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PRO DAIRY Education & Applied Research

HYDROGEN SULFIDE REMOVAL FROM BIOGAS
Part 1B: Measuring Hydrogen Sulfide

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WHY MEASURE BIOGAS HYDROGEN SULFIDE CONCENTRATIONS?

Because of the effect of hydrogen sulfide (H_2S) on biogas equipment longevity, it is important to be able to accurately measure the concentration in biogas.

An accurate measure will provide a means of determining whether concentrations are above thresholds set by equipment manufacturers, and whether scrubber systems to remove H_2S are working as designed, or if they need maintenance.

TYPES OF MEASUREMENTS

H_2S measurements fall into two categories, single use and continuous monitoring.

Single Use measurements

The oldest technology for measuring H_2S relies on colorimetry, which is the reaction of H_2S gas with the reagent to change reagent color. A standard volume of sample gas is drawn through a glass tube filled with reagent, with graduated markings on the side. As the gas passes through the reagent it reacts and changes color. A calibrated gradation gives the concentration.

Because there is a chemical reaction involved, these tubes can only be used one time. It is also critical that the correct volume of biogas be drawn through the tube by using the correct sampler at the recommended settings for the tube. For this reason, when sampling from a biogas line that is under pressure, it is necessary to first collect the biogas sample into a non-reactive Tedlar™ bag from which the sample can then be drawn.

Calibrated tubes come in a variety of measurement ranges from 5 parts per million (ppm) to 40% by volume. This is an important consideration, for the most precise measurement relies on using a tube with the narrowest range, which requires knowledge of what the approximate concentration is before even taking the measurement. Accuracy is ±10% of the range of the tube (i.e. 20 ppm on a 0 to 200 ppm tube).

H_2S tubes are single use and cost $5 to $10 with a shelf life of 2 years. In addition to the sample tubes a calibrated pump is required (~$500).

Pros

- Highly portable and quick to use
- Relatively inexpensive for few measurements
- No need for calibrations/maintenance
- Can measure other gases easily too (with different tubes)
- No need for electricity
- Can be used by non-technical persons

Cons

- For most precise measurements, need to know the approximate range of concentration being measured
- Need to manually sample, measure, and read value off of tube
- Results may not be representative due to changing biogas H_2S concentrations

Continuous Monitoring

When multiple repeated measurements are required a system capable of automatically sampling and measuring is necessary. Typically such systems use either a “tape” based colorimetric system (similar to the single use tubes), or an electrochemical cell. Electrochemical cells operate like a battery, and the change in current between the electrodes is proportional to the concentration of H_2S gas.

Gas monitoring systems are usually set up to measure the concentrations of several gases at the same time (such as CH_4, CO_2, O_2 and H_2S). It is also common for such systems to analyze multiple sampling points, monitoring each for a set period of time (typically a minimum of 15 minutes). It takes time for the sensors to react to a change in concentration and stabilize as well as to purge the gas sample lines of the previous sample gas, and so more frequent switching isn't recommended.

H_2S sensors require frequent calibration both in terms of zero gas or ambient air, to account for zero-drift and temperature effects. Usually this autocalibration is set to occur several times per day, or based on a measured change in ambient temperature.

It is also necessary to calibrate with a known concentration gas that is representative of the range of concentrations measured in the sampled gas. This can be automated, but is usually carried out manually based on a recommended frequency from the manufacturer. For H_2S, monthly calibrations are recommended for best results.

Continuous monitoring is usually performed with in-situ or hand-held units.

In-situ equipment

In-situ measurement systems are generally used for long-term performance monitoring and/or system control. Systems typically cost $20,000 to $30,000 with replacement H_2S sensors approximately $1,000.

Pros

- Automated sampling and data collection
- Data can be viewed/evaluated real-time
- Can be used for process control and compliance monitoring
- Can monitor several gases at once
- Can capture changes over time

Cons

- Expensive to install, requires plumbing connections
- Need to condition gas (remove moisture)
- Regular (monthly) calibrations and sensors need annual replacement
- Sensors are temperature sensitive
- Subject to freezing of sampling lines – specific frost protection required

Hand-held equipment

Hand-held systems are typically used for monitoring several gas concentrations simultaneously, for short periods of time. Units cost approximately $5,000, and factory re-calibration is approximately $1,000.

Pros

- Data can be viewed/evaluated real-time
- Can monitor several gases a once
- Portable and easy to use

Cons

- Unit must be returned for calibration

SAFETY MEASUREMENTS

Simplified continuous measurement systems are also recommended for anyone working in enclosed spaces or in areas where H_2S concentrations may build up (H_2S is heavier than air). These devices are designed to be worn by a worker, and to trigger a vibration, flashing light, and sound when a potentially dangerous level of H_2S is detected. Single gas detectors are typically priced between $250 to $500. For more information please read "Conducting a Safety Walk-Through On a Farm"[1]

[1] http://www.manuremanagement.cornell.edu/Pages/General_Docs/Papers/Self_assessment_Safety_Walk_through_Manure_Systems_2007.pdf

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