

Hydrogen Sulfide:

Real-time Detection Techniques

New TLV® Heightens Industrial Hygiene Monitoring Concerns

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In 2003, an uncontrolled release from a natural gas well in Chongqing, China, led to the deaths of approximately 240 people.¹ Most deaths occurred in the area 200 to 500 m away from the well-head, but exposed individuals as far as 1,200 m away also died. Over 1,000 people were hospitalized, thousands were evacuated, and according to one published report, “dogs, ducks, rabbits and other domestic animals were killed. Even fish did not escape.”¹

The devastation was caused by hydrogen sulfide (H₂S), a colorless gas with a distinctive “rotten egg” odor that often occurs naturally within oil and gas deposits^{2,3} and in downstream transport² and refining operations.³ In occupational settings, H₂S is a serious threat to worker health. It is soluble in water, explosive (with a lower explosive limit concentration of 4.3 percent by volume), corrosive, heavier than air, and highly toxic. Under certain conditions, decaying organic material yields H₂S,³ so it is potentially present in many situations where workers must enter poorly ventilated confined spaces.

In cases where exposure to H₂S is possible, accurate and reliable detection methods are critical. The poor warning properties of H₂S and the extreme hazard posed by even brief exposures to high concentrations literally make recognition of the potential presence of this extremely dangerous gas a matter of life or death.

Health Effects

Hydrogen sulfide interacts with hemoglobin in red blood cells and myoglobin in muscle tissue,³ interfering with oxygen transport and storage. The most discon-

certing health effects from H₂S arise from impairing the body’s ability to use oxygen in the mitochondrial electron transport chain,⁴ disrupting function of the nervous system, and causing olfactory desensitization as the airborne concentration of H₂S increases above ~100 ppm.^{3,5} With exposure to H₂S concentrations greater than ~1,000 ppm, the phrenic nerve, which controls the diaphragm, ceases functioning almost immediately, causing breathing to stop.^{2,3} This effect combined with a sudden loss of consciousness is known as “knock-down.” If the airborne H₂S concentration is not lowered and breathing is not restored, death will ensue quickly. Irritation and damage to pulmonary, skin, and eye tissues is also possible.¹

Because of the effects of H₂S on the nervous system, as well as damage to lung tissues, even aggressive cardiopulmonary resuscitation may not be sufficient to restore breathing or avoid permanent injury. The knockdown effect of H₂S can give rise to multiple deaths when improperly protected co-workers attempt to retrieve a victim from atmospheres with high H₂S levels.⁶

According to the U.S. Bureau of Labor Statistics, H₂S poisoning was the cause of at least 52 occupational-related deaths in the U.S. from 1993 to 1999. Nine of these deaths involved multiple casualties, including those killed while attempting to rescue co-workers.⁶ Deaths from H₂S exposure were noted in waste management, petroleum and natural gas, food processing, asphalt, fishing, and dye industries. In 1998, occupational-related deaths from H₂S were found to be the second leading cause of death from toxic chemicals, behind carbon monoxide (CO).⁷

Real-time H₂S Detection

Portable instruments used to measure H₂S usually include one or two instanta-

neous alarms (peak or ceiling alarms), as well as short-term exposure limit (STEL) and time-weighted average (TWA) alarms based on time-history exposure. In the past, widely recognized occupational exposure limits for H₂S have referenced an 8-hour TWA of 10 ppm and a 15-minute STEL of 15 ppm. Most manufacturers routinely set instrument alarms at these values.

In February 2010, ACGIH® recognized the potential for adverse health effects from H₂S exposure at lower airborne concentrations and adopted new TLV® recommendations, lowering the 8-hour TWA to 1.0 ppm and the STEL to 5.0 ppm.⁸ The new recommendations forced many practitioners to reconsider exposure limit guidelines and alarm set points. A primary concern has been whether detection instruments are capable of operation with alarms set to the new limits. Industrial hygienists may need to verify with manufacturers whether this is feasible with a particular instrument design.

Methods used to detect H₂S include instruments that measure conductivity changes in a gold film upon absorption of H₂S as well as colorimetric tubes and indicators. This article focuses on electrochemical sensors, which are the most widely used means of real-time H₂S measurement.

How Electrochemical Sensors Work

In many situations, a multigas meter is used to simultaneously detect oxygen (O₂) deficiency and the presence of combustible gases and vapors and will also employ one or more compound-specific electrochemical sensors. When it is known that a single gas or vapor is predominantly present without O₂ deficiency or a combustible gas hazard, a single-gas monitor may be used. The ideal compound-specific sensor would

respond only to the specific compound, while the ideal “broad range” sensor would respond to all air contaminants present. In practice, the selectivity of electrochemical sensors designed for detection of a specific airborne compound such as H₂S falls somewhere between these two extremes.

Each electrode in an electrochemical sensor (Figure 1) has a specific purpose. The sensing electrode (Figure 2), often referred to as the “working” electrode, is where the reaction of interest occurs. Depending on the gas being measured, the target gas is either oxidized or reduced on the working electrode, creating a flow of current proportional to the airborne gas or vapor concentration. The counter electrode completes the circuit with the working electrode. If the measured gas is oxidized at the sensing electrode, some other chemical species (often O₂) is reduced at the counter electrode in a balancing half-cell reaction. Conversely, if the target gas is reduced at the sensing electrode, another chemical species is oxidized at the counter electrode. Zero-biased (often referred to as “unbiased”) sensors are normally installed in a circuit that holds the electric potential of the working electrode at a constant value. The potential of the counter electrode is allowed to “float” as a function of the changing concentration of the gas being measured. Three-electrode sensor designs include a reference electrode that provides a stable output signal unaffected by analyte concentration changes. This stable output is a reference point for comparison with the active signal from the sensing electrode as it dynamically changes with analyte concentration fluctuations.

For electrochemical detection of H₂S the only materials consumed are H₂S and O₂, and only a small amount of power from the instrument’s power supply is needed. As long as the sensor is located in an atmosphere with a minimal amount of O₂, the O₂ consumed in these reactions can be replenished.

Figure 3 shows that the instrument readout does not equilibrate instantaneously when an electrochemical H₂S sensor is first exposed to the target compound at 25 ppm, although the “time to alarm” in this case was about 4 seconds. Importantly, the sensor output signal is extremely linear over the full range of the sensor. The ratio of surface area of the sensing electrode is physically quite large compared with the number of H₂S molecules that actually enter the sensor. Even if a substantial frac-

Figure 1. An electrochemical H₂S sensor module.

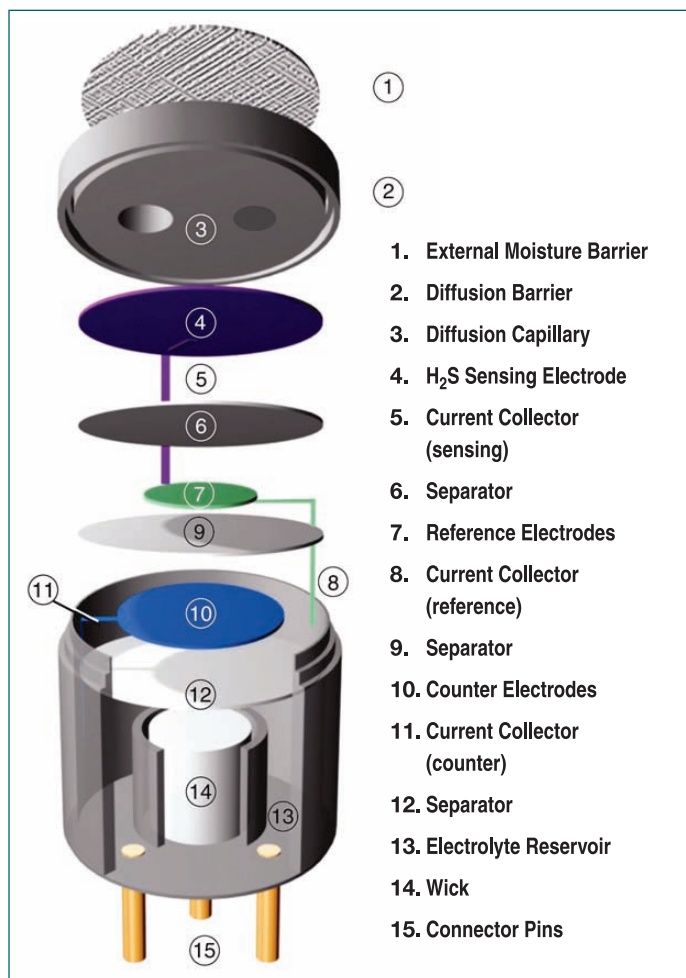


tion of the sensing electrode becomes unusable (for example, from physical damage or poisoning of the catalyst system), the sensor usually has more than enough reserve efficiency to operate normally.

An alternative to the “nonconsuming” type of electrochemical sensor is a detector where a chemical component within the sensor is consumed. In these detectors, the sensor will eventually run out of required reagent. No reagent is consumed within electrochemical H₂S sensors; the oxidation/reduction reactions can theoretically occur indefinitely as long as O₂ is present and even for short periods in oxygen-deficient atmospheres as residual O₂ remains in an electrolyte reservoir present within the detector. Even when exposed to H₂S on a regular basis, electrochemical H₂S sensors routinely last three years or longer. Although these sensors do not lose sensitivity from exposure to H₂S, regularly testing the sensor by exposing it to a known concentration of calibration gas is highly recommended.

All electrochemical sensors employ aqueous chemistry and thus should not be stored at high temperatures, even for brief periods of time. If an electrochemical sensor (see Figure 2) is stored in a hot environment or is left in a car on a warm day, the water within the electrolyte reservoir located within the sensor can evaporate. If the electrolyte dries out beyond a cer-

Figure 2: Schematic diagram showing the components present in an electrochemical sensor module.



tain point, the detector will fail. Also, since the electrochemical H₂S detector requires a small amount of O₂ to function, it will not work correctly for applications where O₂ is absent for extended periods (for example, for H₂S detection within a natural gas pipeline).

Cross-sensitivity

Some cross-sensitivity may occur with electrochemical sensors. Depending on the interfering chemical, either a positive or negative detector response bias is possible. However, in the case of an electrochemical H₂S sensor, because the relative signal strength is much greater for H₂S, a very high concentration of oxidizing gas (for example, Cl₂) would be required to materially affect sensor readings.

A greater concern is the positive interfering effect on electrochemical H₂S sensor readings from certain volatile organic compound (VOC) vapors, such as limonene, methanol or other alcohols, including those present in some hand sanitizers and insect repellents. Always remember to allow these liquids to dry completely before handling gas detectors, and never use methanol to clean or decontaminate gas-detecting instruments. Electrochemical sensors of all types are designed with specific use conditions and requirements in mind, so always follow factory recommendations

regarding cleaning, routine maintenance and calibration.

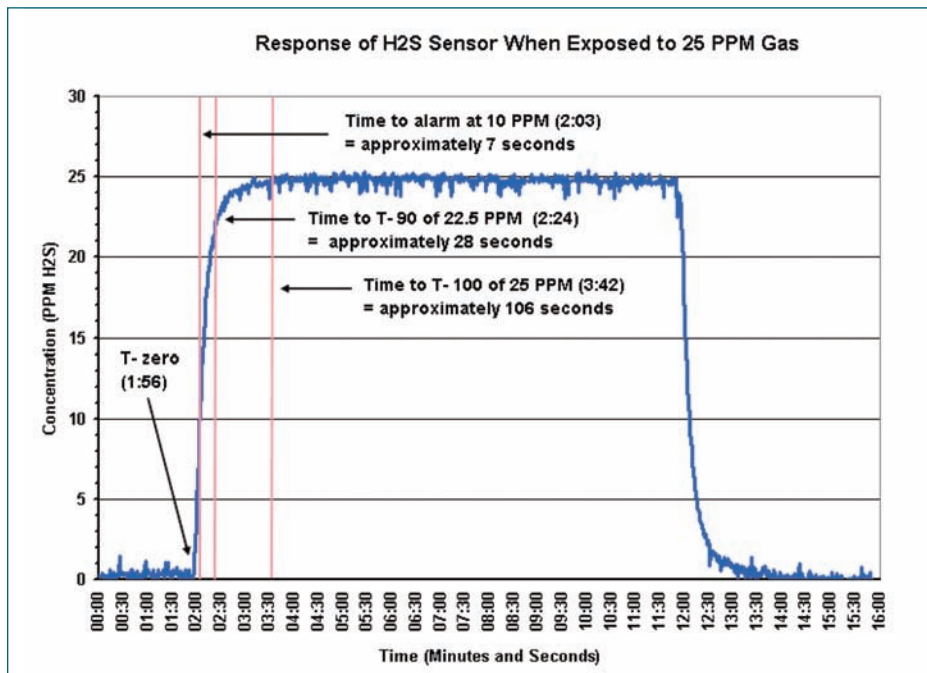
Combined H₂S/CO Sensor Designs

A commonly used variant of the electrochemical H₂S sensor includes a second working electrode for the detection of CO. The sensor includes a single counter electrode, a single reference electrode, and one electrode each for H₂S and CO, thereby providing a separate signal for each detected gas. Typically, once the gas diffuses into the sensor, it first reaches the H₂S working electrode where most of this compound reacts, and the H₂S working electrode is designed not to respond to CO. The sampled air continues to diffuse into the sensor, where it reaches the CO sensing electrode and the CO concentration is then measured.

Four-electrode CO/H₂S sensors usually include an internal filter that limits the amount of VOC interferences and H₂S that reach the CO electrode. However, a certain amount of H₂S is still expected to remain in the gas that reaches the CO electrode. While optimized for the detection of CO, the CO sensing electrode responds to both CO and H₂S. Instruments deduct the effects of H₂S on the CO electrode based on the expected breakthrough ratio. Such a system requires calibration with both gases before use.

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Figure 3. Response of a typical electrochemical H₂S sensor to a stable concentration of 25 ppm H₂S.



H₂S Monitoring Concerns

The lowering of the ACGIH TLV for hydrogen sulfide in 2010 caused concern among industrial hygienists about their detection instruments. Below, manufacturers share their responses to the following question from *The Synergist*: “What is the number one complaint you hear from industrial hygienists about H₂S monitoring?”

Bryan Bates, President and CEO, Gas Clip Technologies, Inc.:

It would have to be a tie between two. The first complaint concerns the problems associated with having to switch out existing “disposable”-type instruments in order to comply with the changing TLV for H₂S, and the second is the hassle and cost associated with enforcing facility SOPs for required bump testing of H₂S monitors/detectors for contractors. To solve these issues, we recommend our customers use disposable H₂S detectors with alarm set points that can be changed and an electronic “bump test” frequency alarm LED-flashing indicator. Both functions require a supervisory action and cannot be changed accidentally by the instrument user.

Bob Henderson, President, GfG Instrumentation:


The most common question is about the new 2010 TLV for H₂S, and whether or not an instrument can be successfully used with take-action alarm settings of 1.0 ppm. The answer is a qualified “yes.” It all depends on the specific instrument. Some gas detectors already have the necessary range and resolution to permit users to set the instantaneous or TWA alarm as low as 1.0 ppm (or lower). In other cases it may be necessary to update the operating software. In some cases, however, it may not be possible to upgrade older instruments to be capable of resetting the alarms to the new limits. The only way to determine whether this is the case for a particular design is to ask the manufacturer.

- REACH's influence in establishing de facto limits (derived no-effect levels, or DNELs)
- a lack of understanding of the difference between acceptable risk and a true threshold of toxic risk

Although these challenges are substantial, the speakers and audience agreed that countries motivated by the common goal of protecting human health can set up a process for sharing scientific information, develop exposure limits, and align on the documentation for those limits. Leadership of this collaborative effort would reside with a neutral third party, preferably an international body. The group also suggested that volunteerism, the hallmark of OEL-setting thus far, could not carry the process forward. And finally, funding must be made available to support this effort for the global community. Presentations are posted at www.ioha.net/internationaloelissues.html.

Future Collaboration

The October 2010 Professional Conference on Industrial Hygiene in Ft. Worth, Texas, continued the dialogue with a half-day session on OELs that included presentations on ACGIH's processes for setting TLVs, OSHA's preliminary deliberations on updating PELs, DNELs as de facto OELs, and the pharmaceutical industry's reliance on control banding and its use of risk modeling when data are limited. These presentations are accessible at www.pcih2011.org.

Efforts to define an "acceptable exposure level" continue at the national and international levels. Although approaches to this task vary, the discussions at IOHA and PCIH revealed that we have a better understanding of the challenges. While no unitary solution is expected immediately, the conversation on OELs enables a more robust future collaboration. 

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Another approach is to take advantage of the cross-sensitivity of the CO working electrode in an unfiltered carbon monoxide sensor. Substance-specific CO sensors normally include a robust internal filter designed to remove H₂S and other contaminants before they reach the sensing electrode. When the filter is left out of the design, H₂S readily diffuses into the sensor and is detected by the CO electrode. The signal output of this type of sensor is generally much stronger for H₂S than for CO. Some manufacturers use the single signal to calculate two readings. Each reading assumes that the entire signal is due to the presence of one or the other gas. Some manufacturers use the ratiometric difference between the signal strength for the two gases and simply set the CO sensor alarm at a concentration equivalent to the desired "take action" concentration limit for H₂S. The obvious drawback with this approach is that the user will not know which gas is present, or the relative concentrations of each. Manufacturers do not usually require calibration of this type of sensor using both gases, but calibration is usually with CO only, which is generally much less expensive and stable for a much longer period than calibration gas that includes H₂S.

Conclusion

Electrochemical H₂S sensors based on oxidation of the target analyte at a working electrode are among the most dependable, stable, and reliable type of gas-detecting sensors available. However, no sensor can detect gas unless it is used. The only way of being sure that toxic contaminants are not present in dangerous concentrations is to look for them with an atmospheric monitor designed for their detection. To protect life and health, it is important for industrial hygienists to understand their detection instrument. Using the instrument when needed to detect a dangerous airborne contaminant such as H₂S is critical. 

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