

AP 1019:

Setting the alarms in electrochemical sensor equipped toxic gas instruments



Recently lowered exposure limits have made taking a more conservative approach to setting alarms mandatory for many instrument users.

Recently lowered exposure limit guidelines for H₂S, SO₂ and NO₂ have forced many instrument users to revisit where to set the alarms in their atmospheric monitors. For other gases, although the exposure limits have not changed, corporate policies as well as enforcement agency decisions have made taking a more conservative approach mandatory for many instrument users.

- **Which exposure limits apply?**

The most important obligation for any employer is to ensure that workers are not harmed by exposure to toxic materials or conditions that may be present in the workplace environment. Exposure limits like the OSHA PEL, NIOSH REL and ACGIH® TLV® provide exposure limits, which if exceeded, may lead to immediate or long term harm. These guidelines and standards set the limits above which conditions are deemed to be hazardous. They are not necessarily the concentrations that should be used when setting alarms. For instrument users there are two obligations. The first is ensuring that workers are not exposed to hazardous conditions. The second is ensuring that workers are able to leave the affected area before becoming affected by a hazardous condition. Workers should be

out of the area before rather than after the concentration of toxic gas exceeds the hazardous condition threshold. Unfortunately, the PEL, REL and TLV® are not always in agreement. Which exposure limit is applicable and enforceable depends on where you are, what you are doing, and who is responsible for enforcing your workplace safety requirements. Even when the applicable (and enforceable) hazardous condition threshold concentrations are unambiguous, setting the alarms can still be a challenge.

United States Occupational Safety and Health Administration (OSHA) regulations use the term Permissible Exposure Limit (PEL) to define the maximum concentration of a listed contaminant to which an unprotected worker may be exposed as an 8 hour time-weighted average (TWA) during the course of his workplace duties. Exposure limits for gases and vapors are usually given in units of parts-per-million (ppm). Limits for mists, fume and particulate solids are expressed in units of mg/m³. In addition to the 8 hour TWA PEL, Ceiling (C), Short Term Exposure Limit (STEL), and peak exposure limits are also specified for some airborne hazards.

OSHA 8 hour TWA PEL and C values are given for some airborne contaminants in Subpart Z (Section 1910.1000), and in substance-specific standards (e.g., methylene chloride, 1910.1052 and benzene, 1910.1028).

OSHA PELs are listed in Subpart Z (Section 1910.1000) of the Code of Federal Regulations, and posted at www.OSHA.gov. Individual states may either follow the Federal regulations, or if they have their own "Approved Occupational Safety and Health Plan" may follow their own, state-specific permissible exposure limits. States may not publish or follow exposure limits that are more permissive than Federal OSHA limits. Twenty-five states (as well as Puerto Rico and the Virgin Islands) have their own approved plan. In many cases the exposure limit in these states for a particular toxic substance is more conservative than the Federal OSHA PEL.

The National Institute of Occupational Safety and Health (NIOSH) develops and periodically revises recommended exposure limits (RELs) for hazardous substances or conditions in the workplace. The NIOSH REL is an occupational exposure limit that has been recommended by NIOSH to OSHA for adoption as a permissible exposure limit. The REL represents a level of exposure that NIOSH believes would be protective of worker safety and health over a working lifetime if used in combination with engineering and work practice controls. The OSHA PELs listed in Subpart Z are the same values originally promulgated in 1971. Because NIOSH RELs are periodically reviewed and updated, they tend to be more conservative than the OSHA exposure limits. Many states with approved occupational safety and health plans use the NIOSH RELs as the basis for their state specific permissible exposure limits. This



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makes the NIOSH REL the enforceable permissible exposure limit in many states. NIOSH and OSHA exposure limits are included in the "NIOSH Pocket Guide to Chemical Hazards," which can be downloaded at <http://www.cdc.gov/niosh/npg/>

• **What are TLVs®, and why do they matter?**

The ACGIH TLVs® are among the world’s most widely used and respected guidelines for workplace exposure to toxic substances. TLVs® are designed to function as recommendations for the control of health hazards, and to provide guidance intended for use in the practice of industrial hygiene. Although ACGIH TLVs® are not expressly developed for use as legal standards; they 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 and NIOSH RELs, many programs, especially the programs of multinational or prominent corporations, use the ACGIH TLVs®. ACGIH® publications may be purchased or downloaded at www.ACGIH.org



TLVs are not consensus standards. They are based solely on peer-reviewed toxicological and epidemiological evidence. The expense of implementing workplace controls, and the feasibility of using currently available monitoring technology are not issues central to the decision of whether or not to release or amend a TLV®. The idea is for science to speak with a neutral voice, and for employers and safety equipment manufacturers to respond as necessary to protect workers. This can create problems when there is a significant drop between the old and the new TLV®.

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

• **How do instruments determine when to go into alarm?**

Most real-time instruments for toxic gas measurement have at least four user settable alarms for each toxic gas sensor. The alarms are usually referred to as the Low alarm, the High alarm, the STEL alarm, and the TWA alarm. There are usually other non-user adjustable alarms as well, such as an alarm for negative readings, and an alarm for over-range conditions that exceed the sensor’s capability to measure.

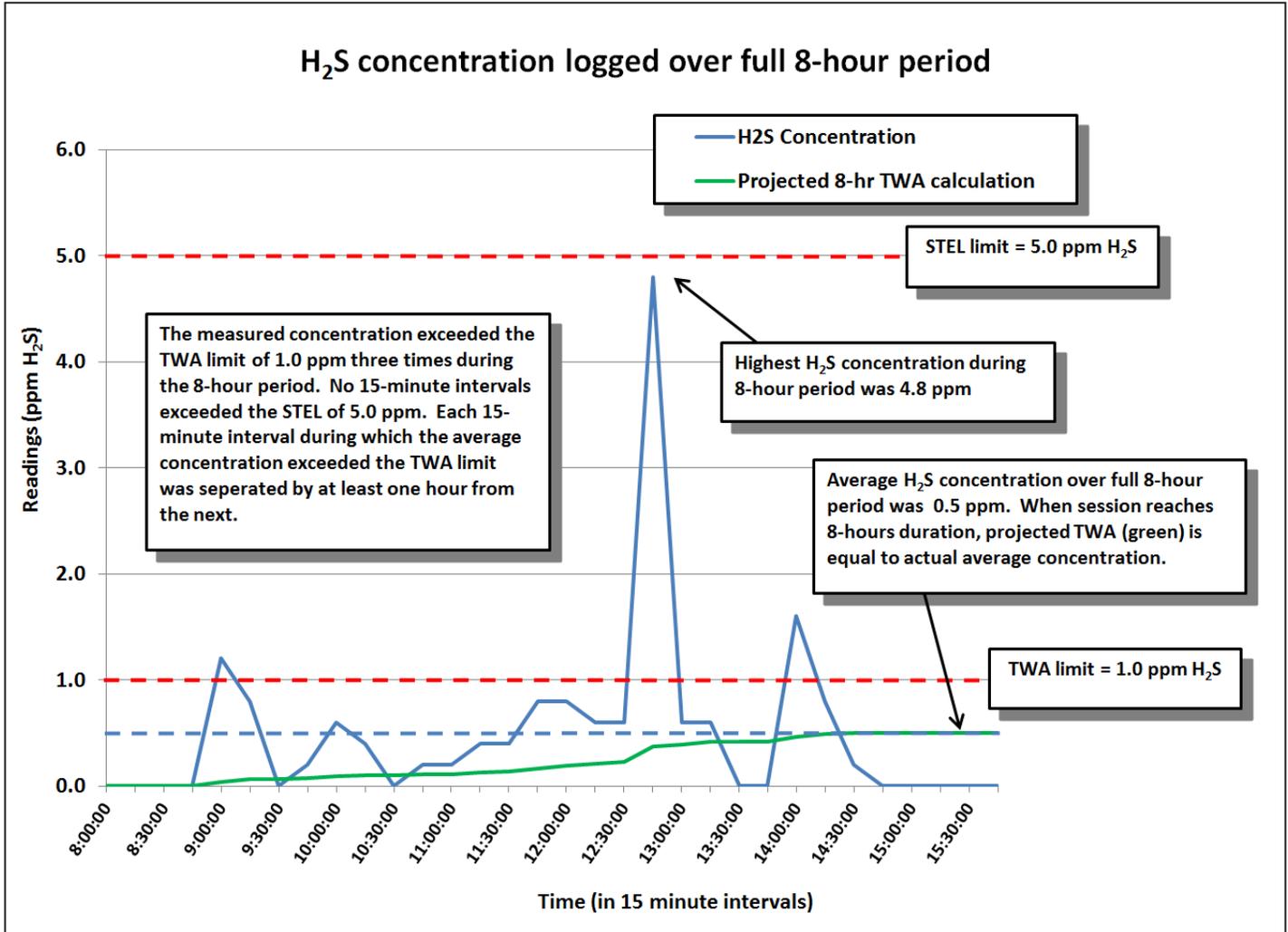
Depending on the manufacturer, however, the Low and High alarms are sometimes also referred to as Ceiling or Peak alarms. Whatever they are called by the manufacturer, the Low and High alarms are based on actual, real-time measured values. The alarm is activated the moment the measured reading exceeds the setting.

The STEL and TWA alarms are based on time history calculations. STEL alarm calculations are generally based on a 15-minute time weighted average. When the instrument is initially turned on (or the monitoring session is initiated), the microprocessor begins calculating the STEL value based on the actual measured concentration projected over a full 15-minute period. Once the duration of the monitoring session exceeds 15-minutes, the STEL calculation is based on the average concentration over the most

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recent 15-minute interval. The STEL alarm is sounded whenever the most recent 15-minute interval average exceeds the alarm setting.

TWA calculations are generally based on an 8-hour time weighted average (TWA). When the instrument is initially turned on, the microprocessor calculates the TWA based on the actual concentration measured projected over a full 8-hour period. Time not measured is projected as zero exposure in most jurisdictions. Thus, for a worker exposed to 100 ppm of contaminant for four hours, the 8-hour TWA would be equal to only 50 ppm at that time. At the end of a full eight hours at 100 ppm, the 8-hour TWA would be equal to 100 ppm.

Once the monitoring session reaches eight hours in duration, most instruments base the TWA reading on the most recent 8-hour

average. (It should be noted that some instrument designs allow users to specify a different TWA calculation interval to facilitate use with extended work shifts and other special applications.) The TWA alarm is sounded whenever the projected or the elapsed exposure exceeds the alarm setting.

In the above chart, the average measured concentration (in blue) over the full 8-hour session was 0.5 ppm H₂S. After 8-hours the projected TWA calculation (in green) equals the average concentration.

An important aspect of the TWA concept is that concentrations above the limit are permitted as long as they are balanced by an equal amount of time that is spent below the limit. Of course, at no time can the the concentration exceed whatever other limits are specified.

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The ACGIH® provides additional guidance for exposures that exceed the TLV®. According to the ACGIH®, exposure above the TWA up to the STEL should be less than 15-minutes, should not occur more than four times per day; and any 15-minute interval which exceeds the TWA limit should be separated by at least one hour from the next.

A complicating factor is that for many gases the TLV® provides only a single part definition. For instance, the 2012 TLV® for NO₂ is a single part recommendation that consists of an 8-hour TWA limit of 0.2 ppm. Although the NO₂ TLV® does not include a STEL or a Ceiling limit, it is still very important to limit the maximum instantaneous exposure.

The ACGIH® “Excursion Limit” applies to those TLVs® that do not have a STEL. According to the ACGIH®, “Excursions in worker exposure levels may exceed 3 times the TLV-TWA for no more than a total of 30 minutes during a workday, and under no circumstances should they exceed 5 times the TLV-TWA, provided that the TLV-TWA is not exceeded.”¹

Using the Excursion Limit concept, setting the Low instantaneous alarm at 0.6 ppm (= 3 times the TWA), the High alarm at 1.0 ppm (= 5 times the TWA), and the TWA alarm at 0.2 ppm would meet both the spirit and letter of the TLV®.

The above example for NO₂ still begs the question of where to set the STEL alarm. One arguably correct approach might be to turn the STEL alarm off, and depend on the other three alarms. The more common approach is for instrument users to set the STEL alarm at the same concentration as the TWA alarm. In this case, as long as the instrument user leaves the affected area immediately upon the activation of any alarm, it is very unlikely that the TWA alarm will ever be activated. This is a very conservative approach to setting the NO₂ instrument alarms:

- Low = 0.6 ppm**
- High = 1.0 ppm**
- STEL = 0.2 ppm**
- TWA = 0.2 ppm**

• **H₂S exposure limits**

H₂S is an extremely common workplace contaminant associated with microbial decomposition. It is a leading cause of injury and death in the oil industry, during confined space entry, and in many other workplace settings.

The Federal OSHA PEL for H₂S is quite different from, and less conservative, than the NIOSH REL and ACGIH® TLV®. The OSHA PEL for H₂S does not include a TWA or STEL, but stipulates that the acceptable Ceiling (C) concentration is 20 ppm, that the maximum

H ₂ S exposure limits					
OSHA PEL					
	TWA	STEL	Acceptable Ceiling (C) Concentration	Acceptable Maximum Peak above Ceiling for an 8-hour shift Concentration	Maximum duration
	NA	NA	20 ppm	50 ppm	10-minutes once only if no other measurable exposure occurs during shift
NIOSH REL					
	TWA	STEL	Ceiling		
	10.0 ppm	15.0 ppm	NA		
2009 ACGIH TLV					
	TWA	STEL	Ceiling		
	10.0 ppm	15.0 ppm	NA		
2010 ACGIH TLV					
	TWA	STEL	Ceiling		
	1.0 ppm	5.0 ppm	NA		

peak above the Ceiling (C) concentration is 50 ppm, and that the maximum duration of exposures above 20 ppm are limited to no more than 10 minutes once per eight hour shift when no other measurable exposures occur during the shift.

Be aware of specific activities may impose additional monitoring requirements and / or take action thresholds. For instance, OSHA 1910.146, "Permit-required confined spaces," Appendix D provides examples of a Confined Space Pre-Entry Check List and Entry Permit. The examples reference 10 ppm H₂S as the maximum permitted concentration during pre-entry testing (after isolation and ventilation), and 10 ppm (TWA) and 15 ppm (STEL) as the maximum concentrations permitted during an entry.

The 2010 TLV® for H₂S has caused much concern among instrument users. The old (2009) TLV®, as well as the current NIOSH REL, reference the same 15.0 ppm STEL and 10.0 ppm TWA limits. In the past, almost all instrument users set the instantaneous Low and High alarms at the STEL and TWA limit values.

Thus, the typical H₂S alarm settings used in most instruments was (and for most users continues to be):

- Low = 10.0 ppm**
- High = 15.0 ppm**
- STEL = 15.0 ppm**
- TWA = 10.0 ppm**

The latest 2010 TLV® comprises a two part definition, with a 15-minute STEL of 5.0 ppm, and an 8-hour TWA of 1.0 ppm. Where to set the instantaneous Low and High alarms is a particular concern for many instrument users. The fear for many instrument users is that if the instantaneous low alarm is set at the 1.0 ppm TLV®-TWA, frequent alarms due to momentary spikes above 1.0 ppm might



cause workers to lose faith in the instrument, or cease taking the correct protective measures.

For instrument users who are unaffected by the new TLV®, the tendency has been to stick with the old alarm settings. For customers affected by the TLV®, many users find the following settings meet the spirit and requirements of the 2010 TLV limit:

- Low = 3.0 ppm**
- High = 5.0 ppm**
- STEL = 5.0 ppm**
- TWA = 1.0 ppm**

- **Are H₂S sensors capable of measuring at the new TLV® limits?**

The answer is “Yes” BUT with qualifications.....

Different H₂S sensors are optimized for different performance requirements (e.g. cost, life, size, response to interfering contaminants, sensitivity, AND ACCURACY!) No single sensor design is equally optimized along all performance dimensions. In particular, the electrical output per ppm of gas varies widely between sensor models. One of the most widely used “miniature” H₂S sensors has an output signal of 0.105 ± 0.025 µA/ppm. Another H₂S sensor manufactured by the same company is optimized for higher sensitivity, and has an output signal of 0.7 ± 0.25 µA/ppm. Both designs are excellent sensors! However, they are designed for use in very different applications.

For an H₂S sensor to be usable with one or more of the alarms set at the 1.0 ppm limit, it needs to be capable of providing low concentration readings with at least ± 0.2 ppm resolution. Some H₂S sensors are easily capable of providing readings with ± 0.1 ppm or ± 0.2 ppm resolution; while others are limited to ± 1.0 ppm resolution. In general, dual channel “COSH” sensors used to simultaneously measure both CO and H₂S have a smaller measurement signal than substance-specific single-channel H₂S sensors.

Besides the sensor limitations, the instrument programming (firmware) must permit setting the alarms at the desired concentration. Depending on the instrument, it may be necessary to update the firmware or even replace an older instrument with a newer model. Instrument users should consult with the manufacturer as to whether or not the instrument can be used with alarms set to the new TLV®.

- **SO₂ exposure limits**

Prior to 2009, the NIOSH REL and the TLV® agreed on the limits for SO₂. In 2009 TLV for SO₂ was significantly reduced from the previous levels.

SO ₂ exposure limits			
	TWA	STEL	Ceiling (C)
OSHA PEL			
	5.0 ppm	NA	NA
NIOSH REL			
	2.0 ppm	5.0 ppm	NA
2009 ACGIH TLV			
	2.0 ppm	5.0 ppm	NA
2010 ACGIH TLV			
	NA	0.25 ppm	NA

The new TLV®-STEL is an extremely challenging limit. Existing instruments may or may not be able to perform at the new limit. Once again, for instrument users who are unaffected by the new TLV®, the tendency has been to stick with alarm settings at the old NIOSH and ACGIH® limits, (Low = 2.0 ppm, High = 5.0 ppm, STEL = 5.0 ppm, TWA = 2.0 ppm).

For customers affected by the TLV®, many users find the following settings meet the spirit and requirements of the 2010 TLV® limit:

- Low = 0.75 ppm**
- High = 1.25 ppm**
- STEL = 0.25 ppm**
- TWA = 0.25 ppm**

- **What is the effect of the accuracy of the sensor and the calibration gas on the accuracy of readings?**

Many instrument manufacturers list the accuracy of the toxic gas sensors in their products as ± 5% of the reading, or the minimum unit of resolution of the instrument, whichever is greater. Thus, for an instrument capable of providing readings in 0.2 ppm H₂S increments, the accuracy for readings between 0 and 2.0 ppm is ± 0.2 ppm. The accuracy of readings above 2.0 ppm will be ± 5% of the measured value.

This statement of accuracy assumes that the sensors are properly calibrated. The effects of the accuracy of the calibration gas on the accuracy of the toxic gas sensor are additive. The higher the accuracy of the calibration gas, the higher the accuracy of the readings.

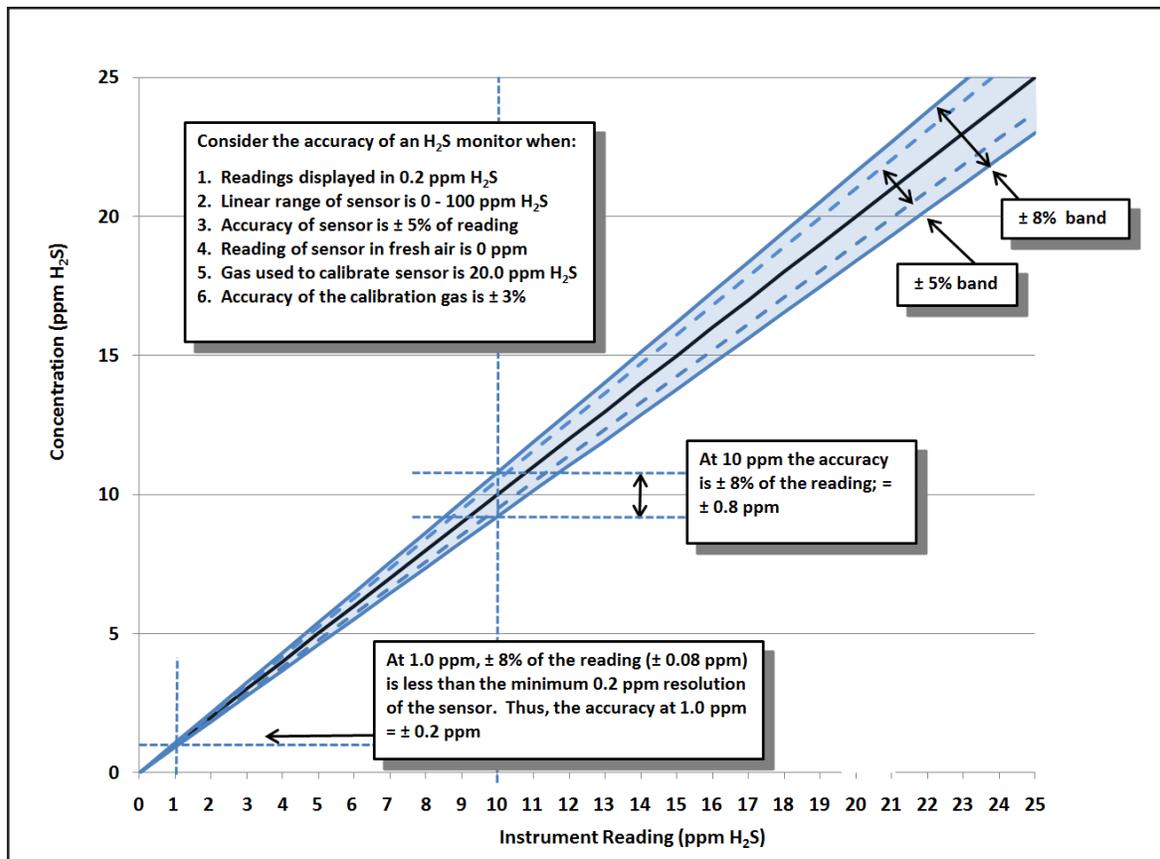
Calibration is minimally a two-point verification of response. In the first step the sensor is zero-adjusted in atmosphere that contains no measurable contaminants. In the second step the instrument is

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adjusted using calibration gas that contains a precise concentration of the toxic gas. Most calibration gas is manufactured and packaged by specialty suppliers to traceable reference standards. The accuracy and the dating (shelf-life) over which the accuracy statement applies are normally printed on the cylinder label. Calibration gas suppliers may offer different levels of accuracy for gas that is used for different purposes. Don't be afraid to ask if you need calibration gas that conforms to a higher level of accuracy.

Several calibration gas manufacturers offer H₂S calibration gas with ±3.0% accuracy with 6-month shelf life dating. They also offer ±10.0% accuracy with up to two-years shelf life dating.

The effect of these relationships on the accuracy of readings can be illustrated graphically. The accuracy of the reading is determined by the accuracy of the sensor (= ±5% of reading) plus the effects of the accuracy of the calibration gas (= ±3% of reading). When the instrument is exposed to 10 ppm H₂S, the concentration is much higher than the minimum unit of resolution (= 0.2 ppm). Thus, at 10 ppm H₂S the accuracy of the reading = ±8% of the reading, or in this case, ±0.8 ppm.

When the instrument is exposed to 1.0 ppm however, the concentration is much closer to the minimum unit of resolution. Since 8% of 1.0 ppm = 0.08 ppm, (which is less than the minimum unit of resolution); at 1.0 ppm the accuracy of the reading becomes ± 0.2 ppm.

• **Conclusion:**

The primary concern for any employer is to ensure that workers are not exposed to hazardous conditions. For many instrument users, recent changes in TLV[®] guidelines may not have a mandatory effect on instrument settings or procedures. Employers whose activities or policies require conformity with TLV[®] exposure limit guidelines may need to evaluate their current monitoring equipment and procedures. If you do need to take action according to the new limits, the equipment is readily available.

¹2012 TLVs[®] and BEIs[®] Based on the Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents; ACGIH[®] Worldwide; Signature Publications; 2012; Cincinnati, OH.

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