



Real-time H₂S Measurement: Issues and Answers

January, 2012

GfG Instrumentation
1194 Oak Valley Drive
Ann Arbor, MI 48108

Toll free: (800) 050-0329
Direct: (734) 761-0573

Internet: www.gfg-inc.com

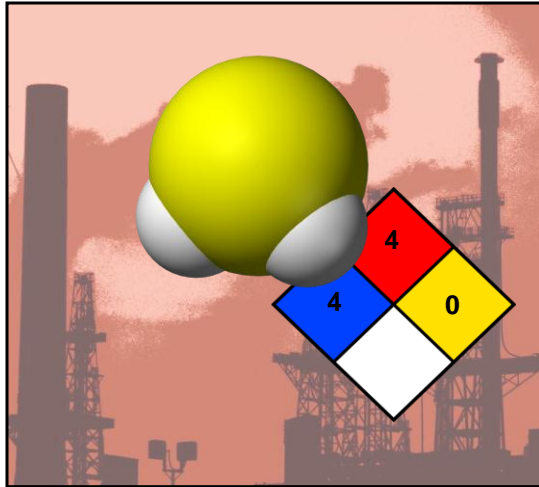
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New TLV Exposure limit for H₂S published in 2010

- **Old TLV:**
 - TWA = 10 ppm
 - STEL = 15 ppm
- **New 2010 TLV:**
 - TWA = 1.0 ppm
 - STEL = 5.0 ppm



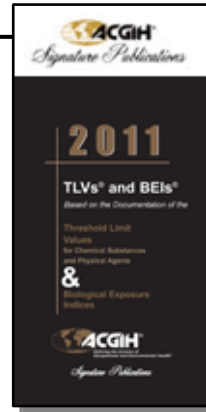
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Threshold Limit Value (TLV[®])

- *Determined by American Conference of Governmental Industrial Hygienists (ACGIH)*
- *Guidelines for control of potential health hazards*
- *Intended as recommendation*
- *Usually more conservative than Federal OSHA PEL, frequently more conservative than NIOSH REL*



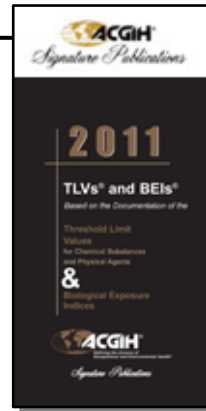
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What are TLVs[®], and why do they matter?

- *In the United States which toxic exposure limits apply depends on:*
 - *The state in which the workplace is located*
 - *The type of work being performed (e.g. shipyard confined space entry versus general industry permit confined space entry)*
 - *Requirements that apply to a specific employer (e.g. US Coast Guard, Navy, Air Force, MSHA regulated worksites, etc.)*
 - *Corporate health and safety policies*



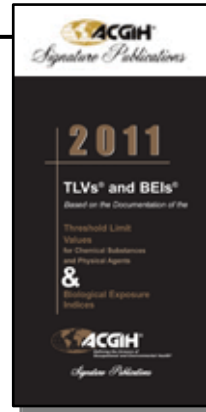
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TLVs[®] Incorporated by Reference in:

- *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*



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Corporate Toxic Exposure Limit Strategy

- *Given the potential for lawsuits, large USA companies with “deep pockets” have to follow the most conservative exposure limit standards*
- *Since ACGIH[®] TLV[®] recommendations are frequently more conservative than OSHA PELs; many corporations use the ACGIH TLVs[®]*
- *Most oil companies in the United States and Canada (where they have no choice) strictly follow the TLVs*



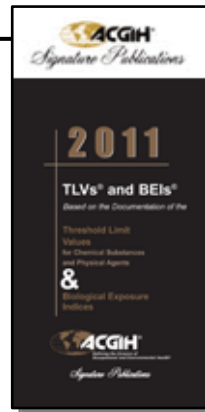
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Why has there been so much controversy?

- *The alarms in many popular H2S instruments cannot be set at the new TLV concentration limit of 1.0 ppm*
- *Customers with sizeable investments in these instruments do not want to have to throw them away*
- *Some (especially oil industry) customers will have a difficult time conforming with the new limits because of the actual presence of gas*
- *Some instrument users have funded studies casting doubt on whether available instruments can actually be used*



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Exposure limits for H₂S

Federal USA OSHA PEL

	8-Hour TWA	STEL	Acceptable Ceiling Concentration	Acceptable Max 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
REL	10 ppm	15 ppm	NA	NA	NA
TLV (2011)	1.0 ppm	5.0 ppm	NA	NA	NA
UK OEL	10 ppm	15 ppm	NA	NA	NA
FR VL	5 ppm	10 ppm	NA	NA	NA
DFG MAK	10 ppm	NA	20 ppm peak in any 10-min period, (as momentary ceiling value), maximum 4 per shift		



H2S Measurement

- **Manufacturers who are not able to set alarms at the new TLV say “Can’t be done.”**
- **Manufacturers who can set the alarms at the new TLV say “Of course you can!!”**
- **What’s the truth and how do we defend our capabilities?**



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Not all electrochemical H2S sensors are created equal!

- **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**
- **The electrical output per ppm of gas varies widely between sensor models:**
 - **City Technology MICROceL™ HS version H2S sensor (used in the BW Technologies by Honeywell MicroClip) has an output signal of $0.105 \pm 0.025 \mu\text{A/ppm}$**
 - **The 4HS/LM CiTiceL® version H2S sensor (used by GfG Instrumentation in the G450) is optimized for higher sensitivity, and has an output signal of $0.7 \pm 0.25 \mu\text{A/ppm}$**

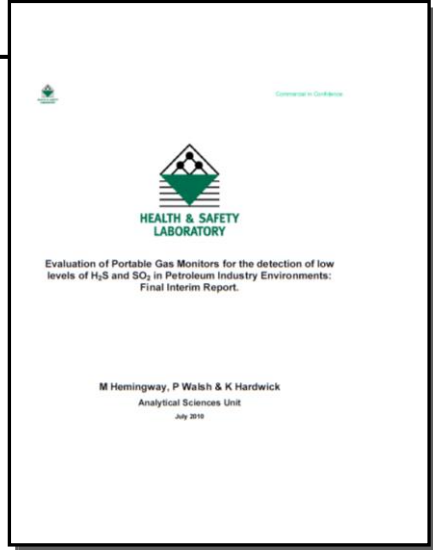
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Accuracy of personal H2S monitors

- **API Conclusions regarding H2S:**
 - **Evaluated 5 models personal H2S monitors (did not disclose brands and models)**
 - **At the new TLV® concentration (1.0 ppm), only some of the monitors responded and alarmed: two of the five tested responded consistently, but only one alarmed consistently**
 - **All the monitors exposed to 5 X TLV® (5 ppm) responded with reasonable accuracy and alarmed.**



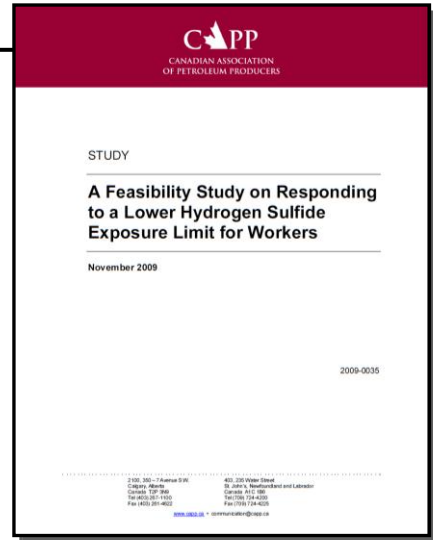
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Accuracy of personal H2S monitors

- **CAPP (Canadian Association of Petroleum Producers) Study**
- **Evaluated 7 models of personal H2S monitors**
- **Two of the instruments found adequate to meet the requirement of a reliable alarm at 1.0 ppm (the other two brands were not found to be adequate)**



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Accuracy of GfG instruments for H2S

- **The G450 and G460 carry third-party performance certifications for H2S from DEKRA-EXAM, a Nationally Recognized Testing Laboratory in Germany**
- **Over the standard full range of 0 – 100 ppm, the stated accuracy of the G450 and G460 when equipped with a City Technology 4HS/LM CiticeL® H2S sensor is $\pm 5\%$ of reading or the minimum increment of measurement, whichever is greater**



Translation 4th Supplement

(Supplement in accordance with Directive 94/9/EC Annex III number 6)

to the EC-Type Examination Certificate
BVS 06 ATEX E 017 X

Equipment: Gas detectors type G450 and G460
Manufacturer: GfG Gesellschaft für Gerätebau mbH
Address: D-44143 Dortmund

Description
The Essential Health and Safety Requirements with respect to the measuring function for explosion protection are accorded by application of:

EN 60795-25-1:2007
EN 50271:2003

The supplement to the EC-type examination certificate covers devices with software version 3.2.1 and infrared-sensors with software version 3.0.

This supplement to the EC-type examination certificate covers the measuring function for methane, propane and isobutane with the measuring range 0 to 100% LEL, sensors MK221-050 and MK211-04-73, for propane with the measuring range 0 to 100% LEL and isobutane with concentrations up to 60% LEL, sensors MK227-5 and MK231-5).

Type report
Type report PFG-no. 41300205P dated 28/11/2009

Special conditions for safe use

- The option "AL locking" shall be set "on".
- After an extreme impact the zero of the sensors shall be checked and, if necessary, adjusted.
- The indications with zero gas and test gas shall be tested before every use.

DEKRA EXAM GmbH
Bochum, dated 30/11/2009

Signed: Müller

Signed: Klauswetter

Certification body

Special services unit

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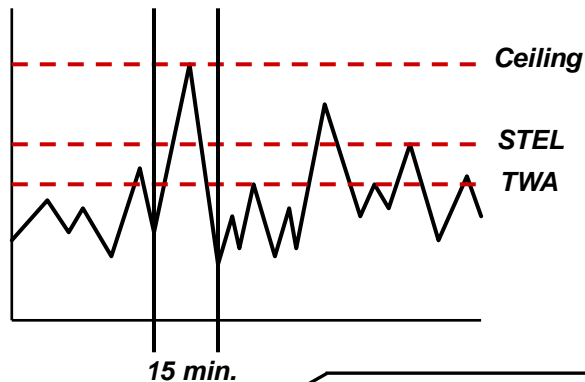
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Exposure Limits defined in three ways:

- **Time Weighted Average (TWA)**
- **Ceiling**
- **Short Term Exposure Limit (STEL)**



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TWA is Projected Value

According to OSHA cumulative TWA exposures for an eight hour work shift are calculated as follows:

$$E = (C_a T_a + C_b T_b + \dots + C_n T_n) / 8$$

Where:

- *E* is the equivalent exposure for the eight hour working shift
- *C* is the concentration during any period of time *T* where the concentration remains constant
- *T* is the duration in hours of the exposure at concentration *C*

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TWA Calculation

<i>Exposure</i>	<i>Concentration</i>	<i>TWA</i>
<i>4 hours</i>	<i>100 ppm</i>	<i>50 ppm</i>
<i>8 hours</i>	<i>100 ppm</i>	<i>100 ppm</i>
<i>12 hours</i>	<i>100 ppm</i>	<i>150 ppm</i>

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Range and resolution of GfG instruments used to detect H2S

- **Standard full range is 0 – 100 ppm. (Users can optionally choose a 0 – 500 ppm extended full range version of the product.)**
- **Standard setup displays readings in 0.2 ppm steps over the 0 – 1.0 ppm range. (Users can optionally choose to display readings in 0.1 ppm increments over the 0 – 1.0 range.)**
- **The method used by the G450 and G460 to calculate STEL and TWA exposure and alarms is based on the actual sensor output, and is not affected by the choice of measurement increment in the 0 – 1.0 ppm range.**
- **From 1.0 – 99.9 ppm measurements are always incremented in 0.1 ppm steps.**



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So how accurate are the readings?

- **Thus, on a standard basis, from 0 – 4 ppm the accuracy is +/- 0.2 ppm; from 4.0 to 100 ppm the accuracy is +/- 5% of reading.**
- **If you choose the 0.1 ppm resolution over the 0 – 1.0 ppm range, from 0 – 2.0 ppm the accuracy is +/- 0.1 ppm, from 2.0 to 100 ppm the accuracy is +/- 5% of reading**
- **Setting ANY of the alarms at 1.0 ppm is NO PROBLEM!**



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How does the accuracy of the cal gas affect the accuracy of the readings?

- GfG Quad Mix cal gas is available with 10 ppm H₂S, +/- 3% accuracy, 6-months shelf life dating
- GfG also supplies 1.0 ppm H₂S in N₂ with +/- 3% accuracy with 6 month dating
- Using +/- 3% accuracy gas means that new accuracy statement for the combined instrument and cal gas system becomes (with standard setup) 0.2 ppm or +/- 8% of reading, whichever is greater
- So from 0 – 2.0 ppm the accuracy is +/- 0.2 ppm
- Once again, setting the alarm at 1.0 ppm is not a problem!

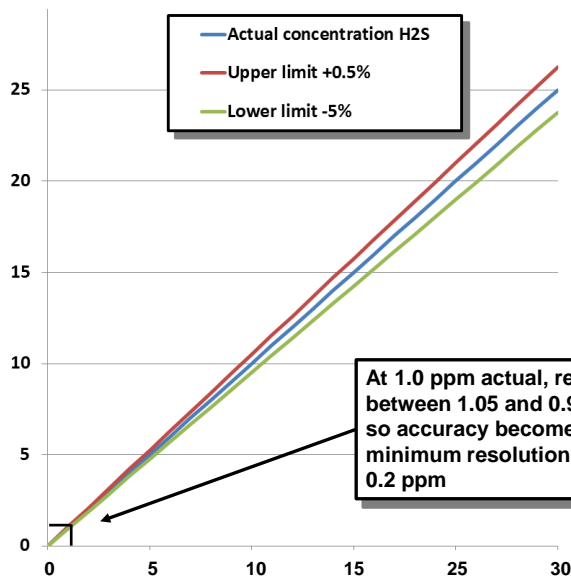


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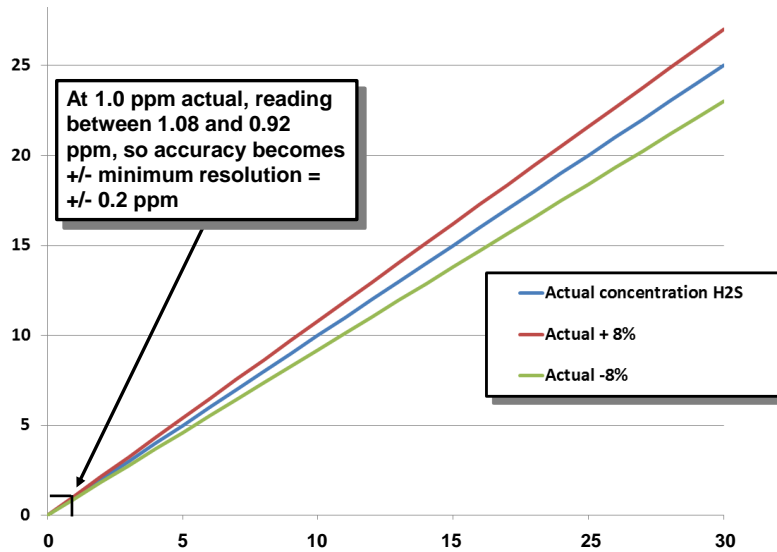


Effect of ± 5% sensor accuracy on readings





Effect of calibration gas ($\pm 3\%$) and sensor accuracy (± 5) on readings: combined effects = $\pm 8\%$



Where should customers who care about the TLC set the alarms?

- TLV only includes STEL and TWA limits; does not include a Ceiling or "Peak" limit
- GfG instruments have 4 user settable alarms (Low, High, STEL and TWA)
- Many customers use the following approach:
 - Low: 5.0 ppm
 - High: 10.0 ppm
 - STEL: 5.0 ppm
 - TWA: 1.0 ppm

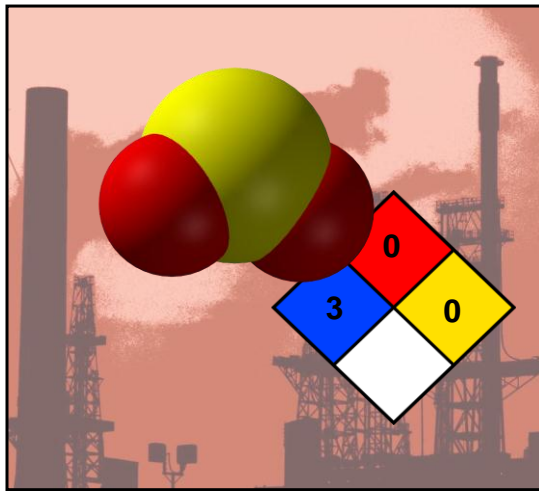


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Exposure limits for SO₂

- **Old TLV :**
 - TWA = 2 ppm
 - STEL = 5 ppm
- **New (2009) TLV:**
 - STEL = 0.25 ppm
- **Suggested GfG alarms:**
 - Low: 2.0 ppm
 - High: 5.0 ppm
 - STEL: 0.25
 - TWA: 0.25 ppm



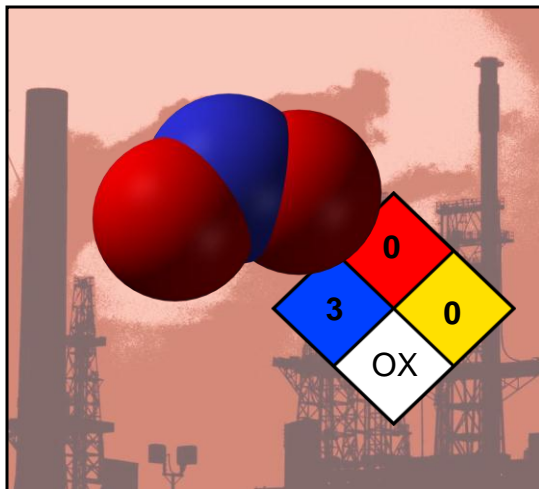
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Exposure limits for NO₂

- **Old TLV:**
 - 8 hr. TWA = 3 ppm
 - 15 min. STEL = 5 ppm
- **Proposed 2012 TLV (NIC)**
 - 8 hr. TWA = 0.2 ppm
- **US OSHA PEL:**
 - Ceiling = 5 ppm
- **US NIOSH REL:**
 - 15 min. STEL = 1 ppm



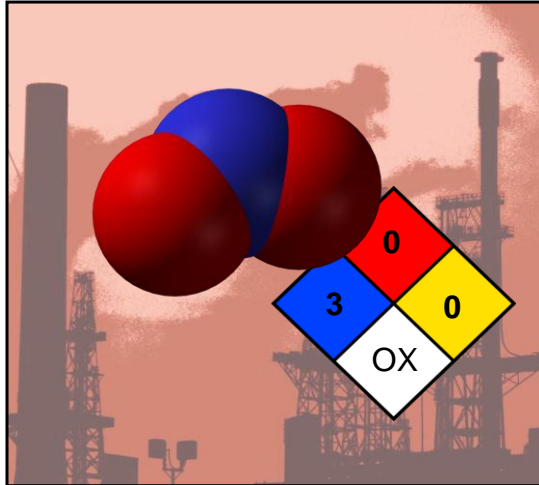
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Exposure limits for NO₂

- **Suggested GfG alarms:**
 - **Low: 3.0 ppm**
 - **High: 5.0 ppm**
 - **STEL: 1.0 ppm**
 - **TWA: 0.2 ppm**



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Questions?



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