

Photoionization Detectors

- *Measuring Solvent, Fuel and VOC vapors in the workplace environment*



Volatile organic compounds (VOCs)

- *VOCs are organic compounds characterized by tendency to evaporate easily at room temperature*
- *Familiar VOCs include:*
 - *Solvent*
 - *Paint thinner*
 - *Nail polish remover*
 - *Gasoline*
 - *Diesel*
 - *Heating oil*
 - *Kerosene*
 - *Jet fuel*
 - *Benzene*
 - *Butadiene*
 - *Hexane*
 - *Toluene*
 - *Xylene*
 - *Many others*



Volatile organic compounds (VOCs)

- ***Solvent, fuel and other VOC vapors common in many workplace environments***
- ***Most have surprisingly low permissible exposure limits***
- ***Long before you reach a concentration sufficient to register on a combustible gas indicator, you will have easily exceeded the toxic exposure limits for most VOC contaminants***
- ***PID equipped instruments generally the best choice for measurement of VOCs at exposure limit concentrations***



VOC Toxicity

- *VOCs present multiple potential threats in the workplace environment*
- *Heavier than air, flammable and toxic*
- *Increased awareness of toxicity is leading to lowered exposure limits*
- *This leads in turn to increased need for direct measurement of VOCs at exposure limit concentrations*



Toxic Exposure Limits

- *Permissible exposure limits (PELs) designed to protect workers against the health effects of exposure to hazardous substances*
- *PEL is maximum concentration of airborne contaminant to which unprotected worker may be exposed*
- *Unprotected workers may not be exposed to concentration that exceeds the limit*
- *It's up to the employer to determine that these exposure limits are not exceeded*
- *In many cases, a direct reading gas detector is the primary means used to ensure that the PEL has not been exceeded*



VOC Toxicity

- *Toxic substances produce symptoms in two time frames: acute and chronic*
- *While some VOCs acutely toxic at low concentrations, most VOCs chronically toxic*
- *Because of long-term nature of the physiological effects, tendency has been to overlook presence in workplace at PEL concentrations*
- *Exposure via skin or eye contact with liquid or aerosol droplets, or inhalation of vapors*



VOC Exposure Symptoms

- ***Symptoms may not become manifest for years***
 - ***Respiratory tract irritation (acute or chronic)***
 - ***Dizziness, headaches (acute or chronic)***
 - ***Long-term neurological: diminished cognition, memory, reaction time, hand-eye and foot-eye coordination***
 - ***Mood disorders: depression, irritability, and fatigue***
 - ***Peripheral neurotoxicity: tremors and diminished fine and gross motor movements***
 - ***Kidney damage and immunological problems, including increased cancer rates***
 - ***Benzene, (toxic VOC found in gasoline, diesel, jet fuel and other chemical products), linked to chemically induced leukemia, aplastic anemia and multiple myeloma (a cancer of the lymphatic system)***

VOCs and Flammability

- **Most VOC vapors flammable at surprisingly low concentrations**
 - **For hexane and toluene 100% LEL = 1.1% (11,000 PPM)**
 - **By comparison, LEL concentration for methane = 5% (50,000 PPM)**
- **Tendency in past has been to measure them by means of percent LEL combustible gas instruments**
- **Combustible gas instrument alarms usually set to 5% or 10% LEL**
- **Unfortunately, most VOC vapors are also toxic, with Permissible Exposure Limit (PEL) values much lower than the 5% or 10% LEL**
- **Toxic exposure exceeded long before LEL alarm concentration reached**



Limitations of LEL sensor

- *Percent LEL sensors detect gas by oxidizing the gas on an active bead located within the sensor*
- *Readings displayed in % LEL increments, with a full range of 0 – 100% LEL*
- *hazardous condition threshold alarm typically set to 5% or 10% LEL*
- *Hot-bead pellistor sensors unable to differentiate between different combustible gases*
- *May be limited or unable to detect vapors of combustible liquids with flashpoint temperatures higher than 38 degrees C*



Limitations of LEL sensor

- *Percent LEL sensors excellent for gases and vapors that are primarily or only of interest from the standpoint of their flammability (like methane)*
- *However, many other combustible gases and vapors fall into a different category*
- *Toxic VOC vapors usually have a PEL that requires taking action at a much lower concentration*



Other Limitations of LEL Sensor

- *Percent LEL sensors have poor sensitivity to the large molecules found in found in fuels, solvents and other VOCs, with flashpoint temperatures higher than 38°C (100°F)*
- *Because percent LEL detectors are poor indicators for the presence of many VOCs, lack of a reading is not necessarily proof of the absence of hazard*
- *Reliance on hot-bead type LEL sensors for measurement of VOC vapors means PEL, REL or TLV® exceeded long before the combustible alarm activated*



Toxic VOC Example: Hexane

- ***Most standards reference an 8-hour TWA for hexane of 50 PPM***
- ***In some, the PEL for hexane is a maximum of only 20 PPM calculated as an 8-hour TWA***
- ***The LEL concentration for hexane = 1.1% (11,000 PPM)***
- ***If combustible sensor alarm is set at 10% LEL, with a properly calibrated instrument, it would take a concentration of:***

$$0.10 \times 11,000 \text{ ppm} = 1,100 \text{ ppm to trigger an alarm}$$

- ***Even if alarm set to 5% LEL, it still would still require a concentration of 550 PPM to trigger the alarm***



Contaminant	LEL (Vol %)	Flashpoint Temp (°F)	OSHA PEL	NIOSH REL	TLV	5% LEL in PPM
Acetone	2.5%	-4°F (-20 °C)	1,000 PPM TWA	250 PPM TWA	500 PPM TWA; 750 PPM STEL	1250 PPM
Diesel (No.2) vapor	0.6%	125°F (51.7°C)	None Listed	None Listed	15 PPM	300 PPM
Ethanol	3.3%	55°F (12.8 °C)	1,000 PPM TWA	1000 PPM TWA	1000 PPM TWA	1,650 PPM
Gasoline	1.3%	-50°F (-45.6°C)	None Listed	None Listed	300 PPM TWA; 500 PPM STEL	650 PPM
Hexane	1.1%	-7°F (-21.7 °C)	500 PPM TWA	50 PPM TWA	50 PPM TWA	550 PPM
Isopropyl alcohol	2.0%	53°F (11.7°C)	400 PPM TWA	400 PPM TWA; 500 PPM STEL	200 PPM TWA; 400 PPM STEL	1000 PPM
Kerosene/ Jet Fuels	0.7%	100 – 162°F (37.8 – 72.3°C)	None Listed	100 mg/M3 TWA (approx. 14.4 PPM)	200 mg/M3 TWA (approx. 29 PPM)	350 PPM
MEK	1.4%	16°F (-8.9°C)	200 PPM TWA	200 PPM TWA; 300 PPM STEL	200 PPM TWA; 300 PPM STEL	700 PPM
Turpentine	0.8	95°F (35°C)	100 PPM TWA	100 PPM TWA	20 PPM TWA	400 PPM
Xylenes (o, m & p isomers)	0.9 – 1.1%	81 – 90°F (27.3 – 32.3 °C)	100 PPM TWA	100 PPM TWA; 150 PPM STEL	100 PPM TWA; 150 STEL	450 – 550 PPM

VOC Exposure Limits

- *Several recently revised VOC exposure limits, including TLVs for diesel vapor, kerosene and gasoline*
- *Because safety procedures for many international corporations are tied to the most conservative published standard, TLVs® receive much attention*
- *Diesel TLV specifies 8-hour TWA for total diesel hydrocarbons (vapor and aerosol) = 100 mg/m³*
- *Equivalent to approximately 15 parts-per-million diesel vapor*
- *For diesel vapor, 1.0% LEL is equivalent to 60 PPM*
- *Even if LEL instrument properly calibrated for diesel – which may not be possible – reading of only 1.0% LEL would exceed the TLV® for diesel by 600 percent!*



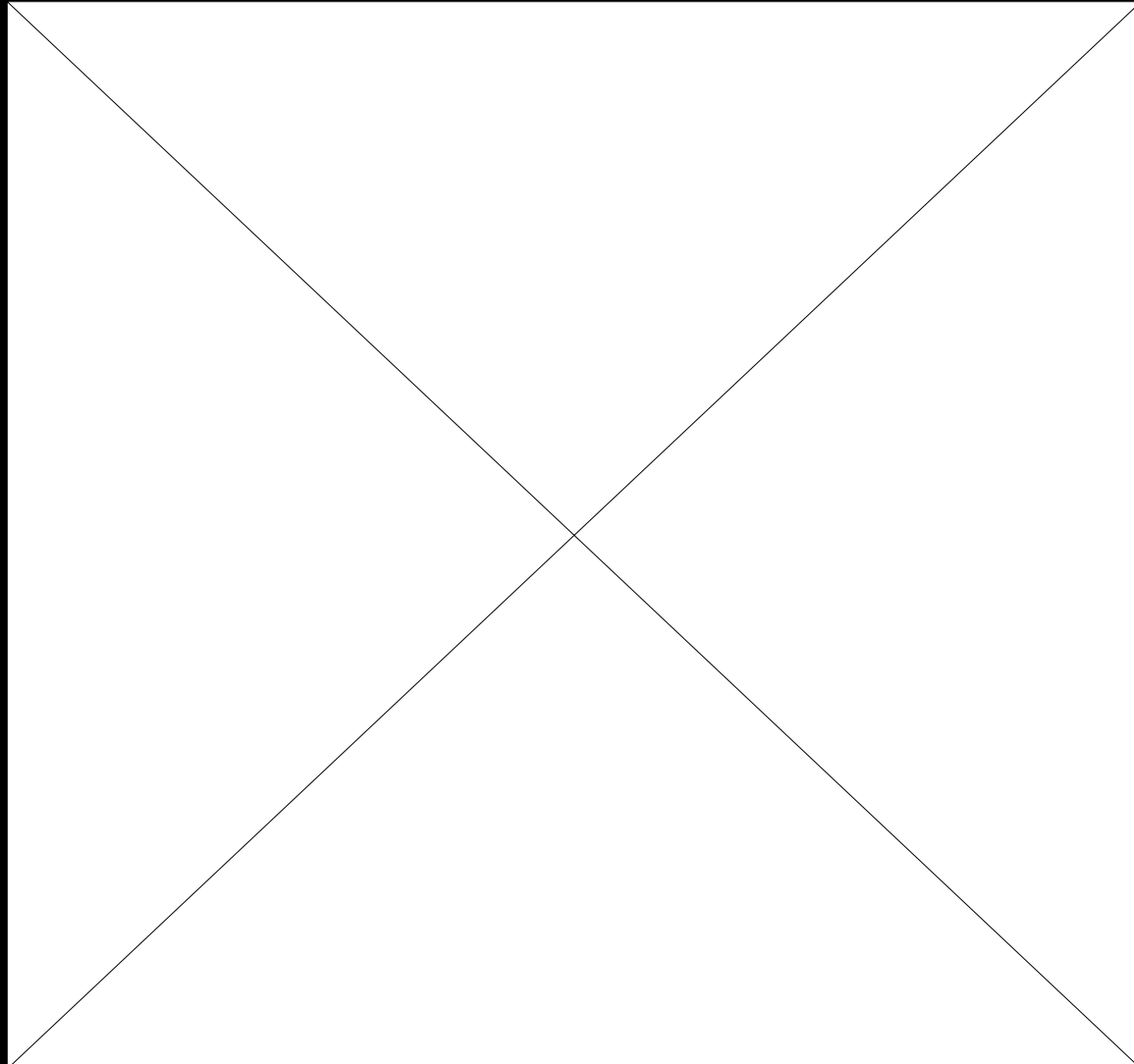
PID - Operating Principle

- *PIDs use ultraviolet light as source of energy to remove an electron from neutrally charged target molecules creating electrically charged fragments (ions)*
- *This produces a flow of electrical current proportional to the concentration of contaminant*
- *The amount of energy needed to remove an electron from a particular molecule is the ionization potential (or IP)*
- *The energy must be greater than the IP in order for an ionization detector to be able to detect a particular substance*



How does a PID work?

- *Ultraviolet light used to remove electron from neutrally charged target molecules creating electrically charged fragments (ions)*



Ionization Potential

- ***IP determines if the PID can detect the gas***
- ***If the IP of the gas is less than the eV output of the lamp the PID can detect the gas***
- ***Ionization Potential (IP) measures the bond strength of a gas and does not correlate with the Correction Factor***
- ***Ionization Potentials are found in the NIOSH Pocket Guide and many chemical texts***



Ionization Potential Values

<i>Substance</i>	<i>Ionization Energy (eV)</i>
<i>carbon monoxide</i>	<i>14.01</i>
<i>carbon dioxide</i>	<i>13.77</i>
<i>methane</i>	<i>12.98</i>
<i>water</i>	<i>12.59</i>
<i>oxygen</i>	<i>12.08</i>
<i>chlorine</i>	<i>11.48</i>
<i>hydrogen sulfide</i>	<i>10.46</i>
<i>n-hexane</i>	<i>10.18</i>
<i>ammonia</i>	<i>10.16</i>
<i>hexane</i>	<i>10.13</i>
<i>acetone</i>	<i>9.69</i>
<i>benzene</i>	<i>9.25</i>
<i>butadiene</i>	<i>9.07</i>
<i>toluene</i>	<i>8.82</i>



Technical Advances in PIDs

- *Miniaturization*
- *Ruggedness*
- *EMI/RFI resistance*
- *Lower humidity interference*



PID Components

- **Detector assembly**
- **Electrodes: sensing, counter and (in some designs) fence**
- **Lamp: most commonly 10.6eV, 11.7eV or 9.8 eV**
 - **Sealed borosilicate glass body**
 - **Window of specific crystalline material**
 - **Filled with specific noble gas or mixture of noble gases**



Photoionization detectors

Nominal Lamp Photon Energies	Gas in Lamp	Major Emission Lines		Relative Intensity	Window Crystal	Crystal transmittance λ Range (nm)
		eV	(nm)			
11.7eV	Argon	11.83	104.8	1000	Lithium fluoride (LiF)	105 - 5000
		11.62	106.7	500		
10.6eV	Krypton	10.64	116.5	200	Magnesium fluoride (MgF ₂)	115 - 7000
		10.03	123.6	650		
9.8eV	Krypton	10.03	123.6	650	Calcium fluoride (CaF ₂)	125 - 8000



PID as “Broad-Range” Sensor

- *VOCs usually detected by means of broad-range sensors*
- *Broad-range sensors provide overall reading for general class or group of chemically related contaminants*
- *Cannot distinguish between different contaminants they are able to detect*
- *Provide single total reading for all detectable substances present*



PID instruments are nonspecific

- *Reading is sum of signals of all detectable substances present, also:*
- *Reading is function of their varying ionization potentials and other physical properties*
- *PID readings always relative to gas used to calibrate detector*
- *Equivalent concentrations of gases other than the one used to calibrate the instrument may not produce equivalent readings!*



PID Correction Factors

- *Correction Factor (CF) is measure of sensitivity of PID to specific gas*
- *CFs do not make PID specific to a chemical, only correct the measurement scale to that chemical*
- *CFs allow calibration on inexpensive, non-toxic “surrogate” gas (like isobutylene)*
- *Most manufacturers furnish tables, or built-in library of CFs to correct or normalize readings when contaminant is known*
- *Instrument able to express readings in true parts per million equivalent concentrations for the contaminant measured*



PID Alarms: Varying Mixtures

- *The Controlling Compound*
 - *Every mixture of gases and vapors has a compound that is the most toxic and “controls” the setpoint for the whole mixture*
 - *Determine that chemical and you can determine a conservative mixture setpoint*
 - *If we are safe for the “worst” chemical we will be safe for all chemicals*



PID Alarms: Varying Mixtures

<i>Chemical Name</i>	<i>10.6eV CF</i>	<i>Exposure Limit Chemical</i>
<i>Ethanol</i>	<i>13.3</i>	<i>1000</i>
<i>Turpentine</i>	<i>0.45</i>	<i>100</i>
<i>Acetone</i>	<i>1.2</i>	<i>750</i>

- Ethanol “appears” to be the safest compound
- Turpentine “appears” to be the most toxic
- This table only provides half of the decision making equation



PID Alarms: Varying Mixtures

- *Set the PID for the compound with the lowest Exposure Limit (EL) in equivalent units and you are safe for all of the chemicals in the mixture*
- *Divide the EL in chemical units by CF to get the EL in isobutylene*

$$EL_{\text{Isobutylene}} = \frac{EL_{\text{chemical}}}{CF_{\text{chemical}}}$$



PID Alarms: Varying Mixtures

<i>Chemical Name</i>	<i>10.6eV CF</i>	<i>EL Chemical</i>	<i>EL Isobutylene</i>
<i>Ethanol</i>	<i>13.3</i>	<i>1000</i>	<i>75.2</i>
<i>Turpentine</i>	<i>0.45</i>	<i>100</i>	<i>222.0</i>
<i>Acetone</i>	<i>1.2</i>	<i>750</i>	<i>625.0</i>

- *Actually, lower sensitivity of the PID makes Ethanol the “controlling compound” when the Exposure Limits are expressed in equivalent “Isobutylene Units”*



PID Alarms: Varying Mixtures

- *Setting the PID to 75 ppm alarm in Isobutylene units protects from all three chemicals no matter what their ratio*
- *IMPORTANT: Equivalent EL_{iso} is a calculation that involves a manufacturer specific Correction Factor (CF)*
- *Similar calculations can be done for any PID brand that has a published CF list*



Questions?

