

**Response to reviewers for the paper “Measurements of hydrogen sulfide (H<sub>2</sub>S) using PTR-MS: calibration, humidity dependence, inter-comparison and results from field studies in an oil and gas production region.”**

**R. Li et al.**

We thank the reviewers for their comments on our paper. To guide the review process we have copied the reviewer comments *in black italics*. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (**in bold text**).

**Anonymous Referee #1**

*General Comments:*

*The authors present the quantification of H<sub>2</sub>S at m/z 35 by PTR-MS including a detailed explanation of isotope interferences at m/z 35 and the measurement’s humidity dependence. Field data of CRDS, ULW-PTR-MS, PTR-MS, and PTR-ToF-MS for H<sub>2</sub>S are intercompared and are used along with methane data for source attribution and characterization. Overall the authors make a strong case for PTR-MS as a valid instrument for H<sub>2</sub>S quantification at sub ppbv mixing ratios. Therefore I recommend this article for publication after the following specific points are clarified.*

*Specific Comments:*

*R1.1 pg 6209-10: As one of the goals of UB-WOS was to quantify ozone precursors as mentioned in the experimental section, information in the introduction concerning the relative ozone production rates of H<sub>2</sub>S reaction vs various VOCs measured at the site should be included if citations are available or mentioned in general if citations are not yet available. Although the thrust of the paper is does not deal with H<sub>2</sub>S as an ozone precursor, the introduction would be well served by including H<sub>2</sub>S relative or expected role in ozone production at UB.*

Thanks for the suggestion. We calculated the OH reactivity due to H<sub>2</sub>S and compared its contribution to the total OH reactivity in the Uintah Basin in winter. The

$k_{\text{OH}}$  of  $\text{H}_2\text{S}$  is  $4.6 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . 1 ppbv  $\text{H}_2\text{S}$  gives  $0.1 \text{ s}^{-1}$  OH reactivity, which is small compared to the total OH reactivity of  $\sim 30 \text{ s}^{-1}$  at the site. The following text has been added to the manuscript (P5, L126).

**“The OH reactivity from  $\text{H}_2\text{S}$  ( $\sim 0.1 \text{ s}^{-1}$ ) is a small fraction of the total OH reactivity ( $\sim 30 \text{ s}^{-1}$ ) observed in the basin, indicating  $\text{H}_2\text{S}$  is not an important precursor for ozone formation.”**

*R1.2 Pg 6210 Although the operating parameters of the ULW-PTR-MS are given in Table 2, the first mention of the instrument requires a citation so that readers will be able to determine the difference in performance and design between it and the PTR-MS (other than its weight as mentioned). This is especially pertinent since the ULW-PTR-MS data is intercompared with the PTR-MS. If no citation yet exists the design and performance difference with the PTR-MS should be noted in this paper.*

*Pertinent sampling details of the NOAA ESRL Mobile Laboratory and Horse Pool location should be given in the experimental section or cited. Of particular interest is information about inlets (sampling flow rate, tubing material type, inner diameter, length, sampling height above ground level, and any known issues (or lack thereof) concerning inlet characteristics that affect sampling  $\text{H}_2\text{S}$ .) Although PTR-MS is a soft chemical ionization mass spectrometer, some fragmentation can still occur especially for VOCs at larger  $m/z$ . Please comment in the paper on the presence or lack any known fragment ions at  $m/z$  35 that could interfere with the  $\text{H}_2\text{S}$  measurement.*

Thanks for the comment and a reference for ULW-PTR-MS instrument has been added. Although a detailed description of the ULW-PTR-MS instrument from the KIT group is not available, a previous paper from our group describes our study surveying the point sources from gas and oil wells in the Uintah basin using the Mobile Laboratory and ULW-PTR-MS (Warneke et al., 2014). This paper includes a description of the instrument and the sampling settings. It is also the first paper with the use of this instrument. A full description of the instrument will be given by our KIT colleagues and is beyond the scope of this paper.

The interference for H<sub>2</sub>S measurement by higher mass fragmentation is not known to occur from compounds like CH<sub>3</sub>SH and CH<sub>3</sub>SCH<sub>3</sub>, which were very low. The following texts were added to the manuscript (P6, L153):

**“The fragmentation from higher molecular weight species to form H<sub>3</sub>S<sup>+</sup> is not known to occur from compounds like CH<sub>3</sub>SH and CH<sub>3</sub>SCH<sub>3</sub>, which were very low at ambient conditions.”**

Reference:

**“Warneke, C., Geiger, F., Edwards, P. M., Dube, W., Pétron, G., Kofler, J., Zahn, A., Brown, S. S., Graus, M., Gilman, J., Lerner, B., Peischl, J., Ryerson, T. B., de Gouw, J. A., and Roberts, J. M.: Volatile organic compound emissions from the oil and natural gas industry in the Uinta Basin, Utah: point sources compared to ambient air composition, *Atmos. Chem. Phys. Discuss.*, **14**, 11895-11927, 2014”**

*R1.3 Pg 6212 It is noted that the H<sub>2</sub>S kinetics are analogous to formaldehyde and HCN as the reverse reaction is important due to proton affinities close to that of water. Later the sensitivity for H<sub>2</sub>S is determined for the ULW-PTR-MS (see figure 9) by comparing it to the PTR-MS sensitivities for various VOCs. It would be useful to see if HCN and formaldehyde follow the same trend as the other VOCs as their sensitivities are also humidity dependent whereas the VOCs used in the figure 9 are presumably not humidity dependent due to their larger proton affinities. In section 3.1 it is stated that the ULW-PTR-MS was calibrated for formaldehyde, was the PTR-MS similarly calibrated for formaldehyde, and if so how did the formaldehyde sensitivity for the ULW-PTR-MS compare to that predicted by the slope in figure 9? Here again the different H<sub>2</sub>O flow rates used (Table 2) between the two PTR-MS instruments may cause the relative sensitivity for H<sub>2</sub>S to deviate from the linear regression line given in Figure 9. It should easy set the PTR-MS to the conditions of the ULW-PTR-MS and verify the sensitivity is not significantly different between the two sets of conditions, was this done?*

Thanks for the comment. We only have formaldehyde calibration factors for PTR-MS, but not for ULW-PTR-MS unfortunately. The detection of formaldehyde by PTR-MS was the subject of a previous paper (Warneke et al., 2011), and we would rather not repeat some of that analysis here, especially since the ULW-PTR-MS instrument was not used for formaldehyde in this study. The following text has been modified to clarify the formaldehyde calibration work (P9, L255):

“Assuming that the sensitivity of the ULW-PTR-MS for H<sub>2</sub>S was similar **with the PTR-MS** and in the same range as for formaldehyde, for which calibration was **performed on PTR-MS**, these...”

Warneke, C., Veres, P., Holloway, J. S., Stutz, J., Tsai, C., Alvarez, S., Rappenglueck, B., Fehsenfeld, F. C., Graus, M., Gilman, J. B., and de Gouw, J. A.: Airborne formaldehyde measurements using PTR-MS: calibration, humidity dependence, inter-comparison and initial results, Atmos. Meas. Tech., 4, 2345-2358, 10.5194/amt-4-2345-2011, 2011

*R1.4 Pg 6212 In 23: the reaction time is stated as \_100 microseconds for the given E/N value of the PTR-MS drift tube. It should also be stated if the reaction time in the ULWPTR- MS drift tube based on the information in Table 2 is significantly different from 100 microseconds.*

Thanks for the suggestion and we have adopted it. The following text has been added to the manuscript (P7, L193):

“These settings give a reaction time  $t$  of ~100 ms, **which is not significantly different from other PTR instruments in Table 2.**”

*R1.5 Pg 6214 In 8: “Little water interference” should be replaced with a more quantitative Statement When referring to a four day period shown in figure 6c the authors state “The measurements from both instruments show reasonable agreement during this short time period, confirming the potential of PTR-MS for*

*accurate H<sub>2</sub>S measurements.” Please state the agreement here quantitatively using regression analysis, or show the residual difference between the two instruments. This is especially pertinent because later when graphing PTR-MS vs CRDS the slope is 1.24 (pg6221 In 1) which denotes an instrument offset or interference in one of the measurements.*

Thanks for the comments. The correlation ( $r^2$ ) between the m/z 35 background signal and the water mixing ratio was 0.005, and this quantitative statement has been replaced with the text “little water dependence” (P14, L391):

**“The correlation between background signals of m/z 35 and water vapor mixing ratio is very small ( $r^2=0.005$ ), indicating that the background data from the catalytic converter serves as a good zero for the H<sub>2</sub>S removal (background < 0.5 ncps).”**

The goal of Fig.6 is to show the detailed processes for interpreting the raw signals from PTR-MS (cps) to H<sub>2</sub>S mixing ratios. The comparison in Fig. 6C verifies the results from these interpretation process for 4 days only. This presentation is then followed by a quantitative comparison of the two measurements for the entire time series in Fig. 7. We feel that adding regression data and correlation analysis for the 4-day period shown in Fig. 6 would be somewhat superfluous and even confusing to the reader, since it would add a second set of statistics to describe the agreement between the two measurements. No change has been made in response to this comment.

*Technical Corrections:*

*R1.6 Pg 6802 Line 18: “160 ppbv to 14 ppbv per 24 h averaging time” should be “14 ppbv to 160 ppbv”*

Thanks for the comment and we have adopted it.

*R1.7 Pg 6811 Line 15: recommend changing “Pt catalyst” to “platinum catalyst”*

Thanks for the comment. We adopted this suggestion by altering the text to:

**“platinum (Pt) catalyst”**

*R1.8 Pg 6811 Line 16: recommend changing “removing VOCS” to “removing VOCs and H<sub>2</sub>S”*

Thanks for the comment and we have adopted it.

*R1.9 Pg 6815 Line 12: I think “(> 18.1 MΩ cm<sup>-1</sup>)” should be “(< 18.1 MΩ cm<sup>-1</sup>)”*

The resistivity of water is a measure of the water pureness. The more pure the water, the higher the resistivity is. Here it shows the purified water has a purity level above > 18.1 MΩ cm<sup>-1</sup>.

*R1.10 In the text most references to humidity (for example pg6215 line 24) are in percent when referring to figures (such as figure 4), however the units of humidity in figure 4 are in g/kg. Units are also in g/kg when stating the range of humidity measured during the campaign (pg6218 line 20). Please revise to be consistent throughout.*

Thanks for the comment. In order to be consistent, the units for water mixing ratios are modified to “g/kg” here and elsewhere in the paper.

*R1.11 Figure 2: the label “equilibrium” could be omitted.*

Thanks for the suggestion, but we would prefer to keep it to indicate the typical conditions in the drift tube are not in equilibrium.

*R1.12 Figures 3,6,7,10: The time axis should be labeled “Time (MST)” or “Local time (MST)” Since MST isn’t defined in the text, a designation relating MST to UTC should be given in the caption (such as Mountain Standard Time (MST) = UTC -7hr)*

Thanks for the comment and we have adopted it. The first place mentioning “MST” in the caption of Figure 3 has been added:

**“Local time, i.e. Mountain Standard Time (MST) = UTC -7hr is used in all the time-series plots.”**

*R1.13 Figure 6c: Please relocate the legend as to not obscure data.*

Thanks for the comment and we have adopted it.

*R1.14 Figure 9: y-axis label should omit “KIT” in “KIT-ULW-PTR-MS” to be consistent with the rest of the manuscript. Sometimes the PTR-MS is called the PTR-QMS such as in figure 9, or as the NOAA PTR-MS, please revise for consistency throughout the article. The CRDS is often just referred to as the “Picarro” instrument, (such as in figure 4, 10, and multiple times in the text) I would consider referring to the instrument as a “CRDS” instrument such as is done in figure 11. This convention gives the reader more information on what type of instrument is used as opposed to the name of an instrument manufacturer. Also the instrument is first introduced in the paper as CRDS (pg6209 line 18, pg6211 line 5, pg62). Furthermore a designation such as H2S/CH4 CRDS can be used to differentiate the two CRDS instruments. In any case the designation of the CRDS instrument should be made consistent throughout the manuscript.*

Thanks for the comment and we changed the Fig. 9 label and other places to be consistent with instrument names throughout the paper. All the “Picarro” are also changed to “CRDS”.

In Fig.9, the y-axis label is changed to **“ULW-PTR-MS”**, and the x-axis label **“PTR-MS”**.

*R1.15 General comment concerning graph axis labels: the format m35, mass 35, and m/z*

*35 for example are used for axis labels. Please revise for consistency. Although  $z=1$  in almost all ions in PTR-MS I would recommend using the convention of "m/z" as opposed to "m".*

Thanks for the comment and we changed all the "m" and "mass" to "m/z".