Decision-making in Chemical Warfare Agent (CWA) Response

In responses to releases of Chemical Warfare Agent (CWA) there may not be one technology or one “answer” that is correct. The responder must take into account all of the clues present to conclude the presence or absence of CWAs and take appropriate action. 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 Personal Protective Equipment (PPE) decisions that are appropriate to the actual hazard. Detection technologies supplement our senses when making decisions in potentially hazardous environments. Relying on our senses alone can be dangerous in chemical response, detectors become our eyes and ears when our senses fail us. Proper use of detection technologies coupled with the clues present at the scene allow us to make better decisions.

Risked Based Response

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.

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. Properly used, detection allows responders to respond at lower levels of PPE to provide the highest levels of safety to themselves and to the community that they protect.

CWA Response Is a 3-Step Process

1. **Location:** one needs to quickly figure out where the problem is coming from using clues, common sense and survey tools. Victims running from a central location, clouds of chemical, and pools of liquid all provide location clues. Survey technologies like Photoionization and Flame Ionization Detectors (PIDs & FIDs) also can help in location. Location should take seconds to minutes and can cost nothing to $3000-5000 for a survey monitor like a PID.
2. **Classification:** one needs to quickly get a general idea of the kind of threat using clues, common sense or classification technologies like colorimetric techniques, Ion Mobility Spectroscopy (IMS), Surface Acoustical Wave (SAW) or Flame Spectrophotometry. In the case of CWAs, at this stage it isn’t necessary to differentiate between Soman (GA) or Sarin (GB) because the initial response protocol is the same. Classification should take seconds to minutes and can cost from $5 to $20,000.
3. **Identification:** using clues, common sense or an instrument, we can gain the specific identity of a chemical or a mixture of chemicals. This can back-up the initial classification and will be helpful in further prosecution of the perpetrators.

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Common technologies include Raman, Fourier Transform InfraRed (FTIR) and Gas Chromatography/Mass Spectroscopy (GC/MS). Response time can range from 60 seconds to more than 15 minutes.

What Are CWAs?

CWAs or Chemical Warfare Agents 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.

Why Worry About CWAs?

In 1994 the Japanese Cult Aum Shinrikyo released a 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. 7 people were killed and 200 hospitalized. Later in 1995 the Aum cult again used Sarin to terrorize the Tokyo subways by simultaneously spilling Sarin liquid in a number of subway cars. 12 people were killed, about 1000 were hospitalized and thousands were made 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.

A Brief History of CWAs

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. John Doughty, a New York City school teacher, proposed chlorine filled 10" shells during the US Civil War but was turned down because the weapon was too inhumane. In 1915 the Germans used Chlorine against the English trenches in Ypres, Belgium. One of the lessons from using Chlorine is that it is not stable and 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.

The Invention of 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.

CWA Classes & Characteristics

CWAs are grouped into three major categories:

Nerve: agents are liquids at normal temperatures that are stable and persistent. Nerve agents are acute (quick acting) and act by inhibiting the chemical actions of the central nervous system. Nerve agents are organophosphates that are similar to insecticides but 100-500 times more powerful. They shut down the nervous system by blocking acetylcholinerase transmission at the nerve synapses (acetylcholinerase inhibitors). At IDLH (Immediately Dangerous to Life and Health) levels they produce muscles twitches, foaming at the mouth, tremors, and lungs constrict & fill with fluids. At 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. One thing to remember is that victims are the ultimate and best nerve agent detector.

Nerve Agent Inhalation Exposure Limits

Agent	LCT50 (ppb)	IDLH (ppb)	TWA (ppb)
GA (Tabun)	20000+	30	0.015
GB (Sarin)	12000	30	0.017
GD (Soman)	9000	8	0.004
VX	2700	1.8	0.00091

LCT50: lethal concentration to 50% of the population for 3 minutes.

Blister: agents are liquids at normal temperatures that are stable and persistent. Blister agents can take minutes to hours to develop blisters. They often don't 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 they can develop pneumonia. Because Blister Agent symptoms take time to develop and it doesn't immediately cause death, many people don't consider blister agents an effective WMD agent. While they can deny usage of an area and they definitely cause pain and suffering, they don't provide the dramatic effects that other WMDs can provide.

Blister Agent Inhalation Exposure Limits

Agent	LCT50 (ppm)	IDLH (ppb)	TWA (ppb)
HD (Mustard)	231	0.46	0.46
HN-1 (nitrogen mustard)			0.43
HN-3 (nitrogen mustard)			0.43
L (Lewisite)	141+	4	0.35

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 they are derived from TICs or still have legitimate industrial uses.

A Brief Review of Chemical Properties

When discussing CWAs it is important to understand their chemical properties. **Vapor Pressure** tells us how readily a liquid (or solid) wants to evaporate into a vapor. Low vapor pressure chemicals don't 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 don't want to become vapors, have relatively low vapor pressures and are harder to measure in air. An example is diesel.

From the following chart, we can see that CWAs all have vapor pressures well below 40mm/Hg and therefore do not present much of a vapor threat. In comparison, while diesel will burn, it doesn't represent much of a flammability threat unless it is sprayed in a mist. Due to their low vapor pressure and high boiling points, CWAs don't represent much of a vapor threat unless they have been aerosolized in some way, otherwise they are heavier than air and tend to stay low to the ground.

A Summary of CWA Chemical Properites

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
Mustard	H	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 (the arbitrary "vapor threat" pressure), less than 20mm/Hg for water (which we all know isn't that volatile), less than diesel and even less than #6 fuel oil (essentially crank case oil) so CWAs are not going to easily move around on their own (unlike gaseous TICs like ammonia or chlorine which move easily).

Water Solubility

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 soak right into these colorimetric technologies. So if a sample beads upon on M8 paper it probably is not a CWA.

A Summary of CWA Chemical Properties

Volatility:

Volatile>**H2O**>G>L>HD>THD >VX>**Non-volatile**

Inhalation threat > Percutaneous **(skin) threat**

Water Solubility:

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

There Is No Such Thing as "Nerve Gas"

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. Without some means of becoming aerosolized, CWAs will take some time to produce vapors that would affect people at room temperature of ~20°C/65°F. 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 and deal with. Finally, unlike most other atmospheric threats (like lack of oxygen) there are antidotes for CWA exposure.

Biological Detection

Nerve agent will kill other species too, 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.

Sensitive>insects>amphibians>birds)>mammals >**Less sensitive**

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.

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 dependant

- 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)*

CWA Accessibility

Abandoned munitions and lab materials at military or research facilities can provide easy access to CWAs. The #1 way to dispose of chemical munitions up until that last few years was to bury and forget them, and because of this we have lost track of some. CWAs can be stolen from poorly maintained regulated stockpiles. CWAs can be obtained from former war zones. Terrorists in Iraq and Afghanistan have used CWAs as IEDs either intentionally or inadvertently. Finally, 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.

Dissemination Is the Key

If one were to solely look at CWAs chemical characteristics they don't appear that threatening. While they are very toxic, they don't want to move and "chase" you 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 technique used to spread the CWAs around. There are four disseminations techniques and they 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. So 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.
2. Pneumatic Dissemination
    - Can be as simple as garden sprayers. Aum's first strike was against judges in Masumoto, Japan using a sprayer that killed 7.
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 may be relatively 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 1000's of fatalities. Poking holes in plastic bags using sharpened umbrellas was not effective in killing large numbers of people, but it did create panic amongst thousands.

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. On their own, survey sensors will not tell you what that "something" is, but they can often quickly (<3-10 seconds) tell you where it is coming from and give you a quick idea of how much is there. "Classification" and "Identification" devices may be too slow to "sniff."

PIDs and FIDs

A PID will provide faster "sniffing" for the location of CWA than most CWA detectors because it not only responds faster but it will display below the alarm threshold so that concentration gradients can be "seen." CWA detectors 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 (like chemical pools, clouds, dead animals, victims, placards and waybills, etc.) that provide identification of a chemical, some survey sensors like Photoionization Detectors and Flame Ionization Detectors (PIDs & FIDs) can quickly tell you how much is there when the proper scaling factors (Correction Factors) are used.

- Advantages:
    - Relatively inexpensive to purchase
    - Can detect CWAs in air
    - Fast response time
    - Store well
    - Inexpensive to use <$0.25/hr for PID <$1.00hr for FID
- Disadvantages
    - PIDs and FIDs are non-specific

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.

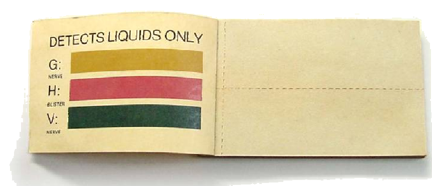
Locate THEN Classify

A PID in the hands of a person trained in identifying CWA signs and symptoms may provide faster screening in a decon line than a CWA detector because no handheld CWA detector can detect below miosis levels. You can see it in their eyes before you can detect it. Locate first, then classify.

CWA Classification Techniques

Classification will typically 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.

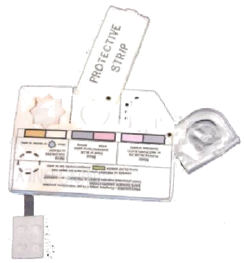
M8 Paper



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/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 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 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 blue band around the dark olive green package. It is very hard to see.
  - Interferants: some smokes, high temperatures and petroleum products
  - Per use cost of $140/use 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 is 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 yrs).

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 & 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 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.

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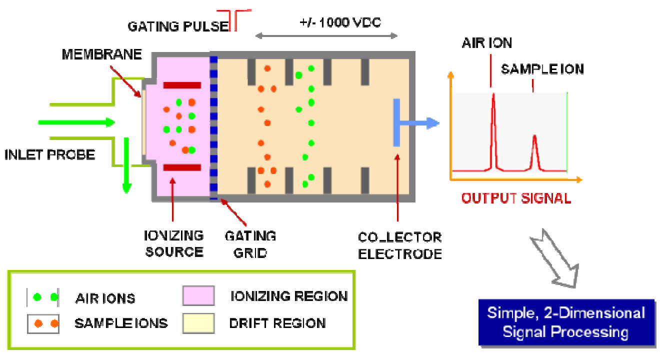
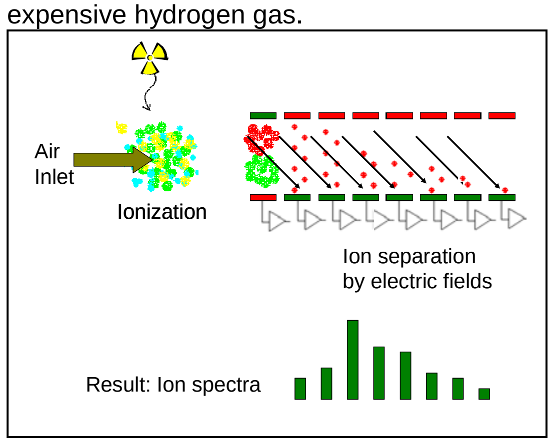


Clean air, provided by a sieve pack, keeps the inside of the ion cell perfectly clean. Sometimes chemical dopants are also used to keep contaminant under control. For example, acetone is used by one manufacturer to help absorb moisture. Membranes, sieve packs and dopants are expensive consumables that 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 day/week/month or else they will not work when an emergency comes. To "exercise" a detector, you turn it on, wait for it to stabilize, challenge it with simulant and then wait for it to clear. This process can 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 & 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 Ion Mobility Spectroscopy (IMS) sensor uses a Nuclear Regulatory Commission (NRC) exempt Am^{241} (Americium) ionization source. As safe as a smoke detector, it doesn't require periodic nuclear wipe tests like Ni^{63} 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. Life-cycle costs and logistical footprint are much less than those of traditional IMS and flame-spectrophotometer based devices because it doesn't require costly membranes and sieves to keep the sensor clean and it doesn't use expensive hydrogen gas.



- 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 (~20)
  - As safe as a smoke detector
  - Predictable service intervals
  - Stores well, no need to exercised
  - Inexpensive to maintain, lifetime costs ~$0.33/hr of use
- Disadvantages
  - False Positives to many common urban chemicals (typically shown as a "Chemical Threat" alarm)

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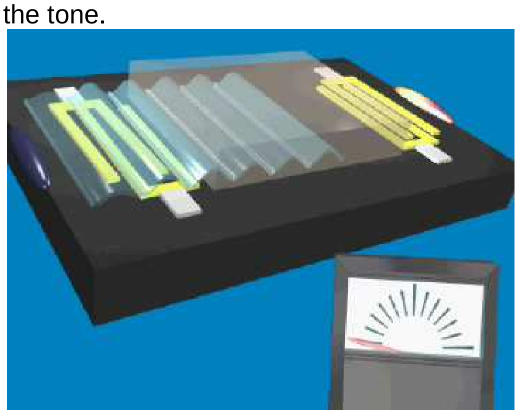
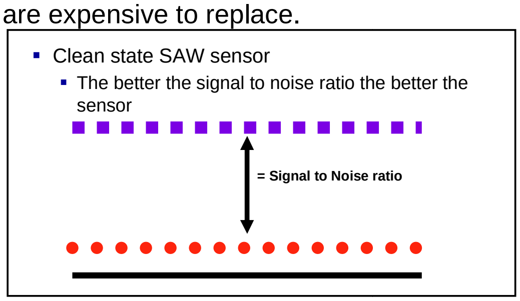
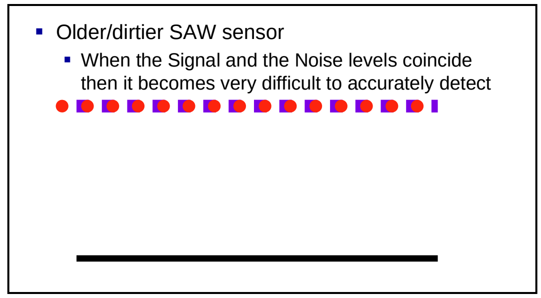
Surface Acoustical Wave (SAW)

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 (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, the problem with SAWs is chemical contamination of their polymer coatings. Consider a handprint by a light switch on the wall. You clean the handprint (but if you have small children) it comes back. Eventually you no longer can clean the handprint and you have to repaint. As the paint (polymer) in a SAW absorbs chemical, some of that chemical (either target or interferant) 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 you cannot detect anymore and you need a new sensor and SAW sensors are expensive to replace.

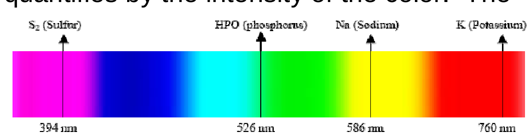




- Advantages
  - Very specific vapor detector
  - Proven Technology
  - Stores well (assuming no contaminants in the air)
- Disadvantages
  - Some common vapors (like alcohols) may ruin the polymer coating
  - While specific, often don't alarm until IDLH levels
  - Unpredictable end of life
  - Lifetime costs can be significantly higher than IMS based products ($2.40 per hour of use)

Flame Spectrophotometry

Flame Spectrophotometry detectors use a colorless hydrogen flame to burn the sample. Chemicals produce characteristic electromagnetic spectra (colors) when they burn. The detector looks for the spectra (colors) that are specific to sulfur and phosphorous compounds that are a defining characteristic of blister and nerve agents. It quantifies 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) and phosphorous (nerve). However, this sensitivity to sulfur and phosphorous compounds can lead to cross-sensitivity and false alarms. Product manuals warn against locating near exhausts which can produce sulfur dioxide as a by-product of the combustion process and give a false positive for blister. Also, phosphorous isn't just in organophosphates. One common use for phosphorous is a whitener in detergents. So if one doesn't rinse their wash thoroughly a Flame Spectrophotometry detector could improperly identify detergent residue as nerve.

- 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 have Sulfur or Phosphorous in them)
  - 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)
  - $9+/hour to run

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

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)
- Anti-Freeze (blister on some IMS)
- Anything with Methyl salicylate (oil of wintergreen) including: Skoal, Wintergreen Altoids, Peppermint Oil, Mennen "Speed Stick", "Deep Heat", Ben Gay, (blister on some IMS)
- 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 (nerve)
  - DMMP: Dimethyl Methyl Phosphonate (nerve)
  - TEP: Triethyl Phosphate (nerve)
  - Sevin (nerve)

CWA Identification

After a chemical has been located and classified in some special situations it is necessary to identify it. Speciation (typically spectroscopy) technologies allow us to identify chemicals so that additional actions can be taken. "Spectroscopy" is the study of

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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
- “Raman” spectroscopy is the study of how laser light interacts with 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 spectra 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

Raman Spectroscopy

In Raman Spectroscopy a laser light source is beamed into a substance. The laser light photons excite the electrons in the sample substance and the electrons reemit photons as they return to their base state. The frequency of the reemitted photons is shifted up or down in comparison with the original laser light and this compound specific characteristic is called the Raman Effect. It is named for one of its discoverers Sir C.V. Raman who won the Nobel Peace Prize in physics for the discovery in 1930.

Raman can be used to identify some solids, pastes and liquids including CWAs. Raman cannot, measure Gases and Vapors (however, while Raman cannot detect gases and vapors it is included because due to the low vapor pressure of CWAs there may be liquid samples present for analysis). Some Raman products have the same issue with mixtures as FTIR and may not be able to see a component if it makes up 10% or less of the mixture.

- Advantages:
    - Can identify many solids, liquids, pastes w/o sample handling or preparation
    - Raman can penetrate many containers
    - Relatively easy to use
    - Stores well
    - Low calibration and logistical requirements
- Disadvantages:
    - Cannot do gases or vapors
    - Very expensive (~$30K) to purchase

Gas Chromatography/Mass Spectroscopy

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

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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 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.

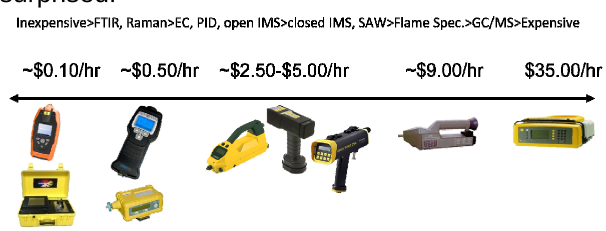
Some portable GC/MS have a **survey mode** in addition to the GC/MS mode. In this survey mode the GC is by-passed and the sample is drawn directly into the MS. This gives quicker response time of about 2 minutes versus the 15-25 minute process time for GC/MS mode. Survey mode can analyze relatively pure 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
  - Doesn't store well (NEG vacuum pumps prefer constant rather than intermittent use)
  - ~$35/hr to use

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 you know the entire story or you could be surprised!



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 use their aptitude when they are not frequently using a detection technology.

Integrating Our 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 15-25 minutes. Metaphorically speaking it can identify the correct "address" in 15-25 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 isn't good enough for evidence and a GC/MS, Raman or FTIR analysis of the sample provides more solid identification.

Speciation

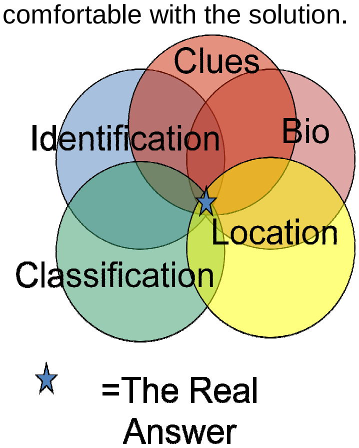
Broadband > PID > IMS, SAW > FTIR, GC/MS> Specific

Country > State > Town > Zip Code > Address

Fast > PID(3 sec)>IMS(10-120sec)>FTIR(30-120sec) > >GC/MS (20min) >Slow

Putting It All Together

In the following diagram, each circle represents whether or not a particular technique/clue is providing a positive response. By overlaying multiple techniques we can zoom in on the solution just like a detective uses multiple clues to solve a crime. Use multiple techniques until you feel comfortable with the solution.



Physical Clues

- Any signs of dissemination techniques?
- What is going on with the weather or indoor environment?
- Are there any physical clues?

Biological clues

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

Location devices

- Using PID, FID, M9 are there any areas of higher concentrations?

Classification devices

- What are the color change technologies telling you?
- What is your CWA detection technology(s) telling you?

Identification devices

- Verify the above clues with an identification technology

In the future represented by the old 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.

About the Author

Christopher Wrenn is the Sr. Director of Sales and Marketing for Environics USA a provider of sophisticated gas & vapor detection solutions for the military, 1st responder, safety and homeland security markets. Previously Mr. Wrenn was a key member of the RAE Systems team, helping to grow RAE's revenues from $1M/yr to nearly $100M/yr in the above mentioned markets. Chris has been a featured speaker at more than 20 international conferences including the American Chemical Society's annual conference, NATO's advanced research workshop and Jane's Defense Weekly WMD conference. He has written numerous articles, papers and book chapters on gas detection in HazMat and industrial safety applications.

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