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Monitoring for Toxic VOC in Oil Industry Applications

Organic chemicals consist of molecules that contain carbon. Volatile organic compounds (VOC) are organic compounds characterized by their tendency to evaporate easily at room temperature.

Crude oil is a complex mixture that includes many different specific hydrocarbons and other chemicals. The hydrocarbons in crude oil are primarily alkanes, (molecules that consist entirely of carbon and hydrogen atoms), cycloalkanes (alkanes that include one or more rings in their structure), and various aromatic hydrocarbons (molecules that include a benzene ring in their structure). The molecules in crude oil present multiple potential hazards. Most of the gases and vapors associated with crude oil are highly flammable. Many hydrocarbon gases and vapors are heavier than air and can displace oxygen containing atmosphere in enclosed environments and confined spaces. In addition, many of the organic molecules associated with crude oil are highly toxic, with exposure limits (in some cases) of less than 1.0 ppm (8 hour TWA).

Toxic VOC exposure is a significant concern at many refineries, chemical plants and oil production facilities. Familiar substances containing VOCs include solvents, paint thinner and nail polish remover, as well as the vapors 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, xylenes, and many others. Most VOC vapors are flammable at surprisingly low concentrations. For most VOCs however, the toxic exposure limit is exceeded long before readings reach a concentration high enough to trigger a combustible range alarm.

Solvent, fuel and other VOC vapors are routinely encountered in many types of procedures undertaken at refineries, chemical plants and oil production facilities. VOC vapors are particularly associated with confined spaces and confined space entry procedures at these same facilities. In some cases the presence of VOCs is due to materials being used or stored in the confined space. In other cases, especially sewers and other large interconnected confined space networks, fuels, combustible liquids or other VOCs accidentally introduced in one location can easily spread to other locations within the system. Increased awareness of the toxicity of these common contaminants has led to lowered



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exposure limits, and increased requirements for direct measurement of these substances at their toxic exposure limit concentrations. Photoionization detector (PID) equipped instruments are increasingly viewed as the best choice for measurement of VOCs at exposure limit concentrations. Understanding the capabilities as well as the limitations of photoionization detectors is critical to interpreting test results and making decisions based on the use this important atmospheric monitoring technology.

Importance and use of “broad-range” sensors

The more unpredictable the hazards, the more important it is to use sensors that are capable of providing alarm notification for a wide range of potential contaminants. Substance-specific sensors, like the ones used to measure oxygen, carbon monoxide and hydrogen sulfide are deliberately designed to limit the effects on readings of other contaminants which may be simultaneously present. Broad-range sensors provide an overall reading for a general class or group of chemically related contaminants. Broad-range sensors are particularly suited for use during initial screening or in situations where the actual or potential contaminants have not been identified because they enable instrument users to obtain an overall reading of the contaminants present in the space. Both traditional LEL and PID sensors are broad-range sensors. They can't determine which type of flammable gas or VOC is being detected, but they are excellent at determining when either of these classes of contaminants is present.

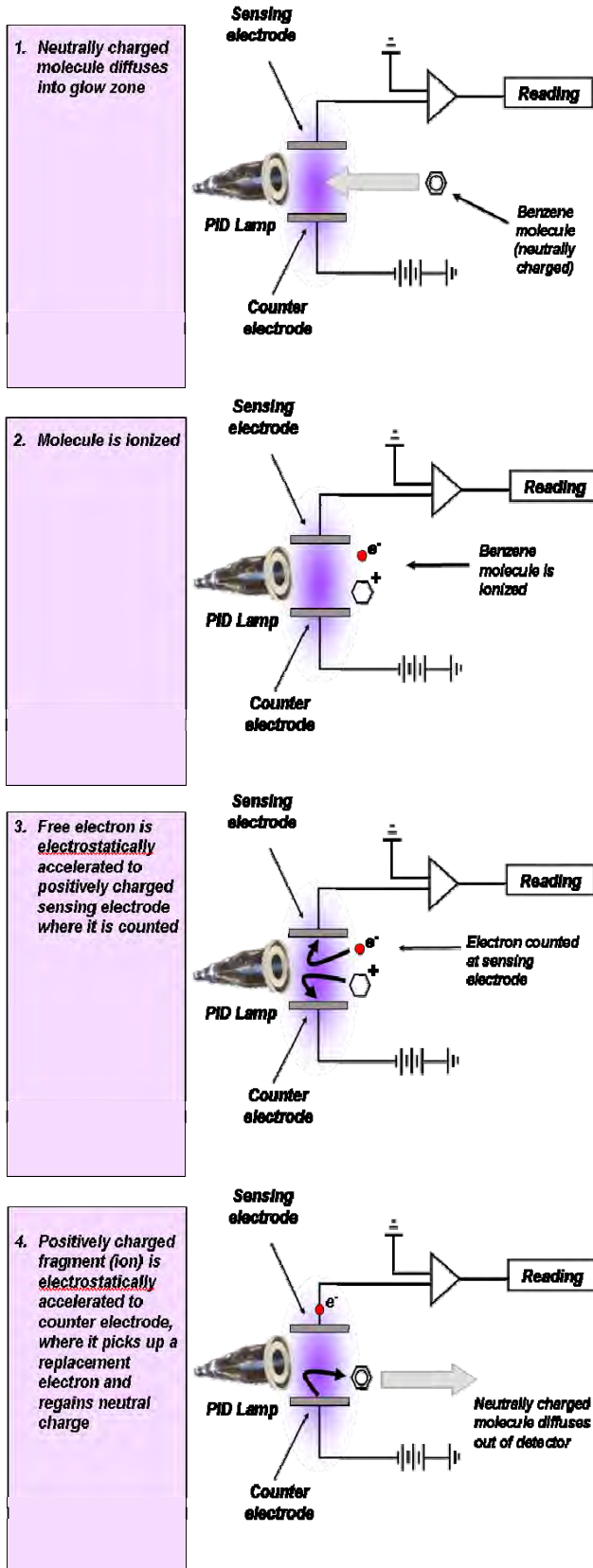
How do PIDs detect VOC?

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 ionization energy (IE) for that substance. The larger the molecule, or the more double or triple bonds the molecule contains, the lower the IE. Thus, in general, the larger the molecule, the easier it is to detect. On the other hand, small hydrocarbon molecules such as methane are not detectable by means of PID.

A PID is only able to detect substances with ionization energies lower than the energy of the ultraviolet photons produced by the PID lamp. The energy required to detect methane exceeds the energy of the ultraviolet light produced by the PID lamp.



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Photoionization detectors may be equipped with a number of different types of lamps that produce photons of various energy ranges. The energy range of the photons produced by the lamp is expressed in “electron volts” or “eV” units of measurement. The most common types of PID lamps produce photons in the 9.8 eV, 10.6 eV or 11.7 eV energy range. By far, the most commonly used PID lamp is one that produces photons in the 10.6 eV energy range. 10.6 eV lamps generally have much longer service lives, and frequently last one to two years in normal operation. At the same time, 10.6eV lamps have an energy output sufficient to detect a wide range of VOCs. As a consequence, 10.6 eV lamps tend to be the most widely used.

What are the differences between PID and LEL sensors?

PID and LEL sensors are based on entirely different detection techniques. Most LEL range sensors detect gas by catalytically oxidizing the gas on a pellistor-bead located within the sensor. Oxidization of the gas causes heating of the active pellistor-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. Pellistor sensors are excellent for the detection of methane, propane, pentane and other small hydrocarbon molecules. However, catalytic-bead sensors, at least when operated in the percent LEL range, are not readily able to detect “heavy” or long-chain hydrocarbons or the vapors from high flashpoint temperature liquids such as turpentine, diesel fuel or jet fuel. Consult the Operator’s Manual, or contact the manufacturer directly to verify the capabilities of the instrument design when using a catalytic-bead LEL sensor to monitor for the presence of these types of contaminants.

Limitations of broad-range sensors

Broad-range sensors provide an overall reading for a general class or group of chemically related contaminants. Both pellistor-bead LEL and PID are broad-range sensors. They cannot distinguish between the different contaminants they are able to detect. The reading provided represents the aggregate signal from all of the detectable molecules present in the monitored environment. Both PIDs and pellistor bead sensors are broad-range sensors. Unless an additional separation technique is used (such as a filter tube or separation column) broad-range detectors are not able to provide substance-specific readings.

Many manufacturers include a user selectable library of correction factors (or “CFs”) in the instrument design. In this case, the user simply selects “methane” or “propane” or any other correction factor in the library, and the instrument automatically



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recalculates readings according to the selected relative response. Changing the CF ONLY changes the scale used to calculate the displayed readings. Selecting the “propane” CF does not prevent the sensor from responding to methane. It just reinterprets the readings as if they were entirely due to propane.

	RAE	BW	Ion	Baseline	IP (eV)
Acetaldehyde	5.5	4.6	4.9	n/a	10.21
Acetone	1.1	0.9	0.7	1.2	9.69
Ammonia	9.7	10.6	8.5	9.4	10.2
Benzene	0.5	0.55	0.5	0.53	9.25
Butadiene	1	0.9	0.85	0.69	9.07
Diesel fuel	0.8	0.93	0.75	0.9	n/a
Ethanol	12	13.2	8.7	10.0	10.48
Ethylene	10	11	8	10.1	10.52
Gasoline	0.9	0.73	1.1	1.1	n/a
n-Hexane	4.3	4	3.3	4.5	10.18
Jet fuel (J.P.8)	0.6	0.51	0.7	0.48	n/a
Kerosine	n/a	1.11	0.8	n/a	n/a
Methylethylketone	0.9	0.78	0.77	0.9	9.53
Naptha (iso-octane)	1.2	1.2	1.1	1.3	9.82
Styrene	0.4	0.45	0.45	0.4	8.47
Toluene	0.5	0.53	0.51	0.53	8.82
Turpentine	0.4	0.45	0.45	0.45	n/a
Vinyl chloride	2	2.19	2.2	1.8	10.0
Xylene	0.4	0.5	0.43	0.5	8.5

Ionization potentials and representative correction factors for several leading brands of photoionization detectors

Using correction factors

Most PID equipped instruments include a built-in library of correction factors. The same principles apply. Changing the PID correction factor (CF) or choosing a chemical from the on-board library does not make the instrument readings specific for that substance! Choosing the “hexane” correction factor does not make the PID a substance-specific detector for hexane. The PID will continue to respond to other detectable VOCs (such as benzene or toluene) which may be simultaneously present. Using the hexane CF simply tells the instrument to display the readings calculated as hexane measurement units.

PIDs are usually calibrated using isobutylene. Thus, the most commonly used measurement scale for most PIDs is isobutylene. It is very important to understand that no matter how comprehensive the list of correction factors, choosing the CF for any particular chemical never makes the readings exclusive or substance-specific for that contaminant.

Also, if the specific nature of the VOC or mixture of VOCs is not known, PID readings are not truly quantified. Unless you



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are able to determine the precise nature of the VOCs being measured, readings should be thought of as "Isobutylene Units", or "PID Units", or units of whatever measurement scale has been selected from the instrument's library of correction factors.

Using broad-range readings to make decisions

Instrument users frequently worry that they can't use a broad-range PID for VOC measurement because they need substance-specific readings for the contaminants present.

PIDs provide a single reading for the total detectable volatile organic contaminants (TVOC) present. In point of fact, many of the most common VOCs do not consist of a single type of molecule. They are comprised of a mixture of, in some cases, a very large number of individual molecular species. For instance, the size distribution of molecules in diesel fuel ranges from molecules with nine carbons (or smaller), to molecules with twenty-three carbons (or larger). However, the ratios of the various molecules present are fairly similar from one batch of diesel to the next. That allows PID manufacturers to experimentally determine a CF for use with this fuel. You don't have to go after the individual molecular types that may be present as a minor fraction of the diesel (such as benzene, toluene, xylenes, etc.) to provide a quantified reading. If you have a CF for the mixture you can use this to quantify the readings for the entire range of molecules present.

Dealing with single-component VOC contaminants or mixtures is easy. Once you know which contaminant you are dealing with, simply assign the correct CF, and set the alarms to the appropriate take action thresholds for that VOC. Dealing with varying mixtures can be a little more challenging. In this case the secret is to identify which chemical is the "controlling" compound.

Every mixture of VOCs has a compound that is the most toxic and / or hardest to detect, and thus "controls" the alarm set-point that should be used for the entire mixture. Once the controlling compound has been identified, it is possible to determine a hazardous condition threshold alarm that will ensure that the exposure limit for any contaminant potentially present is never exceeded.

The first step is to calculate (or look up) the exposure limits in isobutylene units for the VOCs of interest. Remember to leave the PID scale (correction factor) set to isobutylene units when using this measurement technique.

The exposure limit in isobutylene units (ELiso) is calculated by dividing the exposure limit for the VOC by the correction factor (CFiso) for the substance. For instance, the TLV® for



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turpentine is 20 ppm. If the CF for turpentine is 0.45, the $EL_{iso} = 20 \text{ ppm} \div 0.45 = 44.5 \text{ ppm}$. Many PID manufacturers include a table of EL_{iso} values either in the owner's manual or in a separate applications note. Consider a situation where you have three VOCs of interest: ethanol, turpentine and acetone. Let's say the owner's manual of the PID shows the following set of correction factors for the three chemicals of interest:

Chemical Name	CF_{iso} (10.6eV lamp)
Ethanol	10.0
Turpentine	0.45
Acetone	1.2

Correction factors higher than 1.0 indicate that the PID is less sensitive to the substance than to the isobutylene used to calibrate the PID. Correction factors of less than 1.0 indicate that the PID is more sensitive to the chemical than to the isobutylene used to calibrate the detector.

Although turpentine has the lowest exposure limit, it is also the most easily detected substance of the three. Acetone is close to isobutylene in terms of detectability, with an exposure limit that is intermediate between those of the other two chemicals. Although ethanol has the highest exposure limit, it is also the least detectable of the three chemicals.

The following table lists the Correction Factors, the OSHA Permissible Exposure Limit (PEL), the ACGIH TLV®, and the exposure limit or each of chemicals recalculated in isobutylene measurement units (ELISO):

Chemical Name	CF_{iso} (10.6eV lamp)	OSHA PEL (8 hr. TWA)	EL_{iso} (PEL)	TLV® (8 hr. TWA)	EL_{iso} (TLV)
Ethanol	10.0	1000	100.0	1000	100.0
Turpentine	0.45	100	222.3	20	44.5
Acetone	1.2	1000	833.4	500	416.7

If OSHA PEL exposure limits are followed, ethanol is the controlling chemical when the "EL" exposure limits are expressed in equivalent "Isobutylene Units". Setting the PID to go into alarm



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at 100 ppm isobutylene units ensures that no matter which of the three chemicals, or combination of chemicals, is actually present, the exposure limit will never be exceeded.

On the other hand, if ACGIH TLV® exposure limits govern your entry procedures, turpentine is the controlling chemical when exposure limits are expressed in isobutylene units. In this case the alarm must be set at 44 ppm isobutylene units to ensure that the exposure limits are never exceeded for any one (or all) of the three chemicals.

Generally speaking, if a VOC is detectable by one manufacturer's PID when equipped with a 10.6 eV lamp, the same substance will be detectable by any other manufacturer's PID when equipped with a similar lamp. The correction factors may be quite different, however, between different instrument designs. PID users should never use the correction factors from one instrument for another manufacturer's design.

Use PIDs should together with LEL sensors when monitoring atmosphere

Catalytic hot-bead combustible sensors and photoionization detectors represent complementary, not competing detection techniques. PIDs are not able to detect methane and hydrogen, two of the most common combustible gases encountered in industry. On the other hand, catalytic pellistor-bead sensors are excellent for the measurement of methane, propane, and other common combustible gases. And of course, 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 optimal strategy for measurement of combustible range concentrations of combustible gases and VOCs is to include both types of sensors in the same instrument.

Limitations of PID sensors

Humidity and moisture can have a serious effect on PID performance. Water molecules can absorb UV light without becoming ionized, and thus quench the PID signal. The susceptibility of the sensor to humidity is very design dependent. One of the most important determinants is the distance of the sensing electrode in the PID from the surface of the window of the PID lamp. Most PID designs deliberately position the sensing electrode as close as possible to the surface of the lamp window to reduce the effects of humidity. PID manufacturers also provide tables of correction factors that can be used to correct readings for humidity at various temperature and RH conditions. Alternatively, it easy to correct for these ambient conditions simply by



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calibrating the PID in the temperature and humidity conditions in which the instrument is actually used.

A second related issue is the condensation of water on the inside of the PID detector. When dirt or dust particles accumulate on the surface of the lamp, electrodes or PID sensing chamber, they provide points of nucleation around which water vapor can coalesce to produce misting similar to the fog that develops on a bathroom mirror. In two electrode PID designs this can lead to surface electrical current flows directly between the sensing and counter electrodes. This “moisture leakage” can result in a rising signal or positive drift in the PID readings. The potential for moisture leakage can be reduced by cleaning the lamp and / or detector.

Some PID designs include a third electrode that serves as a short circuit path that mechanically interrupts current flow between the sensing and counter electrodes. In the case of three electrode designs, condensation of water vapor does not tend to produce a positive drift, or interfere with the ability of the PID to obtain proper readings.

Pump versus diffusion

Whether or not the PID requires a pump or fan to move the sample through the sensing chamber is a function of the manufacturer’s design. Many PID designs include a built-in pump or fan. Other designs allow the addition of a motorized pump to obtain samples from areas that are remote from the detector. The easiest way to determine whether or not a pump is required is to evaluate the instrument before purchase. Most manufacturers and distributors are more than willing to make instruments available to potential customers for field trialing.

The best approach includes use of both substance-specific and broad-range sensors

PIDs are able to detect a wide variety of VOC and other toxic chemicals including hydrogen sulfide, ammonia, phosphine, chlorine and others. However, PIDs are broad-range sensors that cannot discriminate between a specific toxic contaminant and other detectable chemicals that may be simultaneously present. When a highly toxic specific contaminant like H₂S is potentially present, it is better to use a substance-specific sensor that responds only to that particular hazard.

Fortunately, PID equipped multi-sensor instruments are available that include up to five channels of detection, allowing users the latitude of choosing exactly the combination of sensors they need to keep their workers safe.



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Case study: Using the controlling chemical approach for setting the TVOC_(ISO) alarm for benzene

Because of its very low exposure limits, benzene is frequently seen as the “controlling chemical” in many oil industry and VOC monitoring applications.

Except for facilities that manufacture this chemical, benzene is rarely encountered in pure form. Generally the benzene is present as a minor constituent in the products being manufactured or transported.

The ACGIH has published TLV® exposure limits for several VOC liquids known to include benzene. Generally speaking, the higher the fractional concentration of benzene the lower the exposure limit for the liquid.

Substance	TLV mg/m ³ (8 hr. TWA)	TLV ppm (8 hr. TWA)	CF _(ISO)	EL _(ISO) ppm (8 hr. TWA)
Gasoline	890 mg/m ³	300 ppm	1.1	273 ppm
Kerosene	200 mg/m ³	30 ppm	0.5	60 ppm
Jet Fuel (JP-8)	200 mg/m ³	30 ppm	0.5	60 ppm
Diesel	100 mg/m³	15 ppm	0.9	16.7 ppm

An easy way to deal with many VOC monitoring applications is to simply set the TVOC alarm (in isobutylene units) at the published exposure limit for the substance. The overall exposure limit takes into account not only the fractional concentration due to benzene; it takes into account the fractional concentrations of other toxic VOCs (such as hexane, toluene and xylenes) that may be present as minor constituents in the mixture.

Unfortunately, in many jurisdictions in North America the local regulations do not include exposure limits for these fuel mixtures. On the other hand, in all jurisdictions the exposure limits for benzene are strictly defined. In this case it may be necessary to directly assess the fractional concentration of TVOC due to benzene.

The following table lists actual readings obtained from the cargo tanks of a fuel barge being used to transport fresh gasoline. The fuel barge included five “port side” and five “starboard side” cargo tanks. The cargo tanks had been emptied (drained) and ventilated prior to the following readings being taken. A PID calibrated to isobutylene was used to provide the “Total VOC” (TVOC_{ISO}) readings for each tank. The instrument manufacturer’s



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correction factor (CF) for gasoline was 1.1. This value was used to convert the TVOC readings from isobutylene units to ppm gasoline.

A substance-specific benzene analyzer was used to measure the actual ppm concentration of benzene in each hold. The percentage concentration of TVOC from benzene was then calculated for each cargo tank.

The fractional percentage of benzene as a function of the total VOC reading ranged from 0.0% (in the "Number 1 Port Cargo Tank") to a maximum of 0.58% (found in the "Number 5 Port Cargo Tank"). Thus, in terms of the fractional percentage of benzene, the "worst case" (highest) percentage concentration of benzene was found to be 0.58%.

Cargo Tank	PPM TVOC (isobutylene)	PPM TVOC (gasoline)	PPM Benzene	%TVOC from benzene
No (1) Port Cargo Tank	33.9	37.3	0.0	0 %
No (2) Port Cargo Tank	40.1	44.1	0.1	0.23%
No (3) Port Cargo Tank	48.9	53.8	0.2	0.37 %
No (4) Port Cargo Tank	43.8	48.2	0.1	0.21%
No (5) Port Cargo Tank	62.3	68.5	0.4	0.58 %
No (1) Stbd Cargo Tank	12.0	13.2	0.0	0 %
No (2) Stbd Cargo Tank	26.4	29.0	0.0	0 %
No (3) Stbd Cargo Tank	52.8	58.1	0.1	0.17%
No (4) Stbd Cargo Tank	44.3	48.7	0.2	0.41 %
No (5) Stbd Cargo Tank	57.5	63.3	0.3	0.44%

It is easy to use these measured data to calculate a "worst case" hazardous condition threshold alarm for benzene based on TVOC by using the following formula:

Alarm setting = The desired exposure limit (EL) divided by the "worst case" percentage of TVOC from benzene



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Thus, if the desired exposure limit (EL) for benzene is 1.0 ppm then:

$$1.0 \text{ ppm} / .0058 = 172 \text{ ppm}$$

Setting the TVOC alarm at 172 ppm (gasoline units) ensures that even in the worst case encountered, the exposure limit

$$172 \text{ ppm TVOC}_{(\text{gasoline})} \times .0058 = 0.9976$$

Make sure to pay attention to the measurement scale (correction factor) you will be using during your VOC monitoring. The 172 ppm TVOC limit is in gasoline measurement units. In other words, this is the limit to use when the "gasoline" has been selected from the instrument's built in library of correction factors.

If you leave the correction factor set to isobutylene (the default measurement scale) you will need to convert the alarm setting to isobutylene measurement units. This is done by dividing the TVOC alarm setting in gasoline units by the correction factor for isobutylene.

$$CF_{(\text{iso})} \text{ for gasoline} = 1.1$$

The CF (gasoline) for isobutylene is simply the reciprocal of the number:

$$CF_{(\text{gasoline})} \text{ for isobutylene} = 1 / 1.1 = 0.9091$$

So, if a take action threshold alarm of 1.0 ppm benzene is desired:

$$(1.0 \text{ ppm} / .0058) / 0.9091 = 172 \text{ ppm} / 0.9091 = 189.7 \text{ ppm}$$

It is easy to take action at a lower concentration for benzene simply by dropping the TVOC_(iso) alarm to a lower concentration.

Desired exposure limit for benzene	TVOC _(gasoline) alarm setting	TVOC _(iso) alarm setting
1.0 ppm	172 ppm	190 ppm
0.5 ppm	86 ppm	95 ppm
0.1 ppm	17 ppm	19 ppm



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Simplified approach to VOC measurement and alarm settings

Running through calculations similar to those discussed above can seem quite daunting. However, it should be remembered that for most applications this is a one time exercise. Once the controlling chemical has been identified, the rest is easy.

Many refineries and oil production facilities find that using an alarm setting of 15 ppm TVOC_(iso) is sufficient to ensure that the exposure limits for individual VOCs are never exceeded. Some facilities are able to use an even higher hazardous condition alarm setting of 30 or 50 ppm. In the event that the PID TVOC_(iso) alarm goes off, workers simply leave the area. Subsequent testing can be used to determine the exact nature of the VOC that triggered the alarm.

In the case of the most conservative VOC monitoring program a substantially lower TVOC_(iso) alarm may be specified. Fortunately, the sensors in PID equipped in multi-sensor gas detectors are easily capable of being used for take action settings of 0.5 ppm (isobutylene units) or even lower.

Real-time VOC monitoring doesn't need to be complicated. Simply leave the instrument set to the isobutylene scale and decide on a prudent TVOC alarm setting. All you have to do is use your PID equipped instrument.

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Pictures:

Microtector II G460 with PID
PID sensors

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