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Water vapor inhibits hydrogen sulfide detection in pulsed fluorescence sulfur monitors

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Abstract. The Thermo Scientific 450 Hydrogen Sulfide–Sulfur Dioxide Analyzer measures both hydrogen sulfide (H_2S) and sulfur dioxide (SO_2). Sulfur dioxide 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 was generated and the output of the analyzer recorded as a function of relative humidity (RH). The analyzer underreported 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%. Hydrogen sulfide 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 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 decomposition of organic material, for example in sediments, livestock manure, sewers, and biogas production. In addition, large amounts are given off by hydrodesul-

furization 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 of this work referred to as the 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 (Heber et al., 2009), where odor was also correlated to the measured H_2S concentrations (Akdeniz et al., 2012). These studies all utilized Standard Operating Procedure G5 for H_2S (Diehl et al., 2006) approved by the Environmental Protection Agency (EPA) for monitoring H_2S ; this protocol advises 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 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).

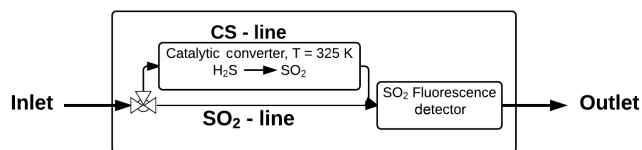


Figure 1. Schematic of the 450 Hydrogen Sulfide–Sulfur Dioxide Analyzer.

The 450 has two internal flow lines: a Combined Sulfur line, referred to as the CS line, and an SO₂ 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 °C, which oxidizes H₂S to sulfur dioxide (SO₂). The SO₂ line bypasses the converter, measuring the sample gas directly, as seen in Fig. 1.

The flow system is used in three different measurement modes: SO₂, CS, and CS/SO₂. The SO₂ mode only uses the SO₂ line, bypassing the converter and therefore only detecting SO₂. The 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/SO₂ mode, the instrument uses a valve to alternate between the two lines, allowing determination of both SO₂ and CS. The CS/SO₂ mode is used to calculate the H₂S mixing ratio by subtracting the measured SO₂ value from the measured CS value, assuming that all converted sulfur is H₂S. However, the converter unit does not oxidize all H₂S to SO₂, 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 H₂S mixing ratio using Eqs. (1) and (2) when measuring in the CS/SO₂ mode.

$$\chi_{\text{H}_2\text{S}} = \frac{\chi_{\text{CS}_{\text{detected}}} - \chi_{\text{SO}_2}}{\delta} \quad (1)$$

$$\chi_{\text{CS}} = \frac{\chi_{\text{CS}_{\text{detected}}} - \chi_{\text{SO}_2}}{\delta} + \chi_{\text{SO}_2} \quad (2)$$

Here χ_{SO_2} is the measured SO₂ mixing ratio and $\chi_{\text{CS}_{\text{detected}}}$ is the non-compensated CS mixing ratio measured by the 450.

In CS mode it is assumed that only H₂S is present. The 450 therefore uses Eq. (3) to calculate the actual CS concentration of the sample air.

$$\chi_{\text{CS}} = \frac{\chi_{\text{CS}_{\text{detected}}}}{\delta} \quad (3)$$

The 450 can also be used to measure other reduced sulfur compounds such as methanethiol (MT), dimethylsulfide (DMS), and dimethyl disulfide (DMDS). Gases such as these have different conversion efficiencies than H₂S.

In this study it is shown that the H₂S 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 H₂S mixing ratios and varying relative humidity, flows combining H₂S and dried, clean, particle-free ambient air (technical air) were generated using three calibrated mass flow controllers (MFC), as shown in Fig. 2. The H₂S concentration was controlled using MFCs 2 and 3, where MFC 3 determined the flow from a 101 ppm H₂S flask, 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 H₂S stream was pulled through a Perma Pure Nafion dryer by the 450, while the rest was led to an exhaust, avoiding overpressure on the sample line. The Nafion dryer was used to humidify the dry test gas from the mixing chamber, by allowing water from a humid purge gas to permeate the Nafion membrane in the dryer. The humid 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.

Preliminary tests showed that the measured H₂S concentration was unaffected by the installation of the Nafion dryer. Thus this system was able to produce a constant H₂S concentration throughout the experiments, while at the same time, vary the relative humidity.

Once the test gas left the Nafion dryer, the relative humidity (RH) was measured, using a Rotronic HC2-C04 probe with an accuracy of (RH ± 1.5) %. After the humidity probe the air stream entered the 450, which measured the H₂S concentration. 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 (data available at <http://data.kb.dk/dvn/dv/AMT-data>).

The humidity response of the 450 was tested at three different H₂S mole fractions, obtained by adjusting the flows from MFCs 2 and 3. All measurements were conducted in CS mode, since only H₂S was present in the sample gas. The three initial H₂S mole fractions were 573 ± 4, 1142 ± 3, and 5145 ± 8 ppb. These measured values are close to the nominal mixing ratios of: 513 ± 26, 1019 ± 51, and 4756 ± 238 ppb, calculated from MFC settings and the stated gas flask concentration. The uncertainties of the MFCs were not included in these calculations, which could explain the observed offset.

In each experiment the H₂S 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 min, ensuring sufficient data for

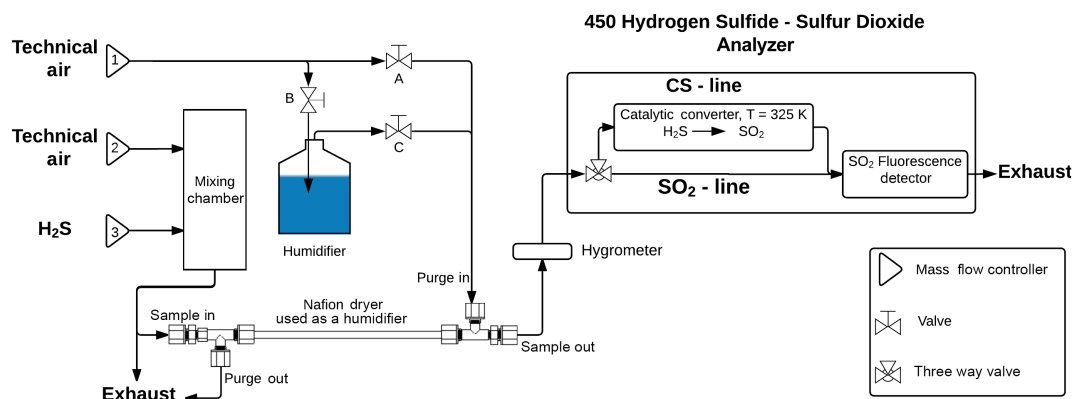


Figure 2. Schematic of the experimental setup.

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

Item	Manufacturer	Description
H ₂ S gas	Yara Praxair	H ₂ S in nitrogen, certified 101 ppm ± 5 %
SO ₂ gas	Yara Praxair	SO ₂ in synthetic air, certified 42 ppm ± 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

analysis. The humidity was then increased by slightly opening valves B and C. The system was allowed to equilibrate, typically for 30–60 min, followed by another 20–30 min of measurements at stable H₂S concentration and humidity. The procedure was repeated for several different humidities, with a stable temperature in all experiments of 294.2 ± 0.8 K.

3 Results and discussion

In all experiments the H₂S mixing ratio decreased within 1–2 min of increasing the humidity of the test gas, showing that the 450 responds very quickly to changes in water content of the sample air.

The ratio between the H₂S mole fractions measured at wet and dry conditions were plotted against the relative humidity in Fig. 3. Even at a very low relative humidity, 5.3 %, H₂S decreased from 5145 to 4718 ppb, corresponding to a reduction of 8.3 % in measured H₂S. Higher reductions were observed when increasing the humidity further, showing an almost linear correlation between the increase in humidity and the decrease in H₂S mole fraction. At all three initial mixing ratios more than 34 % of the H₂S concentration passed the instrument undetected when measuring at relative humidities above 80 %. The largest decrease was observed at the high initial H₂S mole fraction, indicating that the effect could be even greater at higher concentrations.

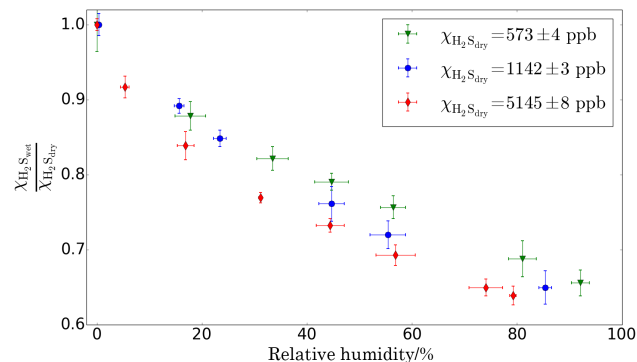


Figure 3. The ratio between measurements of H₂S at wet and dry conditions for three initial mole fractions, plotted against the corresponding humidity at a temperature of 294.2 ± 0.8 K. All error bars have been multiplied by 5 for better visualization.

A similar experiment was conducted with SO₂ instead of H₂S, and no interference from water was observed. This led to the conclusion that the interference from water was produced in the converter unit, possibly due to inhibition of catalytic sites, thereby lowering the conversion efficiency. According to our observations it is not necessary to dry the sample air when measuring SO₂.

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

dry conditions. However, since a significant reduction was observed in H₂S at only 5.3 % relative humidity, virtually all ambient measurements may be complicated by the interference of water vapor. The interference from water is not mentioned in the instrument manual; instead it is stated that the instrument functions at ambient conditions. Therefore most researchers do not dry sample air before measuring, meaning that many earlier studies may have underreported H₂S levels. The fast response to changes in humidity could make events such as rainfall result in significant underreporting of H₂S 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 US Environmental Protection Agency, should be revised to account for the water vapor interference. The water vapor interference may also occur in instruments that utilize a similar technique such as the Teledyne T101 H₂S Analyzer (Teledyne, 2012), but this was not tested in the present study. It should be noted that the magnitude of the effect is likely to vary from one instrument to another, seeing that the effect is determined by the state of the catalyst. Furthermore it is not clear how many instruments are affected, and users should therefore investigate if similar behaviors are observed in their instruments.

4 Conclusions

It has been shown that a Thermo Scientific 450 Sulfur Analyzer shows a significant water vapor interference when measuring H₂S. Reductions of up to 1/3 of the dry H₂S mixing ratio were observed at ambient conditions. Our opinion is that the interference occurs in the catalytic unit converting H₂S to SO₂. These findings indicate that earlier results obtained with the 450 and similar instruments are very likely to have underreported H₂S concentrations and should therefore be re-evaluated. Since the magnitude of the effect is most likely instrument-specific and since it is not clear how many instruments are affected, users of the 450 should investigate the behavior of their own instruments. Based on these findings it is recommended to dry the air stream prior to a catalytic H₂S monitoring instrument using a Nafion dryer, which in this study was shown to produce no change in the measured H₂S concentration. Alternative drying techniques were not tested in this study and should therefore be experimentally verified before use.

5 Data availability

All experimental data is available online (Bluhme et al., 2016; <http://data.kb.dk/dvn/dv/AMT-data>).

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