USING PIDS IN CLAN LAB INVESTIGATIONS

CLAN LABS CAUSE CHEMICAL CONTAMINATION

In the past few years there has been a dramatic rise in the number of clandestine labs ("clan labs") producing methamphetamines and other illegal drugs. The chemical processing at these labs is often carried out by untrained "cooks" who, rather than having an extensive chemical background, just follow a simple "cookbook." This lack of chemical knowledge means that cooks don't have a professional chemist's respect for these toxic and flammable chemicals, and this leads to widespread chemical contamination in and around clan labs.

Measurement is the Key to Risk Reduction

The lack of respect that clan lab cooks have for the chemicals they use requires investigators of these crime scenes to protect themselves from the toxic and flammable gas and vapor threats left behind. Only after making an accurate assessment of the residual levels of contamination can clan lab investigators properly protect themselves from these threats. Because clan labs are crime scenes, investigators often have to make quick decisions. The best way to assess on-scene risk is with a continuous monitor that provides instantaneous readings. Not only can portable monitors decrease risk to personnel; they can also reduce costs. The cost of medical testing for law enforcement personnel that have been exposed to clan lab chemicals can approach six figures in the case of a gross exposure.

Wheatstone bridge Sensor Have Limitations Measuring Flammability and Toxicity in Clan Labs

Not only are many chemicals found in clan labs flammable, but also the toxicity of many of them requires monitoring at parts per million (ppm) levels for toxicity. The most common sensor used for these measurements by law enforcement groups is the Wheatstone bridge/catalytic bead/pellistor sensor ("Wheatstone bridge"). The use of Wheatstone bridge sensors is problematic in the Clan Lab environment because:

1. They can only measure flammable gases and vapors while some clan lab chemicals are not flammable.
2. They have difficulty measuring low vapor pressure and high flashpoints of chemicals found in clan labs.
3. They don't have enough sensitivity for the ppm level measurements that are required for gauging toxicity threats.
4. Chemicals used in clan labs can permanently poison the Wheatstone bridge sensor, rendering it inoperable even for making even gross decisions about combustible gas at lower explosive limit (LEL) levels.

PIDs Reliably Measure Flammability and Toxicity

PIDs (Photo Ionization Detectors) provide an alternative, highly accurate and poison-free means of measuring both chemical toxicity and 10% of LEL for clan lab investigators. They are an excellent means of measuring many of the chemicals commonly found in and around clan labs and provide a basis for an integrated gas monitoring program including other sensing technologies (Wheatstone bridge, electrochemical sensors and colorimetric tubes). Because of their greater sensitivity, PIDs also provide an excellent detection tool to help find cooks and the chemical contamination clues that they leave behind.

1. PIDs can measure flammable and non-flammable gases, liquids and vapors.
2. PIDs can easily measure low vapor pressure/high flashpoint chemicals, providing protection from more clan lab chemicals than Wheatstone bridge sensors.
3. With resolution as low as parts per billion and excellent accuracy, PIDs provide the necessary sensitivity for making toxicity decisions.
4. An optical system, PIDs are immune to the common Wheatstone bridge sensor poisons found in clan labs.

1. Wheatstone Bridge Sensors are Designed to Measure Flammable Gases Like Methane

Combustible gas indicators (CGI) with Wheatstone bridge sensors are often used to detect the flammable solvents and chemicals used in meth labs. The most common are acetone and ether. However, smaller-scale "cookers" use solvents that are more readily available, such as paint thinner, charcoal lighter fluid, Coleman stove fuel, engine starter fluid, naphtha, and even gasoline. While these solvents are flammable, Wheatstone bridge sensors do not have enough sensitivity to accurately measure them. Law enforcement personnel often can see and smell these chemicals without their meter detecting them. This can seriously undermine their confidence in their monitor. Wheatstone bridge sensors were originally designed to solve the problem of measuring methane levels in coal mines and don't have the sensitivity needed to measure these solvents. A Wheatstone bridge sensor is simply a tiny electric stove with two burner elements. One element has a catalyst (such as platinum) and one doesn't. Both elements are heated to a temperature that normally would not support combustion. However, the element with the catalyst "burns" gas at a low level and heats up relative to the element without the catalyst. The hotter element has more resistance, and the Wheatstone bridge measures the difference in resistance between the two elements, which correlates to LEL. Wheatstone bridge sensors cannot measure nonflammable vapors found in clan labs like chloroform and phosphorus trichloride and solids that give off vapors, such as phenylacetic acid, piperonal, and iodine.

2. High Flashpoint Vapors Have Difficulty Diffusing Into Wheatstone Bridge Sensors and Reduce Their Output

Low vapor pressure/high flashpoint vapors have difficulty diffusing through the flame arrestor on Wheatstone bridge sensors. This flame arrestor is necessary to prevent the sensor itself from starting a fire and does not prevent gases like methane, propane and ethane from reaching the Wheatstone bridge. However, low vapor pressure/high flashpoint compounds are "heavier" and "thicker," so they diffuse through the flame arrestor slower. Less vapor reaches the Wheatstone bridge and the sensor gives little to no response.

The following is a brief list of low-vapor-pressure (<10mm Hg)/high flashpoint (>90°F, 32°C) chemicals often found in clan labs (refer to "Clandestine Laboratory Operations and Safety Field Guide" and "Chemical Hazards of Clandestine Drug Laboratories"):

- Acetic acid
- Acetic anahydride
- Benzaldehyde
- Benzyl chloride
- Benzyl cyanide
- Bromobenzene
- Formamide
- Mineral spirits (Stoddard solvent)
- Naphtha
- Phenylacetic acid
- Piperonal
- Toluidine, o-

3. Wheatstone Bridge Sensors Lack Sensitivity at ppm Levels

The Wheatstone bridge sensor currently used by many clan lab investigators has a full-scale range of 0-10,000 ppm and reads in 20 ppm increments. Its accuracy is ±10% of full scale, or ±1,000 ppm. One of the least toxic of the chemicals often found in clan labs is ethyl acetate with a TWA (time-weighted average exposure) of 400 ppm. Many clan lab chemicals have toxicity of less than 10 ppm. Clearly, a sensor with 1,000 ppm accuracy is not an appropriate choice for making toxicity decisions in the clan lab environment.

4. Common Clan Lab Chemicals Can Poison LEL sensors

Under the best circumstances, it is difficult for Wheatstone bridge LEL sensors to measure many chemical vapors found in clan labs. However, common clan lab chemicals can degrade and destroy LEL sensor performance. Some act very quickly ("acute" poisons) and some act over time ("chronic" poisons). As with human toxicity, Wheatstone bridge LEL sensor "poisoning" is dosage dependent. Unfortunately, Wheatstone bridge sensors fail to an unsafe state; when they fail, they indicate safe levels of flammable gas (0% of LEL). Failure and/or poisoning of a Wheatstone bridge sensor can only be determined through challenging it with calibration gas.

Acute LEL Sensor Poisons found in clan labs:

- Lead-containing compounds: Lead acetate
- Phosphates and phosphorous-containing compounds: Red phosphorous and phosphorous trichloride

Just a few parts per million (ppm) of these compounds are sufficient to permanently degrade the sensing performance of a Wheatstone bridge LEL sensor.

Chronic LEL Sensor Poisons found in Clan Labs:

- Hydrides: Ammonia and phosphine
- Halogenated hydrocarbons: Freons, hydrogen chloride gas

Also called "inhibitors" chronic Wheatstone bridge sensor poisons don't act as quickly on the Wheatstone bridge sensor. Often, exposure to clean air allows the sensor to "burn off" these compounds. But with continued operation in an atmosphere containing these chemicals Wheatstone bridge sensor output will ultimately fall to zero (for more information, refer to Technical Note TN-144: Handling LEL Sensor Poisons).

WHAT IS A PID?

A photoionization detector (PID) measures VOCs and other toxic gases in concentrations from ppb up to 10,000 ppm. A PID is a very sensitive broad-spectrum monitor, not unlike a "low-level LEL monitor."

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 measured 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." After measurement, the ions re-form the original gas or vapor. PIDs are non-destructive; they do not "burn" or permanently alter the sample gas, which allows them to be used for sample gathering (PIDs like the MiniRAE 2000 and ppbRAE provide this feature). The optical system of PIDs is immune to the clan lab poisons that affect Wheatstone bridge sensors. It is also intrinsically safe and does not require a flame arrestor. Because the PID does not have the flame arrestor of the Wheatstone bridge sensor, it can easily respond to low vapor pressure/high flashpoint chemicals. RAE PIDs fail "safe." When the PID lamp fails to light the PID provides a "Lamp" alarm, so operators immediately know that it is not working. Therefore, it is not necessary to show PIDs calibration gas just to determine if they are working, unlike a Wheatstone bridge sensor.

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 will be ionized. The most common PID lamp is 10.6 eV. Because PID measurement is based upon Ionization Potential and not flammability it can see many non-flammable chemicals.

A PID is a More Accurate 10% of LEL Sensor

PIDs are sensitive hydrocarbon sensors originally designed to measure ppm levels of hydrocarbons for the environmental industry. PIDs are uniquely suited for measuring hydrocarbon mixtures. Because PIDs use an optical technology, they are resistant to the poisons that can ruin Wheatstone bridge sensors. Recent breakthroughs in PID technology make them compact, rugged and affordable. PIDs provide ±10% of reading accuracy. So if a PID is reading 1,000 ppm, the actual reading could be 900 to 1100 ppm. The Wheatstone bridge sensor has an accuracy of ±10% full scale of 0 to 10,000 ppm. If the Wheatstone bridge sensor is reading 1,000 ppm, the actual reading could be 0 to 2,000 ppm.

Comparison of PID vs Wheatstone Bridge LEL Sensors for Measuring Typical Clan Lab Gases and Vapors

Chemical Name	PID 10.6 eV Lamp Can See	Wheatstone Can See
Acetic Acid	Poor	Poor
Acetic Anahydride	Good	Poor
Acetone	Good	Good
Ammonia	Good	Good-Inhibitor
Ammonium Acetate	No	No
Ammonium Formate	No	No
Benzaldehyde	Good	No
Benzene	Good	Good
Benzyl chloride	Good	No
Benzyl cyanide	Good	No
Bromobenzene	Good	Poor
Butylamine, n-	Good	Good
Chloroform	No	No
Diethyl ether	Good	Good
Ethyl acetate	Good	Good
Ethyl Alcohol	Poor	Good
Formamide	Good	No

Chemical Name	PID 10.6 eV Lamp Can See	Wheatstone Can See
Freon	No	No-Inhibitor
Gasoline	Good	Good
Hexane	Good	Good
Hydriodic Acid	Good	No
Hydrogen Chloride	No	No-Inhibitor
Iodine	Good	No
Isopropyl Alcohol	Good	Good
Isosafrole	Good	Not Enough Data
Lead Acetate	No	No-Poison
Mercuric Chloride	No	No
Methyl Alcohol	No	Good
Methylamine	Good	Good
Naphtha	Good	Poor
Nitroethane	No	Good
Palladium Black	No	No
Phenyl-2-Propanone	Good	Not Enough Data
Phenylacetic acid	Good	No
Phosphine	Good-Inhibitor	Good-Inhibitor
Phosphorus trichloride	Good	No-Poison
Phosphorous, red	No	No-Poison
Piperonal	Good	No
Pyridine	Good	Good
Sodium Acetate	No	No
Sodium Dichromate	No	No
Sodium Hydroxide	No	No
Stoddard Solvent	Good	Poor
Sulfuric Acid	No	No
Tetrahydrofuran	Good	Good
Thionyl Chloride	No	No
Toluene	Good	Good
Toluidine, o-	Good	No

The previous chart of 48 chemicals can be summarized:

	PID w.10.6 eV	Wheatstone
Good Response	29	15
Good Inhibitor	1	2
Poor Response	2	5
No Response	16	21
No-Poison	Doesn't apply	3
Not enough data	0	2

This summary shows that the PID can see more chemicals in a clan lab environment (29 "Good," 2 "Poor," for 31 total) than the Wheatstone bridge sensor (15 "Good," 5 "Poor," for 20 total). In addition, the PID does not have any poisons, and response can be restored by cleaning the PID lamp even if exposed to high levels of an inhibitor (phosphine). If we combine a PID and a Wheatstone bridge LEL sensor, one can measure 34 clan lab chemicals. Neither sensor can measure chloroform, thionyl chloride, hydrogen chloride gas, sulfuric acid and eight solid compounds.

- **Good Response:** PID has at least good sensitivity to the chemical (Correction Factor <10), and for the Wheatstone bridge sensor the chemical is flammable and has a vapor pressure of >10mm Hg and/or flashpoint <90°F (32°C).
- **Good Inhibitor:** PID sensitivity can be degraded by exposure to this chemical (although it can be restored with cleaning). The Wheatstone bridge sensor can measure this chemical, but prolonged exposure degrades the sensor's performance.
- **Poor Response:** PID has poor sensitivity to the chemical (Correction Factor >10) and for the Wheatstone bridge sensor the chemical is flammable and has a vapor pressure of <10mm Hg and/or Flashpoint >90°F (32°C).
- **No Response:** the sensor cannot "see" this chemical
- **No-Poison:** Sensor does not see this chemical, and exposure to this chemical in even small amounts can permanently degrade sensor performance.
- **Not Enough Data:** Not enough information is available.

Guidelines for using PID for 10% of LEL Protection in Clan Labs

At the scene of a clan lab it is possible to encounter approximately 29 flammable gases and vapors and of these the PID can see 27 with a 10.6eV lamp. It may not be immediately obvious what chemical(s) or mixture of chemicals might be present. When measuring unknown chemicals or mixtures PIDs should use an isobutylene measurement scale. Like the Wheatstone bridge sensor, PIDs have varying sensitivity to chemicals. Correction Factors (CF) express the PID sensitivity to a particular gas relative to its calibration gas of isobutylene. (Refer to TN-106: PID Correction Factors.) To determine 10% of LEL in units of isobutylene, 10% of LEL in ppm is divided by the PID Correction Factor (refer to Application Note AP-221: PIDs for Assessment of Exposure Risk in Unknown Environments). Upon examining Table 1:10% of LEL for Clan Lab Chemicals When Measuring on an Isobutylene Scale, one can see that:

- Setting the PID high alarm to a setpoint of 182 ppm provides 10% of LEL protection for 27 chemicals (because PID with a 10.6eV lamp has poor sensitivity to acetic acid, but the Wheatstone bridge sensor also has poor sensitivity to acetic acid)
- Setting the PID high alarm to a setpoint of 250 provides 10% of LEL protection for 26 chemicals
- Setting the PID high alarm to a setpoint of 500 provides 10% of LEL protection for 19 chemicals
- Setting the PID high alarm to a setpoint of 1000 provides 10% of LEL protection for 18 chemicals

Important: In the clan lab environment, a high PID alarm of 250 is the recommended alarm for 10% of LEL.

Table 1: 10% of LEL for Clan Lab Chemicals When Measuring on an Isobutylene Scale"

Chemical Name	Correction Factor	LEL (%)	LEL in ppm	10% of LEL in ppm of Chemical	10% LEL in Units of Isobutylene
Acetic Acid	22.00	4	40000	4000	182
Hexane, n-	4.30	1.1	11000	1100	256
Ethyl alcohol	12.00	3.3	33000	3300	275
Naphtha	2.80	0.9	9000	900	321
Isopropyl Alcohol	6.00	2	20000	2000	333
Ethyl acetate	4.60	2	20000	2000	435
Acetic Anahydride	6.10	2.7	27000	2700	443
Phosphine	3.9	1.79	17900	1790	459
Bromobenzene	0.60	0.5	5000	500	833
Stoddard Solvent	0.71	0.8	8000	800	1127
Tetrahydrofuran	1.70	2	20000	2000	1176
Formamide	4.00	5	50000	5000	1250
Gasoline	1.00	1.4	14000	1400	1400
Butylamine, n-	1.10	1.7	17000	1700	1545
Ammonia	9.70	15	150000	15000	1546
Phenyl-2-Propanone	0.5	0.8	8000	800	1600
Benzyl cyanide	0.60	1	10000	1000	1667
Diethyl ether	1.10	1.9	19000	1900	1727
Benzyl chloride	0.60	1.1	11000	1100	1833
Isosafrole	0.4	0.8	8000	800	2000
Toluene	0.50	1.1	11000	1100	2200
Benzene	0.53	1.2	12000	1200	2264
Acetone	1.10	2.5	25000	2500	2273

Chemical Name	Correction Factor	LEL (%)	LEL in ppm	10% of LEL in ppm of Chemical	10% LEL in Units of Isobutylene
Pyridine	0.68	1.8	18000	1800	2647
Benzaldehyde	0.50	1.4	14000	1400	2800
Toluidine, o-	0.50	1.5	15000	1500	3000
Methylamine	1.2	4.9	49000	4900	4083
Methyl alcohol	NR	6	60000	6000	PID Can't Measure
Nitroethane	NR	3.4	34000	3400	PID Can't Measure

GUIDELINES FOR USING PID FOR TOXICITY DECISIONS IN CLAN LABS

At the scene of a clan lab, it is possible to encounter approximately 48 gases, vapors, liquids and solids. Of these, the PID can see 32. It may not be immediately obvious what chemical or mixture of chemicals might be present. When measuring unknown chemicals or mixtures, PIDs should use an isobutylene measurement scale. PIDs have varying sensitivity to chemicals, Correction Factors express the PID sensitivity to a particular gas relative to its calibration gas of isobutylene. (Refer to TN-106: PID Correction Factors.) To determine toxicity in units of isobutylene the toxicity of a chemical in ppm is divided by the PID Correction Factor for that chemical (Ref: AP-221: Using PIDs for Assessment of Exposure Risk in Unknown Environments,"

Note: CFs are specific to each PID manufacturer. The following data only applies to RAE Systems PIDs.

Upon examining Table 2: "Clan Lab Chemicals Toxicity Limits When Measuring on an Isobutylene Scale, note the following:

- Continuous detection of phosphine is best performed by a phosphine electrochemical sensor.
- Setting the PID low alarm to a toxicity setpoint of 1 ppm in isobutylene units provides toxicity protection for 22 chemicals from iodine to acetone.
- Setting the PID low alarm to a toxicity setpoint of 5 ppm in isobutylene units provides toxicity protection for 16 chemicals from formamide to acetone.
- Setting the PID low alarm to a toxicity setpoint of 10 ppm in isobutylene units provides toxicity protection for 12 chemicals from o-toluidine to acetone.
- The PID can measure additional clan lab chemicals including: bromobenzene, isosafrole, phenyl-2-propanone, phenylacetic acid, piperonal and hydriodic acid. However, no exposure limits (indicated by "NEL" in Table 2) have been found for these chemicals.

Important: In the clan lab environment, a low PID alarm of 5 ppm is the recommended alarm to move from respiratory protection to bareface.

With the RAE Systems PID set to this 5 alarm and with the meter not beeping in alarm. It should be safe to go without respiratory protections.

Table 2: "Clan Lab Chemicals Toxicity Limits when Measuring on an Isobutylene Scale"

Chemical Name	Correction Factor	Exposure Limit (EL)	EL in Units of Isobutylene
Phosphine	3.9	0.3	0.077
Phosphorus trichloride	4.0	0.5	0.125
Acetic acid	22.00	10.000	0.455
Acetic anahydride	6.10	5	0.820
Iodine	0.10	0.100	1.000
Benzyl chloride	0.60	1	1.667
Benzyl cyanide	0.60	1.040	1.733
Benzene	0.53	1.000	1.887
Benzaldehyde	0.50	2.000	4.000
Butylamine, n-	1.10	5	4.545
Formamide	4.00	20.000	5.000
Ammonia	9.70	50.000	5.155
Pyridine	0.68	5.000	7.353
Methylamine	1.2	10	8.333
Hydriodic acid	4	None	NEL
Toluidine, o-	0.50	5	10.000
Naphtha	2.80	100.000	35.714
Isopropyl alcohol	6.00	400.000	66.667
Ethyl alcohol	12.00	1000.000	83.333
Ethyl acetate	4.60	400	86.957
Tetrahydrofuran	1.70	200.000	117.647
Gasoline #2, 92 octane	1.00	300.000	300.000
Toluene	0.50	200	400.000
Stoddard solvent	0.71	500.000	704.225
Acetone	1.10	1000.000	909.091
Bromobenzene	0.60	None	NEL
Isosafrole	0.4	None	NEL
Phenyl-2-propanone	0.5	None	NEL
Phenylacetic acid	0.4	None	NEL
Piperonal	0.4	None	NEL

Measuring Ammonia and Phosphine with a PID

PIDs can readily measure hydrides like ammonia and phosphine. Ammonia can be present in large quantities in labs using the "Nazi" method of production. These cookers often obtain their ammonia illegally and vent their entire supply as a diversionary tactic in a raid. Unlike electrochemical ammonia-specific sensors, PIDs respond instantly to ammonia (versus 150 seconds) and they are not poisoned by large quantities of ammonia (200 or more ppm) like electrochemical sensors (refer to AP-201: Measuring Ammonia with PIDs). While Phosphine is ionizable and can be "seen" by a PID, the specificity and sensitivity of an electrochemical sensor is preferred for phosphine because of its low exposure limit of 0.3 ppm.

PIDs for Use in Clan Labs

PIDs provide a compact, rugged and reliable means of identifying the presence of and quantifying the threat of gaseous threats in clan labs. When combined with a Wheatstone bridge LEL sensor and electrochemical phosphine sensors, PIDs can form the basis of an integrated continuous gas-monitoring program that provides more effective protection than relying solely on Wheatstone bridge sensors.

RAE SYSTEMS PIDS FOR THE CLAN LABS

MultiRAE PID & Multigas Monitor

Combines PID (0 to 2,000 ppm) with four other sensors (O2, LEL and two toxic sensors) in one compact monitor to accurately provide warning when toxic and flammable levels of clan lab chemicals are about to be exceeded. Its internal pump provides for fast response and remote monitoring. For clan lab applications, the MultiRAE Plus is typically purchased with ammonia and phosphine sensors installed in the toxic spots.

ToxiRAE II Pocket PID

A PID that fits into a shirt pocket. The ToxiRAE PGM-30 is the smallest and most affordable PID in the world.

ToxiRAE II NH3 or PH3 Monitor

The ToxiRAE can take ammonia or phosphine sensors but is not interchangeable with the PID sensor. When configured with a phosphine sensor, the ToxiRAE II can provide 0.01 ppm resolution.

MiniRAE 2000 PID

The MiniRAE 2000 is our best detection, or survey, instrument for measuring 0 to 10,000 ppm. Its strong pump makes it our best "Geiger counter" for finding and delineating spilled chemicals.

ppbRAE PID

Our most sensitive PID provides resolution to 1 ppb and a full scale of 0-200 ppm. The low range sensitivity of the ppbRAE lets it measure at or below olfactory thresholds. This makes it an excellent tool for tracking down the characteristic smells given off by many clan labs.

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