

# **Science and Technology**

Chemical Weapons

By

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# Chemical Weapons (CW)

- Chemical weapons are, “Any chemical which through its chemical action on life processes can cause death, temporary incapacitation or permanent harm to humans or animals. This includes all such chemicals, regardless of their origin or of their method of production, and regardless of whether they are produced in facilities, in munitions or elsewhere.” (OPCW)



***Special gas mask  
for dogs-1917***

# Types of Chemical Weapons



- Nerve agents (e.g. sarin and VX)
- Blood agents (e.g. hydrogen cyanide)
- Choking agents (e.g. chlorine or phosgene)
- Blistering agents (e.g. sulfur mustard)
- Tearing agents (e.g. CS)
- Opiate-like agents (e.g. fentanyl)
- Psychochemical Incapacitants (e.g. BZ)
- Toxins (ricin)

# For Terrorists or Countries?

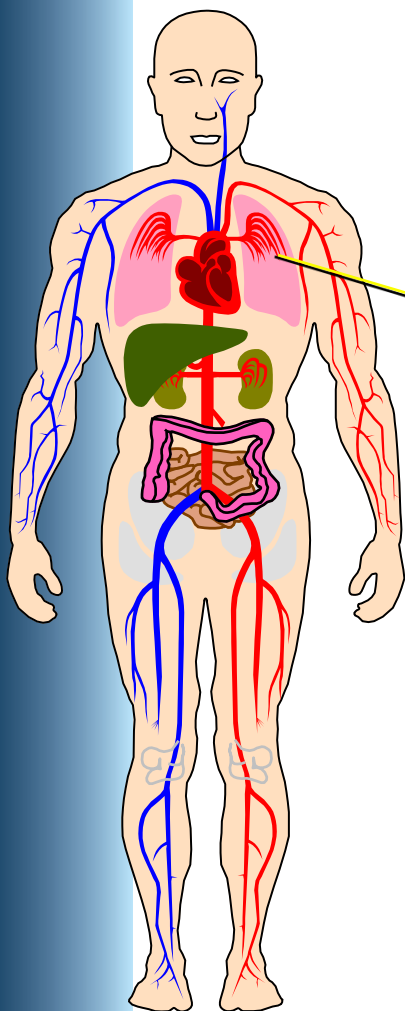
- **Terrorist criteria**

- Either relatively simple to make or relatively simple to divert from industry.
- Relatively simple to disperse
- Can be lethal or incapacitating
- Relatively low cost

- **Government with well developed chemical industry (e.g. North Korea)**

- Can be more difficult to make.
- Can have more sophisticated dispersal techniques.
- More likely to want lethal
- Higher cost may be OK

# Choking Agents



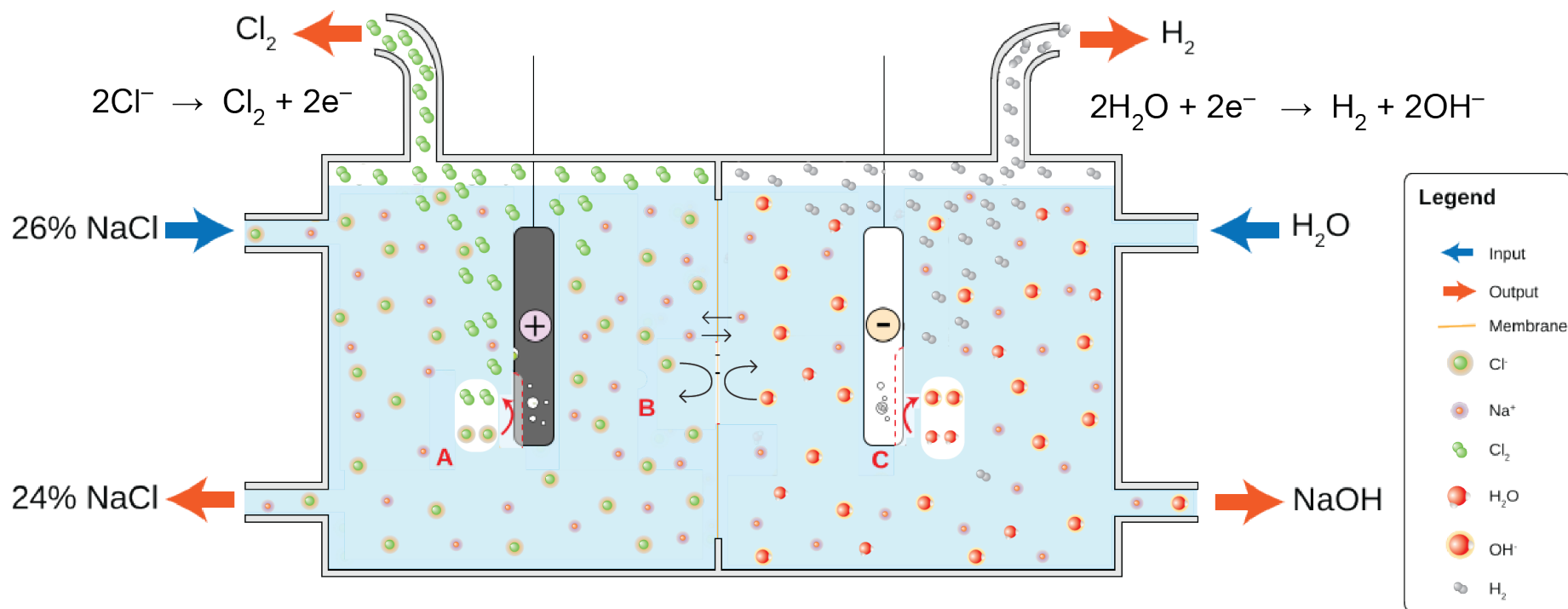
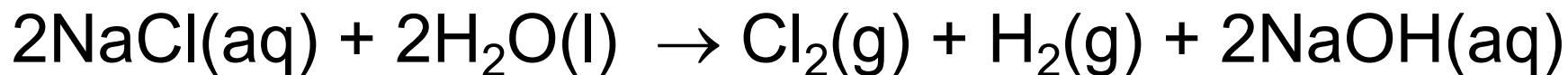
- Diphosgene, **phosgene**, **chlorine**, chloropicrin
- Mode of action: inhalation
- Physiological effects
  - Victim can die of oxygen deficiency via different mechanisms
- Form when disseminated: gas
- Required defensive gear: protective mask

# Ways to Obtain Chlorine, $\text{Cl}_2$

- Produce it
- Capture it from production plant
- Divert it during transportation
- From water treatment plant

# Production of Chlorine

- Compared to other chemical weapons, chlorine is relatively easy to make by electrolysis of sodium chloride in water.



# Chlorine from Captured Production Plant

- December 2012 – a chemical plant east of Aleppo, Syria was taken by rebel fighters from the Al-Nusra Front (now part of Hay'at Tahrir al-Sham, Organization for the Liberation of the Levant). The factory produced chlorine among other chemicals.

<http://www.france24.com/en/20121208-syria-warns-rebels-may-resort-chemical-weapons-assad-united-nations-islamists/>

# Transportation of Chlorine

- By rail in tank cars



- By highway in cargo tanks and cylinders
- By barge

# Chlorine in Water Treatment Plant

- Commonly in one-ton containers



# Ways to Disperse Chlorine, Cl<sub>2</sub>, as a CW

- Stationary device, e.g. pressurized gas tanks
- Car or truck bombs
- Drop containers from planes or helicopters that will burst on impact (barrel bombs)
- Roadside bombs
- Projectiles

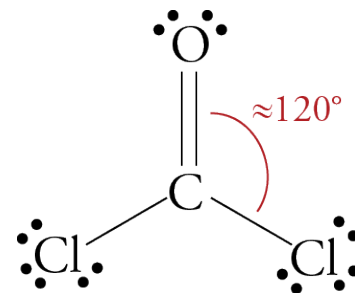
A 120-millimeter mortar shell struck fortifications at a Kurdish military position near the Mosul Dam in June, arms experts said, sickening several Kurdish fighters who were nearby.



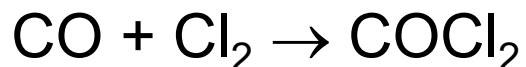
Credit  
Conflict Armament Research and  
Sahan Research

<http://www.nytimes.com/2015/07/18/world/middleeast/islamic-state-isis-chemical-weapons-iraq-syria.html>

# Phosgene, $\text{COCl}_2$

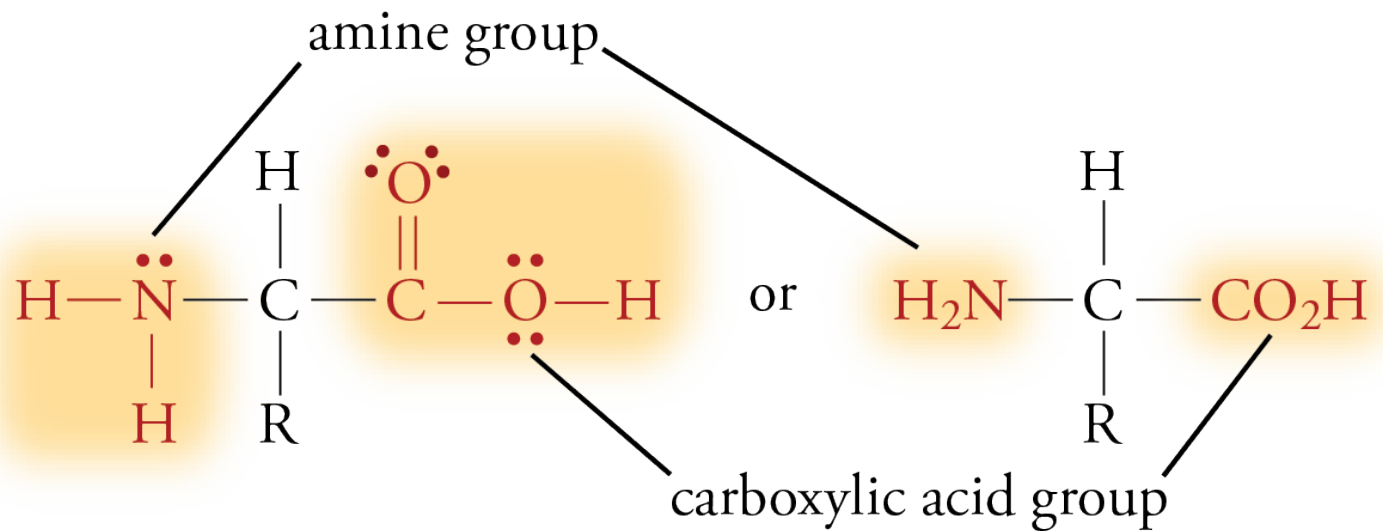


- More difficult to make than chlorine. Produced by passing purified carbon monoxide and chlorine gas through a bed of porous activated carbon, which serves as a catalyst. The reactor must be cooled to prevent phosgene from decomposing.

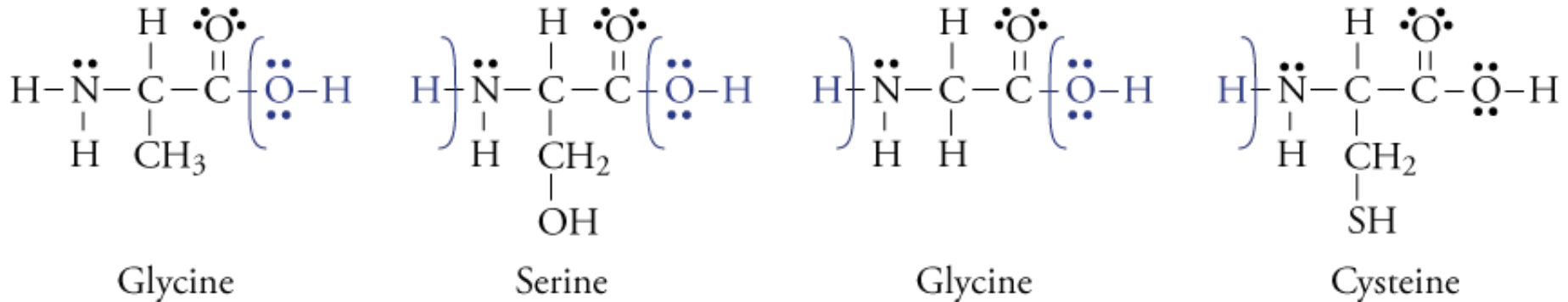


- 18 times more toxic than  $\text{Cl}_2$
- It causes suffocation by reacting with proteins and generating hydrochloric acid in the lungs, leading to pulmonary edema (a buildup of fluid in the lungs), which disrupt the blood-air barrier.
- Smells like new-mown hay
- Less irritating than  $\text{Cl}_2$ , so soldiers were slower to put on their gas masks

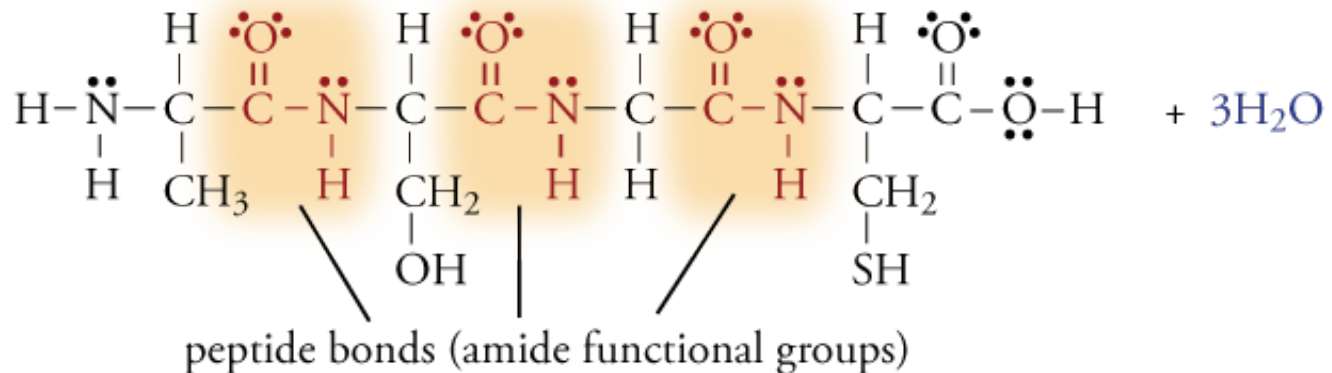
# Amino Acids



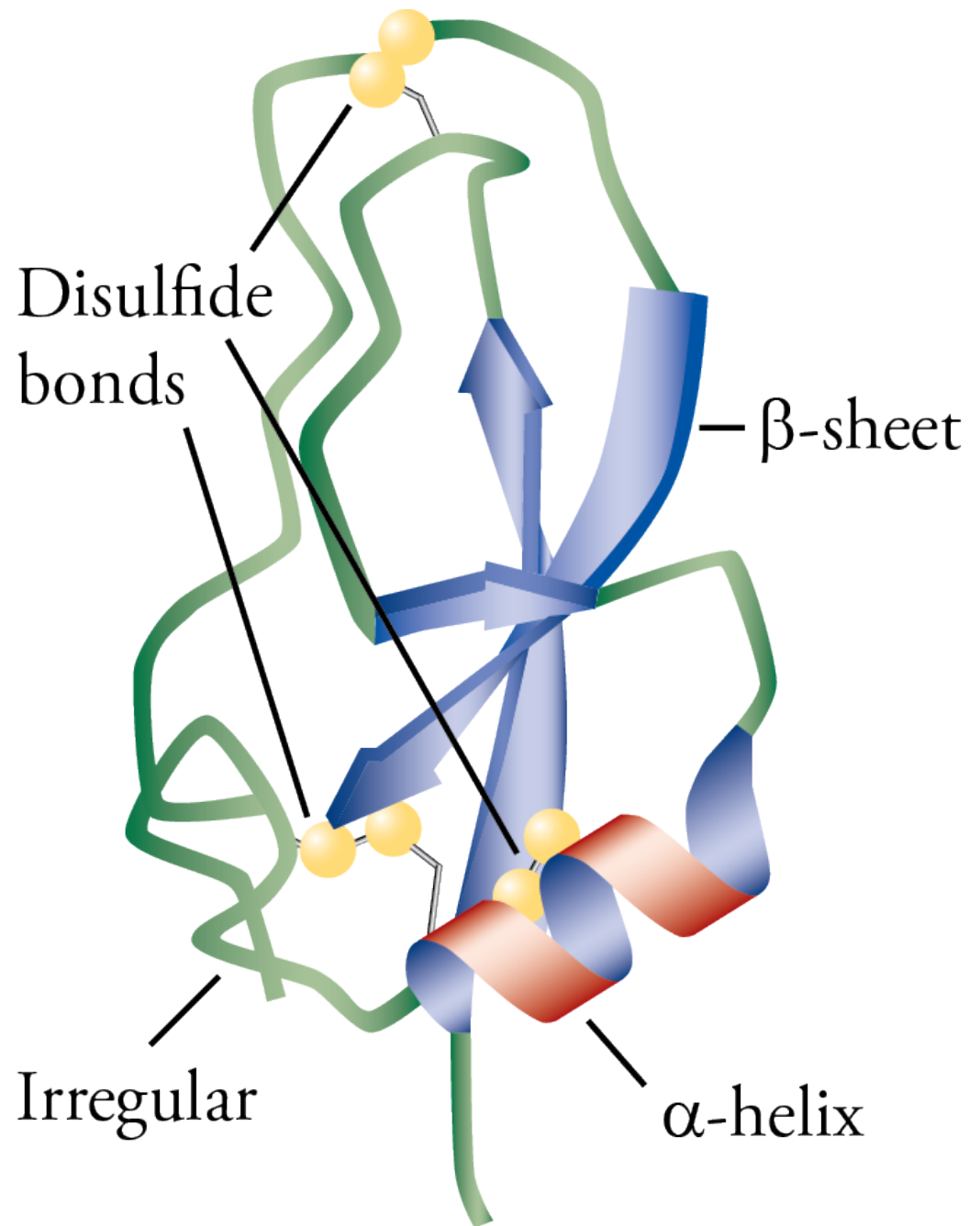
# Formation of Ala-Ser-Gly-Cys



↓ Condensation reaction releases water

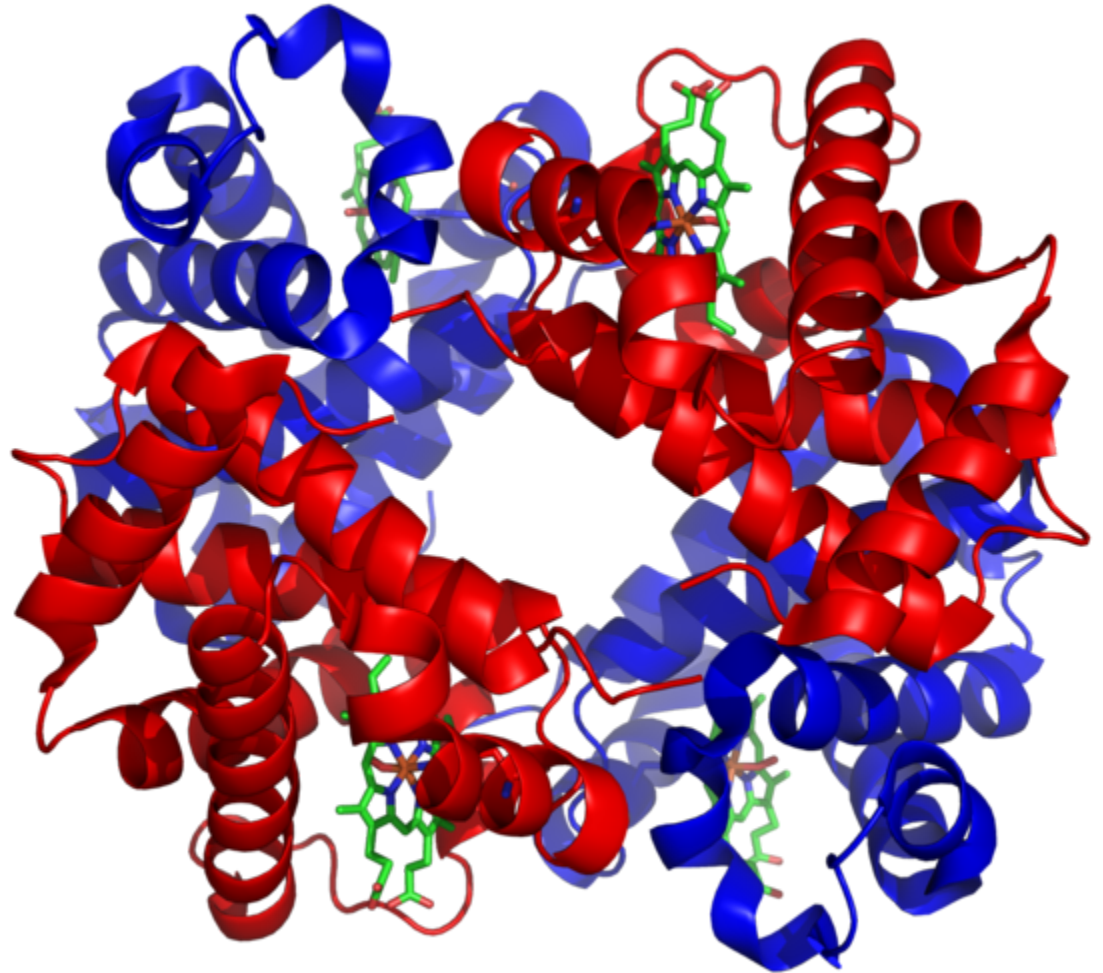


# The Ribbon Structure of the Protein BPTI



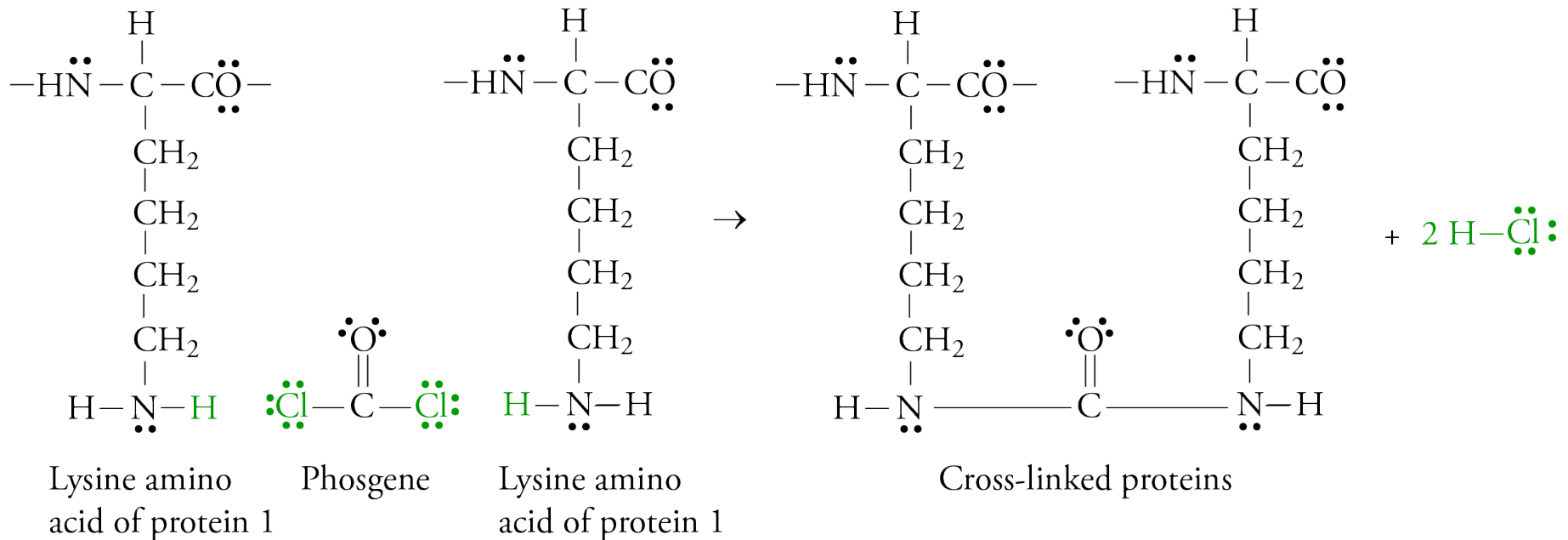
# Hemoglobin

- The protein hemoglobin carries oxygen in the blood.



# Phosgene Reactions with Protein

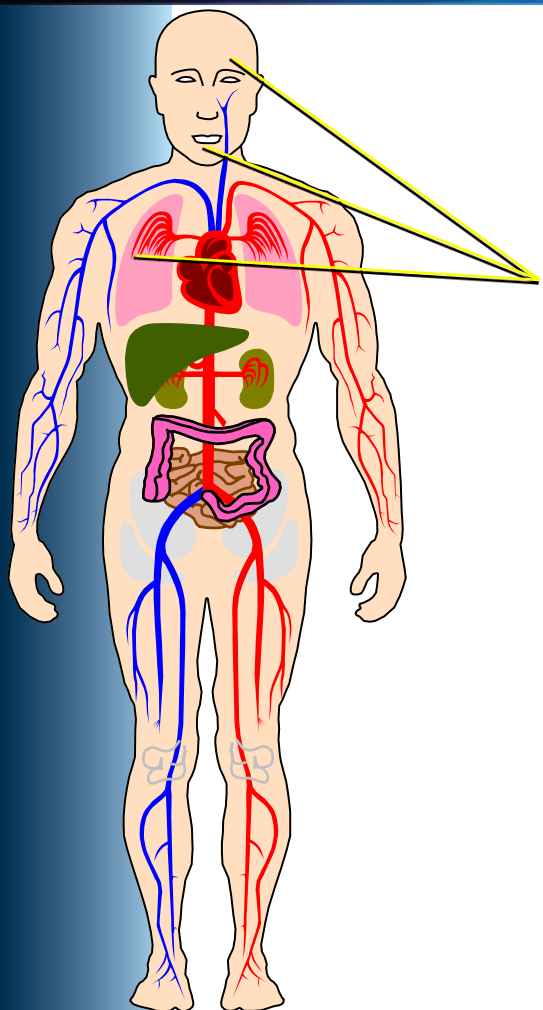
- Phosgene reacts with amino acids in proteins by acylation, adding an acyl group (a group with a CO double bond).
- It also reacts with the amines of the proteins, linking protein together.
- The altered proteins no longer function in their normal way.



# Dual Use

- A small-scale malicious chemical program can easily be hid behind a normal industrial/research chemistry front.
  - Chlorine is used for water purification and to make many other compounds.
  - Phosgene is used to make important compounds, including pharmaceuticals and plastics.

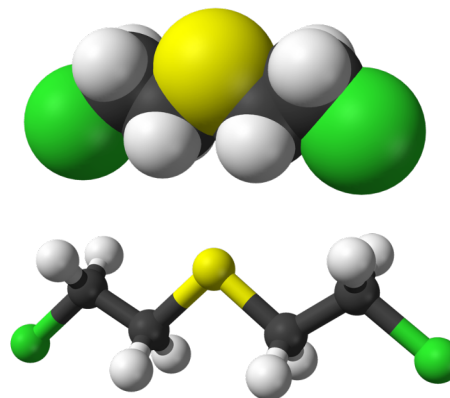
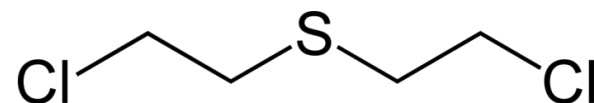
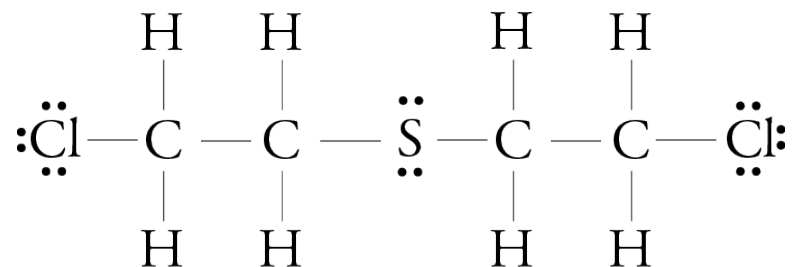
# Blister Agents (Vesicants)



- **Sulfur mustard**, nitrogen mustard, phosgene oxime, Lewisite
- Mode of action: inhalation, skin contact
- Physiological effects
  - Burns skin, mucous membranes, and eyes, causing large water blisters on exposed skin
  - Causes damage to upper airways
  - Primarily used to cause medical casualties, but can be lethal when large amounts are inhaled
- Form when disseminated: liquid, aerosol, vapor, dust
- Required defensive gear: protective mask & clothing

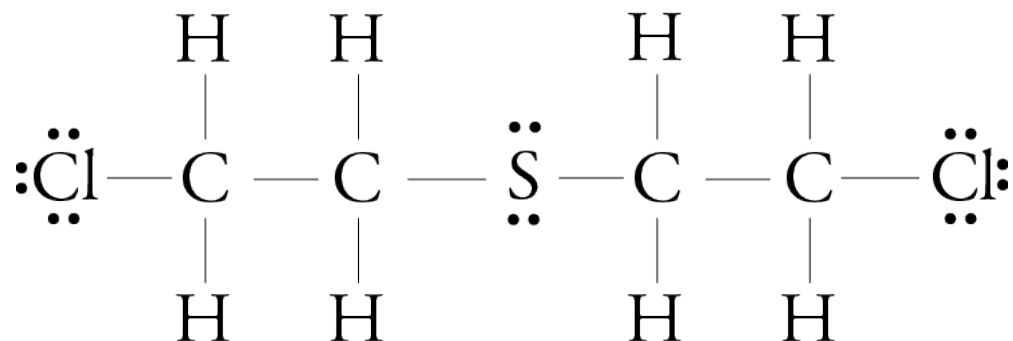
# Sulfur Mustard, H or HD

- Called “mustard” because of its horseradish- or garlic-like smell.
- It is fat-soluble, so it dissolves in the oils in the skin, causing severe chemical burns and blisters.



# Ways to Describe Organic Compounds

- Lewis structures



- Condensed Formulas,  $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$

- Line Drawings 

# Sulfur Mustard (cont.)

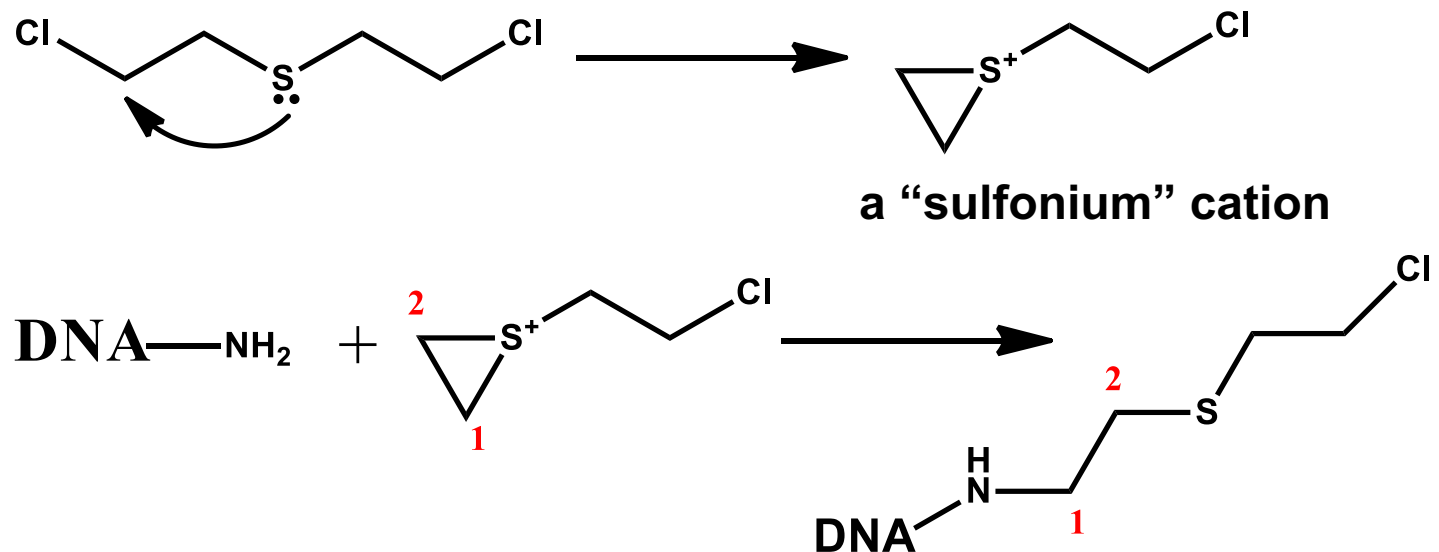
- “H” usually refers to an impure form of sulfur mustard with 20-30% impurities...has short shelf-life. It is relatively easy to make.
- “HD” refers to a more pure form (96% pure) that can be stored longer.
- It can remain on the ground for weeks, making the area dangerous long after its dispersal.



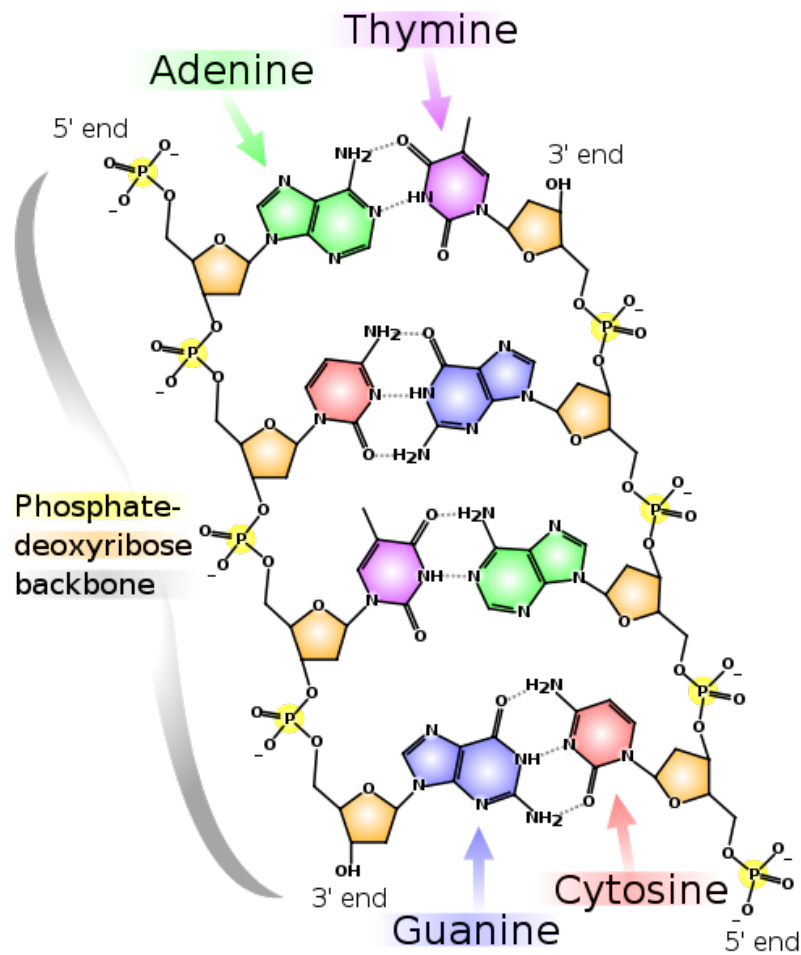
155 mm artillery shells that contained "HD" (distilled sulfur mustard agent) at Pueblo chemical weapons storage facility

# Effect of Sulfur Mustard on DNA

Sulfur mustard forms a sulfonium ion, which attaches to a number of different biomolecules, including proteins and the nucleotides of DNA, disrupting cell division and function. This can lead to cellular death or cancer.



# DNA Segment



# Sulfur Mustard Treatment

- Early rinsing of the exposed area with Betadine (povidone-iodine) dissolved in glycofural will reduce symptoms.
- Can limit the formation of blisters by applying household bleach or a solution called DS2 (2% sodium hydroxide, NaOH, 70% diethylamine,  $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$ , and 28% ethylene glycol monomethyl ether,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ )
- After initial treatment, the patient is treated in the same way that any burn victim would be treated.
- Because the symptoms do not appear for about 24 hours, it is less likely that the treatments would be done in time to avoid problems.
- Fatal in about 2% of exposures, so mostly used as an incapacitating agent.

# Difference Between Theoretical and Actual Effects



- The ability of CW agents to kill or hurt people depends on a number of factors, such as:
  - Quality of agent
  - Means of delivery
  - Environmental factors
- *Illustration:* In theory, less than a teaspoon of mustard agent can kill if it is inhaled into the lungs. Yet in WW I, more than 60 pounds of mustard agent were used for each man killed or wounded by it. Only 2% of the people affected by mustard agent actually died.

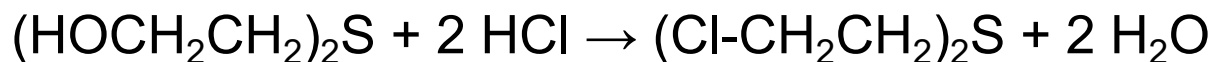
# Factors Affecting the Ability to Make CW



- Scientific and industrial expertise
- Availability of precursors
- Availability of equipment
- Money available
- Desired quantity
- Desired purity
  - For a variety of reasons, products of chemical reactions are rarely pure, so after the initial reactions, steps are taken to purify the product.
- Concern for safety of workers
- Concern for the environment

# Production of Sulfur Mustard

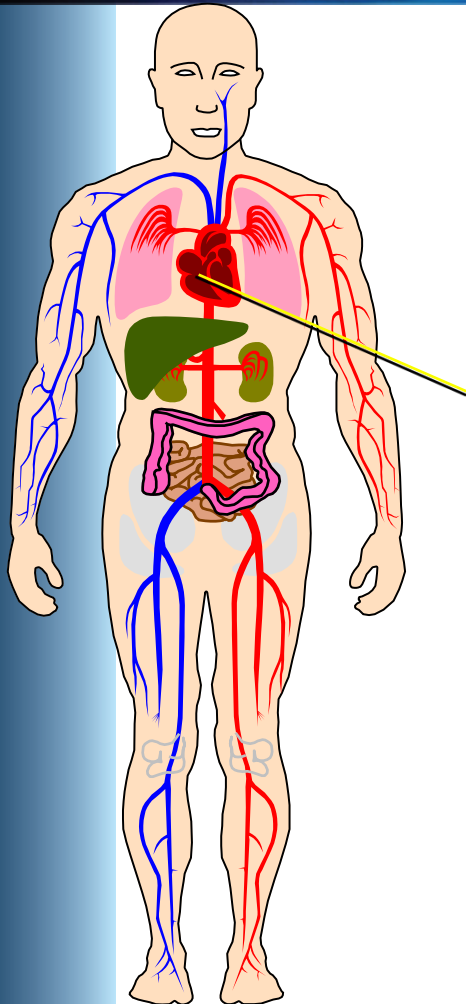
- Thiodiglycol and concentrated hydrochloric acid react to form sulfur mustard.



- Thiodiglycol (CWC Schedule 2 Part B)
  - Used to make many things, including pen inks, plastics, pesticides, dyes, and photographic developing solutions
  - Produced in several countries, including Germany and the UK.
  - Many firms purchase it.
- Does not require sophisticated equipment.
- Distillation leads to improved purity, which allows longer storage.
- Plant cost of \$5-10 million



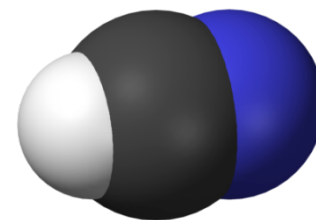
# Blood Agents



- **Hydrogen cyanide**, cyanogen chloride, **sodium or potassium cyanide**, and arsine
- Mode of action: inhalation or ingestion
- Physiological effects of cyanide
  - Disrupts cellular respiration by diminishing the transfer of oxygen into the mitochondria of cells.
- Form when disseminated: gas or solution
- Required defensive gear: protective mask

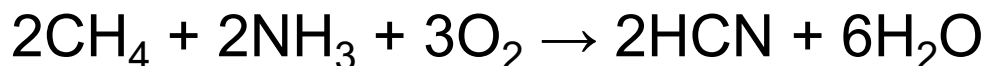
# Hydrogen Cyanide, HCN

- Volatile liquid – boiling point 26 °C (79 °F)
- Used in industry to make many important chemicals
- Fatal at concentrations as low as 300 mg/m<sup>3</sup> in air.
- According to OPCW, there are no confirmed uses as CW, but may have been used by Iraq against Iran and the Kurds.
- Schedule 3, Part A of the CWC



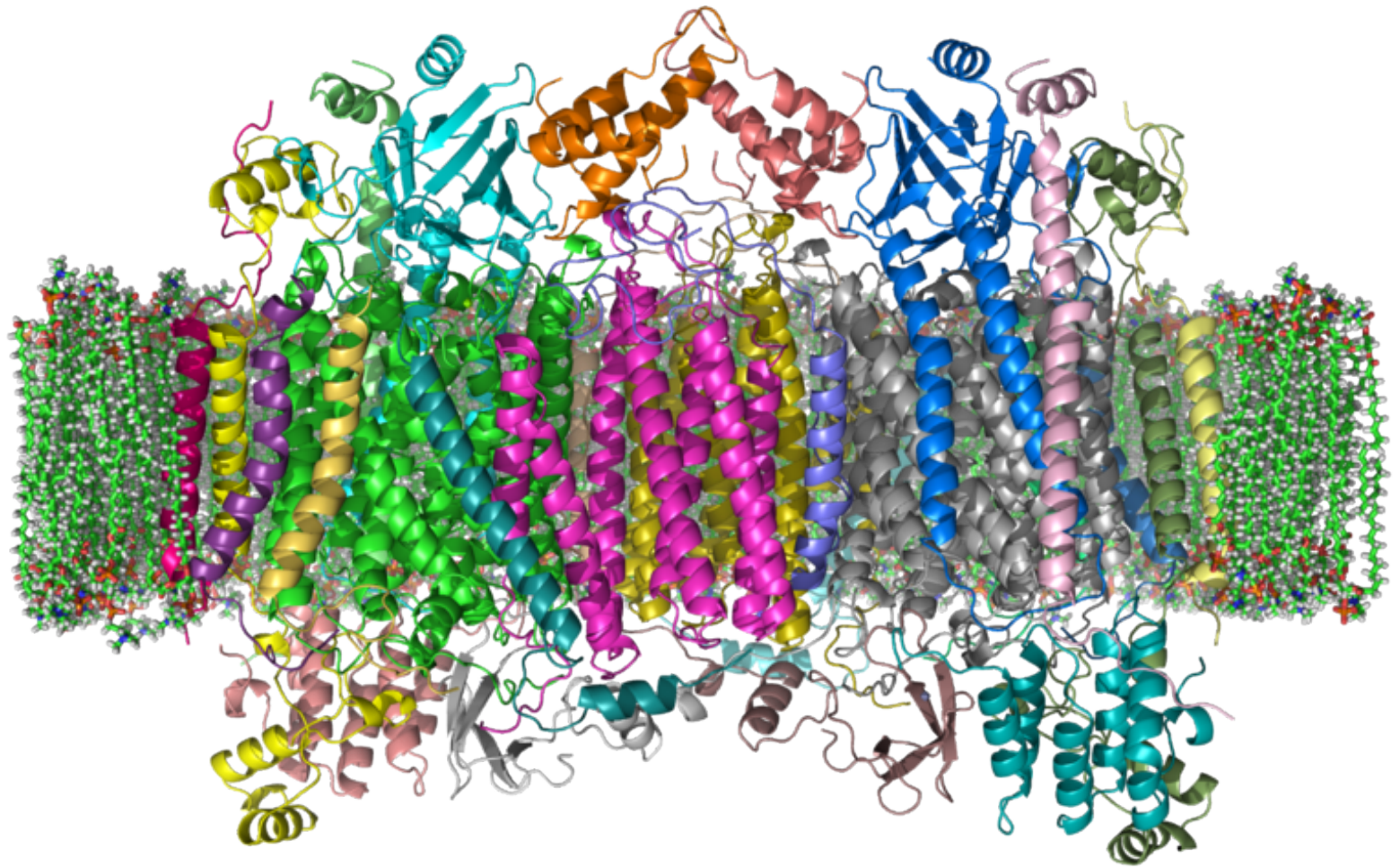
# Hydrogen Cyanide, HCN

- Disrupts cellular respiration (the conversion of nutrients and oxygen into carbon dioxide, water, and energy) by inhibiting an enzyme (cytochrome oxidase) in mitochondria. This enzyme delivers electrons to oxygen, helping to convert O<sub>2</sub> into water molecules.
- Binds to iron in cytochrome oxidase.
- Leads to dizziness, vomiting, loss of consciousness, and death
- Most made from the following reaction at 1200 °C over a platinum catalyst.



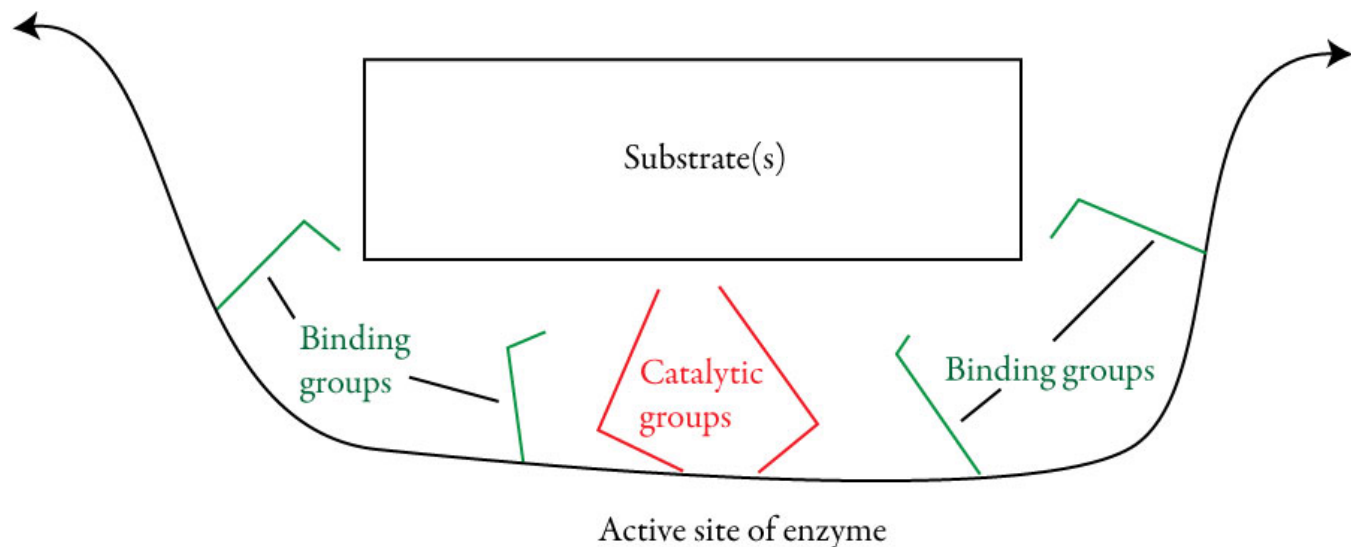
- Converted into sodium cyanide, NaCN, and transported in water solution.

# Cytochrome c Oxidase in cell membrane



# Enzymes

- **Enzymes** are naturally occurring catalysts, primarily composed of protein. **Catalysts** speed chemical changes without being permanently altered themselves.
- The chemicals that they act on are called **substrates**.



# Enzymes



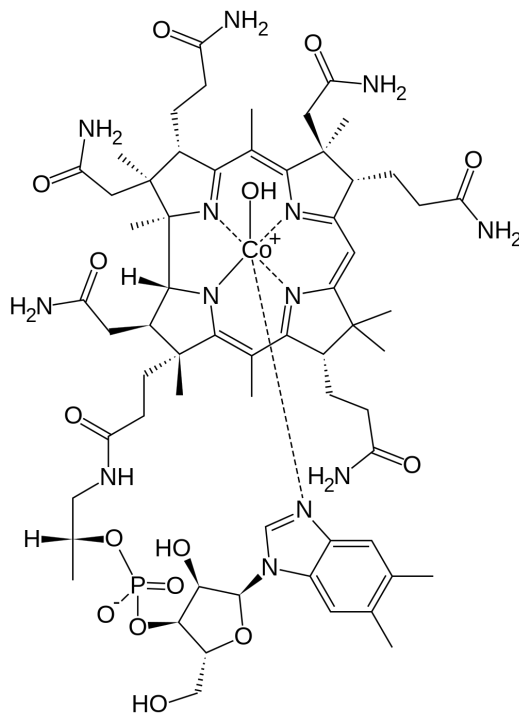
- Very specific due to
  - Substrate shape – “Lock and Key”
  - Positions of binding groups, which attract substrates to the active site.
  - Positions of the catalytic groups that speed the reaction.
- Speed chemical reactions because
  - Provide a different path to products that has more stable intermediates and therefore requires less energy.
  - Give the correct orientation every time.

# One HCN Antidote

- First - a small inhaled dose of amyl nitrite
  - Nitrites oxidize some of hemoglobin's iron from the  $\text{Fe}^{2+}$  state to the  $\text{Fe}^{3+}$  state, converting the hemoglobin into methemoglobin.
  - Cyanide preferentially bonds to methemoglobin rather than the cytochrome oxidase, converting methemoglobin into cyanmethemoglobin.
- Second - intravenous sodium nitrite
- Third - intravenous sodium thiosulfate
  - Converts the cyanmethemoglobin to thiocyanate, sulfite, and hemoglobin. The thiocyanate is then excreted in the urine.

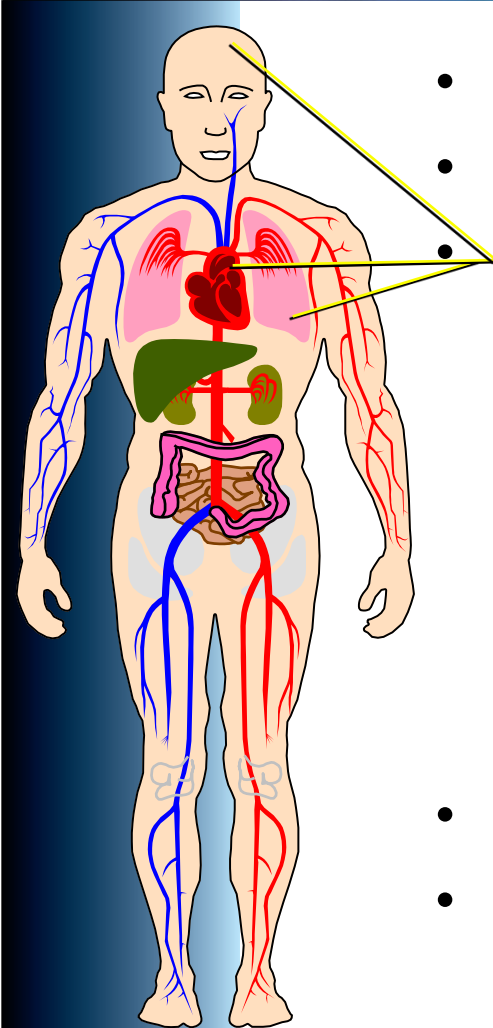
# One HCN Antidote

- Hydroxocobalamin (vitamin B<sub>12a</sub>) is newly approved in the US and is available in Cyanokit antidote kits.



<https://en.wikipedia.org/wiki/Hydroxocobalamin>

# Nerve Agents



- Tabun, **sarin**, soman, cyclosarin, **VX**, Novichok
- Modes of action: contact, inhalation
- Physiological effects
  - Disrupt the mechanism by which nerves transfer messages to organs
  - Causes seizures and loss of body control
  - Exhausts muscles, including heart and diaphragm
  - Lethal dose can cause death from respiratory failure in five minutes
- Form when disseminated: liquid, vapor, aerosol
- Required defensive gear: protective mask & clothing

# Nerve Agents



- Cause contraction of pupils, profuse salivation, convulsions, involuntary urination and defecation, and eventual death by asphyxiation as control is lost over respiratory muscles.
- U.S. and the Soviet Union developed and stockpiled large quantities of nerve agents in a chemical arms race that mirrored the nuclear arms race.

# Nerve Agents – Three Series

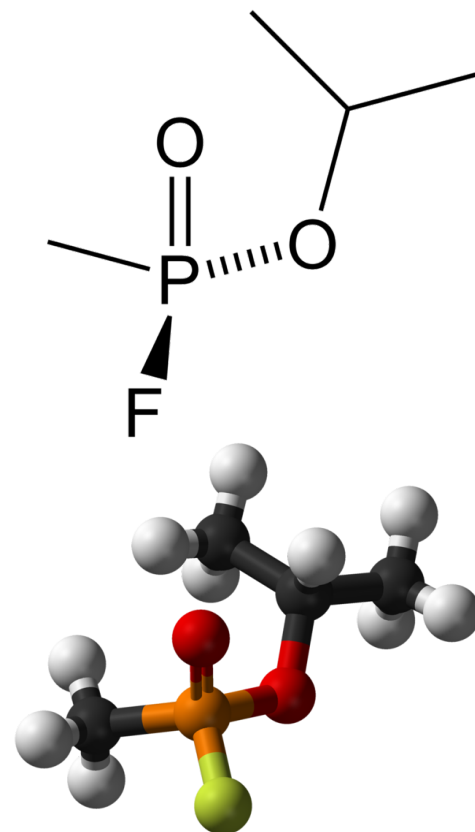


- G-series
  - Produced by Germans
  - 1936 – GA (tabun)
  - 1939 – GB (sarin)
  - 1944 – GD (soman)
  - 1949 – GF (cyclosarin)
  - GA and GB less persistent after dispersal
- V-series
  - More persistent after dispersal
  - VX most important...first produced by the British in the 1950s
- Novichoks

# Sarin (GB)

- Developed by the Germans in 1939
- Odorless
- Hard to make
- Volatility similar to water
- Very potent
- Breaks down fairly rapidly in the environment
- Has antidotes
- Adopted as the standard nerve agent for the U.S. in 1948.

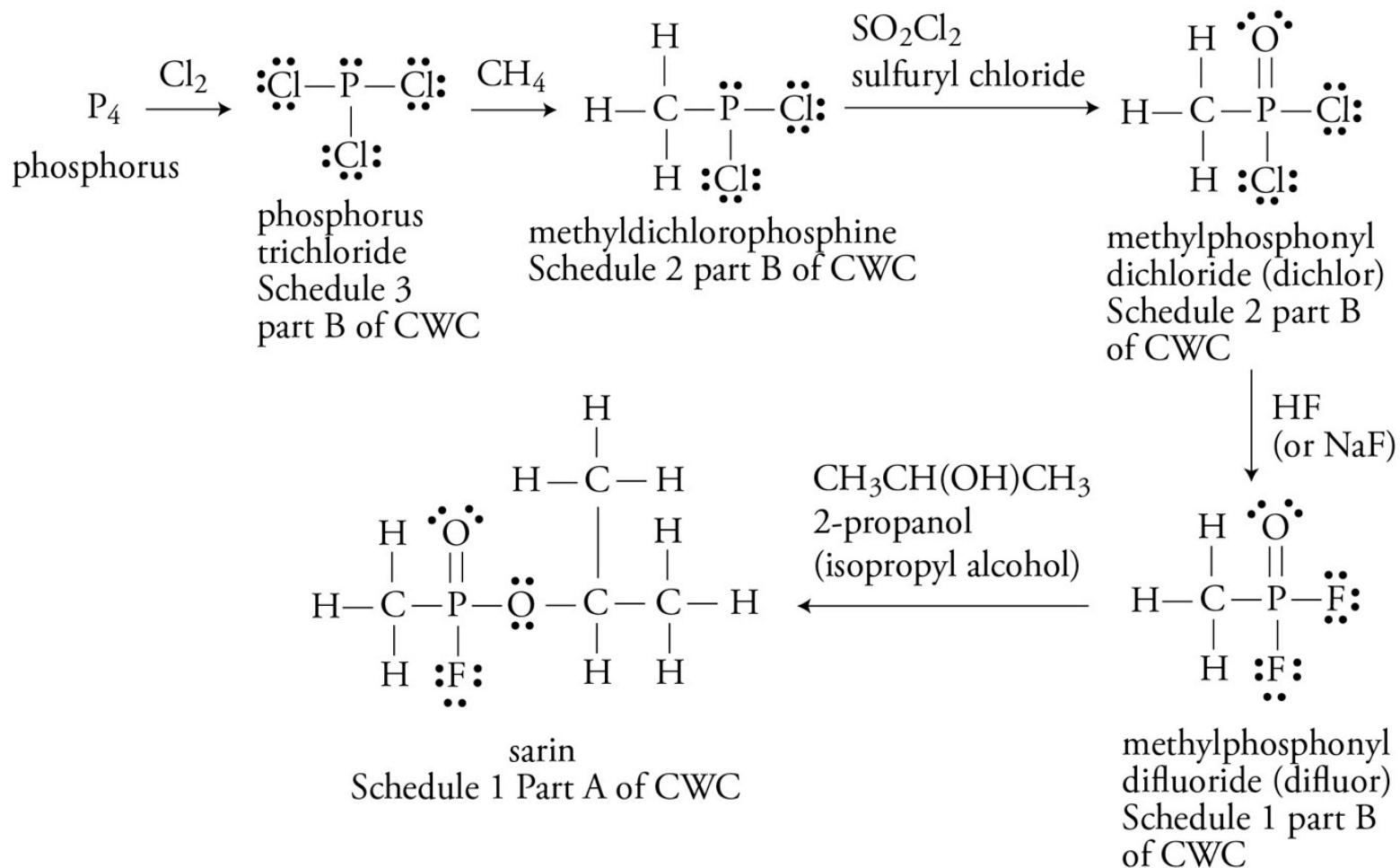
<http://chemapps.stolaf.edu/jmol/jmol.php?model=FP%28%3DO%29%28OC%28C%29C%29C>



# Sarin (GB)

- If sarin does not have a high purity, it degrades fairly rapidly.
- Its shelf-life can be extended with stabilizers.
- A very large amount of sarin has been made, but very little of it has been used.
  - March 1988 - Iraq used against Kurd city of Halabja
  - April 1988 – Iraq against Iran.
  - 1995 - Used in the Tokyo Subway attack by Aum Shinrikyo
  - 2013 - Used in Ghouta, Syria
  - 4/4/2017 – used in Khan Shaykhun, Syria

# Rough Steps in Production of Sarin



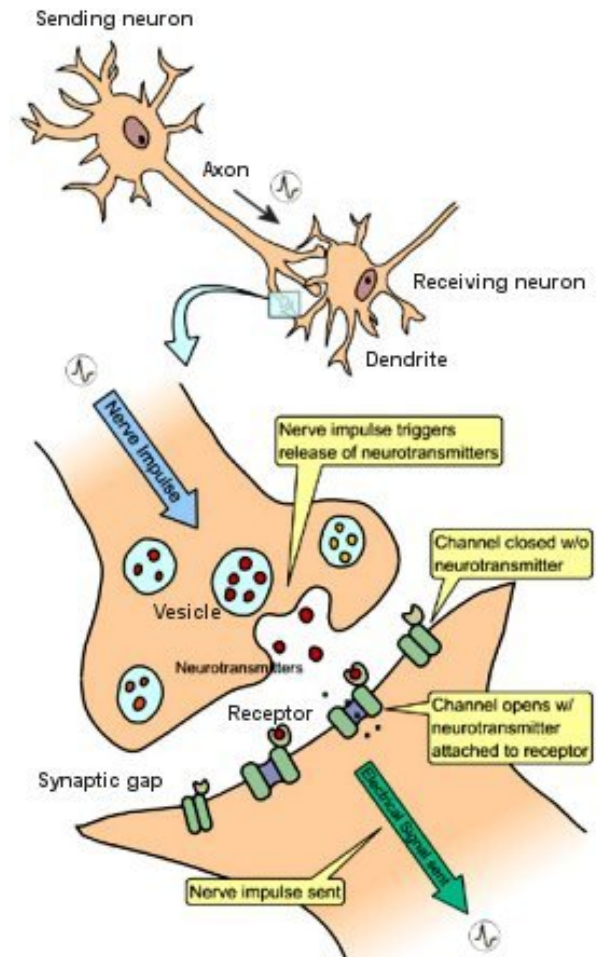
# Production of Sarin

- Most easily prepared from methylphosphonyl difluoride and isopropyl alcohol.  
$$\text{CH}_3\text{P}(\text{O})\text{F}_2 + (\text{CH}_3)_2\text{CHOH} \rightarrow [(\text{CH}_3)_2\text{CHO}]\text{CH}_3\text{P}(\text{O})\text{F} + \text{HF}$$
- Three technical hurdles when making from simpler substances.
  - Involves corrosive hot hydrochloric acid, HCl, and hydrogen fluoride, HF, so need corrosion resistant equipment, e.g. vessels and pipes of an alloy that is 40% nickel...Monel and Hastalloy.
  - To make  $\text{CH}_3\text{P}(\text{O})\text{F}_2$  (schedule 1, part b), alkylation reaction in which methyl,  $-\text{CH}_3$ , group is added to the phosphorus atom is technically difficult.
  - Distillation necessary to produce high-purity necessary for long storage.
- Plant cost \$30-50 million

# Neurotransmitters

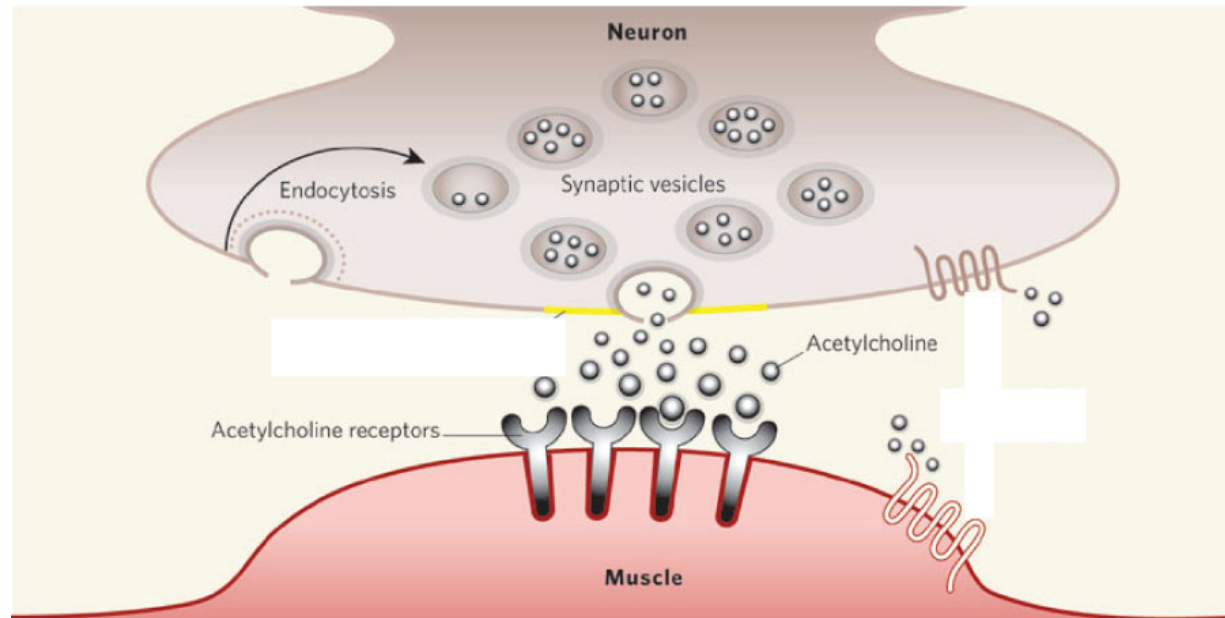
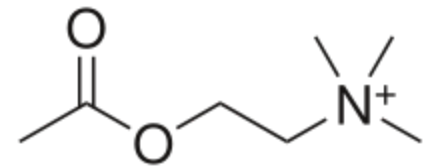
- Neurotransmitters cause nerve cells to fire.

From <http://universe-review.ca/R10-16-ANS.htm>



# Acetylcholine and Muscle Contraction

- Among other things, the neurotransmitter acetylcholine (ACh) stimulates nerve cells that cause muscle contraction.



From Nature 436, 473-474 (28 July 2005)

# Acetylcholine, Acetylcholinesterase, and Transfer of Nerve Information

- Normally, acetylcholine (ACh) is broken down in the active site of an enzyme, acetylcholinesterase (AChE).
- Each enzyme molecule converts about 25,000 molecules of ACh per second.
- Together, ACh and AChE are like an on-off switch for muscles



# Sarin and Acetylcholine-Acetylcholinesterase

- Sarin forms a covalent bond to a serine side chain in the active site of acetylcholinesterase, deactivating it.
- If acetylcholinesterase is deactivated, the acetylcholine levels remain high, and the switch gets stuck in the “on” position.

[http://preparatorychemistry.com/nerve\\_agent\\_sarin.html](http://preparatorychemistry.com/nerve_agent_sarin.html)

# Effects of Nerve Agents



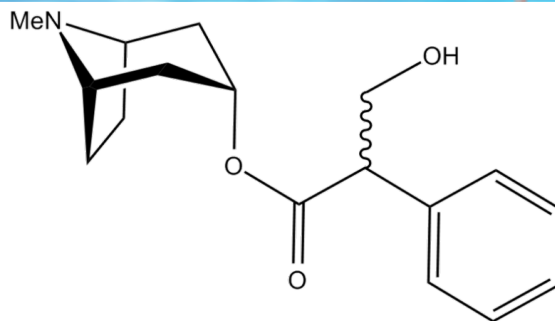
- For skeletal muscles: uncontrolled spasms, followed by paralysis
- For involuntary muscles: pupil contraction, excessive salivation, intestinal cramps, vomiting, and constriction of bronchial tubes
- For central nervous system: overstimulates the brain, causing seizures
- Causes glands to be overactive, secreting excess nasal mucus, saliva, and sweat
- Causes death by asphyxiation through constriction of bronchial tubes, suppression of the respiratory center of the brain, and paralysis of the breathing muscles

# Low-level Exposure to Nerve Agents



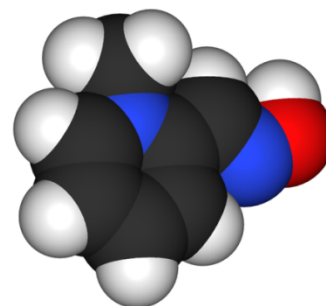
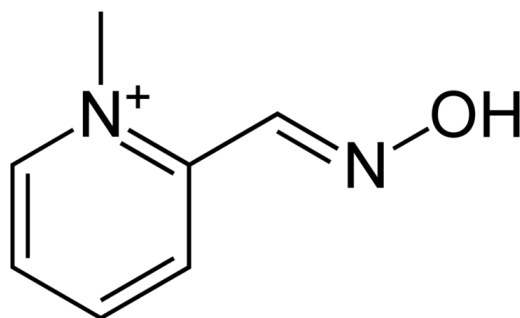
- Low doses lead to inability to think clearly, insomnia, trouble concentrating, and mood swings.
- Continuing exposure to low doses leads to a gradual increase in symptoms.
- It can take up to months for the acetylcholinesterase levels to return to normal.

# Nerve Agent Antidotes - Atropine



- Standard antidote for organophosphate poisoning
- Used in ancient Greece to dilate pupils (to make women's eyes prettier)
- Competes successfully with one type of acetylcholine receptors. This type of receptor is found in smooth muscles and glands.
- Helps relax muscles
- Stops the symptoms from nerve agent poisoning, *not* the cause

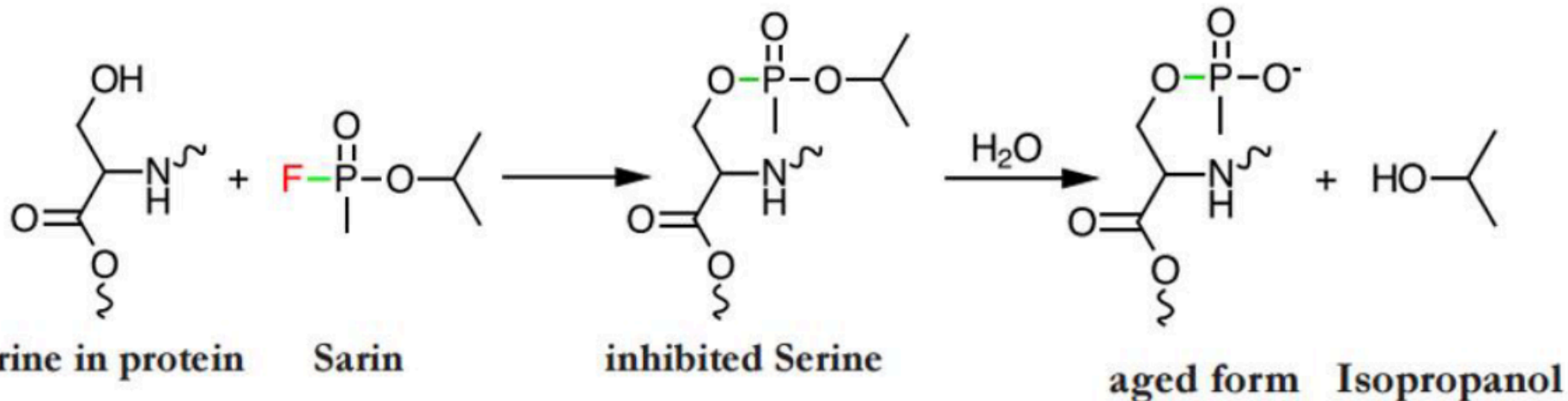
# Nerve Agent Antidotes (2-PAM)



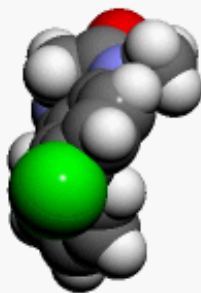
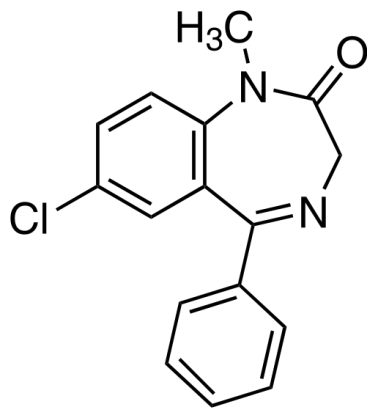
- Pralidoxime (2-pyridine aldoxime methyl chloride,) or 2-PAM
- Removes the nerve agent from the active site of acetylcholinesterase, restoring the enzyme to more normal levels
- Too slow to work well alone
- Works best when administered with atropine, which acts more quickly, giving the slower-acting 2-PAM time to work.
- Does not make it through the blood-brain barrier, so does not alleviate problems within the central nervous system.

# Inhibited and Aged Acetylcholinesterase

- The attachment of sarin to the active site inhibits the action of the enzyme. The sarin can be removed, so the inhibition is reversible.
- The loss of the isopropyl group from the sarin yields the *aged* form of the enzyme. The sarin cannot be removed in this form, so the inhibition of this enzyme is not reversible.



# Diazepam (Valium)



- Anticonvulsant
- Enhances the effect of the neurotransmitter GABA, which slows the transfer of nerve information.
  - Nerve firing is caused by buildup of positive ions in nerve cells.
  - GABA triggers movement of Cl<sup>-</sup> ions into nerve cell, slowing the buildup of positive charge and slowing the firing of the cells.
  - Valium and other benzodiazapines make it easier for GABA to work.

# Treatment for Nerve Agent Exposure

- An individual who is known to be exposed to a nerve agent or who exhibits definite signs or symptoms of nerve-agent exposure should have an immediate injection of the antidotes atropine and pralidoxime (2-PAM) and a sedative/antiepileptic drug, such as diazepam (Valium).
- Can be administered with an autoinjector, such as the United States military Mark I NAAK and CANA (Convulsive Antidote, Nerve Agent).
- Remove as much of the nerve agent as possible before moving to a non-contaminated area.
- Rinse with household bleach and rinse with water.
- Remove contaminated clothing and rinse skin again.



# Nerve Agent Antidotes

- Atropine and 2-PAM can be administered with a pressurized syringe with a spring-loaded, recessed needle.
- A catch is released and when the syringe is pressed against the leg, the spring is released, pushing the needle through clothing and into the leg, releasing the antidote.



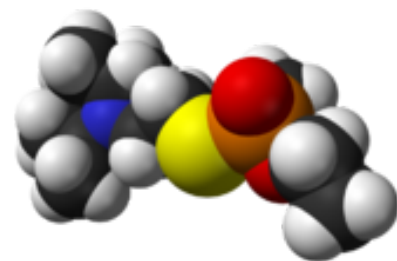
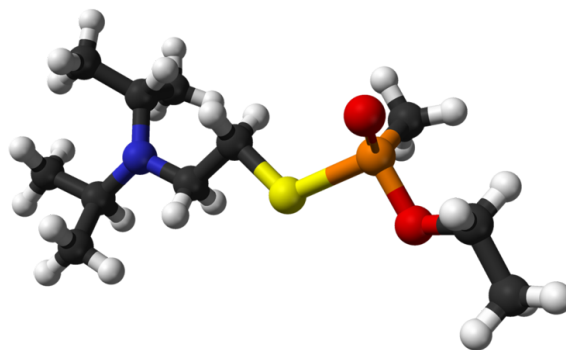
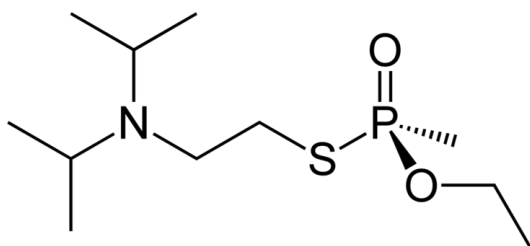
This auto-injector can deliver atropine and 2-PAM to counteract nerve gas or pesticide poisoning.

# CANA

(Convulsive Antidote,  
Nerve Agent)

- Contains diazepam (Valium)
- One CANA kit is typically issued to service members, along with three Mark I NAAK kits, when nerve agents are considered a potential hazard.
- Deliver drugs using autoinjectors
- Intended for use in "buddy aid" or "self aid"

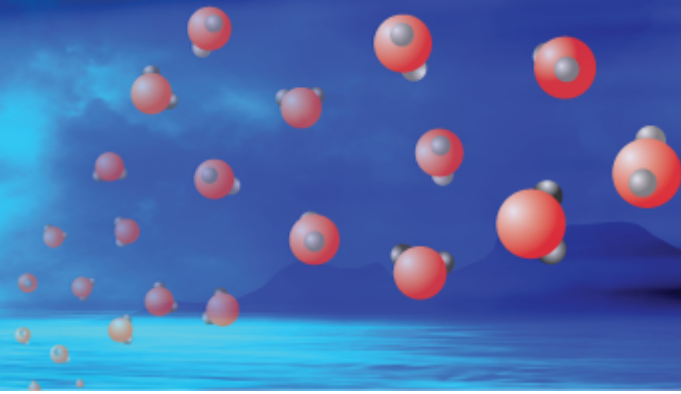
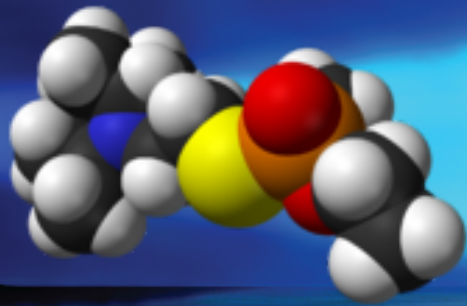
# VX



- One of several similar substances that were considered “venomous” and called V-agents.
- First produced in England in 1954
- Odorless liquid, slightly more dense than water, with a viscosity similar to motor oil.

<http://chemapps.stolaf.edu/jmol/jmol.php?model=CCOP%28C%29%28%3DO%29SCCN%28C%28C%29C%29C%28C%29C>

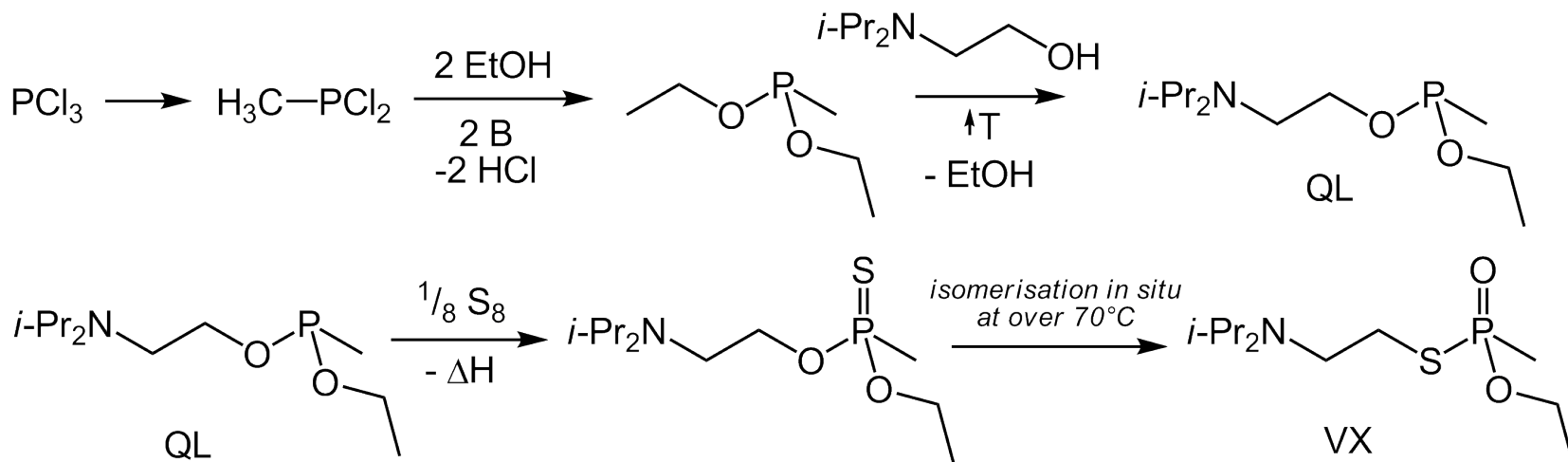
VX



- Three times more toxic than sarin when inhaled and a thousand times more toxic when absorbed by the skin. A small drop on the skin could kill an adult in fifteen minutes.
- Dispersed as an airborne mist or coarse spray.
- Clings to whatever it hits
- When sprayed on the ground, remains lethal for up to three weeks, so it is an *area denial weapon*.

# Production of VX

- Phosphorus trichloride (schedule 3, part b) is methylated, forming methyl phosphonous dichloride, which reacts with ethanol to form a diester. This reacts with N,N-diisopropylaminoethanol (Schedule 2, part b) to produce phosphonite, which reacts with sulfur to form VX.
- Has difficult alkylation step but not corrosive HF gas.



# Dosage Units



- $LD_{50}$  = dose of chemical expected to kill 50% of an exposed population...typical units = mg/kg of body weight
- $LCt_{50}$  = concentration of a chemical (in vapor phase) expected to kill 50% of a population exposed for a specified period of time...often expressed as the product of chemical's concentration in air ( $mg/m^3$ ) and the duration of exposure (min)...units =  $mg \cdot min/m^3$
- $ED_{50}$  = dose of a chemical expected to cause a defined effect in 50% of an exposed population...typically expressed in units of mg/kg of body weight.

# Dosage Units

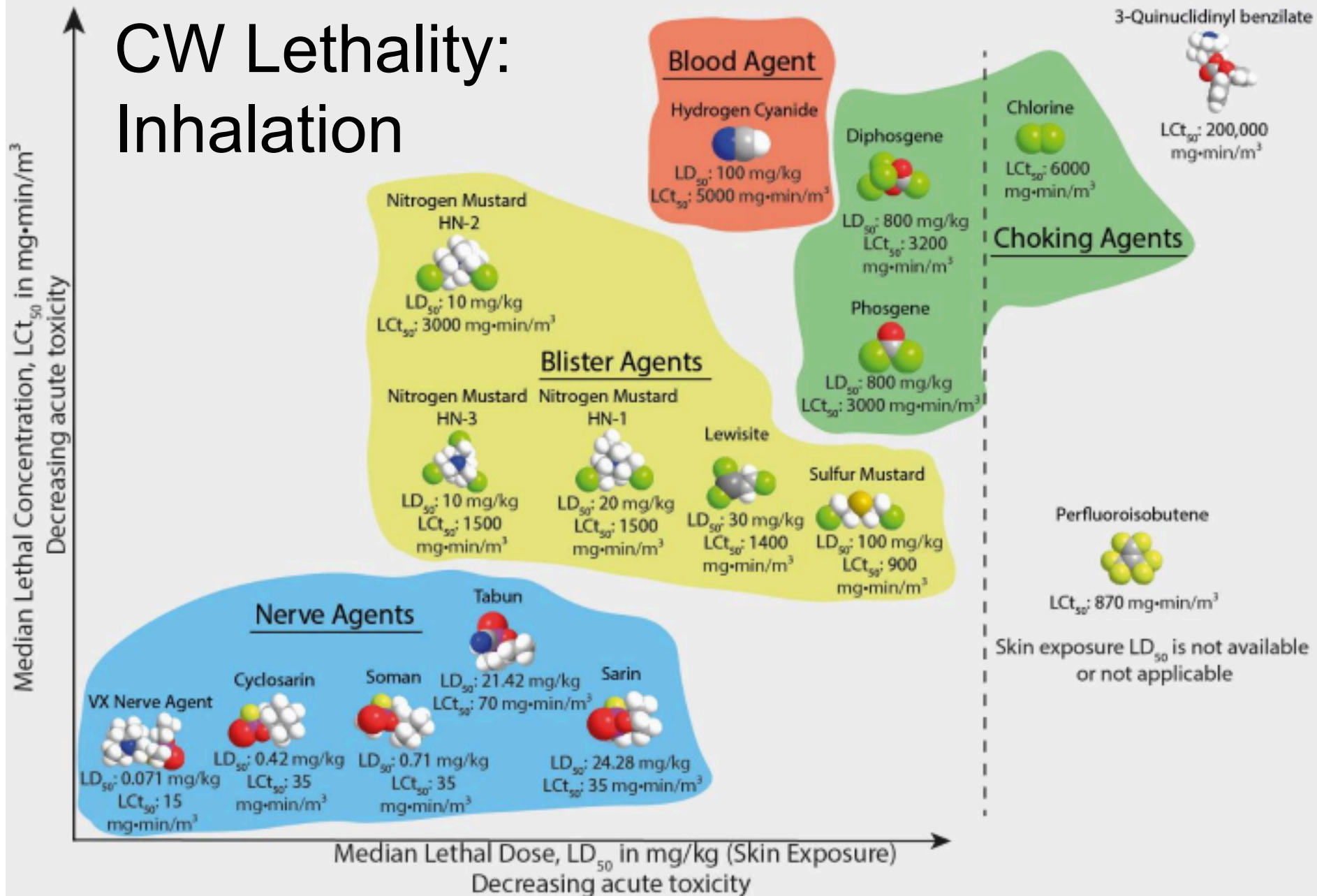
- $ECt_{50}$  = concentration of chemical (vapor phase) expected to cause a defined effect in 50% of a population exposed for a specified period of time; typically expressed as product of chemical's concentration in air ( $mg/m^3$ ) and the duration of exposure (min)...typical units =  $mg \cdot min/m^3$ .
- $ICt_{50}$  = median incapacitation concentration, concentration of chemical (vapor phase) expected to incapacitate 50% of a population exposed for a specified period of time, typically expressed as product of chemical's concentration in air ( $mg/m^3$ ) and the duration of exposure (min)...typical units =  $mg \cdot min/m^3$

# Dosage Units



- $TD_{LO}$  = Lowest toxic dose; the lowest dose of a chemical reported to cause an observable toxic effect in test animals

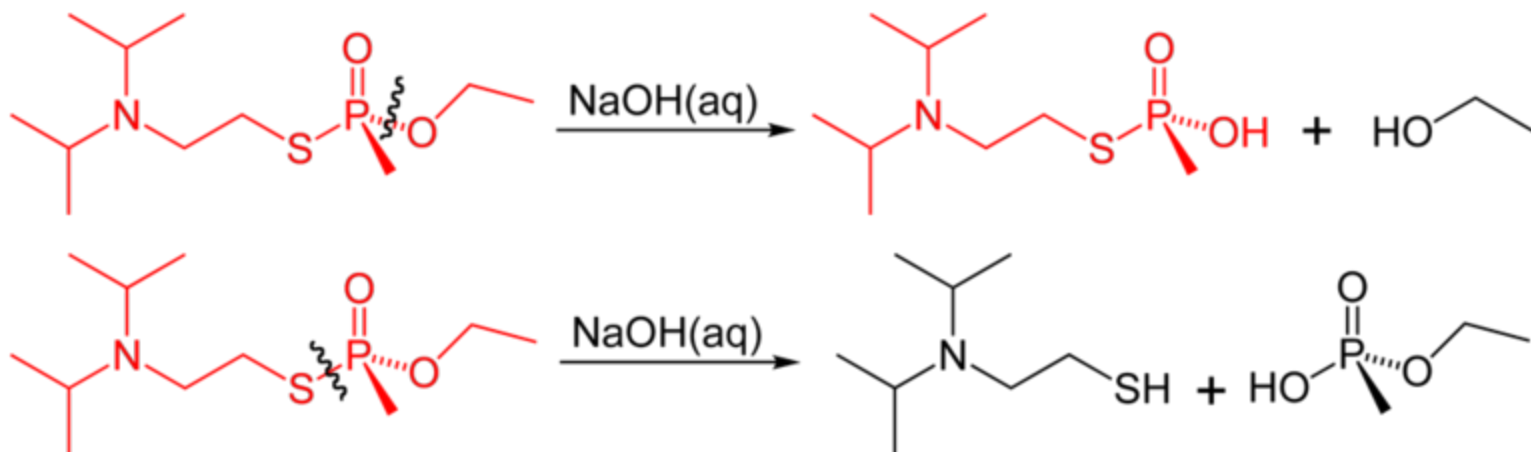
# CW Lethality: Inhalation



Source: Organisation for the Prohibition of Chemical Weapons (OPCW)

# Destruction of VX

- VX can be converted into safer substances by combining it with a concentrated solution of sodium hydroxide, NaOH.
- The reaction is called **hydrolysis**, in which water,  $\text{H}_2\text{O}$ , divides into H, which combines with one part of a molecule, and OH, which combines with another part of the molecule, splitting the molecule into two parts.



# Sarin or VX?

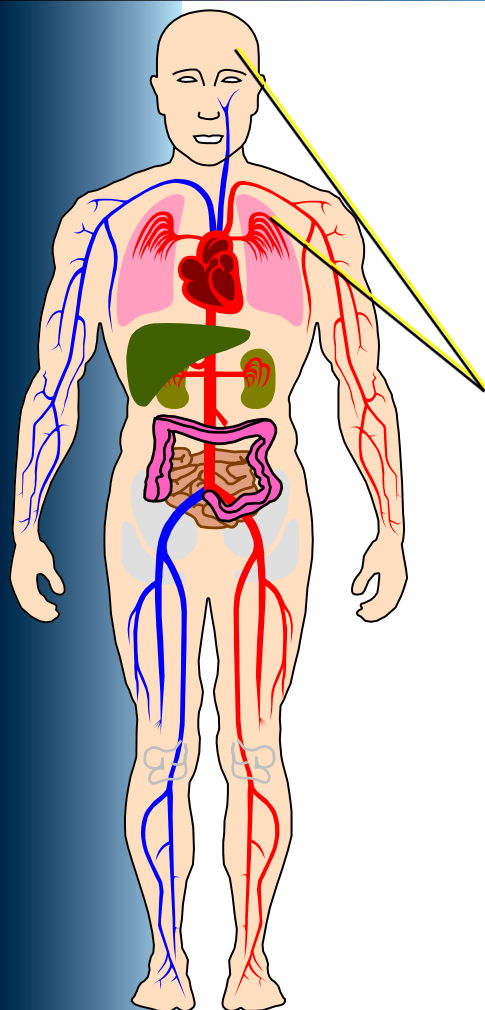
- Sarin –
  - Deadly so inflict high casualties
  - Evaporates about as rapidly as water and reacts fairly quickly with water to form less harmful substances, allowing attacking force to seize territory without major risk to its own troops.
  - Compared to VX nerve agent, sarin is also relatively easy to disseminate.
- VX
  - Due to its viscous nature, VX requires some sort of aerosolization.
  - As little as one drop of VX on skin can be fatal, unless very swift medical treatment.
  - VX nerve agent would require labor-intensive and time-consuming decontamination procedures.

# Incapacitants Classification



- **Irritants** Riot-control agents (CS, CN, etc.); pepper spray
  - The OPCW recognizes 17 riot control agents.
- **Central nervous system stimulants**  
(Amphetamines, cocaine, caffeine, nicotine, strychnine, metrazole)
- **Central nervous system depressants**  
(Barbiturates, opioids, antipsychotics, benzodiazepines)
- **Psychedelics** (LSD-25, psilocybin, ibogaine, harmine, MDMA...“ecstasy”, PCP)
- **Deliriants** (Many, especially anticholinergics, such as BZ)

# Physiological Incapacitants



- CN (mace), CS, pepper spray, fentanyl
- Modes of action: mucous membrane irritation, vomiting inducing, sleep inducing
- Physiological effects - variable
  - Can cause uncontrolled tearing, itching, vomiting, unconsciousness
  - Acts immediately
- Form when disseminated: powder, vapor
- Required defensive gear: protective mask & clothing

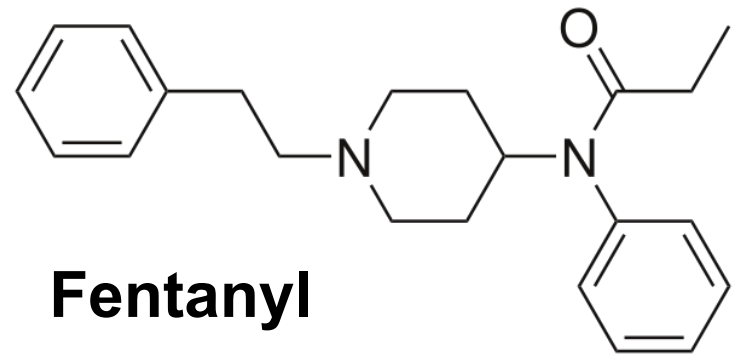
# Opiate-like Agents

- Clinical data for opiate-like compounds, comparing the effective dose ( $ED_{50}$ ) and the lethal dose ( $LD_{50}$ )
- This varies with the health of the subject.

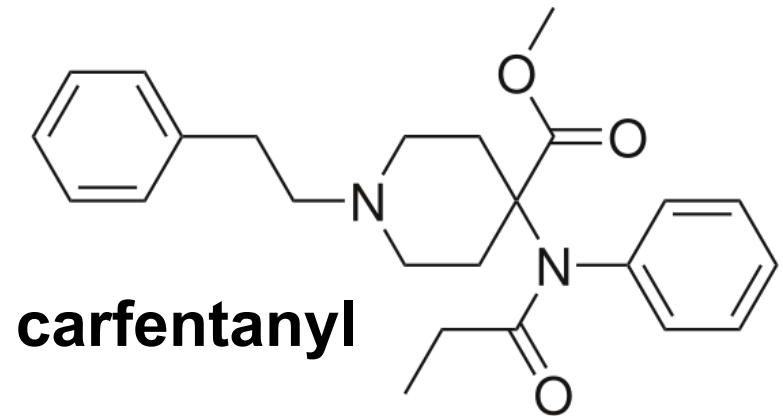
Opiate	Lowest effective dose, $ED_{50}$ mg/kg	$LD_{50}$ , mg/kg	Relative safety index
Meperidine	6.0	29.0	4.8
Alfentanil	0.044	47.5	1,080
Fentanyl	0.011	3.1	277
Sufentanil	0.007	17.9	25,211
Lofentanil	0.0059	0.066	112
Carfentanil	0.0034	3.4	10,000

# Fentanyl and Carfentanyl

- Both potent, synthetic narcotics that stimulate opioid receptors.
- Fentanyl is approximately 100 times more potent than morphine and 50 times more potent than heroin.
- Carfentanyl is about 10,000 times more potent than morphine and 5000 times more potent than heroin.



**Fentanyl**



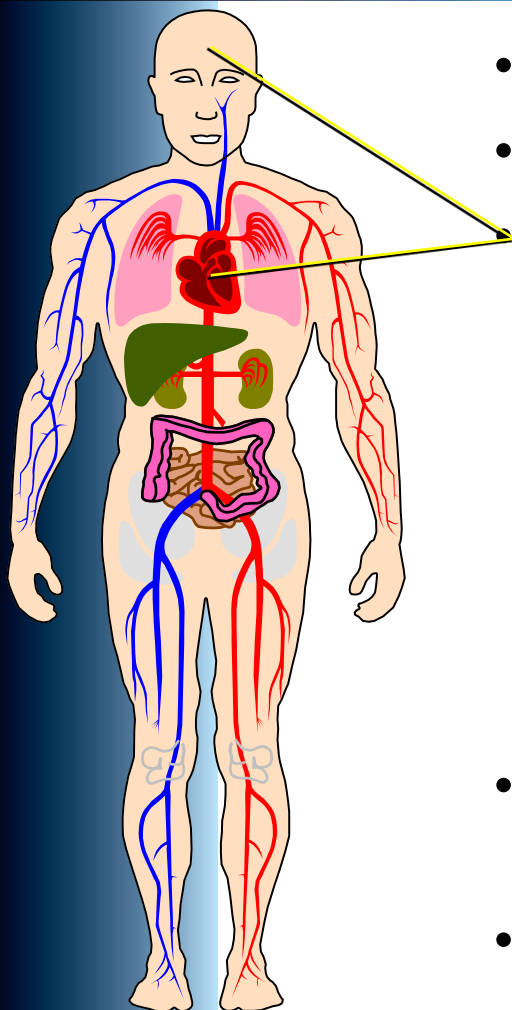
**carfentanyl**

# How Opiates Work



- Bind to the same receptors as natural opioids, such as endorphins, and change how the brain receives pain messages.
- Although the pain information is still transmitted to the brain, a series of changes triggered by the opiate opens channels that slow the transfer of nerve information in the brain.
- They also inhibit the release of GABA, which inhibits the release of dopamine (the feel-good chemical). This leads to an increase of dopamine in the system.
- Dopamine is a neurotransmitter that has many functions, including stimulating the reward system that reinforces behavior necessary for the survival of the species, such as eating, drinking, and sex.

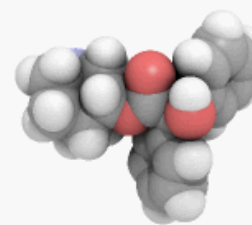
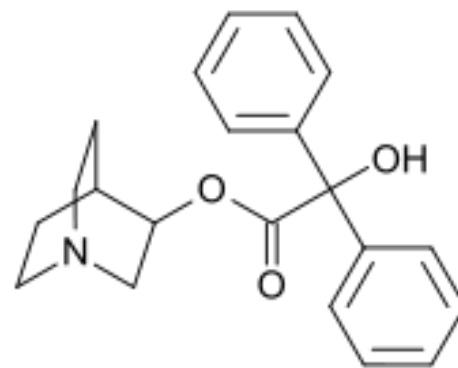
# Psychochemical Incapacitants



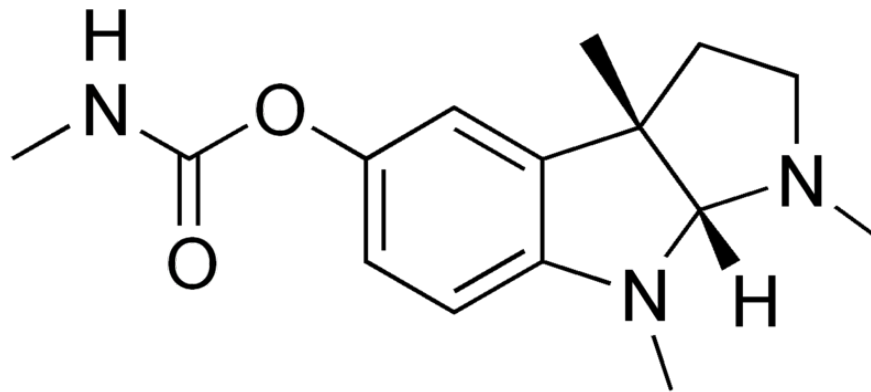
- BZ (3-3-quinuclidinyl benzilate)
  - Modes of action: inhalation, ingestion, injection
- Physiological effects
- Potent anti-cholinergic compound (similar to atropine)
  - Dose  $<1$  mg induces hallucinations and delirium
  - Effects peak at 8 hours and decline over next 48-72 hours
  - Form when disseminated: aerosolized solid, possibly in solvent
  - Required defensive gear: protective mask, suits

# BZ

- **3-Quinuclidinyl benzilate (BZ)** - military incapacitating agent.
- Related to atropine
- Competitive inhibitor of acetylcholine at receptor sites in smooth muscle, exocrine glands, autonomic ganglia, and the brain
- Decreases the effective concentration of acetylcholine seen by receptors at these sites.
- Opposite of effects in nerve agent poisoning.
- Effects include stupor, confusion, and hallucinations.
- Schedule 2 of the Chemical Weapons Convention



# Physostigmine - BZ Antidote



- Anticholinesterase, which temporarily raises acetylcholine concentrations by binding ***reversibly*** to acetylcholinesterase, the enzyme responsible for the breakdown of acetylcholine in the synaptic gap.

# Toxins



- A **toxin** is a poisonous substance produced within living cells or organisms.
- Because toxins are chemicals produced by biological organisms, they can be considered chemical or biological weapons, the use of which would be a violation of both the CWC and the BWC (Biological Weapons Convention).
- As modern chemistry can synthesize an ever-growing number of toxins, they fall under the purview of the CWC.
- Two toxins, ricin and saxitoxin, are listed on Schedule 1 of the CWC.



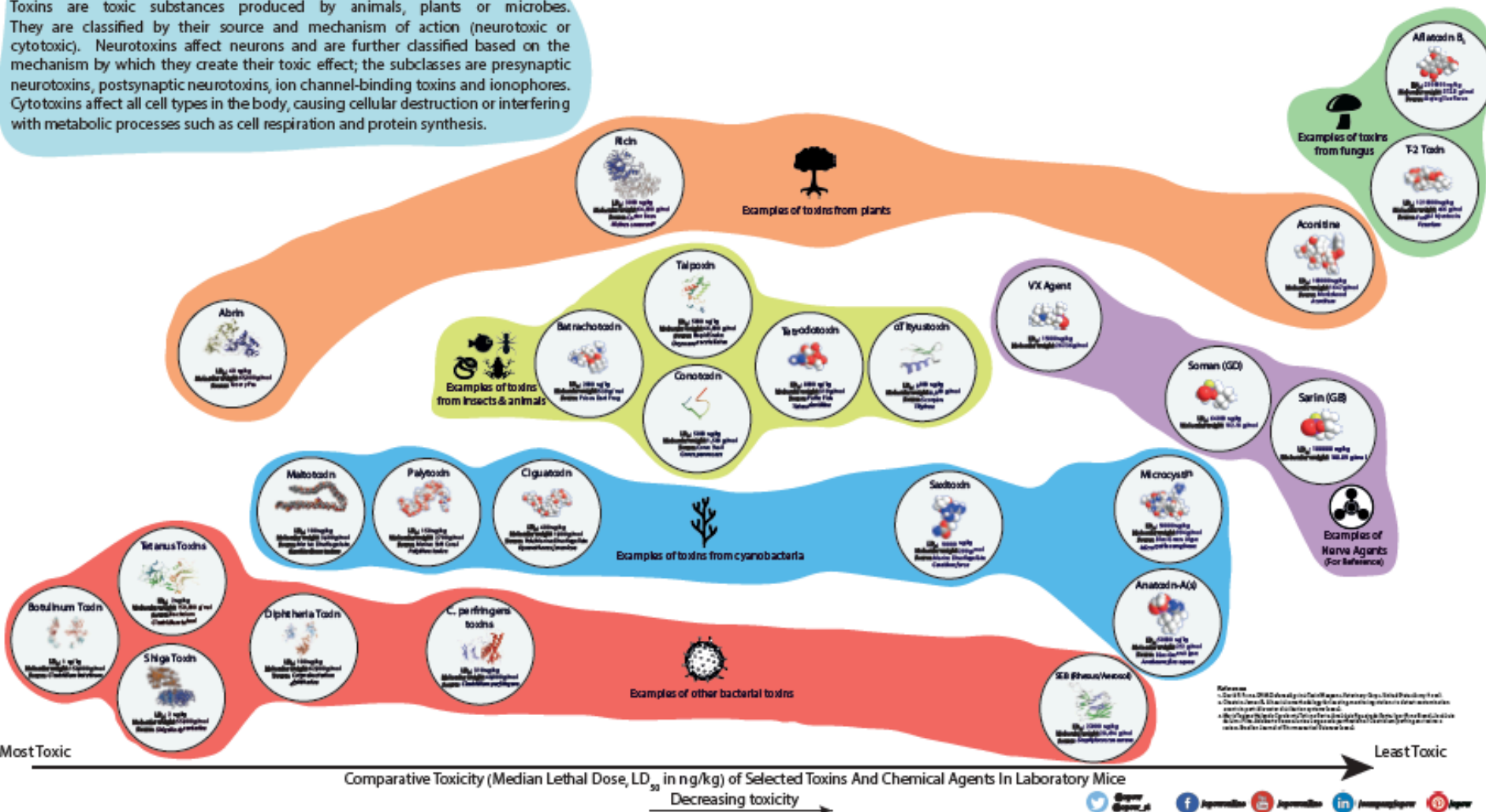
# ORGANISATION FOR THE PROHIBITION OF CHEMICAL WEAPONS

Working Together for a World Free of Chemical Weapons

## Biological Toxins and their Relative Toxicity

### What are Toxins?

Toxins are toxic substances produced by animals, plants or microbes. They are classified by their source and mechanism of action (neurotoxic or cytotoxic). Neurotoxins affect neurons and are further classified based on the mechanism by which they create their toxic effect; the subclasses are presynaptic neurotoxins, postsynaptic neurotoxins, ion channel-binding toxins and ionophores. Cytotoxins affect all cell types in the body, causing cellular destruction or interfering with metabolic processes such as cell respiration and protein synthesis.

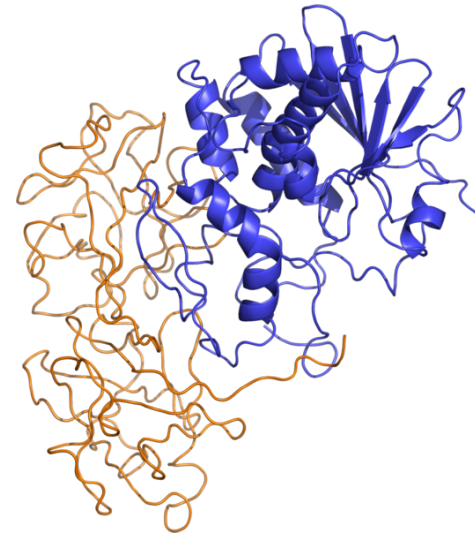


# Ricin

- Naturally occurring protein.
- Can be extracted from castor beans
- The LD<sub>50</sub> of ricin is around 22 micrograms per kilogram in humans if exposure is from injection or inhalation.
- Oral lethal dose is 20–30 milligrams per kilogram.
- The major reason ricin is a public health threat is that it is easy to obtain. (More than 1 million metric tons of castor beans are processed each year.)
- Low thermal stability makes it useless in munitions.
- Ricin is listed as a Schedule 1 controlled substance in the CWC.

<http://en.wikipedia.org/wiki/Ricin>

<https://www.google.com/patents/US3060165>



# Ricin Physiological Effects

- Reacts with ribosomal RNA, deactivates the ribosome, and disrupts protein synthesis.
- Symptoms may take anywhere from hours to days to appear. Death typically occurs within 3–5 days of exposure.
- **Symptoms from inhalation:** respiratory distress (difficulty breathing), fever, cough, nausea, and tightness in the chest. Heavy sweating may follow as well as fluid building up in the lungs (pulmonary edema). Finally, low blood pressure and respiratory failure may occur, leading to death.
- **Symptoms from ingestion:** vomiting and diarrhea that may become bloody. Severe dehydration, followed by low blood pressure....hallucinations, seizures, and blood in the urine. Within several days, the person's liver, spleen, and kidneys might stop working, and the person could die.

# Comparison of Toxins and Chemical Agents

- **Toxins**

- Natural Origin
- Difficult, small-scale production
- None volatile
- Many are more toxic
- Mostly not dermally active
- Legitimate medical use
- Odorless and tasteless
- Diverse toxic effects
- Many are effective immunogens
- Aerosol delivery


- **Chemical Agents**

- Human-made
- Large-scale industrial production
- Many volatile
- Less toxic than many toxins
- Can be dermally active
- Almost no medical uses
- Noticeable odor or taste
- Fewer types of effects
- Poor immunogens
- Mist/droplet/aerosol delivery

# 1925 Geneva Protocol

- Protocol on the Prohibition of the Use in War of Asphyxiating, Poisonous or Other Gases, and of Bacteriological Methods of Warfare
- **Banned first use of chemical and biological weapons but not their production and stockpiling**
- Adopted by the League of Nations
- Within ten years, it was ratified by forty countries, including most of the major powers except the U.S. and Japan.
- U.S. signed with reservations 50 years later (General Fries lobbied against it, aided by a coalition of veterans' groups, the chemical industry, and the American Chemical Society.)
- A number of countries reserved the right to retaliate and therefore stockpiled chemical weapons.

# U.S. Chemical Warfare Service (CWS)



- Formed in 1918
- Headquartered at Edgewood Arsenal
- Headed by General Amos Fries
- Later became the U.S. Army Chemical Corps

*When properly safe-guarded with masks and other safety devices, [chemical weapons give] the most scientific and most ingenious people an advantage over the less scientific and less ingenious...It is just as sportsman-like to fight with chemical warfare material as it is to fight with machine guns.*

General Fries

# Chemical Weapons Convention (CWC)



- **A disarmament agreement that bans the production, stockpiling, transferring, and use of chemical weapons.**
- Approved by the U.N. General Assembly in November, 1992.
- Open for signature in 1993
- The U.S. ratified CWC in 1997.

<http://www.cwc.gov/>

<http://www.opcw.org/chemical-weapons-convention//>

<http://www.opcw.org/news-publications/publications/history-of-the-chemical-weapons-convention/>

# CWC General Obligations



1. Each State Party to this Convention undertakes never under any circumstances:
  - (a) To develop, produce, otherwise acquire, stockpile or retain chemical weapons, or transfer, directly or indirectly, chemical weapons to anyone;
  - (b) To use chemical weapons;
  - (c) To engage in any military preparations to use chemical weapons;
  - (d) To assist, encourage or induce, in any way, anyone to engage in any activity prohibited to a State Party under this Convention.

# CWC General Obligations (cont.)

2. Each State Party undertakes to **destroy chemical weapons it owns or possesses**, or that are located in any place under its jurisdiction or control, in accordance with the provisions of this Convention.
3. Each State Party undertakes to **destroy all chemical weapons it abandoned** on the territory of another State Party, in accordance with the provisions of this Convention.
4. Each State Party undertakes to **destroy any chemical weapons production facilities** it owns or possesses, or that are located in any place under its jurisdiction or control, in accordance with the provisions of this Convention.
5. Each State Party undertakes not to use riot control agents as a method of warfare.

# Organisation for the Prohibition of Chemical Weapons (OPCW)

- Model of multilateralism - 192 member states that contain 98% of the world's population.
- 4 nonmember states
  - Signatory states that have not ratified the CWC
    - Israel
  - States that have neither signed nor ratified the CWC
    - Egypt
    - North Korea
    - South Sudan ("has all but concluded the process of joining the Organisation for the Prohibition of Chemical Weapons" 12/1/17)

# States Outside CWC

- Israel
  - Analysts believe that Israel initiated a CW program between mid-1950s and mid-1980s.
  - Refuses to ratify CWC until there's more regional participation.
  - Israel's chemical industry is advanced and diverse.
  - Although Israel is capable of creating CW weapons, there is insufficient information available to reconstruct their CW program.

<http://www.nti.org/country-profiles/israel/>

# States Outside CWC

- Egypt
  - Used CW in North Yemen
  - Thought to have inherited mustard agent and phosgene from British forces when they withdrew in 1954
  - May have nerve agents
  - Refuses to join CWC until Israel joins the Nuclear Nonproliferation Treaty (NPT)
  - Thought to have helped Iraq get CW production capabilities

[http://www.nti.org/e\\_research/profiles/Egypt/Chemical/index.html](http://www.nti.org/e_research/profiles/Egypt/Chemical/index.html)

# States Outside CWC



- North Korea
  - Thought to have 2500-5000 metric tons of phosgene, hydrogen cyanide, mustard agent, and sarin
  - Has capable but aging chemical industry

<http://www.nti.org/country-profiles/north-korea/>

# CWC

## Definitions

- **Toxic Chemical** = Any chemical which through its chemical action on life processes can cause death, temporary incapacitation or permanent harm to humans or animals.
- **Precursor** = Any chemical reactant which takes part at any stage in the production by whatever method of a toxic chemical.
- **Key Component** of Binary or Multicomponent Chemical System = The precursor which plays the most important role in determining the toxic properties of the final product and reacts rapidly with other chemicals in the binary or multicomponent system.

# CWC

## Schedule 1

<http://www.opcw.org/chemical-weapons-convention/annex-on-chemicals/a-guidelines-for-schedules-of-chemicals/>

- Schedule 1 chemicals have few or no uses other than as chemical weapons agents or to arm chemical weapons.
- Examples include the nerve agents, sulfur mustards, nitrogen mustards, and lewisite
- They are the most highly regulated of all chemicals.

[http://www.cwc.gov/index\\_chemicals\\_sch1.html](http://www.cwc.gov/index_chemicals_sch1.html)

# CWC

## Schedule 2

- Schedule 2 chemicals are chemicals that could be used as weapons or to make weapons, but also have legitimate small-scale uses.
- Examples include Amiton (a V-series nerve agent) and BZ.

[http://www.cwc.gov/index\\_chemicals\\_sch2.html](http://www.cwc.gov/index_chemicals_sch2.html)


# CWC

## Schedule 3

- Schedule 3 chemicals have large-scale uses other than chemical weapons.
  - Chemical plants producing more than 30 Mg per year must report to the Organisation for the Prohibition of Chemical Weapons (OPCW).
  - The plants can be inspected, and there are restrictions on export to countries that have not signed the CWC.
  - Phosgene and hydrogen cyanide are examples.

[http://www.cwc.gov/index\\_chemicals\\_sch3.html](http://www.cwc.gov/index_chemicals_sch3.html)

# CWC Parts A and B



- Each schedule is divided into
  - Part A – toxic chemicals themselves
  - Part B – their precursors (chemicals used to produce the toxic chemicals)

# Organisation for the Prohibition of Chemical Weapons (OPCW)

- Intergovernmental organization located in The Hague, Netherlands
- *“...implementing body of the [CWC]...given the mandate to achieve the object and purpose of the Convention, to ensure the implementation of its provisions, including those for international verification of compliance with it, and to provide a forum for consultation and cooperation among States Parties.”*

<http://www.opcw.org/about-opcw/>

<http://www.opcw.org/>

# OPCW Tasks



- Bring all States into the CWC
- Verifying the destruction of declared chemical weapons, including those in abandoned CW weapons
  - The CWC is unique among disarmament treaties in having a verification regime.
- Verifying the destruction or conversion of CW plants
- Monitoring future compliance with CWC

# Common CW Precursors

- Most precursors have legitimate commercial uses.
- Dual-use nature impedes detection of CW programs.
- Trade in precursors is monitored and controlled.

<i><b>Chemical Compound</b></i>	<i><b>Commercial Uses</b></i>	<i><b>CW Agent</b></i>
Thiodiglycol	plastics, textile dyes, ink	Mustard agent
Phosphorus trichloride	plasticizers, insecticides	Sarin
Sodium cyanide	dyes & pigments, nylon, metal hardening	HCN
Methylphosphonic difluoride	organic synthesis	Sarin, VX
Phosphorus pentasulfide	insecticides, lubricants, pyrotechnics	VX

# Australia Group



- Established 1985
- *“The Australia Group (AG) is an informal forum of countries which, through the harmonisation of export controls, seeks to ensure that exports do not contribute to the development of chemical or biological weapons. Coordination of national export control measures assists Australia Group participants to fulfill their obligations under the Chemical Weapons Convention and the Biological and Toxin Weapons Convention to the fullest extent possible.”*

<http://www.australiagroup.net/en/index.html>

# Australia Group



- *“The principal objective of Australia Group participants’ is to use licensing measures to ensure that exports of certain chemicals, biological agents, and dual-use chemical and biological manufacturing facilities and equipment, do not contribute to the spread of CBW. The Group achieves this by harmonising participating countries’ national export licensing measures. The Group’s activities are especially important given that the international chemical and biotechnology industries are a target for proliferators as a source of materials for CBW programs.”*
- Some of the controlled chemicals are not listed in the CWC.

<http://www.australiagroup.net/en/objectives.html>

# Australia Group

## 43 Participants

- European Union (1985), Germany (1985), United States (1985), United Kingdom (1985), Italy (1985), Japan (1985), France (1985), Spain (1985), Sweden (1991), Poland (1994), Switzerland (1987), Netherlands (1985), Argentina (1993), Republic of Korea (1996), Australia (1985), Latvia (2004), Austria (1989), Lithuania (2004), Belgium (1985), Luxembourg (1985), Bulgaria (2001), Malta (2004), Canada (1985), Mexico (2013), Croatia (2007), New Zealand (1985), Republic of Cyprus (2000), Norway (1986), Czech Republic (1994), Denmark (1985), Portugal (1985), Estonia (2004), Romania (1995), Slovak Republic (1994), Finland (1991), Slovenia (2004), Greece (1985), Hungary (1993), Republic of Turkey (2000), Iceland (1993), Ukraine (2005), Ireland (1985), India (2018)

<http://www.australiagroup.net/en/participants.html>

# Top 10 Chemical-Producing Countries

- In Australia Group:
  - 1. USA
  - 2. Germany
  - 5. Japan
  - 6. United Kingdom
  - 7. Italy
  - 8. France
  - 9. India
- Not in Australia Group:
  - 3. Russia
  - 4. China
  - 10. Brazil

<http://www.australiagroup.net/en/participants.html>

# INCIDENT INVESTIGATION

## WHAT – WHERE – WHO ?



# INCIDENT OCCURS

Science for Diplomats 17 March 2015

[www.opcw.org/fileadmin/OPCW/Science\\_Technology/Diplomats\\_Programme/Science\\_for\\_Diplomats\\_at\\_the\\_OPCW\\_2014\\_2015.pdf](http://www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the_OPCW_2014_2015.pdf)



# FIRST REPPONSE

Science for Diplomats 17 March 2015

[www.opcw.org/fileadmin/OPCW/Science\\_Technology/Diplomats\\_Programme/Science\\_for\\_Diplomats\\_at\\_the OPCW\\_2014\\_2015.pdf](http://www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the OPCW_2014_2015.pdf)

## WORLD &amp; NATION

March 21, 1995

## Boston's Red-Light District Flickers

THE WASHINGTON POST

BOSTON

It is known officially as the Lower Washington Street Adult Entertainment District, but everyone calls it the Combat Zone. It is the place where the commercial sex industry finds its public, and where Boston — a city once synonymous with sexual prudery — has carried out a successful containment strategy by creating one of the few formal red-light districts in North America.

Now the red light is flickering, about to be extinguished by a convergence of trends here. The story of the Combat Zone's brief heyday, long decline, and imminent fall is an instructive tale of sex, money, violence and urban development.

The area acquired its name before it became zoned for sex. Initially, it was home to a number of small tailor shops, and troops shipped through Boston during World War II got their uniforms altered there. When members of different branches bumped into each other on the sidewalks, combat often erupted.

Later, during the 1950s and 1960s, Boston, like many cities, embarked on a large-scale "urban-renewal" effort, which involved leveling districts of the city and replacing them with new office towers and apartment buildings.

One of the last places to go under the wrecker's ball was Scollay Square, which had been home to Boston's burlesque houses. When the area was torn down to make way for the new City Hall and government center, the honky-tonk businesses migrated to the Combat Zone.

During the late 1980s, the Zone's fate was sealed, according to Robert Campbell, the architecture critic for *The Boston Globe* and a student of urban development.

## Rushdie Asks France for Help In Ending Iranian Death Threat

LOS ANGELES TIMES

PARIS

Salman Rushdie — the author whom Iran six years ago marked for death for his book *The Satanic Verses* — met France's highest politicians on Monday, winning assurances they would lead a European effort to persuade Iran to declare a "cease-fire" on him.

"I think we are at the beginning of a very serious step," Rushdie said after meeting with Prime Minister Edouard Balladur, Foreign Minister Alain Juppe and other top French officials.

"This is a situation that can be resolved, but what is needed is the will," the British writer told a well-guarded news conference at the French National Assembly. "And this visit has been an important step in creating the will to remove the deadlock."

After meeting with Rushdie, Juppe, the French foreign minister, said pressure on Iran had failed so far in Rushdie's case. But he declared that France was prepared to bring the issue up again next week.

"We are ready to take any step in this direction," he said. "We are ready to take any step in this direction." "We are ready to take any step in this direction." "We are ready to take any step in this direction."

## Suspect Captured in Fatal Tokyo Subway Gas Attack

By T.R. Reid

THE WASHINGTON POST

TOKYO

Police reportedly had one suspect under guard Tuesday as they searched for a well-organized terrorist gang believed to be responsible for the release of poison gas on the Tokyo subway Monday, which left 8 dead, 76 critically injured and more than 600 hospitalized overnight.

According to the national police agency, the World War II-era nerve gas sarin apparently was released on at least five widely scattered trains during a half-hour period starting around 8 a.m. Monday. Handling this powerful poison — so potent that a single drop on the skin can be fatal — and coordinating its delivery around the city probably required a careful team effort, a police spokesman said.

No one claimed responsibility for the attack, which one official called "a case virtually unparalleled in the history of crime in this country." Police said they were reviewing several other recent cases in which noxious fumes were released — including an incident last June in which seven people died from inhaling what appeared to be the same substance released in the subways on Monday.

The Tokyo Shimbun newspaper reported Tuesday that passengers at the Kodenmacho station in downtown Tokyo spotted and chased a man who had left a vial of vaporous liquid on the train shortly after 8 a.m. The suspect was overcome by the fumes and could not get away. He is now under guard in a hospital, the newspaper said, but was too ill to be questioned Monday.

The poison gas attack was a civil act, courtesy and the low crime rate of any big city on Earth.

Army and other terrorist groups resorted to occasional violence in pursuit of various political aims.

There was little sign of panic in Tokyo following Monday morning's attacks. The thousands of people who came gasping and retching out of the subways — many temporarily blinded by the stinging gas — lined up and waited quietly for on-the-spot treatment or transport to hospitals.

Outside the subway station at Kasumigaseki, bureaucrats sat atop their briefcases while police gave them oxygen. Meanwhile, police and military personnel wearing gas masks and spacesuit-style protective gear searched inch-by-inch through trains and stations.

More than 4,600 people sought hospital treatment. At St. Luke's International Hospital downtown, beds lined the lobby and corridors as nurses washed the eyes of victims and gave them oxygen. Most victims left the hospital under their own power after a few hours. Police said 603 persons were hospitalized overnight.

Service was restored on all but one of the city's 12 subway lines by Monday afternoon, and officials said trains were as packed as usual during the evening rush hour. "Look, I've got to get home," said a woman on the Ginza subway line Monday night. "And it's probably worse if you go up (on the street) and take the bus."

Since the first day of spring is a national holiday in Japan, Tuesday morning was calm and quiet on the subways, with all lines running and all stations open.

In contrast to the delays and confusion that marked the government's response to the disastrous Kobe earthquake in January, rescue efforts for Tuesday's attack seemed to be timely and adequate.

The affected stations.

U.S. government sources in Washington expressed some skepticism that the substance used in the attack was actually sarin. They said they understood that Japanese police had not completed testing needed to prove what chemical was used and that the data collected so far indicate the substance instead may have been a mixture of agricultural chemicals and other hazardous pesticide-like compounds. The U.S. officials also said they believe the number of deaths is low for a genuine sarin-like agent.

Experts said that sarin itself is in relatively scarce supply and would be difficult, though not impossible, for a terrorist group to make. But structurally similar compounds, with similarly lethal properties, can be made relatively easily and cheaply, according to chemists and other experts.

Other than the report that a suspect was under guard, police said almost nothing about their investigation, but other media reports indicated that there were several witnesses who saw unusual actions on the subways Monday morning.

At Nakameguro station, southwest of the city center on the Hibiya subway line, witnesses told police, a man about 40 years old jumped on the train just before 8 a.m. When he got off at Ebisu, the next stop, he left behind on the floor a plastic lunch box wrapped in newspaper. Within eight minutes, or three more stops, a sharp odor coming from the package forced everybody off the train.

At a train on the Marunouchi line, a wad of wet newspaper on the floor began giving off noxious fumes. A similar wad of papers was found inside a plastic trash bag on a different train.

Government and private experts said these reports suggested that the terrorist group may have brought sealed bottles of sarin on the trains, poured the clear, lethal liquid onto newspaper, then left the train.



# SYRIAN ARAB REPUBLIC 2013

Science for Diplomats 17 March 2015

[www.opcw.org/fileadmin/OPCW/Science\\_Technology/Diplomats\\_Programme/Science\\_for\\_Diplomats\\_at\\_the\\_OPCW\\_2014\\_2015.pdf](http://www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the_OPCW_2014_2015.pdf)



# INTERVIEWS AND BIOMEDICAL SAMPLING

Science for Diplomats 17 March 2015

[www.opcw.org/fileadmin/OPCW/Science\\_Technology/Diplomats\\_Programme/Science\\_for\\_Diplomats\\_at\\_the\\_OPCW\\_2014\\_2015.pdf](http://www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the_OPCW_2014_2015.pdf)



# ENVIRONMENTAL SAMPLING

Science for Diplomats 17 March 2015

[www.opcw.org/fileadmin/OPCW/Science\\_Technology/Diplomats\\_Programme/Science\\_for\\_Diplomats\\_at\\_the\\_OPCW\\_2014\\_2015.pdf](http://www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the_OPCW_2014_2015.pdf)



# CHAIN OF CUSTODY!

Science for Diplomats 17 March 2015

[www.opcw.org/fileadmin/OPCW/Science\\_Technology/Diplomats\\_Programme/Science\\_for\\_Diplomats\\_at\\_the\\_OPCW\\_2014\\_2015.pdf](http://www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the_OPCW_2014_2015.pdf)

# OPCW Fact Finding Missions



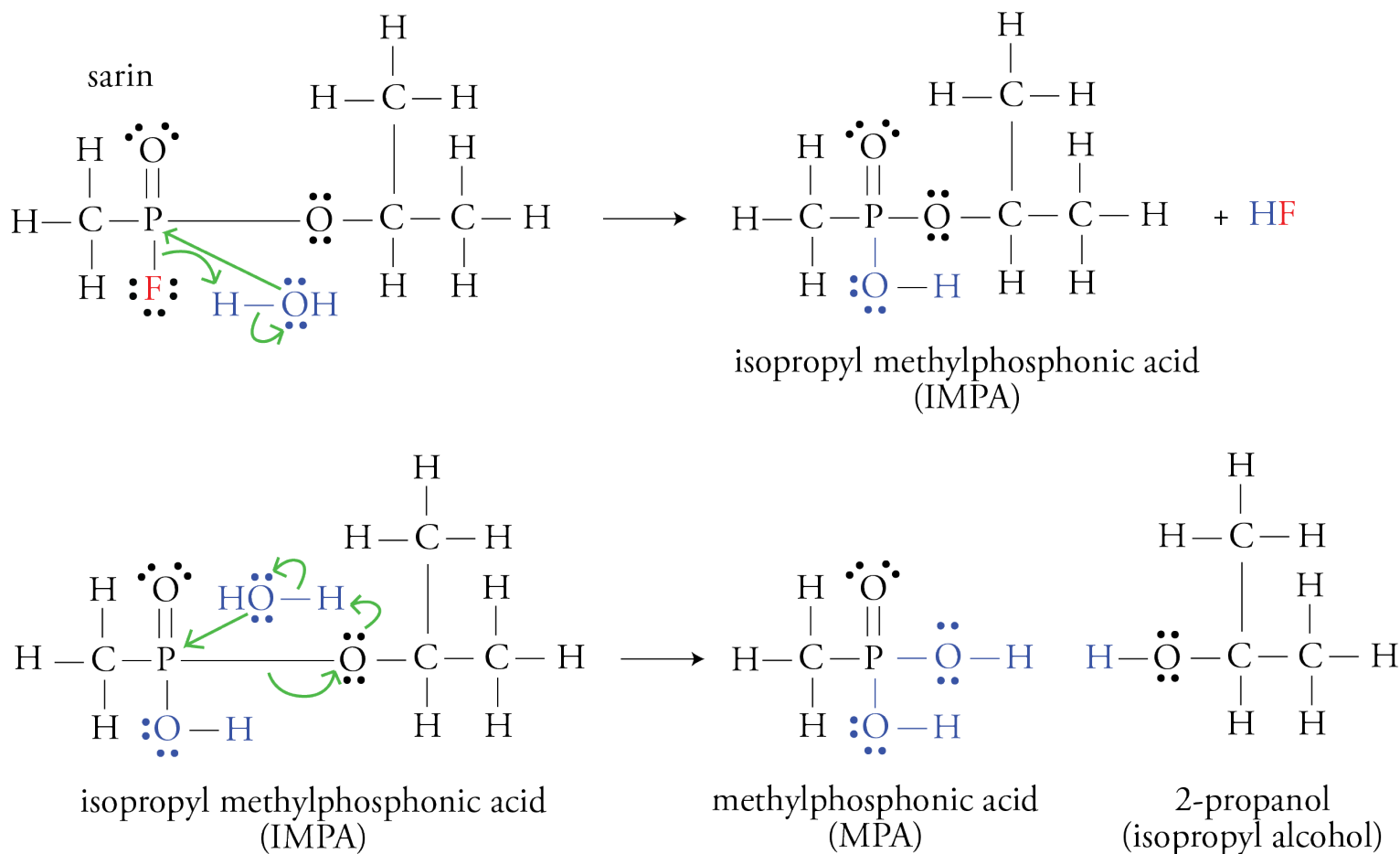
- Collection of evidence
  - Environmental samples
  - Biomedical samples
  - Chain-of custody
  - Interviews
  - Photos, video
- On-site detectors, on-site analysis
- OPCW designated laboratory network

# Sample Types and Assumed Concentrations

- Environmental samples
  - “Neat” agent from a reactor or bomb
  - Residue from a reaction or waste container
  - Contaminated clothing, hair, soil, water, etc.
  - Concentrations usually expected  $>1 \mu\text{g/g}$  (ppm)
  - Survey analysis is possible
- Biomedical samples
  - Urine, blood, plasma, tissue, etc.
  - Intact chemical agent likely not present (degradation/reaction product or metabolite)
  - Concentration levels quite low,  $< 5 \text{ ng/g}$  (ppb)
  - Survey analysis not possible; must use targeted analysis

# Hydrolysis of Sarin

Each arrow represents the movement of a pair of electrons as covalent bonds are broken and made.



# Detection of Sarin Use



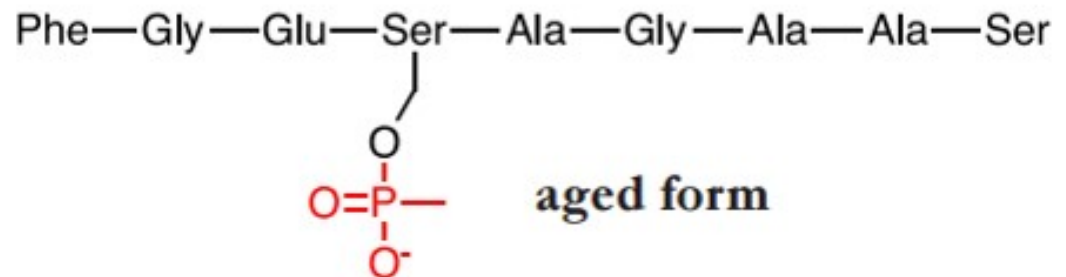
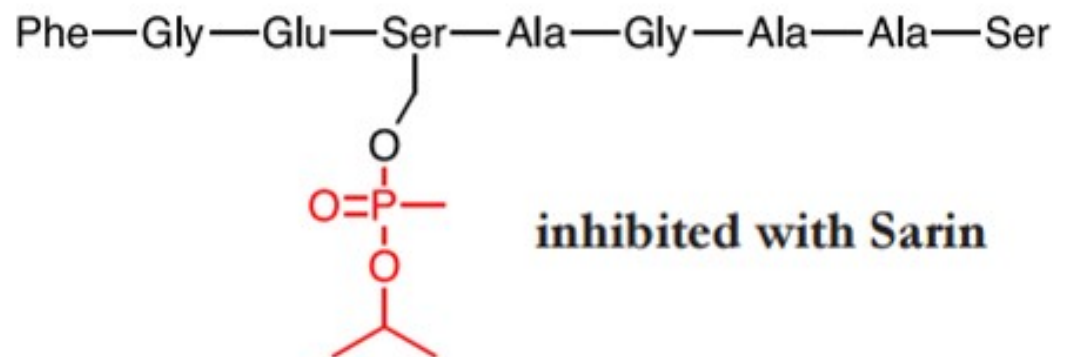
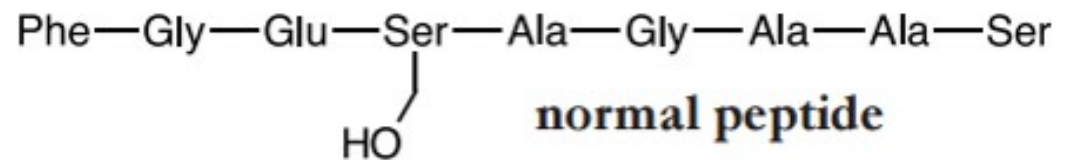
- The product of the first step in the hydrolysis of sarin, isopropyl methylphosphonic acid (IMPA), is a chemical that is not commonly found in nature, so if it is found at the site of a chemical weapons attack, it's an indication of the use of sarin.
- IMPA was detected in 20 of 42 reported environmental samples taken by the OPCW team in Ghouta, Syria.
- The final products of the hydrolysis of sarin are formed from the hydrolysis of other organophosphates.

# Detection of Sarin Use in Biomedical Samples

- Urine or blood samples taken from exposed persons are more difficult than environmental samples to analyze because the chemical agent, its adducts, and metabolites degrade and are excreted from the body, giving a limited time window to collect and analyze samples.
- Concentration levels in these samples are likely to be in the parts per billion range, requiring a targeted rather than a survey approach to the analysis.
- Can look for IMPA and protein adducts, including sarin-AChE or sarin-BChE (butyrylcholinesterase), which may persist for several weeks.
- Unlike the sarin-AChE adduct, sarin-BChE is found in blood serum.

# Detection of Sarin Use in Biomedical Samples

- Can look for protein fragments that come from the partial digestion of the sarin-BChE) in blood serum.
- These fragments can be in the sarin-fragment form or the aged form.



# How does a GC/MS work?

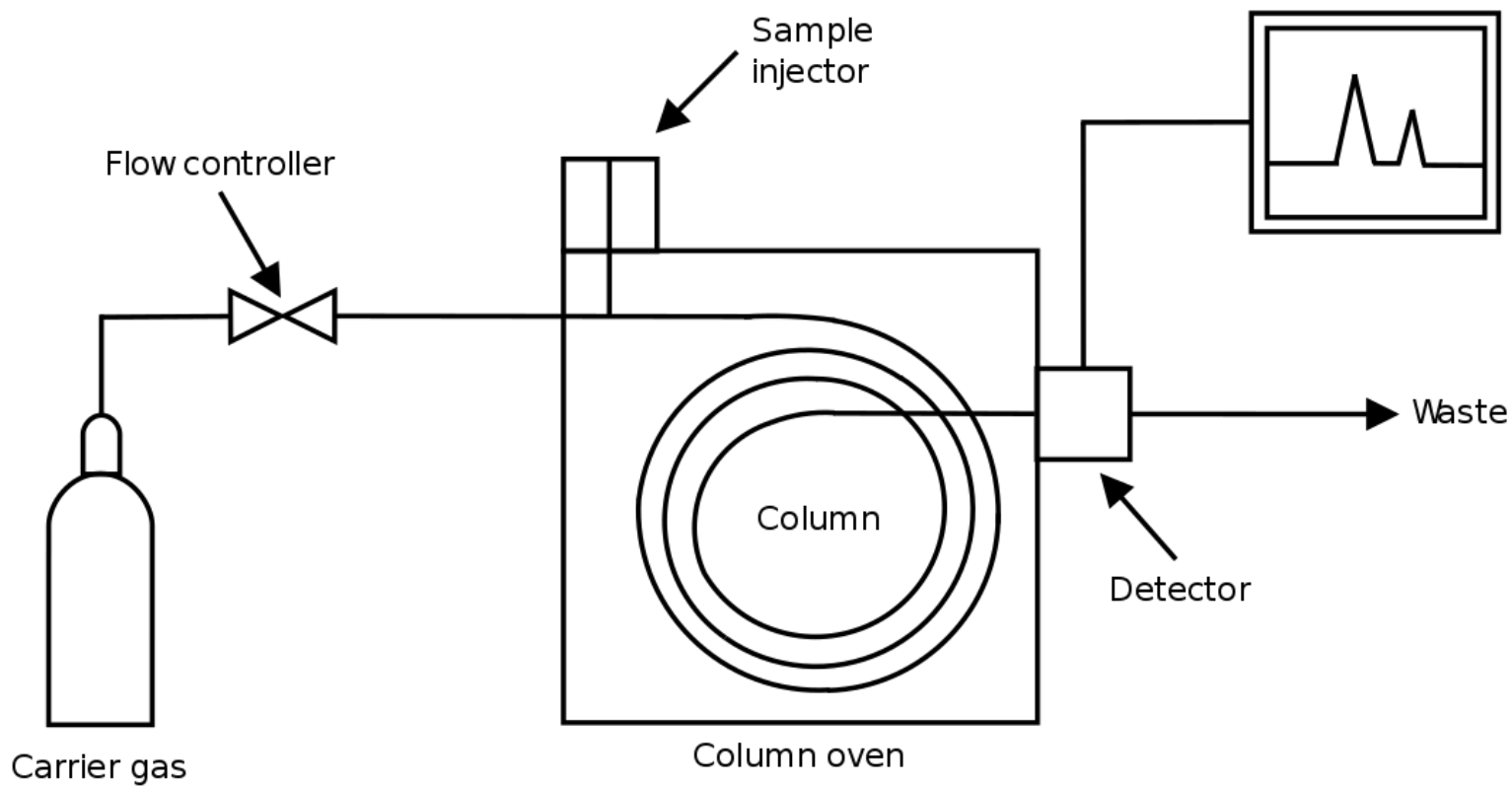


(3) Mass Spectrometer:  
Creates a **spectrum** or “fingerprint” of each compound as it comes from the GC

(1) Autosampler:  
Injects a small amount (1  $\mu\text{L}$ ) of sample into the Gas Chromatograph

(2) Gas Chromatograph:  
Separates chemical species and creates a **chromatogram** of all the species in the sample.

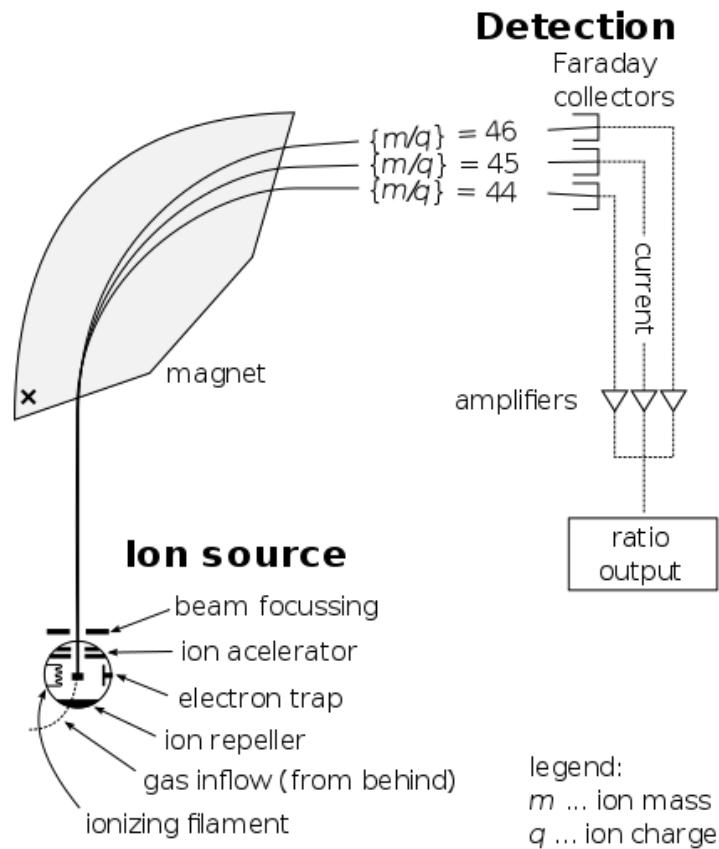
# Gas Chromatograph




# Gas Chromatograph

- Volatile sample injected.
- Carried by an inert or unreactive gas (e.g. helium or nitrogen) through column with solid coated with thin layer of liquid or a polymer.
- Substances move back and forth between moving in the gas and stationary on liquid.
- Different substances have different volatilities and different attractions to liquid or polymer, so they spend different amounts of time moving in gas.
- Substances are separated because they come out of the column at different times

# Mass Spectrometer



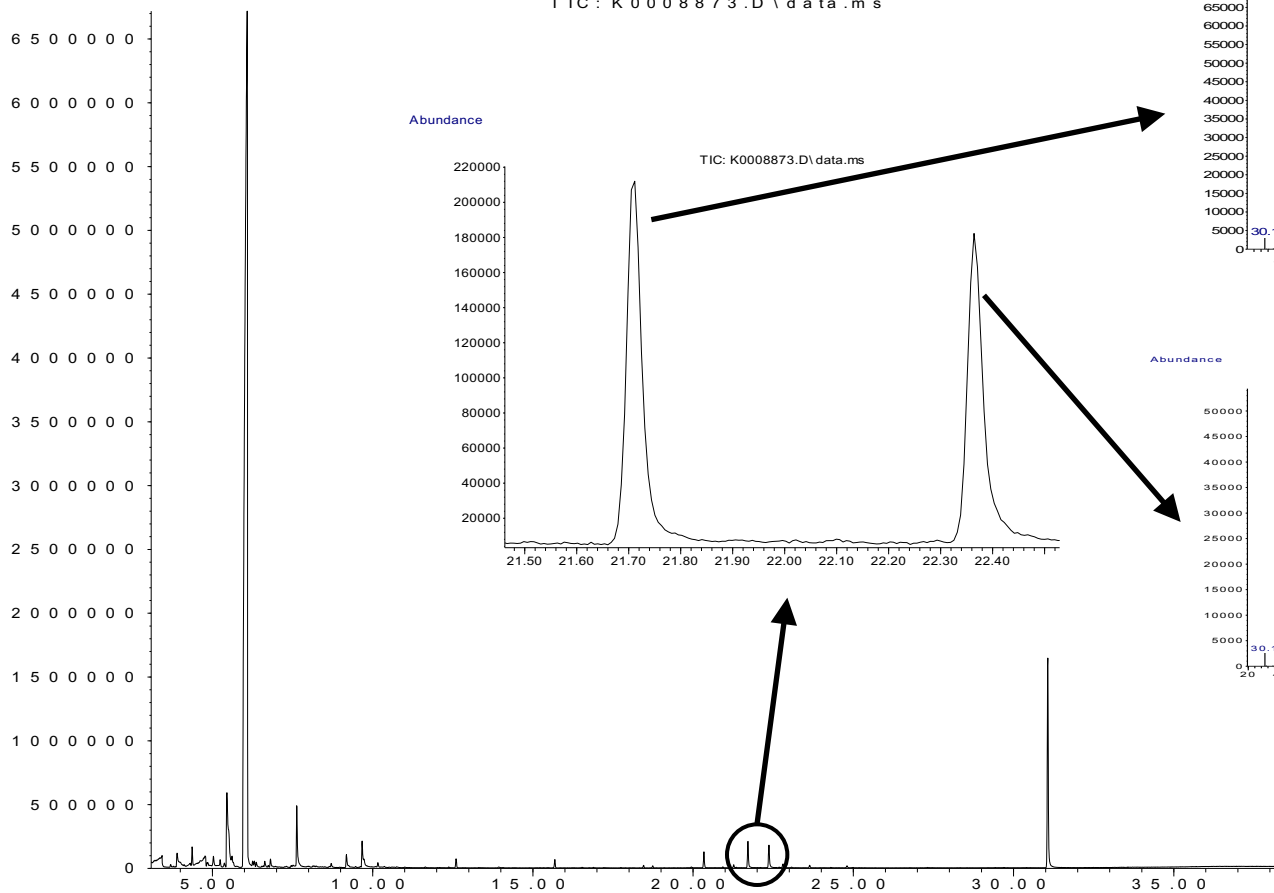
# Mass Spectrometer

The background of the slide features a stylized illustration. On the left, a dark silhouette of a mass spectrometer's ion source and acceleration region is visible against a dark blue background. A bright, glowing blue cloud-like shape represents the ion beam's path as it moves towards the right. On the right side, numerous red and white spheres, representing ions, are shown in various positions, suggesting they are being deflected or detected at different points.

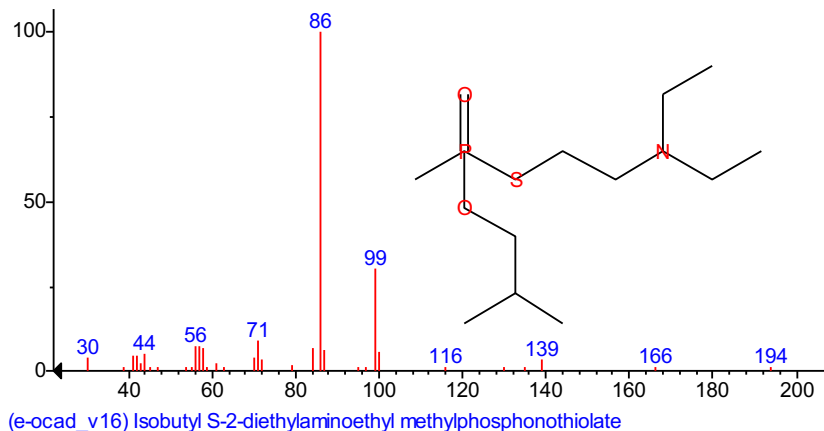
- Substances is ionized and broken into fragments by an electron beam.
- Ions are accelerated into a magnetic field.
- Moving ions create a magnetic field that interacts with the external magnetic field, causing the ions to be deflected.
- The more massive the particle is, the more difficult it is to deflect it, so the less it is deflected.
- Detector finds the ions at different positions, and a mass spectrum is created based on the amount of deflection and the intensity of the ion beam at different degrees of deflection.
- Each substance yields a unique mass spectrum, and comparison of a mass spectrum to mass spectrums of known substances can be done to identify substances.

# GC/MS Data: Chromatograms and Spectra

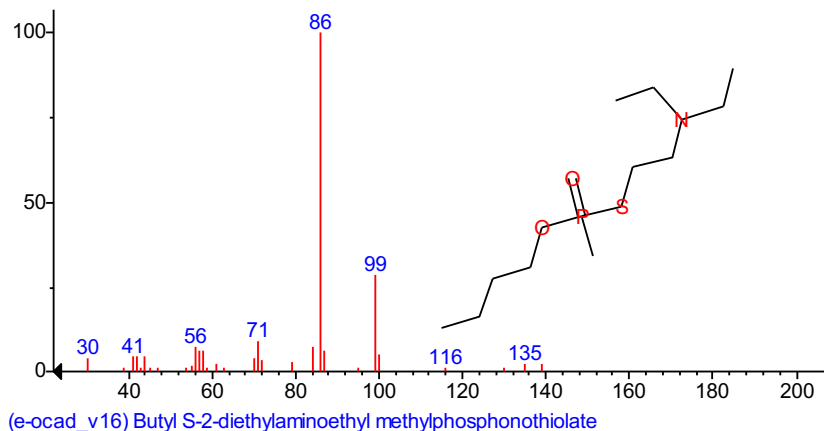
Abundance



# GC/MS Results: Spectra Match to Library

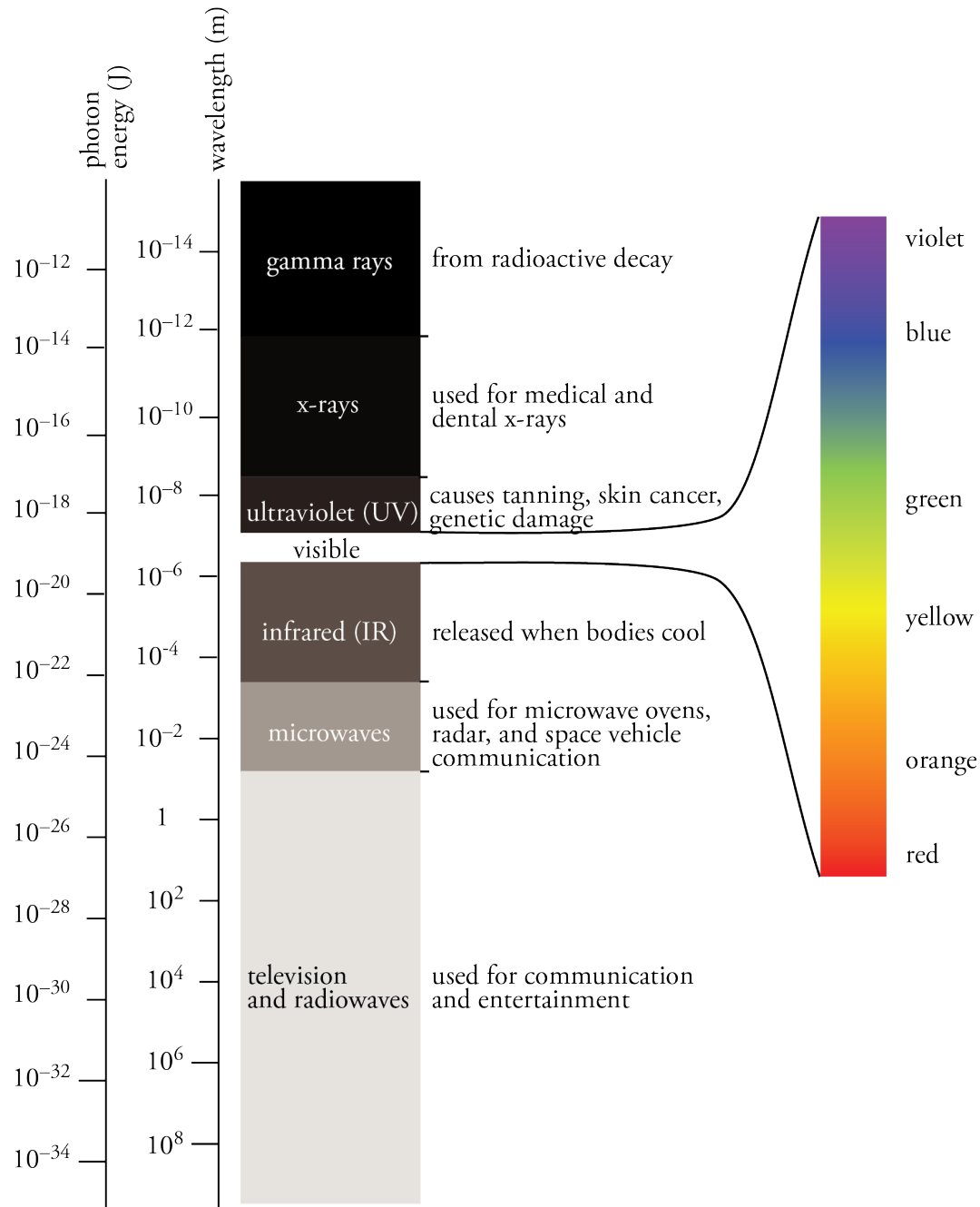


- Small differences in mass spectra indicate different structures
- Both are V-agents

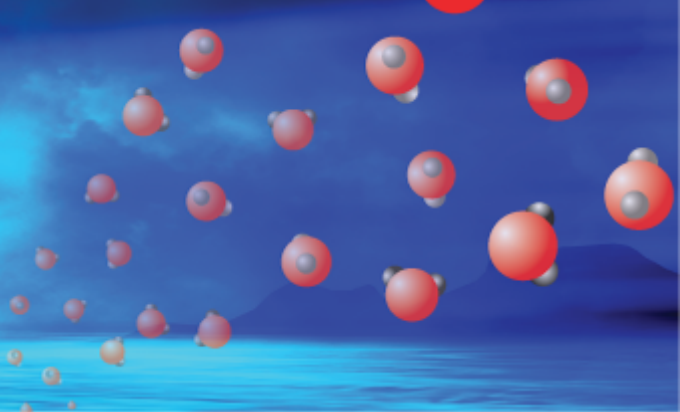


# Infrared (IR) Radiation

- Infrared radiation is longer wavelength and lower energy than visible light.
- There is a range of energies within the IR region of the radiant energy spectrum.



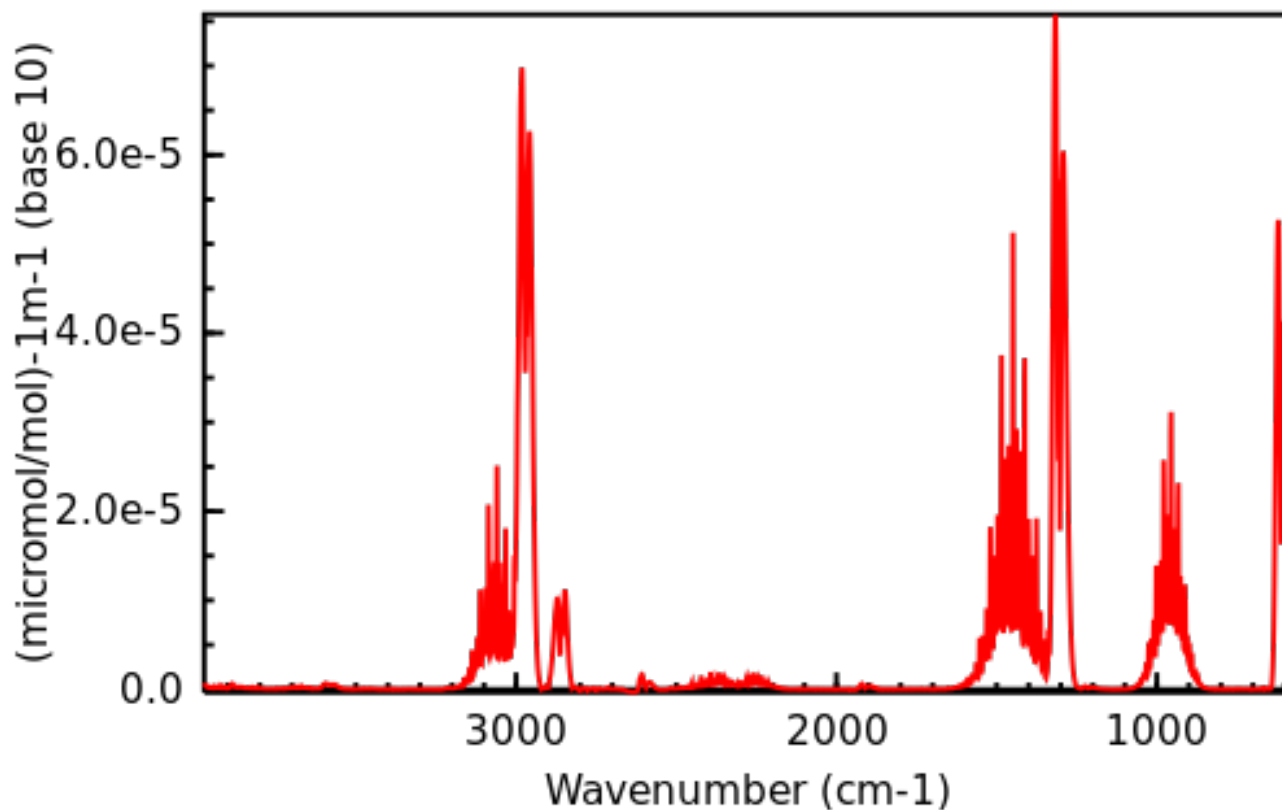
# Infrared (IR) Radiation and Vibrations and Rotations



- Each molecule has a unique set of most stable (ground state) and less stable (excited state) vibrational and rotational energies.
- The molecules can be excited from a ground state to an excited state by infrared radiation.
- Because each substance has a unique set of differences in energy between ground and excited states, each substance absorbs a unique set of IR wavelengths and energies, which can be used to identify substances.

# IR Spectrum

Bromomethane  
INFRARED SPECTRUM



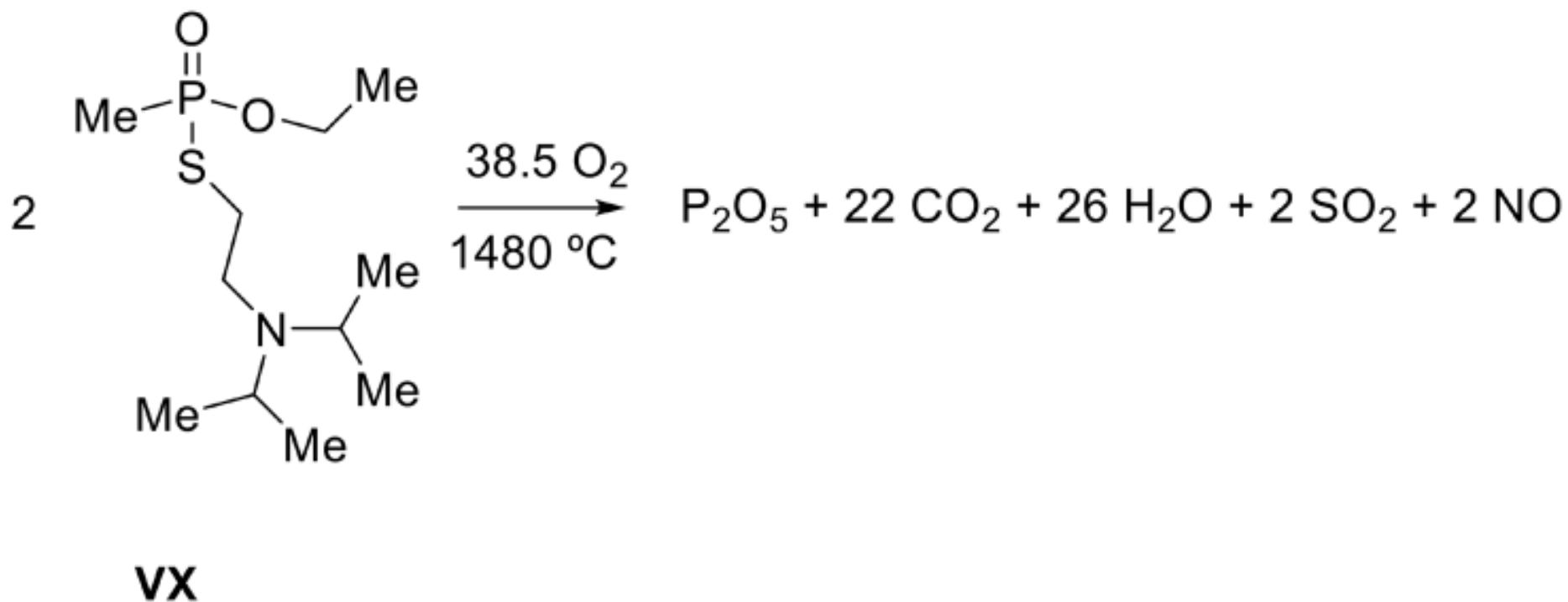
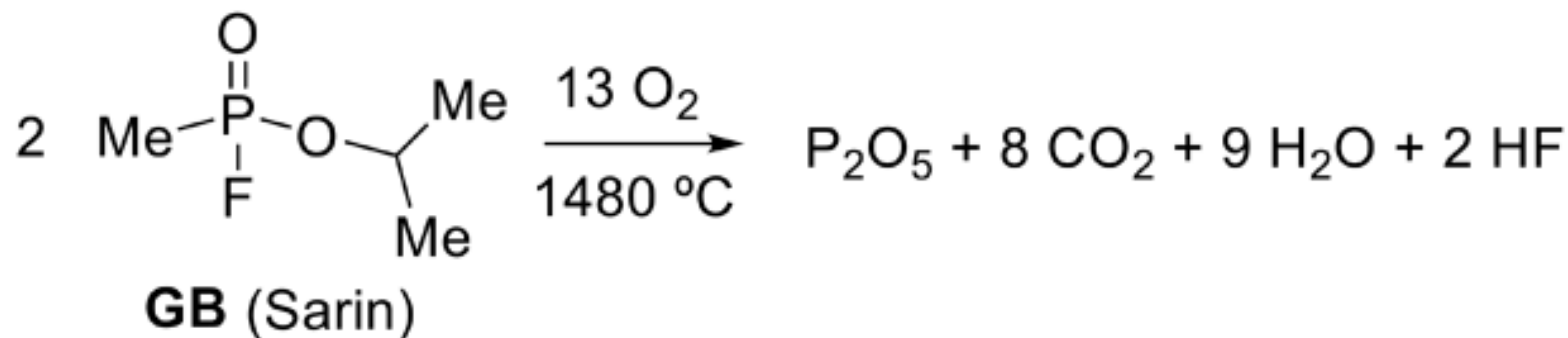
NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

# Three Ways of Disposing of Chemical Weapons



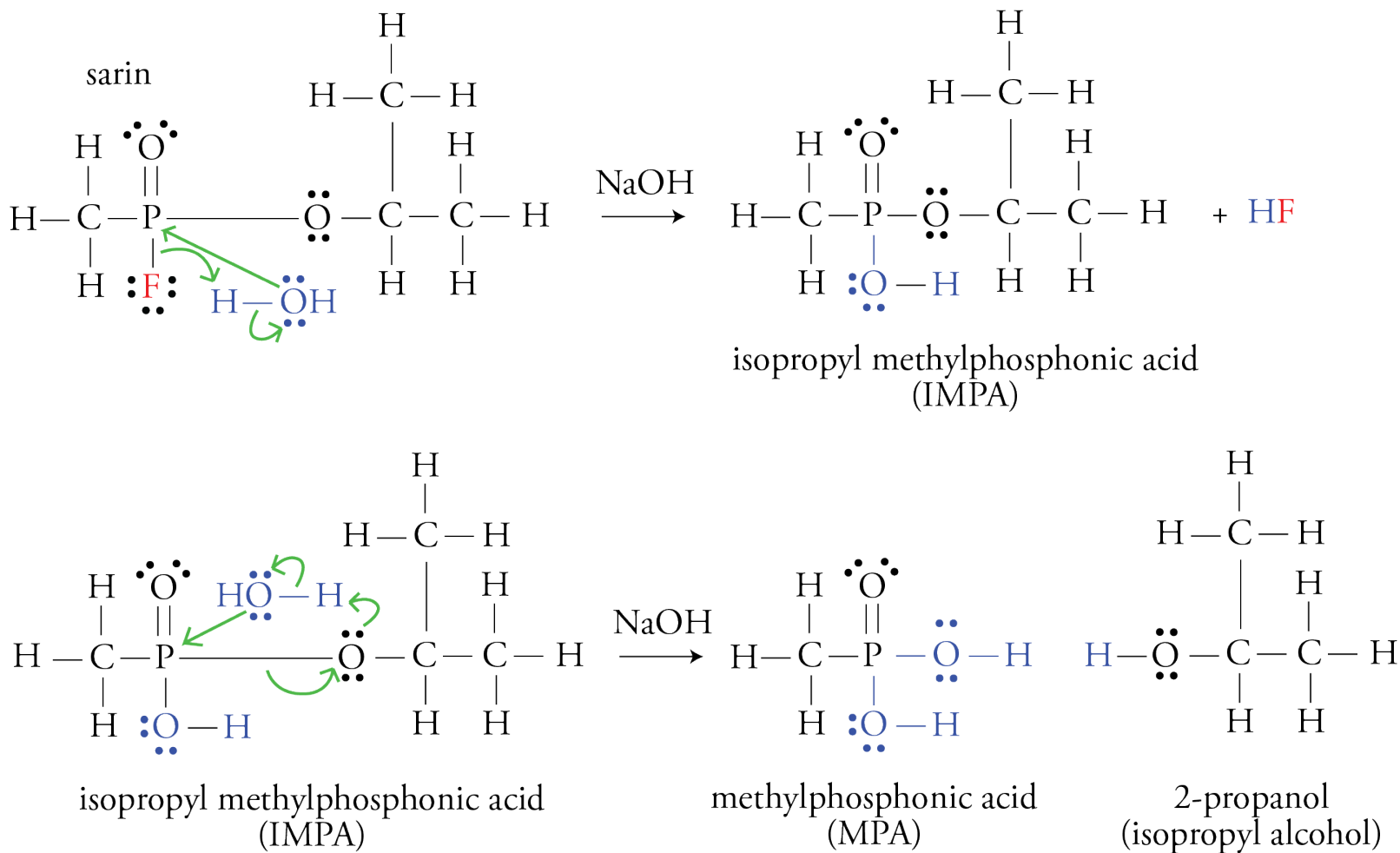
- Ocean dumping (no longer done)
- Incineration
- Chemical neutralization followed by various further treatments (now favored)

# Incineration of Sarin and VX



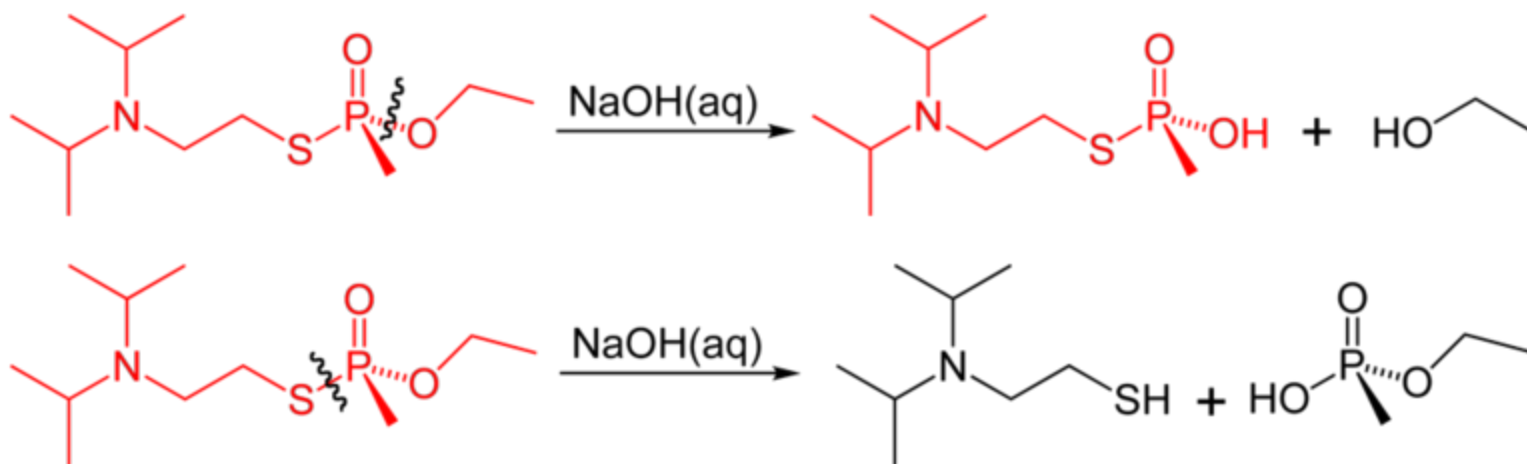
# Hydrolysis of Sarin

Each arrow represents the movement of a pair of electrons as covalent bonds are broken and made.



# Chemical Neutralization of VX

- VX can be converted into safer substances by combining it with a concentrated solution of sodium hydroxide, NaOH.
- The reaction is called hydrolysis, in which water,  $H_2O$ , divides into H, which combines with one part of a molecule, and OH, which combines with another part of the molecule, splitting the molecule into two parts.



# U.S. Army's Chemical Materials Agency (CMA)

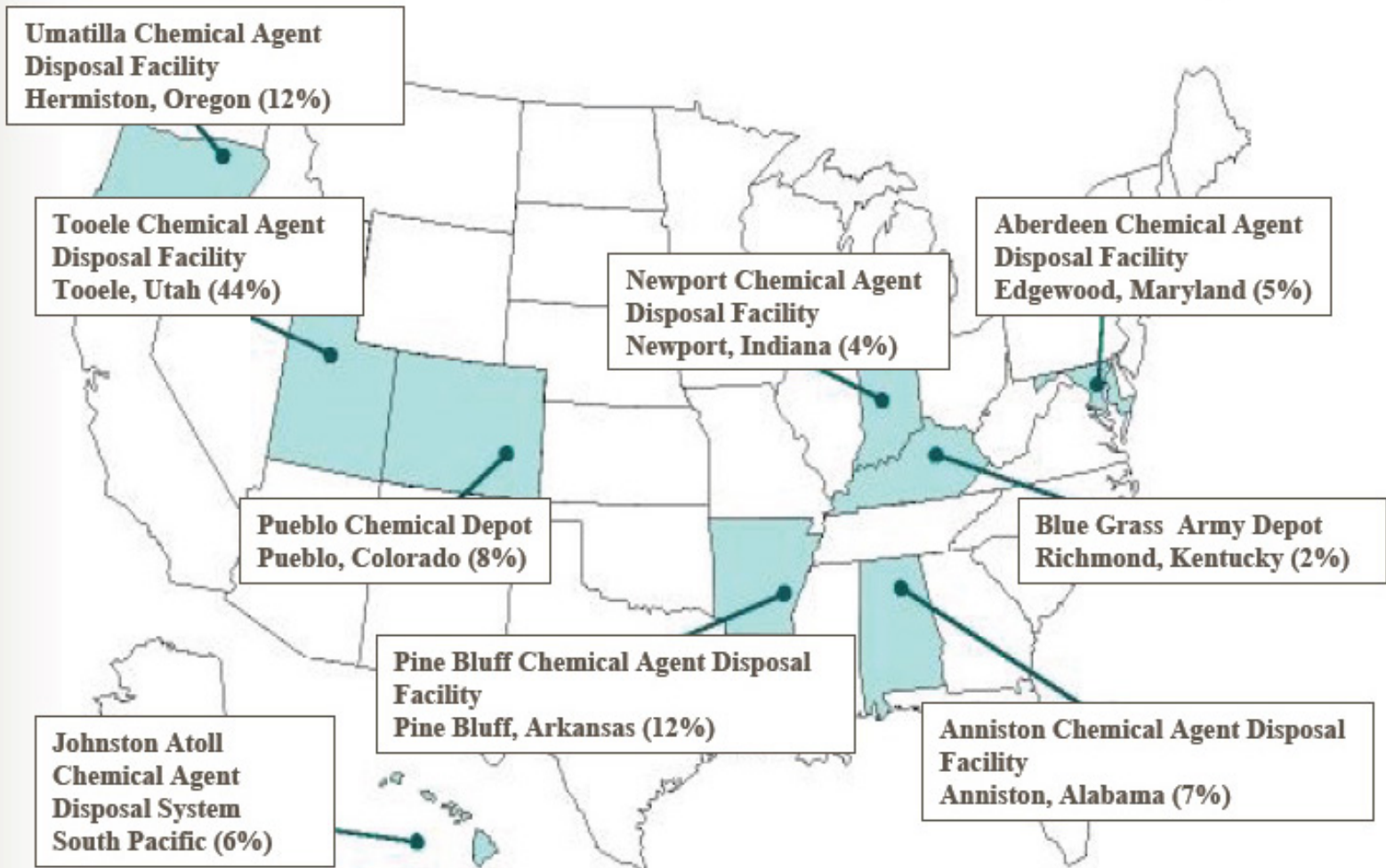
- The CMA stores and destroys the U.S. chemical weapons.

<http://www.cma.army.mil/>

A student fully encapsulated in a protective suit at the Chemical Demilitarization Training Facility at Aberdeen Proving Ground, Md., rolls a simulated waste barrel in the Demilitarization Equipment Room.



# United States CW Disposal Facilities

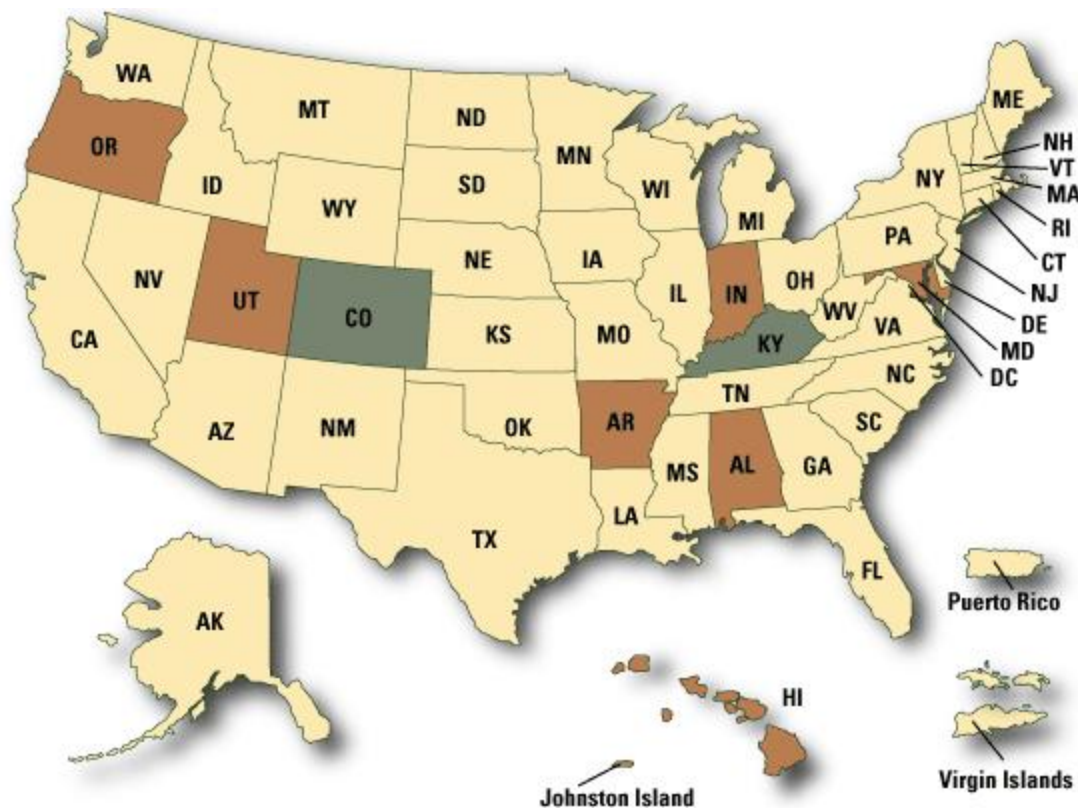


# Status of CW Disposal Facilities

## Green - States and Regions with Chemical Weapons Stockpiles

**Yellow** - States and Regions without Chemical Weapons Stockpiles

## Brown - States and Regions that had Chemical Weapons Stockpiles



<http://www.cma.army.mil/map.aspx>

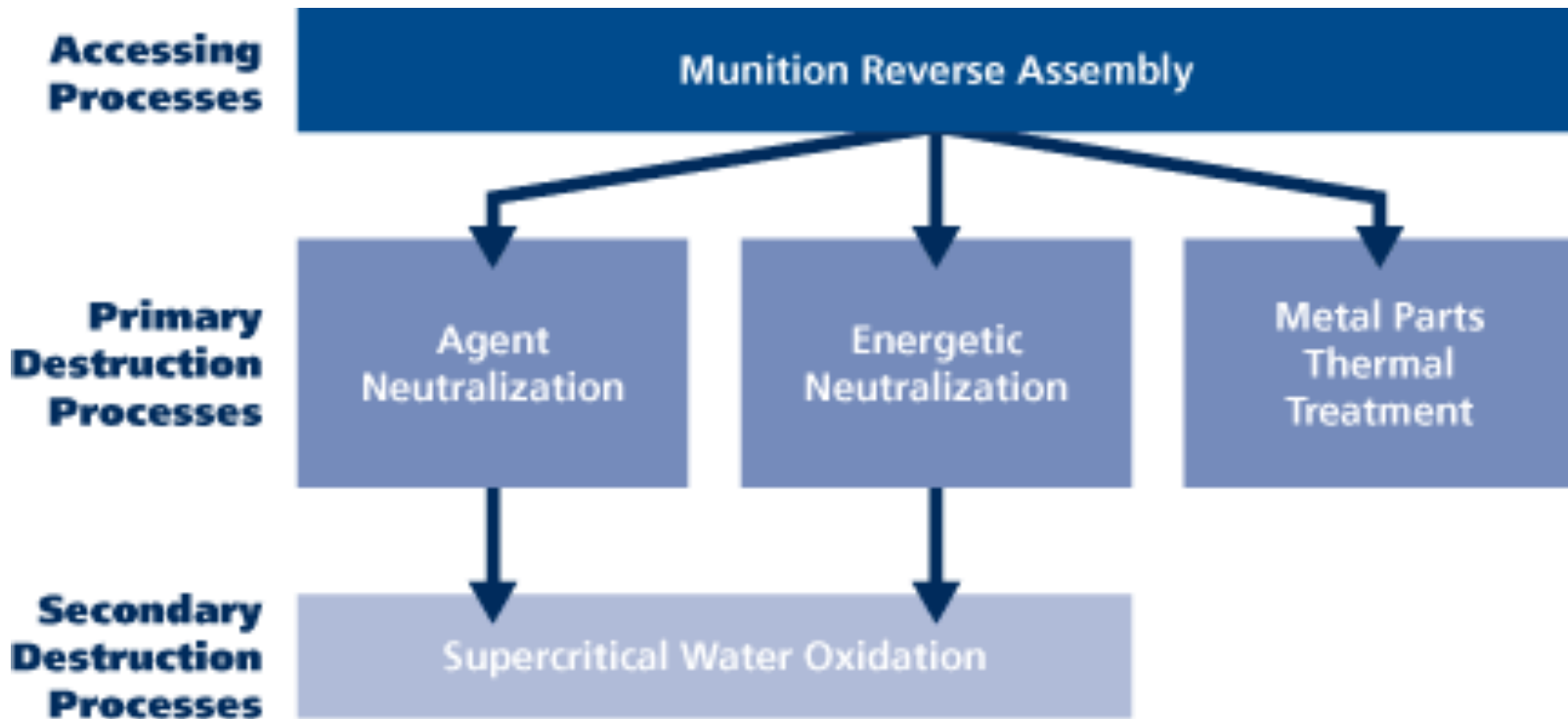
# United States Remaining Chemical Weapons

- Blue Grass Army Depot - Richmond, Kentucky
  - Chemical weapons will be destroyed by chemical neutralization followed by supercritical water oxidation.
  - Has sarin, VX, and mustard agent in projectiles, warheads, and rockets.

<http://www.cma.army.mil/bluegrass.aspx>



# Supercritical Water Oxidation (SCWO)



# Supercritical Water Oxidation (SCWO)

- The chemical agent and energetics are separated.
- Hydrolysis of chemical agent and energetics
- The hydrolysis products are separately fed to the supercritical water oxidation units to destroy the organic materials.
  - SCWO subjects the hydrolysis products to very high temperatures and pressures, breaking them down into carbon dioxide, water and salts.
- Metal parts are thermally decontaminated by high-pressure water washout and heating to 1,000 degrees Fahrenheit for a minimum of 15 minutes.
- Gases are filtered through a series of filters before being released to the atmosphere.
- Water is recycled into the pilot plant facility and reused as part of the destruction process.

<http://www.peoacwa.army.mil/bgcapp/bgcapp-destruction-technology/>

# United States Remaining Chemical Weapons

- Pueblo, Colorado
  - Will destroy 2,371 metric tons of mustard agent stored in different types of projectiles and mortars by neutralization.
  - Started March 2015

<http://www.cma.army.mil/pueblo.aspx>



# Steps for Neutralization Followed by Biotreatment

- Robatically removing the energetics, including the fuse and burster
- Robatically removing the mustard agent
- Hydrolysis of mustard agent
- Biotreatment of remaining organics (mostly thiodiglycol) with microbes (ordinary sewage treatment bacteria)
- Disposal of metal parts after heating to high temperature to complete the decontamination

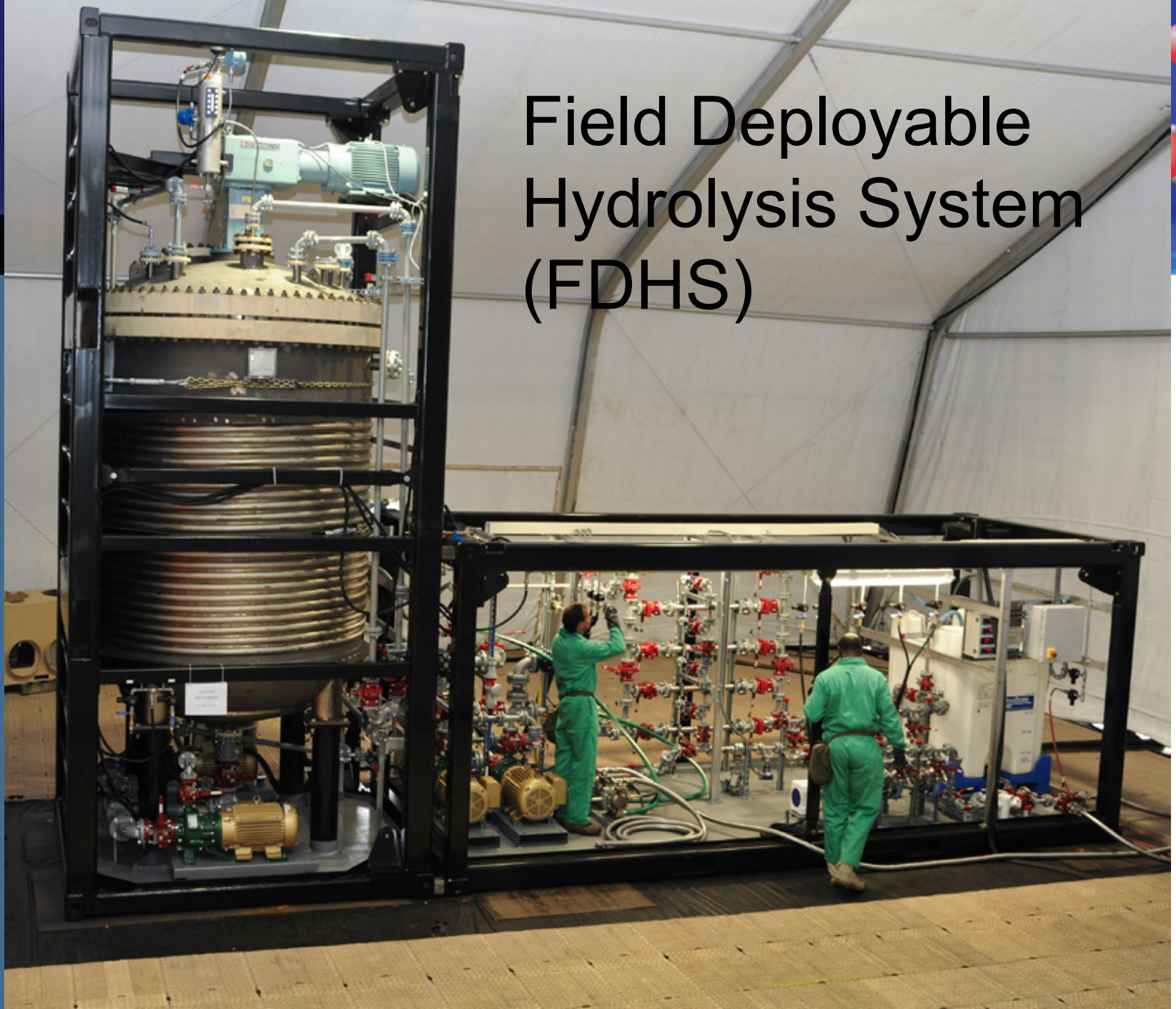
<http://www.peoacwa.army.mil/media-toolkit/facts-pages/facts-page-neutralization-followed-by-biotreatment/>

# Field Deployable Hydrolysis System (FDHS)



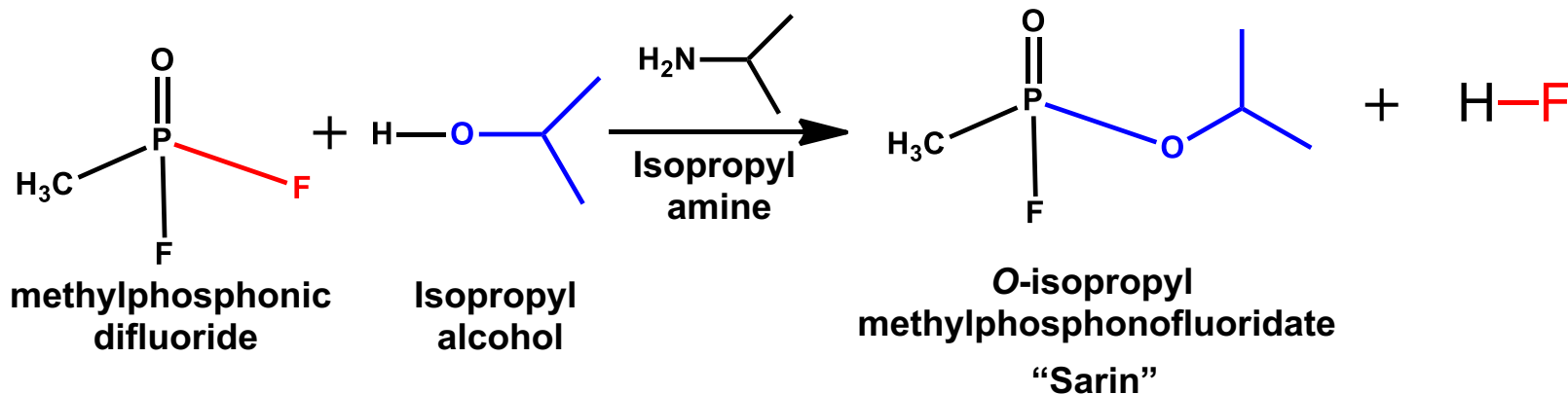
- *Transportable, high-throughput modular demilitarization system designed to render chemical warfare materiel into compounds not usable as weapons.*
- *The system uses neutralization technology to destroy bulk chemical warfare agents and their precursors by heating and mixing with reagents, such as water, sodium hydroxide and sodium hypochlorite to facilitate chemical degradation resulting in a destruction efficiency of 99.9 percent.*

# Field Deployable Hydrolysis System (FDHS)



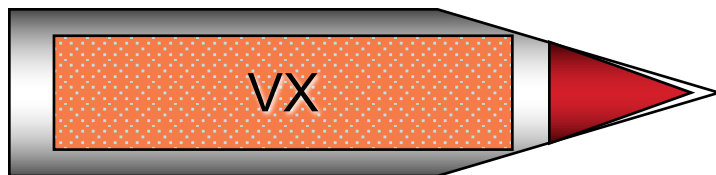
# Binary Chemical Weapons

- In order to minimize the dangers associated with the handling and storage of a nerve agent, the last step in its production can take place after a projectile is launched.



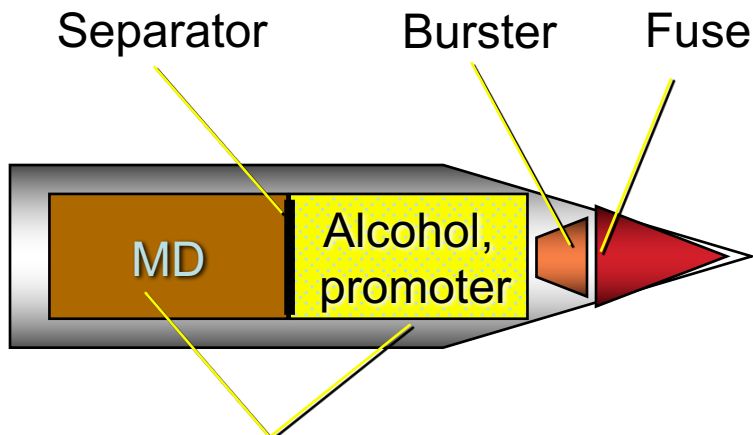
# Common CW Munition Types

## Unitary Munitions



- Easier to produce
- More dangerous to store, handle & transport

## Binary Munitions (sarin)



Two non-lethal compounds

- Firing, spin flight & detonation mix compounds to form agent
- Relatively safer to handle & store
- Munition challenging to manufacture
- Methylphosphonyl difluoride + 72% isopropanol and 28% isopropylamine

# Binary Munitions



- Reactants mixed immediately before firing or mixed in flight
- U.S. - three binary munitions
  - A 155 mm artillery shell to deliver sarin (liquid isopropyl alcohol and liquid methylphosphonic difluoride, DF)
  - BIGEYE spray bomb to deliver VX (solid sulfur and liquid precursor QL)
  - Warhead for Multiple Launch Rocket System (MLRS)