Atmos. Meas. Tech. Discuss., 7, C1887–C1891, 2014
www.atmos-meas-tech-discuss.net/7/C1887/2014/

Atmospheric Measurement Techniques
Discussions

Interactive comment on “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” *by* R. Li et al.

Anonymous Referee #1

Received and published: 27 July 2014

General Comments:

The authors present the quantification of H2S 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 H2S 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 H2S quantification at sub ppbv mixing ratios. Therefore I recommend this

article for publication after the following specific points are clarified.

Specific Comments:

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 H2S 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 H2S as an ozone precursor, the introduction would be well served by including H2S relative or expected role in ozone production at UB.

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 H2S.)

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 H2S measurement.

Pg 6212 It is noted that the H2S 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 H2S 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 H2O flow rates used (Table 2) between the two PTR-MS instruments may cause the relative sensitivity for H2S 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?

Pg 6212 ln 23: the reaction time is stated as $\sim$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 ULW-PTR-MS drift tube based on the information in Table 2 is significantly different from 100 microseconds.

Pg 6214 ln 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 H2S 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 ln 1) which denotes an instrument offset or interference in one of the measurements.

Technical Corrections:

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

160 ppbv”

Pg 6811 Line 15: recommend changing “Pt catalyst” to “platinum catalyst”

Pg 6811 Line 16: recommend changing “removing VOCS” to “removing VOCs and H2S”

Pg 6815 Line 12: I think “(> 18.1MÎŔcm−1)” should be “(< 18.1MÎŔcm−1)”

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.

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

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)

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

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.

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”.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 6205, 2014.