

EFFECTIVE MONITORING OF HYDROGEN SULFIDE GAS IN WASTEWATER FOR ODOR CONTROL; FOR ON-SITE AND LABORATORY ANALYSIS

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Hydrogen sulfide (H₂S) is a colorless hazardous gas known for its “rotten egg” odor that many of us can detect even at low levels.^[1] Every time we pass a landfill, a wastewater facility, or are brave enough to pry open the long-forgotten egg salad container in the back of the fridge, we have encountered H₂S. Although many instruments are available that measure toxic gas in the parts per million (ppm) range, there is a need to detect and measure hydrogen sulfide in the much lower parts per billion (ppb) concentrations due to odor complaints, which are traced to ppb levels. The human odor threshold is 8 ppb and the human annoyance threshold is 40 ppb.^[2] To take control of this problem, many state and local regulations limit the ppb release of hydrogen sulfide into the environment.

Wastewater treatment facilities are therefore required by law to measure and control an acceptable level of H₂S exposure for their employees and surrounding civilians. Protocols established to control and limit the odor of the H₂S generated from decaying organics often include adjusting the pH, adding nitrates or disinfecting the wastewater with chemical additives.^[3] The cost in minimizing hydrogen sulfide odor might be substantial and might place a heavy financial burden on the facility.^[4] Understanding why these protocols are used for odor control as well as accurately and precisely measuring the hydrogen sulfide gas is important for ensuring safety while minimizing the use of expensive additives. This paper briefly outlines how hydrogen sulfide is created in wastewater, how it is controlled and how you can accurately detect its presence using the Jerome® 605 Hydrogen Sulfide Analyzer (J605). Using the J605 as an

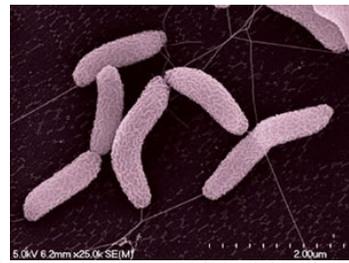
analytical tool may aid in determining the appropriate concentration of additives required to minimize H₂S odor on a laboratory scale. These empirical concentrations could then be extrapolated to full-scale proportions saving the facility time, money and resources.



What are anaerobic bacteria and how do they contribute to H₂S production?

An *anaerobic bacterium* is a term for a species of bacteria that can function in an oxygen-free environment. Many of these bacteria have a distant evolutionary predecessor that thrived 3.5 billion years ago when the earth was mostly barren of oxygen but rich in sulfates.^[5]

Like all forms of life, anaerobic bacteria break down sugars, lipids and proteins for energy but require some form of a chemical electron acceptor to complete their biochemical/metabolic cycles. These sulfates (SO₄⁻²) had become that electron acceptor (reduced) and in the process had created hydrogen sulfide gas by anaerobic fermentation. Today, sulfate reducing bacteria such as *Desulfovibrio*, still play an important role in reducing sulfates in anaerobic conditions (i.e. wastewater).^[5] Scanning electron micrograph shown below.



<https://microbewiki.kenyon.edu/index.php/Desulfovibrio>

Why are anaerobic bacteria important in wastewater treatment?

Most decomposition bacteria can be categorized as chemoheterotrophic, meaning its energy source is derived from organic materials made by other organisms.^[5] Wastewater and gray water are rich with undigested organics and are the proverbial “all you can eat buffet” for bacteria. This is important in reducing the amount of solid organic waste found in wastewater. Early in the bacterial decomposition process, aerobic (oxygen loving) bacteria dominate the feeding frenzy. However, as more and more aerobic bacteria grow and use the dissolved oxygen in the water, an acidic anaerobic environment is created. This acidic, oxygen-depleted environment is now suitable for anaerobic bacteria to proliferate and consume the partially digested organic material left behind.^[3] Having an anaerobic counterpart ensures decomposition is always occurring in any environment.

Why do pH levels, nitrates and disinfectants affect H₂S concentrations?

All forms of life function at an optimal pH. If the pH is too high or low, proteins and lipids may denature and the organism may cease to function properly. In the case of minimizing H₂S odor, pH plays two roles: By increasing the pH (or making the wastewater more alkaline), the anaerobic bacteria stop growing and metabolizing since their optimal pH has been altered. Raising the pH also inhibits the release of dissolved H₂S from solution, so it remains in an aqueous versus gaseous state.^[4]

Nitrates (NO₃⁻¹) can also serve as a final electron acceptor in place of sulfates. Flooding the wastewater with nitrates forces the bacteria to use nitrate instead of sulfates, which minimizes the H₂S fermentation byproduct.^[6] Commercially available nitrates are usually in the form of liquid or powdered calcium or sodium nitrates. Like pH, the addition of nitrates has both a biological and chemical effect on the water. Preventative or curative attempts to minimize H₂S often result in the chemical alteration of hydrogen sulfide back to ionic sulfate in the equation shown below:



The downside of adding too much nitrate is that it may cause problems down the line in purifying the water which is now spiked with excessive amounts of nitrogen.^[6] Preventative nitrate measures also tend to be a major cost in water treatment and when utilized, should only be done sparingly.

Disinfectants such as chlorine, ozone or peroxides essentially break down the cell wall of any microbes present in the water. These reactive compounds also combine with sulfur compounds and other hydrocarbons.^[4] These additives are usually reserved for the final step in processing wastewater but are essential for killing any harmful bacteria. Like any other additives, these chemicals come at a cost and the addition of too much or too little have detrimental effects later in processing.

How can you accurately monitor H₂S?

Monitoring H₂S in your facilities may be as easy as walking around your work site with a handheld H₂S analyzer such as the Jerome® 605. This level of detection is important for ensuring the air quality is safe for all who may be exposed. The J605 uses gold film technology specific for hydrogen sulfide gas with a detection limit as low as 3 ppb. The J605 offers a continuous “autosample” mode option to monitor air quality over a period of time and saves the data, which can be exported onto a spreadsheet for further analysis.

Arizona Instrument LLC (AZI) has performed several studies in which the J605 has been used not only as a safety/odor monitoring tool, but as an analytical instrument in the laboratory. Due to the volatility of hydrogen sulfide (b.p. = -60°C), one effective method for testing the concentration of dissolved H₂S is to test the headspace above a liquid sample. If the temperature and the accumulation time are well controlled, then the concentration of H₂S in the headspace will be proportional to the concentration of H₂S dissolved in the sample. AZI has done extensive studies with dissolved H₂S in liquid samples such as beer and wine. A similar method can be used to detect dissolved H₂S in wastewater. The experimental design is shown below.



To run a test, an Erlenmeyer vacuum flask is connected to a Jerome® J605 Hydrogen Sulfide Analyzer by Tygon® or other suitably sized inert tubing. A liquid sample of wine or beer is poured into an Erlenmeyer flask and allowed to stir for 5 minutes. The instrument is placed in Autorange and Autosample, sampling the headspace above the liquid every 2 minutes. The instrument then samples for 30 minutes, and the results are summed for a total concentration of H₂S.^[7]

Although this particular study relates to alcoholic beverages, anaerobic fermentation still plays a key role in both processes where hydrogen sulfide gas is generated as an unwanted byproduct. By taking in-line samples of wastewater during various stages of processing, it is theoretically possible to maintain an accurate measure of hydrogen sulfide concentration on a laboratory scale. Moreover, scaling down water treatment (addition of base, nitrates and disinfectants) may give you better insight on quantity, the rate of reaction, and the efficiency of each of these additives may be (or any combination).

Understanding the chemistry of hydrogen sulfide *and* the biology of its generation is important in treating wastewater odor control. Moreover, having a reliable and accurate instrument to measure H₂S is paramount for both safety monitoring and analytical measurement. The Jerome® 605 has been shown to be a useful and versatile instrument in determining hydrogen sulfide concentrations in both air and liquid samples. This technique may allow for more efficient bulk usage and purchasing for these odor-inhibiting additives while maintaining a safe and healthy work environment in accordance with the law.

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