

Response to reviewers for the paper “Measurements of hydrogen sulfide (H₂S) 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 #2

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 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.

Thanks for the comment. Briefly, in previous papers we have shown that the sensitivities of a number of VOCs can indeed be calculated using reaction kinetics and showed good agreement with the laboratory calibration results (Warneke, et al., 2003). Please see our response to R2.9 for more details and text revision related to this issue.

Minor Comments

R2.1. 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.

Thanks for the comment and we have adopted it.

R2.2. 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.

Thanks for the comment and we have added the E/N ratio in Table 2 for each instrument.

R2.3. 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.

This issue has been already addressed in response to comment R1.3. In addition, all the water mixing ratios are modified to water mass mixing ratio in g/kg through the paper for consistency.

The mass mixing ratio is used because the H₂S sensitivity equation (Eq. 6) requires water mass mixing ratio in g/kg. Therefore, Fig 4 also uses water mass mixing ratio to display the fit with this sensitivity equation.

R2.4. 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 from the paper when you say things like we tried this but it didn't work.

As described above, reaction kinetics indeed have provided a good basis for understanding the performance of the PTR-MS. While calibrations are needed for the most accurate measurements, we strongly believe that understanding the performance of an instrument in detail is important and ultimately leads to better measurements. [Therefore, we would prefer to keep this section in detail.](#)

R2.5. 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.

This is a good question. Previous study (Tanaka et al., 1978) on rate constant measurements for H₂S proton transfer reaction shows the water cluster ions H₃O⁺•H₂O does not react with H₂S rapidly ($< 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$). No evidence for the occurrence of competing reaction channels and complications were observed in the measurements of the H₂S proton transfer reactions. Therefore, the H₂S protonation by water cluster ions are assumed not to be important. The following text has been added to section 2.1 (P6, L167):

“It should also be noted that H₂S proton transfer reaction with water cluster ions H₃O⁺•H₂O are not important due to a much slower reaction rate ($<10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). No occurrence of competing channels by the water clustering reactions was observed in the measurement for H₂S protonation under a wide range of humidity conditions (Tanaka et al., 1978). Therefore, the H₂S reaction with water cluster is neglected in this work.”

Reference:

Tanaka, K., Mackay, G. I., and Bohme, D. K.: Rate and equilibrium constant measurements for gas-phase proton-transfer reactions involving H₂O, H₂S, HCN, and H₂CO, Canadian Journal of Chemistry, 56, 193-204, 10.1139/v78-031, 1978.

R2.6. Does humidity also impact the reaction time since H₃O⁺ clusters are more important at higher humidity?

This is a good question. The ion mobility of the H₃O⁺.H₂O clusters is lower and thus the reaction time will be slightly higher (Warneke et al., 2001). Another small effect is that ion mobilities in general will be slightly lower in air-water vapor mixtures than in just pure air. But we assume these effects are negligible. The following texts have added to address this issue (P7, L194):

“At higher water concentration, the reaction time is slightly lower due to a higher fraction of water clusters, which have a lower ion mobility (Warneke et al., 2001). Another small effect is that ion mobilities in general are slightly lower in air-water vapor mixtures than in pure air. But these effects are very small and have been neglected in this work.”

Warneke, C., C. van der Veen, S. Luxembourg, J. A. de Gouw, and A. Kok (2001), Measurements of benzene and toluene in ambient air using proton-transfer-reaction mass spectrometry: calibration, humidity dependence, and field intercomparison, *Int. J. Mass Spectrom.*, 207(3), 167–182.

R2.7. 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.

Thanks for the comments. A is the ratio of transmission efficiencies for H₃S⁺ and H₃O⁺ ions, which depends on (i) the extraction efficiency of ions from the drift tube into the quadrupole, (ii) the transmission efficiency of the mass spectrometer, and (iii) the detection efficiency of the electron multiplier for each mass. “Constant” was used for A is because it is relative constant in each instrument compared to the

variables in the sampling conditions. We typically do not change settings on the instrument for that very reason. This includes the high voltage to the detector, which we don't like to change during an experiment. If we do change it, we typically try to follow up shortly with a new calibration. The stability of calibration factors thus obtained have been shown in previous work (de Gouw et al., 2003) (Fig 4). The word "constant" has been changed to "factor", and the following text has been added to the manuscript to clarify A term (P11, L315).

"A is a factor that is determined by the ratio of transmission efficiencies for H_3S^+ and H_3O^+ ions, which varies in different PTR-MS instruments with different settings. Typically, A is relatively constant since the voltages to the detector and ion extraction are not changed frequently, and thus stable calibration factors can be obtained (de Gouw et al., 2003)"

de Gouw, J. A., P. D. Goldan, C. Warneke, W. C. Kuster, J. M. Roberts, M. Marchewka, S. B. Bertman, A. A. P. Pszenny, and W. C. Keene (2003), Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002, *J. Geophys. Res.-Atmos.*, 108(D21), 4682, doi:10.1029/2003JD003863.

R2.8. 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?

Thanks for the comments and the following text has been added to the manuscript to address this issue (P16, L442).

"The impurity ions O_2^+ formed from the air back streaming in the ion sources and can be reduced by tuning the voltages on the intermediate chamber between ion source and drift tube. HO_2^+ is likely generated by endothermic proton transfer during ion extraction at the end of drift tube and this interference can be reduced by optimizing those voltage settings."

R2.9. 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 H₃O⁺ 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 (~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.

The reviewer wonders how well we understand the reaction kinetics, when the sensitivity for similar compounds can vary significantly between campaigns.

We usually tune our instrument specifically for each field campaign. If the focus of a campaign includes for example acetonitrile (mass 42) or methanol (mass 33), we tune the instrument to be more sensitive at lower masses. If the focus is on larger aromatics (m₁₂₁, 135, ...) or monoterpenes (mass 137), we tune the instrument to be more sensitive at higher masses. This is the reason why we have different sensitivities for each campaign.

During each campaign we do not implement changes in the tuning and we calibrate the PTR-MS frequently for compounds with a range of masses, usually at least every

other day. With this calibration, we not only verify our instrument sensitivity for the measured compounds, but can also determine the mass transmission specific for each mass accurately (factor A in Eq 5 of the manuscript). This tuning only effects the extraction from the ions out of the drift tube, but not the conditions where the reactions take place and as a result the reaction kinetics does not change between the campaigns.

As demonstrated in our previous work, reaction kinetics in the PTR-MS instruments are well understood ((Warneke et al., 2003) Fig 3B). Together with the mass transmission efficiency that we determine accurately for each campaign, we have a very good understanding of the reaction kinetics determining the sensitivity for each compound. Therefore we think that the theoretical sensitivity calculation of H₂S is very useful and we would like to keep the discussion. We have added the following explanations to the text.

(P5, L139) “During these studies, regular calibrations were performed using standard gas mixtures every other day.”

(P11, L300) “Previous studies have demonstrated a reasonable agreement between the calibration measurements and the theoretical calculation using rate coefficients for proton transfer reactions for a number of VOCs with little humidity dependence (Warneke et al., 2003). In this study, the theoretical H₂S sensitivities as a function of humidity are also investigated and compared to the laboratory calibration.”

(P12, L317): “For different studies the instruments were usually tuned to optimize the measurement of the compounds of interest, and therefore, the A factor and sensitivities may be different. Using the calibration measurements in the field and the laboratory A is verified for compounds in the calibration standard and can be calculated for all other masses.”

(P39, L793) “The calibration factors shown here are average of calibrations performed during the campaign.”

Reference:

Warneke, C., de Gouw, J. A., Kuster, W. C., Goldan, P. D., and Fall, R.:
Validation of Atmospheric VOC Measurements by Proton-Transfer- Reaction
Mass Spectrometry Using a Gas-Chromatographic Preseparation Method,
Environmental Science & Technology, 37, 2494-2501, 10.1021/es026266i, 2003.