

New TLV® exposure limit: **Measuring** hydrogen sulfide



Photo courtesy of GFG Instrumentation

By BOB HENDERSON

In the past, the most widely recognized occupational exposure limits for hydrogen sulfide (H₂S) have referenced an 8-hour TWA of 10 ppm, and a 15-minute STEL of 15 ppm. In February 2010, the American Conference of Governmental Industrial Hygienists (ACGIH®) adopted a new threshold limit value (TLV®) recommendation for

higher, inhalation of H₂S can cause immediate collapse and unconsciousness. A single breath at a concentration of 1,000 ppm results in immediate loss of consciousness, followed by cardiac arrest and death unless the unconscious individual is successfully revived.

H₂S is produced by the action of anaerobic, sulfur fixing bacteria on materials that contain sulfur. It is commonly associated with raw sewage, animal

“nine involved multiple casualties, some of whom were killed

while attempting to rescue co-workers.” Tragically, hardly a week goes by that does not include a fatal accident somewhere in the world due to H₂S exposure.

What are TLVs® & why do they matter?

OSHA uses the term Permissible Exposure Limit (PEL) to define the maximum concentration of a listed contaminant to which an unprotected worker may be exposed. Depending on the contaminant, the PEL may reference an eight-hour, time-weighted average (TWA), a 15-minute short-term exposure limit (STEL) or an instantaneous ceiling (C) concentration that cannot be exceeded for any period of time. Individual states either follow federal regulations, or follow their own, state-specific permissible exposure limits. States may not publish or follow exposure limits that are more permissive than federal OSHA limits.

The ACGIH TLVs® are guidelines for workplace exposure to toxic substances. TLVs® are developed and designed to function as recommendations for the control of health hazards, and to provide guidance intended for use in the practice of industrial hygiene. But ACGIH

H2S Exposure Limits					
	8-hr. TWA	STEL	Ceiling	Acceptable Max Peak Above Ceiling for an 8-Hour Shift	
				Concentration	Maximum Duration
Federal OSHA PEL	NA	NA	20 ppm	50 ppm	10-minutes once only if no other measurable exposure occurs during shift
NIOSH REL	10 ppm	15 ppm	NA	NA	NA
TLV (2010)	1.0 ppm	5.0 ppm	NA	NA	NA

H₂S, lowering the 8-hour TWA to 1.0 ppm, and the STEL to 5.0 ppm. The new TLV® has forced many companies to reconsider exposure limit guidelines and alarm settings. A major issue is whether a company’s current instruments are capable of operation with alarms set to the new 1.0 ppm limit. Employers may need to verify whether or not this is possible with a particular instrument design.

How dangerous is H₂S?

Hydrogen sulfide is a colorless gas that at low concentrations has an odor similar to rotten eggs. At higher concentrations, H₂S rapidly deadens the sense of smell. For most people, a concentration of 150 ppm is enough to immediately deaden the sense of smell. At a concentration of about 750 ppm or

especially associated with oil production and refining activities. H₂S ranks second behind carbon monoxide (CO) as the leading cause of death from toxic chemicals in the U.S. 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. Of these deaths,

TLVs® Incorporated by Reference in:

- NFPA 306 – Control of Gas Hazards on Vessels
- US Coast Guard regulations (OSHA PEL or TLV, whichever is lower)
- US Army (OSHA PEL or TLV, whichever is lower, or specific Army OEL)
- Some individual state health and safety plans (e.g. California)
- Many international standards and regulations (e.g. Canada)
- Many consensus standards (e.g. ANSI, NFPA)
- Many corporate health and safety plans
- Mine Safety and Health Administration (MSHA) regulations

TLVs® are frequently incorporated by reference into state, federal and many international regulations governing workplace exposure. They may also be cited or incorporated by reference in consensus standards of associations such as the National Fire Protection Association (NFPA), or American National Standards Institute (ANSI).

Given the potential for lawsuits, many employers have made the strategic decision to base their corporate health and safety programs on conservative applicable recognized standards. Since ACGIH recommendations are frequently more conservative than OSHA PELs, many programs, especially the programs of multinational or prominent corporations, use the ACGIH TLV®.

How do H₂S sensors detect gas?

Substance-specific H₂S sensors are compact, require very little power, exhibit excellent linearity and repeatability, and generally have a long life span. The detection technique is very straightforward. Gas that enters the sensor undergoes an electrochemical reaction that causes a change in the electrical output of the sensor. The difference in the electrical output is proportional to the amount of gas present. The detection reaction is a two-step process.

H₂S that enters the sensor is oxidized at the sensing electrode:



The counter electrode balances out the reaction at the sensing electrode by reducing oxygen from the air to water:



Each molecule of H₂S that is oxidized at the sensing electrode produces a current flow of eight electrons. The amount of current produced is a function of the number of H₂S molecules that enter the sensor. For every 1.0 ppm of H₂S in the atmosphere being monitored, a typical hydrogen sulfide sensor shows a raw electrical output of 0.7 µA (micro amps). This relationship is linear over a very wide range such that 10 ppm

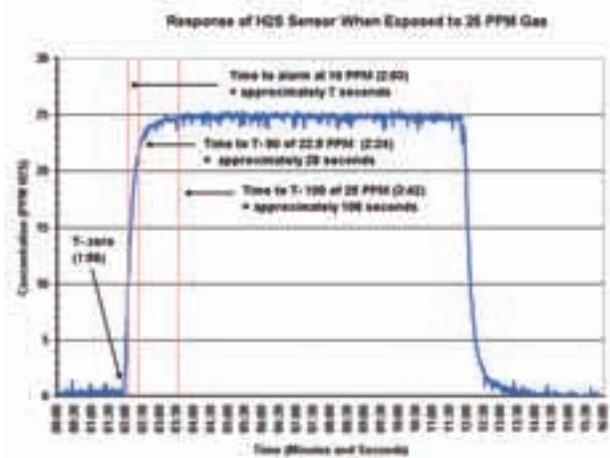
produces 7.0 µA, 100 ppm produces 70.0 µA and so on.

H₂S sensors are usually designed to minimize the effects of interfering contaminants, making the readings as specific as possible for the gas being measured. H₂S sensors are stable, long-lasting, require very little power and are capable of resolution (depending on the sensor and contaminant) to ± 0.1 PPM or even lower. H₂S sensors are normally usable over a wide range of temperatures, depending on the brand of sensor, from as low as - 40°C to 50°C (- 40 to 120 °F).

The sulfuric acid produced in the reaction simply accumulates in the sulfuric acid electrolyte. Water from the electrolyte is used, but is regenerated during the course of the reaction. The only materials consumed during the detection reaction are the molecules of H₂S, power from the battery of the instrument and oxygen. As long as the sensor is located in an atmosphere containing even small amounts of oxygen, the sensor will be able to replenish itself directly from the atmosphere. This is the reason that H₂S sensors have such long life spans. The lifespan of the sensor is not affected by exposure to the contaminant that it measures. No part of the sensor is consumed during the detection reaction. You can expose the sensor to H₂S calibration gas every single day without shortening or affecting the lifespan of the sensor.

Setting H₂S alarms

Most H₂S instruments have four user settable alarms: Low, High, TWA and STEL. The Low and High alarms are instantaneous “Ceiling” type alarms that sound immediately whenever the concentration exceeds the alarm setting. The STEL alarm is a time-history alarm based on the average concentration over the most recent 15-minute period. The TWA alarm is calculated for an 8-hour exposure period. When the exposure is less than 8 hours, the TWA calculation is projected over a full 8-hour period.



Compact electrochemical H₂S sensors can last three years or longer in day-to-day operation.

Until recently, most instrument users (and manufacturers) have set the Low and TWA alarms at 10 ppm, and the High and STEL alarms at 15 ppm. Instrument users who are required to conform to the new TLV will need to use much lower settings. It is possible to set the H₂S alarms (at least on some brands of instruments) as low as 0.5 ppm (one-half the TLV® exposure limit value). How low to set the alarms is a function of legal requirements and company policy. Many instrument users now set the Low and TWA alarms at 1.0 ppm, and the High and STEL alarms at 5.0 ppm. In cases where the ambient concentration of H₂S makes it impractical to set the instantaneous alarms at these very low concentrations, it may make sense to set the TWA at 1.0, and the STEL alarm at 5.0 ppm; but to leave the instantaneous Low and High alarms at the old values of 10.0 ppm and 15.0 ppm.

It's useless unless you use it

Electrochemical H₂S sensors 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, and take action at the appropriate concentration.

Bob Henderson is president of GfG Instrumentation.