

MEASURING H₂S IN CRUDE OIL FOR QUALITY CONTROL & TRANSPORTATION SAFETY

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ABSTRACT

Measurement of hydrogen sulfide (H₂S) is a critical practice for quality control and safety purposes. Without precise quantification of H₂S in a process, efficient processing of crude oil is not possible. To maintain safety when transporting crude oil and condensate, measurement of the H₂S content is vitally important. This is an in-plant case study in the Middle East consisting of the start-up, commissioning, and accuracy field test of four on-line process analyzers measuring H₂S content in crude oil for quality control purposes. The study also validates the calibration method used for the analyzers.

INTRODUCTION

Measurement of hydrogen sulfide (H_2S) is a beneficial practice for product quality control purposes and for personnel safety of those who may come in contact with sometimes fatal sour gas. Crude oil with low levels of H_2S is more valuable than crude with high H_2S as low H_2S level oil can be more readily processed into petroleum products. Without accurate quantification of H_2S in a sample stream, efficient removal of the H_2S is not possible. H_2S analyzers are utilized for this quantification of H_2S in various systems in order to optimize the process and cut costs.

Safely transporting crude oil is becoming an increasingly important requirement in light of recent rail car derailments. Hydrogen Sulfide is a toxic and deadly gas that is often present in crude oil (sour crude) and condensate. Even small amounts of H_2S present a health risk to personnel transporting the sour crude oil and condensate as well as the public in case of accidents. The U.S. Occupational Safety and Health Administration (OSHA) warns H_2S is an irritant and a chemical asphyxiant that can alter both oxygen utilization and the central nervous system. Death can result from exposure to sulfide gas vapors at levels of just 100 ppm. (1)

H_2S is highly corrosive. Over time corrosion from H_2S may occur in pipelines, rail cars, trucks and other transport vessels that deliver crude oil: which may lead to deadly accidents. The Pipeline and Hazardous Materials Safety Administration (PHMSA) recently issued a safety alert on January 2, 2014 following the train car derailments that caught fire west of Fargo, ND, and Lac-Mégantic, Quebec, indicating crude oil being transported from the Bakken region “may be more flammable than traditional heavy crude oil.” (2)

Although there is debate as to whether the flammability of the Fargo cargo was due to high H_2S levels or simply the highly volatile properties of the crude oil, most rail, truck, and pipeline facilities are now requiring low H_2S content in crude oil and condensate. Some institutions and companies have implemented policies to turn away crude oil with more than 5 ppm H_2S content. The U.S. Federal Energy Regulatory Commission (FERC) is standing behind Enbridge Energy Partners by ruling that Enbridge reserves the right to reject crude that does not contain a hydrogen sulfide content of 5 parts per million (ppm) or less.” (3) The rule went into effect in May of 2013. The FERC also approved a 5 ppm H_2S limit by Tesoro Corp. effective January 1, 2014 and True companies at 10 ppm H_2S limit effective April 1 of 2014. (4) OSHA has set the maximum exposure limits of hydrogen sulfide “at either 10 or 20 ppm...with an absolute prohibition of exposure above 50 ppm.” (5)

Continuous online monitoring of hydrogen sulfide can pay for itself by preventing product loss, meeting sales specifications, and protecting personnel by verifying hazardous amounts of hydrogen sulfide are not present in the product before transportation. Continuous analyzers also eliminate costly and timely lab analysis costs which cannot offer real-time measurement of hydrogen sulfide in the crude.

METHODS OF SAMPLING

Because of the opaque nature and complex compositional characteristics of crude oil, direct optical measurement is difficult. To circumvent this problem, the composition of the crude oil (including the hydrogen sulfide) can be representatively “stripped” from the liquid phase into the vaporous gas phase for precise measurement by a gas detector. Two primary methods exist for stripping (or recovering the composition of) the crude oil for measurement by a gas detector for continuous analysis: The ‘headspace’ stripping column; and the use of the Sample Transfer Stripper™ utilizing a variety of proprietary membrane technologies. Both of these methods are based in part on Henry’s Law and partial pressures of the components in the sample:

"At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."

The headspace stripping column requires crude oil to continuously flow into a temperature controlled pipe (several inches in diameter) while a stripping gas flows in the opposite direction against the crude oil. The combining agitation of the stripping gas and the constant heat and pressure of the column persuade the compositional vapor of the crude oil to strip from the crude oil and into the stripping gas which then carries the vapor to the detector for analysis. The headspace stripping column system requires a multitude of parts to maintain constant flow, heat and pressure of the crude oil sample. The column is normally a large component. Several feet of length is normally required to effectively serve its purpose. Oftentimes, multiple columns are required. Much care must be given to the headspace column to prevent the crude oil from “carrying-over” into the stripping gas line which requires cleanup of crude oil in the air sampling lines and the contaminated detector and/or flow cell. Precise control of sample flow and pressure; carrier flow and pressure; and temperature becomes critical to the proper functionality of the headspace column stripper system. It is important the crude oil is evenly dispersed inside the column to ensure the stripping gas effectively contacts all of the crude oil sample. In reality, this is difficult to accomplish with the headspace column stripper system as the crude oil tends to clump to one side of the column instead of being evenly distributed. Inaccurate measurements are frequent with this method.

Alternatively, the membrane Sample Transfer Stripper™ is a simple and straight forward approach to extracting a proportional compositional vapor from the crude oil for quantification. The Sample Transfer Stripper™ employs the use of membranes to efficiently and proportionately separate the crude oil composition from the liquid sample for analysis. The device is a simple and elegant. At only 5” high and 3.5” wide it provides an ultra-clean and dry sample to the detector for analysis without demanding valuable real-estate. The Sample Transfer Stripper™ operates based in part on Henry’s Law and employs the partial pressure of the sample for compositional extraction into the vapor phase. The crude oil sample flows into the heated membrane stripper where it continuously sweeps one side of the membrane. The composition of the sample then permeates through the membrane into vapor-phase where the carrier gas sweeps the sample to the detector for analysis.

The membrane in the Sample Transfer Stripper™ acts as a physical block, preventing mists and other contaminants from passing through the carrier gas tubing lines and onto the detector. There is no risk of “carry-over” from the crude oil. This prevents buildup of contamination in the sample line which would otherwise cause in/out gassing and inaccurate readings over time due to gradual contamination of sample tubing walls. Because the membrane technology uses 90% fewer parts than the headspace column stripper, maintenance requirements are radically reduced.

METHODS OF ANALYSIS

There are three primary detection methods to continuously quantify the hydrogen sulfide gas vapor after it has representatively been extracted from the liquid sample. These methods are absorption spectroscopy, electrochemical sensor cell, and the colorimetric-rateometric tape method of detection. Primary considerations for an analyzer include low maintenance and accurate measurements. Whereas low maintenance relies on the sampling system (described earlier), the accuracy of the system also lies in the detection technology. Users demand a highly versatile analyzer that maintains accuracy despite process changes.

The absorption spectroscopic method operates in conjunction with Beer-Lambert law: “the absorbance of a solution will depend directly on the concentration of the absorbing molecules and the path length traveled by light through the solution.” The sample enters a flow cell where a light source is shined across the sample. As the light is absorbed by components of interest, such as hydrogen sulfide (normally in the UV region), the spectrometer quantifies the resulting absorbance as concentration.

H₂S analyzers with electrochemical cells are also sometimes used to measure H₂S in crude oil. These cells measures concentrations of a component by oxidizing the component at an electrode and measuring the current that results.

Hydrogen sulfide is a difficult component to measure due to the presence of similar background components in samples such as methyl-mercaptan and ethyl-mercaptan, other sulfur species and organics. Problems arise with the aforementioned absorption spectroscopy and electrochemical sensor cells due to these interfering components. Attempts have been made to reduce ‘false positives’ with absorption spectroscopy but this requires complicated chemometric modeling that is static and not always reliable. When the process stream naturally changes over time, even slightly, chemometric model updates and new calibrations are required. This is difficult to perform in the field and often requires the labor support of the manufacturer. Furthermore, suppliers of absorption spectroscopy analyzers guard chemometric models as intellectual property and the user has little control over or access to these models. Unfortunately, the user usually cannot apply new modeling in attempt to negate interfering components and require the assistance of the manufacturer. Because many processes are time critical, time spent waiting for the arrival of a

manufacturer's representative becomes burdensome. Zero reading 'drift' is routine with these methods of analysis. Manufacturers of electrochemical sensor cells offer disclaimers showing an array of interfering compounds with their sensor cells including hydrogen, ethyl-mercaptan, methyl-mercaptan, ammonia, carbon monoxide, ethylene, chlorine, methane, methanol, nitrogen dioxide and other sulfur species. Attempts have been made to "scrub" out these interfering compounds. However, these scrubbers tend to unintentionally scrub the very H₂S components attempting to be measured. Furthermore, as the scrubbing media becomes spent, the degree of scrubbing the components becomes less effective over time.

The colorimetric-rateometric tape method of detection is unique in its ability to measure hydrogen sulfide directly without any practical cross-interference from other components based on thousands of worldwide applications. State-of-the-art developments have improved the tape method to a straightforward and simple design, resulting in reliable operation with very minimal maintenance requirements. Life span for a single tape reel is extended up to 6 months in some cases. Measurement of hydrogen sulfide concentration by the use of the ASTM approved colorimetric-rateometric tape is based on physical constants and chemical factors. The following mathematical formulations demonstrate the calculation precision that is achieved by this application.

Detection of H₂S concentrations by the use of H₂S sensing tape is achieved by exposing the film to the H₂S sample through an aperture in the sample flow system, called the sample chamber. The reaction of photographic film to the light is analogous to the way that chemically saturated H₂S sensing tape reacts to hydrogen sulfide. The chemical formulation for this reaction is as follows:



This reaction has three characteristics which allow it to be applied with unique analytical precision:

1. The reactants are colorless (white).
2. The product (PbS) is colored.
3. In more than a century of use, hydrogen sulfide is the only practical reactant found that produces a colored product on lead acetate Pb(OAc)₂ tape.

The analytical precision of this technology is ASTM approved (ASTM 4084-82).

The rate (r) of this reaction (forming PbS) is as follows:

$$r = k \text{ Pb(OAc)}_2 \times \text{H}_2\text{S} \quad [2]$$

Where k, the proportionality factor, is called the rate constant.

NOTE: The very large (more than 1000 times) concentration of Pb(OAc)₂ on the H₂S sensing tape simplifies the reaction as follows:

$$[\text{Pb(OAc)}_2]_0 = [\text{Pb(OAc)}_2]_1 - \text{PbS}_1 = K_2 (<.1\%) \quad [3]$$

$$\text{Therefore, } r_n = k k_2 (\text{H}_2\text{S} - \text{PbS}_n) \quad [4]$$

For simplicity:

$$k_2 = K \quad [5]$$

$$r_n = K(H_2S - PbS_n) \quad [6]$$

By maintaining a constant H_2S concentration, with continuous flow of the sample into the sample chamber, the rate of reaction equation is further reduced to:

$$r = KH_2S \quad [7]$$

Therefore, by maintaining the control conditions of:

1. A large quantity of $Pb(OAc)_2$
2. Constant H_2S concentration.
3. Sufficient moisture.

The rate of reaction (i.e. the rate of darkening) is linearly proportional H_2S concentration. Measuring the rate of darkening is therefore directly equivalent to measuring the H_2S concentration.

TEST PROCEDURE

The following is an in plant case study in the Middle East consisting of the start-up, commissioning, and accuracy field test of four on-line process analyzers measuring H_2S content in crude oil for quality control purposes. The Model 205 H_2S in Crude Oil Analyzer utilizes the Sample Transfer Stripper™ with ASI Membrane Technology to extract the composition of the crude oil from the liquid phase into the vaporous gas phase; and the colorimetric-rateometric tape method detector to quantify the H_2S . The study also validates the calibration method used for the analyzers. The Analyzer was cross checked for analytical accuracy. The test was witnessed and conducted by several plant Engineers, lab supervisor, and the Process Analyzer Engineer.

This procedure included 3,760 ml of crude sample with an unverified concentration of H_2S . This sample was continuously pumped into the Analyzer and recycled (via analyzer drain) into a suitable container. The Analyzer had an initial reading of 5.72 ppm by weight H_2S based on the concentration of H_2S in the crude sample.

Next, the same sample container holding the same crude sample was sealed and carefully and quickly delivered to the on-site laboratory in attempt to minimize H_2S decay. The laboratory supervisor and assistant analyzed a representative portion of the sample in two separate beakers with two separate manual lab analysis units. The result of the first reading was 4 ppm by weight H_2S . The second lab unit measured 5 ppm by weight H_2S . The difference in measurement between

the Analyzer and the lab units is attributed the escape and decay of H₂S over time and other accuracy factors involved with the lab procedure.

VERIFICATION OF CALIBRATION METHOD

The Volumetric Blending method of calibration was utilized for the Analyzer. The calibration procedure calls for a known concentration of H₂S, which is injected into the crude sample in a container. This was performed by inserting the needle and syringe into a septum connected to a pure source of H₂S while the gas was verified to be fully flowing. After the known volume of pure H₂S was obtained, the H₂S was then introduced into the container with the crude sample via a septum (this was performed under the laboratory vent hood for safety).

ADDITIONAL TESTS

The Analyzer measured continuously while two field samples were taken by lab personnel which were tested in the laboratory. The cross reference of the readings of the analyzer and the lab results can be seen below:

Table I. Comparison of results from the 205 Analyzer and the Lab.

SAMPLE #/ TIME	MODEL 205	LAB
Sample 1: 12:00	5.201 ppm/w	4 ppm/w
Sample 2: 15:00	15.02 ppm/w	14 ppm/w
ASI Prepared Standard 10 ppmw	10.07 ppm/w	14 ppm/w

The differences in Sample 1 and Sample 2 were accounted for by participants as indicated previously and the above lab collection method. The sample was taken in a refinery spout which was poured into an open container which results in the rapid decay of H₂S into the ambient air. The transportation time to the lab, and the time it took to pour the sample into a beaker to be analyzed by the lab also resulted in some decay.

FIELD TEST CONCLUSION

The Analyzer utilizing the Sample Transfer Stripper™ membrane stripper and colorimetric-rateometric tape method of detection was tested by the plant laboratory specialists and found to be

accurate. The Volumetric Blending method of calibration was also verified for accuracy. Both the plant engineers and Process Analyzer Engineer specialists along with ASI engineers were very pleased with the testing method and the accuracy of the Analyzer.

Accurate measurement of low ppm levels of H₂S in a complex liquid stream (such as crude oil) on line is a major challenge. Consequently, the colorimetric-rateometric paper tape combined with the proprietary membrane technology in the Sample Transfer Stripper™ method remains as sensitive and reliable a method as is practically achievable in today's environment.



THE ANALYZER IS PICTURED ABOVE

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