RAE SYSTEMS by Honeywell

USING PIDS IN TERRORIST CHEMICAL ATTACKS

Terrorist attacks in the United States on both the Federal Building in Oklahoma City (1995) and the World Trade Center (1993) in New York City along with international incidents like the Sarin attack in the Tokyo subway, prompted the United States Congress to look at domestic preparedness for attacks utilizing Weapons of Mass Destruction (WMD). The initial response by the U.S. Congress was legislation called "Nunn-Lugar," then "Nunn-Lugar-Domenici II" (also known as the Domestic Preparedness Act.) These bills funded training of domestic cities and acquisition of products for them. Since then, money has been spent in the following markets:

- Fire/HazMat (hazardous materials)
- Police
- EMS (emergency medical services)
- Hospitals

As sensitive chemical monitors, photoionization detectors (PIDs) are versatile tools that have an important place in preparedness for terrorist chemical threats. (For a comprehensive overview of PIDs and how they work, see Application Note AP-000.)

CHEMICAL WARFARE AGENTS (CWA)

Chemical Warfare Agents (CWA) are chemical compounds designed to either kill or debilitate opposing military forces, and today they pose a lethal threat to civilians as well. Developed from compounds in the civilian chemical industry (toxic industrial chemicals, or TICs, also known as toxic industrial materials, or TIMs), these agents have been subsequently refined for their particularly gruesome purpose. With terrorist groups having demonstrated their ability to make and use chemical warfare agents, responders at the federal, state and local levels must look at ways to effectively measure these CWA compounds so that decisions can be made with confidence.

Many TICs are CWA

Industry continues to use and make TICs that have been used as CWA or are similar to CWA without much fanfare. A TIM is defined as a industrial chemical that has a LCt50 (lethal concentration for 50% of the population multiplied by the exposure time) less than 100,000 mg-min/m3 in any mammalian species and is produced in quantities exceeding 30 tons per year at one production facility[1]. Chlorine gas has been used as a CWA, yet it is found in large quantities at many water treatment facilities. Phosgene gas was used extensively as a CWA in World War I, yet it continues to be used in many chemical processes. CWAs like Sarin can be simply described as powerful insecticide, and similar compounds are used in the agriculture industry (like Parathion). The chemical leak in Bhopal, India, that killed 3,000 has been described by some as a chemical agent "attack" on the poor of India. Yet processes like the Bhopal plant continue to be used in the United States today. United States Presidential Decision Directive 39 identified a toxic industrial chemical (TIC) threat list of compounds that can be used as effective chemical weapons. The line between TIC and CWA often is defined only by how the chemical is utilized.

CHEMICAL AGENT: A POLITICAL PROBLEM

Chemicals such as TDI (toluene diisocyanate) are used daily to catalyze urethanes, yet TDI is extremely toxic. However, we don't hear about TDI spills on the national news. The reason for this is political. Chemical Warfare Agents are a political problem. More people died in the Tokyo Sarin attack from being trampled to death than from exposure to Sarin. CWA scares people to death! Yet most people don't know enough about TICs to know any better. A Sarin release can cause a riot (witness the Tokyo subway Sarin release where less than half of 12 fatalities were because of direct exposure to the chemical agent). A chlorine gas release is typically just a news item.

WHY USE PIDS TO MEASURE CWA?

HazMat responders are the front line of chemical response in the US. One of the primary tools that HazMat responders use to measure toxic chemicals at ppm (parts per million) and now ppb (parts per billion) levels is a PID. Many HazMat responders use PIDs with confidence on almost every call as a screening tool to see if something is there and as a tool to accurately measure concentrations after a chemical has been identified. If chemical agent response is just an extension of normal hazardous chemical response (some say, "HazMat with an attitude"), then responders should be able to use PIDs on these responses. The familiarity and confidence gained in daily usage is a valuable asset when presented with the political problems of responding to a terrorist release of a CWA or a TIC. PIDs are dual-use instruments, which are equally effective for day-to-day HazMat applications and for chemical terrorist responses.

Terrorists Do Not Have To Follow the Military's Example

While responder familiarity with PIDs is an important consideration, as sensitive broadband chemical monitors, PIDs offer another important advantage. Perhaps in part because most of the WMD coordination has been overseen by the military, the assumption is that a chemical attack will take place in the form of "normal" military-grade chemical agent like Sarin, Soman, etc. However, as WMD programs have developed, it has been recognized that there are many more chemicals available to terrorists than CWAs. CWAs are tightly controlled and difficult to synthesize. However, many toxic chemicals are present in industry and terrorists have much better access to these chemicals than to CWAs. The book *Chemical And Biological Terrorism* describes the situation like this: "Would-be terrorists have a much longer list of agents from which to choose than does a military force, which must be concerned with the production in quantity, weaponization, storage, safety of their own personnel and civilian noncombatants, and contamination of desired physical and geographical objectives."[2] There is no terrorist "rule book" that limits terrorists' chemical choices to the same list used by the military.

CWA Detectors May Not "See" TICs

Toxic chemicals like ammonia and chlorine are found in large quantities in virtually every community. Highly toxic chemicals like pesticides (e.g., Parathion) and chemical catalysts (e.g., toluene diisocyanate, or TDI) are only slightly less common. PIDs are not limited in their detection capabilities to a few selected CWAs. surface acoustical wave (SAW) and ion mobility spectroscopy (IMS) chemical agent detectors have algorithms to identify and measure specific CWAs. If a terrorist were to choose a TIC that falls outside of these algorithms, these meters are not useful. The Tokyo Sarin attack was just 37% Sarin the balance being a relatively common industrial chemical, acetonitrile.

"INTENT" MAKES A HAZMAT INCIDENT A TERRORIST EVENT

"Intent" is the only word that separates a HazMat incident from a WMD incident. If a rail car carrying anhydrous ammonia derails and leaks, causing injuries and evacuations in a community, then we call this a "HazMat." Yet if an explosive device caused the derailment we call this "terrorism." If the intent is to create fear, then it's called "terrorism." If there is no intent, then it's a "HazMat."

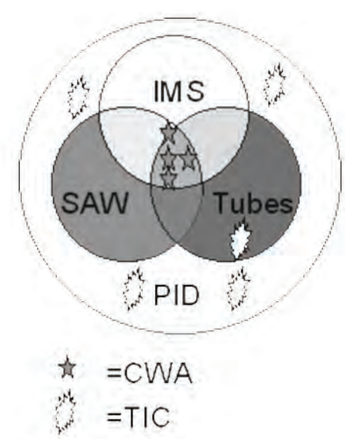
DIRECT-READING CHEMICAL AGENT DETECTORS CAN BE EASILY FOOLED

IMS CWA detectors were designed to operate in a military environment where CWA can be expected, not the urban environment where virtually any chemical can be found. The developers of military CWA detectors assume the presence of battlefield-deployed, high-quality CWA. Yet they don't take into account that many common chemicals can fool the algorithms in CWA detectors. Low vapor pressure for most CWAs complicates their measurement. This leaves very little in the air to measure. Other low-vapor-pressure chemicals (including many everyday substances) can fool the IMS algorithm:

- Brake fluid
- Diesel additives
- Paint fumes
- Glycol ethers and vinyl esters in cleaning products
- Wintergreen/spearmint oils in mouthwash and breath mints

UNDERSTANDING "DETECTION CIRCLES"

In the following diagram, each circle represents the range of chemicals that each detector technology can "see." Each "detection circle" includes the chemical that the detector was designed to "see" along with cross-sensitive compounds (like brake fluid, etc.). Cross-sensitivity isn't always bad In fact, it is utilized with gas detection tubes to measure CWA. For example, the Dräger™ Phosphoric Acid Esters Tube (p/n 6728461)[3] is designed to measure dichlorvos, a TIC, but it does an excellent job measuring Sarin, Soman and Tobun. While there is a finite number of CWAs, the list of TICs is huge, and TICs can easily fall outside of the "detection circle" of CWA detectors, and yet still are readily measured by a PID. This diagram illustrates two key concepts:



1. PIDs can measure both CWAs and the TICS that can fall outside of the design parameters of military CWA specific measurement tools.
2. Multiple CWA-specific devices are often required to account for cross-sensitivity and to provide a reliable determination of the CWA.

PID SENSITIVITY TO CHEMICAL AGENTS

In February 1999, the US Army Soldier and Biological Chemical Command (SBCCOM) released a study of PID sensitivity to chemical agents entitled *Testing of Commercially Available Detectors Against Chemical Warfare Agents: Summary Report.* This report is perhaps the first printed study of PID response to chemical agents. This testing showed that a RAE Systems MiniRAE Plus PID had good to excellent sensitivity to HD (Mustard), GA (Tobun) and GB (Sarin) chemical agents. Testing with other brands of PIDs employing 11.7eV lamps provides indication that PID sensitivity to Sarin is slightly better with an 11.7eV lamp[4].

Low CF = High PID Sensitivity To A Gas

CF stands for *Correction Factor*. CF is a measure of the PID's sensitivity to a particular gas or vapor. The lower the number, the greater PID sensitivity is to that compound.

- Mustard's CF with 10.6eV lamp is 0.6, so a PID is very sensitive to mustard.
- Sarin's CF with 10.6eV lamp is 3.0, so a PID is less sensitive to Sarin.
- Use PIDs for Exposure limit decisions when a CF <10.
- Use PIDs for gross leak detectors when a CF >10.

Summary of Chemical Agent and Simulant Properties and PID Response

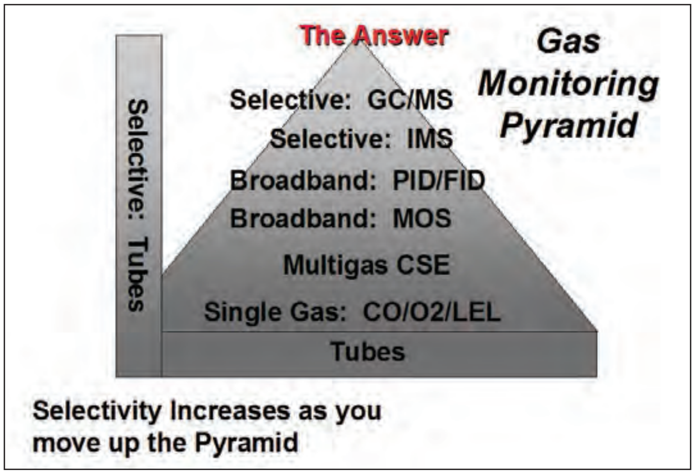
Data from the SBCCOM report has been integrated with our estimates and laboratory testing below. A PID generally gives good to excellent results in screening for chemical agents as seen in the following table:

Compound	Structure	m.w.	Vapor Press. (ppmv)	Lamp (eV)	CF	8-h TWA (mg/m^3)	8-h TWA (ppbv)	LCt50 (ppmv-min.)
Arsine (SA)	AsH_3	78	Gas	10.6	1.9	0.16	0.05	
Cyanogen Chloride	ClCN	61.5		ND**	ND**	0.6 Cξ	300 Cξ	
DMMP	$O{=}P(Me)(OMe)_2$	124		10.6	4.3			
GF	O=PF(Me)(O-Cyclohex)	180		10.6	~3*			
Hydrogen Cyanide	HCN	27	Gas	ND**	ND**	11	10,000	270
Lewisite	$ClCH{=}CHAsCl_2$	207	460	10.6	~1*	0.003	0.35	140
Methyl salicylate	$2\text{-}(HO)C_6H_4CO_2Me$	152		10.6	0.9			
Mustard (HD)	$S(EtCl)_2$	159	95	10.6	0.6	0.003	0.46	>230
N Mustard (HN-1)	$N(Et)(EtCl)_2$	172		10.6	~1*			
Phosgene	$O{=}CCl_2$	99	Gas	11.7	~2*	0.4	100	2
Sarin (GB)	O=PF(Me)(OiPr)	140	3800	10.6	3	0.0001	0.017	12
Soman (GD)	O=PF(Me)(OCH(Me)(tBu))	182	530	10.6	~3*	0.00003	0.004	9
Tabun (GA)	$O{=}P(CN)(OEt)(NMe_2)$	162	48	10.6	0.8	0.0001	0.015	20
Triethyl phosphate	$O{=}P(OEt)_3$	182		10.6	3.1			
VX	$O{=}P(Me)(OEt)(SetN(iPr)_2)$	267	0.92	10.6	~0.5*	0.00001	0.00091	2.7

* Estimated value. ** ND = Not Detectable by PID. ξC = ceiling value

WHERE DO PIDS FIT INTO A WMD GAS MONITORING PROGRAM?

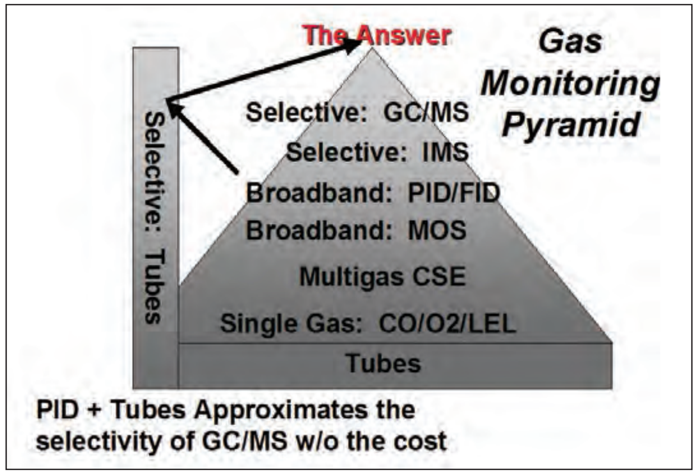
PIDs are the choice of many WMD programs to provide fast, low-level on-site screening for chemical contamination. PIDs can be a very important part of a WMD gas monitoring program containing a variety of options that build towards specificity and sensitivity.



A gas-monitoring program can be represented by a pyramid that builds upon techniques that increase in cost and sophistication until the answer is reached at the top of the pyramid. At its foundation are colorimetric tubes; then it builds to single-gas monitors (like CO monitors) and progresses to multi-gas confined space monitors. From there, a gas-monitoring pyramid can add broadband monitoring of chemicals (via PIDs) and finally move on to the top of the pyramid with specific techniques from colorimetric tubes to IMS and GC/MS (gas chromatography/mass spectroscopy). However, it is dangerous to jump to the top of the gas-monitoring pyramid if one has not established a proper foundation. For example, if one's entire budget is spent on an expensive GC/MS, then little or none might be left for important broadband scanning devices. For those without the budget or the demand for costly CWA-specific monitors, the same ground can be covered with a continuous monitoring PID and a simple specific detector like a colorimetric ("Dräger") tube as can be seen in the previous diagram.

PIDs are "Scouts" for GC/MS

Broadband scanning devices like PIDs are important, because they are simpler and can be fielded in greater quantities to provide more widespread protection. In addition, broadband detectors like PIDs can provide clues that a more specific measurement technique like GC/MS or even colorimetric tubes may be needed. In this case PIDs act as "scouts" or "survey" instruments for the more specific and complicated detectors. Many people don't realize that the well-known Tokyo subway Sarin attack was the third such incident, and that there were injuries and fatalities in the previous two incidents. Perhaps if "survey" instruments like PIDs were available, these injuries and fatalities could have been reduced or prevented.



PIDs will not provide a selective measurement technique for CWA. Instead a PID is a "broad band" monitor that provides very accurate measurement down to ppm and ppb levels. A PID is effectively the detector out of a gas chromatograph, and like a GC, has been shown to deliver excellent accuracy even below 1 ppm. Many experts feel that the PID is an excellent field-screening tool to help establish the absence of CWA or TICs. Therefore, if a PID can help to establish the lack of CWA or TICs, it can quickly quell a potential political problem. However, if an agent has been identified by CWA-specific techniques like M-256, SAW, or CAM, then the PID can readily provide accurate and continuous measurement of the identified compound.

Day-To-Day Use Builds Confidence In PIDs

PIDs have been proven rugged and reliable, and are accepted by most HazMat responders for the bulk of HazMat responses. By using PIDs for common HazMats (like fuels, paints, etc.), responders can build confidence in PID detection capability. The more esoteric measurement techniques required by CWA detection (M-256, SAW or CAM) are rarely if ever used, so responders cannot build confidence with these techniques as easily. Many WMD teams are using PIDs as part of their preparedness for terrorist chemical events. Some of these teams include:

- US Army National Guard Civil Support Teams (CST)
- Numerous city HazMat teams including New York City and Washington, DC.
- Marines Corps CBIRF Team
- FBI HazMat team
- US Secret Service
- Department of Homeland Security

REFERENCES

1. **Guide for the Selection of Chemical Agent and Toxic Industrial Material Detection Equipment for First Responders**, National Institute of Justice, June 2000
2. **Chemical and Biological Terrorism**: National Academy Press, Washington, DC, 1999. Page 20
3. **Dräger Tube Handbook**: 11th Edition, Drägerwerk, AG., Page 206
4. **Testing of Commercially Available Detectors Against Chemical Warfare Agents: Summary Report**: Terri L. Longworth, Juan C. Cajigas, Jacob L. Barnhouse, Kwok Y. Ong, Suzanne A. Procell, SBCCOM, Aberdeen, MD, February 1999. Table 3.

RAE Systems: PIDs as a HazMat Response Tool (Application Note AP-203)

RAE Systems: Correction Factors and Ionization Potentials (Technical Note TN-106)

RAE SYSTEMS SOLUTIONS FOR MEASURING CHEMICAL AGENTS

ppbRAE Plus PID: Breakthrough technology to measure VOCs and other ionizable compounds in parts per billion. The ppbRAE provides unsurpassed accuracy and is capable of continuous detection down to 1 ppb with a range of 0 to 200 ppm.

MiniRAE 2000 PID: The MiniRAE 2000 is our best detection, or survey, instrument.

- **Linear from 0-10,000 PPM with 3-second response.**
- **Quick lamp and sensor access:** Access the lamp and sensor in seconds without tools. Other PIDs have quick lamp access, but what is the point if you can't clean the sensor. Cleaning the lamp without cleaning the sensor is like taking a shower and then putting on the same sweaty clothes!
- **Nickel Metal Hydride Drop-in Battery:** has no memory effects, unlike NiCds.
- **Intelligent:** User-friendly screens make it easy to take advantage of the sophisticated options in the MiniRAE 2000, including the 100 Correction Factors in memory.
- **Rugged Rubber Boot:** Protection in the roughest conditions.
- **Bags Samples:** the standard sample bagging attachment of the MiniRAE 2000 lets you bag unknown positive results for further lab testing.

MultiRAE Plus: Combines a 0 to 2,000 ppm PID with the "standard" four gases (O_2, LEL, CO and H_2S) in one compact monitor, to provide accurate warning that threshold levels (ppm) of chemicals (and other toxic gases) are about to be exceeded. The MultiRAE Plus has two specific toxic sensor sockets that can draw from 10 specific toxic sensors (CO, H_2S, SO_2, NO, NO_2, Cl_2, HCN, PH_3 and NH_3). This allows both "broad-band" monitoring with the PID and specific toxic chemical monitoring.

AreaRAE: A ruggedized MultiRAE with radio-frequency (RF) capability. Up to 16 AreaRAEs can communicate continuously with a modem-equipped computer at a central command post. Voice and GPS options make the AreaRAE a highly versatile gas monitoring/communications system. The AreaRAE is perfect for defining perimeters in extended HazMat operations or for pre-positioning for proactive monitoring of special events in sports and convention venues.

ToxiRAE II Pocket PID: This instrument is for those who want the sensitive broadband capabilities of the 0 to 2,000 ppm PID/VOC detector in our MultiRAE, but they already have a 4-gas monitor. The ToxiRAE is the most affordable PID in the world.