

Interactive comment on “Ethane measurement by Picarro CRDS G2201-i in laboratory and field conditions: potential and limitations” by Sara M. Defratyka et al.

Anonymous Referee #2

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Defratyka et al. report ethane measurements from a spectroscopic instrument originally not designed to make an ethane measurement. Ethane has a small interfering absorption peak for an instrument that reports isotopic measurements of CO₂ and CH₄. Defratyka et al. quantify this peak, and although the ethane measurement has low precision, use it to quantify the ethane to CH₄ ratio from natural gas emissions.

Although the ethane measurement is not very good, and the application of this measurement is limited, it nonetheless could be of some use to the scientific community. However, before this paper is ready for publication, I think some issues must be addressed.

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The Picarro 2201 website (https://www.picarro.com/sites/default/files/product_documents/Picarro_%20G2201-i%20Analyzer%20Datasheet_053017.pdf) says there are interferences from “other organics”, as well as ethane, ammonia, ethylene, and sulfur-containing compounds. Might some of these other organics exist in natural gas? Have the authors looked at propane interferences?

I was confused in the second sentence of the Abstract by the use of the word “dedicated”, which is also used throughout the paper. To me, “dedicated” means it only measures that to which it is dedicated, in this case CO₂ and CH₄. I suggest the authors use “originally designed to measure” or some such phrase. And it wasn’t until line 84 on page 3 that the authors mention for the first time that the G2201-i was actually used to measure ethane. The authors should explicitly state that the G2201-i was used to measure ethane in the Abstract, rather than hiding it in terms of “consider[ing] the possibility” of measuring ethane.

Generally, I thought the paper needed more statements of introduction and conclusion in many paragraphs. There are a lot of paragraphs explaining what the authors did related to the measurement. What is missing is information on why they are doing this, and what are the results of this part of the experiment.

I also would like to see this paper act more as a stand-alone work. As written, it is tied heavily to Assan et al. (2017) in too many places. In many cases, a sentence or two summarizing the results of the cited work would be helpful.

Other comments:

line 36, somewhere it should be stated that the ratios referred to in the paper are molar ratios, as opposed to mass ratios

line 58, instead of simply stating “good agreement”, add what measurements agreed well in case the reader is not familiar with Assan et al. (2017)

line 66, again, please list the measurements that were compared

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line 88, Equation 1: rather than a generic equation, please fill in the parameters A, B, and C so that one does not have to look at the paper by Assan et al. to find these numbers

line 97. Agreed. What have the authors done to ensure comparability and traceability?

line 105, if CMR is commonly known as precision, why not use the phrase precision?

line 153, vibrations of the instrument probably lead to instrument noise regardless of whether then instrument is “dedicated” to an ethane measurement. And are the authors referring to the ethane measurement noise when referring to “instrument readouts”? Or all measurements? And in line 154, this is referred to as a “constraint”. Does this mean the mobile data were noisy to the point of being unusable?

line 162, are these two-sided fits? Weighted by anything?

line 174, what is “skc”?

line 181, where has this publication been submitted? Is it available to read?

line 185, what is the purpose of this sentence? Was the change in drying intentional? If so, for what reason? Was it regular?

line 201, the authors should define a “low” amount of ethane. It seems like they are referring to 23 ppb, which is not low. But reading later, it appears they are referring to 2.2 ppb? But that is in the next section, so I’m not sure if that is the same working standard referred to in this section. Regardless, the authors should start with their best estimate of the tank mixing ratio. This puts the G2201-i performance in perspective. Otherwise, the reader has to read several paragraphs to discover a 2.2 ppb standard reads as 23 ppb on this instrument.

For Table 1 and Figure 1, Was this the working gas used as part of the dilution system described on page 4/equation 1? In general, I think whenever the authors mention a working gas, they should state what the nominal ethane mixing ratio is.

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line 210, can you add an uncertainty to the 2.2 ppb?

line 212, this was a surprisingly high offset. I am also still getting confused by the working gases used. This is apparently not the same one used for Figure 1? And if Figure 1 averaged 23 ppb, presumably you were giving it less than 2.2 ppb ($2.2 * 23/33 = \sim 1.5$ ppb?).

line 218 and 220, there are a lot of Picarro model numbers in this paragraph. Perhaps the authors could add a table to show what models measure what species, since I am not familiar with all the models.

Figure 2, what units are the Allan deviation plots in? I assume they are all ppm?

line 240, in some cases such as these, a standard error of the mean would also be worth reporting, along with the standard deviation

Figure 3, are the differences between Protocol 2 and 3 simply linear fits, i.e., Protocol 2 fits a line to all the data, and Protocol 3 fits a line to data $< 0.16\%$ H₂O? If so, what would a higher-order fit to H₂O do – could you use that for both high and low humidity cases? I'm also not sure of the benefit of naming these "Protocol X", since every time they are mentioned, a description of the Protocol is also given. It seems easier to mention "no correction", etc. every time, and the reader wouldn't have to remember what arbitrary Protocol number this was given.

line 255, what does a release with a C₂H₆:CH₄ equal to 0 mean? No ethane was released, but methane was? Or nothing at all was released?

line 264, when absolute deviations are on the order of 10 ppb, an "improvement" of 0.4 ppb seems like simple statistical variation. In other words, I think the authors are assigning significance to the insignificant digits of these numbers.

Table 3, Why do the authors report the residuals, and not the ratio itself? And how are the residuals defined? Is a linear fit performed on the data, and these are the residuals when the fitted line is subtracted from the data?

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Table 4, referring to the different sites as A, B, C, and D only further complicates this table. Also, I'm not yet sure what difference the survey number makes. I think it would be easier to refer to these as compressor 1, 2, 3, and landfill. Use abbreviations if necessary. Also, move the * information from the title of the table to below the table.

Figure 5, how are these slopes calculated? Are the data weighted in the fit? And are the uncertainties reported in Table 4 just the slope uncertainties, or do they tie in the uncertainties of the C₂H₆ measurement?

line 407, it might be best to reiterate the requirement that CH₄ be greater than 1 ppm here, as mentioned previously in the paper

Grammar suggestions/typos:

line 28, it looks like “sources” is possessive, needs apostrophe

line 34 and elsewhere, I think “ethane:methane ratio” is redundant. Suggest either “ethane:methane” or “the ethane to methane ratio”. But to me, using a colon implies ratio.

line 42–43, change “methane enhancement source” to “methane source”

line 45, remove “access to”

line 56, change “biogenic or thermogenic” to “biogenic from thermogenic”

line 85, add “1” to H in CH₄ for consistency

line 124, change to “Equation”

line 133, change “has been measured during” to “was sampled for”

line 152, change “the previous works” to “previous work”

line 155, change “standing some” to “spending”

line 155, change “accumulating air in” to “sampling air using”

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line 159, add “the” before “C2H6:CH4”

lines 164–5, start sentence “A description of the experimental. . .”, replace “find” with “found”, and add period after “(2017)”

line 167, suggest “up to” instead of “until”

line 169, suggest “C2H6:CH4” instead of “ethane:methane” for consistency

line 170, suggest “stationed in the plume”

line 171–172, suggest “. . . the time spent within the plume was approximately 15 to 20 minutes.”

line 173, suggest “tracer release”

line 174, change “5 liters” to “5-liter”. Also line 284.

line 175, change to “. . . bags were sampled inside . . . and one was sampled . . .”

line 175, change “bags” to “bag samples”

line 180, delete “real”. I think “field” is sufficient.

line 183, add “the” before “C2H6:CH4”

lines 185–186, change “part of measurements without dryer” to either “part with a dryer” or “part of the measurements without a dryer”

Figure 1 caption, I would re-word and make two sentences, change “20 minutes” to “20-minute”, start new sentence with “For each measurement point, squares represent. . .”

line 214, change to “As a result. . .”

line 218, change “dedicated to the measure of ethane” to “designed to measure ethane”

line 227, change “ethane absolute value” to “an absolute value of ethane”

line 229, change “deduct” to “deduce”

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line 259 and elsewhere, suggest “stationary in-plume situation” instead of “plume standing situation”

line 273, suggest something like: “For the higher emission, the measurements and results were combined when the emission rates were 70, 72, and 73 L/min.”

line 276, add “the” before “AirCore”

line 285–286, add “to” after “equal”

Table 4, change “Data” to “Date”

line 321, change “due the very” to “due to the very”

line 329, change “ratio” to “ratios”

line 356–357, the time of sampling is confusing. The first sentence makes it sound like the instrument spends 10 minutes online, followed by 10 minutes offline. The next sentence makes it sound like the instrument spends 10 minutes online, followed by 20 minutes offline.

line 358, perhaps just describe the CRDS data as being averaged over the sampling time of the GC-FID

line 360–361, change to “. . . to use a CRDS G2201-i to measure C₂H₆:CH₄, . . .”

line 366, change to “. . . on the TILDAS method . . .”

line 367, change to “tracer release”

line 384–385, a word is missing here, perhaps “allowed us to”, change “measurements point” to “measurement points”

line 391, change to either “allow us to separate” or “allow the separation”

line 394, change to “flask samples”

line 398, indicative of what?

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for the tables in the Appendix, I would put the * asides below the table, rather than part of the table title

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