to make up a cylinder of MIS or GIS for regular analysis?

P3508 – Line 6 – reference gas peaks are rarely square but thay are always flat-topped unlike the sample peaks. P3508 – Lines 9-12 - This discussion implies that both mass specs must give the same d13C value for pure CO2. Has the same pure CO2 gas been measured directly by injection into both mass specs? P3508 – Line 25 – Table 2 shows that multiple analyses of the samples have been made so why is the precision identical for every standard measured?

P3509 – Line 14 – Please name the IT-principle in full, not just the abbreviation. P3509 – Line 16 – how constant is the daily offset? Is there any evidence of drift during the day.

P3510 – Lines 17-18 – Producing reference gases at various mixing ratios and within



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a 17 ‰ range is clearly demonstrated. What needs to be clearly stated are the volumes of reference gas that can be offered. Can 30 litre cylinders be filled to 200 bars for example? Some extraction methods require large volumes (2-5 L) for extraction and standards need to be measured on a regular basis. Offering the fossil and biogenic standards diluted in zero air would also be useful for the atmospheric community. P3510 – Line 22 – You could finish by mentioning the next steps to produce a useful product for the community.

Table 2 – Is the 4.4 ‰ offset defined using the same reference gas as on the GC-IRMS? Table 2 – How can the precision be the same for all standards when multiple analyses have been made on each?

Figure 2 – It is not clear where the 1 ml H2O vial is attached. Is the whole of the CO2 trap removed and taken to the mass spec for analysis? It should be made clear where the collection vials are located and at what point they are disconnected.

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