Is There Something Out There?

Handheld survey sensing technologies, how to apply them and get the most from them

Why are Survey Sensors Important?

- 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
- On their own, survey sensors will not tell you what that “something” is, but they can often quickly tell you where it is coming from and give you a quick idea of how much is there
- Coupled with clues (like placards, waybills, etc.) that provide identification of a chemical some survey sensors (PIDs & FIDs) can quickly tell you how much is there (quantification)

Why are Survey Sensors Important?

- 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
- Survey sensors are our best “Sniffers”

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.

Topics: Survey Sensors

- Quantifiable Survey Tools
  - What is a PID?
  - What is a FID?
  - The Power of Correction Factors in PIDs & FIDs
- Non-quantifiable Survey Tools
  - What is a MOS?
  - What are Orthogonal Detectors?
- Tips for Using and Maintaining Sniffers
- Putting it all together

What is Quantification ?

- PIDs and FIDs are single sensor detectors that are relatively linear
- When a single species of a detectable chemical gas/vapor is present they can easily provide an accurate ppm/ppb measurement using Correction Factors (CFs)
- Under certain conditions they can be helpful with quantification of mixtures

Parts Per Million (ppm)

- 1 ppm is the same as 1 inch in 16 miles
- 1 ppm is the same as 1 oz in 10,000 gallons
- ppm (and ppb or parts per billion) are commonly used to express concentrations of gases and vapors

  - 1 pbb is the same as 7 people out if the entire earths population

Parts Per Billion (ppb)

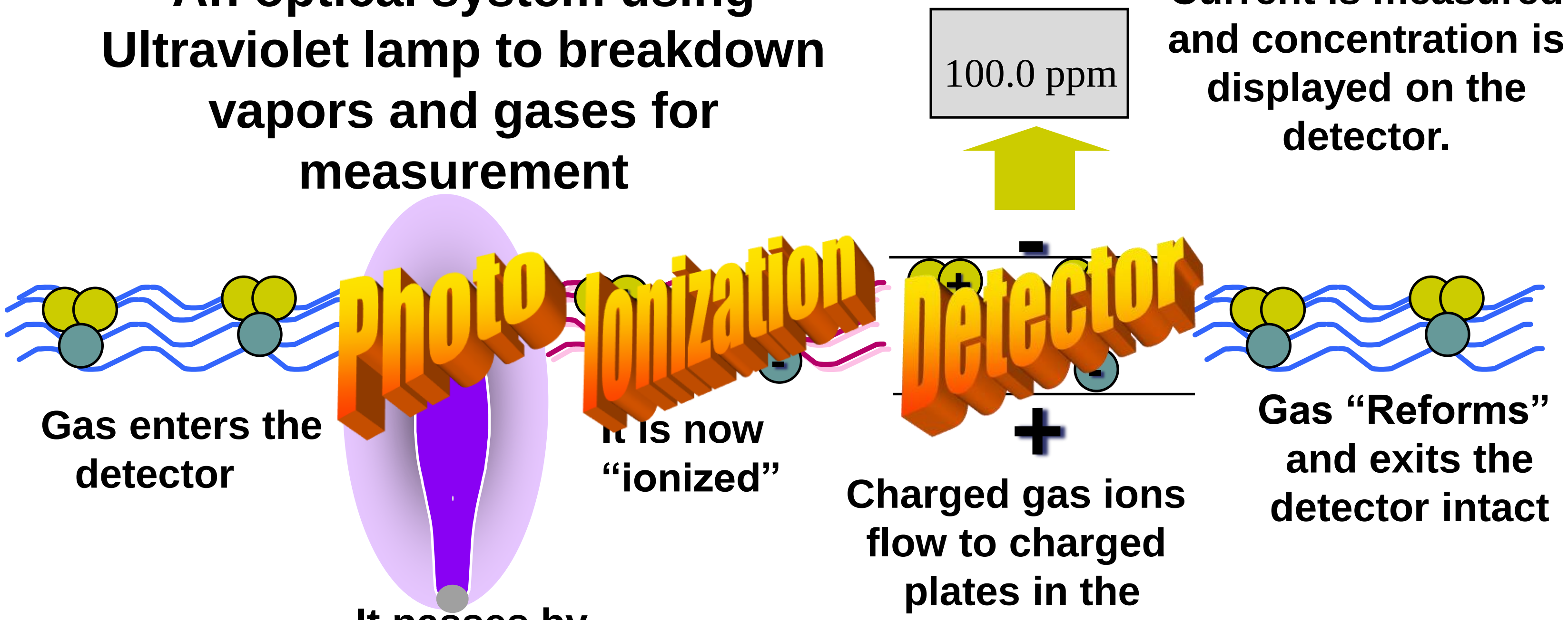
- Some survey detectors are ppb capable
  - PIDs like ppbRAE
  - Orthogonal detectors like ChemPro100i
- PPB capable products help you to even “see” smells

What is a PID?

- **PID** = Photo-Ionization Detector
- Detects VOCs (volatile organic compounds) and Toxic gases from <10 ppb to as high as 10,000 ppm
- Fuel products are easily measured with a PID
- A PID is a very sensitive broad spectrum monitor, like a “low-level LEL”

How does a PID work?

An optical system using Ultraviolet lamp to breakdown vapors and gases for measurement



Current is measured and concentration is displayed on the detector.

Gas enters the detector

It passes by the UV lamp

It is now "ionized"

Charged gas ions flow to charged plates in the sensor and current is produced

Gas "Reforms" and exits the detector intact

What does a PID Measure?

- Organics: Compounds Containing Carbon (C)
  - **Aromatics** - compounds containing a benzene ring
    - BETX: benzene, ethyl benzene, toluene, xylene
  - **Ketones & Aldehydes** - compounds with a C=O bond
    - acetone, MEK, acetaldehyde
  - **Amines & Amides** - Carbon compounds containing Nitrogen
    - diethyl amine
  - **Chlorinated hydrocarbons -** trichloroethylene (TCE)
  - **Sulfur compounds –** mercaptans, carbon disulfide
  - **Unsaturated hydrocarbons** - C=C & C C compounds
    - butadiene, isobutylene
  - **Alcohol's**
    - Ethanol, IPA
  - **Saturated hydrocarbons**
    - butane, octane
- Inorganics: Compounds without Carbon
    - Hydride Gases
      - Ammonia. Phosphine, Arsine

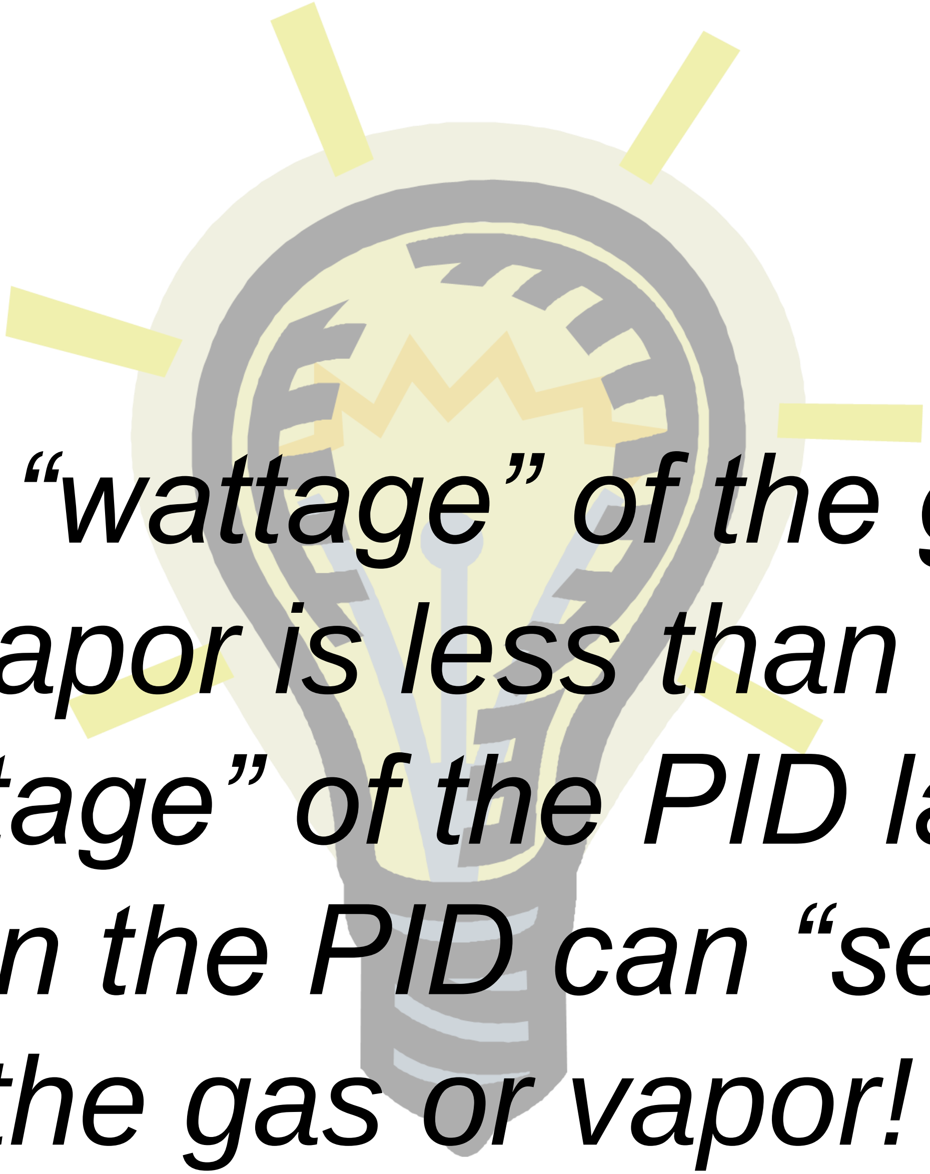
What PIDs Do Not Measure

- Radiation
- Air
  - N_2
  - O_2
  - CO_2
  - H_2O
- Toxics
  - CO
  - HCN
  - SO_2
  - Cl_2
- Non-volatiles:
  - PCBs
  - Greases
- **Pure** Short Chain Saturated Hydrocarbons
  - Pure Methane (CH_4)
  - Pure Ethane (C_2H_6)
  - Pure Propane (C_3H_8)
- Acids Gases
  - HCl
  - HF
  - HNO_3
- Others
  - “Freons”
  - Ozone O_3
  - Hydrogen Peroxide

What does a PID Measure?

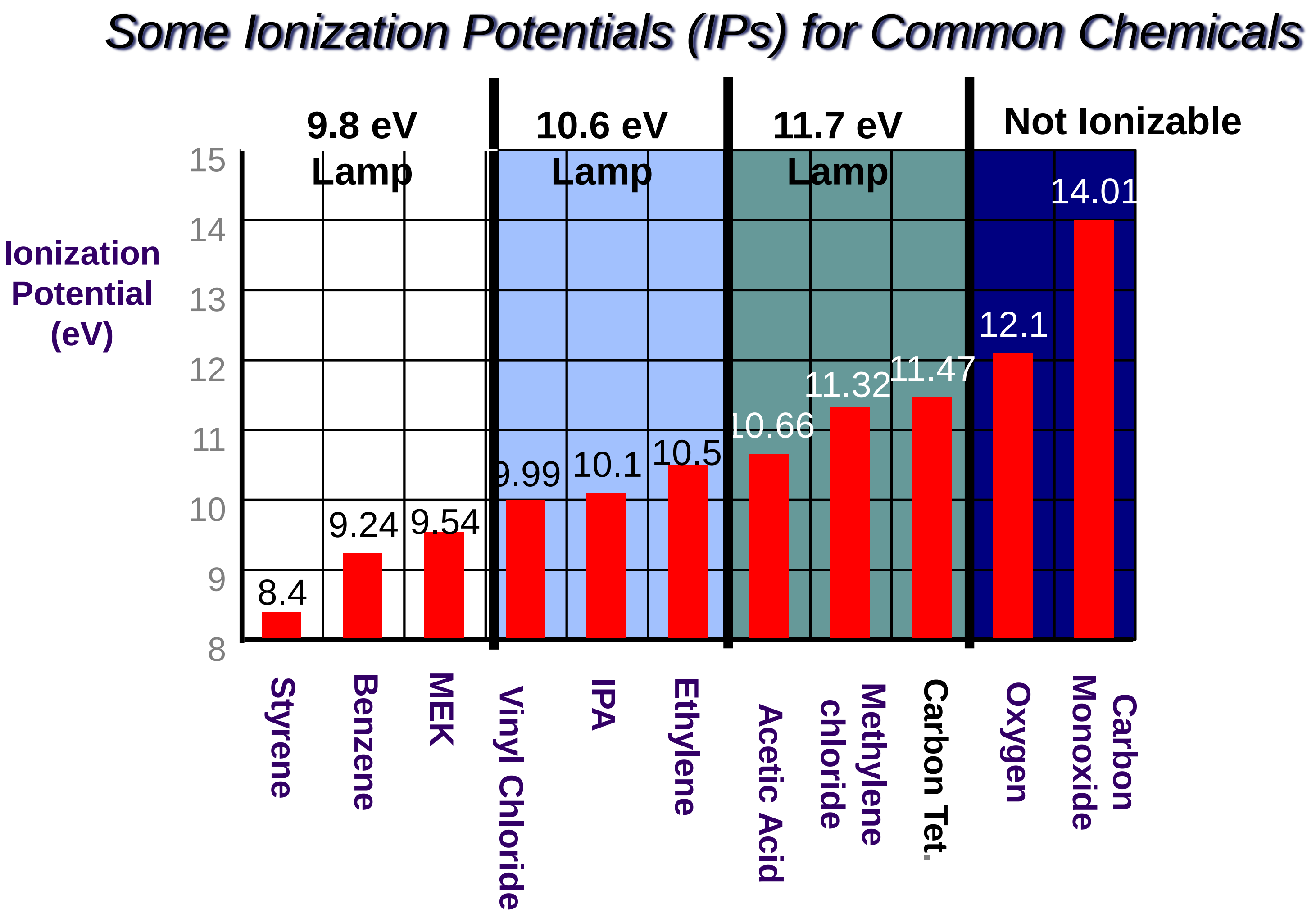
Ionization Potential

- IP determines if the PID can “see” the gas
- If the IP of the gas is less than the eV output of the lamp the PID can “see” it
- Ionization Potential (IP) does not correlate with the Correction Factor
- Ionization Potentials are found in the NIOSH Pocket Guide, many chemical texts and PID manufacturer correction factor charts (for example RAE System TN-106)



If the “wattage” of the gas or vapor is less than the “wattage” of the PID lamp then the PID can “see” the gas or vapor!

What does a PID Measure?



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”
- 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
- Generally speaking a PID with a 10.6eV lamp is largely a liquid hydrocarbon detector

Why mostly 10.6 eV and not 11.7 eV Lamps?

- 9.8 & 10.6 provide more specificity
- 10.6 lasts 24-36 months
- 10.6 provides best resolution
- 10.6 costs less ($195)
- 11.7 is required for high energy compounds like Methylene Chloride
- 11.7 crystal absorbs water and degrades
- 11.7 lasts about 2-3 months
- 11.7 costs more ($295 and higher)

Short 11.7 eV lamp life

- Remediation contractor complained about short (<30-day) lamp life used on the PIDs they were using to alert workers to mask up
- Investigation found that the contractor was using 11.7eV lamps in a very hot, very humid environment
- The contractor was remediating a gunnery range where vehicles were shot up, the threat appeared to just be hydrocarbon contamination of the swampy soil with a high water table

Short 11.7 eV lamp life

- When asked why they were using an 11.7eV lamp, the contractor replied that it was required by the SOP (Standard Operating Procedures)
- After a week of trying the Industrial Hygienist responsible for the SOP was located, when asked why an 11.7eV lamp was specified the IH replied “if 10.6 was good, I figured 11.7 would be better”
- More power doesn’t necessary work when specifying PID lamps
- When changed over to 10.6eV lamp they had great performance

11.7 Lamp Calibration Concerns

- While isobutylene is commonly used to calibrate all PIDs it is recommended to calibrate 11.7 lamps with propane (at the same calibration values)
- Isobutylene is easily seen by a 10.6 lamp but propane is only seen by an 11.7 lamp
- Much like calibrating a LEL sensor with methane is a more robust calibration, calibration with propane makes sure that the 11.7 lamp is “seeing” 11.7 gases/vapors

PID “Quenching”

- Some gases and vapors absorb ultraviolet light without ionizing in the PID sensor
  - Methane, ethane, moisture and high analyte concentrations are examples
  - Modern PID sensor designs with very small lamp to sensor volumes minimize this effect
  - Some modern PIDs continuously measure moisture and adjust PID gain on the fly in response to changes in humidity
    - Older non-compensated PIDs may read less than newer units in these kinds of atmospheres

Which PID for Me?





- Multigas with PID
  - Like your Swiss Army Knife or Leatherman
  - If you have only one tool this should be it


- Straight PID
  - Like your DeWalt 18volt driver
  - While the Leatherman has a Phillips screwdriver on it you wouldn’t hang drywall with it
  - Best for decon and leak detection or situations where the gas in question could kill other sensors

PID Summary

<u>Advantages</u>

- + 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
- + Doesn't require O_2
- + Stores well
- + Low consumables (cal gas)
- + Largely poison resistant

<u>Disadvantages</u>

- – Has many "Blind Spots" and will not measure many toxic chemicals (like Cl_2) and short change 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)

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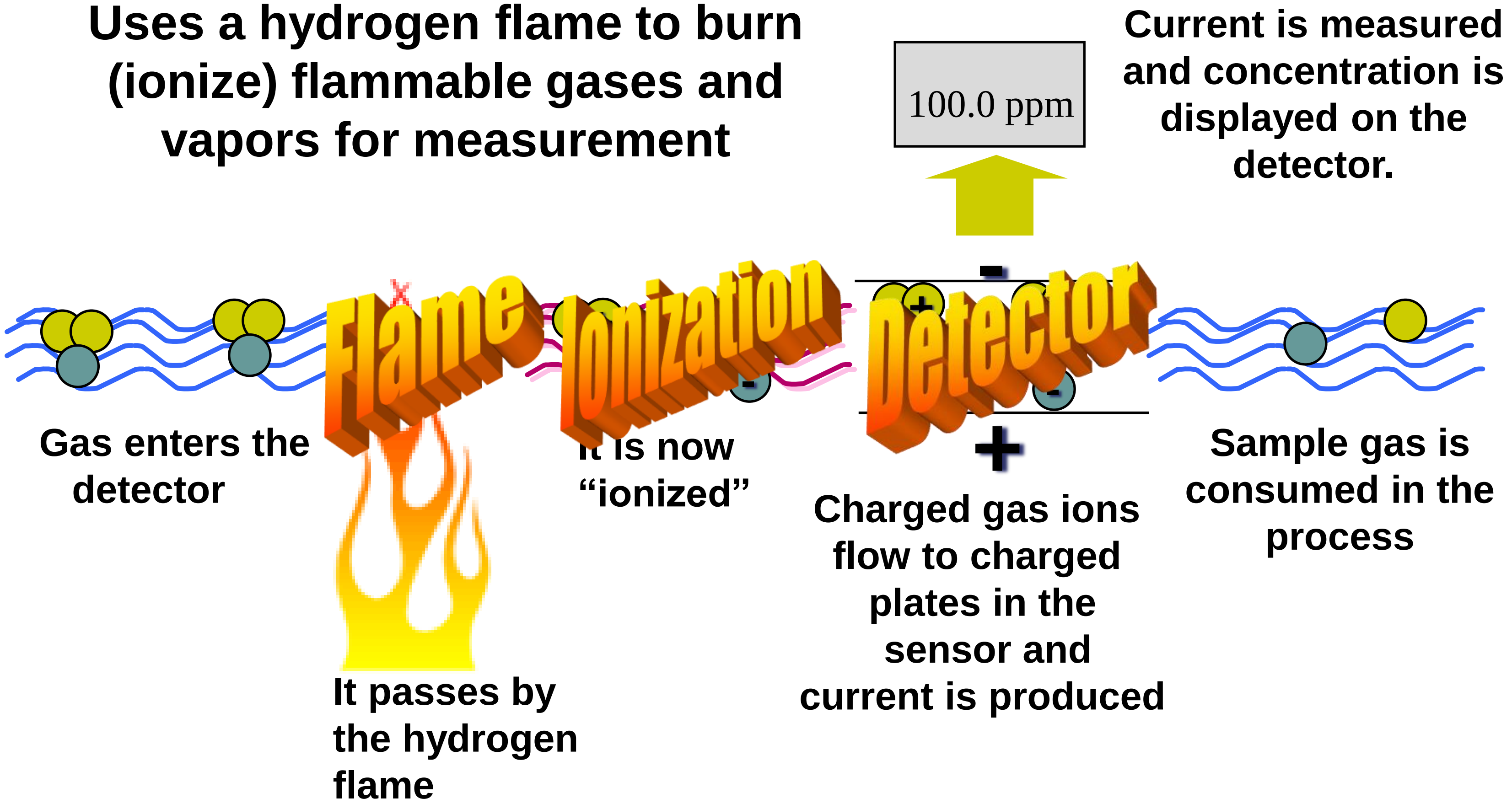
What is a FID?

- **FID** = Flame Ionization Detector
- Detects flammable carbon containing gases and vapors from ppm to as high as 50,000 ppm (5% by volume)
- Like the PID, the FID is a very sensitive broad spectrum detector, like a “low-level LEL”

How does a FID work?

Uses a hydrogen flame to burn (ionize) flammable gases and vapors for measurement



What does a FID Measure?

- Organics: Compounds Containing Carbon (C)
  - **Aromatics** - compounds containing a benzene ring
    - BETX: benzene, ethyl benzene, toluene, xylene
  - **Ketones & Aldehydes** - compounds with a C=O bond
    - acetone, MEK, acetaldehyde, formaldehyde
  - **Amines & Amides** - Carbon compounds containing Nitrogen
    - diethyl amine
  - **Chlorinated/halogenated hydrocarbons -** trichloroethylene (TCE), freons can cause problems because the halogen released in combustion can destroy the FID sensor
  - **Sulfur compounds –** mercaptans, carbon disulfide
  - **Unsaturated hydrocarbons** - C=C & C C compounds
    - butadiene, isobutylene
  - **Alcohol's**
    - Ethanol, IPA, methanol,
  - **Saturated hydrocarbons**
    - butane, octane, methane, propane, ethane
- Inorganics: Compounds without Carbon cannot be burned and cannot be detected with FID
- FID gains formaldehyde, methanol, methane, propane and ethane while losing the hydride gases compared to the PID

What FIDs Do Not Measure

- Inorganics: Compounds without Carbon cannot be burned and cannot be detected with FID
- Air
  - N_2
  - O_2
  - H_2O
- Toxics w/o C
  - HCN
  - SO_2
  - Cl_2
- Acids
  - HCl
  - HF
  - HNO_3
- Others
  - Ozone O_3

FID Summary

Advantages

- + Linear, quantifiable measurements (although multiple CFs may be required)
- + Measure from ppm-5% vol (0.5-50,000 ppm)
- + Measures CH_4 and nearly all organic gases and vapors
- + Stores well

Disadvantages

- – Has many “Blind Spots” and will not measure many toxic chemicals (like Cl_2)
- – Lacking in low-end sensitivity (<10ppm)
- – High consumables (H_2 & Cal gas)
- – Requires O_2 > 14%
- – Halogens can destroy the FID sensor
- – Expensive to purchase

PIDs vs. FIDs

- 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

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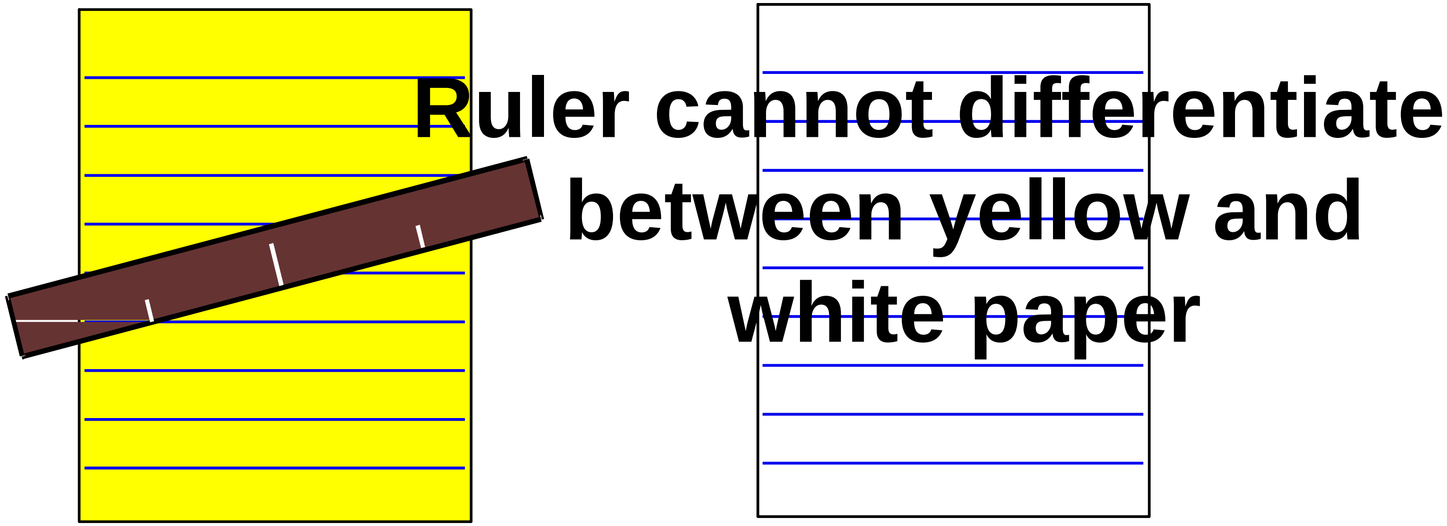
Selectivity Vs Sensitivity

- PIDs & FIDs are very sensitive and accurate
- PIDs & FIDs are not very selective



PIDs & FIDs can't differentiate between acetone & xylene

Selectivity Vs Sensitivity

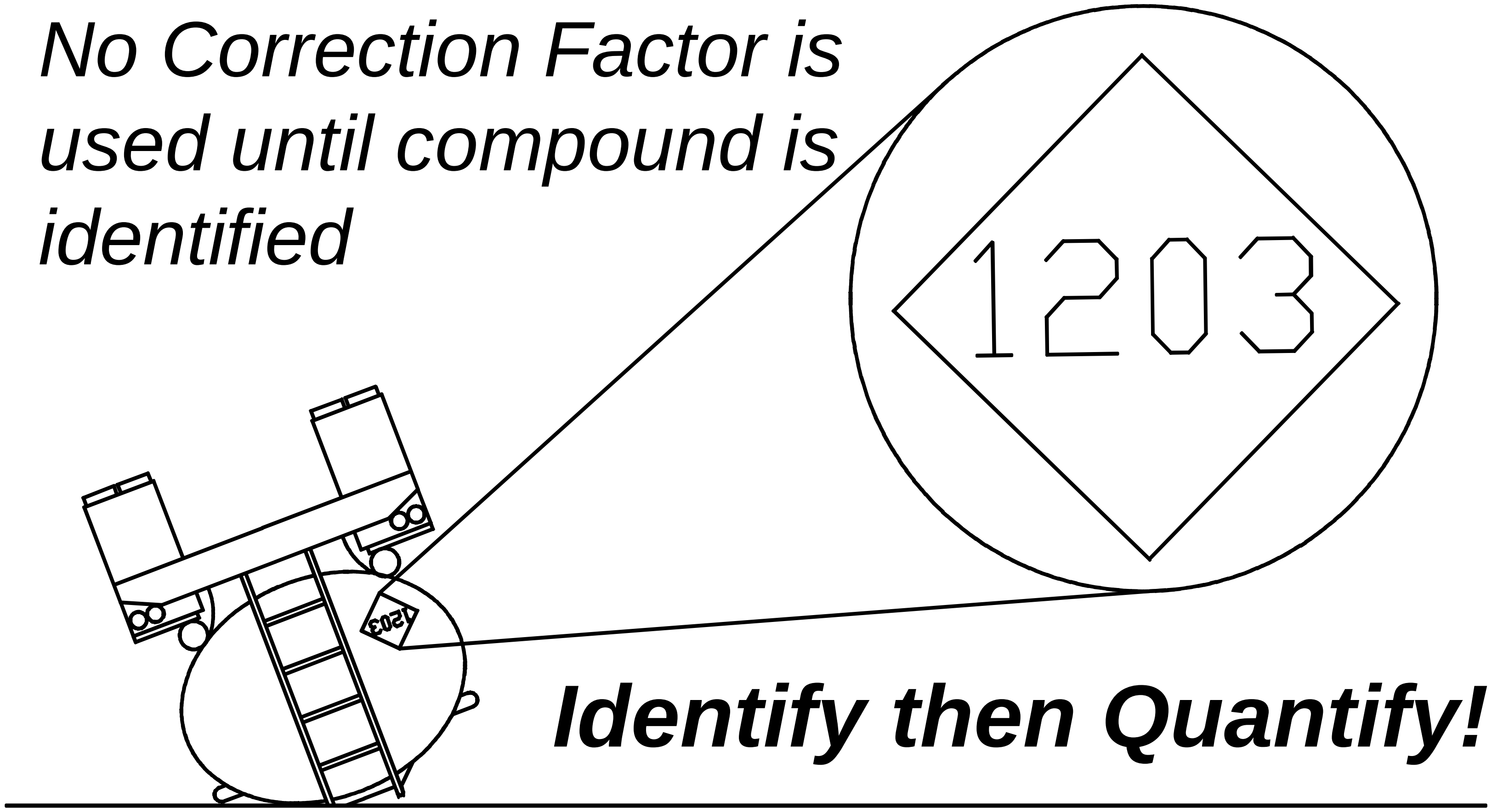
Use your head for Selectivity and the PID or FID for Sensitivity

- PIDs & FIDs are sensitive to chemicals but not specific
- Correction Factors set correct PID or FID scale
- PID or FID should stay on Isobutylene or Methane (Calibration gases) until unknown is identified

PIDs & FIDs are a Gas Chromatograph where the column is between your ears!

Selectivity Vs Sensitivity

No Correction Factor is used until compound is identified



Identify then Quantify!

What is a Correction Factor?

Correction Factors are the key to unlocking the power of PIDs & FIDs for Assessing Varying Mixtures and Unknown Environments

What is a Correction Factor?

- **Correction Factor** (CF) is a measure of the sensitivity of the PID or FID to a specific 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 turn the “volume” up or down depending on how “loud” or “quiet” a gas or vapor is on the detector
- Correction Factors allow calibration on cheap, non-toxic “surrogate” gas
  - Originally PIDs were calibrated to a benzene scale
  - Now all PIDs are calibrated to an isobutylene scale
  - FIDs are calibrated to a methane scale

Multiplier Response Factors

- Most common type
- Calculated by dividing the actual concentration of a chemical by the detector response
  - MRF = Actual Concentration/Measured Response
- If 100 ppm of a chemical produces 50 ppm reading in isobutylene units then the response factor would be 2
  - $50ppm_{iso}$ x 2 = $100ppm_{chemical}$
- Multiply the reading in calibration gas units by the correction factor to arrive at the actual concentration
- Used by Biosystems, Industrial Scientific, Ion Science, MSA, Photovac, RAE & Thermo

10.6eV Lamp MRFs Compared

Chemical	RAE	Ion Science	Photovac (2020-Pro)	MSA (Sirius)	HNu*	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

Why do CFs vary between manufacturers?

- Variation in CFs is due to differences in sensor and lamp design
- Some sensors are big and some have a smaller volume and are more efficient
- Then you also have lamp variation.
  - HNU rates their magnesium fluoride lamp as a 10.2eV lamp because it's not as efficient between 10.2-10.6eV
  - RAE rates its magnesium fluoride crystal as a 10.6 lamp, you can see that the correction factors between 10.2-10.6eV are higher on the RAE 10.6eV lamp than below 10.2eV which indicates that it is less efficient
  - Some 11.7eV lamps are better than others
  - Lamp differences include how the lamp is built, the gas mixture inside the lamp and even how the crystals are prepared
- The design choices that manufacturers make result in differences in CFs
  - That's why manufacturers determine CFs by lab testing on the chemicals of interest
  - For some manufacturers you see tight clusters of CFs, then you see them vary at the extremes

Know your response factors

- Don’t interchange response factors, 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 has 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

CF's measure sensitivity

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***
- 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 $\leq$ 10***
- Use PID/FIDs for gross leak detectors when CF > 10

CF's measure sensitivity

- You can think of CFs like combs
  - If you only have a few hairs (a toxic chemical) you need a fine tooth comb, this is a low CF

  - If you have a lot of hair (a less toxic chemical) a more coarse comb will do, this is a higher CF

Should I Use a PID?

- Benzene
  - CF with a 10.6 lamp is 0.5
  - Exposure limit is 1.0 ppm
    - ***If Exposure limit is < 10 ppm, CF ≤ 1***
  - PID is a good choice for exposure limit decisions & sniffing
- Ethylene Oxide
  - CF with a 10.6 lamp is 13
  - Exposure limit is 1.0 ppm
    - ***If Exposure limit is < 10 ppm, CF ≤ 1***
    - Use PIDs for gross leak detectors when CF > 10
  - PID is NOT a good choice of exposure limit decisions
  - Still ok as a “sniffer”

Should I Use a PID?

- Ammonia
  - CF with a 10.6 lamp is 9.7
  - Exposure limit is 25 ppm
    - ***If Exposure limit is > 10 ppm, CF $\leq$ 10***
  - PID is a good choice for exposure limit decisions & sniffing
- Acetic Acid
  - CF with a 10.6 lamp is 22, CF with 11.7 lamp is 2.6
  - Exposure limit is 10 ppm
    - ***If Exposure limit is < 10 ppm, CF $\leq$ 1***
  - 10.6 lamp is definitely NOT a good choice of exposure limit decisions
  - 11.7 lamp isn’t any better,
  - This MAY NOT be a good PID application

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

$$0.5_{CF} \times 100\ ppm_{iso} = 50\ ppm_{toluene}$$

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

$$9.7_{CF} \text{ x } 100 \text{ ppm}_{iso} = 970 \text{ ppm}_{ammonia}$$

Correction Factors

- CFs are scaling factors
- Imagine that your PID is a car radio
  - You need to turn the volume down by ½ (multiply by 0.5) to accurately "hear" toluene relative to isobutylene units
  - You need to turn the volume up 9.7 times to accurately "hear" ppm of ammonia relative to isobutylene units

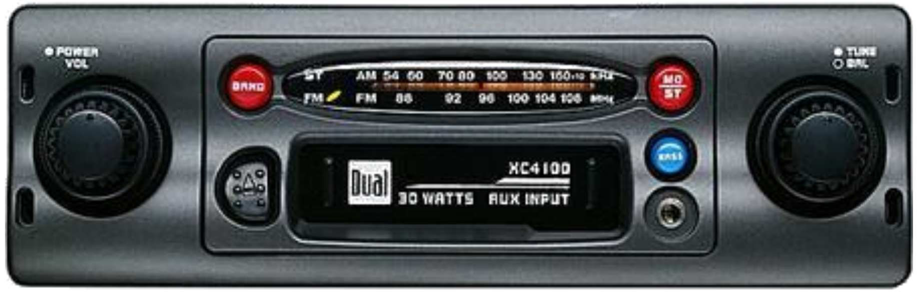


Photo courtesy
www.crutchfield.com

Making a Decision with a PID/FID

Two sensitivities must be understood to make a decision with a PID/FID

- **Human Sensitivity:** as defined by AGCIH, NIOSH, OSHA or corporate exposure limits
- **PID Sensitivity:** correction factor as defined through testing by the manufacturer of your PID/FID

ONLY USE A CORRECTION FACTOR FROM THE MANUFACTURER OF YOUR PID/FID!

Making a Decision with a PID/FID

Three scenarios on how to make a decision with a PID/FID

- Single Gas/Vapor
- Gas/Vapor mixture with constant make-up
- Gas/Vapor mixture with varying make-up

PID/FID Alarms: Single Chemical

Single Chemicals are easy

- Identify the chemical
- Set the PID/FID Correction Factor to that chemical
- Find the Exposure Limit(s) for the chemical
- Set the PID/FID alarms according to the exposure limits

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

Solving a Paint Smell issue

- As the final step of restoring a Victorian house, the radiators had to be painted
- Latex paint is not recommended for this task as it puts an insulating layer of paint on the radiator making them less efficient
- Either a silver or gold paint solvent based paint is recommended for this task
- Once painted and with the heat back on, an occupant of the house complained of the “toxic” atmosphere
- So we start by looking at the contents of the can of paint

PID Alarms: Constant Mixtures

Paint: 15% Styrene and 85% Xylene

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

First calculate the exposure limit (EL) Where:

- 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
- Ref: NIOSH Pocket guide

PID Alarms: Constant Mixtures

Paint: 15% Styrene and 85% Xylene

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

Then calculate the Correction Factor (CF) Where:

- 0.15 is 15% styrene
- 0.4 is the CF* styrene
- 0.85 is 85% xylene
- 0.6 is the CF* for xylene
- Referencing the PID manufacturer’s correction factor chart

* Relative sensitivities are for example only, please consult your detector manufacturer for sensitivities specific to your product

PID Alarms: Constant Mixtures

Paint: 15% Styrene and 85% Xylene

- The sealed living room read 120_{iso} on the PID in Isobutylene units
- Multiplying it by the correction factor of 0.56_{mix} the real reading on the mixture was 67.2_{mix} ppm
- This is under the calculated exposure limit of 87_{mix} ppm for the mixture
- However, styrene has an olfactory threshold of ~2ppm, so even at safe levels the paint vapors have a distinct smell and the difference between olfactory threshold and toxicity was discussed

PID Alarms: Constant Mixtures

Constant Mixture Shortcut #1

Paint: 15% Styrene and 85% Xylene

- Lets consider it to be just Xylene because the toxicity of styrene and xylene is in the same power of ten (styrene = 50, xylene = 100)
- In the sealed up living room I got a reading of 120 on the PID in Isobutylene units
- Multiplying it by Xylene CF* of 0.59 my real reading as Xylene is 70.8 ppm
- This is under the Xylene exposure of 100 ppm

* Relative sensitivities are for example only, please consult your detector manufacturer for sensitivities specific to your product

PID Alarms: Constant Mixtures

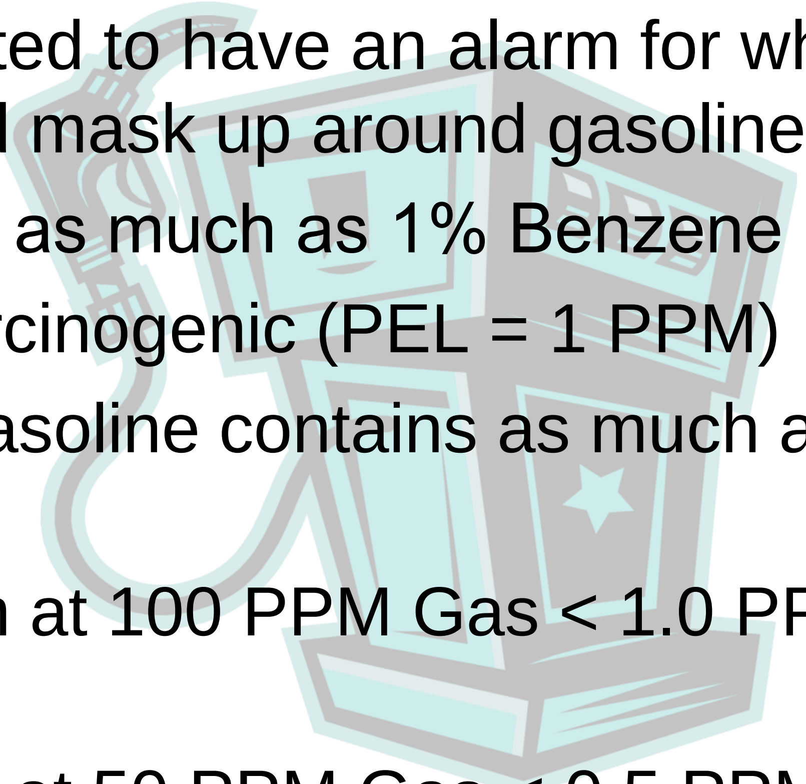
Constant Mixture Shortcut #2

- Find the average make-up of the mixture
- Determine the most toxic VOC
- Base setpoints on the most toxic VOC

WARNING: Shortcuts only provide a quick guideline!

PID Alarms: Constant Mixtures

Gasoline



- A refinery wanted to have an alarm for when workers should mask up around gasoline vapors
- “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

PID Alarms: Varying Mixtures

The Controlling Compound

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

PID Alarms: Varying Mixtures

- A vitamin C plant wanted to find a way to alert their workers when it was safe to take their respiratory protection off in areas that contained ethanol, toluene and acetone vapors
- A PID salesman said this was easy to do because workers could set the “smart” PID up as an ethanol, toluene or acetone detector
- But management didn’t want the workers “messing” with their detectors and workers really couldn’t know exactly which solvent vapor they had, it could vary a lot
- So the salesman sought a simple solution

PID Alarms: Varying Mixtures

Chemical Name	10.6eV CF	Exposure Limit Chemical
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
- This table only provides half of the decision making equation
- Might as well compare 1000 apples to 100 oranges

* Relative sensitivities are for example only, please consult your detector manufacturer for sensitivities specific to your product

PID Alarms: Varying Mixtures

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

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

PID Alarms: Varying Mixtures

Chemical Name	10.6eV CF*	EL Chemical	EL Isobutylene
Ethanol	12	1000	83.33
Toluene	0.50	100	200.00
Acetone	1.1	750	681.82

- Now one can compare “Apples to Apples”
- Its lower sensitivity on the PID makes Ethanol the “controlling compound” when the Exposure Limits are expressed in equivalent “Isobutylene Units”

* Relative sensitivities are for example only, please consult your detector manufacturer for sensitivities specific to your product

PID Alarms: Varying Mixtures

- Setting the PID to 83 ppm alarm in Isobutylene units protects from all three chemicals no matter what their ratio
- 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 brand that has a published CF list.

PID Alarms: Varying Mixtures

- EL_{iso} thresholds are a tool to help characterize unknown environments
- If the reading on your PID is below the EL_{iso} for a chemical there isn’t a threat
- The lower the reading in isobutylene units on your PID the less risk
  - 100 ppm EL_{iso} should be safer than 1000
  - 10 ppm EL_{iso} should be safer than 100
  - 1 ppm El_{iso} should be safer than 10

PID Alarms: Varying Mixtures

A RAE 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 solvents like Xylene, Toluene, MEK, Acetone
- **65 chemicals at a 50 ppm alarm**, from Cyclohexanone to Acetone.
- **81 chemicals at a 25 ppm alarm**, from Diethylamine to Acetone.
- **105 chemicals at a 10 ppm alarm**, from Toluidine to Acetone.
- **140 chemicals at a 1 ppm alarm**, from Diethylenetriamine to Acetone

Ref: RAE AP-221

PID Alarms: Varying Mixtures

- Setting an alarm to 1 ppm provides the highest protection, but it also causes the most alarms.
- An alarm point of 1 ppm would be similar to always wearing a Level A suit!
- A 50 ppm EL_{iso} alarm is appropriate for going to respiratory protection in a fuel tanker roll-over because an EL_{iso} alarm of 50 is very conservative for all hydrocarbon fuels

PID Alarms: 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

- **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

PID Alarms: Varying Mixtures

- EL_{iso} are only one gauge of the threat level in any circumstance
- The PID user must use all of the clues present to reach a decision

Topics: Survey Sensors

- Quantifiable Survey Tools
  - What is a PID?
  - What is a FID?
  - The Power of Correction Factors in PIDs & FIDs
- Non-quantifiable Survey Tools
  - What is a MOS?
  - What are Orthogonal Detectors?
- Tips for Using and Maintaining Sniffers
- Putting it all together

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

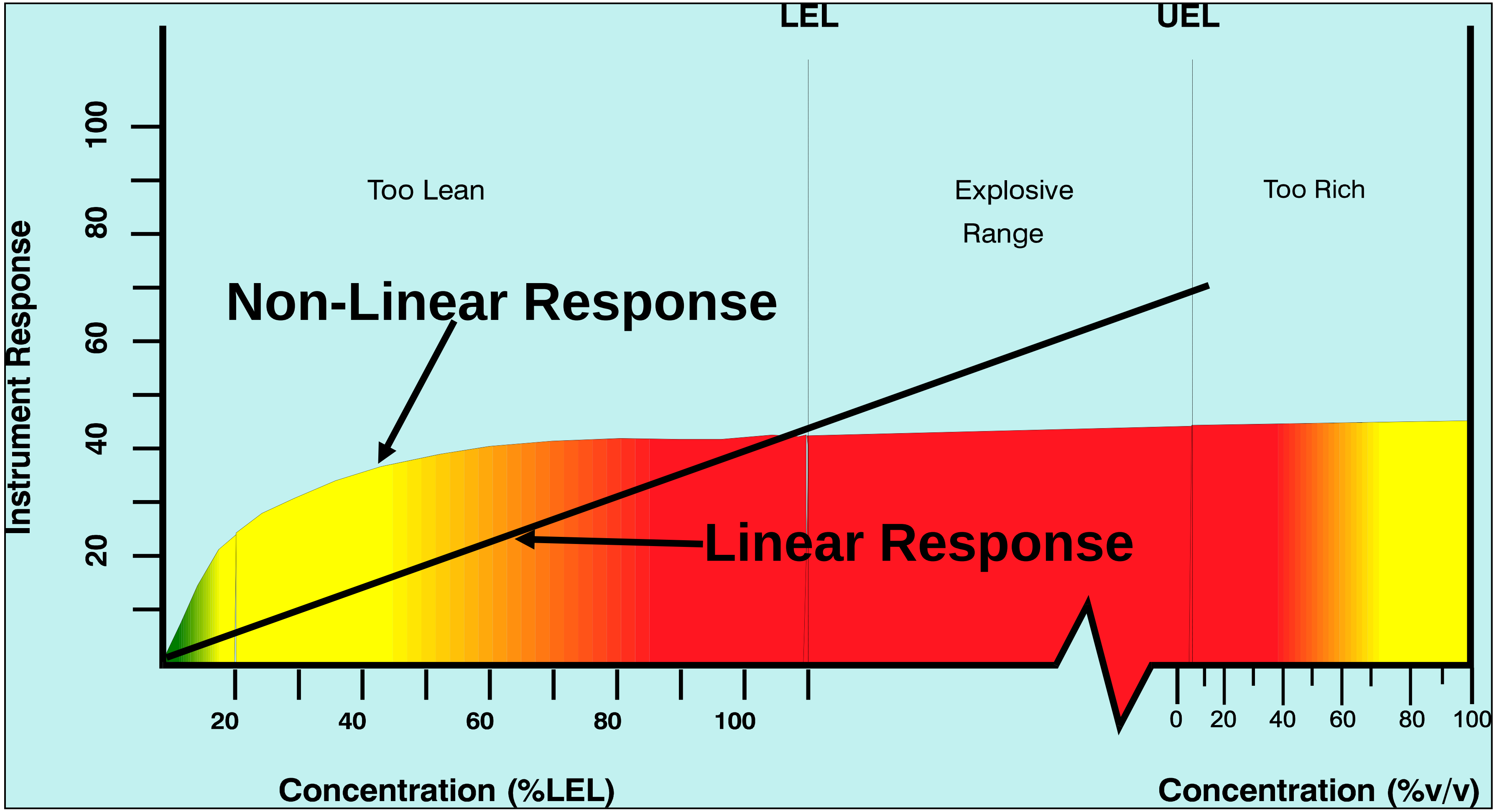
MOS Sensors

- 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
  - Halogenated hydrocarbons: refrigerants (“Freons”)
  - Hydrocarbons: alcohols, ethers, ketone, aromatics
  - 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

MOS Sensors

- Affordable: (some people call them the “Poor Man’s PID”)
- Non-linear output limits accuracy (they are a rubber ruler) and prevents accurate (quantifiable) ppm readings
  - Leads to Audible “Geiger Counter” style of user interface because non-linearity makes a ppm display problematic
- Sensitive to Temperature and Humidity which can lead to false alarms when not compensated
- Can be poisoned & ruined by over-ranging like LEL sensors

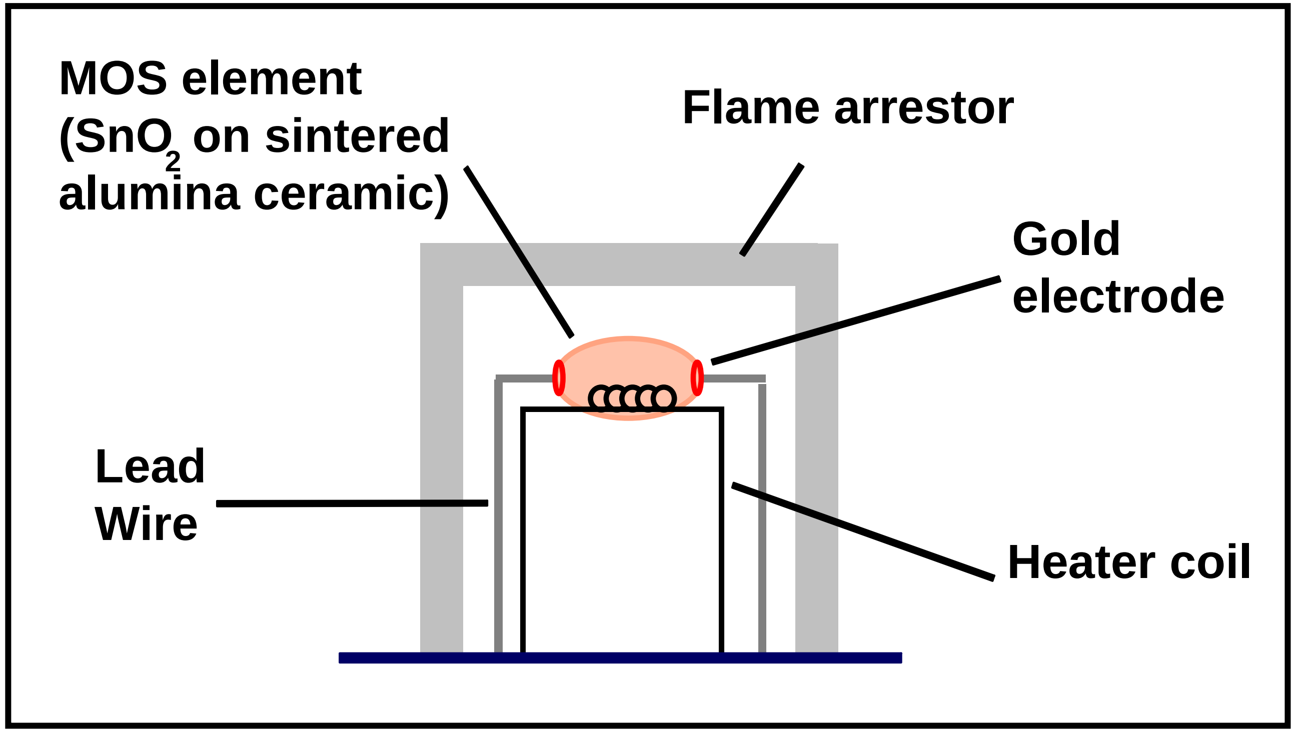
MOS Sensor Response Curve



What is a MOS Sensor?

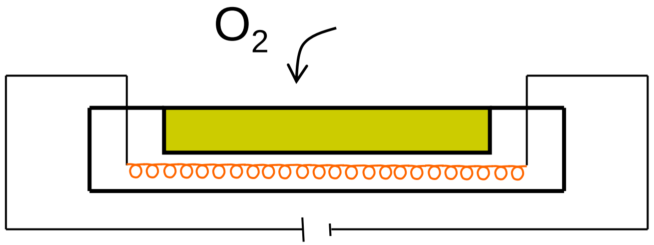
- Tin dioxide (SnO_2) on sintered alumina ceramic that is heated
  - Essentially it is a porous metal sponge on a stove
- In clean air electrical resistance is high
- Contact with reducing gases (such as CO or combustibles) increases conductivity
- Sensitivity to specific gases depends on temperature of sensing element and how the substrate is doped

MOS Sensors

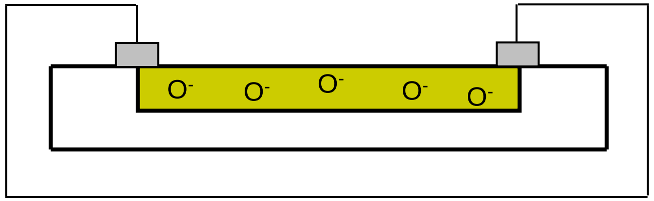


MOS element
(SnO2 on sintered
alumina ceramic)
Flame arrestor
Gold
electrode
Lead
Wire
Heater coil

MOS Sensors



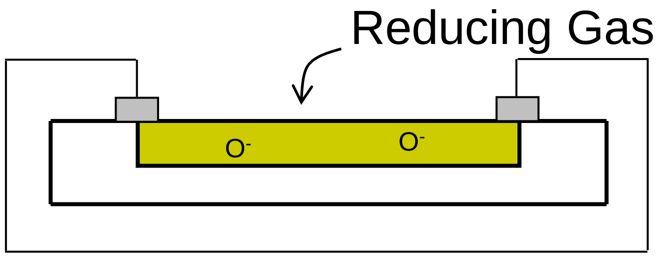
1. Heating
2. O_2 absorption



Big Resistance

3. Oxygen barrier

→ High resistance



Resistance Decreases

4. Reducing gas

→ Resistance decreases

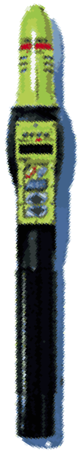
MOS Summary

Advantages

- + Very sensitive detectors
- + Selectivity may be changed by temperature or the doping of the sensor
- + Most inexpensive survey detector
- + Store well
- + No consumables

Disadvantages

- – Non-linear measurement, can't accurately tell you how much is there once you identify it
- – Requires O_2
- – Will not measure all chemicals



Topics: Survey Sensors

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  - What are Orthogonal Detectors?
- Tips for Using and Maintaining Sniffers
- Putting it all together

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
- Because all the sensors contribute on any single decision the orthogonal detector is much more than the sum of the individual sensors
- 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.

Natural Gas doped MOS

+

Refrigerant doped MOS

+

FID

+

PID

=

Orthogonal

Orthogonal “Sniffers”

- 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}Am NRC exempt source of the ChemPro100i produces approximately 60KeV (60,000eV) so it can “see” hundreds 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

Orthogonal “Sniffers”

- The ChemPro100i can be easily used as a survey tool, much like a PID “on steroids” to quickly “see” concentration trends
- The graphical “Trend” screen facilitates finding the source
- 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

Orthogonal Detectors as a Sniffer

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 you how much is there once you identify it
- Requires O_2

Topics: Survey Sensors

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Cleanliness is Next to Godliness

- Sniffers are sensitive devices, how they are used or misused can affect their immediate and future performance.
- While said by millions of mothers this statement was originally said by John Wesley, the founder of Methodism, in a sermon in 1778, but it remains current in its applicability to our sniffers
- If we get contamination in or on our sniffers they will continue to try to sniff that contamination until it evaporates or we clean it

Tips for keeping your Sniffers clean

- Do not store sniffers in areas where there are strong odors
- Avoid handling the detector's inlet or filter if your hands might be contaminated with chemicals
- Poor sampling technique leads to drift
  - ***Do not aspirate (suck) any liquids into your sniffers***
  - Watch out for hot vapors that might condense in the sniffer
  - Do not touch contaminated surfaces with your sniffer
- Clean probes and filters first before going into the unit

Sniffing Tips

- When sniffing from vessels always sniff just outside of the mouth of the vessel or just barely in the mouth, don’t stick the probe too far into the vessel
- This helps to prevent the aspiration of liquids into the detector
- This also assures that the detector (particularly FIDs) gets enough oxygen for its sensors to operate properly because the headspace of many vessels lack oxygen

YES

NO

FID Flameout

- An FID user wanted to replace his FID with a PID because he routinely experienced flameouts when sampling old 55 gallon drums
- When asked to demonstrate his technique it was found that he would insert the probe of the FID way into the bung of the 55 gallon drum
- Most likely the old 55 gallon drums had a no oxygen atmosphere in their headspaces because it had been consumed by rust and the FID was simply flaming out due to lack of oxygen
- Proper sample technique, just at the entrance to the bung, prevented flameouts and the risk of sucking old nasty liquids into the FID

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

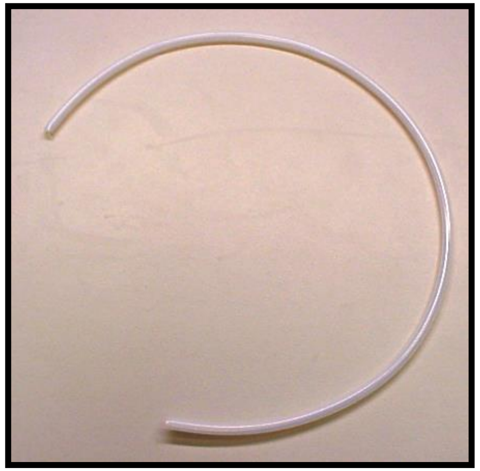
Cleaning a Dirty Sniffer

- Always start with filters and probes
- PID lamps and sensors can often benefit from cleaning
  - PIDs have charged plates in them that can accumulate particles on them just like the charged plates in the “smoke-eaters” that used to be in bars
  - These particulates can become “nuclei of condensation” that allow moisture to condense in the sensor and provide high values on some PIDs
  - This is diagnosed by putting the PID in a high humidity environment which can be easily simulated by exhaling into the PID. If the PID responds strongly to the humidity in exhalation, then the PID sensor should be cleaned or replaced
  - Some PID manufacturers make it easy for users to clean the lamp and sensor of their products
    - Follow your manufacturers cleaning directions, some recommend methanol others polishing with alumina powder
- Other products may need to be returned to the manufacturer for service

A PID that would not Zero

- 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 such 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

Tubing MAY affect Performance



- Never Use Tygon tubing with sniffers!
  - Absorbs chemicals like a “sponge”
  - Can reduce readouts when chemicals exist
  - Can causes “false positives” when chemicals don’t exist
- Always use Teflon or similar non-reactive tubing
  - Will not absorb chemicals but might get coated
  - Clean with anhydrous methanol if it gets dirty

Jet Fuel Measurements

- Customer wanted to use PIDs for wingtank entry LEL readings
- During a trial 3 PIDs were used with 3 different readings
  - MultiRAE flows at 125cc/min, lowest reading
  - Photovac 2020 flows at 250cc/min, mid reading
  - MiniRAE 2000 flows at 500cc/min, highest reading
- The Tygon tubing absorbed the jet fuel based upon residence time in the tubing, lower flow means longer residence time and less reading at the detector
- Replacing the Tygon tubing with Teflon tubing solved the problem

Filters MAY Affect Performance

- "Heavy/Sticky" chemicals with high boiling point/low vapor pressure may get eliminated/reduced by filters
  - Phenols & heat transfer fluids are examples of times when you may need to remove the filter to get accurate readings
  - When in doubt remove the filter and see if the reading changes
  - Filters can hold these compounds and make the survey detector indicate chemical when there is none present

Filters MAY Affect Performance

- Reactive chemicals like Monomethyl Hydrazine (MMH) may react with filters and the sniffer may not measure MMH until the MMH has "broken-through" the filter
  - When detecting MMH it is recommended to remove all filters including stainless steel frit
  - This may require more cleaning of the sniffer

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Integrating Gas Detection Techniques

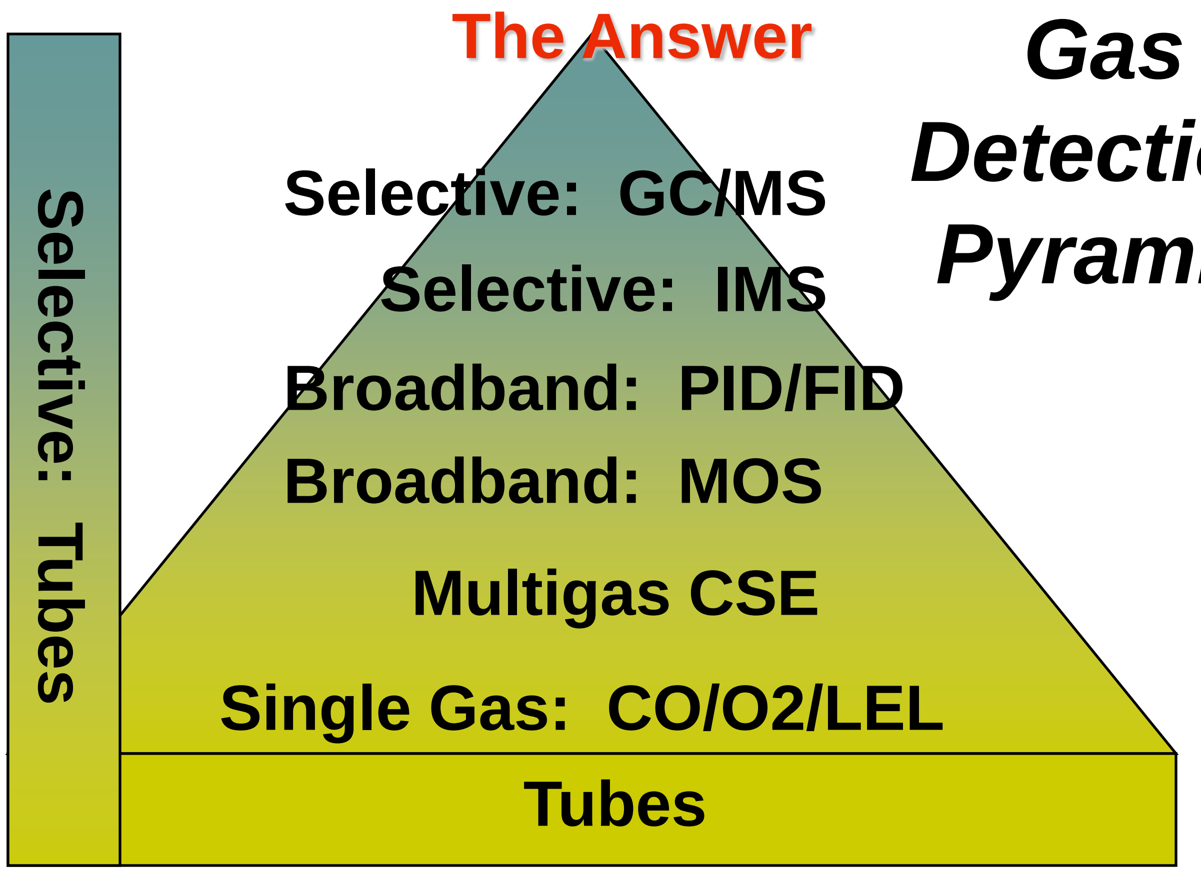
Sniffers can be an important part of any gaseous risk assessment and should be used with other clues present:

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

Integrating Gas Detection Techniques

The Gas Detection Pyramid is a graphic depiction of how to integrate various gas detection techniques in order to more quickly move from detection to decision

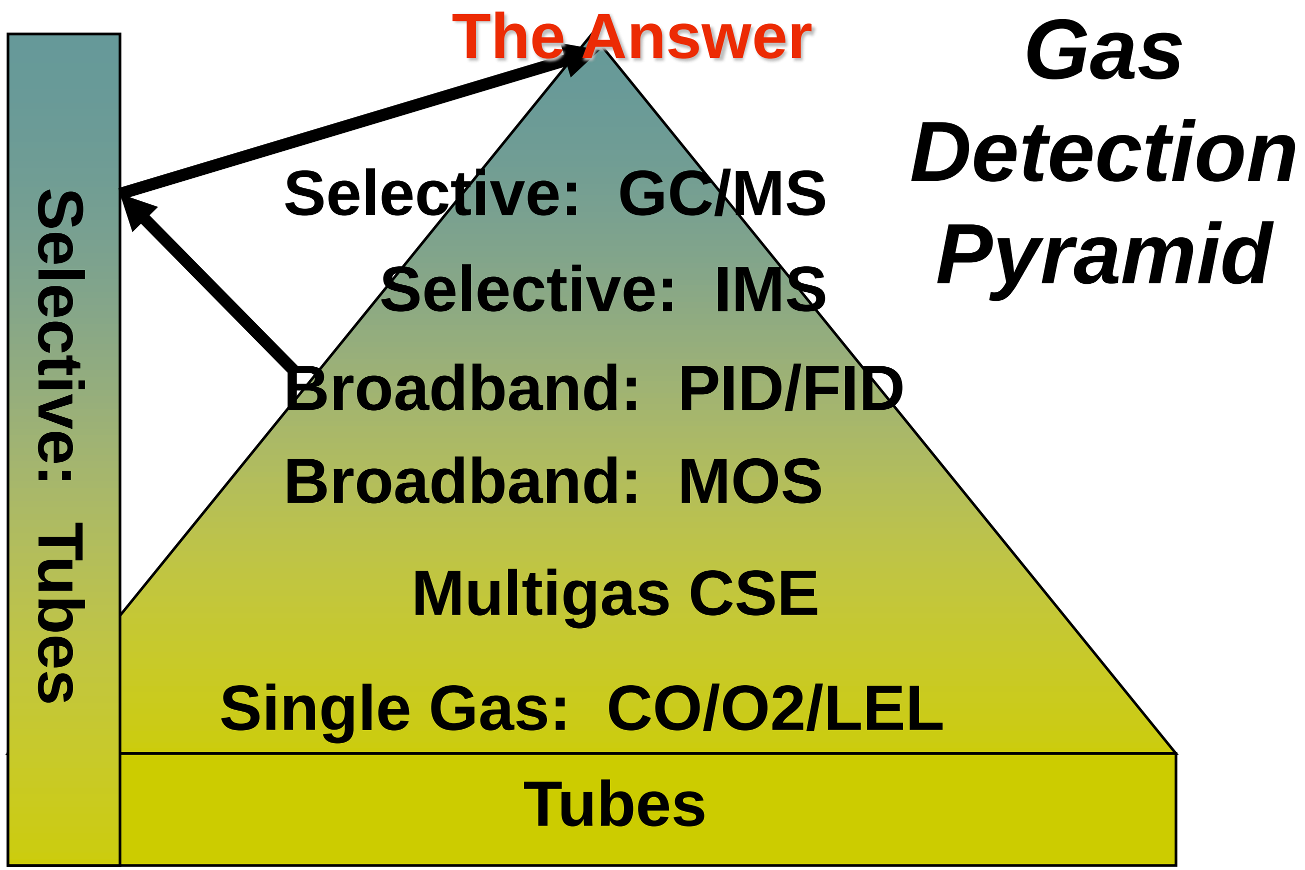
Integrating Gas Detection Techniques



Gas Detection Pyramid

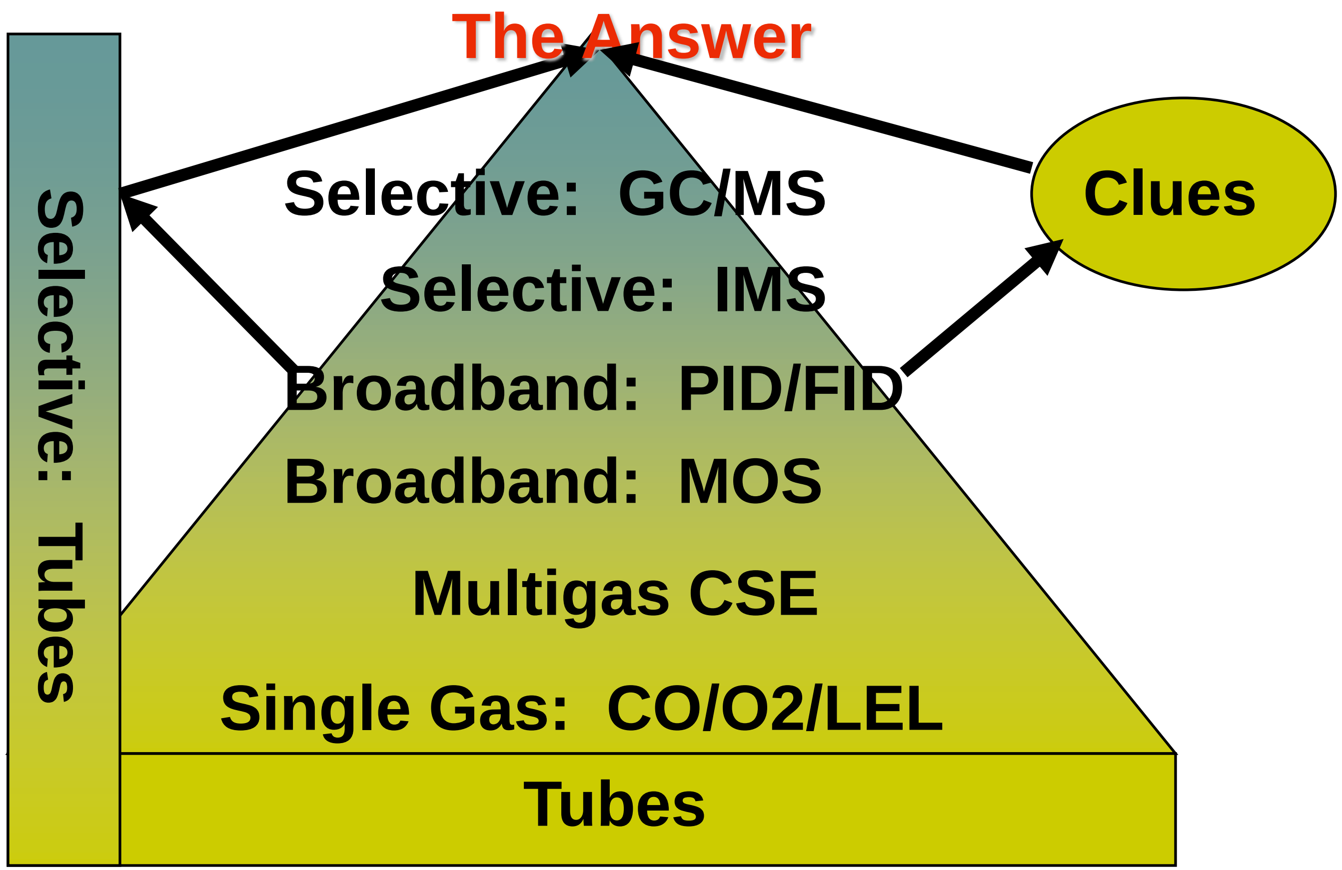
Selectivity Increases as you move up the Pyramid

Integrating Gas Detection Techniques



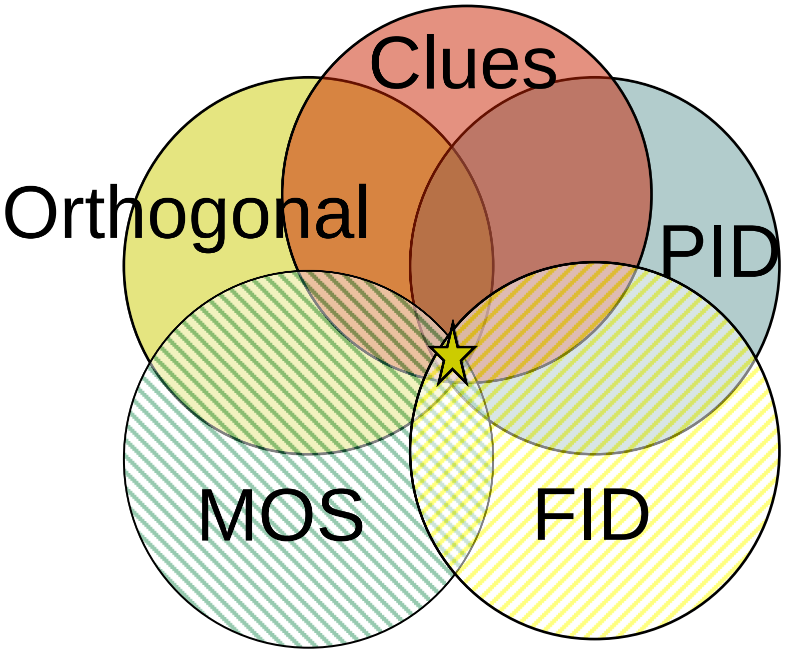
PID + Tubes Approximates the selectivity of GC/MS w/o the cost

Integrating Gas Detection Techniques



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

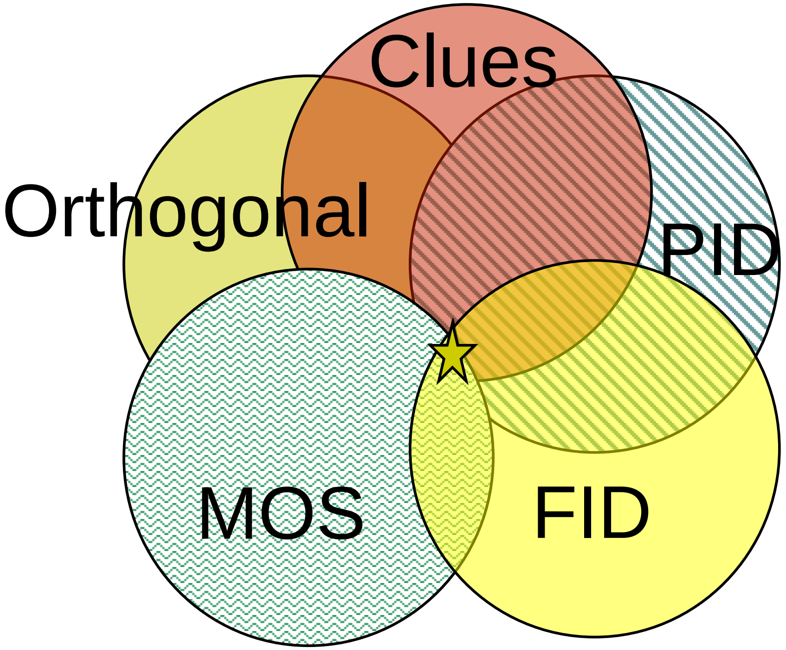
Leaking Fuel Oil Tank



★=PID probably the best

- 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

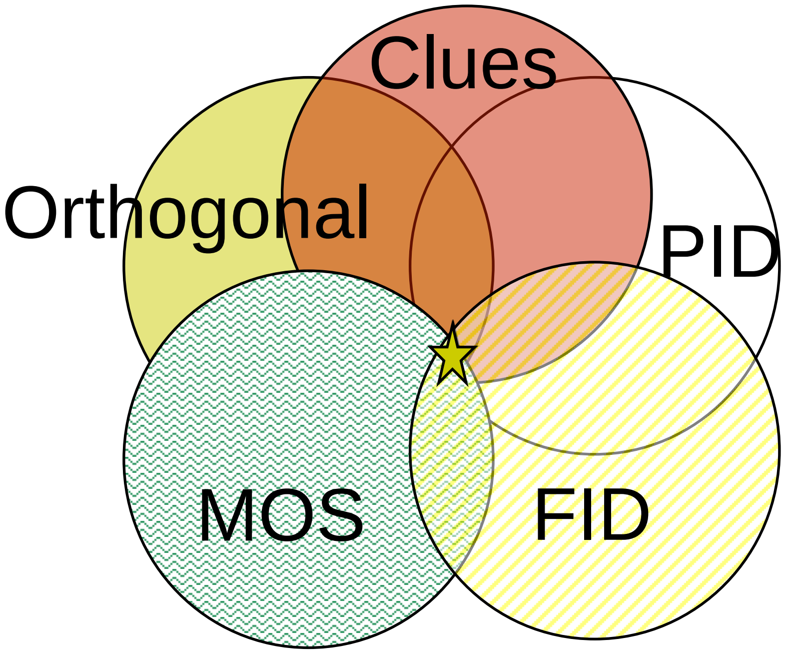
Natural Gas Leak



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

- 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

Refrigerant Leak



= MOS for Refrigerant is the cheap option if you have one, Orthogonal will work fine

- **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 Refrigerant model
- **Orthogonal:** strong response

Ice Plant Ammonia Leak

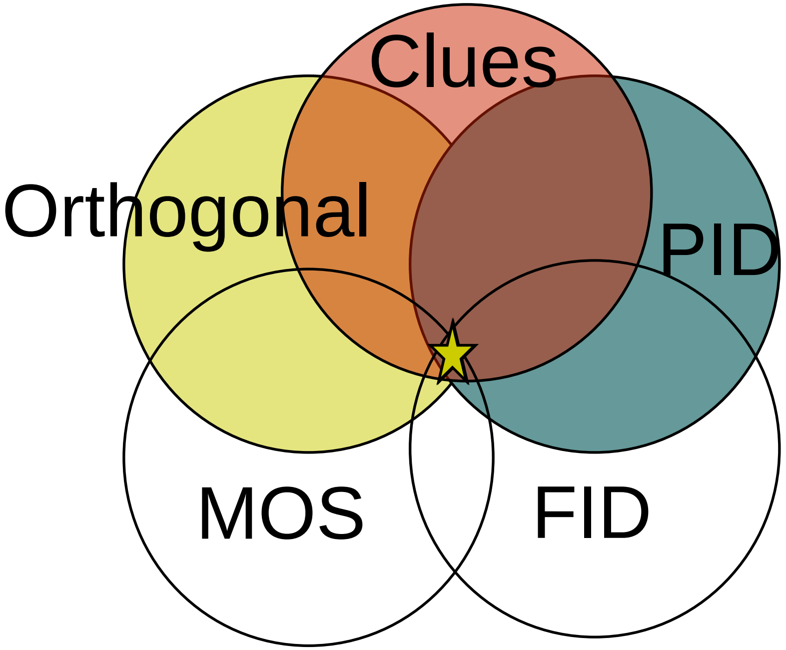
- **Problem**
  - An ice plant had a large leak in its ammonia refrigeration system
- **Response**
  - Regional and state HazMat assets responded primarily using PIDs to find the leaks and access exposures levels for PPE decisions
  - After sealing off the leak the PIDs continued to read high levels of “something” but given that the leak was sealed up responders thought that perhaps there was another chemical leaking that they were not aware of

Ice Plant Ammonia Leak

- They used a ChemPro100i to find areas of higher concentration using its “Trend” or “Sniffer” screen. The ChemPro100i was also able to confirmed that the high concentrations were “Ammonia” and that they were coming from ammonia diffusion out of the large amounts of ice that were stored on site

- **Conclusion**
  - The high concentrations of ammonia had infiltrated the large store of ice
  - After the leak was sealed, the PID was able to quantitate that 150 ppm of ammonia was diffusing out of the ice and the ChemPro100i was able to identify the ammonia
  - ***This is an excellent example of using two different technologies to solve a problem***

Ice Plant Ammonia Leak



★ = Layering gas detectors is sometimes the best solution

- **Clues:** Ammonia plant leak
- **PID:** strong quantitative readings both before & AFTER the ammonia leak was sealed
- **FID:** no response
- **MOS:** no response
- **Orthogonal:** strong response and could identify the presence of ammonia, but can't quantitate

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

Sick Building

- **Response**
  - The building was an office/warehouse for our state Department of Environmental Protection (DEP) and it was in a flex warehouse complex
  - 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

Sick Building

- **Response (continued)**
  - 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.

Sick Building

- **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”

Sick Building

- **Actions Taken (continued)**
  - 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

Sick Building

- **Actions Taken (continued)**
  - 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, 6 buildings away, had fired up a kiln at 0800 and had cremated several animal carcasses

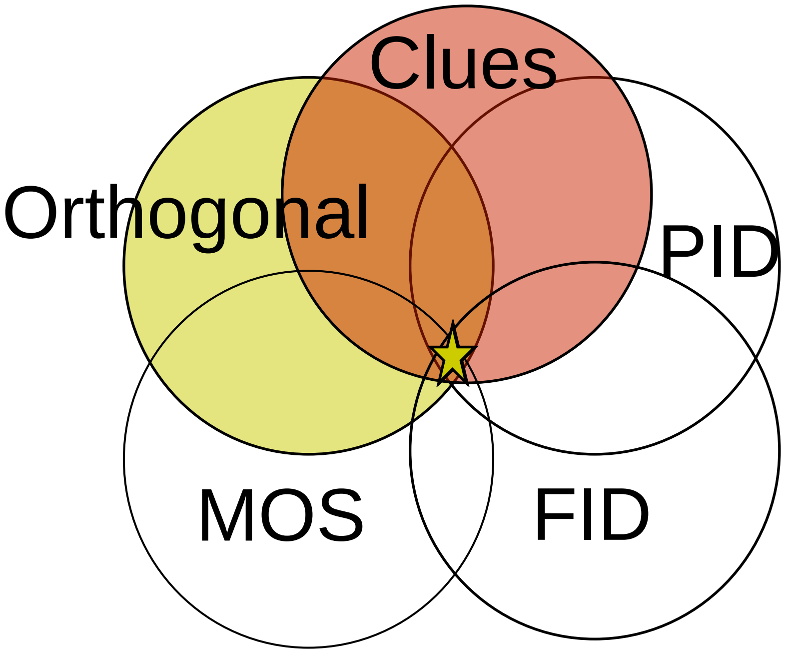
Sick Building

- **Conclusions**
  - It was determined that the byproducts of the cremation of animals had been drawn into the fresh air intake of the HVAC system because of a temperature inversion and distributed them 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 (LOD > 2-50 ppm) as well as an FID with no results

Sick Building

- **Conclusions (continued)**
  - ***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

Sick Building



☆ = Orthogonal detector found the problem in minutes

- **Clues:** workers got sick in an office building
- **PID:** didn't detect at all
- **FID:** no response
- **MOS:** not used, but can't see acids
- **Orthogonal:** strong response
- This is an excellent example of adding another angle to the problem to find the solution

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

Questions?

chriswrenn@att.net

"Still confused but at a higher level"

If you'd like a copy of this presentation or the white papers mentioned please email me or give me your information

If you are ever challenged with a gas detection problem, call, text or email me and we'll work through it

610-659-4507

Please fill out your course evaluation and hand it in before you leave

Check out www.DetectionGeek.com for downloads of slides and whitepapers