

Interactive comment on “Characterisation of interferences to in-situ observations of $\delta^{13}\text{CH}_4$ and C_2H_6 when using a Cavity Ring Down Spectrometer at industrial sites” by Sabina Assan et al.

Anonymous Referee #2

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This is a potentially interesting paper that has still has serious issues that I feel need addressing. I think that research into levels at which various gases interfere with the accuracy of CRDS instruments is important, as these instruments become more ubiquitous both in the field and in the lab (where extreme concentrations of interfering gases are more likely to be seen). Overall, to me, the focus of this paper is not quite right. A g2201i measures $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, $^{12}\text{CH}_4$, $^{13}\text{CH}_4$ and water vapour concentration (and is then able to calculate the C13 isotope ratios for CO_2 and CH_4). It is interesting that this unit can, in a simpler way, measure the concentration of C_2H_6 as well. As the measurement of C_2H_6 is secondary, it seems to me that this paper should concentrate

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on how excess quantities of any of these gases affect the accuracy and precision of the other gases that are measured. This should include C_2H_6 as well, as that is a known interferer (and can be measured). The C_2H_6 analysis presented in this paper would fit into this structure and make more sense to me. Following are comments on areas that need to be addressed or corrected. 1. It was interesting to me to find out that the instruments used in this research are G2201i's and are not designed to measure C_2H_6 concentration. This is stated only once (I think) in this paper, but is a very important point that should be stressed more. It explains the negative C_2H_6 concentrations, etc. Picarro may not be that happy that all of this work is being done on correcting gas concentrations that this unit is not designed to measure, but without that emphasis on the extracurricular nature of the measurement makes it look as if the machine is poorly calibrated, etc. 2. Why are all of the interference experiments on C_2H_6 (i.e. sections 3.1.1 – 3.1.3) all done on gases that contain no C_2H_6 ? While it is interesting that there are (repeatable) effects on C_2H_6 concentrations when other gases are added to the zero air (most occur when C_2H_6 concentrations are negative), I think that these results need to be confirmed at C_2H_6 levels similar to atmospheric background and at anomalous levels as well. 3. I would like to see the correction systems for C_2H_6 and $\delta^{13}\text{C}$ CH_4 tested on “real” mixtures of the standard gases (i.e. with varying known concentrations of CH_4 , CO_2 , C_2H_6 and H_2O). Confirmation of concentrations with the GC would then add confidence. I am sure that this sort of work was done, but these results are not presented, and this detracts from the paper. The field examples do suggest that the corrections work, but showing test results would help. 4. Minor – Lines 384-386 – This statement sounds very speculative and should either be improved or removed. 5. Minor – the caption in Figure 6 states that “For each plot the bottom axis indicates the increase in concentration of the targeted gas (CO_2)”. Doesn't the bottom axis just show the concentration (not the increase) of CO_2 in each sample? 6. Minor – the caption for Figure 9 is confusing. Isn't the concentration of CH_4 being diluted from ~1.95ppm? 7. Very minor – Carbon dioxide is capitalised on line 349. 8. Very minor – Line 436 – “single event” not singular. 9. Line 478 – presentation of the negative ratio

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implies that a researcher would accept and use the negative concentration of C2H6, which of course they would not. Needs to be deleted.

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