



Measurements of
hydrogen sulfide
(H₂S) using PTR-MS

R. Li et al.

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

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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AMTD

7, 6205–6243, 2014

Measurements of hydrogen sulfide (H₂S) using PTR-MS

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Natural gas production is associated with emissions of several trace gases, some of them classified as air toxics. While volatile organic compounds (VOCs) have received much attention, hydrogen sulfide (H₂S) can also be of concern due to the known health impacts of exposure to this hazardous air pollutant. Here, we present quantitative, fast time-response measurements of H₂S using Proton-Transfer-Reaction Mass-Spectrometry (PTR-MS) instruments. An Ultra-Light-Weight PTR-MS (ULW-PTR-MS) in a mobile laboratory was operated for measurements of VOCs and H₂S in a gas and oil field during the Uintah Basin Winter Ozone Study (UBWOS) 2012 campaign. Measurements of VOCs and H₂S by a PTR-MS were also made at the Horse Pool ground site in the Uintah Basin during UBWOS 2013. The H₂S measurement by PTR-MS is strongly humidity dependent because the proton affinity of H₂S is only slightly higher than that of water. The H₂S sensitivity of PTR-MS ranged between 0.6–1.4 ncps ppbv⁻¹ (normalized counts per second/parts per billion by volume) during UBWOS 2013. We compare the humidity dependence determined in the laboratory with in-field calibrations and determine the H₂S mixing ratios for the mobile and ground measurements. The PTR-MS measurements at Horse Pool are evaluated by comparison with simultaneous H₂S measurements using a PTR Time-of-Flight MS (PTR-ToF-MS) and a Picarro cavity ring down spectroscopy (CRDS) instrument for H₂S/CH₄. On average 0.6 ± 0.3 ppbv H₂S was present at Horse Pool during UBWOS 2013. The correlation between H₂S and methane enhancements suggests that the source of H₂S is associated with oil and gas extraction in the basin. Significant H₂S mixing ratios of up to 9 ppmv downwind of storage tanks were observed during the mobile measurements. This study suggests that H₂S emissions associated with oil and gas production can lead to short-term high levels close to point sources, and elevated background levels away from those sources. In addition, our work has demonstrated that PTR-MS can make reliable measurements of H₂S at levels below 1 ppbv.

Measurements of hydrogen sulfide (H₂S) using PTR-MS

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1 Introduction

Hydrogen sulfide (H_2S) is a flammable gas that is highly toxic at low concentrations; e.g., at 10–20 ppmv H_2S starts causing eye irritation and at levels above 150 ppmv it is life threatening. The primary emission sources of H_2S to the atmosphere include volcanic eruptions, natural decomposition of sulfates and sulfur-containing organic compounds by anaerobic bacteria, and anthropogenic release from industrial processes. H_2S is also emitted from coal pits, landfills, livestock manure, thermal or polluted waters and septic systems (Environmental Protection Agency et al., 1993). Hydrogen sulfide is a major impurity in natural gas that needs to be removed prior to use. In oil and gas operations, H_2S can be released routinely or accidentally at wellheads, piping, separation and storage tanks (Environmental Protection Agency et al., 1993; Tarver and Dasgupta, 1997). Previous H_2S studies in oil fields indicated that hydrogen sulfide was the dominant reduced sulfur gas in all the sampled oil producing locations (Tarver and Dasgupta, 1997).

One study showed that the mixing ratios of H_2S in ambient air range from 0.02–0.07 ppbv in undeveloped rural areas to 0.11–0.33 ppbv in urban areas (ATSDR, 2006). Ambient air quality guidelines for H_2S have been developed in many states, which range from 160 ppbv to 14 ppbv per 24 h averaging time. H_2S is regulated under a number of United States statutes, including Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Emergency Planning and Community Right-to-Know Act (EPCRA), and the Prevention of Significant Deterioration (PSD) program of the EPA for regulation of new oil and gas well sources (Dubyk, 2002; ATSDR, 2006). The familiar “rotten egg” odor of H_2S becomes detectable by humans at concentrations of 3–20 ppbv. However, higher concentrations of H_2S in the 150–250 ppmv range can cause olfactory paralysis. At these concentrations, the olfactory sense may be lost and exposed persons may be unaware of the presence of the toxic gas. Thus, odor cannot be relied upon as a warning sign of possible exposure to H_2S (Environmental Protection Agency et al., 1993). Little public data exist to determine

AMTD

7, 6205–6243, 2014

Measurements of hydrogen sulfide (H_2S) using PTR-MS

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



laboratory settings in spite of various analytical challenges (Feilberg et al., 2013). In this work, we characterized the humidity dependence of the instrument responses to H₂S of PTR-MS, and explored its application for quantitative measurements of H₂S in the air over an oil and gas field.

2 Experimental

The Uintah Basin in northeastern Utah (Fig. 1), a region with approximately 8000 gas wells and 2000 oil wells in operation, experienced high wintertime surface ozone concentrations in the winters 2009/2010 and 2010/2011 (Martin et al., 2011). Two field intensives, the Energy and Environment – Uintah Basin Winter Ozone Study (UBWOS), were conducted in the winters of 2012 (15 January–28 February) and 2013 (15 January–28 February). An extensive suite of research instruments were deployed by a large group of scientists from different institutions at a well pad (named Horse Pool, 40.143° N; 109.468° W; 1530 m elevation) located on the northern edge of the gas field, 20 miles south of Vernal, UT in both years. The NOAA Earth System Research Laboratory (ESRL) also surveyed the Uintah Basin with an instrumented van, called here the Mobile Laboratory, to document ambient levels of methane and ozone precursors downwind of various point sources. The main goals of this project were to quantify the emission of ozone precursors from the oil and gas wells, and to understand the mechanisms of ozone formation in the basin in winter.

Measurements of H₂S were made in the oil and gas field in the Uintah basin during the UBWOS 2012 and 2013, and during a laboratory study on H₂S detection by PTR-MS after the 2013 UBWOS campaign (all measurements used here are summarized in Table 1). During UBWOS 2012 an Ultra-Light-Weight Proton-Transfer-Reaction Mass Spectrometer (ULW-PTR-MS, ~ 55 kg) was fielded together with a PTR-MS (de Gouw and Warneke, 2007). The ULW-PTR-MS was installed in the NOAA ESRL Mobile Laboratory for two weeks in February 2012 to make measurements downwind of point sources in the Uintah basin. In 2013, we further explored H₂S detection by

Measurements of hydrogen sulfide (H₂S) using PTR-MS

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



PTR-MS is affected by humidity and has a relatively low sensitivity. However, drying the sample flow to eliminate the humidity dependence of the sensitivity is not an option, because it will also result in losing many VOCs along with the water. The kinetics of the analogous reactions with formaldehyde (HCHO) has been studied in detail by Vlasenko et al. (2010), Warneke et al. (2011b), Inomata et al. (2008) and for HCN by Knighton et al. (2009). In a manner analogous to that work, the humidity dependent concentration of H_3S^+ ion in the drift tube is given by:

$$[\text{H}_3\text{S}^+] = [\text{H}_3\text{O}^+] \frac{k_1[\text{H}_2\text{S}] (1 - e^{-k_{-1}[\text{H}_2\text{O}]t})}{k_{-1}[\text{H}_2\text{O}]} \quad (1)$$

Where $[\text{H}_2\text{S}]$, $[\text{H}_2\text{O}]$ and $[\text{H}_3\text{O}^+]$ are drift tube concentrations of H_2S , water and hydronium ions, respectively, and t is the reaction time. Although the rate coefficient of the forward reaction (Reaction R1) is higher than of the reverse reaction rate coefficient (Reaction R-1) (i.e. $k_1 \gg k_{-1}$), the mixing ratio of water (typically 1%) in the drift tube is much higher than H_2S (< 10 ppbv) (i.e. $[\text{H}_2\text{O}] \gg [\text{H}_2\text{S}]$). The ratio $(k_1 \times [\text{H}_2\text{S}]) / (k_{-1} \times [\text{H}_2\text{O}])$ determines the final $[\text{H}_3\text{S}^+]$ in the drift tube. It should be noted that the ion kinetic energy is elevated in the drift tube, and that the endothermic reactions (i.e. Reaction R-1) may be more important than based solely on the reaction enthalpy. As a result of back reaction (R-1), the production of protonated H_2S is much less efficient than production of most protonated VOCs. In Eq. (1), $[\text{H}_3\text{S}^+]$ is strongly dependent on the H_2O concentration and the reaction time t . In Fig. 2, the $[\text{H}_3\text{S}^+]$ in the drift tube calculated from Eq. (1) is plotted as a function of reaction time at various humidity conditions. The reaction time t is determined by the ion drift velocity, which is a function of the parameter E/N , where E is the electric field and N the number density of the gas in the drift tube (de Gouw and Warneke, 2007). The instrument settings used in this study are typical for the PTR-MS and are given in Table 2. These settings give a reaction time t of $\sim 100 \mu\text{s}$. It is worth noting that the forward and backward reactions are not necessarily in equilibrium. From Fig. 2 it is clear that at low water

Measurements of hydrogen sulfide (H_2S) using PTR-MS

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



an enhancement of 3 orders of magnitude over ambient levels. Because the ULW-PTR-MS was not calibrated, the mobile laboratory H₂S data is shown here in cps. Assuming that the sensitivity of the ULW-PTR-MS for H₂S was in the same range as for formaldehyde, for which calibration was made, these occasionally high count rates suggested that H₂S was in the ppmv range. Such high mixing ratios were the motivation for the measurements described in the following. We will return to these data at the end of this paper.

3.2 Laboratory calibration

Laboratory calibrations for H₂S were performed after UBWOS 2013 using the PTR-MS and PTR-ToF-MS at different humidities. Zero air was split using two mass flow controller (Tylan FC-260) channels, one of which passed air through a water bubbler filled with purified water (> 18.1 MΩ cm⁻¹) at 20 °C for humidification. Assuming near-saturation (23.3 mbar vapor pressure at an ambient pressure of 844 mbar and 20 °C) the water mixing ratio in the humidified channel was 2.84 %. The humidified zero air was mixed with dry zero air. This way the water vapor mixing ratio in the dilution gas was held at a constant level for individual calibration runs and could be changed rapidly from one setting to the next. The total flow rate of the humidified dilution gas stream was kept at approximately 500 sccm (cm³ min⁻¹ at STP) and was measured volumetrically (Bios DryCal Definer 220) for each humidity setting. Up to 5 sccm (Unit Mass Flow Controller) of H₂S from a calibration standard (10.08 ppmv ± 2 % H₂S in N₂; Scott-Marrin, Inc, Riverside, CA) was dynamically diluted with the humidified zero air and was sampled by both PTR instruments simultaneously. Calibrations with four concentration levels (between 41 ppbv and 100 ppbv H₂S) were performed at 6 humidity levels (water mixing ratios between 0 and 2.61 %). In Fig. 4, the signals on *m/z* 35 normalized to primary ion signals H₃O⁺ (in units of 10⁶ counts s⁻¹) from (Fig. 4a) PTR-MS and (Fig. 4b) PTR-ToF-MS are plotted vs. the mixing ratio of H₂S at different humidities. Calibrations at each individual humidity levels are fit separately by linear regression

Measurements of hydrogen sulfide (H₂S) using PTR-MS

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(lines in Fig. 4a and b, respectively). Observed slopes are the instrument sensitivities for different humidities and are plotted vs. water vapor mixing ratio in Fig. 4c and d.

The PTR-MS had an average primary ion signal of 25 million cps and the PTR-ToF-MS had 8.8 million cps with duty cycle corrected (about 1.2 million cps actual counts) on average during UBWOS 2013. The differences in normalized sensitivities (in ncps ppbv⁻¹) are likely due to the ion extraction and discrimination against smaller masses that are different between the quadrupole and time-of-flight mass spectrometers. As the absolute signal of the PTR-MS is higher, the sensitivity of the PTR-MS (in cps ppbv⁻¹) can be higher than that of the PTR-ToF-MS.

As shown in Eq. (1), the H₃S⁺ ion signals are dependent on water concentration in the drift tube, which is governed by the water vapor concentration in the sample gas and by the amount of water vapor from the ion source leaking into the drift tube (Vlasenko et al., 2010; Warneke et al., 2011b). The resulting water vapor concentration in the drift tube is expressed as water vapor mass mixing ratio instead of water vapor number concentration, because mixing ratio is a conserved value as gas moves from ambient pressure into the drift tube at lower pressure. The calibration curves in Fig. 4 are color-coded with the water vapor mixing ratio in the sample gas. The sensitivity decreases when sample air humidity increases as the reverse proton transfer reaction (R-1) becomes more important with higher humidity. An exponential fit derived from Eq. (1) is used to describe the humidity dependence of the H₂S sensitivities. From the definition of the sensitivity, which is defined as the signal of RH⁺ ions (*I*_{RH⁺}) obtained at a mixing ratio of 1 ppbv and normalized to a H₃O⁺ signal (*I*_{H₃O⁺} of 10⁶ cps; de Gouw and Warneke, 2007), the H₂S sensitivity can be expressed as

$$\text{H}_2\text{S Sensitivity} = \frac{I_{\text{H}_3\text{S}^+}}{I_{\text{H}_3\text{O}^+}} \times \frac{10^6}{\text{H}_2\text{S}_{\text{VMR}}} \quad (2)$$

Where H₂S_{VMR} is the H₂S volume mixing ratio (VMR) in ppbv

$$\text{H}_2\text{S}_{\text{VMR}} = \frac{[\text{H}_2\text{S}]}{N \times 10^{-9}} \quad (3)$$

Measurements of hydrogen sulfide (H₂S) using PTR-MS

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and N is the air number concentration in unit of molecule cm^{-3} in the drift tube. H_3S^+ and H_3O^+ signals are related to their ion concentrations in the drift tube

$$\frac{I_{\text{H}_3\text{S}^+}}{I_{\text{H}_3\text{O}^+}} = \frac{[\text{H}_3\text{S}^+]}{[\text{H}_3\text{O}^+]} \times A \quad (4)$$

A is a constant that is determined by the ratio of transmission efficiencies for H_3S^+ and H_3O^+ ions. A previous study has shown A is mass dependent and increases with molecular weight (Warneke et al., 2011a). In this study of H_2S , A is assumed to be ~ 1.5 for PTR-MS based on the measured value of 1.6 for acetonitrile (mass 42) (de Gouw et al., 2003). For PTR-ToF-MS, A is 1 for H_3S^+ vs. H_3O^+ due to duty cycle correction on the ToF data (Müller et al., 2013). By substituting Eqs. (1), (3) and (4) into Eq. (2), the H_2S sensitivity can be described as an exponential function of water:

$$\text{H}_2\text{S Sensitivity} = A \times 10^6 \times \frac{k_1 \left(1 - e^{-k_{-1}[\text{H}_2\text{O}]t}\right)}{k_{-1}[\text{H}_2\text{O}]} \times N \times 10^{-9} \quad (5)$$

The water concentration in the drift tube includes water vapor from the sampled air and from the ion source, which can be expressed as mass mixing ratio ($\text{H}_2\text{O}_{\text{sample}}$ and $\text{H}_2\text{O}_{\text{ion source}}$ in unit of g kg^{-1})

$$[\text{H}_2\text{O}] = (\text{H}_2\text{O}_{\text{sample}} + \text{H}_2\text{O}_{\text{ion source}}) \times \frac{M_{\text{air}}}{M_{\text{water}}} \times 10^{-3} \times N \quad (6)$$

The molecular masses of air (M_{air}) and water (M_{water}) are 29 g mol^{-1} and 18 g mol^{-1} . Using known coefficients k_1 and k_{-1} from literature, reaction time t , air number concentration N and the sampled air humidity ($\text{H}_2\text{O}_{\text{sample}}$), the H_2S sensitivity can be fit by Eq. (5) as a function of $\text{H}_2\text{O}_{\text{sample}}$ for the data shown in Fig. 4c and d. The free parameters in the fit are the transmission ratio A and $\text{H}_2\text{O}_{\text{ion source}}$, which is the offset

AMTD

7, 6205–6243, 2014

Measurements of hydrogen sulfide (H_2S) using PTR-MS

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Measurements of
hydrogen sulfide
(H₂S) using PTR-MS**

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(x_{offset}) on the x-axis resulting from the additional water vapor from the ion source. The fit results give values for A of 0.3 ± 0.03 and 0.06 ± 0.006 for the PTR-MS and PTR-ToF-MS, respectively. These are unrealistic values suggesting that the known coefficients that were used for the fit were not all appropriate. As mentioned earlier, the coefficients of k_1 and k_{-1} obtained at 296 K may be different for the collision conditions in the drift tube. In fact, it is likely that they increase due to the elevated ion kinetic energy in the drift tube. Therefore, we re-fit the sensitivities by holding the transmission ratio A fixed with more reasonable values (1.5 and 1 for PTR-MS and PTR-ToF) and allowing k_{-1} as free parameters in the fit instead. As shown in Fig. 4c and d, the fit gives the same k_{-1} of $(3.0 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for PTR-MS and $(3.0 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for PTR-ToF, which are 2 orders of magnitude higher than the value obtained at ambient temperature ($4.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Tanaka et al., 1978). Such high values may also be unrealistic, so the most likely explanation may be a combination of uncertainties in the reaction rate coefficients as well as the mass transmission. The fit offsets of the water mixing ratio from ion source are $3.3 \pm 0.4 \text{ g kg}^{-1}$ and $1.1 \pm 0.2 \text{ g kg}^{-1}$ (corresponding to $(86.9 \pm 10.4) \%$ and $(29.1 \pm 5.2) \%$ RH at STP) for PTR-MS and PTR-ToF-MS, respectively. The exponential decay of the sensitivity from the laboratory calibration is well represented by the fit derived from the proton transfer Reactions (R1 and R-1).

As shown in Fig. 4c, the water vapor mixing ratios ranged from 1 to 6 g kg^{-1} during UBWOS 2013, which gives H₂S sensitivities ranging from $0.6\text{--}1.4 \text{ ncps ppbv}^{-1}$ (and $20\text{--}34 \text{ cps ppbv}^{-1}$) for PTR-MS and $0.5\text{--}1.9 \text{ ncps ppbv}^{-1}$ (and $1.0\text{--}2.2 \text{ cps ppbv}^{-1}$) for PTR-ToF-MS. This is much lower than for other VOCs, which typically have sensitivities ranging from $13.3 \text{ ncps ppbv}^{-1}$ for methanol to $31.3 \text{ ncps ppbv}^{-1}$ for acetone by PTR-MS (Warneke et al., 2011b). Figure 4c also shows a calibration conducted at the Horse Pool site during UBWOS 2013 (triangle point). A resulting sensitivity of $1.03 \text{ ncps ppbv}^{-1}$ was determined under ambient conditions. This value agrees within 20% with the laboratory calibration results.

The H₂S detection limit by PTR-MS was determined from the laboratory calibration measurements at H₂S VMR = 0. For the ambient humidity conditions during UBWOS 2013 (2.8 g kg⁻¹ on average), the H₂S detection limit by PTR-MS is 0.35 ppbv (signal-to-noise = 3).

3.3 Ambient measurements and inter-comparison

Here we demonstrate how the H₂S mixing ratios were determined from the ambient measurements by PTR-MS during a 4 day period between 29 January and 1 February 2013 at the Horse Pool site. This period was selected because it covered a wide range of humidities, H₂S and methanol levels. As described earlier, because of the high levels (100 s ppbv) of methanol from the gas and oil production in Uintah basin, there is interference in the H₃S⁺ signal from the methanol isotope containing oxygen isotope ¹⁸O. In Fig. 5, the measured signals at *m/z* 35 are plotted against the methanol signals at *m/z* 33 color-coded with H₂S mixing ratios measured by the Picarro during UBWOS 2013. For the data with low H₂S levels (purple-blue points), the signals at *m/z* 35 show a linear relationship with the signals at *m/z* 33. The linear slope, ~ 0.002, is equal to the natural abundance of the isotope ¹⁸O in methanol (0.2 %) and indicates that the signal CH₃¹⁸OH is dominating *m/z* 35. Of course there are also the ¹⁴C (carbon), ²D (deuterium) and ³T (tritium) isotopes, but their abundance is much smaller so we will ignore those here to simplify the discussion. It is clear that much of the signal at *m/z* 35 is from CH₃¹⁸OH. As the H₂S mixing ratio increases (yellow-red points), the relationship between signals at *m/z* 35 and *m/z* 33 diverts from the line attributed to the CH₃¹⁸OH signal. In these cases, H₂S is a significant contributor to the *m/z* 35 signals. This shows that the H₂S can be detected by PTR-MS at *m/z* 35. At several hundred ppbv of methanol as often observed at Horse Pool, the signal at *m/z* 35 was corrected for the contribution from CH₃¹⁸OH before the *m/z* 35 signal is used to obtain H₂S, which was calculated by subtracting the product of the methanol signal at *m/z* 33 multiplied by the natural abundance of the isotope ¹⁸O (0.2 %, Fig. 6a).

Measurements of hydrogen sulfide (H₂S) using PTR-MS

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4 Conclusion

In this paper we demonstrate fast time response measurements of H₂S using three different PTR-MS instruments that were operated at standard instrument settings for various VOCs detection in the Uintah Basin with oil and gas producing wells during two wintertime field studies in 2012 and 2013. Mobile laboratory measurements were made possible using a compact and lightweight ULW-PTR-MS during UBWOS 2012. The ULW-PTR-MS was not calibrated but showed varying levels of H₂S across the field and provided evidence for the existence of multiple point sources in oil and gas field, which prompted more work to explore the performance of PTR instruments for H₂S. During UBWOS 2013, H₂S was measured by the PTR-MS together with the PTR-ToF-MS for inter-comparison purposes. A specific calibration study for H₂S was undertaken for these field measurements. The humidity dependence of H₂S detection by PTR-MS was determined in the laboratory and agreed within 20 % with the calibration determined in the field for the PTR-MS instrument. The observed sensitivities at various humidities appear to be explained by kinetics when we allow for a higher backward reaction rate and an offset in water vapor concentration in the drift tube. The PTR-MS H₂S sensitivity was determined to be 0.6–1.4 ncps ppbv⁻¹ during UBWOS 2013, about 3–10 % of the sensitivity to most other compounds detected by PTR-MS. This is due to the proton affinity of H₂S that is only slightly higher than that of water, leading to a non-negligible backward proton transfer reaction. Inter-comparison of H₂S measurements shows the PTR-MS as a valid method for the measurement of H₂S. On average 4 ± 2 ppbv H₂S was observed from the NOAA ESRL Mobile Laboratory close to well-pads during UBWOS 2012 and 0.6 ± 0.3 ppbv H₂S at the Horse Pool site during UBWOS 2013 in the Uintah Basin, most likely due to routine emissions from oil and gas facilities, which was supported by evidence of the correlation between H₂S and CH₄. Significant H₂S mixing ratios up to 9 ± 4 ppmv from a condensation tank being serviced were observed during the mobile measurements. This study suggests that H₂S emissions associated with oil and gas production can lead to short-term high levels

Measurements of hydrogen sulfide (H₂S) using PTR-MS

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



close to point sources, and elevated background levels away from those sources. This study shows PTR-MS is able to make reliable measurements of H₂S down to levels of 350 pptv. Potentially better measurements are possible if the PTR instrument settings were optimized for H₂S.

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Measurements of hydrogen sulfide (H₂S) using PTR-MS

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Measurements of
hydrogen sulfide
(H₂S) using PTR-MS**

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Measurements of
hydrogen sulfide
(H₂S) using PTR-MS**

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Measurements of
hydrogen sulfide
(H₂S) using PTR-MS**

R. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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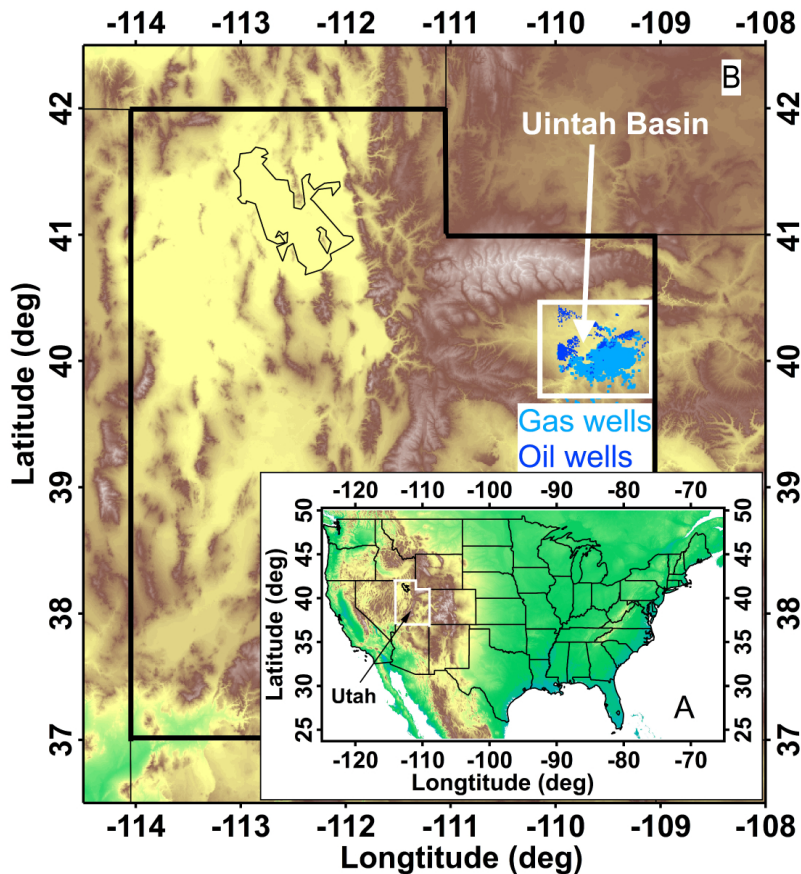


Figure 1. (A) The location of Utah in the overview map of United States. (B) The oil and gas wells in Uintah Basin, Utah.

Measurements of hydrogen sulfide (H₂S) using PTR-MS

R. Li et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Measurements of hydrogen sulfide (H_2S) using PTR-MS

R. Li et al.

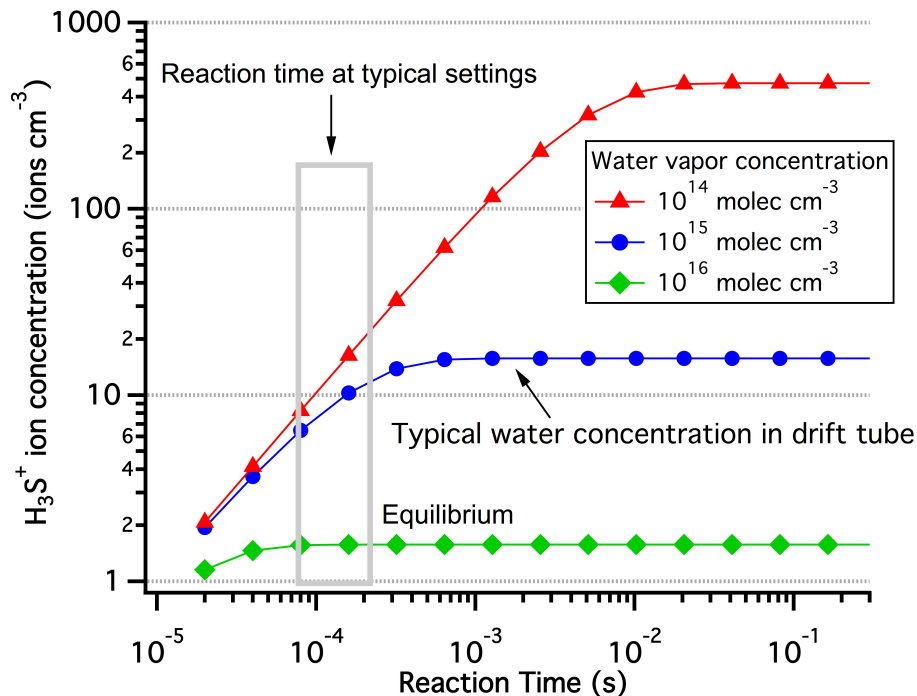


Figure 2. The concentration of H_3S^+ ions as a function of reaction time in the drift tube at different humidities. The water vapor concentration in the drift tube ranges from 0.5×10^{15} to 2×10^{15} molec cm^{-3} (equivalent to water vapor mixing ratio of 0.9–4.7 %).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Measurements of hydrogen sulfide (H_2S) using PTR-MS

R. Li et al.

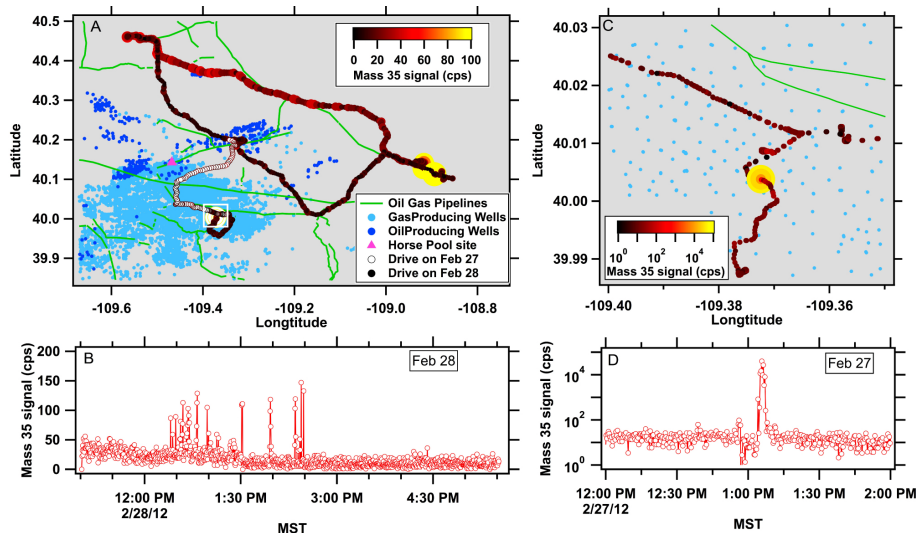


Figure 3. (A) Mobile laboratory tracks color- and size-coded with H_2S signal at m/z 35 by ULW-PTR-MS among the oil and gas wells in Uintah Basin during UBWOS 2012. (B) Time series of H_2S signal at m/z 35 on 28 February 2012 (solid points in A). (C) The area indicated by the white square in (A) for the drive on 27 February 2012. Note that the color scale of H_2S signals is in log scale. (D) The time series of H_2S measurements shown in (C). The peak H_2S mixing ratio observed during this drive was determined to be 9 ppmv using the calibrations developed further below in this paper.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


Measurements of hydrogen sulfide (H_2S) using PTR-MS

R. Li et al.

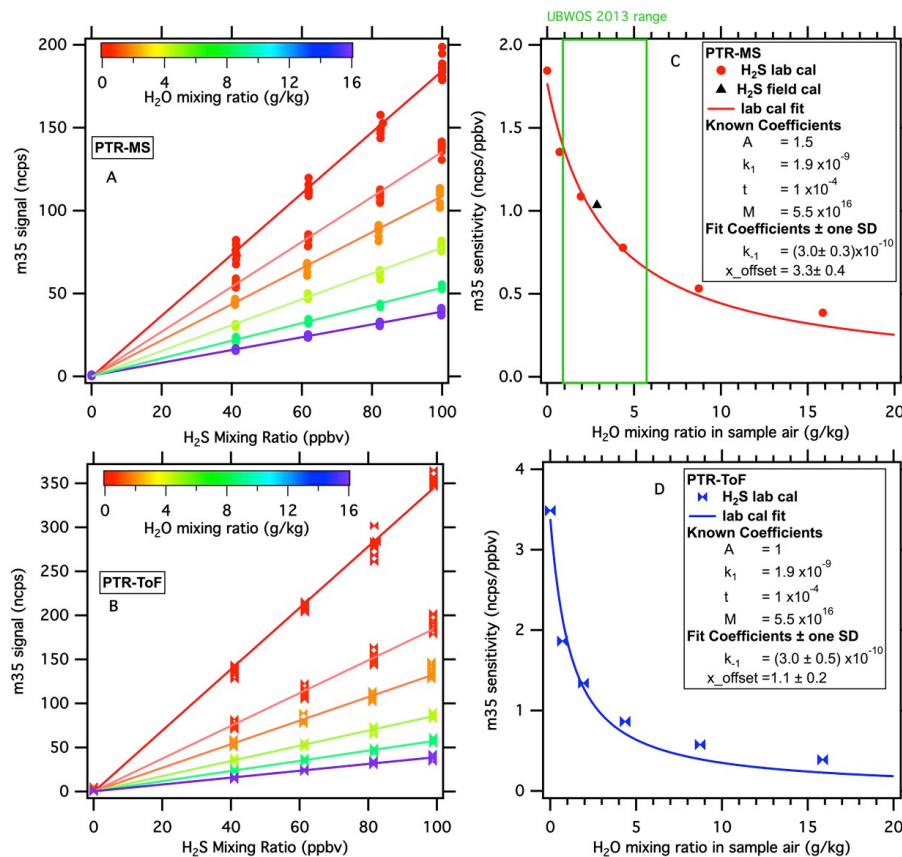


Figure 4. H_2S laboratory calibration curves at different humidities for (A) PTR-MS with an average H_3O^+ ion signals of 25 million cps and (B) PTR-ToF-MS with an average H_3O^+ of 8.8 million cps duty cycle corrected and 1.2 million cps actual counts. The sensitivity of (C) PTR-MS and (D) PTR-ToF-MS for H_2S measurement dependent on humidity with the exponential fit of Eq. (6).

Measurements of
hydrogen sulfide
(H₂S) using PTR-MS

R. Li et al.

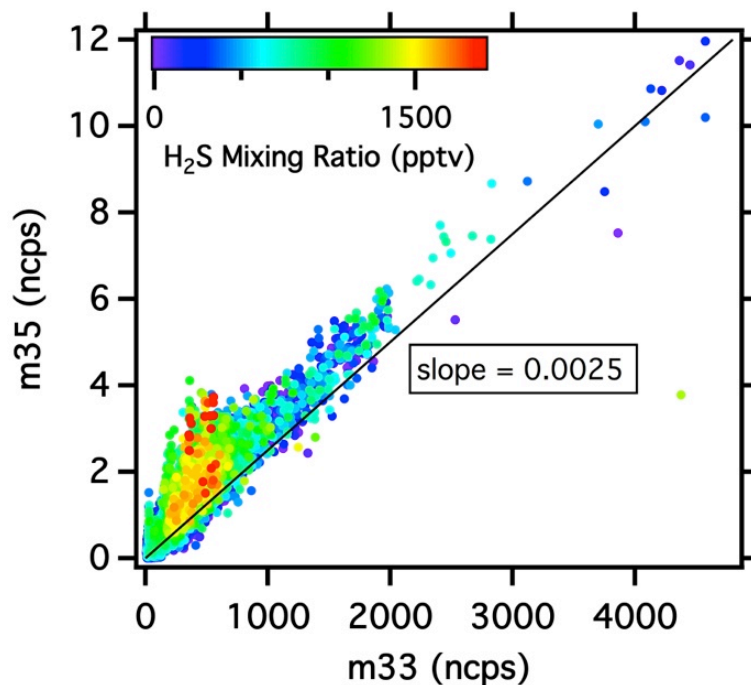


Figure 5. The relationship between m/z 35 and m/z 33 color-coded by the H₂S mixing ratio measured by the Picarro instrument. The line with a slope of 0.0025 that is the ¹⁸O natural abundance overlaps with the measurements at zero H₂S mixing ratio levels (purple points).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Measurements of hydrogen sulfide (H_2S) using PTR-MS

R. Li et al.

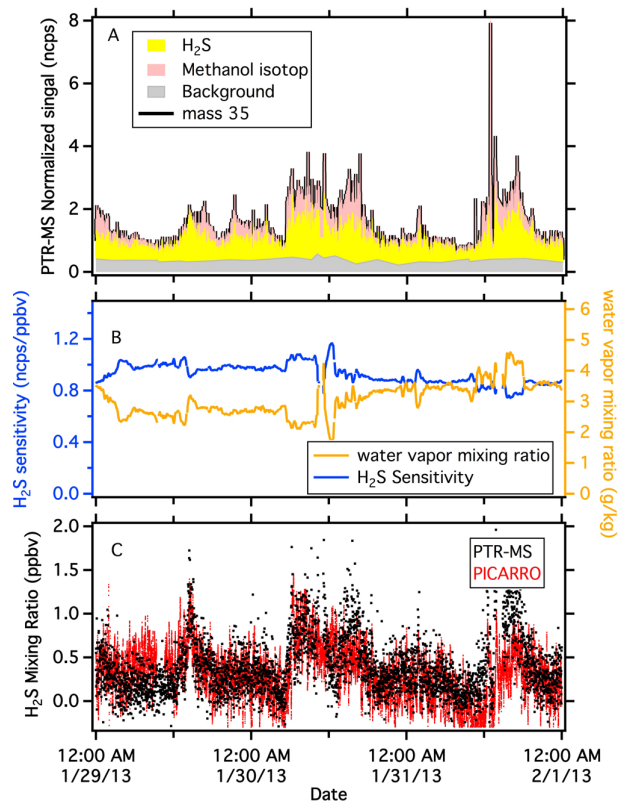


Figure 6. Time series of H_2S measurements during UBWOS campaign 2013. **(A)** PTR-MS raw signals at m/z 35 and the contributions from H_2S , $\text{CH}_3^{18}\text{OH}$ and instrument background. **(B)** Calibration factor estimated from the water vapor mixing ratio by the fit in Fig. 4. **(C)** H_2S mixing ratio comparison between the resulting PTR-MS and Picarro measurements. The signal from PTR-MS is 1 min average, and Picarro is an average of the last 5 min measurements over 5 s intervals.

Measurements of hydrogen sulfide (H₂S) using PTR-MS

R. Li et al.

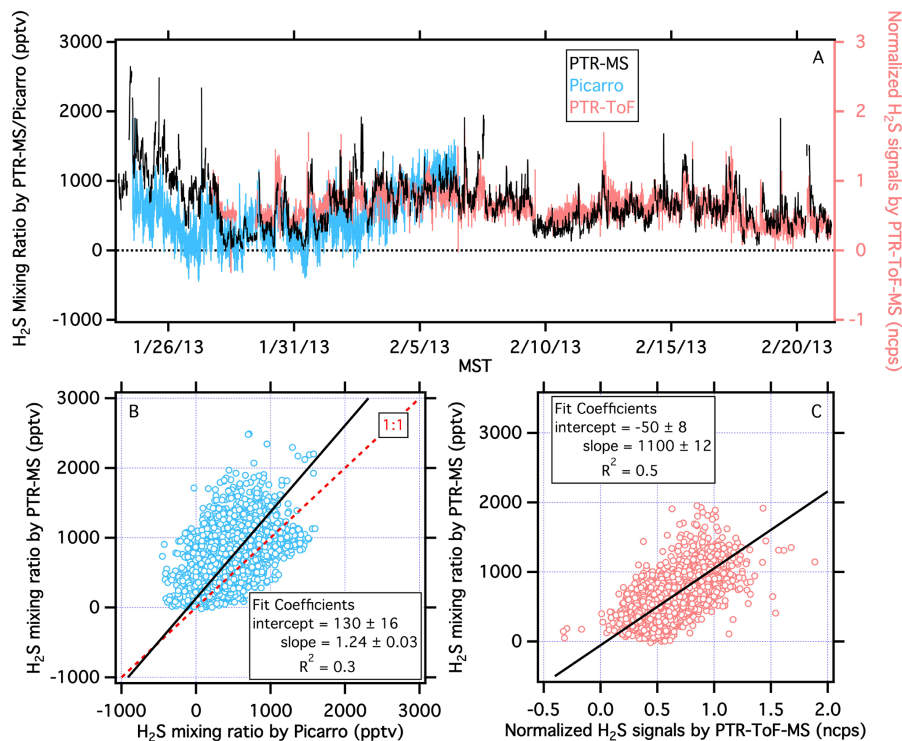


Figure 7. (A) Inter-comparison of H₂S measurements from PTR-MS, PTR-ToF-MS and Picarro during UBWOS 2013 at Horse Pool ground site. All the measurements are 5 min averaged. The PTR-MS and Picarro measurements are plotted in mixing ratio on the left axis. PTR-ToF-MS measurements are in normalized counts per second (ncps) on the right axis. (B) Scatter plot of H₂S measurements by PTR-MS vs. by Picarro. (C) Scatter plot of H₂S measurements by PTR-MS vs. by PTR-ToF-MS.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Measurements of hydrogen sulfide (H_2S) using PTR-MS

R. Li et al.

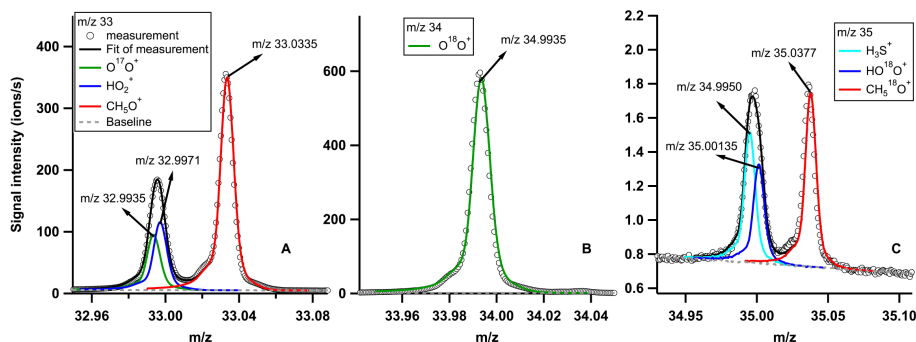


Figure 8. A common example of the mass spectra and peak fit for different species at m/z 33, 34 and 35 from the measurements of PTR-ToF-MS. **(A)** Two peaks are shown in the raw measurements at m/z 33. The first peak is contributed by both O_2^+ with ^{17}O isotope and HO_2^+ . The second peak is by methanol. **(B)** The signals at m/z 34 are from O_2^+ with ^{18}O isotope. **(C)** There are two peaks in the raw measurements at m/z 35. The first peak is contributed by a sum of H_3S^+ (protonated H_2S signal) and HO_2^+ with ^{18}O isotope. The second peak is from methanol with ^{18}O isotope.

Measurements of hydrogen sulfide (H₂S) using PTR-MS

R. Li et al.

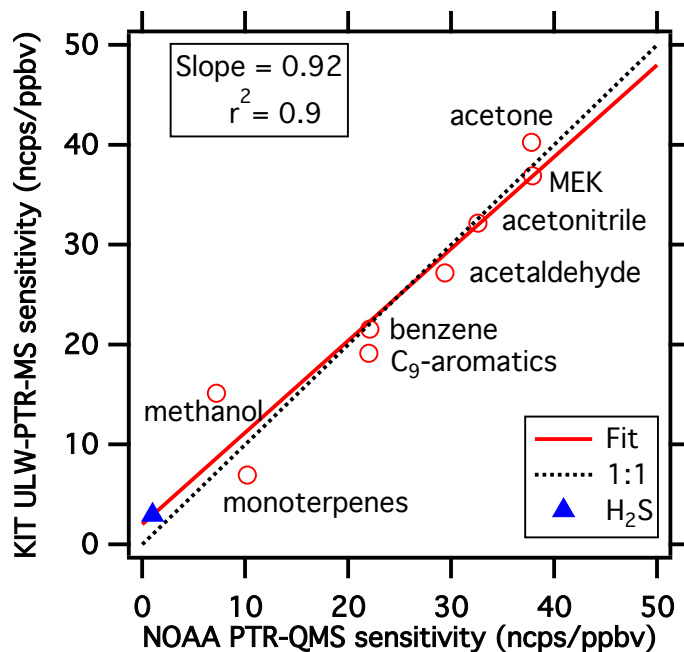


Figure 9. The estimate of ULW-PTR-MS calibration factor for H₂S (blue triangle) from NOAA PTR-MS calibration at the field site during the UBWOS 2013, based on the comparison of calibration results for other compounds between the two PTR-MS instruments (red fit line).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Measurements of hydrogen sulfide (H_2S) using PTR-MS

R. Li et al.

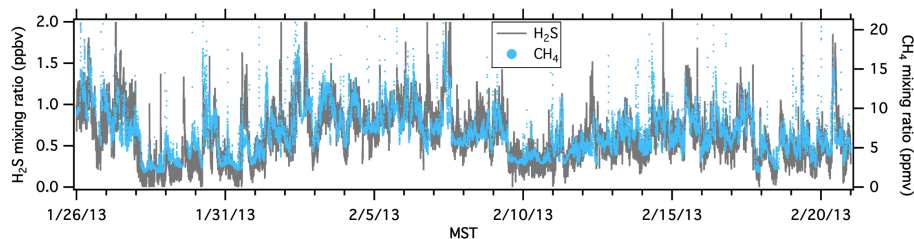


Figure 10. Time series of H_2S measurements by PTR-MS and CH_4 mixing ratios by Picarro during UBWOS 2013 at Horse Pool ground site.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Measurements of
hydrogen sulfide
(H₂S) using PTR-MS

R. Li et al.

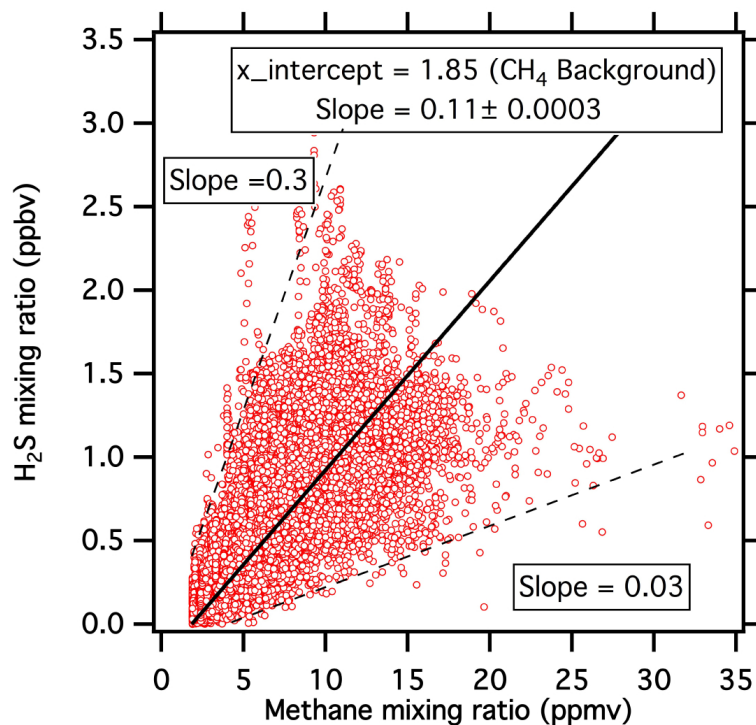


Figure 11. Scatter plot of H₂S mixing ratio measured by PTR-MS vs. methane measured by CRDS with linear fit to the data shown in Fig. 10. The slope values are in units of ppbv ppmv⁻¹. The dashed lines represent the maximum and minimum enhancement ratios.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

