Effect of Condensed Water on Hydrogen Sulfide Concentration in Raw Biogas Samples

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Background

The analysis of sulfur compounds is essential to the production and distribution of Renewable Natural Gas (RNG). However, the reactivity of sulfur compounds with sample container surfaces and water poses a significant challenge to the accuracy and reliability of this analysis. ASTM Standard Test Methods for sulfur determination (D5504, D6228) emphasize the importance of both appropriate sampling conditions and the timely analysis of samples to minimize the deterioration that occurs between sampling and analysis. Specifically, it is essential to use inert/passivated containers for collecting and transporting samples, and samples should be analyzed as soon as possible (ideally within 24 hours). However, rapid analysis is not always possible due to transportation distance and costs.

To address the issue of reactivity with sample container surfaces, Ohio Lumex collects pressurized gaseous fuel samples in stainless steel high-pressure cylinders (HPCs) that have been treated with a chemically inert coating, which is a proven method to preserve samples for analysis of sulfur compounds in RNG, which is a relatively clean and dry gas.

However, Ohio Lumex has observed decreased stability when using HPCs for the sampling of raw biogas. Raw biogas typically contains high amounts of hydrogen sulfide (H_2S), which is one of the most reactive sulfur compounds. Although HPCs are inert containers, we have observed H_2S concentrations decreasing below detectable levels in a matter of days. While expedited analysis may help ensure samples are analyzed prior to complete H_2S deterioration, logistical limitations prevent this from being an option for all samples. Additionally, repeat analyses have shown that some raw biogas samples deteriorate quickly, even within the first 24 or 48 hours after sampling.

Investigation

Initially, it was suspected that rapid deterioration was due to a reaction between H_2S and oxygen, which is typically present at around 1% concentration in raw biogas. Testing confirmed that higher oxygen concentrations in biogas contribute to a decrease in H_2S over time. However, the rate of decrease was relatively slow compared to the sharp drop in concentration observed in field samples.

The tested hypothesis is that moisture in the sample gas is responsible for the loss of H_2S. Raw biogas is often saturated with water vapor. We theorized that pressurizing wet raw gas in the HPCs was causing condensation within the cylinder. The vapor pressure of water is independent of the total pressure in the container, and thus additional water beyond 100% humidity would return to liquid phase. The condensed water could then be responsible for the increased rate of H_2S degradation as it acts as a catalyst by providing a site for reactions to occur more quickly than in the gas phase.

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Experimental

To confirm the effect that water has on H_2S degradation rate, two gas samples were prepared in HPCs in parallel – one absent of any water, and another with water added. Both were then analyzed for sulfur compounds for several days to see the differences in stability. To simulate the composition of raw biogas, the basis of the gas mixture was a standard containing primarily methane, along with small amounts of hydrogen and hydrocarbons. A small but meaningful amount of oxygen (<0.5%) was added, then each sample was spiked with a standard of several sulfur compounds in nitrogen, including H_2S, with an initial target concentration of approximately 4 ppmv. To determine the amount of water to add to the wet sample, we calculated the volume of water that would be present as vapor, in gas with 100% relative humidity, in the volume of an HPC, at room temperature; then multiplied that volume by the ratio of the (absolute) pressure of the pressurized HPC, and atmospheric pressure. This represents the water that would accompany the gas being pumped into the HPC to pressurize it. To absolutely ensure the presence of liquid water in the sample for testing purposes, the final volume added was greater than that calculated amount; thus arriving at 50 µL of water.

50 µL of DI Water was added to the HPC by injection with a gastight syringe through a septum fitting into a short line connected to the HPC, while the HPC was under vacuum. The water was then flushed into the HPC with the methane gas mixture when the HPC was filled. Lines were heated >100°C during this step to facilitate evaporation of the water and effective transfer into the cylinder.

The same setup was used for the dry sample when filling with the methane gas mixture; note that the dry sample was filled first, before any water was introduced to the system.

Both the dry and wet samples then had a small amount of oxygen added, then the sulfur standard, to bring the samples to the final target pressure and H_2S concentration.

Samples were then analyzed for sulfur compounds using GC-PFPD following modified ASTM D6228. Analysis was repeated several times daily for both samples, up to 5 days after sample preparation. The date and time for each analysis were recorded alongside the measured sulfur concentrations.

Both samples were also analyzed for major gas components by ASTM D1945, primarily to confirm the concentration of oxygen present. Major gas analysis was performed on the first and last days of the testing period for both samples.

Results
Effect of Water on H$_2$S
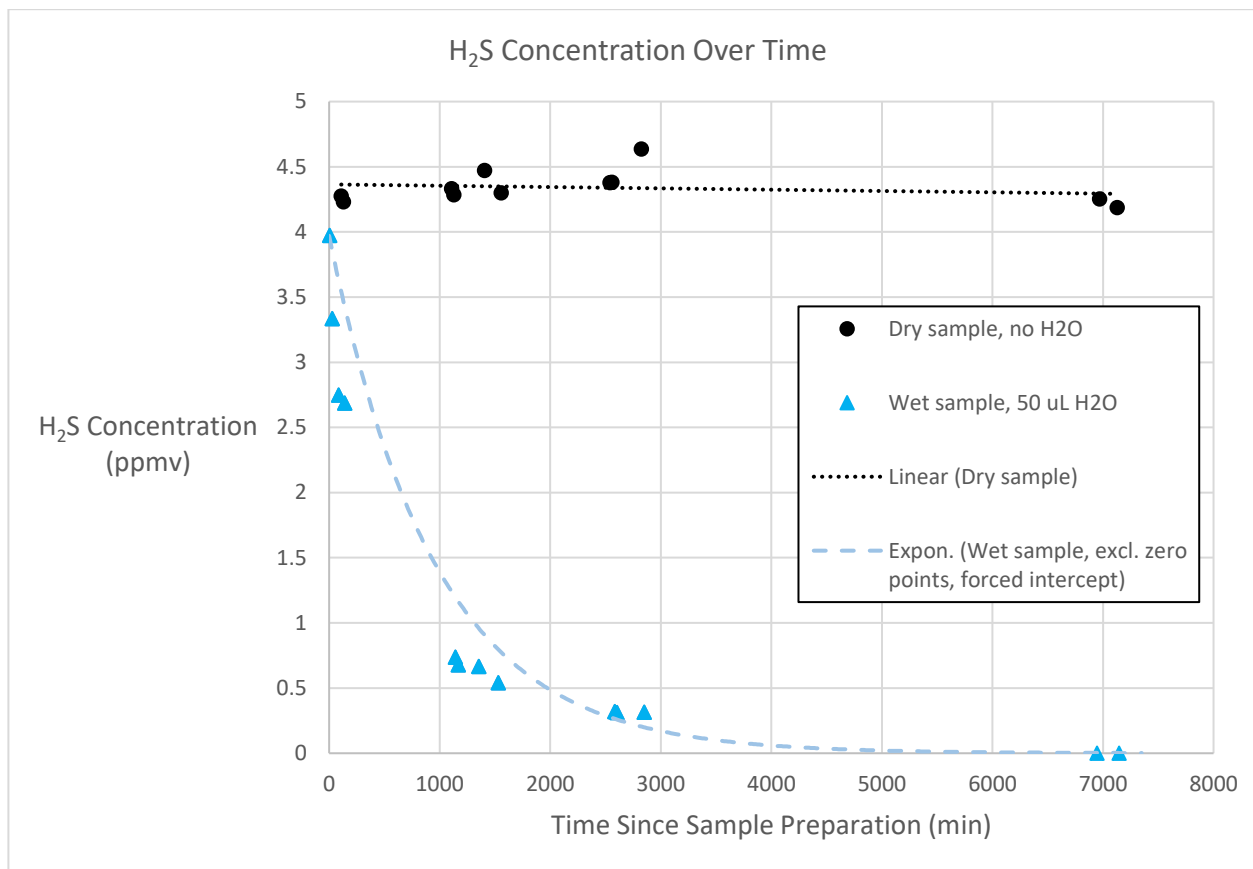
Consecutive analyses immediately after preparation of the wet sample showed a rapid decrease in H$_2$S concentration, while no such decrease was observed for the dry sample. After less than one day, H$_2$S in the wet sample had dropped from an initial concentration of 3.97 ppmv to 0.67 ppmv – a loss of 83.25%. The rate of degradation slowed as concentration decreased; after a second day, the concentration was 0.32 ppmv. Analysis 5 days after sample preparation did not detect any H$_2$S remaining in the wet sample.

Wet Sample H$_2$S Loss (selected measurements)

Hours since sample preparation	Measured H$_2$S Concentration (ppmv)	% H$_2$S Lost
0.07	3.9744	---
0.45	3.3341	16.11%
2.37	2.6859	32.42%
22.58	0.6659	83.25%
47.50	0.3163	92.04%
115.78	0	100%

H$_2$S concentration in the dry sample remained statistically consistent over the 5-day testing period. The average of all the measurements was 4.34 ppm; each individual measurement was within the 10% method uncertainty of this value.

Conclusion

The results of our testing demonstrate that liquid water in the sample container produces a rapid decrease in the concentration of H_2S in a gas sample. H_2S will react with liquid water at a rate significant enough to compromise measurement accuracy even if the analysis is performed within 24 hours of sampling. This experiment demonstrated an unacceptable H_2S loss of more than 83% prior to the 24-hour mark.

Accurate sulfur analysis of raw biogas cannot be performed in the presence of condensation. Raw biogas is typically saturated with water vapor at a higher temperature than the temperature of the laboratory where analysis is performed, and the unheated FedEx warehouses and trucks during transportation to the laboratory, especially in winter months. Therefore, condensed water is almost certain to exist in the sample container before sulfur analysis is performed.

Solution

In order to prevent condensation from affecting hydrogen sulfide measurements for raw biogas, a sampling system must be used that alters the dewpoint of the sample gas. The simplest solution is to collect and store raw biogas samples **below** atmospheric pressure, using a container such as a SUMMA canister. At partial vacuum the dewpoint of water is reduced significantly, and condensation will be prevented, even after the temperature of the SUMMA canister is reduced to laboratory temperature.

As a result of this investigation, Ohio Lumex has switched to using SUMMA canisters for sulfur samples at raw biogas sources. This ensures excellent sample stability and the accurate measurement of sulfur compounds.

Referenced Methods

- ASTM D6228-19 Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection
- ASTM D5504-20 Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence