Decision-Making in Chemical Warfare Agent (CWA) Response

There is a lot of fear associated with Chemical Warfare Agents (CWAs). The misnomer "Nerve Gas" quickly brings horrible images to the minds of many civilians. But if we lay aside the politics and fear, CWA detection should treated like other gas/vapor detection challenges. It should be a collaborative process encompassing physical clues, threat scenario, biological clues, and a variety of sensing technologies. No one clue or technology is always correct. Experience and the use of multiple clues and technologies are the keys to successful CWA response. Understanding what the clues are and how to layer them to make a decision is critical to successful CWA response.

Why is Gas Detection Important?

Responders cannot rely on their senses for decision-making. Without effectively knowing how to use detection techniques responders are unable to properly identify threats and make decisions that are appropriate to the actual hazard. Detection technologies supplement the responder's senses when making decisions in potentially hazardous environments. Relying on the senses alone can be dangerous in chemical response; detectors become our eyes and ears when those senses fail us. Proper use of detection technologies coupled with the clues present at the scene allow for better decision making.

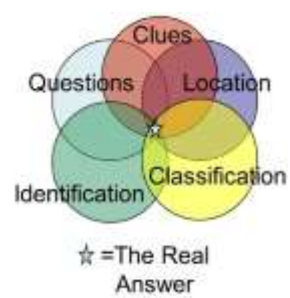
Over Responding Can Be Dangerous to the Community

Risked Based Response (RBR) is a common concept in the first responder community. The idea is to respond at the lowest level necessary to prevent undue risk to the responder whilst protecting the public. Over-responding can be dangerous to the community because panic is as effective a killer as bullets, bombs or chemical attacks. One example of how panic can kill occurred in 2003 when more than 1,500 people were in the Epitome Night Club in Chicago when someone released pepper spray into the air. 21 people were crushed to death in the resulting stampede to evacuate the club from the unknown chemical release. The community will echo how the first responders act. If the first responders are calm, civilians will act accordingly. If the first responders over-react and immediately jump into full encapsulation protection it could panic the public and cause unnecessary worry and even injury.

Over Protection Can Be Dangerous to the Responder

Heat stress is the number one injury in HazMat response and immediately jumping into full Level A encapsulation is a good way of overheating oneself. Level A encapsulation also makes one much more susceptible to slip, trip and fall injuries. Finally, over protection makes it harder to get things done. When properly used, detection allows responders to respond at lower levels of Personal Protective Equipment (PPE) to provide the highest levels of safety to themselves and to the community that they protect.

CWA Response Is a 5-Step Process



1. **Clues:** are the physical clues, threat scenario and biological clues consistent with a CWA release
2. **Location:** survey tools or "sniffers" will help find out where "it" is coming from. If you can find "it" you have a much better chance to figure out what "it" is
3. **Classification:** will narrow down the problem to give a general idea of the chemical you are dealing with to understand how to proceed. It is not necessary to differentiate between GA and GB to administer antidote!
4. **Identification:** using clues, common sense or an instrument to gain the specific identify of a chemical or a mixture of chemicals

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5. **Ask the Right Questions:** responders have to interpret the clues AND ask the right questions.

Why Worry About CWAs?

CWAs are chemicals designed to either kill or debilitate an opposing military. They are often derived from civilian Toxic Industrial Chemicals (TICs) such as insecticides, chlorine and hydrogen cyanide. In 1994 the Japanese Cult Aum Shinrikyo released Sarin spray from a refrigerated box truck in a quiet neighborhood of Matsumoto, Japan with the intent to kill three judges who were due to rule against the cult. Seven people were killed and 200 hospitalized. In 1995, the Aum cult again used Sarin to terrorize the Tokyo subways by simultaneously spilling Sarin liquid in a number of subway cars. Twelve people were killed, about 1000 were hospitalized and thousands became ill. In Iraq, insurgents have used chemical munitions to make roadside IEDs (Improvised Explosive Devices). With terrorist groups having demonstrated their ability to make and use CWAs, responders must look at ways to effectively detect and respond to these compounds.

CWAs are Accessible

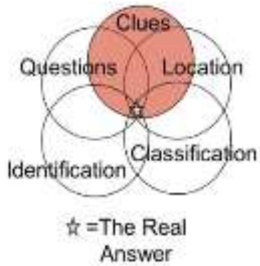
Until that last few years one of the most common ways to dispose of chemical munitions was to bury it, or dump it off our coasts, and it often has been lost track of. Abandoned munitions and lab materials at military or research facilities can provide easy access to CWAs.

- After WWII the Germans left 296,103 tons of chemical weapons. The US share was 30-40K tons which they disposed of in 6/1946-8/1948 by sinking 9 ships in the Baltic Sea and 2 in the North Sea in operation “Davy Jones Locker”
- From 1967-68 four ships containing CWAs were sunk in a three mile area between Florida and the Bahamas as part of “Operation CHASE” (Cut Holes and Sink ‘Em)
- In 1995 “mustard” shells from WWI were dug up during the construction of subdivision outside of Washington, DC
- In 2003 US made Chloropicrin shells were found in a Baltimore, MD basement, live but not armed
- In 2010 Mustard contaminated clams were dredged out of Long Island Sound and burned some of the fishermen

- CWAs can be stolen from poorly maintained regulated stockpiles. Terrorists in Iraq and Afghanistan have used CWAs as IEDs either intentionally or inadvertently.
- Aum Shinrikyo has twice demonstrated that they can make and disperse Sarin and it can be expected that others can and will follow Aum’s example.

Physical Clues

- Any signs of dissemination techniques?
- Is there a valid/credible threat?
- Is there any physical evidence?
- Are there any dead animals or ones that display SLUDGEM /DUMBBELLS type symptoms?
- Are there any human victims displaying SLUDGEM /DUMBBELLS symptoms?



A Brief History of CWAs

CWAs are chemical compounds designed to either kill or debilitate opposing militaries. With terrorist groups having demonstrated their ability to make and use CWA, responders must look at ways to effectively measure these compounds. Chemical warfare is not a 20th century development:

- The Chinese used arsenical smokes in 1000 BC.
- The Spartans used noxious smoke and flame against the Athenian allied cities in the Peloponnesian War in 429 and 424BC.
- Leonardo DaVinci proposed a powder of sulfur and verdigris (oxidized copper) as a weapon in the 17th century.
- The **Strasbourg Agreement of 1675** is the first international agreement banning the use of chemical weapons and was created in response to the use of poisoned bullets
- John Doughty, a New York City school teacher, proposed chlorine filled 10 inch shells during the US Civil War but was turned down because the weapon was too inhumane.
- **The Hague Convention of 1899** prohibited "the Use of Projectiles the Object of Which is the Diffusion of Asphyxiating or Deleterious Gases"
- On April 22, 1915 the Germans used chlorine against the Allied trenches in Ypres, Belgium with 5,000 fatalities and an additional 10,000 casualties. One of the lessons from using chlorine is that it is not persistent. Wind easily carried the chlorine gas over to the English trenches. However, the weather is fickle, and when the wind changed it carried the chlorine gas back over to the Germans.
- What was needed was a stable and persistent chemical that would stay where it was needed. Mustard "gas," also called Yperite or Ypercite, was used for the first time near Ypres in the autumn of 1917. Mustard is a liquid at normal temperatures and it is very persistent. That is, it is not a gas and it stays where it is put. Mustard is so pervasive that is still remains in the soil and water around Ypres. Modern farmers have sat down on freshly cut tree stumps and suffered severe burns to their rear ends because the trees draw up the mustard in the soil and water and concentrate it in their sap. In Edgewood, MD, Mustard contaminated soil is remediated with trees.
- Chemical Weapons came of age in WWI
    - By the beginning of 1918 one in four projectiles were chemical
    - By November 1918 one in two shells were chemical
    - While Phosgene caused the most deaths in WWI, Mustard caused the most casualties
- 6/17/1925 **The Geneva Protocol** prohibits the first use of chemical and biological weapons

Modern "Nerve Agents"

- On December 23, 1936 Dr. Gerhard Schrader of I.G. Farben invented Tabun (GA) as an insecticide. Because of a 1935 Nazi decree it was reported to the Ministry of War as an invention of possible military significance.
- In 1938 Sarin was invented and was named for its discoverers ***S***chrader, ***A***mbros, ***R***igriger and Vad Der L***in***de.
- The V-series of agent was invented by the US in the 1960s.
- Novichok was invented by the Russians in the 1990s.
- On January 13, 1993 the US and Russia entered into the **Chemical Weapons Convention (CWC)** that prohibits the use and manufacture of chemical weapons.

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CWA Classes and Characteristics

- Nerve
  - Liquids at normal temperatures
  - Stable & persistent
- Blister
  - Liquids at normal temperatures
  - Stable & persistent
- Choke/Blood
  - Gases at normal temperatures that are normally treated by first responders as TICs
  - As the gas detection protocols for TICs are well developed the balance of this paper will only address nerve and blister agents

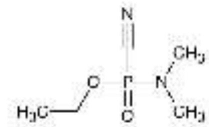
Nerve: agents are more toxic than other agents. At sufficient concentrations they can cause effects within seconds and death within minutes. Nerve agents are divided into two classes G and V agents:

1. **G**, or "German" agents are older and more volatile and are more of a vapor hazard
2. **V** or "Venom" agents are newer, less volatile, more persistent, more toxic (~2x) and more of a contact hazard

Nerve agents are stable and persistent liquids at normal temperatures that can vary from clear & colorless to light amber to dark brown depending on purity and age. GB recovered from Guam during the US demilitarization process was the color of coffee and still 98% pure.

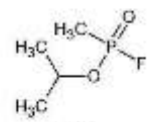
Nerve agents are organophosphates which are defined by a phosphorous-oxygen double bond at the heart of their chemical structure. They are similar to insecticides but 100-500 times more powerful, although technical grade, highly concentrated organophosphate pesticides, such as parathion, are only about 3 times less toxic than military nerve agents. Because of this EMS in big agricultural states routinely carry and use the same atropine/2 pam auto-injectors that are used for military nerve agents to address organophosphate pesticide exposures. Nerve agents are cumulative hazards, repeated exposures to low concentrations may produce symptoms.

- **GA/Tabun**
  - **Chemical Name**: Ethyl N, N-dimethylphosphoroamidocyanidate



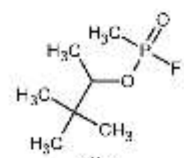
GA

  - **Synonym**: Dimethylaminocyanophosphoric acid ethyl ***ester***
- **GB/Sarin**
  - **Chemical Name:** Isopropyl methylphosphonofluoridate



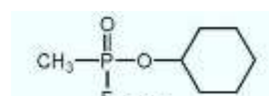
GB

  - **Synonym**: Methylphosphonofluoridic acid isopropyl ***ester***
- **GD/Soman**
  - **Chemical Name:** Pinacolyl methyl phosphonofluoridate
  - **Synonym**: Methylphosphonofluoridic acid 1,2,2-trimethylpropyl ***ester***



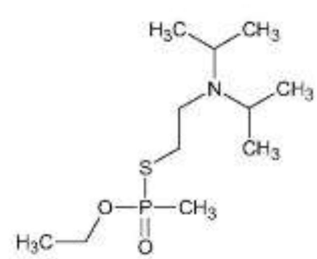
GD

- **GF/Cyclo-sarin**
  - **Chemical Name:** Cyclohexyl methylphosphonofluoridate



GF

  - **Synonym:** Phosphonofluoridic acid, methyl-, cyclohexyl ***ester***
- **VX**
  - **Chemical Name:** O-Ethyl-S-(2-diisopropylaminoethyl) methyl phosphonothiolate



VX

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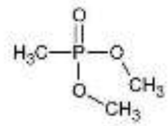
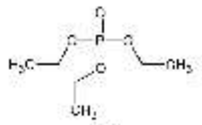
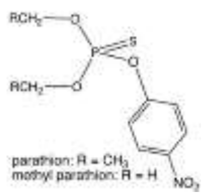
- **Synonym:** Phosphonothioic acid, methyl-, S-(2-(diisopropylamino)ethyl) O-ethyl ***ester***

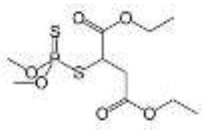
In all of the "Nerve" agents we can see that chemically they all contain phosphorous (P) , which we will later see is important for at least one detection technology, and they are all organophosphates. Other organophosphates such as DMMP (Dimethyl methylphosphonate commonly used as a flame retardant) and TEP (Triethyl phosphate often used as a plasticizer) can be used as Nerve agent simulants.


DMMP


TEP

Organophosphate pesticides are chemically similar to nerve and will often give nerve alarms on CWA detectors.




Malathion

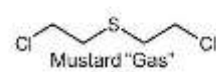
We can also see that all the Nerve agents are complicated acidic ***esters*** (the author has added bold italics to the ester parts in each of the synonyms to illustrate that they are all complicated organic, acidic esters).

- **GA/Tabun**
  - **Chemical Name**: Ethyl N, N-dimethylphosphoroamidocyanidate
  - **Synonym**: Dimethylaminocyanophosphoric acid ethyl ***ester***
- **GB/Sarin**
  - **Chemical Name**: Isopropyl methylphosphonofluoridate
  - **Synonym**: Methylphosphonofluoridic acid isopropyl ***ester***
- **GD/Soman**
  - **Chemical Name:** Pinacolyl methyl phosphonofluoridate
  - **Synonym:** Methylphosphonofluoridic acid 1,2,2-trimethylpropyl ***ester***
- **GF/Cyclo-sarin**
  - **Chemical Name:** Cyclohexyl methylphosphonofluoridate
  - **Synonym:** Phosphonofluoridic acid, methyl-, cyclohexyl ***ester***
- **VX**
  - **Chemical Name:** O-Ethyl-S-(2-diisopropylaminoethyl) methyl phosphonothiolate
  - **Synonym:** Phosphonothioic acid, methyl-, S-(2-(diisopropylamino)ethyl) O-ethyl ***ester***

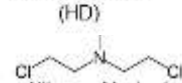
That fact that all of the Nerve agents are esters may be the cause of cross-sensitivities with other compounds that are or contain esters such as some cleaning compounds and brake fluids.

Blister: Agents are colorless to dark brown oily liquids at normal temperatures (HD Gels below 50ºF,14.5ºC) that are stable and persistent. Blister agents can take minutes to hours to develop blisters. They often do not immediately kill their victims like nerve agents. But blister agents certainly make it difficult for soldiers to perform their tasks. When inhaled, blister agents can fill their victims' lungs with fluid and can cause chemical pneumonia. Because Blister Agent symptoms take time to develop and it does not immediately cause death, many people do not consider blister agents an effective WMD agent.

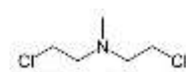
- **HD/Mustard**
  - **Chemical Name**: Bis (2-chloroethyl) sulfide

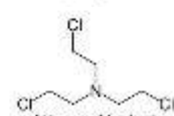

Mustard "Gas" (HD)

- **HN-1/Nitrogen Mustard-1**
  - **Chemical Name:** 2,2'-Dichlorotriethylamine


Nitrogen Mustard (HN1)

- **HN-2/Nitrogen Mustard-2**
  - **Chemical Name:** Bis-(2-chloroethyl)methylamine


Nitrogen Mustard (HN2)


Nitrogen Mustard (HN3)

- **HN-3/Nitrogen Mustard-3**
  - **Chemical Name:** 2, 2', 2"-Trichlorotriethylamine

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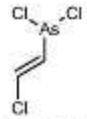
- **L/Lewisite**
  - **Chemical Name:** Dichloro(2-chlorovinyl)arsine



Lewisite (L)

The "blister" agents don't have a common defining chemical element like the nerve agents. From the previous brief summary we can see that blister agents can be sulfur (HD), amine (HN) or arsine (L) based. We will later see how these elements/compounds are important for at least one detection technology and they also can lead to some cross-sensitivities with other compounds that contain sulfur and amines.

Nitrogen Mustard is known to depress white blood cell count. Because Leukemia is too many white blood cells in 1954 doctors in the US Army's Edgewood labs tried injecting Nitrogen Mustard into a critically terminal leukemia patient and found the first effective chemotherapy for leukemia. Nitrogen Mustard is still an ingredient in some oncology drugs and has been found in the personal effects of retired oncologists

Blood or Choke: agents are gases at normal temperatures that are neither stable nor persistent. They include chlorine, phosgene, hydrogen cyanide and cyanogen chloride. They act by choking, or preventing the blood stream from taking up oxygen by preferentially binding to hemoglobin. Typically these TICs still have legitimate industrial uses and can be encountered in "routine" HazMat calls so they will not be focused on in the rest of this paper.

A Brief Review of Chemical Properties

When discussing CWAs it is important to understand their chemical properties. CWAs are complex organic compounds and are **not very water soluble**. This can provide a clue. For example, water will bead up on M8 paper and M9 tape while organic chemicals and CWAs quickly soak right into these colorimetric technologies. So if a sample beads upon on M8 paper it probably is not a CWA.

Soluble > G > VX > L >> HD > Insoluble

Vapor Pressure tells us how readily a liquid (or solid) wants to evaporate into a vapor. Low vapor pressure chemicals do not want to make vapors while high vapor pressure chemicals want to become gases. Any chemical with a vapor pressure over 1 ATM, 760 mm/Hg, 14.7 PSIA or 1,701 mb is a gas. Vapor pressures of over 40 mm/Hg are more likely to move around and are considered to be an inhalation or vapor hazard. As a reference point, water has a vapor pressure of 20 mm/Hg.

A chemical's **boiling point** is another way to understand how readily a liquid wants to move to a vapor state. A liquid's boiling point is the temperature at which it transitions to a gas. Low boiling point chemicals want to become vapors and have relatively higher vapor pressures making them easier to measure in air. An example is gasoline. High boiling point chemicals do not want to become vapors, have relatively low vapor pressures and are harder to measure in air. An example is diesel.

A Summary of CWA Chemical Properties

Name	Abbreviation	Melting Point (°C)/ (°F)	Vapor Pressure mm/Hg (@20°C)	Boiling Point °C/ °F
Tabun	GA	-50/-58	0.07	246/475
Sarin	GB	-57/-70	1.48	147/297
Soman	GD	-80/0112	0.92	190/374
Cyclo-Sarin	GF	-12/10	0.93	228/442
Mustard	HD	14/57	0.11	217/422
Lewisite	L	-18/-0.4	0.35	190/374
VX	VX	-51/-59	0.0007	298/568
Water	H_2O	0	17.54	100/212
Diesel	Diesel		0.40	160-371/ 320-700
Heavy Fuel Oil	#6 Fuel Oil		<5.2	176-648/ 350-1200

All of the CWAs have vapor pressures less than 40mm/Hg (an arbitrary "vapor threat" pressure), less than 20mm/Hg for water (which is not that volatile), less than diesel,

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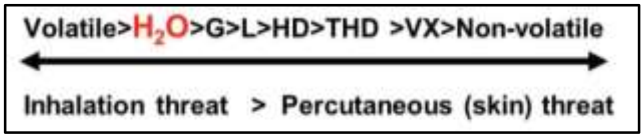
and even less than #6 fuel oil (essentially crank case oil).



There Is No Such Thing as “Nerve Gas”

Owing to their low vapor pressure and high boiling points, CWAs do not represent much of a vapor threat unless they have been aerosolized in some way. They are heavier than air and tend to stay low to the ground.

CWAs are stable and persistent liquids, as opposed to gases, because the army that deploys them wants them to stay on their enemy and not float back. Compared to gases like chlorine, hydrogen fluoride, and ammonia, which all can move readily in air, CWAs are very toxic but they are not that tough to contain. Unlike most other atmospheric threats (like lack of oxygen) there are antidotes for CWA exposure. Without some means of dissemination via aerosolization, CWAs will take some time to produce vapors that would affect people at room temperature of ~20ºC/65ºF.

Dissemination Is the Key

If one were to solely look at CWAs chemical characteristics they do not appear that threatening. While they are very toxic, they do not want to move and “chase” us as gases like chlorine and ammonia can and will do. The key to successful deployment of CWAs is dissemination, which is a fancy name for the techniques used to spread the CWAs around. There are four dissemination techniques which can provide a clue as to the nature of the attack/event:

1. **Explosive Dissemination**
   - The military has honed their skills on using low level explosive (dispersant) charges to disseminate chemicals. A CWA shell is lofted into the air by its propellant charge. Then when it reaches the proper altitude a secondary “dispersant” charge is detonated to turn the heavy liquid into a mist or a spray that spreads out over the opposing military.
   - Big explosions burn up chemical like a fuel-air bomb, but small ones spread it effectively. The army will dispose of unstable chemical ordinance in place, rather than taking the risk of transporting it, by blowing it up in place.
   - If witnesses/victims talk of hearing a “pop” without a fireball that is a good sign of a dispersant charge
   - If they speak of a big boom or whoomp followed by a fireball it is highly probable that the explosion consumed the CWA
   - Explosions that dispense liquids, mists or gases should be suspected dispersant charges.
   - Explosions that seem to only destroy a package or bomb itself should be suspected as dispersant charges.
2. **Pneumatic Dissemination**
   - Can be as simple as garden sprayers. Aum’s first strike was against judges in Masumoto, Japan using a garden sprayer that killed 7.
   - Unscheduled or unusual sprays should be suspected as dispersant incidents
   - Abandoned spray devices should be suspected as dispersant devices.
3. **Mechanical Action Dissemination**
   - Plastic bags inside paper bags or boxes that were poked with sharpened umbrella tips in Tokyo proved to be a poor dissemination method. This seems to indicate that their intent may have been to create more of a distraction than to kill large numbers of people.
   - Glass bottles dropped from above or plastic bottles with holes in them that allow agent to splash down the station steps may have been more effective.
4. **Chemical Reaction Dissemination**
   - Cyanide tablets plus acid = gas

Dissemination is the key to killing a lot of people. With proper dissemination, Tokyo could have been the first 9/11 type of event with thousands of fatalities. However,

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because CWAs all have low vapor pressures, after effective dissemination it is likely that a film will be left on flat, smooth, non-porous surfaces. CWAs are not gases, and they will take hours to days to break down even in direct sunlight. If there has been a valid dissemination technique used then look for clues on surfaces in the area near the dissemination.

Is There a Valid Threat Scenario?

When responding to potential CWA releases responders should first think about what the potential threat scenario is. Terrorists are most likely to use CWAs against high-visibility targets:

- **Transportation:** subways in Tokyo
- **Public venues:** sports arenas, conventions
- **Dignitary visits**

Terrorists are not as likely to use CWAs against normal everyday people unless they are part of a large crowd, big event or part of the transportation system (like subways).

Nerve Agent Actions

Vertebrate nervous systems are hybrid electrical-chemical systems. Electrical pulses travel down the neurons and chemicals complete the transfer to the next nerve at the synapses. Organophosphates Nerve agents quickly shut down the nervous system by blocking acetyl cholinesterase (AChE) transmission at the nerve synapses and because of this they are also known as acetyl cholinesterase inhibitors. AChE normally binds and hydrolyzes the neurotransmitter ACh, which ends the activity of ACh at the receptor sites. Nerve agents bind to AChE, making it unable to bind with ACh. ACh is not hydrolyzed and it builds up causing an hyperactivity/ overstimulation of the body organs stimulated by cholinergic neurons. Essentially the affected nerves go into “overdrive.” At high dose IDLH (Immediately Dangerous to Life and Health) levels they produce muscles twitches, foaming at the mouth, tremors, and lungs constrict & fill with fluids. At low dose TWA (Time Weighted Average or 8 hour dosage) levels they can produce pinpoint pupils, watery eyes, stomach cramps or can feel like a bad hangover. Nerve agents are cumulative poisons, repeated exposures to low concentrations may produce symptoms. Animals displaying the characteristic symptoms of organophosphate exposure (DUMMBELLS or SLUDGEM) are good clues to a Nerve agent release. But human victims displaying the characteristic symptoms of organophosphate exposure (DUMMBELLS or SLUDGEM) are always the ultimate and best nerve agent detector.

Agent Toxicity

Before discussing the toxicity of the CWAs it’s important to understand how toxicity is defined:

- **Dosage:** is the amount of substance administered per body weight
- **ECt_{50}:** Median Effective Dosage of a vapor or aerosol is the effective dosage that will cause some defined effect in 50% of exposed, unprotected people
- **ED_{50}:** Median Effective Dosage of a liquid agent is the amount expected to cause some defined effect (like collapse or convulsions) in 50% of exposed, unprotected people
- **LCt_{50}:** Medial Lethal Dosage of a chemical agent vapor or aerosol is the dosage that is lethal to 50% of exposed, unprotected people for a defined minute volume (MV) and exposure duration
- **LD:** Lethal Dose
- **LD_{50}:** Median Lethal Dosage of a liquid chemical agent is the amount expected to kill 50% of a group of exposed, unprotected people
- **MV(L):** Minute Volume in liters
- **ROE:** Route Of Entry

GB Toxicity Estimates

Endpoint	Toxicity (mg-min/m^3)	MV (L)	Exposure Duration	ROE
Lethality	LD_{50}: 1700 mg	N/A	N/A; 70-kg man	Percutaneous Liquid
	LCt_{50}: 35	15	2 min	Inhalation/ Ocular
	LCt_{50}: 12,000	N/A	30-360 min	Percutaneous Vapor
	LCt_{50}: 6000 (provisional)	N/A	30-360 min	Percutaneous Vapor
Severe effects, includes some deaths	ED_{50}: 1000 mg	N/A	N/A; 70-kg man	Percutaneous Liquid
	ECt_{50}: 25	15	2 min	Inhalation/ Ocular
	ECt_{50}: 8000	N/A	30-360 min	Percutaneous Vapor
	ECt_{50}: 4000 (provisional)	N/A	30-360 min	Percutaneous Vapor
Threshold effects (Slight ChE inhibition)	ECt_{50}: 1200	N/A	30-360 min	Percutaneous Vapor
	ECt_{50}: 600 (provisional)	N/A	30-360 min	Percutaneous Vapor
Mild effects (miosis, rhinorrhea)	ECt_{50}: 0.4	N/A	2 min	Inhalation/ Ocular

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VX Toxicity Estimates

Endpoint	Toxicity (mg-min/m³)	MV (L)	Exposure Duration	ROE
Lethality	LD_{50}: 5 mg	N/A	N/A; 70-kg man	Percutaneous Liquid
	LCt_{50}: 15	15	2-360 min	Inhalation/ Ocular
	LCt_{50}: 150	N/A	30-360 min	Percutaneous Vapor
	LCt_{50}: 75 (Provisional)	N/A	30-360 min	Percutaneous Vapor
Severe effects, includes some deaths	ED_{50}: 2 mg	N/A	N/A; 70-kg man	Percutaneous Liquid
	ECt_{50}: 10	15	2-360 min	Inhalation/ Ocular
	ECt_{50}: 25	N/A	30-360 min	Percutaneous Vapor
	ECt_{50}: 12 (Provisional)	N/A	30-360 min	Percutaneous Vapor
Threshold effects (Slight ChE inhibition)	ECt_{50}: 10	N/A	30-360 min	Percutaneous Vapor
	ECt_{50}: 5	N/A	30-360 min	Percutaneous Vapor
Mild effects (miosis, rhinorrhea)	ECt_{50}: 0.1	N/A	2-360 min	Inhalation/ Ocular

HD Toxicity Estimates

Endpoint	Toxicity (mg-min/m³)	MV (L)	Exposure Duration	ROE
Lethality	LD_{50}: 1400 mg	N/A	N/A; 70-kg man	Percutaneous Liquid
	LCt_{50}: 1000	15	2 min	Inhalation/ Ocular
	LCt_{50}: 10,000	N/A	30-360 min	Percutaneous Vapor
	LCt_{50}: 5000 (Provisional)	N/A	30-360 min	Percutaneous Vapor
Severe effects (vesication)	ED_{50}: 600 mg	N/A	N/A; 70-kg man	Percutaneous Liquid
	ECt_{50}: 500	N/A	30-360 min	Percutaneous Vapor
	ECt_{50}: 200	N/A	30-360 min	Percutaneous Vapor
Severe effects (eyes)	ECt_{50}: 75	N/A	2-360 min	Ocular
Mild effects (erythema, itching, some pain)	ECt_{50}: 50	N/A	30 min	Percutaneous Vapor
	ECt_{50}: 25	N/A	30 min	Percutaneous Vapor
Mild effects (eyes)	ECt_{50}: 25	N/A	2-360 min	Ocular
Odor detection	EC_{50}: 0.6-1mg/m	N/A	Few seconds	Inhalation

HN1 Toxicity Estimates

Endpoint	Toxicity (mg-min/m³)	MV (L)	Exposure Duration	ROE
Lethality	LD_{50}: 1400 mg	N/A	N/A; 70-kg man	Percutaneous Liquid
	LCt_{50}: 1000	15	2 min	Inhalation/Ocular
	LCt_{50}: 10,000	N/A	30 min	Percutaneous Vapor
	LCt_{50}: 5000	N/A	30 min	Percutaneous Vapor
Severe effects (vesication)	ED_{50}: 600 mg	N/A	N/A; 70-kg man	Percutaneous Liquid
	ECt_{50}: 500	N/A	30 min	Percutaneous Vapor
	ECt_{50}: 200	N/A	30 min	Percutaneous Vapor
Severe effects (eyes)	ECt_{50}: 75	N/A	2 min	Ocular
Mild effects (pain, erythema, itching)	ECt_{50}: 50	N/A	30 min	Percutaneous Vapor
	ECt_{50}: 25	N/A	30 min	Percutaneous Vapor
Mild effects (eyes)	ECt_{50}: 25	N/A	2 min	Ocular

Biological Detection

Humans can smell Sulfur Mustard (HD) at about 0.1 ppm while the LCt_{50} is 1500 ppm. Smell is not a reliable indicator as it can vary with individual, batch, purity. Exposure to even very low levels of nerve agent vapor produces:

- Observable signs: Miosis and runny nose
- Symptoms: Headache, blurred or dim vision

Nerve agent will kill other species, and dosage is dependent on the size and the metabolism of the animal. Smaller animals with fast metabolisms will be affected faster than large animals with slower metabolisms. Insects, amphibians, reptiles, birds and small mammals will all be affected by nerve agents before humans. However, humans are biological indicators for large animals like horses and elephants. Because of its low vapor pressure and high vapor density, nerve

agents will not stay aerosolized, meaning that they will quickly fall to the ground, affecting ground dwelling and grazing species first. The characteristic symptoms of CWA exposure, both in humans and in animals, are one of the best and most unequivocal means of establishing the presence of CWAs.

Nerve Agent Symptoms

There are two major mnemonics used to remember human (and animal) nerve agent symptoms: DUMBBELLS and SLUDGEM. Each captures many of the same symptoms somewhat differently. ***Irritated eyes and throats are NOT found in the SLUDGEM or DUMBBELLS acronyms and are NOT valid clues to the presence of CWAs.***

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DUMBBELLS
D - Diarrhea (Diaphoresis-excessive sweating)
U - Urination (peeing)
M - Miosis (constriction of the pupil of the eye)
B - Bronchospasm (difficulty breathing)
B - Bradycardia (slow heart beat)
E - Excite skeletal muscle and CNS emesis (vomiting)
L - Lacrimation (tearing)
L - Lethargy (fatigue)
S - Salivation (excessive drooling)

SLUDGEM
S - salivation (excessive drooling)
L - lacrimation (tearing)
U – urination
D - defecation / diarrhea
G - GI upset (cramps)
E - emesis (vomiting)
M - muscle (twitching, spasm, "bag of worms")

Severity of symptoms is dose dependent. Here are some more specific symptoms to look for:

- Nose: runny nose (Rhinorrhea)
- Airways: tightness in chest, difficulty breathing, wheezing (Dyspnea)
- GI Tract: nausea, vomiting, diarrhea
- Glands: increase of secretions sweat, nasal, salivary, bronchial
- Skeletal: muscle twitching
- Central Nervous System (CNS): confusion, agitation, forgetfulness, insomnia, irritability, impaired judgment, seizures, coma
- Eyes: pinpoint pupils (Miosis)

"The eyes may be the window to the soul, but they also can serve as an agent alarm" *(i.e. Miosis) (Brad Rowland, DPG)*

Bird Kill Examples
In 12/2000 there was a bird kill at the Texas State house in Austin, TX. As George H.W. Bush was governor and president-elect there was a viable threat scenario in this case. Upon questioning the building maintenance people it was found that they had baited the area for "nuisance" birds. In about the same time there was a bird kill at a low-income apartment complex in Woonsocket, RI. Upon questioning the building maintenance people it was found that they had baited the area for "nuisance" birds.

Certainly the Austin response had a higher threat scenario and required a higher level of response. However, over-responding in the Woonsocket scenario could have caused fearful apartment dwellers to harm themselves even when there was no threat to them.

Clues Summary
- Any signs of dissemination techniques?
  - A dissemination technique MUST be used to effectively spread CWAs
    - Explosion that dispensed liquids, mists or gases
    - Explosion that seemed to only destroy a package or the bomb itself
    - Unscheduled or unusual spray
    - Abandoned spray devices
- Is there a valid/credible threat?
- Is there any physical evidence?
  - If liquid samples are found do they bead up or are they quickly absorbed into M8?
  - Classic CWAs are not "gasses" and there will be strong clues if they have been used
  - CWAs are heavy, low-vapor pressure liquids, after effective dissemination the area should appear to be coated with it
  - Days after dissemination/spills CWAs on outdoor surfaces exposed to sunlight will have degraded but CWAs can still be found in protected areas such as soils, groundwater
- Are there any biological clues?
  - Are there any dead animals or ones that display SLUDGEM /DUMBBELLS type symptoms?
  - Are there any human victims displaying SLUDGEM /DUMBBELLS symptoms?
  - ***Irritated eyes and throats are NOT found in the SLUDGEM or DUMBBELLS acronyms and are NOT valid clues to the presence of CWAs***
  - If no human signs or symptoms take a breather and figure it out, do not rush to antidotes and decon

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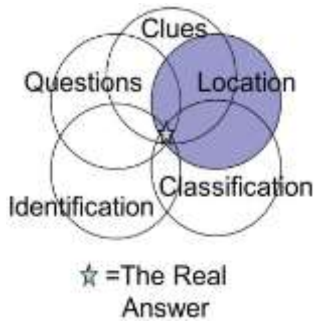
CWA Location

Why Are Survey Sensors Important?



Survey sensors or “sniffers” are one of the best tools to quickly identify if something is out there and where it is located. If you can’t find “it” you will never figure out what “it” is. On their own, survey sensors will not tell what that “something” is, but they can often quickly (<3-10 seconds) tell where it is coming from and how much is there. “Classification” and “Identification” devices may be too slow to “sniff.”

M9 tape

M9 is a “dumb” survey technique. M9 tape is a simple colorimetric technology. It is designed to be taped to personnel (on boots and the bottom of pant legs) and to vehicle bumpers. It only indicates red as a positive response and is best used with a classification technology.

- Advantages
  - Simple
  - Stores well (keep cool)
  - Inexpensive (<$7 for 10m roll)
- Disadvantages
  - A liquid sample is required
  - Red color change can’t be read with night vision filters (red) on flashlights
  - Many organics will provide positive response including cleaning solvents, ammonia, some petroleum products and even high temperatures.

PIDs and FIDs

A Photoionization Detector (PID) or Flame Ionization Detector (FID) may provide faster “sniffing” for the location of CWA than most CWA classifiers because they not only respond faster but can display below the alarm threshold so that concentration gradients can be “seen.” CWA classifiers often require more time to detect, therefore, when sampling, the user often must check for potential contamination slowly and methodically, much like when checking for alpha radiation contamination. Coupled with clues (e.g. chemical pools, clouds, dead animals, victims, placards and waybills) that provide identification of a chemical, some survey sensors like PIDs and FIDs can quickly tell how much is there when the proper scaling factors (Correction Factors) are used, but they are broad-band detectors that respond to a wide variety of chemicals other than CWAs.

- Advantages
  - Relatively inexpensive to purchase
  - Can detect many CWAs in air
  - Fast response time
  - Store well
  - Inexpensive to use <$0.25/hr for PID <$1.00hr for FID
- Disadvantages
  - PIDs with 10.6eV lamps can’t “see” hi IP chemicals (Sarin is borderline, can’t see chlorine or phosgene)
  - Non specific

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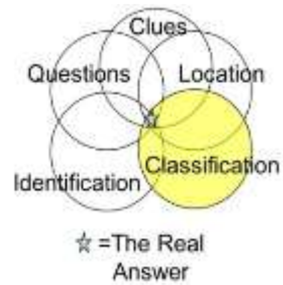
The ChemPro100i can Locate and Classify Simultaneously

One product, the ChemPro100i, can locate or “sniff” and classify simultaneously. It provides a rolling line graph and audible “Geiger-Counter” style beep so users can “see” and “hear” areas of higher concentrations. It can be easily used as a survey tool, much like a Photoionization Detector (PID) “on steroids” to quickly “see” concentration trends. The ^{241}AM (Americium-241) 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.

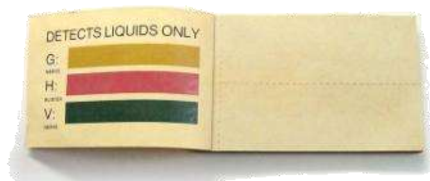
CWA Classification

Classification may take more time than location. Classifiers will typically come up with an answer quicker on real agent than on cross-sensitive chemicals. There are two fundamental types of CWA classification techniques, chemical color change technologies (colorimetrics) and direct reading devices. Properly used in conjunction with each other and the other clues at a scene, these technologies can provide a very high degree of confidence.



M8 Paper

M8 Paper is one of the simplest means of classifying CWAs. Some have called it “pH paper” for CWA. Detection is based upon solubility of dyes in CWA. Nerve indicates yellow, Blister indicates red and VX indicates green.



- Advantages
  - Simple
  - Stores well (when kept cool)
  - Inexpensive (<$5 per book)
- Disadvantages
  - A liquid sample is required
  - Many organics will also dissolve the dyes including cleaning solvents, ammonia, some petroleum products and even high temperatures.

M256A1 Kit

The M256A1 kit is an organic chemistry set on a paper card to provide classification of nerve, blister and blood agent gas, vapors and liquids (an undocumented feature of the M256A1 kit is that drops of chemical samples can be put on the sample pads for faster response than waiting for an airborne sample). The test

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process takes 12-25 minutes and the instructions are complicated and hard to read off of the dark green packaging material. It is counter-intuitive that the G series indication is a lack of color change where the other pads do change colors. Most colorimetric techniques make a positive color change, from white to a new color, in the presence of the target chemical.

- Advantages
  - Cheapest way into vapor detection of CWAs ($140 per kit)
  - Can do liquids too
  - Stores well (keep cool)
- Disadvantages
  - 15-25 minute test time
  - Complicated instructions
  - “Trainer” kits are only differentiated from the real thing by a hard to see blue band around the dark olive green package.
  - Interferents: some smokes, high temperatures and petroleum products
  - Per use cost of $140 is high if multiple samples are required

Colorimetric Tubes

Often referred to as “Draeger” tubes after the German manufacturer, a colorimetric tube is a glass tube filled with a silica substrate coated with reagent that will produce a color change when exposed to the chemical of interest. The user draws a predetermined sample through the tube and reads the scale like reading an old glass thermometer. The tube is calibrated at the factory and this calibration is printed on the side of the tube as a scale. Calibration is typically valid for operation life of tube (2 years).

Some common Tubes for WMD

Chemical Species	Draeger PN	Sensidyne PN	Detects
Phosphoric esters	6728461	(132LL) Dichlorovos/ Trichloroethylene	GA, GB, GD
Carbon Tetrachloride	8101791		Chloropicrin
Organic Arsenic Compounds	CH26303	(19LA) Arsine	Lewisite
Thioether (Qualitative)	CH25803	N/A	Mustard (HD)
Organic Basic Nitrogen (Qualitative)	CH25903	Mustard	Nitrogen Mustard
Phosgene	CH28301	(16)	Blood/Choke
HCN	CH25701	(12L)	Blood/Choke
Cyanogen Chloride	CH19801		Blood
Cyanide	6728791		Blood/Choke
Chlorine	6728411		Blood/Choke

- Advantages
  - Proven technology
  - Factory calibrated (no expensive calibration gas required)
  - Relatively inexpensive vapor detection technique ($2-10 per sample)
- Disadvantages
  - “Snap Shots,” non-continuous, no alarms can result in sampling error
  - Respond in minutes rather than seconds
  - 15-25% accuracy Piston/Bellows style
  - Readings subject to interpretation
  - Does not store well, tubes expire and a large stock is expensive to keep up to date (keep cool)

Traditional “Closed Loop” IMS

Ion Mobility Spectroscopy (IMS) uses a radiation source (ionizing and non-ionizing) to break down a sample into ions that then travel down a magnetic drift tube where the ions are separated to generate a characteristic spectra or “picture.” This picture is matched up against pictures in the detector’s library to provide a positive identification. One simplistic way to look at IMS is “ion distillation.” In traditional closed loop IMS, the ion cell is separated from ambient air by a membrane to keep contaminants from affecting the signal. Clean air, provided by a sieve pack, keeps the inside of the ion cell perfectly clean.

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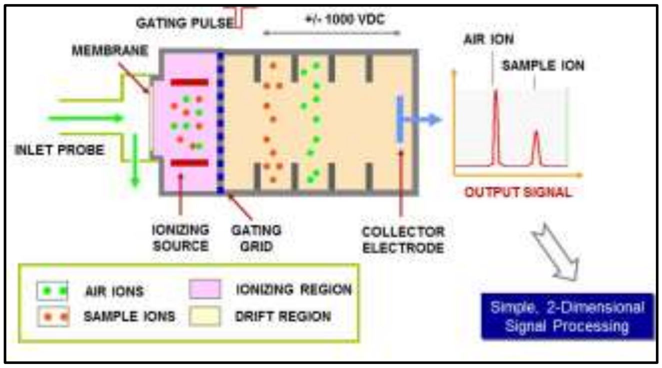
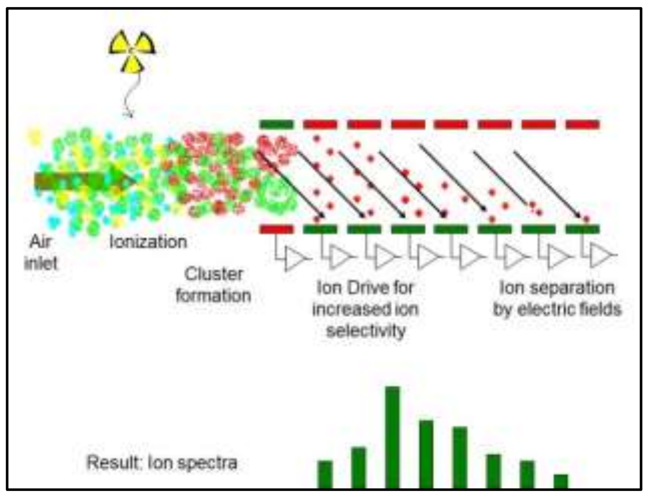


Sometimes chemical dopants are also used to keep contaminant under control. For example, acetone is used by one manufacturer to help absorb moisture. Membranes, sieve packs and dopants are expensive consumables that have to be periodically replaced (typically annually depending on use). Sometimes change out is predictable but they can fail unpredictably when presented with gross contaminants. The membrane slows response time, especially on VX, and also slows recovery when the detector is exposed to high chemical concentrations. Some closed loop IMS CWA detectors need to be "exercised" or run once per day/week/month or else they will not work when an emergency comes. To "exercise" a detector, turn it on, wait for it to stabilize, challenge it with simulant and then wait for it to clear. This process may take over an hour.

- Advantages
  - Sensitive Instrument good for vapor detection
  - Military proven technology
  - Quick response time
  - Good detection of class (i.e., G vs. H)
- Disadvantages
  - False positives to many common urban chemicals
  - Small to none TIC capability until $20-30K detectors
  - Some use radioactive sources that require NRC license and periodic wipe testing
  - Unpredictable maintenance intervals, if the sieve gets chemically contaminated it will not work
  - Membranes slow response time
  - Stores poorly, must be exercised
  - Can be expensive to maintain lifetime costs of +$2/hr of use

Open Loop or "Aspirated" IMS

The open-loop IMS sensor uses a Nuclear Regulatory Commission (NRC) exempt ^{241}Am (Americium) ionization source. As safe as a smoke detector, it does not require periodic nuclear wipe tests like ^{63}Ni (Nickel) sources in some other IMS products. The IMS sensor is open to the environment, no membrane or sieve pack is used to maintain cleanliness in the sensor. Because of this, the open loop IMS can provide much faster response and clearing times than closed loop IMS, allowing for open-loop IMS to also be used for location or "sniffing." The high ionization potential of its ^{241}Am source allows it to be used to sniff for GB, chlorine and other high ionization potential chemicals largely unseen by PIDs with a 10.6eV lamp. Life-cycle costs and logistical footprint are much less than those of traditional closed-loop IMS and flame-spectrophotometer based devices because it does not require costly membranes and sieves to keep the sensor clean and it does not use expensive hydrogen gas.



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- Advantages
    - Sensitive instrument good for vapor detection
    - Military proven technology
    - Quick response time
    - Good detection of class (i.e., G vs. H)
    - Good TIC capability (>40)
    - As safe as a smoke detector
    - Predictable service intervals
    - Stores well, no need to exercised
    - Inexpensive to maintain, lifetime costs <$0.50/hr of use
- Disadvantages
    - False positives to many common urban chemicals (typically shown as a “Chemical Threat” alarm)

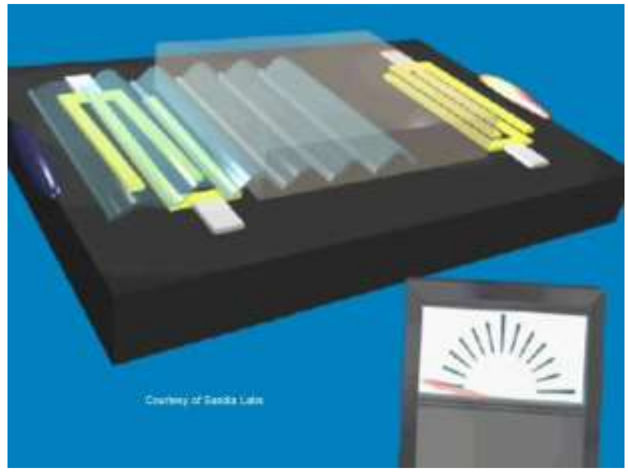
Surface Acoustical Wave (SAW)

SAW sensors convert acoustic waves to electrical signals by exploiting the piezoelectric effect of certain materials. Their use for CWA detection originated in the US Naval Research Labs. A waveform (sound) is generated on a quartz substrate. The substrate is coated with a polymer that has an affinity with the chemical to be detected. When the target chemical bonds with the polymer coating, the wave form frequency changes

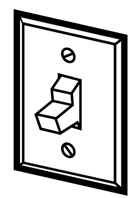
Individual SAW ~0.3"

Array of 4 SAWs with 2 heaters

(tone changes) indicating that the target chemical is present. Selectivity comes from the choice of the polymer coating. Simplified, a SAW is essentially a polymer (“paint”) on a quartz substrate; the chemical of interest is absorbed into the paint and changes the tone.



While an elegant solution SAWs have two problems. First, while specific they lack low end sensitivity relative to IMS and flame spectrophotometry. Second they are very susceptible to chemical contamination of their polymer coatings. To illustrate this, consider a handprint by a light switch on the wall. After cleaning the handprint (especially with small children) it eventually comes back. Eventually cleaning the handprint is not enough and the wall must be repainted. As the paint (polymer) in a SAW absorbs chemical, some of that chemical (either target or interferent) is left behind. As chemical is left behind the baseline signal rises, eventually the baseline signal rises to the point that it equals the signal level and detection is no longer possible. A new sensor is needed and SAW sensors are expensive to replace.



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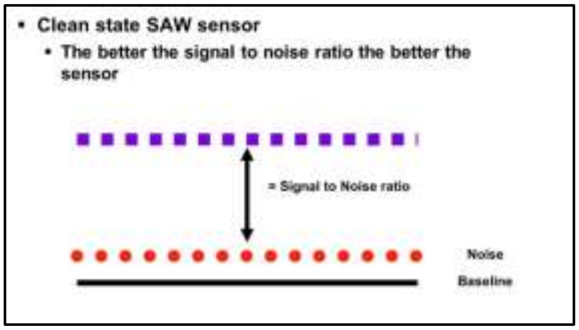
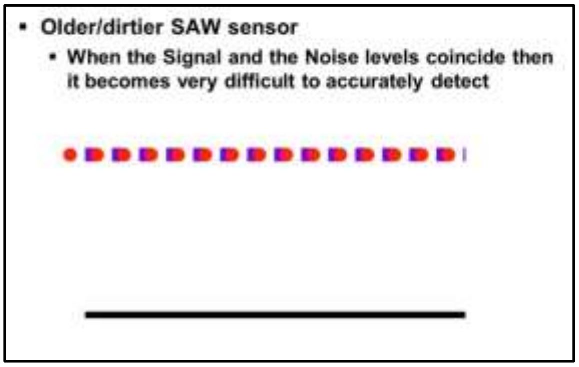
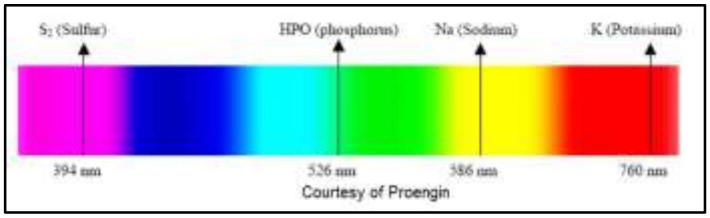




- Advantages
  - Specific vapor detector
  - Proven technology
  - Stores well (assuming no contaminants in the air)
- Disadvantages
  - Some common vapors (like alcohols) may ruin the polymer coating
  - Less sensitive, alarms well above military levels
  - Unpredictable end of life
  - Lifetime costs can be significantly higher than IMS based products (~$9/hour of use)

Flame Spectrophotometry

Chemicals produce characteristic electromagnetic spectra (colors) when they



Courtesy of Proengin

burn in a colorless hydrogen flame. Fireworks take advantage of this characteristic to produce the desired colors. In the case of spectrophotometry for CWA detection the detector looks for the spectra that are specific to phosphorous, sulfur, arsine and nitrogen compounds that are a defining characteristic of nerve and blister agents. It provided relative quantification by the intensity of the color. The brighter the color the more chemical is present. It is very sensitive and quick to respond to chemicals that contain sulfur (blister), phosphorous (nerve), amines (nitrogen mustard) and arsine (lewisite). However, this technology is perhaps the least specific to CWAs of any of the competing technologies because ANY chemical containing phosphorous, sulfur, amines and arsine will give false positive alarms. Product manuals warn against locating near exhausts which can produce false blister alarms because sulfur dioxide is a by-product of the combustion process. Phosphorous is not just in organophosphates. The second largest use of phosphorous in the world is as a fabric safe whitener in detergents. So if one does not rinse clothing thoroughly, a Flame Spectrophotometry detector could improperly identify detergent residue as nerve agent contamination. These devices only classify to the main chemical species and are not as specific as IMS and SAW detectors, which are much more specific to organophosphates and blister agents.

- Advantages
  - Military proven technology
  - Quick response time
  - Stores well, no memory affect
- Disadvantages
  - EXPENSIVE to purchase
  - False positives to exhausts, fuel spills and detergent
  - Does not measure TICs (unless they contain sulfur, phosphorous, amines or arsine)
  - Run time constrained by hydrogen size to 12 hours per cylinder (@$100 per cylinder)
  - Long-term operations can be hindered by the requirement for hydrogen gas
  - Hydrogen gas is difficult to ship by air, which hinders air deployment of this technology (hydrogen fill station costs $75K)
  - >$12/hour to run

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Orthogonal Detectors

"Orthogonal" means to look at something from many different angles and orthogonal detectors do this by using a variety of sensors rather than just one type to come to a conclusion. Each sensor has its strengths and weaknesses. "Sensor fusion" takes advantage of this by utilizing the strengths of a number of sensors to come to a final conclusion. Advanced signal processing is used to match the pattern from the sensor array to a library of compounds. 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.

- Advantages
  - Less false alarms
  - More chemicals detected than just a short CWA list
  - Great when they cost less or the same as the sum of the various detectors that they replace
- Disadvantages
  - Can be very expensive
  - Can be larger and heavier
  - Their value is questionable when they cost much more than the sum of the detection technologies they include

CWA Classifiers Can Be Fooled

Every detector will have some false positives. Typically different detector technologies will have different false positives. Most CWA classification techniques were designed for the battlefield environment and do not always take into account cross-sensitivities from common chemicals found in the urban environment. Low vapor pressure for most CWAs complicates classification because other low vapor pressure chemicals can fool the algorithms. This is not a condemnation of CWA classifiers, just a realization that multiple confirmational techniques may be required in CWA response. CWA classifiers tend to take longer to come up with a solution when presented with simulants than if presented with the real thing.

CWA Simulants/Cross-sensitivities for Classifiers

- Brake fluid (nerve on some IMS, SAW and M8 paper)
- Anti-freeze (blister on some IMS, nerve on some SAW)
- Anything with methyl salicylate (oil of wintergreen) including: Skoal, Wintergreen Altoids, Peppermint Oil, Mennen "Speed Stick," "Deep Heat," Ben Gay, (blister on some IMS and SAW)
- Detergent residue on clothing due to the phosphorous in "whiteners" (nerve-Flame Spectrophotometry)
- Sulfur compounds in fuel products or exhaust (blister-Flame Spectrophotometry)
- Fingernail polish remover (nerve-M8)
- Cleaners that containing esters including: "Super Gleam" glass cleaner, ACE Brand window cleaner, "Spray-9" industrial cleaner (nerve on some IMS)
- Real toxic materials (chemically similar to nerve)
  - Parathion, Malathion (nerve)
  - DMMP: Dimethyl Methyl Phosphonate (nerve) also possibly found in flame retardants
  - TEP: Triethyl Phosphate (nerve) also found in plasticizers so decon tents and Level A suits possibly could give "nerve" alarms on some detectors
  - Tributoxyethyl phosphate (TBEP) found in Acolade floor polish is also US Army VX simulant

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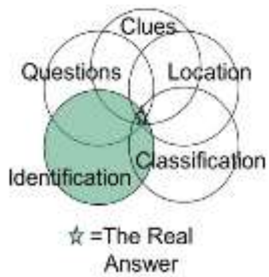
CWA Identification

After a chemical has been located and classified in some special situations it is necessary to identify it. Speciation (typically spectroscopy) technologies are used to identify chemicals so that additional actions can be taken. "Spectroscopy" is the study of how electromagnetic radiation interacts with the atoms and molecules:

- "Infrared" or FTIR spectroscopy is the study of how infrared light is absorbed by the bonds between atoms that form molecules
- Mass Spectroscopy ionizes pure chemical peaks, produced by a gas chromatograph, which breaks down into characteristic and identifiable pieces; this spectral "fingerprint" is unique to a particular chemical and can be matched to a library.



Essentially spectroscopy is the science of taking a "picture" and matching that picture to another known "picture" in a library. Once a spectrum is acquired the system software can perform a search analysis for the "unknown" in question.

FTIR Spectroscopy

In Fourier Transform Infrared (FTIR) spectroscopy, infrared (IR) radiation is passed through a sample. Wavelengths of IR light that a chemical absorbs determines what that chemical is (fingerprint). Each molecular structure has a unique combination of atoms and produces a unique infrared spectrum (identification = qualitative). When FTIR is used for gas/vapor measurement, thanks to the ***Beer-Lambert Law*** the amount of IR that is absorbed (intensity) determines how much chemical is there (concentration = quantitative). FTIR is a proven technology for chemical identification used for over 50 years in applications from laboratories to law enforcement and industry.

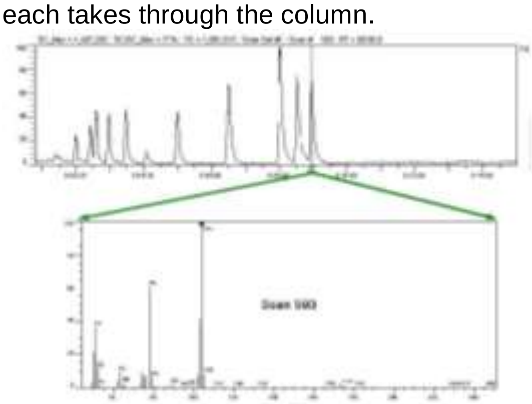
FTIR can be used to identify some solids, pastes and liquids including CWAs. FTIR can also be used to identify some gases and vapors including CWAs. FTIR analyzers are typically fast acting and easy to use. Their ability to handle mixtures varies with vendor although some products will not be able to see a component in a mixture if it accounts for 10% or less of the mixture. They typically have the advantage of low lifetime costs but they can be expensive ($10's of thousands) to purchase.

- Advantages
  - Can identify many solids, liquids, pastes, gases & vapors
  - Relatively easy to use
  - Low calibration and logistical requirements
  - Stores well
- Disadvantages
  - Either solids or gases not both
  - Some difficulty with mixtures
  - Some are heavy and bulky
  - Very expensive to purchase

Gas Chromatography/Mass Spectroscopy

GC/MS is the combination of two technologies to help identify gases or vapors:

Gas Chromatography (GC): separates high boiling from low boiling chemicals (low vapor pressure from high vapor pressure) and puts them into "peaks" that represent their characteristic travel time through a chromatography column (a small very small capillary tube). High boiling (low vapor pressure) compounds have longer retention time in the capillary than low boiling (high vapor pressure) compounds. The resulting graph is called a "chromatogram" which shows a series of peaks representing different chemicals separated by the time that each takes through the column.



Mass Spectroscopy (MS): ionizes these pure chemical peaks which break down into characteristic and identifiable pieces. This spectral "fingerprint" is unique to a particular chemical and can be matched to a spectral library. In the *Ionizer* a corona discharge

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ionizes the peaks into ions. In the *Quadrupole Rods* the ions are electronically filtered and separated before they reach the *Detector* which measures their response.

Some portable GC/MS have a **survey mode** in addition to the GC/MS mode. In this survey mode the GC is by-passed and the sample is drawn directly into the MS. This gives quicker response time of about 2 minutes versus the 15-25 minute process time for GC/MS mode. Survey mode can analyze relatively pure samples to 10's of ppm but had difficulty with mixtures and providing low levels of sensitivity.

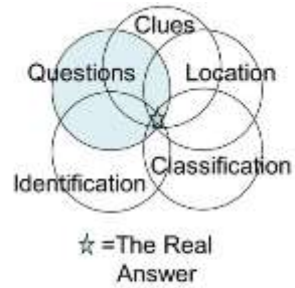
In **GC/MS mode** the GC separates each chemical into peaks and then each peak is further separated into ions for identification by the MS. This mode is most useful for separating mixtures and has high sensitivity (10's of ppb) but it takes much longer, 15-25 minutes per sample.

- Advantages
  - The "Gold Standard" of gas detection
  - Very accurate
  - Very specific
- Disadvantages
  - Very expensive to purchase ($60-$100K)
  - "Snap Shots," non-continuous (MS can run continuous)
  - Respond in minutes rather than seconds (~2 min in survey ~20 min in GC/MS mode)
  - Very complicated & training intensive
  - Very heavy and bulky
  - Does not store well (NEG vacuum pumps prefer constant rather than intermittent use)
  - ~$35/hr to use

CWA Identification Technology Summary

While typically more expensive to purchase and while they may take longer to make a measurement, they provide a "quality check" on faster and cheaper colorimetric and direct reading technologies.

Ask the Right Questions



Asking the proper questions may be the key to an effective CWA response. We can't be overly dependent on technology. We have to also use common sense. If the classical signs of CWA exposure are NOT present in both animal and human victims then it can be assumed that CWAs are NOT present no matter what other detection techniques are showing.

- Take a "breather" and work the clues to solve the problem

If it is not an obvious CWA attack, but some detection technologies are giving false alarms, responders need to ask questions to see if there have been any recent changes to the environment that are causing the false alarms:

- Dissemination questions
  - Has there been an explosion that dispensed liquids, mists or gases?
  - Has there been an explosion that seemed to only destroy a package or the bomb itself?
  - Has there been an unscheduled or unusual spray?
  - Has there been any abandoned spray devices?
- Is there a valid/credible threat?
  - Are there any high profile individuals visiting?
  - Is a high profile event taking place?
- Is there any physical evidence?
  - If liquid samples are found do they bead up or are they quickly absorbed into M8?
  - CWAs are heavy, low-vapor pressure liquids, is the area coated with anything, are droplets or pools of liquid present?
  - Days after dissemination/spills CWAs on outdoor surfaces exposed to sunlight will have degraded but CWAs can still be found in protected areas such as soils, groundwater

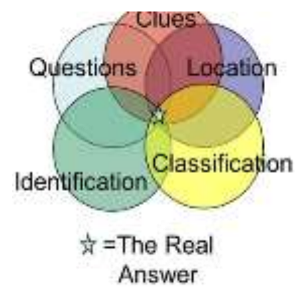
- **What has changed, what is different from before the incident?**
  - SHOW ME
- **Have there been any recent cleaning activities?**
  - Esters in some professional cleaners can mimic G-series agents because nerve agents are esters
  - Some professional floor waxes/sealers contain VX simulant
  - SHOW ME
- **Have there been any recent construction activities?**
  - Can include gluing, painting, cleaning and exhausts from construction machinery
  - SHOW ME
- **Have there been any recent applications of pesticides?**
  - Some pesticides are chemically similar to G-series and they will alarm as "Nerve" even if levels are not high enough to provide symptoms in human victims
  - SHOW ME
- **Have there been any recent attempts at removal of nuisance species using chemicals or bait?**
  - Dead birds, rodents and small animals probably are not signs of chemical agent attack if people are not affected
  - SHOW ME
- **Are there any internal combustion engines running nearby?**
  - Diesel exhaust can set off some CWA detectors
- **Could there be a lot of plastics in the area?**
  - Plasticizers like TEP, used in rubberized tents and Level A suits can simulate nerve agents

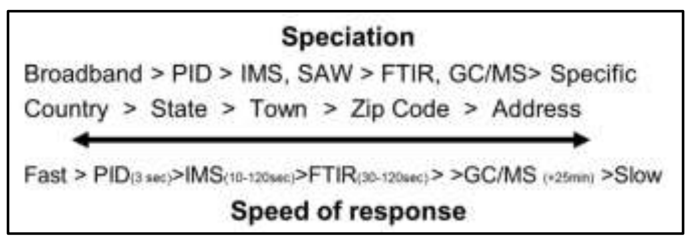
Ask the Right Questions Summary

The questions you ask are perhaps the most important part of CWA response. If the answer to any of these questions is "yes," investigate further before concluding the presence of CWAs. If you find chemicals, look at their ingredients or MSDS to see if they contain any compounds that might provide a cross-sensitive response.

Integrating Gas Detection Technologies

Every technology has its strengths and weakness. In the following chart there are three continuums. The top line moves from broadband detection to very specific gaseous detection. The second line is a metaphoric line and the lowest line represents speed of detection. A PID can locate contamination in seconds. Metaphorically speaking the PID can get to the right state in seconds. An IMS product can classify in 10's of seconds. Metaphorically speaking it can get to the right town in 20-30 seconds. A GC/MS can identify a gas/vapor in 25 minutes. Metaphorically speaking it can identify the correct "address" in 25 minutes. So a PID can be used to find contamination while an IMS can classify it. While classification is adequate for making antidote decisions in the field it is not good enough for evidence and a GC/MS or FTIR analysis of the sample provides more solid identification.





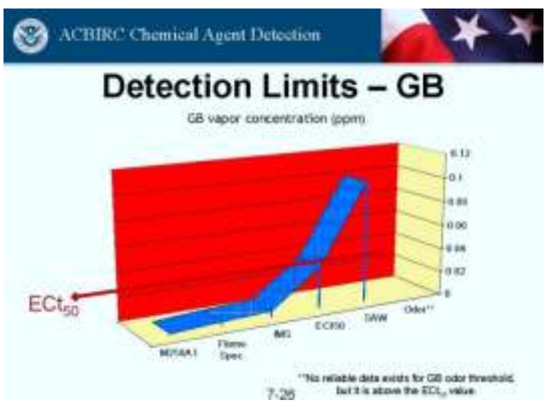
Detection Limits are Important

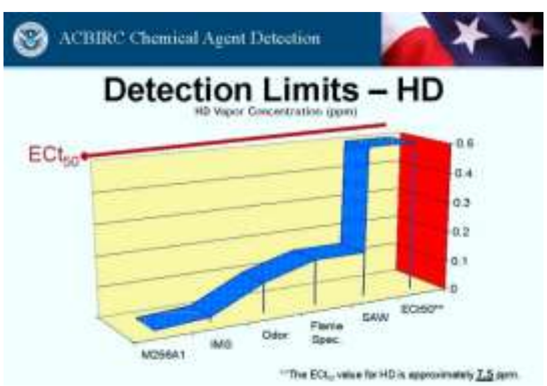
Make sure that you understand the detection limits of your CWA detection technology. Limits of Detection (LOD) can vary widely with detection techniques. IMS and Flame Spectrophotometry can provide fast results to very low levels. SAW detectors can have much higher limits of detection as the following two charts demonstrate. While FTIR can be very accurate, one common gaseous FTIR detector has a LOD of 50ppm!

Handheld CWA Classifier Sensitivity Comparison

Agent Mild Effects	Environics	Bruker	MSA	Proengin	Smiths
	CP100i	RAID-M 100	HazMat CAD Plus	AP2C	LCD 3.3
GB (0.4 mg/m3)	0.04-0.1 mg/m³	0.05 mg/m³	0.2-0.9/0.13-25 mg/m³	0.01 mg/m³	0.1 mg/m³
VX (0.1 mg/m3)	0.04-0.1 mg/m³	0.05 mg/m³	0.2-0.9/0.13-25 mg/m³	0.03 mg/m³	0.1 mg/m³
HD (25 mg/m3)	0.5-2.0 mg/m³	0.35 mg/m³	1.2-1.4/0.23-0.31 mg/m³	1 mg/m³	1 mg/m³
HN1 (25 mg/m3)	0.5-2.0 mg/m³	0.35 mg/m³	1.2-1.4/0.23-0.31 mg/m³	-	2 mg/m³

Sensitivity is nothing without specificity for classifiers. One of the most sensitive detectors is the least specific.



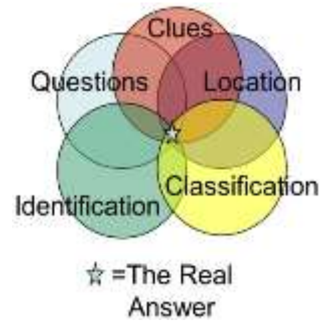


Life Cycle Costs and Sustainability

When purchasing expensive detection technologies for CWA response one should consider not only the cost of acquisition but also the cost of ownership. Some products need expensive consumables or services which can mean very expensive hourly run- rate costs. Some products have unusual logistics demands (like requiring unusual gases to operate) that may not be readily available during a national emergency. Some products may not store well (requiring weekly/monthly "exercising") or may need a long time to "warm up" (as long as an hour or two) after extended periods of storage. When looking to purchase, make sure the entire story is revealed! The following chart compares CWA detectors as cost per hour of use:

In addition to purchase cost, look for products that have low cost of ownership (if all else is equal). Look for products that have multiple uses. This allows operators to become familiar with their performance across a wide range of applications. Single use products like CWA only detection technologies tend to get underutilized and users quickly lose their aptitude when they are not frequently using a detection technology. Another way of looking at this is that multi-use products don't not have to sit around and "gather dust" waiting for a CWA response. The other side of this is that with routine use the user skills on the product don't gather dust either.

Putting It All Together



In this diagram, each circle represents whether or not a particular technique/clue is providing a positive response. By overlaying multiple techniques one can zoom in on the solution just like a detective uses multiple clues to solve a crime. Use multiple techniques until the solution reveals itself.

1. **Clues**
   - Any signs of dissemination techniques?
   - Is there a valid/credible threat?
   - Is there any physical evidence?

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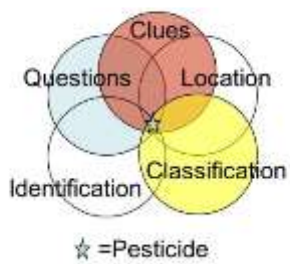
- Are there any dead animals or ones that display SLUDGEM /DUMBBELLS type symptoms?
- Are there any human victims displaying SLUDGEM /DUMBBELLS symptoms?

2. **Location devices**
   - Using PID, FID, M9 are there any areas of higher concentrations?
3. **Classification devices**
   - What are the color change technologies telling you?
   - What is your CWA detection technology(s) telling you?
4. **Identification devices**
   - Verify the above clues with an identification technology
5. **Ask the Right Questions**

Nerve alarm in a Sports Stadium

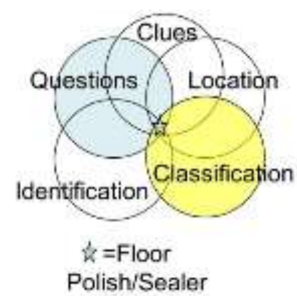
The HazMat team for a state capitol did a security sweep for the local college football team prior to a big game. On a sweep the day before an event they consistently got "Nerve" alarms on their ChemPro100. Upon questioning the custodial staff they found that they had just sprayed the stadium with pesticide. By closely inspecting the pesticide they found that it was an organophosphate pesticide that should give "Nerve" alarms. They scanned the morning of the day of event and found no pesticide readings. If they had found pesticide readings the day of event the ChemPro100 allows users to zero out this background and still alarm if levels were to rise.



1. **Clues**
   - Any signs of dissemination techniques? ***NO***
   - Is there a valid/credible threat? ***YES***
   - Is there any physical evidence? ***NO***
   - Are there any dead animals or ones that display SLUDGEM /DUMBBELLS type symptoms? ***NO***
   - Are there any human victims displaying SLUDGEM /DUMBBELLS symptoms? ***NO***
2. **Location devices**
   - Using PID, FID, M9 are there any areas of higher concentrations? ***NO***
3. **Classification devices**
   - What are the color change technologies telling you? ***Not used***
   - What is your CWA detection technology(s) telling you? ***"Nerve" alarm on a ChemPro100***
4. **Identification devices**
   - Verify the above clues with an identification technology ***Not used***
5. **Ask the Right Questions** ***Pesticide***

Irritated Eyes & Throats in an Office Building

A fire department was called to an office building for irritated eyes and throats; no classic CWA toxicity symptomology was noted. There was no threat scenario, no dispersant technique, no other physical evidence. No reading on the PID but an APD2000 gave a "Nerve" alarm. The floors were very shiny. HazMat asked building maintenance if anything had changed overnight (no symptoms were noticed the prior day). Building maintenance said that a floor contractor had polished the floor overnight. HazMat found some of the floor polish and found that it contained Tributoxyethyl phosphate (TBEP). Not knowing that TBEP was VX simulant, the HazMat officer concluded that the phosphorous in the floor polish was setting off their APD2000.



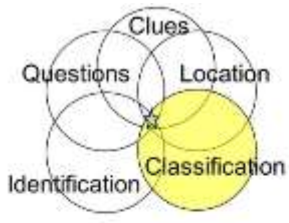
1. **Clues**
   - Any signs of dissemination techniques? ***NO***
   - Is there a valid/credible threat? ***NO***
   - Is there any physical evidence? ***NO***
   - Are there any dead animals or ones that display SLUDGEM /DUMBBELLS type symptoms? ***NO***
   - Are there any human victims displaying SLUDGEM /DUMBBELLS symptoms? ***NO***
2. **Location devices**
   - Using PID, FID, M9 are there any areas of higher concentrations? ***NO***
3. **Classification devices**

- What are the color change technologies telling you? ***Not used***
- What is your CWA detection technology(s) telling you? ***"Nerve" alarm on an APD2000***

4. **Identification devices**
   - Verify the above clues with an identification technology ***Not used***
5. **Ask the Right Questions *TBEP in the floor polish***

Nerve Gas in a Catholic High School

A HazMat team was called to a Catholic High School for "irritated throats." They checked with a PID and found nothing. They checked with a 4 gas monitor and found nothing. They checked with an APD2000, came up "Nerve." Based upon this single reading they called the local CST, set up a mass decon line and decontaminated approximately 300 students. Let's review the clues:

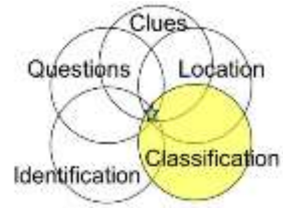


☆ = Never found out

1. **Clues**
   - Any signs of dissemination techniques? ***NO***
   - Is there a valid/credible threat? ***NO***
   - Is there any physical evidence? ***NO***
   - Are there any dead animals or ones that display SLUDGEM /DUMBBELLS type symptoms? ***NO***
   - Are there any human victims displaying SLUDGEM /DUMBBELLS symptoms? ***NO***
2. **Location devices**
   - Using PID, FID, M9 are there any areas of higher concentrations? ***NO***
3. **Classification devices**
   - What are the color change technologies telling you? ***May have been a good next step***
   - What is your CWA detection technology(s) telling you? ***"Nerve" alarm on an APD2000***
4. **Identification devices**
   - Verify the above clues with an identification technology ***May have been a good next step for the CST***
5. **Ask the Right Questions *NOT DONE***

Irritant in a Thrift Shop

A major metropolitan HazMat team was called to a thrift shop for "irritated throats." They checked with PID and found nothing. They checked with a RAID-M and found Mace/Pepper Spray. They checked with an HGVI that came up "Nerve," and they checked with AP2C and got nothing. Most HazMat teams don't have access to this many meters, but in this case the multiple meters help to define the problem. Let's review the clues:



☆ =Never found out, ventilated and employees returned to work

1. **Clues**
   - Any signs of dissemination techniques? ***NO***
   - Is there a valid/credible threat? ***NO***
   - Is there any physical evidence? ***NO***
   - Are there any dead animals or ones that display SLUDGEM /DUMBBELLS type symptoms? ***NO***
   - Are there any human victims displaying SLUDGEM /DUMBBELLS symptoms? ***NO***
2. **Location devices**
   - Using PID, FID, M9 are there any areas of higher concentrations? ***NO***
3. **Classification devices**
   - What are the color change technologies telling you? ***Not used***
   - What is your CWA detection technology(s) telling you? ***HGVI: "Nerve, " Bruker: "Mace," AP2C nothing (very good layering of classifiers)***
4. **Identification devices**
   - Verify the above clues with an identification technology ***Not used***
5. **Ask the Right Questions *Never proved it but suspect that Pepper spray went off in a purse***

There is No "Tricorder":

In the future represented by the classic TV show "Star Trek," one of the characters "Mr. Spock" used a "Tricorder" to analyze unknown environments. But even in this future the Tricorder was given to the smartest guy on the spaceship. In present day CWA response we must be smart in coming to decisions using not only the high-tech detection technologies that we are provided with, but also the clues that we can see with our own eyes.

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About the Author

Christopher Wrenn is the Vice President of Americas Sales for AEssense Corp., a Silicon Valley developer and manufacturer dedicated to providing innovative technological solutions for plant growers worldwide. Previously Chris was 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. Chris was also a key member of the RAE Systems team, helping to grow RAE's revenues from $1M/yr to nearly $100M/yr in the above mentioned markets.

Chris has extensive experience teaching gas and vapor detection and has been a featured speaker at more than 100 international conferences. He has written numerous articles, papers and book chapters on gas/vapor detection. Mr. Wrenn has received the following awards:

- 2011 "Outstanding Project Team Award," in recognition of outstanding service and dedication to the Real Time Detection Registry Team presented by the AIHA (American Industrial Hygiene Association) President
- 2015, received the James H. Meidl "Instructor of the Year" award at The Continuing Challenge, Sacramento, CA presented by CA State Fire Marshal
- 2016, received the "Level A Award" from the International Hazardous Materials Response Team Conference "For your Leadership Service and Support to the Hazardous Response and Training Program."

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