H_2S DETECTION AND DETERMINATION

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INTRODUCTION

Hydrogen Sulfide (H_2S) is a gas composed of one Sulfur Atom and two Hydrogen Atoms. H_2S is formed by the decomposition of organic matter and is therefore, found naturally in crude oil and natural gas deposits. H_2S 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 H_2S within natural gas pipelines. This paper will discuss the Properties, Purpose of Measurement and Measurement Technologies for H_2S and discuss how these technologies can be adapted for measurement of Total Sulfur.

PROPERTIES

H_2S is also known as Sour Gas, Swamp Gas, Sulfuretted Hydrogen, and Hydrosulfuric Acid. H_2S has a familiar odor of rotten eggs at low concentrations. At high concentrations, H_2S is highly toxic and often deadly.

Physical Properties

Boiling Point	-76.60°F
Freezing Point	-121.9°F
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

PPM/V = Parts Per Million by Volume

PPM/W = Parts Per Million by Weight

Grains/100 ft^3 = Grains per 100 cubic feet

Percent = % of total gas

Conversion Factors

1 Grain/100 ft^3 = ~15.7 PPM/V

10,000 PPM/V = 1%

¼ Grain/100 ft^3 (quarter grain) = ~4 PPM/V

WHY MEASURE?

- Personal Safety – H_2S is a toxic gas and can cause severe illness and/or death.
- Corrosion Protection – H_2S is a caustic chemical that can cause embrittlement of steel pipelines.
- Contractual Agreements – FERC requires that pipeline gas be less than 4 PPM/V. 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 H_2S in fuel gas.

MEASUREMENT TECHNOLOGIES

Many different technologies for measuring concentrations of H_2S have been used. This sections briefly describes some of the more popular technologies that have been used:

Lead Acetate Tape – Perhaps the best analytical method available for H_2S measurement and certainly the most widely used over the past 30+ years. Paper tape is chemically impregnated with Lead Acetate. When exposed to H_2S, 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 H_2S present. Chemical preparation advances and electronics innovations have improved this technology for response times less than 10 seconds and sensitivities below 10 ppb.

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 H_2S 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 H_2S present in the known volume of gas. Stain tubes are generally ± 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 H_2S. Particular attention should be given to the potential interferences of other gas components that report false positive readings for H_2S.

Titration – Titrators operate on the principle of the oxidation-reduction reaction of Sulfurs 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 (H_2S) 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.

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.

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
- Keep a written record of maintenance performed

CONCLUSION

Measurement of H_2S 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 H_2S analyzer are accurately calibrated and are maintained for optimal performance.