Water Vapor Inhibits Hydrogen Sulfide Detection in Pulsed Fluorescence Sulfur Monitors

Anders B. Bluhme[1], Jonas L. Ingemar[1], Carl Meusinger[1], and Matthew S. Johnson[1]

[1]Department of Chemistry, Universitetsparken 5, University of Copenhagen, Copenhagen, Denmark

Correspondence to: Carl Meusinger (came@chem.ku.dk)

Abstract. The Thermo Scientific 450 Hydrogen Sulfide - Sulfur Dioxide Analyzer measures both H_2S and SO_2. SO_2 is measured by pulsed fluorescence, while H_2S is converted to SO_2 with a molybdenum catalyst prior to detection. The 450 is widely used to measure ambient concentrations, e.g. for emissions monitoring and pollution control. An air stream with a constant H_2S concentration

5 was generated and the output of the analyzer recorded as a function of relative humidity. The analyzer under-reported H_2S as soon as the relative humidity was increased. The fraction of undetected H_2S increased from 8.3 % at 5.3 % RH (294 K) to over 34 % at RH > 80 %. H_2S mole fractions of 573, 1142, and 5145 ppb were tested. The findings indicate that previous results obtained with instruments using similar catalysts should be re-evaluated to correct for interference from water vapor. It is

10 suspected that water decreases the efficiency of the converter unit and thereby reduces the measured H_2S concentration.

1 Introduction

Hydrogen sulfide (H_2S) is a malodorous, very poisonous, and flammable gas first described by Swedish chemist Carl Wilhelm Scheele (Scheele, 1777). It is produced by the anaerobic bacterial

15 decomposition of organic material, for example in sediments, livestock manure, sewers, and biogas production. In addition, large amounts are given off by hydrodesulfurization in petroleum refineries. It is therefore of great interest to monitor H_2S in the atmospheric environment.

Analytical instruments used to quantify H_2S include pulsed fluorescence gas analyzers (Harman, 1981), e.g. the Thermo Scientific 450 Hydrogen Sulfide - Sulfur Dioxide Analyzer, in the remainder

20 of this work called 450. This model has been used in many measurement campaigns worldwide, due to its broad detection range, sensitivity, durability, and reasonable cost. Examples include monitoring H_2S emissions from poultry egg laying houses in California (Lin et al., 2012; Ni et al., 2012) as part of the National Air Emissions Monitoring Study (Cortus et al., 2010), where also odour was correlated to measured H_2S concentrations (Akdeniz et al., 2012). These studies all utilized Standard

25 Operating Procedure G5 for H_2S (Diehl et al., 2006) proposed by the Environmental Protection

Agency (EPA) for monitoring H_2S; this protocol advices the use of the 450. The instrument has also been used to study H_2S emissions from anaerobic swine waste treatment (Blunden and Aneja, 2008), and to monitor emissions when altering diets of livestock including cows and pigs (Li et al., 2011; Liu et al., 2012). Furthermore the 450 has been used to determine H_2S removal efficiencies

30   for several air cleaning techniques, including biofilters at pig finishing facilities and swine waste water pits (Akdeniz et al., 2011; Janni et al., 2014; Lim et al., 2012), as well as biotrickling filters in laboratory studies (Liu et al., 2013). Another study monitored H_2S concentrations in Reykjavik resulting from two nearby geothermal power plants (Thorsteinsson et al., 2013).

The 450 has two internal flow lines: a Combined Sulfur-line, referred to as the CS-line, and an

35   SO_2-line (Thermo Fisher Scientific, 2008). The CS-line directs the sample gas through a converter unit, consisting of a molybdenum catalyst at variable temperatures between 310 and 340 ^{o}C, which oxidises H_2S to SO_2. The SO_2-line bypasses the converter, measuring the sample gas directly, as seen in Fig. 1. The flow system is used in three different measurement modes: SO_2, CS, and CS/SO_2. The
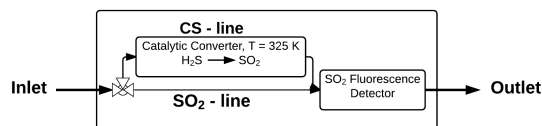
Figure 1. Schematic of the 450 Hydrogen Sulfide - Sulfur Dioxide Analyzer.

SO_2 mode only uses the SO_2-line, bypassing the converter and therefore only detecting SO_2. The

40   CS mode uses only the CS-line, passing the gas stream through the converter unit before analysis, thereby detecting the amount of total sulfur in the air stream. When measuring in CS/SO_2 mode, the instrument uses a valve to alternate between the two lines, allowing determination of both SO_2 and CS. The CS/SO_2 mode is used to calculate the H_2S mixing ratio by subtracting the measured SO_2 value from the measured CS value, assuming that all converted sulfur is H_2S. However, the

45   converter unit does not oxidise all H_2S to SO_2, rather it uses a conversion efficiency, δ, determined by the manufacturer. The conversion efficiency varies from instrument to instrument, and is typically above 80 %. The conversion efficiency is taken into account when calculating the actual H_2S mixing ratio using Eqs. 1 and 2 when measuring in the CS/SO_2 mode.

$$\chi_{H_2S} = \frac{\chi_{CS_{detected}} - \chi_{SO_2}}{\delta} \tag{1}$$

50   $$\chi_{CS} = \frac{\chi_{CS_{detected}} - \chi_{SO_2}}{\delta} + \chi_{SO_2} \tag{2}$$

Here χ_{SO_2} is the measured SO_2 mixing ratio and $\chi_{CS_{detected}}$ is the non compensated CS mixing ratio measured by the 450.

In CS mode it is assumed that only H_2S is present. The 450 therefore uses Eq. 3 to calculate the actual CS content of the sample air.

$$55 \quad \chi_{CS} = \frac{\chi_{CS_{detected}}}{\delta} \tag{3}$$

The 450 can also be used to measure other reduced sulfur compounds such as Methanethiol (MT), Dimethylsulfide (DMS), and Dimethyldisulfide (DMDS). Gases such as these have different conversion efficiencies than H_2S.

In this study it is shown that the H_2S response of the 450 has a significant interference from water vapor, even at ambient humidities.

2 Method

In order to generate test gasses with predetermined H_2S mixing ratios and varying relative humidity, flows combining H_2S and technical air, were generated using three calibrated mass flow controllers (MFC), as shown in Fig. 2. The H_2S content was controlled using MFCs 2 and 3, where MFC 3 determined the flow from a 100 ppm H_2S bottle, while MFC 2 determined the flow of technical air for dilution. A mixing chamber was installed after the two MFCs, which ensured a homogeneous mixture before continuing. Part of the diluted H_2S 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. Preliminary tests showed that the measured H_2S concentration was unaffected by the Nafion dryer. The purge gas was produced with technical air using MFC 3, where valves A, B, and C controlled the amount of air bypassing or entering a humidifier, before reaching the purge inlet of the Nafion dryer. This made it possible to alter the humidity of the purge gas, and thereby also the amount of water transferred across the Nafion membrane into the test gas. Since H_2S cannot permeate the Nafion membrane, the setup allowed a constant H_2S concentration, while altering the relative humidity.

Once the test gas left the Nafion dryer, the relative humidity was measured, using a Rotronic HC2-C04 probe with an accuracy of (RH $\pm$ 1.5) %. After the humidity probe the air stream entered the 450, which measured the H_2S content. The instrument used in this study was a model 450i purchased in late 2014, with a stated conversion efficiency of 93.1 %. All other materials and instruments used in the experiments are listed in Table 1.

The humidity response of the 450 was tested at three different H_2S mole fractions, obtained by adjusting the flows from MFCs 2 and 3. All measurements were conducted in CS mode, since only H_2S was present in the sample gas. The three initial H_2S mole fractions were: 573 $\pm$ 4, 1142 $\pm$ 3, and 5145 $\pm$ 8 ppb. These measured values are close to the nominal mixing ratios of: 513 $\pm$ 26, 1019 $\pm$ 51, and 4756 $\pm$ 238 ppb, calculated from MFC settings and stated gas bottle concentration. The
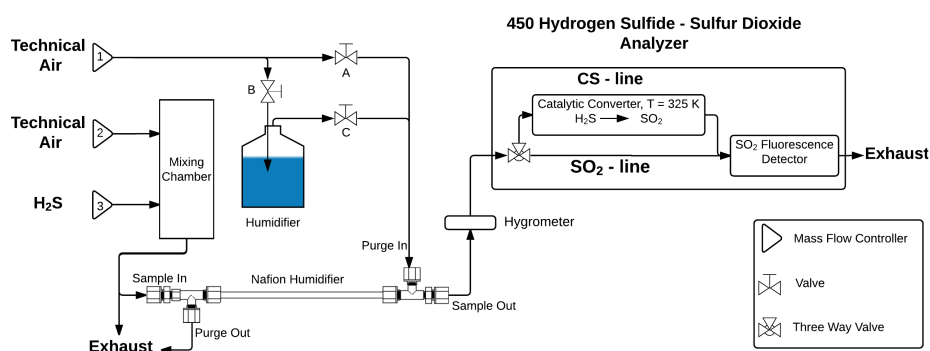
Figure 2. Schematic of the experimental setup.

Table 1. List of materials and instruments used in the experimental setup.

Item	Manufacturer	Description
H_2S gas	Yara Praxair	H_2S in Nitrogen, certified 101 ppm $\pm$ 5 %
SO_2 gas	Yara Praxair	SO_2 in Synthetic air, certified 42 ppm $\pm$ 5 %
MFC-1	Brooks Instrument	Model: 4800 0-3 L min^{-1}
MFC-2	Brooks Instrument	Model: 5850TR 0-10 L min^{-1}
MFC-3	Brooks Instrument	Model: 5850S 0-100 mL min^{-1}
Nafion dryer	Perma Pure	Model: MD-110-24F-4, 24″ dryer

uncertainties of the MFCs were not included in this calculations, which could explain the observed offset.

In each experiment the H_2S mixing ratio was measured initially under completely dry conditions, meaning that the two valves leading to and from the humidifier (valves B and C) were closed, while the bypass valve (A) was open. Once a stable concentration was obtained, measurements continued for 20-30 minutes, ensuring sufficient data for analysis. The humidity was then increased by slightly opening valves B and C. The system was allowed to equilibrate, typically for 30-60 minutes, followed by another 20-30 minutes of measurements at stable H_2S concentration and humidity. The procedure was repeated for several different humidities, with a stable temperature in all experiments of 294.2 $\pm$ 0.8 K.

3   Results & Discussion

In all experiments the H_2S mixing ratio decreased within 1-2 minutes of increasing the humidity of

100   the test gas, showing that the 450 responds very quickly to changes in water content of the sample

air.
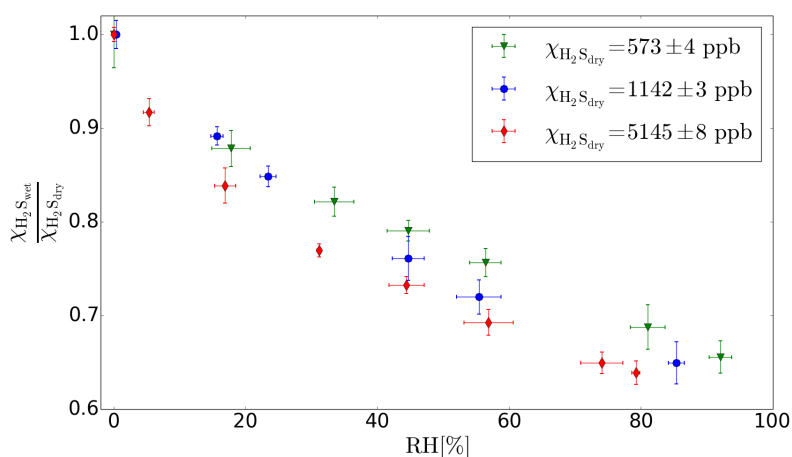
Figure 3. The ratio between measurements of H_2S at wet and dry conditions for three initial mole fractions, plotted against the corresponding humidity at a temperature of 294.2 ± 0.8 K. All errorbars have been multiplied by 5 for better visualization.

The ratio between the H_2S mole fractions measured at wet and dry conditions were plotted against the relative humidity in Fig. 3. Already at a relative humidity of 5.3 %, a clear decrease from 5145 to 4718 ppb was observed, corresponding to a reduction of 8.3 % in measured H_2S. Higher reductions

105   were observed when increasing the humidity further, showing an almost linear correlation between the increase in humidity and the decrease in H_2S mole fraction. At all three initial mixing ratios more than 34 % of the H_2S content passed the instrument undetected when measuring at relative humidities above 80 %. The largest decrease was observed at the high initial H_2S mole fraction, indicating that the effect could be even greater at higher concentrations.

110   A similar experiment was conducted with SO_2 instead of H_2S, and no interference from water was observed. This lead to the conclusion that the interference from water was produced in the converter unit, possibly due to inhibition of catalytic sites, thereby lowering of the conversion efficiency. According to our observations it is not necessary to dry the sample air when measuring SO_2.

The interference from water calls earlier studies into question, unless sampling was performed

115   under completely dry conditions. However a significant reduction in measured H_2S was observed already at 5.3 % relative humidity, which might pose difficulties for ambient sampling. The inter-

ference from water is not mentioned in the instrument manual, instead it is stated that the instrument functions at ambient conditions. Therefore most studies do not dry sample air before measuring, meaning that many earlier studies may have under-reported H_2S levels. The fast response

120   to changes in humidity, could make events such as rainfall result in significant under-reporting of H_2S concentrations. Furthermore the interference could result in overestimations of removal efficiencies for certain biofilters, where high humidities are necessary for the filters to function. Our measurements indicate that the Standard Operating Procedure provided by the U.S. Environmental protection agency, should be revised to account for the water vapor interference. The water vapor

125   interference may also occur in instruments that utilize a similar technique such as the Teledyne T101 H_2S analyzer (Teledyne, 2012), but this was not tested in present study. It is not clear how many instruments are affected, and users should therefore investigate if similar behaviours are observed in their instruments.

4   Conclusions

130   It has been shown that the Thermo Scientific 450 Sulfur analyzer shows a significant water vapor interference when measuring H_2S. Reductions of up to 1/3 of the dry H_2S mixing ratio have been found at ambient conditions. Our analysis is that the interference occurs in the catalytic unit converting H_2S to SO_2. These findings indicate that earlier results obtained with the 450 and similar instruments are very likely to have under-reported H_2S concentrations and should therefore be re-

135   evaluated. Since it is not clear how many instruments are affected, users of the 450 should investigate if similar behaviour are shown with their instruments. Based on these findings it is recommended to dry the air stream prior to a catalytic H_2S monitoring instrument using a Nafion dryer or another appropriate drying technique.

Acknowledgements. The authors would like to thank the CCAR group at KU for their help and support. Fur-

140   thermore they would like to thank the Innovation Fund Denmark (grant number 156-2013-6) for their financial support.

References

Akdeniz, N., Janni, K. A., and Salnikov, I. A.: Biofilter performance of pine nuggets and lava rock as media, Bioresource Technology, 102, 4974–4980, 2011.

145 Akdeniz, N., Jacobson, L. D., Hetchler, B. P., Bereznicki, S. D., A. J. Heber, Koziel, J. A., Cai, L., Zhang, S., and Parker, D. B.: Odor and Odorous Chemical Emissions from Animal Buildings: Part 6. Odor Activity Value, American Society of Agricultural and Biological Engineers, 55, 2357–2368, 2012.

Blunden, J. and Aneja, V. P.: Characterizing ammonia and hydrogen sulfide emissions from a swine waste treatment lagoon in North Carolina, Atmospheric Environment, 42, 3277–3290, 2008.

150 Cortus, E., Lin, X.-J., Zhang, R., and Heber, A.: National Air Emissions Monitoring Study: Emissions Data from Two Layer Houses in California - Site CA2B, Tech. rep., 2010.

Diehl, C. A., Bogan, B. W., Grant, R. H., and Boehm, M. T.: EPA Standard Operating Procedure G5: Measurement of Hydrogen Sulfide (H_2S) with the Thermo Electron Corporation Model 450I Pulsed-Fluorescence Analyzer, Tech. rep., Agricultural and Biological Engineering, Purdue University, 2006.

155 Harman, J. N.: Interference reactor to provide selective SO_2 measurement by fluorescent methodology, 1981.

Janni, K. A., Jacobson, L. D., Hetchler, B. P., Oliver, J. P., and Johnston, L. J.: Semi-Continuous Air Sampling versus 24-Hour Bag Samples to Evaluate Biofilters on a Swine Nursery in Warm Weather, American Society of Agricultural and Biological Engineers, pp. 1501–1515, 2014.

Li, W., Powers, W., and Hill, G. M.: Feeding distillers dried grains with solubles and organic trace mineral 160 sources to swine and the resulting effect on gaseous emissions, Journal of Animal Science, 89, 3286–3299, 2011.

Lim, T. T., Jin, Y., Ni, J. Q., and Heber, A. J.: Field evaluation of biofilters in reducing aerial pollutant emissions from a commercial pig finishing building, Biosystems Engineering, 112, 192–201, 2012.

Lin, X. J., Cortus, E. L., Zhang, R., Jiang, S., and Heber, A. J.: Ammonia, hydrogen sulfide, carbon dioxide and 165 particulate matter emissions from California high-rise layer houses, Atmospheric Environment, 46, 81–91, 2012.

Liu, C., Liu, J., Li, J., He, H., Peng, S., Li, C., and Chen, Y.: Removal of H_2S by co-immobilized bacteria and fungi biocatalysts in a bio-trickling filter, Process Safety and Environmental Protection, 91, 145–152, 2013.

Liu, Z., Powers, W., Oldick, B., Davidson, J., and Meyer, D.: Gas emissions from dairy cows fed typical diets 170 of Midwest, South, and West regions of the United States., Journal of Environmental Quality, 41, 1228–37, 2012.

Ni, J. Q., Chai, L., Chen, L., Bogan, B. W., Wang, K., Cortus, E. L., Heber, A. J., Lim, T. T., and Diehl, C. A.: Characteristics of ammonia, hydrogen sulfide, carbon dioxide, and particulate matter concentrations in high-rise and manure-belt layer hen houses, Atmospheric Environment, 57, 165–174, 2012.

175 Scheele, C. W.: Die stinckende Schwefel luft, Chemische abhandlung von der luft und dem Feuer, 97, 149–155, 1777.

Teledyne: Operation Manual Model T101 UV Fluorescence H_2S Analyzer, 2012.

Thermo Fisher Scientific: Model 450i - Instruction Manual, 2008.

Thorsteinsson, T., Hackenbruch, J., Sveinbjörnsson, E., and Jóhannsson, T.: Statistical assessment and model- 180 ing of the effects of weather conditions on H2S plume dispersal from Icelandic geothermal power plants, Geothermics, 45, 31–40, 2013.