

DETERMINATION OF HYDROGEN SULFIDE AND TOTAL SULFUR IN NATURAL GAS

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INTRODUCTION

Hydrogen Sulfide (H₂S) is a gas composed of one Sulfur Atom and two Hydrogen Atoms. H₂S is formed by the decomposition of organic matter and is therefore, found naturally in crude oil and natural gas deposits. H₂S is a highly toxic, transparent, colorless and corrosive gas. Due to the toxic and caustic properties of this gas and its natural presence within natural gas, it is imperative to measure and control the concentration levels of H₂S within natural gas pipelines. This paper will discuss the Properties, Purpose of Measurement and Measurement Technologies for H₂S and discuss how these technologies can be adapted for measurement of Total Sulfur.

TOTAL SULFUR MEASUREMENT

Total sulfur measurement is critical in processed gas for refinery applications, pharmaceutical and beverage as well. Additional sulfurs present in most natural gas formations can be mercaptans, sulfides, disulfides and thiophenes. The use of odorants (which is a form of mercaptans) puts further emphasis on the need for Total Sulfur analysis.

PROPERTIES

H₂S is also known as Sour Gas, Swamp Gas, Sulfuretted Hydrogen, and Hydrosulfuric Acid. H₂S has a familiar odor of rotten eggs at low concentrations. At high concentrations, H₂S is highly toxic and often deadly.

Physical Properties

- Boiling Point -76.60°F
- Freezing Point -121.9°
- Molecular Weight 34.08 g/mole
- Specific Gravity 1.1895
- Lower Explosive Limit 4.0%
- Upper Explosive Limit 44.0%

Danger Levels

- 10 ppm Unpleasant Odor, Safe for 8 hour exposure
- 100 ppm Kills sense of smell in 3-15 minutes, stings eyes and throat
- 200 ppm Rapidly kills sense of smell, severely stings eyes and throat
- 500 ppm Immediate dizziness, breathing ceases in a few minutes
- 700 ppm Quick unconsciousness, death results if not immediately rescued
- 1,000 ppm Immediate unconsciousness, followed by death within minutes

CONCENTRATION UNITS

PPMN = Parts Per Million by Volume

PPM/W = Parts Per Million by Weight

Grains/100 ft³ = Grains per 100 cubic feet

Percent = % of total gas

CONVERSION FACTORS

1 Grain/100 ft³ = -15.7 PPMN

10,000 PPMN = 1%

¼ Grain / 100 ft³ (quarter grain) = -4 PPM

WHY MEASURE?

- Personal Safety – H₂S is a toxic gas and can cause severe illness and/or death.
- Corrosion Protection – H₂S is a caustic chemical that can cause embrittlement of steel pipelines.
- Contractual Agreements – FERC requires that pipeline gas be less than 4 PPMN. Most custody transfer contracts also state this limit.
- Feedstock Quality - Protection of catalysts in refinery and petrochemical processes is economically important.
- Legal Requirements – Sulfur emissions can be controlled by measuring concentrations of H₂S in fuel gas prior to combustion.

MEASUREMENT TECHNOLOGIES

Many different technologies for measuring concentrations of H₂S and Total Sulfur have been used. This section briefly describes some of the more popular technologies that have been used:

Lead Acetate Tape – The most widely used method available for H₂S measurement over the past 30+ years. Paper tape is chemically impregnated with Lead Acetate. When exposed to H₂S, a chemical reaction on the tape occurs forming a colored reactant, Lead Sulfide (PbS). Optics are used to measure the rate of formation of the colored stain, which is directly proportional to the H₂S present. Chemical preparation advances and electronics innovations have improved this technology for response times less than 10 seconds and sensitivities below 50 ppb. Lead Acetate tape can be used to measure total sulfur by mixing the sample stream with hydrogen and passing it through a furnace (pyrolyzer) at elevated temperatures. The sulfur compounds found in the sample stream are converted to hydrogen sulfide and then read as total sulfur.

Stain Tubes – Glass tubes filled with a lead acetate impregnated substance. A measured amount of gas is pulled through the glass tube by a hand-held pump. The lead acetate reacts with any present H₂S and forms a stain changing the color of the substance within the tube. The length of the stain through the tube is proportional to the amount of H₂S present in the known volume of gas. Stain tubes are generally $\pm 25\%$ of reading and should therefore only be used as a spot check technique.

Solid State Sensors – Normally this technology is used to measure different gases in ambient air, however, in recent years this technology has been adapted for use in pressurized systems such as pipelines. When exposed to low-pressure flow of the gas stream, this sensor outputs a signal to an electronic controller that reports a value for H₂S. Particular attention should be given to the potential interferences of other gas components that report false positive readings for H₂S.

Titration – Titrators operate on the principle of the oxidation-reduction reaction of Sulfur free Bromine, which is generated by electrolysis. A sample is bubbled through a solution of Hydrobromic Acid within a reaction cell. The amount of current required to generate enough free Bromine to react with all sulfur present is recorded and is indicative of the amount of sulfur present.

Flame Photometric Detector – Sulfur compounds are thermally decomposed in a hydrogen flame with excess hydrogen, and light (energy) is emitted when recomposed sulfur molecules revert from its excited state into the ground energy state.

X-Ray Absorption Detector – Radiation from the source passes through a sample to a detector where it is converted into a digital signal, which is a measure of the sample absorption.

UV Fluorescence – All sulfurs are converted to sulfur dioxide in a pyrolyzer furnace. The combustion gases then flow into a fluorescence chamber where they are exposed to ultra violet radiation. The ultra violet light emission provides an instrumental method for sulfur analysis.

Chemiluminescence – Involves the flameless combustion of the sample in a reducing atmosphere of air and hydrogen at near vacuum conditions to produce sulfur monoxide. The sulfur monoxide produced is transferred to a reaction cell where it is combined with ozone to produce an excited form of sulfur dioxide, which releases light upon relaxation.

Conductimetric Detector – The target gas (H₂S) is defused through a porous filter or membrane then contacts the surface of a sensor element where a change in resistance occurs that is proportional to the concentration of the target gas. The signal (current) is then amplified and sent to a microprocessor. The sensor element could be an electrochemical cell, metal oxide cylinder or a combination of the two sensors.

Diode Tuned Laser - Utilizes laser absorption spectroscopy to detect the presence of one or more gases in a mixture of other gases

Silver Nitrate Tape- A relatively new method, developed from the above mentioned lead acetate tape. The silver nitrate tape retains the same interferent-free analysis capability, but also eliminates the need for a humidifier. The spent silver nitrate tape is EPA classified as non-hazardous, and can be disposed of without concern or regulation. This method does not require scrubbers, dilution systems, pyrolyzers or heaters.

CALIBRATION

Regardless of the technology employed, it is imperative that calibration be performed periodically to insure accuracy. Some analyzers are susceptible to calibration drift, zero drift, desensitizing or interferences. Periodic calibration assures the user that the calibration of the analyzer stays accurate. Depending on the analyzer make and model, a calibration once a month or once a quarter is typically sufficient.

When sampling for on-line H₂S analysis, it is critical that the gas sample containing a representative concentration of H₂S reach the analyzer in the shortest period of time possible. The response time of most analyzers is typically many times faster than the delivery time of the gas sample from the sample tap to the analyzer:

Tube diameter	Pressure	Length/ft	Flow/SCFH	Lag Time/minutes
0.25	800#	100'	0.4 SCFH	144 minutes
0.25	200#	100'	0.4 SCFH	36 minutes
0.25	50#	100'	0.4 SCFH	9 minutes
0.25	20#	100'	0.4 SCFH	3.5 minutes

Table 1. Gas Sample Lag Time Estimates

The quality of natural gas sample points range from the basic sample tap with a weldolet to sample taps equipped with membrane probe regulators.

Unfortunately, many of the taps through which samples are drawn for on-line H₂S analysis are the basic sample taps without a probe. The gas sampled through a basic sample tap with only a weldolet and no probe is likely to contain liquid contaminants as the liquids typically travel along the pipe walls and may easily enter the sample line. Much of the liquid contaminants can be avoided simply by installing a probe through the weldolet to draw the sample from near the center of the pipe. The use of a probe will ensure a more representative sample of the flowing gas will be presented to the H₂S analyzer. However, in many applications, the sample quality can be further improved by installing a membrane probe regulator assembly. The addition of the membrane will prevent droplets of liquid traveling in the gas stream away from the pipe walls from entering the sample line. The regulator portion of the assembly makes the pressure cut inside the pipe at flowing temperature and therefore the temperature drop and resulting liquid drop out associated with the pressure cut is minimized.

Reducing the sample pressure at the line tap will reduce the amount of gas packed in the sample line and decrease the time it takes for the sample to reach the Analyzer. The delivery time of the sample to the analyzer can be further improved by utilizing the analyzer's speed loop.

PREVENTATIVE MAINTENANCE

Analytical instrumentation requires routine maintenance to insure proper performance. Operators responsible for maintenance should set up their own Preventative Maintenance (PM) schedule. A checklist of services to be performed should include the following:

- Detector assembly verification, adjustment and replacement as required
- Consumables replacement

- Sample flow system inspection and cleaning, as required
- General instrument performance evaluation
- Verify certification of calibration standards
- Complete calibration using a certified known-value calibration standard
- Keep area around analyzer clean and organized

CONCLUSION

Measurement of H₂S is a necessary and sometimes dangerous process. It is critical for personal safety and pipeline quality reasons. Many technologies exist to perform this function and care should be taken to select the technology and brand of instrument that best suits the application requirements, whether it is for safety, quality, legal, contractual, or other purposes. Well-trained operating personnel can assure that the H₂S analyzer are accurately calibrated and are maintained for optimal performance.