DETERMINATION OF H_2S AND TOTAL SULFUR IN NATURAL GAS

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Introduction

Hydrogen Sulfide (H_2S) is a chemical compound comprised of one Sulfur Atom and two Hydrogen Atoms. It is a colorless, extremely poisonous gas that reeks of rotten eggs. H_2S is formed when bacteria breaks down organic matter and is found in natural oil and gas deposits. Hydrogen Sulfide is highly corrosive and renders some steels brittle, leading to sulfide stress cracking which can lead to damage to operational equipment. Natural gas producers, gas processors and pipeline operators measure H_2S to protect equipment and to conform to buyer specifications or government limits. Sometimes, H_2S concentration is used as a feedback parameter to control and optimize sweetening and sulfur recovery processes. Due to the toxic and corrosive properties of Hydrogen Sulfide and its presence in natural gas, it is imperative to measure and control the concentration levels of this compound within natural gas pipelines.

This paper will address the properties, purpose of measurement and measurement methods for H_2S and discuss how these methods can be adapted to the measurement of Total Sulfurs as well as H_2S in natural gas streams.

Key Information

H_2S is also known as Sour Gas, Acid Gas, Swamp Gas, and Sulfuretted Hydrogen. H_2S has a familiar odor of rotten eggs and is detectable by most people at concentrations as low as 5 ppb. Above a concentration of a few hundred parts per million, H_2S is highly toxic and often deadly.

In raw natural gas and gas gathering fields, H_2S concentrations can be as lows as 1 ppmv and as high as 20%, or more. In “sales gas” (e.g. in transmission and distribution pipelines), the maximum allowable concentration is 4 ppm in the US, but H_2S levels are often maintained around 1 or 2 ppmv.

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 (depends on values used for standard conditions)

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.

Sampling for On-line Measurement

When sampling for on-line H_2S analysis it is critical that the gas sample containing a representative concentration of H_2S reach the analyzer in the shortest period of time possible. The response time of most analyzers can be many times faster than the delivery time of the gas sample from the sample tap to the analyzer. The Manufacturer's recommendations must be observed as there may be slight differences with different analyzer types.

The stream composition, associated phase diagrams and ambient temperatures should be considered when designing the sample system to ensure that the sample remains in vapor phase during pressure reduction and sample transport.

Unfortunately, many of the taps through which samples are drawn for on-line H_2S 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 H_2S analyzer. Additionally 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 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. Sometimes the regulators must be multistage depending on the dew point of the sample and the stream pressure and temperature.

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.

Measurement Technologies

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

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 relates 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.

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.

Tunable Diode Laser - Utilizes laser absorption spectroscopy to detect the presence of a specific target analyte in a mixture of other gases. For very low measurement levels, differential spectroscopy is sometimes used to subtract the effects of background interference.

Gas Chromatograph with Thermal Conductivity 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.

Gas Chromatograph with 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.

Gas Chromatograph with 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.

Lead Acetate Tape – 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. When the surface of the tape becomes too dark, the tape indexes forward to a clean spot with a reel-to-reel tape feed system.

Calibration or Validation

Regardless of the technology employed, it is imperative that calibration or validation be performed periodically to ensure accuracy. Some analyzers are susceptible to calibration drift, zero drift, desensitizing or interferences. Periodic validation & 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:

- Assembly verification, adjustment and replacement as required for moving parts and spare parts as recommended by the manufacturer.
- Consumables replacement (if applicable)
- Sample flow system inspection and cleaning, as required
- General instrument performance evaluation
- Verify certification of calibration standards
- Complete validation and/or 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 gas quality. Many technologies exist to perform this function and care should be taken to select the technology and manufacturer 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 H_2S analyzers are accurately calibrated and are maintained for optimal performance.