Determination of Hydrogen Sulfide and Total Sulfur in Natural Gas

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Introduction

Hydrogen sulfide and other sulfur bearing compounds exist naturally in many natural gas fields throughout the world. It is generally necessary to remove these sulfur bearing compounds from the gas in order to preserve public safety, reduce corrosion in pipelines, meet contractual agreements and to control odor in the gas. Thus the determination of hydrogen sulfide and total sulfur in natural gas is critical to the natural gas industry.

Hydrogen Sulfide Measurement Requirements

Hydrogen sulfide (H_2S) is a clear, colorless, extremely toxic gas that has a rotten egg smell at low concentrations. The human nose can detect H_2S at concentrations below 100 parts per billion. Caution must be used when relying on the sense of smell to detect H_2S because fatal concentrations of H_2S anesthetize the sense of smell.

H_2S is generally present in raw natural gas reserves in varying concentrations ranging from parts per million to percentage levels. There are several processes in gas refining facilities designed to remove the H_2S from the gas. The measurement of H_2S is critical in ensuring that processed natural gas meets contractual specifications for their customer. Typical allowable limits of H_2S range from 4 to 16 ppm by volume.

Total Sulfur Measurement Requirements

In most natural gas reserves, the majority of sulfur is present as H_2S. However, in some reserves there may be significant concentrations of other sulfur bearing compounds. These “other sulfurs” can generally be divided into four main groups: 1) mercaptans or thiols, 2) sulfides, 3) disulfides and 4) thiophenes. There are also processes in gas refining facilities designed to remove these other sulfur compounds. Total sulfur measurement is also critical in ensuring that processed gas meets contractual pipeline specifications. Typical allowable limits for total sulfur range from 16 to 80 ppm by volume. Total sulfur measurement is further complicated by the issue of gas odorization. Odor is imparted to natural gas in populated areas for safety reasons by the addition of sulfur compounds. Typical odorant compounds are iso-propyl mercaptan, normal-propyl mercaptan, tertiary-butyl mercaptan and thiophene. Total sulfur measurement and/or individual sulfur compound analysis may be required to balance odor injection levels.

Overview of Sulfur Measurement Technology

Listed below are some of the commonly used sulfur measurement techniques with their key features and limitations.

Lead Acetate Tape.

Methodology. This method relies on the chemical reaction of H_2S with lead acetate impregnated paper tape to form lead sulfide. The lead sulfide appears as a brown stain on the paper tape. A light source is used to illuminate the tape where the reaction is to occur and light detector is used to monitor the reflection of the source from the tape. A concentration of H_2S can be determined by the rate of staining on the tape.

Lead acetate tape can be used to measure total sulfur by mixing the sample stream with hydrogen and passing it through a quartz tube heated to 1000 ^oC. This process quantitatively converts sulfur bearing compounds to H_2S which can then be measured at the tape.

Key Features and Limitations. The lead acetate tape method is H_2S specific, very sensitive, and has an equimolar response to sulfur when used in the total sulfur mode. Tape is typically linear up to 50 ppm. Higher ranges can be achieved with dilution systems.

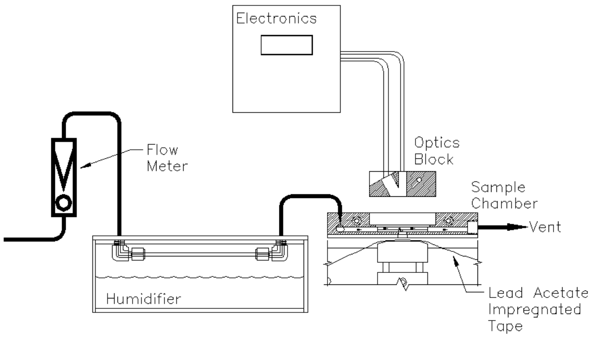

Figure 1: Lead Acetate Tape Analyzer

Sulfur Chemiluminescence.

Methodology. This is a two step measurement process in which a small amount of sample is injected into a hydrogen rich flame or an enclosed combustion assembly. The hydrogen to air ratio combined with the presence of a vacuum allow for the formation of sulfur monoxide (SO) in the combustion assembly. The combustion gases from the flame or combustion assembly are then drawn under vacuum to a reaction cell where ozone from an ozone generator is continuously added. SO reacts with ozone to form an electronically excited state of sulfur dioxide (SO_2) which releases ultraviolet (UV) radiation upon relaxation. The released UV radiation is detected with a photomultiplier tube and is linearly proportional to the amount of sulfur present in the sample. Sample can be injected directly to the analyzer to arrive at a total sulfur concentration. The addition of a chromatograph column prior to the detector allows for the measurement of individual sulfur compounds.

Key Features and Limitations. The sulfur chemiluminescence detector is linear over a large range, very sensitive and has an equimolar response to sulfur compounds. This allows for the use of a single component, single point calibration which greatly simplifies the calibration process.

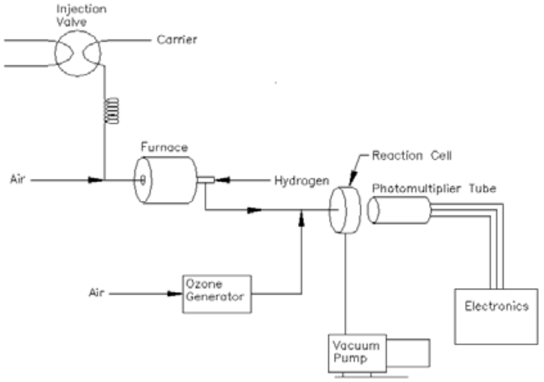

Figure 2: Sulfur Chemiluminescence Analyzer

Flame Photometric Detector (FPD).

Methodology. FPDs are generally employed as chromatograph detectors. The effluent from a chromatograph column is passed through a hydrogen rich, low temperature flame. Sulfur species are converted to S_2 which becomes excited and emits radiation upon relaxation. The emitted radiation is monitored by a photomultiplier tube.

Key Features and Limitations. The FPD is very sensitive and selective to sulfur. Its response to sulfur is, however, non linear and non equimolar which makes it difficult to calibrate because several multi-component standards of varying concentration are required.

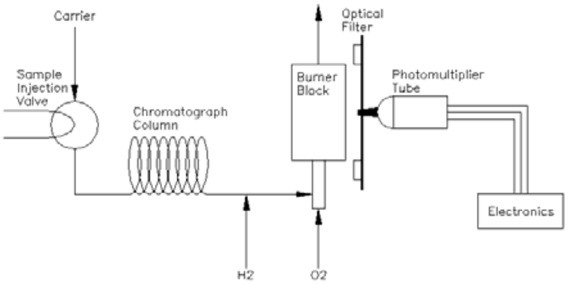

Figure 3: Flame Photometric Analyzer

Ultraviolet (UV) Absorption.

Methodology. This method relies on the ultraviolet absorption characteristics of H_2S. The optical system consists of a UV lamp as a source, a transparent sample cell through which the sample gas flows, and a single photomultiplier tube detector. In front of the detector is a motor driven beam splitter which alternately directs the source beam to a reference filter and a measurement filter. The measurement filter is selected to correspond to an absorbency peak of H_2S while the reference filter is selected to correspond to some non-absorbing region of the spectrum for H_2S. In this way the absorption of the sample can be measured and is proportional to the amount of H_2S present in the sample.

Key Features and Limitations. The UV absorption method is typically used at percentage levels of H_2S, however, by lengthening the cell and pressurizing the sample in the cell, measurement at ppm levels is possible. This method is subject to strong positive interference from olefins and aromatic compounds. Chromatographic techniques are sometimes employed to separate the H_2S from interfering species.

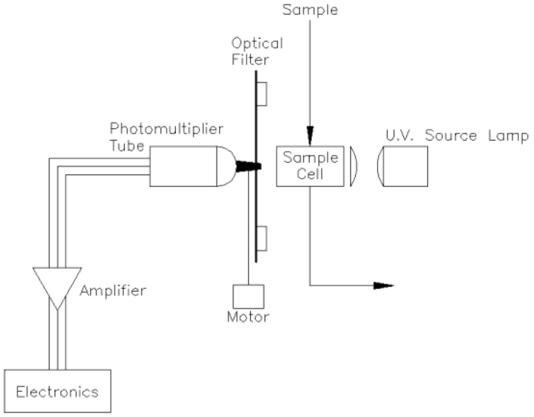

Figure 4: Ultraviolet Absorption Analyzer

Wet Electrochemical Detectors.

Methodology. The wet electrochemical detector relies on the reduction/oxidation reaction between reduced sulfur compounds and a solution of chromic acid. This method is used as a chromatograph detector for the measurement of individual sulfur compounds and has widespread use in odorant analysis. The sulfur compounds are eluted from a column and passed through a measurement electrode assembly. The electrode assembly consists of two platinum mesh electrodes, one of which is immersed in the chromic acid solution while the other is suspended above the solution. The two electrodes are held in contact by a layer of the solution which is suspended between the two electrodes by capillary action. The column effluent is passed over the upper electrode. The chromic acid near the surface of the electrode is reduced, creating an excess of electrons at the upper electrode. The strength of the resulting current between the two electrodes is proportional to the amount of sulfur compound present.

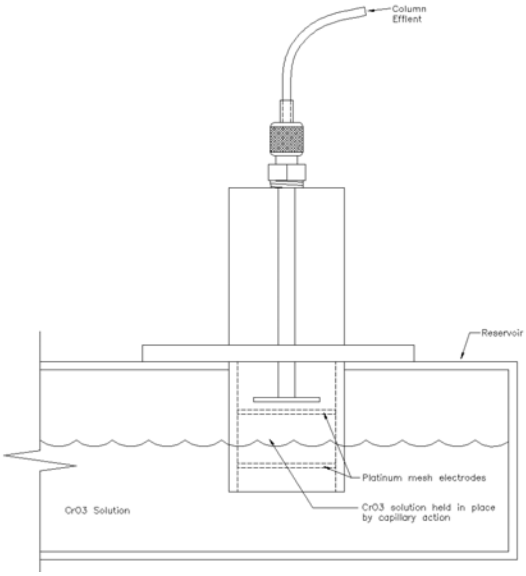

Figure 5: Wet Electrochemical Detector

Key Features and Limitations. This method offers linear response to sulfur compounds in the low ppm range, however the response is not equimolar. It only responds to reduced sulfur species and thus cannot measure carbonyl sulfide, making a true total sulfur analysis impossible.

Solid State Electrochemical Sensors.

Methodology. Solid state sensors are constructed using a semi-conductor material that is applied to a non-conducting substrate between two electrodes. The substrate is heated to a temperature such that the gas being monitored can cause a reversible change in the conductivity of the semi-conductor material. Under zero gas conditions, oxygen molecules tie up free electrons in the semi-conductor material by absorbing to its surface, thus inhibiting electrical flow. As H_2S molecules are introduced, they replace the oxygen molecules releasing the free electrons thus decreasing the resistance between the two electrodes. This change in resistance is measured directly and is proportional to the concentration of H_2S in the gas.

Key Features and Limitations. Solid state sensors are typically used for ambient air monitoring for protection of personnel and equipment. They generally have high zero drift and are susceptible to poisoning, making them ineffective as process analyzers.

Sulfur Titrators.

Methodology. Sulfur titrators operate on the principle of the reduction-oxidation reaction between sulfur bearing compounds and bromine (Br_2) and are typically used in chromatographic applications. Bromine gas (Br_2) is generated electrochemically from a solution containing hydrobromic acid (HBr). The titrametric cell is basically a three electrode coulometric titration. Three electrodes are used: the first serves as a common, the second is used to generate the Br_2, and the third is a hydrogen generating electrode. The titration proceeds by flowing the chromatograph column effluent through the titrametric cell at a fixed flow rate. The Br_2 that is generated in the cell reacts with the sulfur compound as it elutes from the column, and both are consumed. The electrical current necessary to generate just enough Br_2 to react with all of the sulfur compound is measured and is proportional to the amount of sulfur compound present.

Key Features and Limitations. Sulfur titrators are typically used as chromatograph detectors which provides measurement of individual sulfur compounds. They do not respond to carbonyl sulfide (COS) or carbon disulfide (CS_2), thus making a true total sulfur measurement impossible.

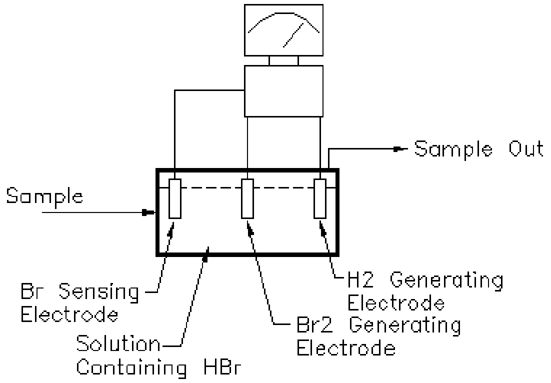

Figure 6: Sulfur Titrator

Tunable Laser Diode (TDL).

Methodology. The tunable laser diode relies on the absorption characterizes of H_2S in the near infrared. A laser is used as the light source instead of traditional infrared sources. The gas sample flows through a cell where is it irradiated by the laser and any H_2S in the sample will absorb energy from the laser. The amount of light absorbed is proportional to the concentration of H_2S in the sample.

Features and Limitations. Tunable laser diode is a direct spectroscopic method and thus requires no consumable components. Sensitivity into the ppm range can be achieved by the use of multipath cells. The TDL is subject to interferences from the hydrocarbon matrix and thus it is required to know the concentration of the specific hydrocarbons in the sample. The analyzer results are subject to change if the hydrocarbon matrix changes. The TDL is also subject to positive interferences from other sulfur compounds in the gas, such as mercaptans. A scrubber is required to remove H_2S from the sample and then compare the spectra of the sample against the sample with H_2S removed.

Length of Stain Tubes.

Methodology. These are glass tubes filled with lead acetate impregnated onto an inert substrate. A fixed volume of sample gas is drawn into the tube by means of a hand held pump. Any H_2S present in the sample will react with the lead acetate to form lead sulfide, which can be seen as a brown stain inside the tube. The length of the stain inside the tube is proportional to the amount of H_2S in the sample.

Features and Limitations. Accuracy of stain tubes is +/- 25% and are only useful as a rough estimate of H_2S concentration. Stain tubes are also available which respond specifically to mercaptans or thiophene. Stain tubes do not provide complete total sulfur measurement because they do not respond to carbonyl sulfide or sulfides and disulfides.

Calibration of Sulfur Analyzers

All sulfur analyzers rely on known reference standards for their calibration. Proper calibration is essential for good analyzer accuracy. There are several methods available for generating H_2S and total sulfur calibration standards, which are listed below.

Permeation Devices. A small amount of the pure compound of interest is encapsulated in a reservoir. One end of the reservoir is sealed against a semi-permeable membrane. The surface area and chemical characteristics of the membrane allow a small amount of the compound to permeate through the membrane at a known rate. A carrier gas flowing at a known rate picks up the permeated sample and thus generates a gas stream of known concentration.

Permeation devices are generally temperature and flow dependent, so care must be exercised to ensure that proper temperature control and flow rates are used for a specific device.

Dilution Techniques. Dilution techniques can be used to generate calibration standards of a desired concentration on site. Typically, a small amount of pure H_2S is injected via a syringe into a large cylindrical container and then diluted with air. By varying the amount of H_2S injected and the amount of air used for dilution, virtually any desired concentration can be generated.

Standards generated in this manner should be used immediately because they tend to degrade over time. Also, great caution must be exercised when using pure H_2S, due to its high toxicity.

Prepared Cylinders. Many gas supply companies offer prepared pressurized cylinders of H_2S and total sulfur standards of any desired concentration. Bottled gases are the most convenient and easy to use standards. There are, however, several points to consider when choosing and using bottled sulfur standards.

Prepared H_2S and sulfur standards have a shelf life. Most manufacturers will guarantee an H_2S standard for 6 months at a concentration below 10 ppm and for one year at concentrations above 10 ppm. Standards should be replaced according to the manufacturers specified shelf life. Bottled standards are available in many sizes, so the amount of calibration gas can be purchased according to your specific requirements.

H_2S standards should be packed in a background of nitrogen, as opposed to methane or any other hydrocarbon background. H_2S in nitrogen standards are more stable because nitrogen is generally available in purer and drier grades than most hydrocarbons. It is the trace amounts of moisture in the background gas that contribute the most to the standard's degradation.

Where possible, mixing several different sulfur compounds in the same gas mixture should be avoided. Sulfur compounds are very reactive and will tend to react with each other, the cylinder walls and trace levels of impurities in the background gas. One example of this occurs in mixtures containing hydrogen sulfide and carbonyl sulfide (COS). The COS tends to hydrolyze at high pressure in the presence of trace amounts of moisture to form H_2S. Therefore, over time, the COS concentration in the bottle will fall while the H_2S concentration will increase.

Avoid the use of any brass components in your calibration system. This includes the valve stem on the bottle, pressure regulators, associated tubing and flow devices. Brass will absorb significant amounts of sulfur, leading to erroneous calibration. 316 stainless steel should be used for all sample wetted parts.

One should constantly be aware of the reactive nature of H_2S and sulfur compounds in general. Even 316 stainless steel will absorb sulfur. It is a good idea to thoroughly purge regulators and tubing with the calibration gas before performing a calibration routine.

Sample Conditioning Systems

The purpose of the sample conditioning system is to deliver a clean, particulate free, dry sample to the analyzer that is representative of the gas in the pipeline. Once again, due to the reactive nature of sulfur compounds, there are some special considerations when designing a sample system for sulfur measurement.

Sample gas will typically be extracted from the pipeline by means of a probe regulator. The probe will typically extend into the middle 1/3 of the pipeline to avoid extracting any contaminants from the inside of the pipeline wall. The probe regulator will also reduce the pressure of the sample from pipeline pressure down to 10 – 50 psig. Making the pressure drop right at the pipeline is desirable for two reasons: 1) the pressure drop occurs right at the probe tip where the gas temperature is likely to be higher thus minimizing the Joules-Thompson effect and 2) packing the sample transport lines with a lower pressure greatly reduces sample transport times.

Once the sample is transported to the analyzer, any particulate or entrained liquids can be removed with a coalescing filter. Typically this filter is equipped with a sweep valve which sweeps away any removed liquids and also acts as a speed loop, ensuring that the sample in the transport line is representative of the sample in the pipeline. In cases where there are large amounts of entrained liquids, a gas permeable membrane filter can be used which will allow only the gas portion of the sample to pass to the analyzer.

As with the calibration system, all sample wetted parts should be of 316 stainless steel construction.

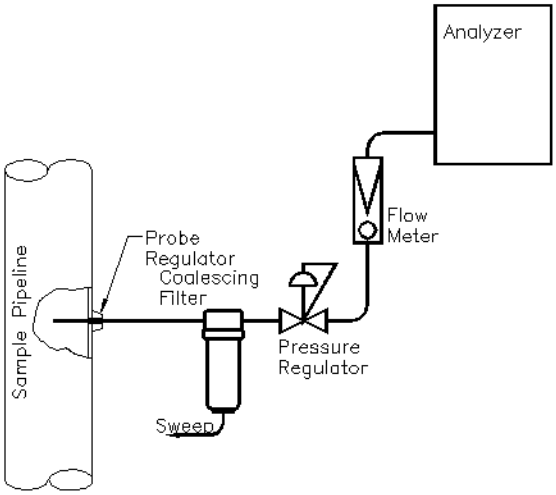

Figure 7: Typical Sample Conditioning System

Getting Good Sulfur Numbers: Verification and Troubleshooting of Sulfur Analyzers

Due to the reactive nature of sulfur compounds it can be difficult to obtain reliable H_2S and/or total sulfur analysis results. Verification of sulfur analyzers can be equally as difficult. The discussion below addresses some of the issues that may arise when attempting to interpret the results of a sulfur analyzer.

Keep the calibration standard current. The calibration standard is the most important trouble shooting tool available to ensure that the sulfur analyzer is operating within its specifications.

It is very important when doing sulfur measurement to keep the sample transport lines free of contaminants such as water, glycol, amine and condensed hydrocarbon liquids. Keep the sample transport lines as direct and as short as possible from the sample point to the analyzer. Also, avoid low spots or cold spots in the sample transport lines where liquids are likely to collect. If liquids do collect in the sample system, H_2S is likely to be absorbed by the liquids, possibly causing false low readings. A liquid pool may also absorb a certain amount of H_2S and then release it upon a change in temperature or pressure, causing temporary false high readings. Choosing an appropriate sample point will also help in minimizing sample line contamination. Putting the sample point slightly farther away from the process may compromise the analyzer's response time slightly, but may greatly improve analyzer reliability.

At certain times it may be necessary or desirable to verify the reading of an on line instrument. Two common ways of doing this are by length of stain tubes or by sending a sample to a laboratory. When using length of stain tubes, be sure to take the sample from the same point that the analyzer does. Where possible, take the sample from the analyzer's actual sample system to eliminate any problems that may be associated with the sample system itself. Bear in mind that length of stain tubes are accurate to +/- 25% of reading and only provide an estimate of theH_2S concentration. When taking a sample to send to a laboratory, also use the same sample point that the analyzer uses and where possible take the sample from the analyzer's sample system. Some consideration must also be given to the sample container itself. Due to their reactive nature the sulfur compounds of interest may be absorbed by the container, leading to false low or even zero readings from the laboratory analysis. If using a sample bomb, it should be of 316 stainless steel construction and must be clean. It should also be sufficiently purged to allow for absorption of the sulfur compounds in the walls of the bomb. Teflon lined sample bombs are available that will minimize sample absorption, however, Teflon is still susceptible to absorption. A sample container deactivation process is now available that will virtually eliminate sulfur absorption. The container is deactivated by applying a microthin layer of silica to the container wall, thus eliminating contact between the sample and the container. Sample transport tubing treated with this process is also available. An alternative to sample bombs where the sample is available at low pressure (less than 2 psig) is the sample bag. These bags are typically made of an inert polymer (usually Tedlar) and are fitted with a valve for sample introduction.

Summary

Determination of hydrogen sulfide (H_2S) and/or total sulfur content in natural gas pipelines is necessary to preserve public safety, reduce corrosion in pipelines and related equipment, meet contractual agreements and to control odor of the gas. There are several different methods for the measurement of sulfur in pipelines, each with its own inherent advantages and disadvantages. Calibration and sample handling systems are an integral part of the sulfur measurement system. Due consideration must be given to the reactive nature of sulfur compounds when designing sulfur measurement systems and when verifying and troubleshooting these systems.