

Interactive comment on “Water Vapor Inhibits Hydrogen Sulfide Detection in Pulsed Fluorescence Sulfur Monitors” by Anders B. Bluhme et al.

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Interactive comment on: “Water Vapor Inhibits Hydrogen Sulfide Detection in Pulsed Fluorescence Sulfur Monitors” by Anders B. Bluhme et al.

Anonymous Referee #1

Received and published: 31 March 2016

This is an excellent and very important piece of work. I do have only one suggestion namely that when the authors suggest drying the incoming sample air they mention that doing so by means of a nafion drier is not likely to alter the concentrations of either of the important analytes. If they have other drying suggestions they should also insert

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them and the relevant supporting data.

Author Response: The authors would like to thank the reviewer for the positive evaluation.

There are many alternative drying techniques available; however this study has only tested the Nafion dryer. The authors found that there was no interference between the Nafion tube and the measured H₂S or SO₂ concentrations and can therefore verify the Nafion dryer as a viable technique. Since no other techniques were tested in the present study, the authors cannot currently verify any alternative drying techniques.

Anonymous Referee #2

Received and published: 11 April 2016

General comments: This paper reported an interesting and important issue of H₂S measurement using the pulsed fluorescence technology. The findings of the paper reveal a possible under-estimation of true H₂S concentrations in some previous research using this type of H₂S analyzers. However, the paper should be improved and a careful check to correct some errors in it is necessary.

Author Response: The authors thank the reviewer for their comments and address further questions below.

Title: The word “inhibit” appears in the paper more as “interfere”. It is not consistent as what is described in the research.

Author Response: Several suggestions for the title were discussed including “interfere” as an alternative to “inhibit”. However, the authors agreed that the word “inhibit” better fits the observations, since the H₂S response of the instruments is inhibited by water vapor.

Line 2 and throughout the manuscript: Normally, a sentence should not be started with

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an abbreviation or a chemical formula.

Author Response: Changes have been made throughout the paper to avoid starting sentences with abbreviations and chemical formula.

Line 4 and throughout the manuscript: The “e.g.” should usually followed by a “,” as in “e.g.,”.

Author Response: The comma has been added after each e.g.

Line 23: A more representative publication for the National Air Emissions Monitoring Study is: Heber, A.J., B.W. Bogan, J.-Q. Ni, T.-T. Lim, E.L. Cortus, J.C. RamirezDorronsoro, C.A. Diehl, S.M. Hanni, C. Xiao, K.D. Casey, C.A. Gooch, L.D. Jacobson, J.A. Koziel, F.M. Mitloehner, P.M. Ndegwa, W.P. Robarge, L. Wang, and R. Zhang. 2008. The National Air Emissions Monitoring Study: overview of barn sources. In: The Eighth International Livestock Environment Symposium (ILES VIII). Iguassu Falls, Brazil, September 1-5: St. Joseph, Mich.: ASABE.

Author Response: The more representative publication is now used instead of the earlier reference.

Line 25: “proposed by” should be “approved by”.

Author Response: This has been corrected

Line 65: Explain about “technical air”. “. . . a 100 ppm H₂S bottle”; in Table 1, it is 101 ppm.

Author Response: A description of technical air has been added to introduce the term technical air. Furthermore “a 100 ppm H₂S bottle “ has been corrected to “a 101 ppm H₂S bottle” as stated in the Table – The flask was purchased as a 100 ppm H₂S flask with the actual content determined to be 101 ppm by the manufacturer.

Lines 66 to 70: Make the names and verbs in the text the same as used in the Figure. It is difficult to follow your description as it is now when referring the figure. . .

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.mixture before continuing. Part of the diluted H₂S stream was lead through a Perma Pure “Nafion dryer” by the 450, while the rest was “bled” into a “fume hood”, avoiding overpressure on the sampling line. The “Nafion dryer” was used to humidify the “dry test gas”, by allowing water to permeate the Nafion membrane from a “humid purge gas”.

Author Response: The verbs in the text and some of the labels in the Figure have been altered to better fit each other. This should make it easier to follow the description given in the text when referring to the Figure.

Line 76: “H₂S concentration”, not “H₂S content”.

Author Response: Content has been changed to concentration in several places throughout the paper

Line 88: Do not cut the sentence by a Figure and a Table.

Author Response: As authors we only have limited power over the layout. The changes from the earlier comments have fixed this as well. During the final proof reading, we will make sure that no such cuts remain.

Lines 103 and 116: What does “Already at a relative humidity of 5.3 %,” mean? Does it mean “As low as at 5.3 % relative humidity”?

Author Response: The sentence has been altered to read: “Even at a very low relative humidity, 5.3 \%, the H₂S response decreased from 5145 to 4718 ppb, corresponding to a reduction of 8.3 \% in measured H₂S”

Line 113: “. . . when measuring SO₂” or “. . . when measuring H₂S”?

Author Response: Here it should be “when measuring SO₂” as is written. This section describes the experiment conducted with SO₂ instead of H₂S. When measuring SO₂ no effect was observed when increasing the humidity.

Line 123: Should be “approved by”.

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Author Response: This has been changed

Lines 137 to 138: “. . .using a Nafion dryer or another appropriate drying technique.”
Was it tested? If not, it should not be as a conclusion.

Author Response: It has been specified that the Nafion dryer was tested and found to produce no change in the measured H₂S concentration and that other drying techniques were not tested in this study and should therefore be experimentally verified before use. References: Please carefully check the format and correctness of the cited references. Some examples are: Lines 145 and 156: Not the correct journal names. Format the article titles consistently with other titles. Line 155: What is the source of this publication?

Author Response: The references have been carefully reviewed and corrected. _____

April 10, 2016 Comments

There appeared to be a critical experimental design or calculation issue that could invalidate the conclusions of the study. As shown in Figure 2, the concentrations of H₂S determined by MFCs 2 and 3 for dry samples were used as “baseline” concentrations. However, when the dry sample air passed through the Nafion Humidifier (should be marked something like “Nafion dryer used as humidifier” to agree with the description or “Nafion dryer” in Table 1), the mass of water vapor was added to the mass of mixed dry air and H₂S. This process could decrease the mass concentrations of H₂S in the “Sample out” to the analyzer. It should be explained and considered in the study.

Author Response: First it should be noted that the concentrations are given in mixing ratios and not in mass concentrations, but the addition of water could still decrease the measured concentrations. To investigate a calculated was performed to determine the highest effect associated with the addition of water:

At 294 K and an atmospheric pressure of 760 Torr the saturation vapor pressure of water is 18.46 Torr. Therefore if the dry air concentration of H₂S is 5145 ppb, the

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concentration of H₂S adjusted for dilution by H₂O vapour is:

$$(5145 \text{ ppb} * (760 - 18.48) \text{ Torr}) / (760 \text{ Torr}) = 5020 \text{ ppb}$$

Thus a change of 2.4 % is the highest possible effect associated with the addition of water. This is furthermore supported by the experiments conducted with SO₂, where the addition of water to the air stream was found to have no effect on the measured concentrations. This slight modification does not change the main result of the paper which is to recommend that users examine their own instruments as the behaviour of individual catalysts may vary.

Lines 109 – 110: “A similar experiment was conducted with SO₂ instead of H₂S, and no interference from water was observed.” The results of the SO₂ tests are better to be presented for comparison.

Author Response: The SO₂ experiments compared dry air and air at 60 % RH. The effect due to water vapour dilution was within the error of the RH probe and the 450.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-357, 2016.

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