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Interactive comment on "Measurements of hydrogen sulfide (H$_2$S)) using PTR-MS: calibration, humidity dependence, inter-comparison and results from field studies in an oil and gas production region" *by* R. Li et al.

Anonymous Referee #2

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General Comments

The paper is well written and provides a useful description of using a PTR-MS instrument to measure hydrogen sulfide. The paper is appropriate for AMT. The paper includes details on measurement methodology, intercomparison with another measurement method, and field results from an oil and gas development field. My main criticism is that the paper presents a lot of discussion on analyzing H2S sensitivity based on reaction kinetics that is overdone. Can other compound sensitivities be analyzed in

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terms of ion molecule reaction kinetics? In the interest of presenting a clear enough description and representation of the facts so that the experimental methodologies can be reproduced by others some clarification is required. So I have some minor comments to improve clarity of the presentation. Overall this is a good paper and worthy of publication.

Minor Comments

1. Abstract. You have "normalized counts per second / parts per billion by volume" in brackets to clarify units of ncps / ppbv but you fail to mention what the counts are normalized to. Perhaps best to leave this definition out of the abstract to avoid cumbersome nature of explaining your units.

2. Section 2.1. You should also list the E/N ratio in Table 2. This metric is more to the point to describe drift tube conditions. Drift tube lengths can vary so stating the voltage is not enough.

3. p6215. In the experimental section the water abundance is described in the text as 2.8% and in the figure shown as a mass based mixing ratio. You should specifically state in the text that it is mass based. Why use mass based mixing ratios for water and molar mixing ratios for H2S? This is somewhat confusing.

4. p6217. I thought the discussion and presentation of the H2S sensitivity was a bit overdone. In the end you don't know what the k-1 rate constant is for the conditions of your drift and the sensitivity and fit shown in Figure 4 is essentially empirical. So a lot of page 6217 and page 6218 sounds like "homework" and detracts form the paper when you say things like we tried this but it didn't work.

5. Could ligand switching reactions be important for H2S protonation and thus be a second means to protonate H2S? This channel would also have a water vapor dependence.

6. Does humidity also impact the reaction time since H3O+ clusters are more important

at higher humidity?

7. The A term in equation (4) is the relative transmission efficiency and you call it a constant but only if voltages settings of the ion transfer lens and detector are the same. Presumably this can change as detector voltage is often changed. Calling it a constant oversimplifies things. For example, there is no reason to believe that the relative ion transmission efficiency would be the same for different PTR-MS instruments.

8. p6221. You should perhaps state the source of HO_2+ and whether this interference in the ToF could be reduced by tuning the ion source?

9. p6223. Figure 9 shows response factors for 2 different PTR-MS instruments that are quite similar despite apparently different drift tube states – again need to list E/N in Table 2. Given that H2S kinetics was used to explain sensitivity based on an H_3O+ rate coefficient and reaction time I'm puzzled how the ncps values can be so similar between these instruments and how these sensitivities relate to the kinetic parameters discussed. For example acetone has a smaller rate coefficient than acetonitrile ($\sim$ 50%) yet in your figure acetone has a much larger sensitivity. Perhaps this is due to humidity dependent calibration factors for these compounds (what RH level were calibrations) or to transmission efficiency effects. The Warneke 2011 paper referenced for transmission effects has a much different looking plot of relative sensitivities. For example in Warneke 2011 the C9-aromatics have a much greater sensitivity (> factor of 2) than benzene but in your paper they are about the same. Presumably this is the same instrument so how can the relative sensitivities be so different? Does your PTR-MS instrument sensitivity display understandable relationships to ion molecule kinetics? If not then discussion of theoretical H2S sensitivities is not useful. To frame a discussion of PTR-MS instrument sensitivities in term of reaction kinetics it would be prudent to show that you understand the sensitivity for compounds that don't have a back reaction issue (say benzene, how do drift tube kinetics yield a 22 ncps compared to acetone's 40?) then proceed to H2S. Otherwise you have an empirically based result, nothing wrong with that, but the kinetic discussion is uninformative, and just

makes the paper longer.

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