

## Is there Something Out There?

### If you can't see "it" you can't find "it"

After oxygen, flammability and your basic electrochemical toxic sensors, survey sensors are one of your best tools to quickly identify if something is out there. Survey sensors are our "Sniffers." On their own, survey sensors may not tell you what that "something" is, but they can often quickly tell you where it is coming from. Coupled with clues (like placards, waybills, etc.) that provide identification of a chemical some survey sensors can even tell you how much is there.

- If you can't see "it" you can't find "it"
- If you can't find "it" you can never clean "it" up
- If you can't see "it" you can't fix the problem

## Quantifiable vs. Non-quantifiable Survey Sensors

Some survey sensors can accurately quantify, providing measurements in precise units of measure, like parts per million (ppm) or even parts per billion (ppb). Some survey sensors are great for finding "it" but they are not linear so they may not be suitable for measuring or "quantifying" "it." Most of the time finding "it" is the biggest part of the battle.

### PIDs and FIDs are Quantifiable Survey Sensors

When a single species of a detectable chemical gas/vapor is present Photoionization Detectors (PIDs) and Flame Ionization Detectors (FIDs) can easily provide an accurate ppm/ppb measurement using Correction Factors (CFs). Under certain conditions they can even be helpful with quantification of mixtures.

### Survey sensors detect at least in ppm

Survey meters measure in ppm and some, like a RAE Systems ppbRAE or an EnviroNics ChemPro100, are capable of detecting at ppb levels. PPB capable products even allow one to "see" smells. PPM is a very small unit of measure, and 10,000 ppm equals 1% by volume:

ppm	%
1,000,000	= 100
500,000	= 50
250,000	= 25
100,000	= 10
10,000	= 1
5,000	= 0.5
500	= 0.05
100	= 0.01
10	= 0.001
1	= 0.0001

- 1 ppm is the same as 1 inch in 16 miles
- 1 ppm is the same as 1 oz. in 10,000 gallons
- $\text{ppm} = \frac{\text{mg/m}^3 \times 24.5}{\text{Molecular weight}}$

As people become more concerned with the toxicity of gases and vapors survey sensors provide a means of detecting and protecting ourselves, our workers and our constituents from a wide variety of chemicals.

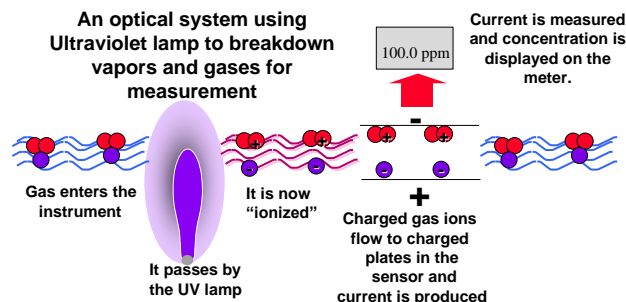
## What is a PID?

A PID measures VOCs and other toxic gases in low concentrations from ppb (parts per billion) up to 10,000 ppm (parts per million or 1% by volume). A PID is a very sensitive broad-spectrum monitor that is much more sensitive than a Lower Explosive Limit (LEL) sensor. If toxic gases and vapors could be considered alligators, the LEL monitor does not respond until the user is swimming with alligators, while the PID lets you know when your foot is wet!

### How Does a PID Work?

A PID uses an ultraviolet (UV) light source (**Photo**=light) to break down chemicals to positive and negative ions (**ionization**) that can easily be counted with a **Detector**. The detector measures the charge of the ionized gas and converts the signal into current. The current is then amplified and displayed on the meter as "ppm." PIDs are non-destructive; they do not "burn" or permanently alter the sample gas, which allows them to be used for sample gathering. PIDs can operate independently of oxygen concentration.

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### Ionization Potential

All elements and chemicals can be ionized, but they differ in the amount of energy they require. The energy required to displace an electron and "ionize" a compound is called its Ionization Potential (IP), measured in electron volts (eV). The light energy emitted by a UV lamp is also measured in eV. If the IP of the sample gas is less than the eV output of the lamp, then the sample gas can be ionized.

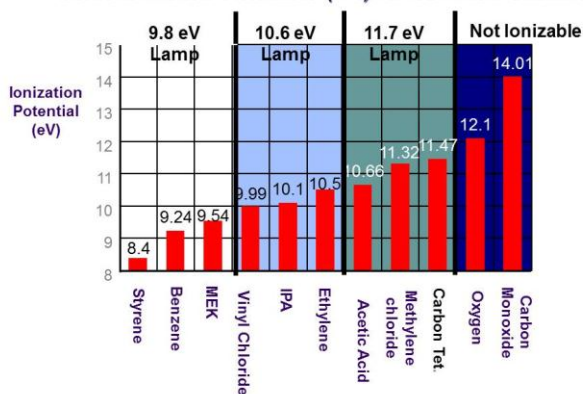
### PID Operation Simplified

While this sounds complicated, it is very simply explained. A PID uses an ultraviolet lamp to break down gases and vapors.

- If the "wattage" of a gas or vapor is less than the "wattage" of the PID lamp, then the PID can "see" the gas or vapor.
- If the "wattage" of the gas or vapor is greater than that of the PID lamp the PID cannot "see" the vapor.

Therefore, a PID with a "75 watt" lamp could see a "50 watt" gas but could not "see" an "85 watt" gas. "Wattage" for PIDs is expressed in "Electron Volts" or eV and is known as the Ionization Potential (IP) for a particular gas or vapor. Ionization Potential is a measure of the bond strength of a gas, or how well it is "built."

Some Ionization Potentials (IPs) for Common Chemical



Benzene has an IP of 9.24 eV and can be seen by a 10.6 eV lamp. Methylene Chloride has an IP of 11.32 eV and can only be seen by an 11.7 eV lamp. Carbon Monoxide has an IP of 14.01 eV and cannot be ionized by a PID lamp. IPs can be found in the NIOSH Pocket Guide, PID manufacturer literature or in many chemical texts.

### Why don't we ionize above 11.7 with a PID?

There are 209,000 ppm (20.9%) of oxygen in air. Once we ionize above 12 eV we will ionize oxygen in air and it will be difficult to separate the gases and vapors (like 1 ppm of benzene) we are looking for from the 209,000 ppm of background "noise" of the ionized oxygen. In order to improve the signal to noise ratio when ionizing above 12 eV other speciation (separation/identification) techniques like gas chromatography (GC) or ion mobility spectroscopy (IMS) must be used.

### What Does a PID Measure?

The largest group of compounds measured by a PID are the Organics: compounds containing Carbon (C) atoms. These include:

- **Aromatics** - compounds containing a benzene ring including: benzene, toluene, ethyl benzene and xylene.
- **Ketones & Aldehydes** - compounds with a C=O bond including: acetone, methyl ethyl ketone (MEK) and acetaldehyde.
- **Amines & Amides** - Carbon compounds containing nitrogen, like diethylamine.
- **Chlorinated hydrocarbons** - trichloroethylene (TCE), perchloroethylene (PERC)
- **Sulfur compounds** – mercaptans, sulfides
- **Unsaturated hydrocarbons** – like butadiene and isobutylene
- **Alcohol's**- like isopropanol (IPA) and ethanol
- **Saturated hydrocarbons** - like butane and octane

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In addition to organic compounds, PIDs can be used to measure some inorganics. These are compounds without carbon and include:

- Ammonia
- Semiconductor gases: Arsine, Phosphine
- Hydrogen sulfide
- Nitric Oxide
- Bromine and Iodine

### What PIDs Do Not Measure

- Radiation
- Air (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O)
- Common Toxics (CO, HCN, SO<sub>2</sub>)
- Non-volatiles: PCBs, Greases
- Pure Short Chain Saturated Hydrocarbons like Methane, Propane & Ethane)
- Acid Gases (HCl, HF, HNO<sub>3</sub>)
- Others- Freons, Ozone (O<sub>3</sub>), Hydrogen peroxide

### PID Lamps, 9.8& 10.6 eV versus 11.7 eV

At first glance, it may appear that to measure the broadest range of gases with a PID an 11.7eV lamp should be used instead of a 10.6eV lamp. However, the following must be considered:

- 9.8 and 10.6 can provide more specificity because they ionize less chemicals
- 9.8 and 10.6 last 12-24 months (about the same as a CO sensor)
- 9.8 and 10.6 costs about the same as a CO sensor
- 9.8 and 10.6 are more accurate
- 11.7 eV lamps costs more and typically have a shorter life than 9.8 or 10.6 lamps. All 11.7 lamps have a window made of Lithium Fluoride to transmit the high energy UV light. Lithium Fluoride is harder to seal to the lamp glass, is very hygroscopic and readily absorbs water from air even when not in use. This causes the window to swell and decreases the amount of light transmitted through the window. Lithium Fluoride also is degraded by UV light, the more the instrument is used the greater the damage. These factors contribute to a shortened lamp life for the 11.7 lamps of some PID manufacturers
- 11.7 lamps can provide lower resolution than the 9.8 and 10.6 lamps of some manufacturers
- 11.7 eV bulbs should only be used when compounds with IPs over 10.6 eV are

expected (e.g.: methylene chloride, chloroform, and formaldehyde).

- As a solution to the problem of short lifetime for 11.7 lamps, one manufacturer offers them packaged in sealed glass ampoules. The gas in the ampoule is the same as in the lamp. The ampoule effectively packages a new lamp in a lamp. When the 11.7 lamp is required, the ampoule is broken, the lamp removed and inserted into the PID.
- 11.7eV lamp life may be extended if the lamp is stored in a desiccant environment (in or out of the PID) between uses. This can simply be a container containing "silica gel" drying packs like those that ship with electronic and camera equipment. It is not recommended to store multisensor products that have oxygen and electrochemical sensor in them in a desiccant environment because this will decrease the life of these sensors by drying out their aqueous electrolytes.

### Which PID for Me?

- Multigas with PID
  - Like a Swiss Army Knife or Leatherman
  - If you have only one tool this should be it
- Straight PID
  - Like a DeWalt 18volt driver
  - While the Leatherman has a Phillips screwdriver on it one wouldn't want to hang drywall with it
  - Best for decon and leak detection because they can be more sensitive and have faster response time than multisensory products
  - Best for uses that will not kill the PID but may kill other sensors. For example high levels of ammonia or hydrogen sulfide

### PID Summary

- Advantages
  - + Linear, quantifiable measurements
  - + Measure from ppb/ppm-2% vol (0.001-20,000 ppm)
  - + Doesn't require a consumable gas to work
  - + Will measure some inorganics

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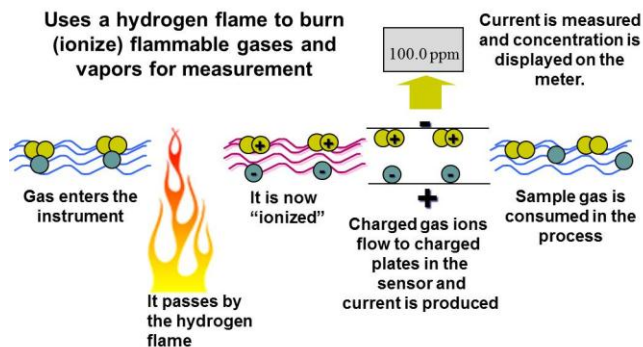
- + Doesn't require O<sub>2</sub>
- + Stores well
- + Low consumables (they only require calibration gas)
- + PIDs are largely poison resistant
- Disadvantages
  - Has many "Blind Spots" and will not measure many toxic chemicals (like Cl<sub>2</sub>) and short chain saturated hydrocarbons like methane, propane and ethane
  - Can be affected by humidity
  - Largely limited to 10.6eV lamps (11.7eV life is too short for wide use for many PID manufacturers)
  - 11.7 lamps may have 10x less resolution than 10.6 and 9.8 lamps

## What is a FID?

A Flame Ionization Detector (FID) detects flammable carbon containing gases and vapors from ppm to as high as 50,000 ppm (5% by volume).

### How Does a FID Work?

A FID uses a hydrogen **flame** to **ionize** (or burn) organic (carbon containing) gases and vapors. Because combustion is essential to support a flame FIDs must be used in areas containing sufficient oxygen (typically > 14% oxygen). These ions are easily counted with a **Detector**. The detector measures the charge of the ionized gas and converts the signal into current. The current is then amplified and displayed on the meter as "ppm." FIDs burn the sample, so they are a destructive process and the sample is consumed in the process of detection so they may not be used for gathering samples of unknowns. FIDs ionize organic materials with an IP of 15.4 or less.



### What Does a FID Measure?

The largest group of compounds measured by a FID are the Organics: compounds containing Carbon (C) atoms. These include:

- **Aromatics** - compounds containing a benzene ring including: benzene, toluene, ethyl benzene and xylene.
- **Ketones & Aldehydes** - compounds with a C=O bond including: acetone, methyl ethyl ketone (MEK) and acetaldehyde.
- **Amines & Amides** - Carbon compounds containing nitrogen, like diethylamine.
- **Chlorinated/halogenated hydrocarbons** - trichloroethylene (TCE), perchloroethylene (PERC) and Freons can cause problems because the halogen released in combustion can damage the FID sensor
- **Sulfur compounds** – mercaptans, sulfides
- **Unsaturated hydrocarbons** – like butadiene and isobutylene
- **Alcohol's**- isopropanol (IPA), ethanol, methanol
- **Saturated hydrocarbons**
  - butane, octane, methane, propane, ethane

### What FIDs Do Not Measure

- **Inorganics:** Compounds without Carbon cannot be burned and cannot be detected with FID
- Air
  - N<sub>2</sub>
  - O<sub>2</sub>
  - H<sub>2</sub>O
- Toxics w/o C
  - HCN
  - SO<sub>2</sub>
  - Cl<sub>2</sub>
- Acids
  - HCl
  - HF
  - HNO<sub>3</sub>
- Others
  - Ozone O<sub>3</sub>

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## FID Summary

- Advantages
  - + Quantifiable measurements (although multiple CFs may be required)
  - + Measure from ppm-5% vol (0.5-50,000 ppm)
  - + Measures CH<sub>4</sub> and nearly all organic gases and vapors
  - + Stores well
- Disadvantages
  - Has many “Blind Spots” and will not measure many toxic chemicals (like Cl<sub>2</sub>)
  - Lacking in low-end sensitivity and linearity (<10ppm) compared to PIDs
  - High consumables (H<sub>2</sub> & Cal gas)
  - Requires O<sub>2</sub> > 14%
  - Halogens can destroy the FID sensor
  - Expensive to purchase

## FIDs vs. PIDs

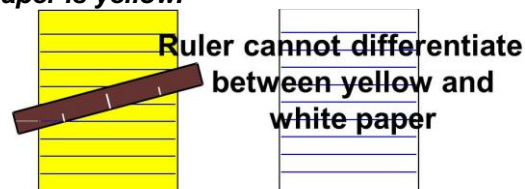
The difference between FID and PID is like the difference between a meter stick and a yardstick. While a PID with a 10.6eV lamp is largely considered a liquid hydrocarbon detector the FID is largely thought of as a gaseous hydrocarbon detector. PIDs are less expensive to purchase and are less expensive to own because they don't use a consumable gas like the hydrogen used by FIDs. The petroleum industry uses FIDs to do accurate ppm level leak detection of gaseous hydrocarbons like methane, propane and ethane under EPA method 21. However some users of gas detection don't often need accurate ppm measurement of methane, propane and ethane, they can get by with LEL for flammability decisions and MOS sensors for leak detection of these chemicals.



## Sensitivity vs. Selectivity

PIDs and FIDs are very *sensitive* monitors that can accurately measure gases and vapors in ppm or even ppb levels in the case of some PIDs. However, PIDs and FIDs are not *selective* monitors. They have very little ability to differentiate between chemicals. To visualize this, let's compare them to a ruler. A

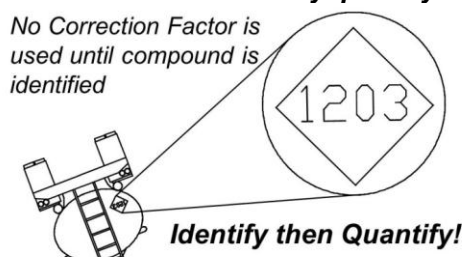
ruler is a sensitive and accurate means of measuring the width of a sheet of paper. But it cannot tell the difference between yellow and white paper. Therefore, if one wants to know the width of the yellow sheet of paper, that person must first select the proper sheet of paper before measuring with the ruler. **We use our head to determine which sheet of paper is yellow.**



## PIDs & FIDs can't differentiate between acetone & xylene

PIDs and FIDs are similar to the ruler. They can tell us how much of a gas or vapor is present, but we must use our head to determine the exact gas or vapor present. When approaching an unknown chemical release, the PID is set to its calibration gas of isobutylene or a FID is set to methane. Once the chemical is identified by means of placard, manifest, waybill or other means, the PID or FID sensitivity can be adjusted to that chemical so that it reads in an accurate scale. For example, if we calibrate on isobutylene and happen to measure a toluene leak of 1 ppm the PID will display 2 ppm because it is twice as sensitive to toluene as it is to isobutylene. Once we have identified the leak as toluene, then the PID scale can be set to a toluene Correction Factor and the PID will accurately read 1 ppm if exposed to 1 ppm of toluene.

**Remember that we use our head for “selectivity” and the PID “sensitivity.” With PIDs and FIDs one must identify first before one can accurately quantify.**



## The Power of Correction Factors in PIDs and FIDs

Correction Factors are the key to unlocking the power of PIDs & FIDs for assessing varying mixtures and even unknown environments. Correction Factors (CF), also known as Response Factors, are a powerful tool in the use of PIDs and FIDs. They are a measure of PID or FID sensitivity to a particular gas or vapor. CFs are scaling factors, they do not make a PID or FID specific to a chemical, they only correct the scale to that chemical. CFs permit calibration on one gas while directly reading the concentration of another gas/vapor. This eliminates the need for multiple calibration gases. Originally PIDs were calibrated to a benzene scale, but because benzene is a carcinogen, now all PIDs are calibrated to an isobutylene scale. FIDs are calibrated to a methane scale. Manufacturers determine CFs by measuring their meters response to a known concentration of a target gas. CFs tend to be instrument and/or manufacturer specific so it is best to use the CFs from the manufacturer of the PID or FID that one is using.

### Types of Correction Factors

Response factors are expressed in 2 major formats:

1. Multiplier Response Factor (MRF)
2. Relative Response Factor (RRF)

### Multiplier Response Factors (MRF)

MRFs are the most common type of Correction Factor. They are calculated by dividing the actual concentration of a chemical by the detector response:

- $MRF = \text{Actual Concentration} / \text{Measured Response}$
- If 100 ppm of a chemical produces 50 ppm reading in isobutylene units then the response factor would be 2
  - $50\text{ppm}_{\text{iso}} \times 2 = 100\text{ppm}_{\text{chemical}}$

To use a MRF one multiplies the reading in calibration gas units by the correction factor to arrive at the actual concentration. MRFs are used by RAE Systems, Ion Science, Photovac, MSA, and Thermo. As MRFs are much more common they will be used in the examples throughout the rest of this chapter.

### Relative Response Factors (RRF)

RRFs are expressed as a percent or a ratio of a chemical's response to that of the calibration gas. They are calculated by dividing the detector response by the actual concentration of the chemical of interest:

- $RRF = \text{Measured Response} / \text{Actual Concentration}$
- If 100 ppm of a chemical of interest produces a response of 50 ppm then the relative response factor would be 50/100 or 0.5 or 50%
  - $50\text{ppm}_{\text{iso}} / 0.5 = 100\text{ppm}_{\text{chemical}}$

The relative response factor is the reciprocal of the response factor multiplier ( $1/RRF = MRF$ ). RRFs are used by Hnu (Thermo provides them in addition to MRFs).

### 10.6eV Lamp MRFs Compared

Chemical	RAE	Ion Science	Photovac (2020 Pro)	MSA (Sirius)	HNu <sup>+</sup>	Thermo** (TVA-1000)
Acetone	1.1	1.1	1.2	1.12	1.3	1.4
Benzene	0.53	0.53	0.5	0.53	0.55	0.75
Diesel #2	0.7	0.7	NA	0.80	NA	NA
Ethanol	10	12	8.8	9.25	2.24	5.38
Styrene	0.4	0.4	0.4	0.32	0.37	0.58
Vinyl chloride	2.0	2.0	1.7	1.47	1.71	2.42

\* Converted from RRFs relative to benzene using 10.2eV lamp

\*\* At 100 ppm

As you can see on the proceeding chart, while Correction Factors seem to want to trend together amongst manufacturers, there are times when they can vary greatly. Don't use CFs from one manufacturer on another's PID because they can differ and errors can be quickly multiplied. Using a Relative Response Factor as a Multiplier Response Factor can give grossly inaccurate readings. Make sure that the manufacturer of your PID or FID has the CFs for the chemicals you need to measure. When in doubt it may be best to choose one of the companies with an extensive list of CFs. Some older PIDs (TVA-1000) and most FIDs are not linearized across their entire measurement range so they will have different CFs depending on the concentration of the chemical as can be seen in the following chart:

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Acetone				
Challenge Concentration (ppm)	Thermo/TVA-1000A (or equivalent)		EPA/TVA-1000B (or equivalent)	
	Relative Response Factor		Response Factor Multiplier	
	PID	FID	PID	FID
10	0.748	1.230	1.342	0.901
50	0.731	1.231	1.375	0.900
100	0.711	1.233	1.417	0.899
250	0.658	1.237	1.544	0.897
500	0.585	1.244	1.754	0.892
1000	0.479	1.258	2.174	0.884
2000	0.352	1.286	3.015	0.866
5000		1.371		0.815
7500		1.442		0.772
10000		1.513		0.728

CFs can be implemented in the use of FIDs similarly to how they are implemented on PIDs and LEL sensors. It is common for FIDs to have different correction factors for different ranges (100, 500, 2000, 5000 ppm) while new PIDs are more linearized than FIDs so they typically only have one correction factor for their entire measurement range.

### CF Measures Sensitivity

Correction Factors are scaling factors used to adjust the sensitivity of the PID or FID to directly measure a particular gas compared to the calibration gas. The lower the MRF CF the more sensitive the detector is a gas or vapor. In the following examples the CF's are for example only, always use CFs provided by the manufacturer of your PID or FID:

- Toluene's CF is 0.5 so the PID is very sensitive to Toluene
- Ammonia's CF is 9.7 so PID is less sensitive to Ammonia

The PID is approximately 19 times more sensitive to Toluene as it is to Ammonia ( $9.7/0.5=19.4$ ).

### Guidelines for using Correction Factors

**Low  $CF_{MRF}$  = high sensitivity to a gas**

- If the chemical is bad for you then the PID/FID needs to be sensitive to it
  - **If Exposure limit is < 10 ppm,  $CF \leq 1$**
  - Therefore, if the chemical has an **exposure limit of 10 ppm** or less, a PID or FID is an appropriate tool for personal safety decisions if the chemical's **CF is less than 1.0**.
  - e.g.: Benzene has an exposure limit of 1 ppm and a CF of 0.5 on a PID so this is a good fit of sensitivity to toxicity

• If the chemical isn't too bad then the PID/FID doesn't need to be as sensitive to it

- **If Exposure limit is > 10 ppm,  $CF < 10$**
  - Therefore, if the chemical has an **exposure limit of over 10 ppm**, a PID or FID is an appropriate tool for personal safety decisions if the chemical's **CF is less than 10**.
  - e.g.: Ammonia has an exposure limit of 25 ppm and a CF of 9.7 on a PID so this is a good fit of sensitivity to toxicity
- Use PID/FIDs for gross leak detectors when  $CF > 10$
- If the chemical's **CF is greater than 10** PIDs and FIDs are still appropriate as gross leak detectors and are only appropriate for personal safety decisions for chemicals with very high exposure limits.
  - e.g.: Ethylene oxide has a CF of 13 with a 10.6 lamp so it would not be appropriate to use this PID for toxicity decisions but it could still be used as a leak detector.

### CF Example: Toluene

- Toluene CF with 10.6eV lamp is 0.5 so a PID is very sensitive to Toluene
- If PID reads 100 ppm of isobutylene units in a Toluene atmosphere then the actual concentration is 50 ppm Toluene units
- $0.5_{CF} \times 100 \text{ ppm}_{iso} = 50 \text{ ppm}_{toluene}$

### CF Example: Ammonia

- Ammonia CF with 10.6eV lamp is 9.7 so PID is less sensitive to Ammonia
- If PID reads 100 ppm of isobutylene units in an Ammonia atmosphere then the actual concentration is 970 ppm Ammonia units
- $9.7_{CF} \times 100 \text{ ppm}_{iso} = 970 \text{ ppm}_{ammonia}$

### How to determine if a PID can Measure a Particular Gas

1. Is the IP of the gas less than the eV output of the lamp?
  - **Yes:** go to step 2.
  - **No:** Select a higher energy lamp. If none available, then the PID cannot measure that gas.

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- **Don't Know:** Most PID manufacturers can help
2. Is the CF less than 10?
- **Yes:** a PID is an appropriate way of measuring that gas.
  - **No:** a PID is not an accurate means of measuring that gas, but it could still be a good way of gross measurement like leak detection.
  - **Don't Know:** Most PID manufacturers can help

### Making a Decision with a PID/FID: Setting Alarms

Two bits of information are required to make a decision with a PID or FID:

1. Human Toxicity: as defined by ACGIH, NIOSH, OSHA or corporate guidelines
2. PID Sensitivity: as defined through testing by the manufacturer of your PID/FID, **ONLY USE A CORRECTION FACTOR FROM THE MANUFACTURER OF YOUR PID/FID!**

PID/FID sensitivity + Human Sensitivity =  
Decision

**Or**

CF + Exposure Limit = Decision

### Three Scenarios for Setting PID/FID alarms:

1. Single Gas/Vapor
2. Gas/Vapor mixture with Constant make-up
3. Gas/Vapor mixture with Varying make-up

#### 1) PID/FID Alarms for a Single Gas/Vapor

Single chemicals are easy:

- Identify the chemical
- Set the PID/FID correction factor to that chemical from the PID/FID manufacturer's listing
- Find the Exposure limit(s) for the chemical (ref. ACGIH/NIOHS/OSHA)
- Set the PID alarms according to the exposure limits

***The "Real World" is rarely this easy!  
Most applications are a "Witches Brew" of chemicals***

#### 2) PID/FID Alarms for a Gas/Vapor Mixture with Constant Make-up

Often a gas/vapor detection problem does not involve a single chemical, but may involve a

compound that is a mixture of toxic chemicals. This "witches brew" of toxic compounds requires greater care in determining alarm set points. If the mixture is identifiable, then the individual chemicals and their concentrations should be easily determined through a contents label or Safety Data Sheet (SDS formally MSDS). If the chemical contents are identifiable then the following equation can be used to determine the toxicity of the mixture:

$$EL_{mix} = 1 / (X_1/EL_1 + X_2/EL_2 + X_3/EL_3 + \dots + X_i/EL_i)$$

Where "EL" is the Exposure Limit and X is the mole fraction of each volatile chemical.

Similarly, the Correction factor for the mixture can be calculated using the virtually the same equation:

$$CF_{mix} = 1 / (X_1/CF_1 + X_2/CF_2 + X_3/CF_3 + \dots + X_i/CF_i)$$

Where "CF" is the MRF Correction Factor and X is the mole fraction of each volatile chemical.

To clarify the usage of these equations let's take an example. Suppose that you have a complaint of paint odors and upon investigating you find that the paint contains 15% styrene and 85% xylene. Then the exposure limit is calculated as follows:

$$EL_{mix} = 1 / (0.15/50 + 0.85/100) = 87 \text{ ppm}$$

- 0.15 is 15% styrene
- 50 is the 50 ppm exposure limit for styrene
- 0.85 is 85% xylene
- 100 is the 100 ppm exposure limit for xylene

In a similar manner the Correction Factor is calculated:

$$CF_{mix} = 1 / (0.15/0.4 + 0.85/0.6) = 0.56$$

- 0.15 is 15% styrene
- 0.4 is the CF styrene
- 0.85 is 85% xylene
- 0.6 is the CF for xylene (in this case it is the average of the three isomers of xylene listed in the reference CF chart)

The reading in the area with the paint odors was 120 on the PID in Isobutylene units. Multiplying this reading by the correction

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## AP-105: Is There Something Out There?

factor of 0.56 the real reading for the mixture was 67.2 ppm. This is under the calculated exposure limit of 87 ppm for the mixture. However, styrene has an olfactory threshold of less than 2 ppm so even at safe levels the paint vapors have a distinct smell.

### Alarm Shortcuts for Constant Mixtures

Set points can often be based on the concentration of the most prevalent or most toxic compound. Many times this determination is as simple as reading the SDS.

### Shortcut for the most Prevalent Compound

- Find the average make-up of the mixture
- Determine the most prevalent VOC
- Base set points on the most prevalent VOC

Let's take a look at the same paint odor example, but instead of doing the math we look at as the most prevalent chemical: xylene. The reading in the area with the paint odors was 120 on the PID in Isobutylene units. Multiplying it by the xylene correction factor of 0.59 the real reading for the reading in xylene units is 70.8 ppm which is under xylene's exposure limit of 100 ppm. This shortcut can save time, but it is not without its pitfalls. In this case it works because styrene and xylene have exposure limits that are within the same power of 10 with an exposure limit of 50 for styrene and 100 for xylene. When a very toxic chemical is present in a mixture it can drastically change the mixture set points. For example if this mixture had contained a very toxic compound like benzene (exposure limit of 1) or Toluene Diisocyanate (exposure limit of 0.02 ppm) the following short cut might be considered.

### Short cut for the most Toxic Compound

For example, while the typical TWA for gasoline is 300 ppm, we can set alarms based upon the relative concentration of chemicals in gasoline. Gasoline is a mixture of hydrocarbons including benzene, ethyl benzene, toluene and xylene. These are all readily ionizable by a PID so we will measure a total of all these compounds. But benzene is by far the most toxic of these chemicals so we will first focus on it. Studies have shown that Gasoline (and other fuel products) contains approximately 1% benzene. Benzene's permissible limit is only 1 ppm due to its potentially carcinogenic properties.

Therefore, in a "worst case" scenario where gasoline has 1% benzene, 100 ppm of gas means an exposure to as much as 1 ppm of benzene! 50 ppm of gasoline contains approximately 0.5 ppm of benzene and would be an appropriate level to go from "bareface" to respiratory protection like Self-Contained Breathing Apparatus (SCBA). While this example ignores differing vapor pressures, this logic is used by some petroleum plants to determine worker respiratory protection requirements.

- "Gas" contains as much as 1% Benzene
- Benzene is carcinogenic (PEL = 1 PPM)
- 100 PPM of Gasoline contains as much as 1 PPM Benzene
- Set High Alarm at 100 PPM Gas < 1.0 PPM Benzene
- Set Low Alarm at 50 PPM Gas < 0.5 PPM Benzene

### 3) Setting PID/FID Alarms for a Gas/Vapor Mixture with Varying Make-up: The "Controlling Compound"

Setting alarms in a varying mixture means that one has to simultaneously interpret both the toxicities of the gases/vapors on humans and their relative sensitivities (Correction Factors). People are accustomed to making decisions solely on human sensitivity but users of meters also need to take into account meter sensitivity. In this case to make a decision it is necessary to simultaneously interpret both human and meter sensitivity. Fortunately this is easier than it sounds. Every mixture has a compound that is the most toxic and "controls" the set point for the whole mixture. Determine that chemical and one can determine a conservative set point for that mixture.

1. Express all Exposure Limits (EL) in equivalent units (divide the exposure limit by the CF)  
$$EL_{\text{isobutylene}} = EL_{\text{chemical}} / CF_{\text{chemical}}$$
2. Look for the compound with the lowest Exposure Limits in equivalent units
3. Set the PID for that set point and we are safe for all of the chemicals in the mixture

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## AP-105: Is There Something Out There?

### Addressing Vapor Exposures in a Vitamin C Plant

A vitamin C plant sought a way for its workers to safely work without respiratory protection so they contacted a PID sales rep. Upon visiting the plant and understanding that the vapors present were ethanol, toluene and acetone, the sales rep suggested that operators could “easily” reset the CFs and alarm limits of the PID as the solvents changed. The plant safety manager pointed out that the solvents were often co-mingled and that the operators may lack the sophistication to reliably make changes to the PID. Given this problem, how could the sales rep proceed with making a sale? First we look at all three chemicals and their exposure limits:

Chemical Name	10.6eV CF	Exposure Limit
Ethanol	12	1000
Toluene	0.50	100
Acetone	1.1	750

- Ethanol “appears” to be the safest compound
- Toluene “appears” to be the most toxic
- But one might as well be comparing apples to oranges to pomegranates

To make a decision of which chemical is the “worst” one we have to take another step. By dividing the exposure limit by the CF we get the exposure limit in units of isobutylene (calibration gas units).

Chemical Name	10.6eV CF	Exposure Limit	10.6 Lamp Iso Units
Ethanol	12	1000	83.33
Toluene	0.50	100	200.00
Acetone	1.1	750	681.82

Now one can compare apples to apples by comparing the 10.6 Lamp Iso Units column. Even though it has the highest exposure limit, ethanol’s lower sensitivity on the PID makes it the “controlling compound” when the Exposure Limits are expressed in equivalent isobutylene units. “Iso Units” or Isobutylene Units are determined by dividing the Exposure Limit by the Correction Factor (CF) to provide us with a number that combines human toxicity with PID sensitivity. Therefore, if the PID is set to an alarm of 83 ppm, it will protect workers from all three chemicals no matter what the relative concentration of the chemicals might be. **IMPORTANT:** in the rest of this discussion,

“Exposure Limit in Isobutylene” will be called or  $EL_{iso}$ .  $EL_{iso}$  is a calculation that involves a vendor specific Correction Factor (CF). Similar calculations can be done for any PID/FID brand that has a published CF list.

$EL_{iso}$  thresholds are a tool to help characterize unknown environments. The lower the reading in isobutylene units on a PID the less risk. If the reading on a PID is below the  $EL_{iso}$  for a chemical there isn’t a threat.

For example, a chemical plant uses styrene, toluene and cumene. A PID gives a reading of 45 ppm. Is this an atmosphere that requires respiratory protection or not?

Chemical Name	10.6eV CF	Exposure Limit	10.6 Lamp $EL_{iso}$
PID in Iso			45
Styrene	0.4	100	250
Toluene	0.50	100	200.00
Cumene	0.54	50	92

In this case because the exposure limits in isobutylene are all above the PID isobutylene unit reading of 45, it is safe to be without respiratory protection.

### The 50/50 Rule

Using the Isobutylene or Iso Unit logic allows one to use the PID to help determine Standard Operating Procedures because one can know exactly what chemicals the PID will provide protection from given a particular reading in isobutylene units. Using this logic with the CF chart of a popular PID manufacturer one can come to the following conclusion:

### ***A RAE Systems PID with a 10.6eV lamp set to the following alarms and not beeping provides protection from:***

- **44 chemicals at a 100 ppm alarm**, includes major solvents like Xylene, Toluene, MEK, MPK, Acetone
- **65 chemicals at a 50 ppm alarm**, from Cyclohexanone to Acetone.
- **81 chemicals at a 25 ppm alarm**, from Diethylamine to Acetone.
- **Over 105 chemicals at a 10 ppm alarm**, from Toluidine to Acetone.
- **Over 140 chemicals at a 1 ppm alarm**, from Diethylenetriamine to Acetone

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Of course setting an alarm to 1 ppm would provide the highest level of protection, but it would also provide the most alarms. Too many alarms would be like “the boy who cried wolf” and would reduce user confidence in the PID. An alarm point of 1 ppm would be similar to always wearing a Level A suit! A 50 ppm EL<sub>iso</sub> alarm is appropriate for going to respiratory protection in a fuel tanker roll-over because an EL<sub>iso</sub> alarm of 50 is very conservative for all hydrocarbon fuels. This alarm point provides protection from some of the most common chemicals in industry and is a good balance point between too many and too few alarms. **One way of looking at this is with an alarm in isobutylene units set to 50 ppm and the PID is not beeping, responders don’t have to worry over 50 common chemicals or the “50/50 Rule.”**

### When Measuring in Isobutylene Units and set to 50 ppm RAE PIDs will protect from over 50 of the most common Chemicals:

- Acetone
- Cyclohexane
- Diesel Fuel
- Ethyl alcohol
- Ethylbenzene
- Gasoline
- Heptane, n-
- Hexane, n-
- IPA
- Jet Fuel
- MEK
- MIBK
- MPK
- Nonane
- Octane, n-
- Pentane
- Stoddard Solvent
- Styrene
- Tetrahydrofuran
- Toluene
- Trichloroethylene
- Xylene

### Guidelines for PID use

When using a PID measuring in units of isobutylene

- **1 ppm:** may be nothing in outdoor environment but for IAQ it definitely means that something is going on (assumes properly calibrated PID)
- **10 ppm:** something is definitely going on outside
- **50 ppm:** mask up (or 50% of most TWAs)
- **100 ppm:** TWA has most likely been exceeded
- **1000 ppm:** 10% of LEL and therefore IDLH has most likely been exceeded
- **10,000 ppm (or 1% by volume):** 100% of LEL has most likely been exceeded

The PID reading is just one clue about the atmosphere; users of detectors must be good detectives to utilize all of the clues present to reach a decision.

## Non-Quantifying Survey Sensors

Some survey sensors are great for finding “it” but they are not linear so they may not be suitable for measuring or quantifying “it.” Most of the time finding “it” is the biggest part of the battle.

## Metal Oxide Sensors

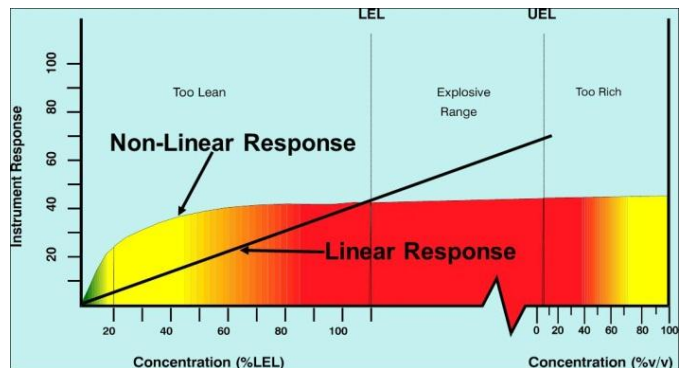
Metal Oxide Sensors (MOS) are one of the most common and affordable survey sensors. Depending on how they are doped they can provide non-specific leak detection of:

- Natural gas: methane, propane, ethane
- Hydrocarbons: alcohols, ethers, ketones, aromatics
- Halogenated hydrocarbons
- Many other chemicals

Doping can limit cross-sensitivity, so a MOS sensor for leak detection of halogenated hydrocarbon refrigerants will not work for natural gas leak detection

### Affordable: (“Poor Man’s PID”)

The non-linear output of MOS sensors limits their accuracy. Essentially they are a rubber ruler and this prevents accurate or quantifiable ppm readings. Because of this many survey meters that use MOS sensors provide only an audible “Geiger Counter” style of user interface because non-linearity makes a ppm display problematic. MOS sensors can be sensitive to temperature and humidity which can lead to false alarms when the sensor is not compensated for these parameters. Finally MOS sensors can be poisoned & ruined by over-ranging just like LEL sensors.



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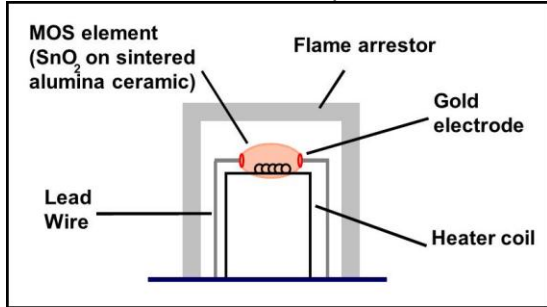
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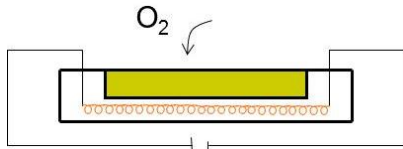
**What is a MOS Sensor?**

In MOS sensors a metal oxide like tin dioxide ( $\text{SnO}_2$ ) is put onto a sintered alumina ceramic that is heated. In clean air electrical conductivity is low, but contact with reducing gases (such as CO or combustibles) increases conductivity. Sensitivity to specific gases depends on temperature of sensing element and how the substrate is doped.

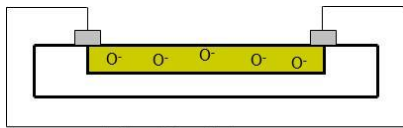


- The metal oxide surface absorbs sample gas molecules
- The absorbed molecules change the electrical resistance
- Decrease in resistance correlates with greater concentrations of the targeted gas/vapor

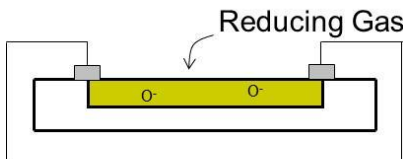
1. Heating and Oxygen absorption



2. In a clean atmosphere an Oxygen barrier in the MOS sensor creates high resistance.



3. As targeted reducing gases (like CO) "deoxidize" the heated substrate the resistance will decrease as the reducing gases increase.

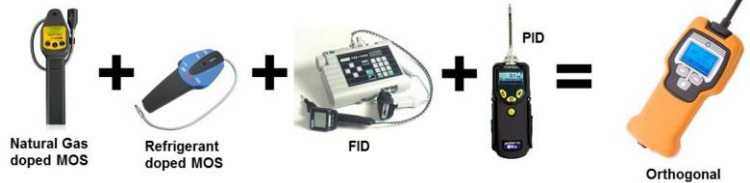


**MOS Summary**

- Advantages
  - + Very sensitive detectors
  - + Selectivity may be changed by temperature or the doping of the sensor
  - + Most inexpensive survey monitor
  - + Store well
  - + No consumables
- Disadvantages
  - Non-linear measurement, can't accurately tell how much is there once it is found
  - Requires  $\text{O}_2$
  - Will not measure all chemicals

**Orthogonal Sniffers**

Orthogonal detectors use a variety of sensors rather than just one type to come to a conclusion. "Orthogonal" means to look at something from many different angles. Sometimes these types of sensors may also be called "electronics noses." Each sensor has its strengths and weaknesses, but assembling a number of sensors "Sensor fusion" takes advantage of this by utilizing the strengths of a number of sensors to come to a final conclusion. By using multiple sensors the goal is to increase sensitivity while reducing false alarms. Another way of looking at this is that redundancy is built into the detector and they have the opportunity to "sniff" for many more chemicals than a single sensor product like a PID, FID or MOS.



**The ChemPro100i Orthogonal Sniffer**

The Trend display in the ChemPro100i totals the absolute outputs of all of the following 7 sensors: aspirated Ion Mobility Spectrometry (IMS), Field Effect, Metal Oxide (3) and Semiconductor (2). The  $^{241}\text{Am}$  NRC exempt source for the aspirated IMS in the ChemPro100i produces approximately 60KeV (60,000eV) so it can "see" hundreds

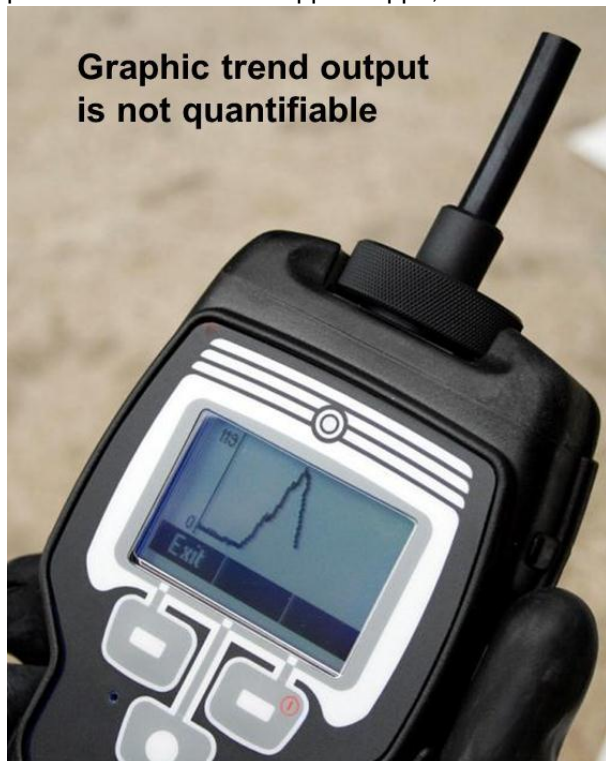


## AP-105: Is There Something Out There?

of gases & vapors with high ionization potentials (like chlorine, carbon tetrachloride, etc.) that go unseen by most PIDs which are limited to just 10.6eV.



The ChemPro100i can be easily used as a survey tool, much like a PID “on steroids” to quickly “see” concentration trends. The graphical “Trend” function facilitates finding the source (leak detection). Elapsed time forms the X axis and the relative concentration forms the Y axis so that leaks are shown as a peak in the running graph. Trend is relative not quantitative, the numbers on the Y axis are relative concentration units and are not a precise concentration in ppm or ppb, but the



ChemPro Trend display can resolve to approximately the ppb level.

### Orthogonal Sniffer Summary

- Advantages
  - + With more sensors have the ability to “see” more of “it” than other sniffers
- Disadvantages
  - Relatively more expensive
  - Non-linear measurement, can't accurately tell how much is there once it is found
  - Requires O<sub>2</sub>

### Uses of Sniffers

With the ability to detect from ppb to 1% by volume, sniffers can provide a powerful tool for the following activities:

- PPE assessment
- Leak detection
- Perimeter establishment and maintenance
- Spill delineation
- Decontamination
- Remediation

### PPE Assessment

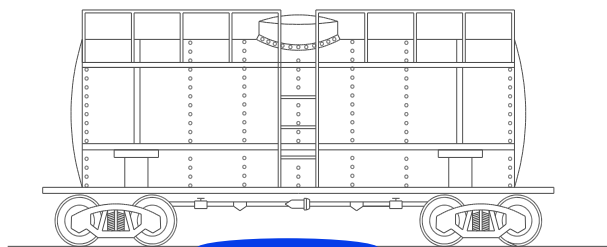
When approaching a potential chemical release, a responder must make a PPE (Personal Protective Equipment) decision. Some potential releases may not be an “incident” at all and may not require any PPE. Some releases may initially appear to have no contamination yet require significant levels of PPE. Sniffers let responders identify the presence or absence of potentially toxic gases or vapors.

### Leaking Railcar

A HazMat contractor was called by a railroad to respond to a leaking tank car on a hot (95°F/35°C), humid (95%RH) summer day. According to the manifest, the tank car was loaded with benzene. Due to the carcinogenic nature of benzene (PEL of 1 ppm) the contractor chose to dress-out in Level A.

## AP-105: Is There Something Out There?

But, because it was a hot summer day, this potentially exposed the responders to heat stress injuries. In the assessment of the “leaking” tank car it was found that the puddle under the car was coming from condensation not dripping benzene. The car had been loaded at 65°F (18°C) and the high ambient temperature combined with relative humidity above 95% produced a puddle of water not benzene.



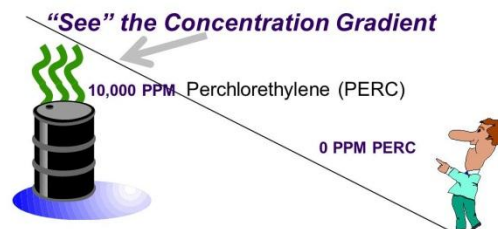
Using a sniffer would have helped the contractor determine if there was a vapor present. Because the manifest identified the tank car contents as benzene, and benzene is readily ionizable, the contractor could have ruled out the presence of benzene vapors using a PID, FID or orthogonal sniffer. With both the PID and the FID the responder could have used a Correction Factor to scale the sniffer to benzene units. Effective use of sniffers would reduce the cost of the response and prevent the potential of heat-stress injuries from dressing out in full Level A encapsulation.

### PPE Assessment Sniffer Summary

- **FID:** often helpful but can miss some chemicals, and can make exposure limit decisions
- **MOS:** often helpful but can miss some chemicals
- **Orthogonal:** usually helpful but can't make exposure limit decisions
- **PID:** often helpful but can miss some chemicals, and can make exposure limit decisions

### Leak Detection

Often a leak is not readily apparent and it must first be located before it can be effectively stopped. Anytime that a gas or vapor is released into air it disperses outwards from the source of the leak. As the gas or vapor disperses it is diluted by ambient air until at some point the gas or vapor cannot be detected. This process establishes a concentration gradient where the concentration of the gas or vapor is greatest at the source of the leak and the concentration is effectively zero when the gas or vapor is fully dispersed. Our sniffers allow us to detect and “see” concentration gradients for many gases and vapors that we would otherwise be unable to detect.

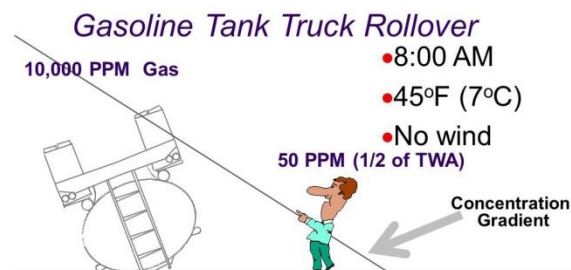


### Leak Detection Summary

- **FID:** often helpful but can miss some chemicals
- **MOS:** often helpful but can miss some chemicals
- **Orthogonal:** usually helpful
- **PID:** often helpful but can miss some chemicals

### Perimeter Monitoring

HazMat technicians assess the incident and set a perimeter based upon the toxicity of the gas or vapor, the temperature, wind direction and other factors. However, perimeters are usually manned by people without a high degree of experience.



- Perimeter = 100 feet

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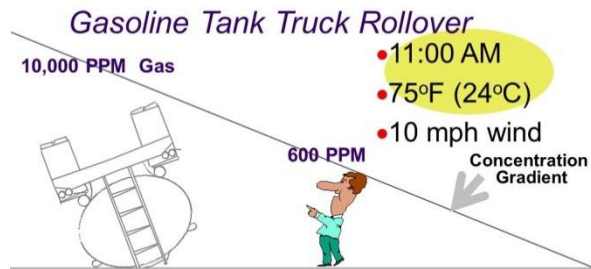
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As conditions change, perimeters often are not adjusted because perimeter workers do not have the experience to recognize that the conditions have changed. The experienced HazMat technicians are typically focused upon the problem of dealing with complications of the original spill. Therefore, perimeter workers are often unprotected from changing conditions that may require movement of a perimeter away from the spill site. Because they are small, affordable and they can quantify, PIDs allow those manning a perimeter line to adjust the line in response to changing conditions. and can be scaled to many chemicals PIDs can provide instantaneous alarms that can warn perimeter workers when to retreat from the



- Perimeter now should be 300 feet
- Perimeter worker overexposed

incident for everything from ammonia to xylene.

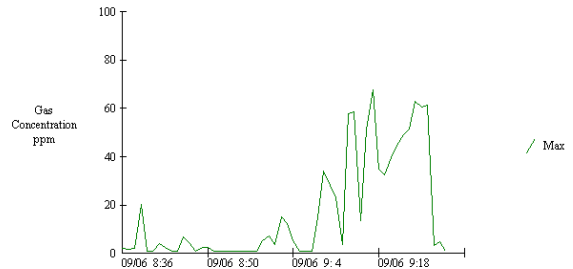
### Perimeter Monitoring Summary

- **FID:** often helpful but big and expensive, can quantitate but can miss some chemicals
- **MOS:** often helpful but can miss some chemicals and can't quantitate
- **Orthogonal:** usually helpful, but can't quantitate but can alarm at specific alarm limits for some chemicals
- **PID:** often helpful, can quantitate, but can miss some chemicals

### Datalogging as a Tool

Datalogging provides supervisors with documentation of exposure levels and provide evidence to justify evacuations should they be required. Some people only datalog when they know that they have a gas/vapor release.

Tanker Spill Northern Perimeter



This misses more than half of the value of datalogging. Many times a negative result on a datalog is more beneficial than a positive result. Saving a "non-detect" can help to quickly establish that a spill was promptly and properly contained. This can save time and money if the spill ever results in legal action.

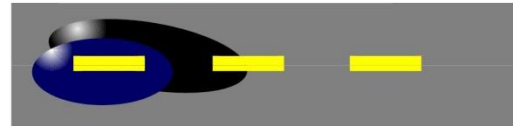
### Datalogging Summary

- **FID:** often helpful, can quantitate but can miss some chemicals
- **MOS:** can't quantitate
- **Orthogonal:** usually helpful, but can't quantitate but can alarm at specific alarm limits for some chemicals
- **PID:** often helpful, can quantitate, but can miss some chemicals

### Spill Delineation

In the course of a spill many liquids can be present such as water, fuel, engine fluids and firefighting foam. With all these liquids present, our sniffers provide an excellent tool for responders to zero in on the spill.

**Sniffers can help separate the "Water" from the "Oil"**



**Limited Absorbent can be Efficiently used only on the Diesel Spill**

### Spill Delineation Summary

- **FID:** often helpful, but can miss some chemicals
- **MOS:** often helpful, but can miss some chemicals
- **Orthogonal:** usually helpful
- **PID:** often helpful, but can miss some chemicals

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## Using Sniffers in Decon

Hazardous materials often get on responders. Our sniffers provide quick and effective means of determining if a responder requires decontamination, and if decontamination has been complete. This may make it easier for a HazMat team to make a decision to reuse an encapsulation suit because it was not contaminated. The sniffer is swept over areas of suspected contamination. It will respond positively to areas that are contaminated and will not respond to clean or properly decontaminated

area or to products that it cannot "see." Because of this it's often best to choose the sniffer that can "see" the most chemicals and this product is the orthogonal detector.



Often a first responder to a fuel spill incident gets gasoline on his flame-retardant turnout clothing. Absorbed gasoline will compromise the flame-retardant properties of turnout gear. PIDs, FIDs and Orthogonal sniffers will quickly respond to contamination and identify this dangerous condition so that the turnout gear can be properly laundered before going into a structural firefighting situation.

## Decon Summary

- **FID:** often helpful, but can miss some chemicals
- **MOS:** may be helpful, but can miss some chemicals
- **Orthogonal:** usually helpful
- **PID:** often helpful, but can miss some chemicals

## Using a PID/FID for Remediation

While the goal of any HazMat response team is to contain and prevent spills, hazardous materials often evade containment; contaminating nearby soil and water. Many jurisdictions (counties, states, countries) have defined the concentration at which remediative action must take place. If there has been a fuel spill that has been contained to the road

surface and it has been completely removed by absorbent, further remediative action may not be required. However, if fuel product has evaded the best efforts for containment, the fuel may have contaminated the surrounding soil or water. Some jurisdictions have an action level of 100 ppm TPH in a sample headspace (Total Petroleum Hydrocarbons) for further remediation. If soil samples show only 10 ppm of contamination in the headspace of a sample, remediation may not be required. Soil samples of 200 ppm would require further remediation.

The PID and FID are the best-recognized tools for making such a determination for environmental officials and environmental contractors. Because of variations in the weather and soil conditions it is best to do a headspace sample on suspect soil or water rather than just waving the PID or FID probe over the suspicious area. This is because on a cold day, VOCs are less likely to evaporate and waving the probe over the area might miss contamination. Conversely, on a hot day, waving the probe over a contaminated area could overestimate contamination.

## How to Do a Headspace Sample

1. Put contaminated soil or water in a container or even a plastic bag
2. Cover/seal the container and bring it to room temperature (65-75°F/18-24°C) for about 5-15 minutes
3. Put PID/FID probe into container and sample
4. Generally <100 ppm is good (Caution: 100 ppm is a general guideline. Check local regulations for specific rules).





**Remediation Summary**

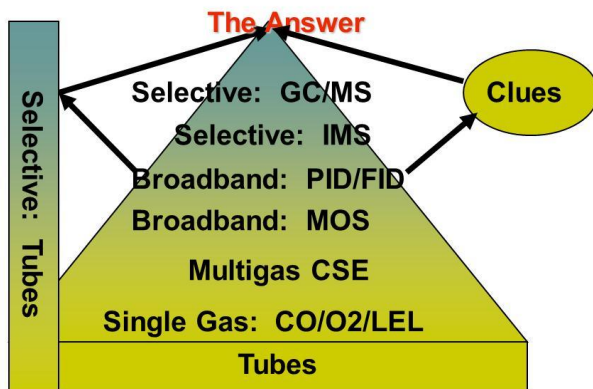
- **FID:** often helpful, can quantitate but can miss some chemicals
- **MOS:** not helpful because it cannot quantitate
- **Orthogonal:** not helpful because it cannot quantitate
- **PID:** often helpful, can quantitate but can miss some chemicals

**Integrating Gas Detection Techniques**

Sniffers can be an important part of any gaseous risk assessment and should be used with other clues present:

- Response from other types of meters
- Response from colorimetric tubes
- Physical clues
- Worker/Victim symptoms

The Gas Monitoring Pyramid is a graphic depiction of how to integrate various gas monitoring techniques in order to more quickly move from detection to decision. In the following example a PID/FID plus the use of a colorimetric tube or the clues at the scene can come to the same conclusion as using a highly selective but very expensive Gas Chromatograph/Mass Spectrometry (GC/MS) detector.



**PID + Tubes Approximates the selectivity of GC/MS w/o the cost**

**Tips for Using and Maintaining Sniffers**

Sniffers are sensitive devices, how they are used or misused can affect their on-scene and future performance.

**“Cleanliness is Next to Godliness”**

While said by millions of mothers this statement was originally coined by a rabbi in ancient times but it remains current in its applicability to our sniffers. Our sniffers are very sensitive devices. So if we get contamination in them or on them they will continue to try to sniff that contamination until it dissipates or we clean it. Once, a PID user asked a salesperson to demonstrate how to zero a new PID. The salesperson did this repeatedly but the PID user didn't want to believe that this was an easy task. It turns out that the PID user was used to using an old style of PID that was very difficult to clean. Because of this it was never cleaned so it would never zero properly. Here are some tips to keep sniffers clean:

- Do not store sniffers in areas where there are strong odors
- Avoid handling the detector's inlet with hands that might be contaminated with chemicals
- Ensure your hands are clean before changing the inlet filter
- Do not touch contaminated surfaces with a sniffer's probe
- **Do not aspirate (suck) any water or liquids into sniffers**

**Diagnosing a Dirty Sniffer**

Sniffers are sensitive devices and in their use they could become inadvertently contaminated. Here are some tips to know when you have contaminated your sniffer:

- It will not hold a good zero: after zeroing the display creeps up even in a clean environment
- Moving it will give positive readings: contamination may be bouncing around inside
- Readings drop when the probe or filter(s) are removed: the probe or filters are probably dirty
- It will not calibrate: contamination may be coating or may have permanently ruined sensors

## AP-105: Is There Something Out There?

### Cleaning a Dirty Sniffer

Always start with filters and probes. Some PID manufacturers make it easy for users to clean the lamp and sensor of their products. Other products may need to be returned to the manufacturer for cleaning or service. So it is particularly important to be vigilant on cleanliness if your sniffer can only be cleaned by sending it away for service.

### Tubing May Affect Performance

Because Tygon sample tubing quickly absorbs many chemical vapors, it should **NEVER** be used with sniffers. While it is easier to use because it doesn't kink like Teflon tubing, Tygon tubing absorbs many chemicals like a "sponge." This can reduce a sniffer's readouts when chemicals exist and it can cause "false positives" when chemicals don't exist in the environment but are just out-gassing out of the Tygon tubing. Tygon tubing is very common because it is found as the remote sampling tubing supplied with most confined space monitors. Only Teflon, Teflon lined tygon or similar non-reactive tubing should be used with sniffers. Teflon will not absorb chemicals but might get coated. It is recommended to clean Teflon a high vapor pressure solvent that will evaporate quickly if it gets dirty.

### Tygon Tubing Absorbs Jet Fuel

A customer was doing a trial of three different PIDs because they were interested in using a PID for LEL readings for confined space entry into aircraft wing tanks. While all three PIDs were calibrated to the same isobutylene standard, all three gave a different reading when sniffing the wing tank. Using Tygon tubing one PID read low, one high and one in the middle. An investigation demonstrated that the three PIDs had three different pump flows. One at 150 cc/min, the other at 250 cc/min and the third at 500 cc/min. When the pump flow was compared to the PID reading it was shown that the low flow pump had the lowest reading and the PID with the highest flow had the highest reading with the medium flow in the middle. This is because the low flow PID gave the jet fuel the most time to absorb into the tygon tubing so it had the lowest reading and the high flow PID gave the jet fuel the least amount of time for the jet fuel to absorb into the tubing. When the Tygon tubing was replaced

by Teflon tubing all the PIDs read the same when sampling the jet fuel environment.

### Filters May Affect Performance

Heavy/Sticky" chemicals with high boiling point/low vapor pressure may get eliminated/reduced by filters. Sniffing low vapor pressure chemicals like phenols & heat transfer fluids are examples of times when one may need to remove the filter to get accurate readings because the filter may prevent these chemicals from getting to the sensor in the sniffer. When in doubt remove the filter and see if the reading changes. Not only can filters keep chemical from getting to a sniffer but dirty filters can hold these compounds and make the survey meter indicate chemical when there is none present as the contamination out-gasses from the filter.

### MMH, an extreme example of Filters Impacting Performance

Measuring Monomethyl Hydrazine (MMH) with a PID represents an extreme example of how filters can prevent the sniffer from "seeing" a chemical. Theoretically, PIDs with a 10.6 eV lamp can readily detect MMH. However, even with the external filter removed one ppb capable PID took 20 minutes to detect MMH. Upon inspection a small stainless steel "frit" filter was found in the probe. When this filter was removed the PID responded to the MMH in less than 20 seconds. In this case the low vapor pressure and high reactivity of MMH meant that it didn't get to the sensor of the PID until it had completely reacted with the stainless steel frit. Removing all filters will require more frequent cleaning of the PID.

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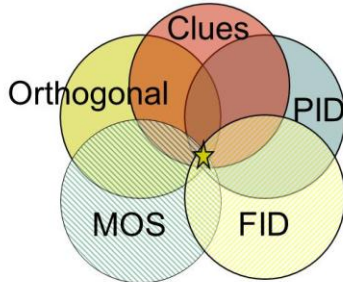
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## Which Sniffer should I use?

### Leaking Fuel Oil Tank

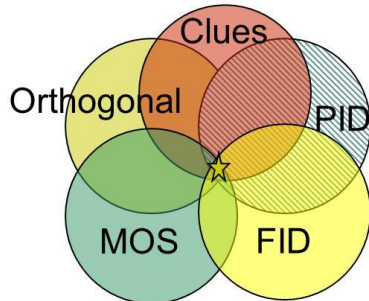
- Clues: smells like oil
- PID: strong, linear reading with good low-end sensitivity
- FID: strong, linear reading with poor low-end sensitivity
- MOS: possible, non-linear reading from natural gas model
- Orthogonal: strong response



★=PID probably the best

### Natural Gas Leak

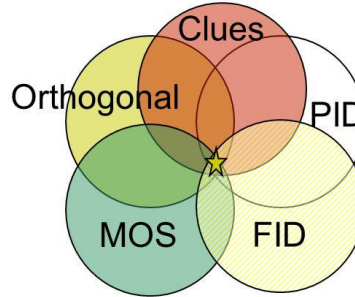
- Clues: smells like “rotten eggs”
- PID: can’t read methane but gives poor reading based on odorants & contaminants (~100s of ppm at LEL levels)
- FID: strong, linear reading
- MOS: excellent leak detector if you have the natural gas model
- Orthogonal: strong response



★= MOS/natural gas is the cheap option if you have one, but FID and Orthogonal will work fine

### Freon Leak

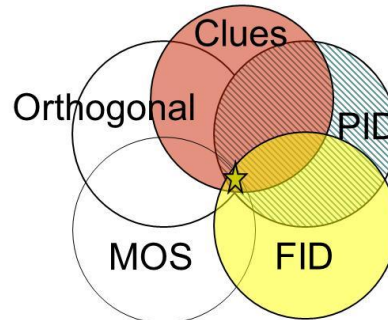
- Clues: hissing/leaking HVAC system
- PID: can’t detect at all
- FID: Possibility of a little detection because the refrigerants all contain carbon, but the freed halocarbons will destroy the FID sensor
- MOS: excellent leak detector if you have the Freon model
- Orthogonal: strong response



★= MOS/Freon is the cheap option if you have one, Orthogonal will work fine

### Refinery EPA Leak Detection

- Clues: Method 21 leak detection
- PID: can do liquid fuels but can’t measure methane, propane and ethane
- FID: strong, linear reading
- MOS: non-linear not appropriate for EPA reports
- Orthogonal: non-linear not appropriate for EPA reports



★=FID is the accepted standard

## AP-105: Is There Something Out There?

### “Chlorine” Smell in a House

#### Problem

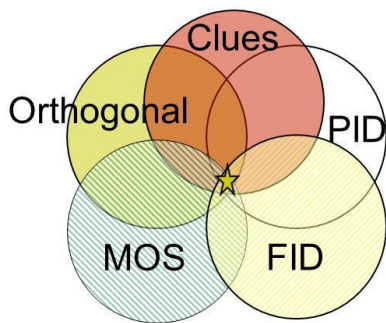
- Fire department responded to a house with complaints of a chlorine smell

#### Response

- “Received call for odor of chlorine in the residence. Homeowner and his wife had been home for about an hour and a half when she noticed a haze in the kitchen and smelled chlorine”
- “On arrival we sent in a two man recon team with ph paper, a single gas electrochemical chlorine meter and 2 multisensor meters with chlorine sensors in them”
- After doing a recon of the dwelling and getting no readings we deployed a second recon team with the ChemPro”
- “In trend mode it began to get readings that spiked in the kitchen and then came down elsewhere in the house. ...we did a quick check without SCBA and found a burnt electrical odor. Upon closer inspection we found it to be the refrigerator-freezer.”

#### Conclusion

- The initial search with chlorine sensors took about 1.5 hours. Using their ChemPro100 they found the smell in 5 minutes
- They determined that the refrigerator motor had burned out and this acrid smell had been confused with the smell of chlorine by the homeowner
- Acrolein and Acrylonitrile can be generated when plastic electrical components overheat and burn, the smell of these chemicals could be confused with chlorine but are not seen by the electrochemical



★ = Orthogonal detector found the problem in 5 minutes

chlorine sensors

- None of the first in sensors could see these chemicals
- Clues: homeowner reports “chlorine” smell
- PID: didn’t detect at all
- FID: not used, but possibly could see it
- MOS: not used, but possibly could see it
- Orthogonal: strong response

### Sick Building

#### Problem

- We responded at approximately 0830 for a report of occupants of an office building experiencing symptoms consistent with a corrosive atmosphere
- The occupants were experiencing respiratory distress as a result of exposure to an unknown chemical.
- While responding our dispatcher notified us that two occupants were being transported to local hospitals for evaluation via personal vehicle

#### Response

- The building was an office/warehouse for our state Department of Environmental Protection (DEP)
- There were no chemicals on scene except common cleaning and household chemicals
- As workers were sitting at their desks they started to experience respiratory discomfort including burning of the eyes, nose, throat, and mouth
- The problem was concentrated in one specific area of the building approximately 60’ x 200’ in size
- A uniformed police officer of the DEP was already on scene as a worker had been dismissed the previous day
- The worker was dismissed for erratic behavior that included drug and alcohol issues and extremely poor performance
- He indicated as he was escorted from the building that they would be sorry
- Based on this information we assumed this threat was followed through on and took every precaution to identify the product.

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## AP-105: Is There Something Out There?

### Actions Taken:

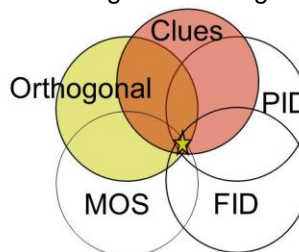
- The initial action was a recon of the building in full firefighting PPE with SCBA
- As part of the Recon the initial entry crew took a four gas, pH paper (wet and dry), PID with a 10.6 lamp, and a radiation detector with a scintillator probe
- Throughout the entire building the readings for all these devices were normal
- The occupancies on either side of the target building was metered as well with the same result
- We decided to try the ChemPro as a last resort using the trend display
- We were able to get an unknown chemical detected alarm in the area where the occupants experienced symptoms
- Directly above the desk area was a discharge for the HVAC system and when the probe of the ChemPro was placed near the discharge grate the trend display increased and went into an alarm
- The assumption was made that the HVAC system was to blame and we activated the system to reproduce the results
- The readings initially increased and then actually went down after activating the system
- After a thorough review of the system it was determined that the system drew fresh air from the outside via a fresh air intake
- An investigation of the surrounding properties revealed that a large cloud had passed by the building at approximately 0815
- The adjacent occupancy had fired up a kiln at 0800 and had cremated several animal carcasses

### Conclusions

- It was determined that the byproducts of the cremation of animals had been drawn into the fresh air intake of the HVAC system and distributed into the office area in question
- As the cloud was gone there was no way to capture readings directly from the kiln. Tedlar samples were taken and ran on a GasID as well as an FID with no results
- ***If not for the ChemPro we may have mistaken this event for a psychosomatic sick building call and would have never found the source of the problem.*** We

simply would have ventilated and had the occupants go about their day with no definitive answer

- Our findings were able to help the emergency department of the receiving hospital treat the patients that were transported
- While we were not able to definitively ID the product we were able to rule out several other products and locate the source of the problem using the ChemPro
- Clues: workers got sick in an office building
- PID: didn't detect at all
- FID: not used, but can't see acids
- MOS: not used, but can't see acids
- Orthogonal: strong response



★ = Orthogonal detector found the problem in minutes

### If you can see "it" you can find "it"

Survey sensors are one of your best tools to quickly identify if something is out there. Survey sensors are our "Sniffers."

- If you can see "it" you can find "it"
- If you can find "it" you can clean "it" up
- If you can see "it" you can fix the problem

### About the Author

Christopher Wrenn is the Sr. Director of Sales and Marketing for Environics USA a provider of sophisticated gas & vapor detection solutions for the military, 1st responder, safety and homeland security markets. Previously Mr. Wrenn was a key member of the RAE Systems team. Chris has been a featured speaker at more than 20 international conferences and has written numerous articles, papers and book chapters on gas detection in HazMat and industrial safety applications.

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