HYDROGEN SULFIDE MEASUREMENT AND DETECTION

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INTRODUCTION

The impetus for measuring and detecting hydrogen sulfide, H_2S, as it relates to the production and distribution of natural gas, is rooted in two primary concerns. The first concern deals with protecting personnel from the lethal effects of H_2S. Typically, the maximum pipeline H_2S concentration is around 0.25 grains per 100 SCF, nominally 4 ppm/volume. At these concentrations H_2S is not lethal and its presence can be detected by the sense of smell with its characteristic rotten egg odor. At the higher lethal H_2S concentrations, typically found at production and acid gas removal installations, the nose becomes desensitized. Unable to smell the H_2S, a worker breathing such an atmosphere is oblivious to the life threatening danger.

The second concern deals with preventing hydrogen embrittlement of the natural gas transmission lines. When hydrogen sulfide reacts with the metal in the transmission line to form a metallic sulfide, the released hydrogen is then free to migrate within the molecular structure of the pipe. Transmission lines weakened by embrittlement are susceptible to rupture failure allowing for large clouds of gasses to escape and accumulate in the atmosphere. Not only are such release clouds lethal by the depravation of life sustaining oxygen, a single spark can set off a devastating explosion.

Various technologies are available for measuring and detecting H_2S. These technologies include on-line continuous analyzers, area monitors, test methods, and personal monitors. Proper use of these technologies can contribute to the safe delivery of natural gas from the well head to the consumer.

H_2S

Though H_2S is a flammable gas, the flammable limits of 4.3% (43,000 ppm) to 46%, (46,0000 ppm) far exceed the concentrations of concern for personnel protection, nominally 10 ppm, and pipeline transmission, 4 ppm. Because H_2S is heavier than air, it will tend to accumulate near the ground when leaked into the atmosphere. A standing individual overcome by H_2S will most likely collapse to where the H_2S concentration is even greater. The H_2S toxicity danger is a function of the concentration and the time of exposure. Concentrations on the order of 500 ppm can result in rapid collapse, unconsciousness and death. Prolonged exposure to lower concentrations can also lead to hemorrhaging and death. At low concentration H_2S has a characteristic rotten egg odor though, with sufficient exposure time, low H_2S concentrations can also deaden the sense of smell. High H_2S concentrations rapidly deaden the sense of smell. Disturbed respiration, throat and eye irritation, sleepiness, headache, and pain in the eyes are all symptoms of hydrogen sulfide exposure.

There is plenty of available information regarding H_2S safety. Some of the web sites containing information on H_2S are listed in Table 1 – H_2S Web References.

Table 1 – H2S Web References

Agency	Web Address
USEPA	www.epa.gov/swercepp/ehs/profile/7783064.txt www.atsdr.cdc.gov/tfacts114.html
OSHA	www.osha-slc.gov/SLTC/etools/oilandgas/general_safety/h2s _monitoring.html
NIOSH	www.cdc.gov/niosh/npg/npgd0337.html

H_2S DETECTION FOR PERSONNEL PROTECTION

Personnel protection devices provide information to a worker regarding a contaminating component concentration in the air so that appropriate actions can be taken in the event an undesirable contaminant concentration is detected. Such actions include, but are not necessarily limited to, evacuation of the area, using a self-contained breathing apparatus, turning on emergency ventilation system, and eliminating the source of the leak. H_2S monitors for personnel protection can be carried by the individual or fixed mounted for area monitoring. H_2S monitors typically use colorimetric or electrical sensors.

An example of a colorimetric H_2S sensor is an encased roll of lead acetate impregnated paper tape, an exposure window, and a color chart. When moistened, the lead acetate impregnated paper tape will change color from white to brown when exposed to H_2S. Tape moisturization is achieved by exhaling on the exposure window. The amount of H_2S present dictates how fast the color changes. The rate of tape color change and the stain darkness is directly proportional to the H_2S concentration. The advantage of the colorimetric H_2S sensor is that electrical power is not required for operation.

Electrical H_2S sensor technologies include metal oxide sensors, sometimes called solid ceramic-metallic (cermet) film devices, and electrochemical cells. Each of these devices depends on the migration of H_2S from its source to the sensor and can be incorporated into a fixed-point detection system or carried by the individual. A personal protection monitor, sometimes referred to as a multimeter, will typically contain a flammable gas detector and an oxygen deficiency sensor in addition to a device to detect H_2S. The migrated H_2S reacts with the surface of the metal oxide sensor, or the reagent chemical in the electrochemical cell, to create an electronic signal. In order for the generated signal to have any meaning, the response of the device must be calibrated with a gas containing a known concentration of H_2S. The surface of the metal oxide sensor regenerates itself in the presence of air. Electrochemical cells have a fixed quantity of reagent that must be replaced when consumed.

Fixed mounted electrical H_2S sensors, powered by a battery or a fixed electrical source, sound an alarm when the H_2S concentration reaches a predetermined level. By using relays, the electrical H_2S sensors can also activate emergency control apparatus, such as, ventilation and alarm systems, when an alarm condition is detected.

H_2S MEASUREMENT IN GASES

Various organizations, such as ASTM, UOP, and GPA, to name three, publish test methods for measuring not only hydrogen sulfide but also a wide range of components and properties. Published test methods provide a way to standardize test procedures so that the results from one location are comparable to the results from another location. Some of the available test methods for measuring and detecting hydrogen sulfide are listed in Tables 2-4.

Table 2 – ASTM Methods for Measurement of H_2S

ASTM Methods	Description
D2420-91 (1996)e1	Standard Test Method for Hydrogen Sulfide in Liquefied Petroleum (LP) Gases (Lead Acetate Method)
D4084-94 1999	Standard Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels (Lead Acetate Reaction Rate Method)
D4323-84 (1997)e1	Standard Test Method for Hydrogen Sulfide in the Atmosphere by Rate of Change of Reflectance
D4913-00	Standard Practice for Determining Concentration of Hydrogen Sulfide by Direct Reading Length of Stain, Visual Chemical Detectors
D4952-02	Standard Test Method for Qualitative Analysis for Active Sulfur Species in Fuels and Solvents (Doctor Test)
D5504-01	Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence
D6228-98	Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection

Table 3 – GPA Methods for Measurement of H_2S

GPA Methods	Description
Standard 2285	GPA Standard for Determination of Hydrogen Sulfide and Mercaptan Sulfur in Natural Gas (Cadmium Sulfate-Iodometric Titration Method)
Standard 2377	Test for Hydrogen Sulfide and Carbon Dioxide in Natural Gas Using Length of Stain Tubes

Table 4 – UOP Methods for Measurement of H_2S

UOP Methods	Description
9-85	Hydrogen Sulfide in Gases by the Tutwiler Method
41-74	Doctor Test for Petroleum Distillates

Selecting a test method to detect and measure hydrogen sulfide will depend on the desired degree of precision. Some test methods are designed to provide approximate results while others are design to provide a greater degree of precision.

An example of an approximate method is the Doctor Test. The Doctor Test involves passing a H_2S containing gas across a filter paper wetted with an aqueous lead oxide solution and observing a color change. The lower detectable limit is about 0.03 grains per 100 SCF, or about 0.5 ppm/v. A dark brown color is indicative of concentrations above 0.5 grains per 100 SCF, or about 8 ppm/v (Pender, 1986).

Another approximate method involves using glass stain tubes filled with lead acetate. As a known volume of gas is drawn through the tube, the lead acetate changes from white to brown. The amount of color change depends on the amount of H_2S in the gas. The greater the H_2S concentration the greater the color change. Tubes for various concentration ranges are available.

Some methods to detect and measure H_2S are based on wet chemical procedures. An example of a wet chemical method is GPA Standard 2285 which is applicable for determining the H_2S content of natural gas. In this method an extracted sample is passed through a cadmium sulfate ($CdSO_4$) solution. The absorbed H_2S reacts to form cadmium sulfide (CdS) which is then measured iodometrically. Another example of a wet chemical method is the portable titrator that uses an electric current passing through a reagent electrolytic solution, such as bromine, while the H_2S containing gas is bubbled through the solution. The net generating current needed to maintain a slight excess of reagent solution is directly proportional to the concentration of the reactant (H_2S).

Some of the methods listed in Tables 2-4 are available as on-line instrumentation. On-Line instruments offer the advantage of providing analytical information twenty-four hours a day seven days a week. Included in this category are gas chromatographs and lead acetate analyzers.

Each is an extractive type analyzer in that the sample is extracted from the process and is transported to the analyzer for analysis.

Gas chromatography involves injecting a known volume of sample into a carrier stream. The sample-containing carrier then passes through a column where the components of the sample are separated from each other. Porous polymers, such as Poropack, are used as the column material when analyzing for sulfur compounds. Typically, the column is operated under constant temperature and pressure conditions as this simplifies the analyzer design. A fairly simple design is preferred due to the potential for remote installations. As each component exits the column, it passes across a detector that, generates a Gaussian (peak) shaped signal. The identity of a given component is determined based on the time it takes to pass through the column. The concentration of the component is determined by integrating the area under the peak and comparing this area to the area obtained using a gas with a known concentration of the specific constituent. A distinct advantage of the gas chromatograph is its ability to provide a complete compositional analysis in addition to the determination of H_2S concentration. The major disadvantages of gas chromatographs include their relatively high purchase price and operational complexity. The major components of a simple gas chromatography system are shown in Figure 1.

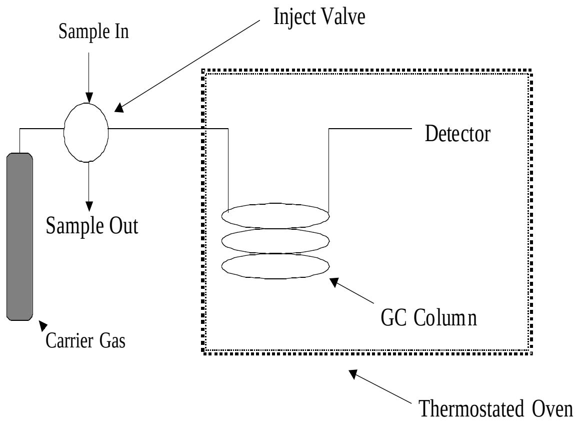

FIGURE 1. Basic Gas Chromatograph

As the name implies, hydrogen sulfide analyzers using the lead acetate detector are based on the reaction of hydrogen sulfide with lead acetate. The initially white lead acetate turns brown when exposed to hydrogen sulfide in the presence of water. The greater the amount of H_2S in the sample, the darker the stain that forms on the tape. Lead acetate is impregnated onto a roll of paper tape that is installed in the analyzer. Only a small portion of the roll is exposed to the sample during an analysis cycle. This is accomplished by using a window in a sample chamber. Before exposure to the tape, the sample gas passes through a humidification bubbler containing a 5% by volume acetic acid in water solution. Being acidic, the bubbler solution prevents the loss of H_2S during the humidification process. After passing past the exposed portion of the tape, the sample gas is vented from the analyzer. At the start of each analysis cycle a fresh piece of the tape is pulled in front of the window.

To be useful as an on-line analyzer, the color change caused by the reaction of H_2S with lead acetate must be converted into an electrical signal. Earlier analyzer designs used a lens to focus a whitish light onto the reaction window. As the initially white surface changes color it absorbs some of the incident light. Two photocells, one measuring the other reference, initially balanced in a Wheatstone bridge arrangement, detected the drop in incident light. The now out of balanced Wheatstone bridge creates a voltage signal that is then processed by the electronic portion of the analyzer. More recent lead acetate analyzer designs utilize a tailored incident light frequency, a bifurcated fiber optic cable for light transmission to and from the reaction window, a photodiode for detecting the drop in the incident light intensity, and an analogue to digital converter for microprocessor signal processing.

Tape transport on the first generation of lead acetate analyzers was continuous. Because the tape was always moving, the motor used to transport the tape was subject to mechanical wear necessitating its periodic replacement. The H_2S concentration was determined by the difference between the reflected light intensity at the beginning of the analysis cycle to that at the end of the analysis cycle. This difference was proportional to the concentration of H_2S in the sample. On subsequent generations of the lead acetate analyzer the tape is stationary during the analysis cycle. By only having to use the motor for a short time between analysis cycles, it is subject to very little mechanical wear. Combined with employing periodic tape transport, a differentiating circuit was also added. Instead of looking at the change in reflected light intensity during an analysis cycle, differentiating the reflected light intensity meant that the rate of change of reflected light intensity was being measured. The rate of change is also proportional to the concentration of H_2S in the sample. Both means of H_2S measurement yielded one result per analysis cycle, which typically lasted for 3 minutes.

With the advent of microprocessors it became possible to slice the analysis cycle into smaller segments. Instead of having one result per analysis cycle, multiple intermediate values of the rate of change could be calculated and then averaged at the end of the analysis cycle to report a result. Alarm outputs could be determined using the intermediate values, which meant that the analyzer could respond to an upset condition just as fast as, and sometimes faster than, the earlier designs. By reporting an average of the intermediate results at the end of the analysis cycle, the total analysis time could be increased. An increased analysis time meant that the time between tape replacement was increased from about two weeks to about a month. Figure 2 illustrates a modern lead acetate tape analyzer for determination of H_2S in natural gas.

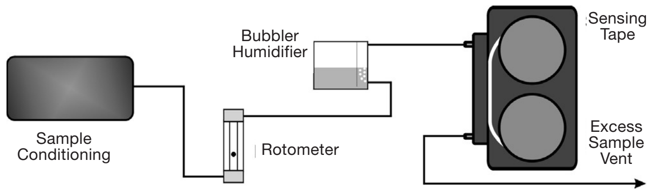

FIGURE 2. Lead Acetate Tape Analyzer for Determination of H_2S in Natural Gas

Lead acetate analyzers cannot provide a complete compositional analysis as with gas chromatographs. These analyzers are typically configured to provide a H_2S and/or total sulfur analysis. Key advantages of lead acetate tape analyzers include their relatively low purchase price and operational simplicity.

CALIBRATION

Instrument calibration is required so that the electronic signal generated by the analyzer can be interpreted intelligently. Calibration requirements are similar for all types of H_2S analyzers. Basically, a span gas with a known H_2S concentration is introduced into the analyzer and the response is recorded. Many H_2S detectors, such as, the flame photometric detector used with gas chromatographs and the lead acetate tape can produce a non-linear detector counts vs. H_2S concentration curve. Therefore, it is often desirable to check the measurement linearity in addition to calibrating with a span gas. A linearity check can be performed with a gas containing at least 50% less H_2S than the span gas.

The typical units of measure for H2S in gases is parts per million, ppm. For gases ppm is commonly expressed as a volume/volume or mole/mole basis. For gases the units of ppm (volume/volume) and ppm (mole/mole) are equal. The concentration of H2S in ppm (v/v), that is, ppm by volume is calculated according to the equation shown in figure 3. Note that the calculation of ppm is very similar to well known percentage calculations, for ppm we multiply by 1,000,000, for percent we multiply by 100. In fact, another name for percent is pph or parts per hundred.

$$\left[\frac{\text{cm}^3\ H_2S}{(\text{cm}^3\ H_2S + \text{cm}^3\ \text{diluent gas})}\right]\left[1{,}000{,}000\right] = \text{ppm } H_2S\ (v/v)$$

FIGURE 3. Calculation of Parts Per Million, ppm

Critical to obtaining a good calibration is the quality of the H_2S standard gasses. These gasses can be obtained in three ways: 1) purchase custom blends from a gas supplier, 2) using a permeation tube, and 3) preparing a blend by using a calibration kit.

A purchased calibration blend is typically under pressure allowing the user to have a long term supply of standard in a single cylinder. Low level blends, 1-10 ppm H_2S (v/v), do require the cylinder to be stabilized which adds to the delivery time. Such blends most likely carry a limited validity time. Storage conditions for low level blends also need to be seriously considered. A low level cylinder exposed to extremes in cold or hot temperatures can result in reduced or excess amounts of H_2S actually in the gas phase within the cylinder. Under these conditions, what comes out of the cylinder may not be the concentration indicated or desired. The net result is a faulty calibration.

Permeation tubes contain a small amount of the pure compound of interest, for example H_2S. The tube is sealed at its ends with a membrane that allows the H_2S to permeate across the membrane at a known rate. The permeation rate is usually low enough compared to the amount of pure compound in the tube that the tube has an extended lifetime. An H_2S free carrier gas at a known flow rate is required to utilize a permeation tube for calibration. The carrier gas mixes with the permeated H_2S resulting in an H_2S blend of a known composition. The permeation rate is characterized and certified at a fixed temperature, which is typically 30 °C to 40 °C. This means that a temperature controlled oven is required so that the permeation rate obtained is the same as the permeation rate expected.

Permeation tubes also require a stabilization time, sometimes as long as 4 to 10 hours after they are installed in a temperature controlled oven. It is important to recognize that a permeation tube permeates all of the time until the material inside of the tube is exhausted. Even in standby mode a carrier gas flow rate is required to pass through the oven when a permeation tube is installed in it. Without a carrier gas flow in standby mode, the concentration of H_2S accumulates. When the carrier gas is finally turned on the H_2S concentration in the ensuing blend will far exceed what is expected. If the carrier gas flow is off while the permeation tube is in the oven for an extended period of time, it may be necessary to replace parts of the oven. These parts will be so saturated with H_2S that they are essentially useless for producing low level calibration blends. Permeation tubes also need to be stored at the recommended temperature so as not to damage or alter the permeation characteristics of the tube.

Preparing calibration blends with a calibration kit requires an H_2S free blending gas and a source of either pure H_2S or a cylinder blend with a known elevated H_2S concentration, for example 1000 ppm/volume. A large plexiglas cylinder with a piston with a typical volume of

10 liters is used to make the desired blend. The technique involves introducing a small amount of either pure H_2S or the H_2S blend using a syringe into the 10 liter cylinder and diluting this to the correct volume with the blending gas to obtain the desired H_2S concentration. Because the blend is at atmospheric pressure, the amount of the standard is limited and a pump is required to introduce it into the analyzer system. Some skill is required to achieve repeatable blends. Figure 4 depicts a typical calibration kit.

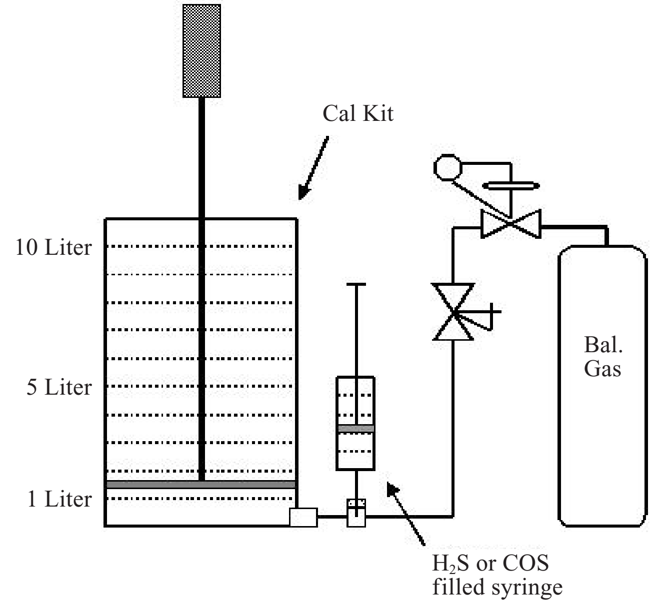

FIGURE 4. A Typical Calibration Kit

Regardless of the source of the calibration standard, attention must be paid to the composition of the background gas used to make the standard. This is especially true when the sample flow rate is important for the successful operation of the analyzer. For example, a H_2S analyzer configured for a methane sample should be calibrated with a H_2S in methane calibration standard. Another point to consider when using calibration blends is where they are introduced to the analyzer. Process sample normally flows through a sampling system prior to being introduced into the analyzer. For purposes of consistency a calibration blend should be introduced into the sampling system at the sample tap, if possible. In this way the calibration blend that arrives at the analyzer has been exposed to the same conditions as the sample. A drifting analyzer response, under these conditions, could suggest the presence of a contaminant in the sampling system as well as an analyzer malfunction. Once a stable analyzer response to a calibration blend is achieved, the unit can then be calibrated.

SAMPLE CONDITIONING SYSTEMS

Independent of the type of extractive on-line analyzer employed, the process sample must be transported from the sample point to the analyzer so as to maintain the integrity of the sample. Sample integrity is obtained by installing a properly designed sample conditioning system. Process variables taken into account when designing a sampling system are the composition, temperature, and pressure at the sample point. One also must know the outside ambient temperature as well as the temperature inside of the analyzer shelter, if one is utilized. With this information it is possible to calculate the hydrocarbon and water dew points of the sample as a function of the pressure along the sample delivery system. Dew points are important because the presence of liquid and gas phases impedes the ability to accurately monitor the flow rate of sample to the analyzer. When measuring hydrogen sulfide, liquids can act as absorption sites thus reducing the amount of H_2S that arrives at the analyzer. Thus, the analyzer can yield a legitimate result based on what is introduced to the analyzer when in fact the actual concentration in the process is higher. Since gas chromatographs use injection valves to introduce sample to the column, two phase sampling leads to erratic results.

Natural gas pipelines tend to operate at elevated pressures, nominally on the order of 1000 psig. When the pressure is reduced from 1000 psig to the typical analyzer inlet pressure of 50 psig, the gas cools. This phenomenon is known as the Joule-Thompson effect. Depending on the composition of the process and the total pressure drop, cold spots in the sampling system can cause liquid formation. Since H_2S is soluble in liquid water and liquid hydrocarbon, the amount of H_2S reaching the analyzer is reduced. Again, the analyzer can yield a legitimate result based on what is introduced to the analyzer when in fact the actual concentration in the process is higher. Sample probes that take the pressure drop inside of the process pipe are available. These operate on the premise that the total heat flow across the outside of the probe is very large compared to the heat flow requirement to reheat the cooled gas at the lower pressure inside the probe. Because probes can extend into the process pipe a third to 1/2 of its diameter, they may not be desirable in some installations. Under these circumstances, taking the needed pressure drop in stages can mitigate the potential for cold spots and/or condensation.

If there is a chance for any particulate matter coexisting with the sample, it needs to be removed prior to the analyzer. Particulate matter can plug injection valves, pressure regulators, and flow control devices. Self-cleaning and cartridge type sample filters are available. Self-cleaning filters have a sweep line that is usually returned to the process. In some natural gas installations a sweep line is not practical because the needed pressure drop in the process line is not available or venting to the atmosphere is not desirable. In these cases, two parallel cartridge filters with isolation and depressurization provisions can provide the needed filtration and maintenance access.

Every sample system has a lag time, the time between when the sample exits the process and when the analyzer observes it. Factors that impact the lag time for a single analyzer system include: 1) the analyzer location relative analyzer system include: 1) the analyzer location relative to the sampling point, 2) the sample line pressure, 3) the sample flow rate to the analyzer, and 4) line bulges such as filter bodies. A long sample line at an elevated pressure means a large sample inventory between the sample tap and the analyzer. Calculating the lag time involves determining the sample system volume. With the sample system volume, the total gas volume in the sample system can be calculated by correcting for the sample line temperature and pressure. Dividing the sample system gas volume by the sample flow rate to the analyzer, at the same conditions of temperature and pressure, yields the lag time to the analyzer. The total lag time of the system is the sum of the sample system lag time and the lag time within the analyzer itself.

MAINTENANCE

Stated simply, routine maintenance on H_2S analyzers, as well as any other analyzer, is a must. Without routine maintenance, problems can develop that can compromise the integrity of the results. Changes in sample and/or carrier flow, as well as sample pressure and temperature can cause calibration drift. Failure of an injection valve on a gas chromatograph or failure to replace the tape when it is consumed and/or replenishing the bubbler solution on a lead acetate H_2S analyzer can cause the analyzer to read zero even though there is H_2S in the sample. Malfunctioning alarms can prevent desired diversion or shutdown actions from occurring in the event out of specification gas passes the sampling point. Sample system contamination and/or leakage can reduce, and possibly eliminate, the concentration of H_2S that actually arrives at the analyzer. Plugging or accumulation in vent lines can increase sample lag times in addition to altering the response of the detector. In general, the recommended maintenance practices of the manufacturer should be followed and supplemented by site and/or company specific requirements and practices.

CONCLUSION

The requirement for measuring and detecting H_2S in natural gas is motivated by personal protection concerns and the need to maintain gas quality. Though the challenges associated with measuring and detecting H_2S can seem daunting, the good news is that there are successful H_2S in natural gas analyzer applications installed in the field. Good maintenance practices, trained personnel, well designed sample systems, proper calibration techniques, understanding the employed methodology, and being cognizant of the dangers of H_2S combine to provide for a reliable and safe H_2S measurement.

REFERENCES

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ADDITIONAL READING

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