

# Measuring Solvent, Fuel and VOC Vapours IN THE WORKPLACE ENVIRONMENT



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**GAS** Detection

Solvent, fuel and many other VOC vapours are pervasively common in many workplace environments. Most have surprisingly low occupational exposure limits. For most VOCs, long before you reach a concentration sufficient to register on a combustible gas indicator, you will have easily exceeded the toxic exposure limits for the contaminant.

A wide range of techniques and equipment are available for measuring the concentrations of these contaminants in air. However, PID equipped instruments are generally the best choice for measurement of VOCs at exposure limit concentrations. Whatever type of instrument is used to measure these hazards, it is essential that the equipment is used properly, and the results are correctly interpreted.

Volatile organic compounds (VOCs) are organic compounds characterised by their tendency to evaporate easily at room temperature. Familiar substances containing VOCs include solvents, paint thinner and nail polish remover, as well as the vapours associated with fuels such as gasoline, diesel, heating oil, kerosene and jet fuel. The category also includes many specific toxic substances such as benzene, butadiene, hexane, toluene, xylene, and many others. Increased awareness of the toxicity of these common contaminants has led to lowered exposure limits, and increased requirements for direct measurement of these substances at their exposure limit concentrations. Photoionization detector equipped instruments are increasingly being used as the detection technique of choice in these applications.

VOCs present multiple potential threats in the workplace environment. Many VOC vapours are heavier than air, and can act to displace the atmosphere in an enclosed environment or confined space. Oxygen deficiency is a leading cause of injury and death in confined space accidents. The literature contains many examples of fatal accidents caused by oxygen deficiencies due to displacement by VOC vapours.

Most VOC vapours are flammable at surprisingly low concentrations. For instance, the lower explosion limit (LEL) concentrations for toluene and hexane are only 1.1% (11,000 PPM). By comparison, it takes 5% volume methane (50,000 PPM) to achieve an ignitable concentration in air. Because most VOCs produce flammable vapours, in the past, the tendency has been to measure them by means of combustible gas measuring instruments. Combustible gas reading instruments usually provide readings in percent LEL increments, where 100% LEL indicates a fully ignitable concentration of gas. Combustible gas instrument alarms are usually set to go off if the concentration exceeds 5% or 10% LEL. Unfortunately, most VOC vapours are also toxic, with Occupational Exposure Limit (OEL) values much lower than the 5% or 10% LEL hazardous condition threshold for combustible gas. The toxic exposure limits are exceeded long before the LEL alarm concentration is reached.

Occupational exposure limits (OELs) are designed to protect workers against the health effects of exposure to hazardous substances. The OEL is the maximum concentration of an airborne contaminant to which an unprotected worker may be exposed during the course of workplace activities. In the United Kingdom, OELs are listed in the EH40 Maximum Exposure Limits and Occupational Exposure Standards. EH40 currently lists exposure limits for about 500 substances. These OELs are enforceable. Unprotected workers may not be exposed to a concentration of any listed substance 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 OEL has not been exceeded.

OELs are generally defined in two ways, by means of a Long Term Exposure Limit (LTEL) calculated as an 8-hour Time Weighted Average (TWA), and / or a Short Term Exposure Limit (STEL) that represents the maximum allowable concentration over a shorter, usually 10 or 15-minute period of time. Exposure limits for gases and vapours are usually expressed in parts per million (PPM) or mg/m<sup>3</sup> increments. The TWA concept is based on a simple average of worker exposure during an 8-hour day. The TWA concept permits excursions above the TWA limit only as long as they do not exceed the STEL or ceiling, and are compensated by equivalent excursions below the limit. For VOC vapours without a STEL, depending on the jurisdiction, the generally suggested approach is to limit excursions above the TWA to a maximum of two

to five times the 8-hour TWA OEL, averaged over a 10 to 15 minute period.

Most direct reading instruments include at least three separate alarms for each type of toxic gas measured. Typically, a toxic gas instrument will include an 8-hour TWA alarm, a STEL alarm, and an instantaneous Ceiling alarm, (sometimes called the "Peak" alarm), that is activated immediately whenever this concentration is exceeded. Most gas detector manufacturers set their initial instantaneous "Peak" alarm to the 8-hour TWA limit. This is a very conservative approach. Although it is legally permissible to spend an entire 8-hour day at this concentration, most direct reading VOC instruments are set to go into alarm the moment the instantaneous concentration exceeds the TWA limit. Instrument users, of course, are free to modify factory alarm settings to meet the demands of their specific monitoring programs.

Airborne toxic substances typically are classified on the basis of their ability to produce physiological effects on exposed workers. Toxic substances tend to produce symptoms in two time frames: acute and chronic. Hydrogen sulphide (H<sub>2</sub>S) is a good example of an acutely toxic substance that is immediately lethal at relatively low concentrations. Exposure to 1,000 PPM produces rapid paralysis of the respiratory system, cardiac arrest, and death within minutes. Carbon monoxide (CO) also can act rapidly at high concentrations (1,000 PPM) although not as rapidly as hydrogen sulphide.

While some VOCs are acutely toxic at low concentrations, most are chronically toxic, with symptoms that may not become fully manifest for years. Exposure can be via skin or eye contact with liquid or aerosol droplets, or via inhalation of VOC vapours. Inhalation can cause respiratory tract irritation (acute or chronic) as well as effects on the nervous system such as dizziness, headaches and other long-term neurological symptoms. Long-term neurological symptoms can include diminished cognition, memory, reaction time, and hand-eye and foot-eye coordination, as well as balance and gait disturbances. Exposure can also lead to mood disorders, with depression, irritability, and fatigue being common symptoms. Peripheral neurotoxicity effects include tremors, and diminished fine and gross motor movements. VOCs have also been implicated in kidney damage and immunological problems, including increased cancer rates. Benzene, a notoriously toxic VOC found in gasoline, diesel, jet fuel and other chemical products, has been linked to chemically induced leukemia, aplastic anaemia and multiple myeloma (a cancer of the lymphatic system). There is good reason that the occupational exposure limits for VOC vapours are as low as they are. Unfortunately, because of the chronic or long-term nature of the physiological effects of exposure, the tendency in the past has been to overlook their potential presence in the workplace environment at OEL concentrations.

## Real-Time Measurement Techniques for VOC Vapours

Commonly used techniques used to measure VOC vapours include colorimetric detector tubes, passive (diffusion) badge dosimeters, sorbent tube sampling systems, combustible gas monitors that use catalytic "Hot Bead" combustible gas sensors to detect vapours in percent LEL or PPM ranges, photoionization detectors (PIDs), flame ionisation detectors (FIDs) and infrared spectra-photometers. All of these techniques are useful, or even mandatory in specific monitoring applications. However, the balance of this article will deal with the most widely used types of portable instruments used for VOC measurement in industrial safety applications: compact multi-sensor instruments equipped with oxygen, LEL, combustible, electrochemical toxic and miniaturised photoionization detectors (PIDs). Portable gas detectors can be equipped with a number of different types of sensors. The type of sensor used is a function of the specific substance or class of contaminant being measured. Many toxic contaminants can be measured by means of substance-specific electrochemical sensors. Direct reading sensors are available for hydrogen sulphide, carbon monoxide, chlorine, sulphur dioxide, ammonia, phosphine, hydrogen, hydrogen cyanide, nitrogen dioxide, nitric oxide, chlorine dioxide, ethylene dioxide, ozone and others.





The best approach to VOC measurement is often a multi-sensor instrument equipped with both LEL and PID sensors

Although some of these sensors are cross sensitive to other substances, there is very little ambiguity when it comes to interpreting readings. When you are interested in hydrogen sulphide, you use a hydrogen sulphide sensor. When you are interested in phosphine, you use a phosphine sensor. In many cases, however, a substance-specific sensor may not be available.

Volatile organic contaminants (VOCs) are quite detectable, but usually only by means of broad-range sensors. Broad-range sensors provide an overall reading for a general class or group of chemically related contaminants. They cannot distinguish between the different contaminants they are able to detect. They provide a single aggregate reading for all of the detectable substances present at any moment.

The most widely used technique for the measurement of combustible gases and volatile organic contaminants continues to be use of a hot-bead pellistor type combustible gas sensor. Pellistor sensors detect gas by oxidising the gas on an active bead located within the sensor. Oxidation of the gas causes heating of the active bead. The heating is proportional to the amount of gas present in the atmosphere being monitored, and is used as the basis for the instrument reading. Most combustible gas reading instruments display readings in % LEL increments, with a full range of 0 - 100% LEL. Typically these sensors are used to provide a hazardous condition threshold alarm set to 5% or 10% of the LEL concentration of the gases or vapours being measured. Readings are usually displayed in increments of  $\pm 1\%$  LEL. Hot-bead pellistor combustible gas sensors are unable to differentiate between different combustible gases.

Hot-bead pellistor sensors that display readings in  $\pm 1.0\%$  LEL increments are excellent for gases and vapours that are primarily or only of interest from the standpoint of their flammability. Many combustible gases, such as methane, do not have a permissible exposure limit. For these gases using a sensor that expresses readings in percent LEL increments is an excellent approach. But many other combustible vapours fall into a different category. Although VOC vapours may be measurable by means of a hot-bead sensor, they may also have an OEL that requires taking action at a much lower concentration.

Hexane provides a good example. Most internationally recognised standards, such as the Federal Republic of Germany Maximum Concentration Value (MAK), the American Conference of Governmental Hygienists (ACGIH®) Threshold Limit Value (TLV®) and the United States National Institute of Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL) reference an 8-hour TWA for hexane of 50 PPM. In the United Kingdom, the OEL for hexane is even more conservative. In the UK, the Long Term Exposure Limit (LTEL) for hexane is a maximum of only 20 PPM calculated as an 8-hour TWA.

The lower explosive limit concentration for hexane is 1.1%. Below 1.1% volume hexane the concentration of hexane vapour to air is too low to form an ignitable mixture. Assuming the combustible sensor alarm is set at 10% LEL, with a properly calibrated combustible gas reading instrument, it would take a concentration of 10% of 1.1% = 0.11% volume hexane to trigger an alarm. Since 1% volume = 10,000 parts-per-million (PPM), every 1% LEL increment for hexane is equivalent to 110 PPM. It would therefore take a concentration of 1,100 PPM hexane to trigger an alarm set to the standard 10% LEL hazardous condition threshold. Even if instruments are set to alarm at 5% LEL, it still would still require a concentration of 550 PPM to trigger the alarm.

Using a combustible gas monitor to measure VOCs presents a number of other potential problems. To begin with, most combustible sensors have poor sensitivity to the large molecules found in fuels, solvents and other VOCs, with flashpoint temperatures higher than 38°C (100°F). But even when the span sensitivity of a properly calibrated instrument has been increased sufficiently to make up for inherently lower sensitivity, an instrument that provides readings incremented in 1.0% LEL steps cannot resolve changes in concentration smaller than  $\pm 1.0\%$  of the LEL concentration of the substance being measured. 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 vapours means in many cases that the OEL, REL or TLV® is exceeded long before the concentration of vapour is sufficient to trigger the combustible hazardous condition threshold alarm. When toxic VOCs are potentially present it is necessary to use additional or different detection techniques that are better suited for direct measurement of VOCs at PPM toxic exposure limit concentrations. Photoionization detectors are becoming increasingly popular for this application.

It should be noted that other combustible gases and vapours may be present at the same time as toxic VOCs. Although catalytic-bead sensors may have limitations with concern to the

measurement of toxic VOCs at exposure limit concentrations, they are by far the most widely used and dependable method for measuring methane and other combustible gases and vapours with smaller, lighter molecules.

Increasing concern with the toxicity of VOCs has led to a number of newly revised exposure limits, including the TLVs® for diesel vapour, kerosene and gasoline. Because the safety procedures for many international corporations are tied to the most conservative published standard, these new TLVs® have been receiving a lot of attention around the world. The TLV® for diesel vapour adopted in 2002 has proven to be particularly problematic, and has led to the revision of numerous oil industry, maritime, and military health and safety monitoring programs. The ACGIH TLV® specifies an 8-hour TWA for total diesel hydrocarbons (vapour and aerosol) of 100 mg/m<sup>3</sup>. This is equivalent to approximately 15 parts-per-million diesel vapour. For diesel vapour, 1.0% LEL is equivalent to 60 PPM. Even if the instrument is properly calibrated for the detection of diesel - which is not possible for many designs - a reading of only 1.0% LEL would exceed the TLV® for diesel by 600 percent!

Table 1 lists ten common VOCs, their LEL concentration, flashpoint temperature, and their exposure limits per the UK OEL, NIOSH REL and ACGIH TLV®. The table also identifies those contaminants (highlighted) with toxic exposure limits lower than 5% LEL.

Table 1: Exposure Limits and Physical Constants for Ten Common VOCs

Contaminant	LEL Concentration (Vol %)	Flashpoint Temp (°C)	UK OEL	NIOSH REL	TLV	5% LEL expressed in PPM
Acetone	2.5%	-20°C	500 PPM TWA; 1500 PPM STEL	250 PPM TWA	500 PPM TWA; 750 PPM STEL	1250 PPM
Diesel (No.2) vapour	0.6%	52°C	None Listed	None Listed	15 PPM	300 PPM
Gasoline vapour	1.3%	-38°C	None Listed	None Listed	300 PPM TWA; 500 PPM STEL	650 PPM TWA 500
Hexane	1.1%	-22°C	20 PPM TWA	50 PPM TWA	50 PPM TWA	550 PPM
Isopropyl alcohol	2.0%	12°C	400 PPM TWA; 500 PPM STEL	400 PPM TWA; 500 PPM STEL	200 PPM TWA; 400 PPM STEL	1000 PPM
Kerosene/ Jet Fuel vapour	0.7%	38 - 72°C	None Listed	100 mg/M3 TWA (approx. 14.4 PPM)	200 mg/M3 TWA (approx. 29 PPM)	350 PPM
MEK	1.4%	-9°C	200 PPM TWA; 300 PPM STEL	200 PPM TWA; 300 PPM STEL	200 PPM TWA; 300 PPM STEL	700 PPM
Styrene	0.9%	31°C	100 PPM TWA; 250 PPM STEL	50 PPM TWA; 100 PPM STEL	20 PPM TWA; 40 PPM STEL	450 PPM
Toluene	1.1	4°C	50 PPM TWA; 150 PPM STEL	100 PPM TWA; 150 PPM STEL	50 PPM TWA	550 PPM
Turpentine	0.8	35°C	100 PPM TWA; 150 PPM STEL	100 PPM TWA	20 PPM TWA	400 PPM

It goes beyond the scope of this article to argue how long it might be permissible to remain at 5% or 10% LEL without actually exceeding the 8-hr TWA or STEL. What is most striking about the list is how few VOCs have 8-hour TWA exposure limits higher than 5% LEL. None of the VOCs on the list have exposure limits higher than 10% LEL.

### Using Photoionization Detectors to Measure VOCs

Photoionization detectors use high-energy ultraviolet light from a lamp housed within the detector as a source of energy used to remove an electron from neutrally charged VOC molecules, producing a flow of electrical current proportional to the concentration of contaminant.

The amount of energy needed to remove an electron from the target molecule is called the ionisation potential (IP) for that substance. The larger the molecule, or the more double or triple bonds the molecule contains, the lower the IP. Thus, in general, the larger the molecule, the easier it is to detect! This is exactly the opposite of the performance characteristics of the catalytic hot-bead type combustible sensor.

Photoionization detectors are easily able to provide readings at or below the OEL or TLV® for all of the VOCs listed in Table 1, including diesel. The best approach to VOC measurement is often a multi-sensor instrument equipped with both LEL and PID sensors

### Multi-sensor Detectors with PIDs

Catalytic hot-bead combustible sensors and photoionization detectors represent complementary, not competing detection techniques. Catalytic hot-bead sensors are excellent for the measurement of methane, propane, and other common combustible gases that are not detectable by means of a PID. On the other hand, PIDs can detect large VOC and hydrocarbon molecules that are effectively undetectable by hot-bead sensors, even when they are operable in PPM measurement ranges.

The best approach to VOC measurement in many cases is to use a multi-sensor instrument capable of measuring all the atmospheric hazards that may be potentially present. Having a single instrument equipped with multiple sensors means no condition is accidentally overlooked.