Science and Technology

Chemical Weapons Part 1

By

Mark Bishop

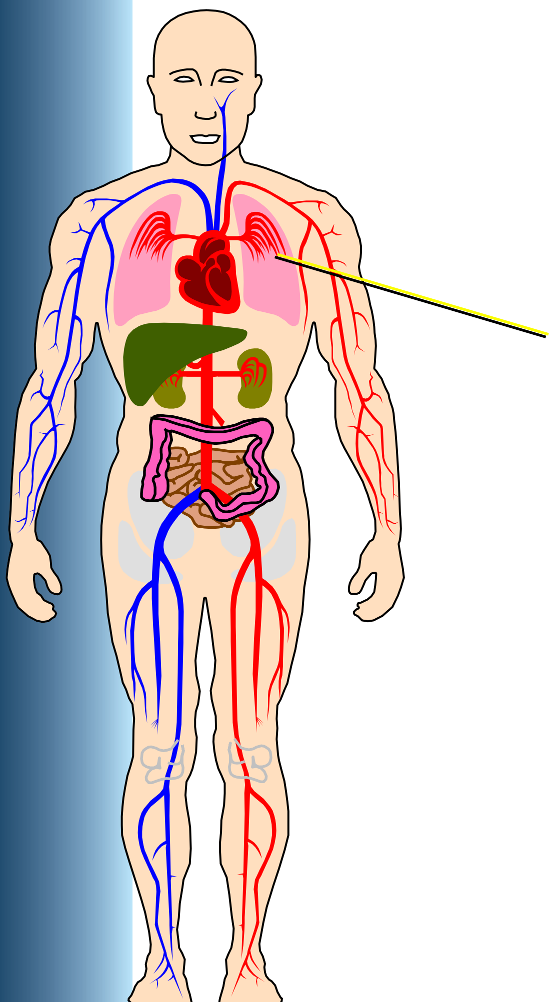
Types of Chemical Weapons

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

For terrorists or governments?

- **Terrorist criteria**
  - Either relatively simple to make or obtain in some other way.
  - Relatively simple to disperse
  - Can be lethal or incapacitating
  - Relatively low cost
- **Government with well-developed chemical industry (e.g. North Korea or Syria)**
  - 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

Chlorine as a Chemical Weapon

- Reacts with water to form hydrochloric acid and hypochlorous acid, which damage tissues in the lungs and draw water into the lungs.

$$Cl_2 + H_2O \rightarrow HCl + HClO$$

Chlorine Lethality

- Death can come from asphyxia due to at least three possible mechanisms
  - Water in lungs displaces air ("*dry land drowning*").
  - Chlorine is more than twice as dense as air, so it displaces the air in the lungs.
  - Oxidative injury to the airways and lungs.
- Cardiac toxicity can lead to cardiac dysfunction.

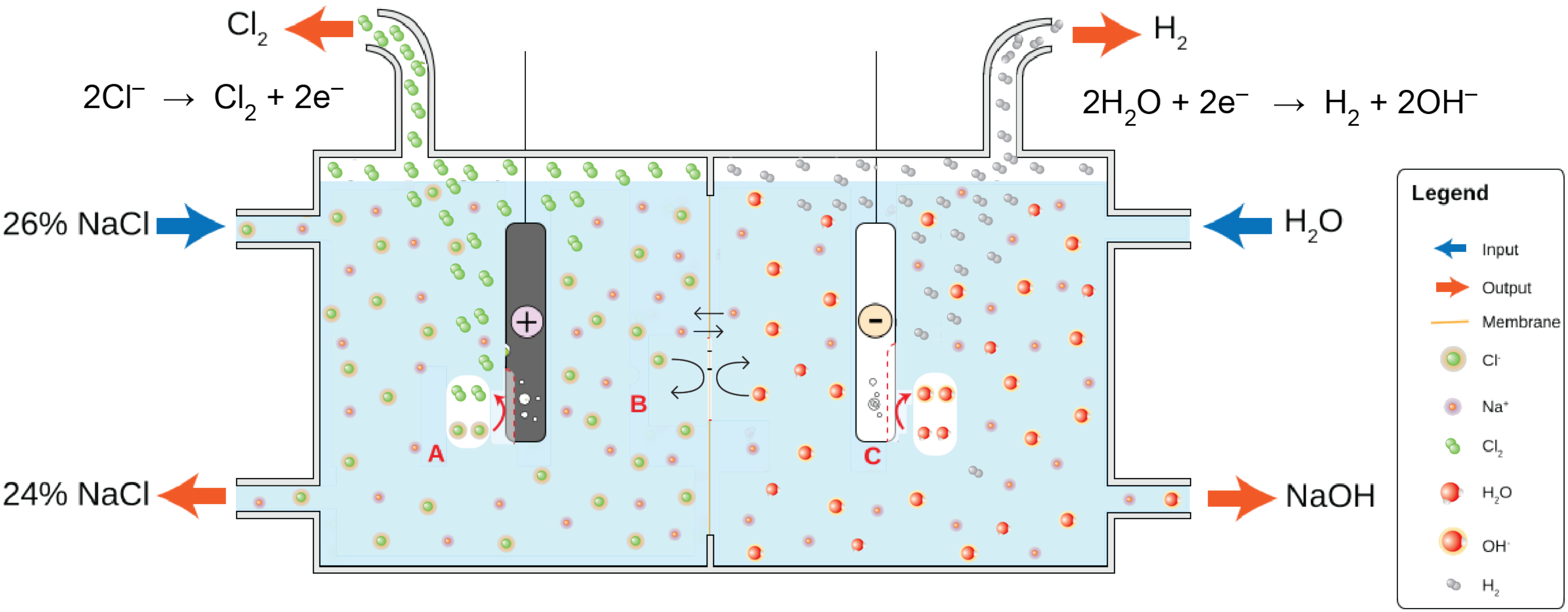
Ways to Obtain Chlorine, Cl_2

- 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.

$$2NaCl(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2NaOH(aq)$$



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 produces 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_2, as a CW

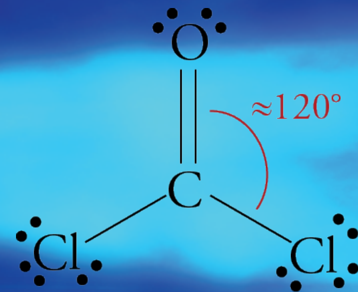
- Stationary device, e.g. pressurized gas tanks
- Car or truck bombs
- Drop containers from planes or helicopters that will burst on impact (barrel bombs)
- Roadside bombs
- Projectiles

A 120-millimeter mortar shell struck fortifications at a Kurdish military position near the Mosul Dam in June, 2015, 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

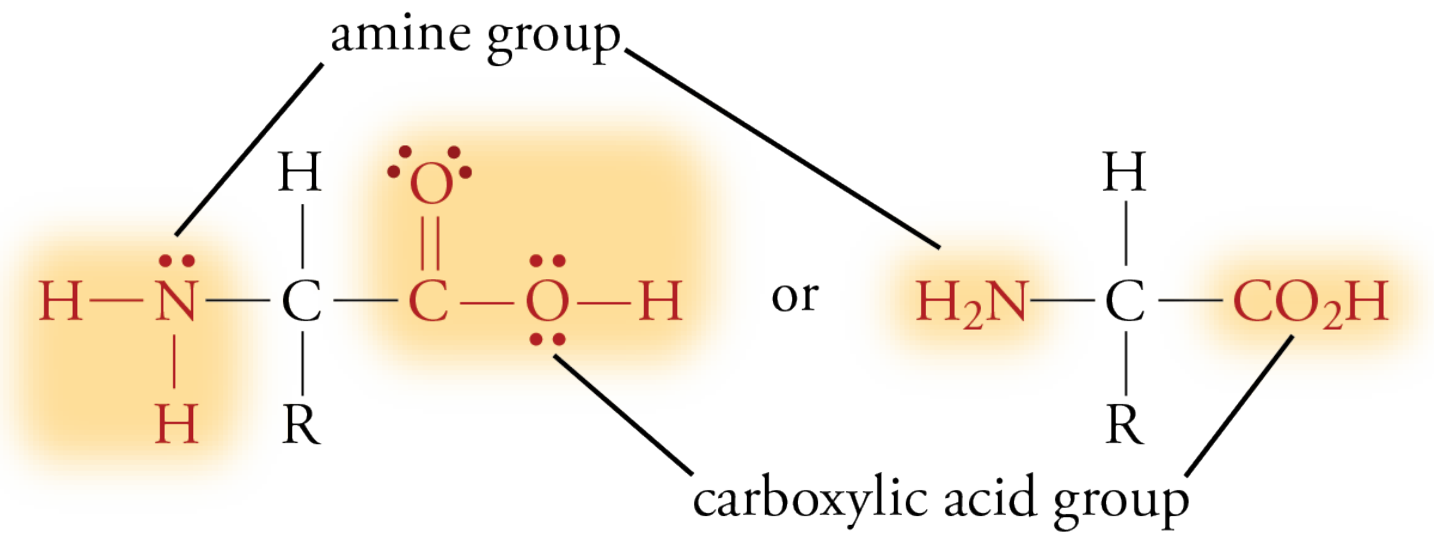
Phosgene, $COCl_2$



- Less irritating than Cl_2, so soldiers were slower to put on their gas masks
- Smells like new-mown hay
- 18 times more toxic than Cl_2
- It causes suffocation by reacting with proteins and disrupting the transfer of oxygen to the body.
- 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 catalyst. The reactor must be cooled to prevent phosgene from decomposing.

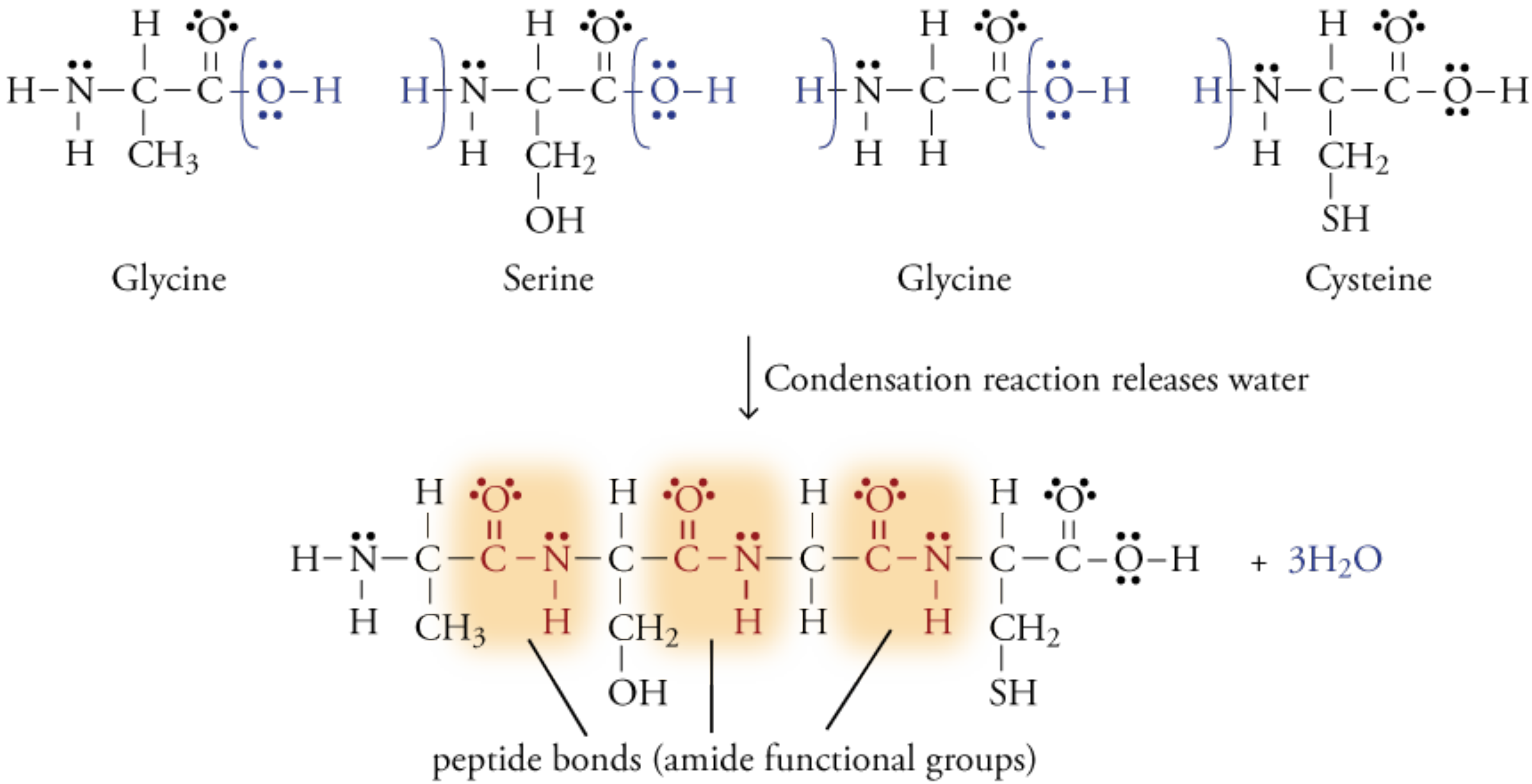
$$CO + Cl_2 \rightarrow COCl_2$$

Amino Acids

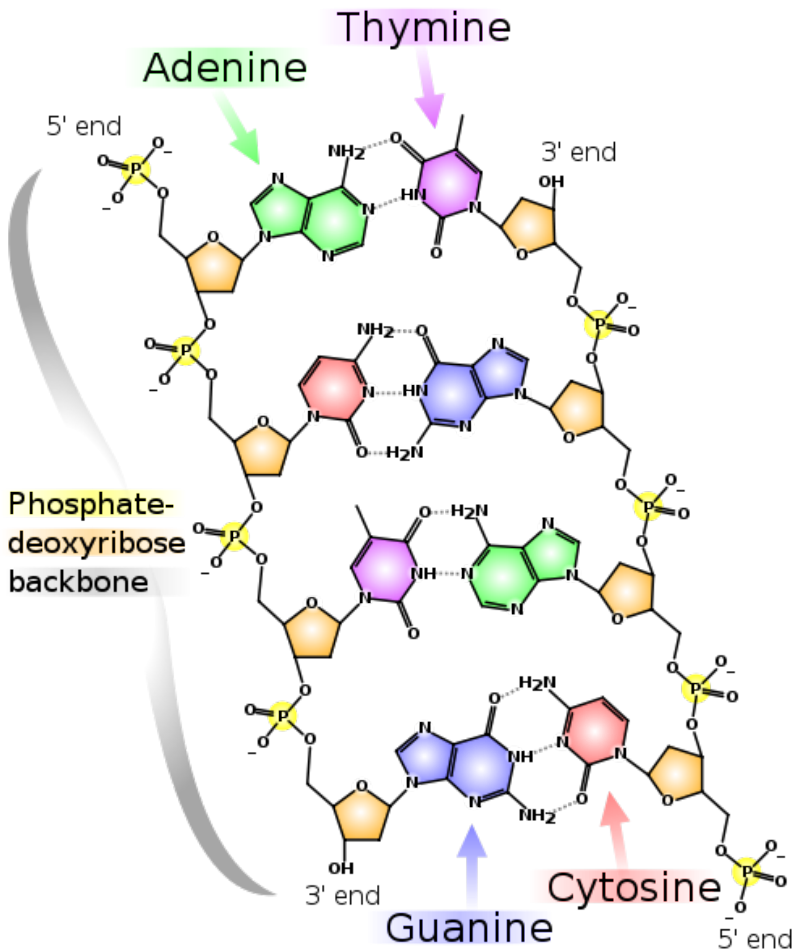


amine group
H
H—N—C—C—O—H
O
H R
or
H
H_2N—C—CO_2H
R
carboxylic acid group

Formation of Ala-Ser-Gly-Cys

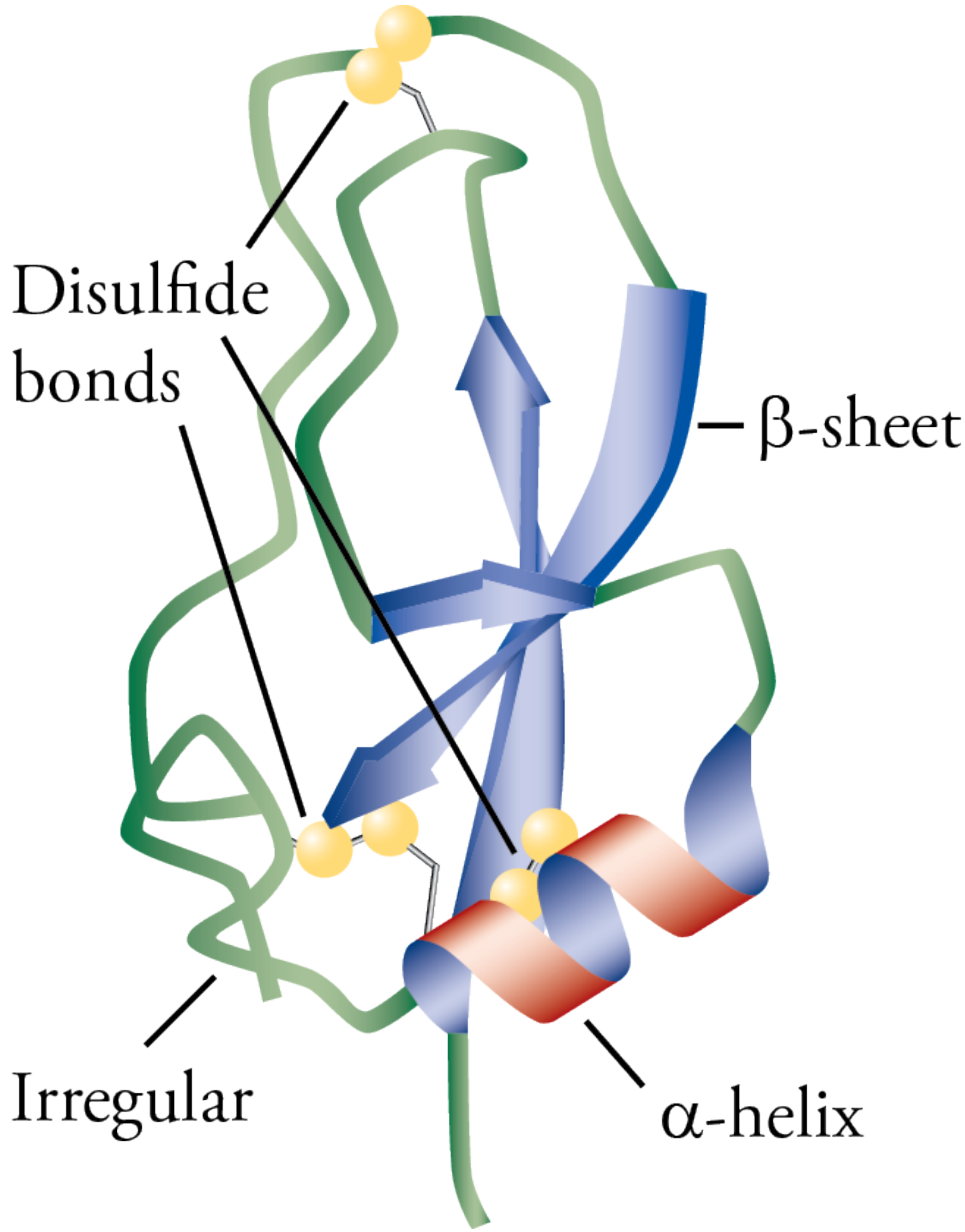


DNA Segment



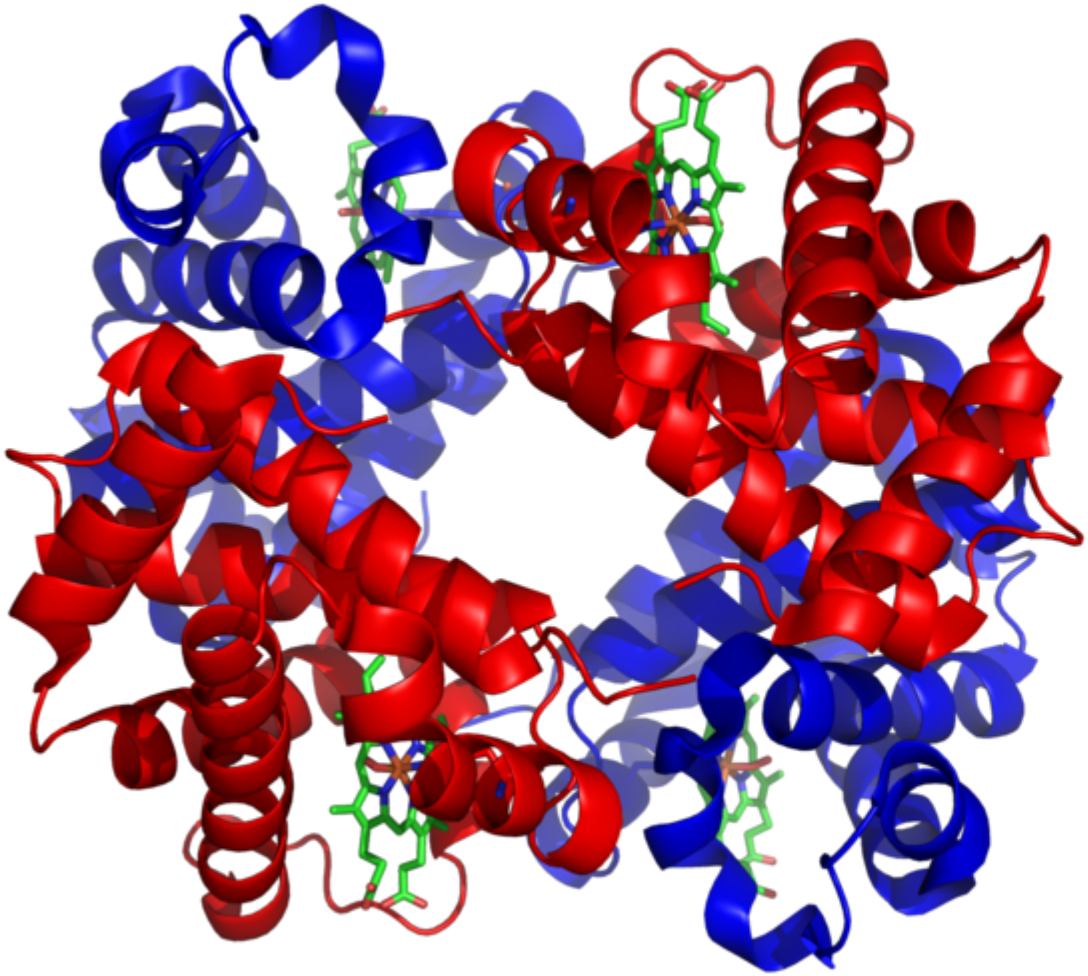
Thymine
Adenine
5' end
3' end
OH
Phosphate-
deoxyribose
backbone
3' end
Guanine
Cytosine
5' end

The Ribbon Structure of the Protein BPTI



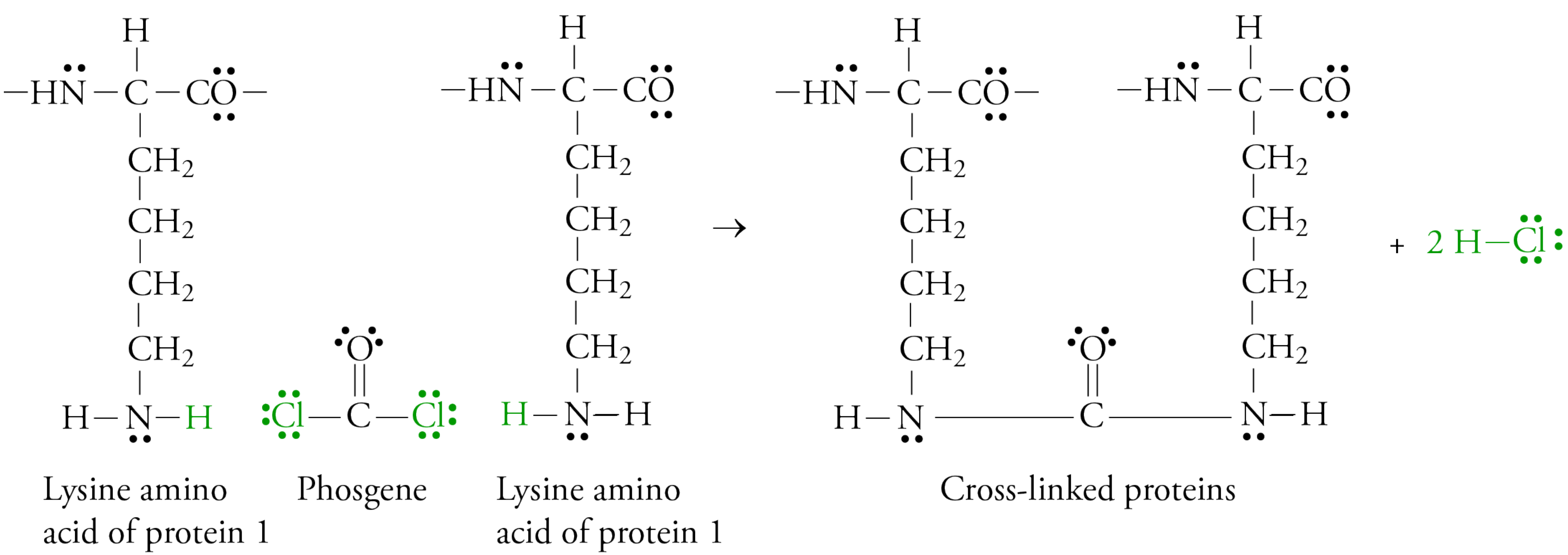
Hemoglobin

- The protein hemoglobin carries oxygen in the blood.



Phosgene Reactions with Protein

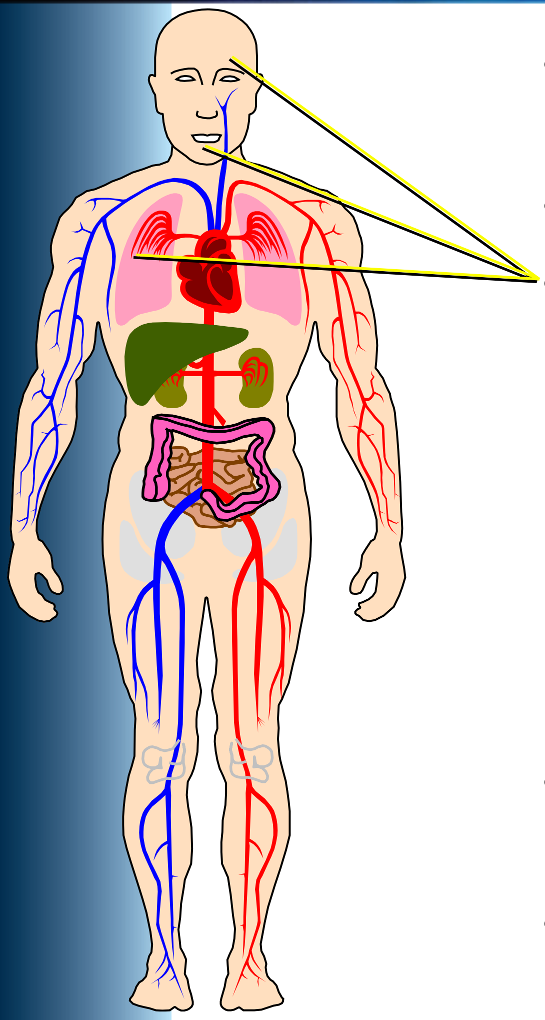
- Phosgene reacts with amino acids in proteins by acylation, adding an acyl group (a group with a CO double bond).
- It also reacts with the amines of the proteins, linking protein together.
- The altered proteins no longer function in their normal way.



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.

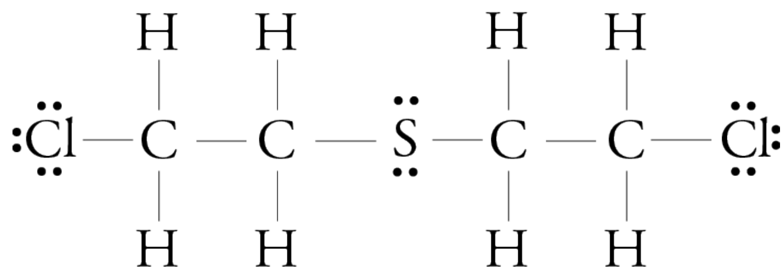
Blister Agents (Vesicants)

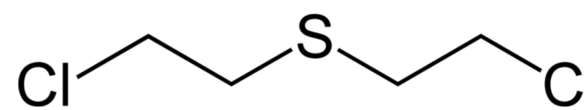


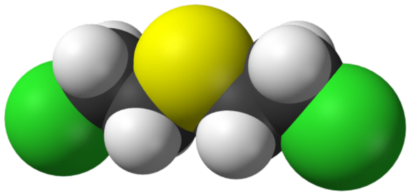
- **Sulfur mustard**, nitrogen mustard, phosgene oxime, Lewisite
- Mode of action: inhalation, skin contact
- Physiological effects
  - Burns skin, mucous membranes, and eyes, causing large water blisters on exposed skin
  - Causes damage to upper airways
  - Primarily used to cause medical casualties,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

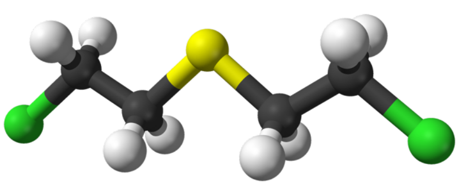
Sulfur Mustard, H or HD

- 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.



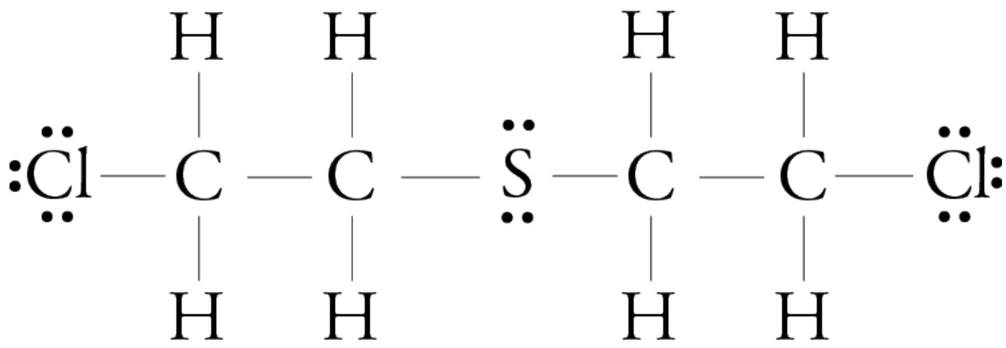






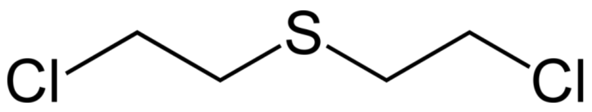
Ways to Describe Organic Compounds

- Lewis structures



- Condensed Formulas, $ClCH_2CH_2SCH_2CH_2Cl$

- Line Drawings



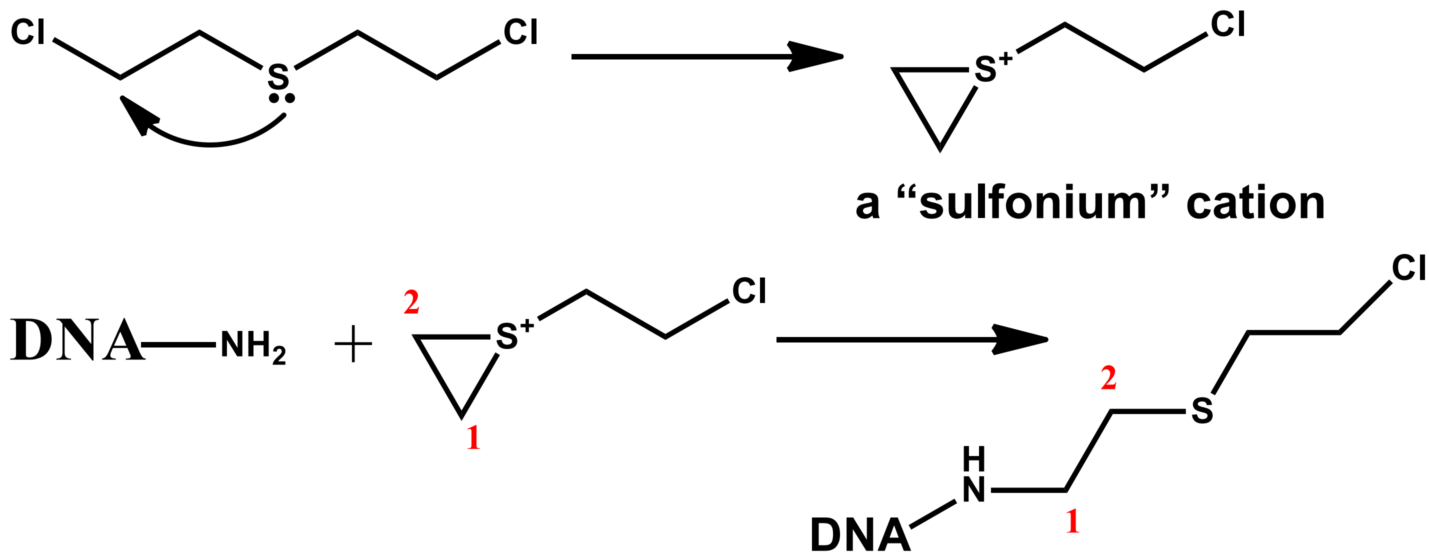
Sulfur Mustard (cont.)

- "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.

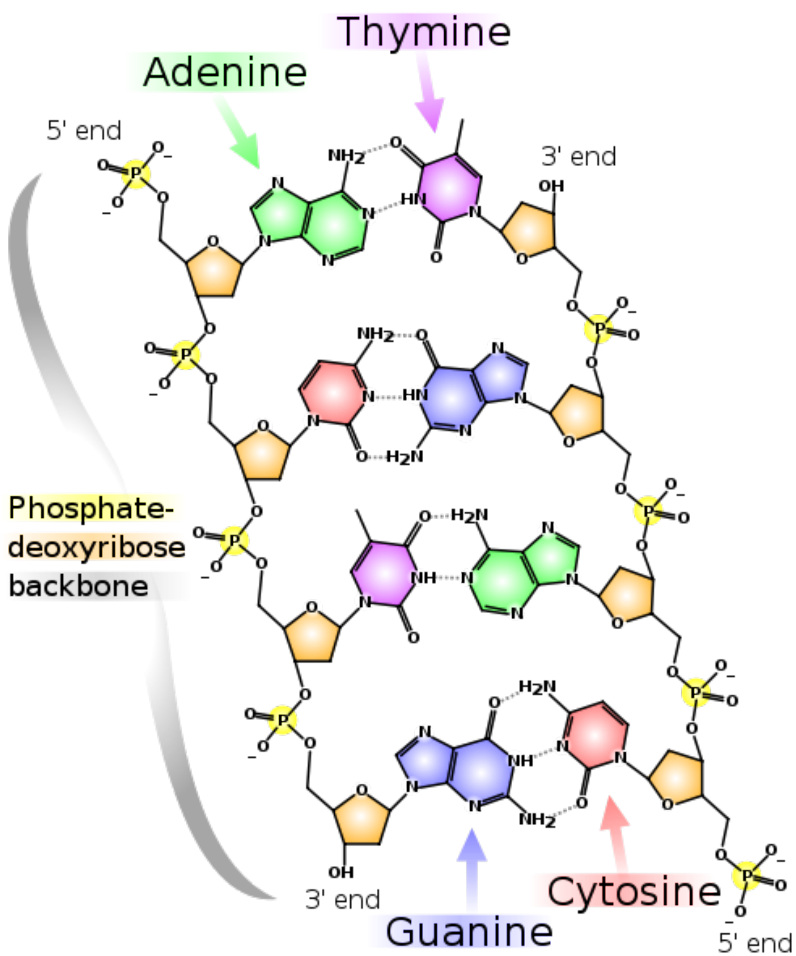
155 mm artillery shells that contained "HD" (distilled sulfur mustard agent) at Pueblo chemical weapons storage facility

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



Thymine
Adenine
5' end
3' end
OH
Phosphate-
deoxyribose
backbone
3' end
Guanine
Cytosine
5' end

Sulfur Mustard Treatment

- Can limit the formation of blisters by applying household bleach or a solution called DS2 (2% sodium hydroxide, NaOH, 70% diethylamine, $CH_3CH_2NHCH_2CH_3$, and 28% ethylene glycol monomethyl ether, $CH_3OCH_2CH_2OH$)
- Early rinsing of the exposed area with Betadine (providone-iodine) dissolved in glycofurol will reduce symptoms.
- 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 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.

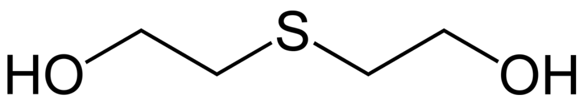
Factors Affecting the Ability to Make CW

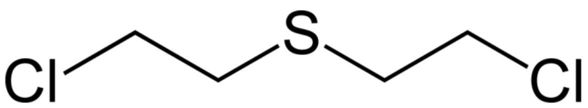
- Scientific and industrial expertise
- Availability of precursors
- Availability of equipment
- Money available
- Desired quantity
- Desired purity
  - For a variety of reasons, products of chemical reactions are rarely pure, so after the initial reactions, steps are taken to purify the product.
- Concern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

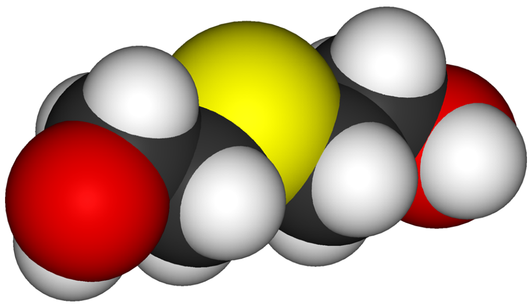
Production of Sulfur Mustard

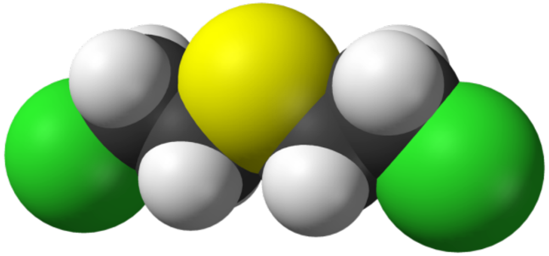
- Thiodiglycol and concentrated hydrochloric acid react to form sulfur mustard.

$$(HOCH_2CH_2)_2S + 2HCl \rightarrow (Cl\text{-}CH_2CH_2)_2S + 2H_2O$$









Production of 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.

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 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

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 for potential chemical weapons and thiodiglycol for a precursor.

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.

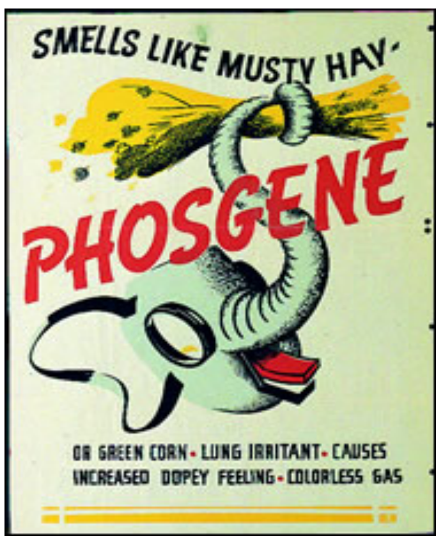
http://www.cwc.gov/index_chemicals_sch3.html

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)

Description of Toxicity

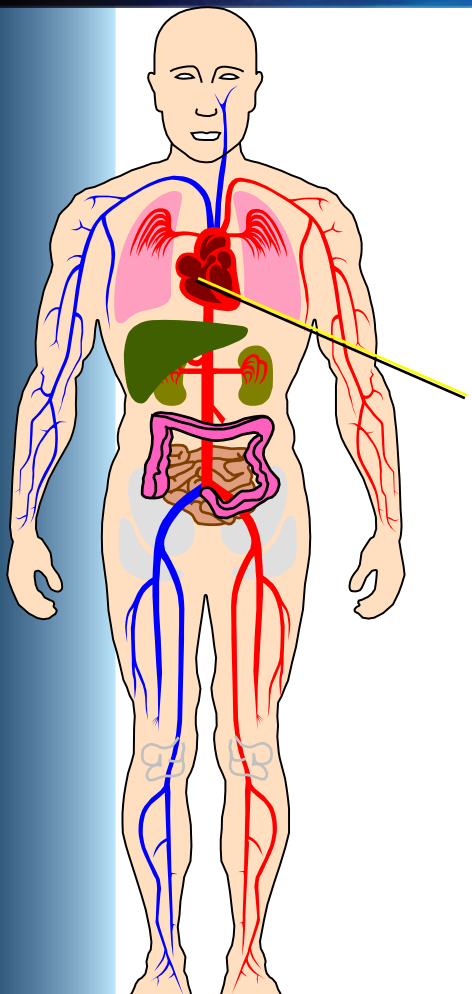
LD_{50} (median lethal dose) = the dose expected to kill 50% of the population exposed; typically in mg/kg of body mass



800 mg/kg (ppm)

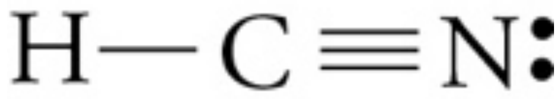
100 mg/kg (ppm)

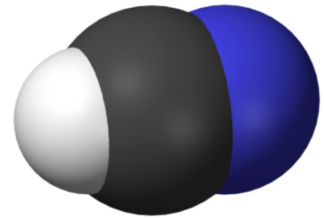
Blood Agents



- **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^3 in air.
- According to OPCW, there are no confirmed uses as CW, but may have been used by U.S., France, and Italy in WWI and by Iraq against Iran and the Kurds.
- Unlike chlorine and phosgene, it’s less dense than air, so it disperses too quickly to be effective outside.
- Schedule 3, Part A of the CWC

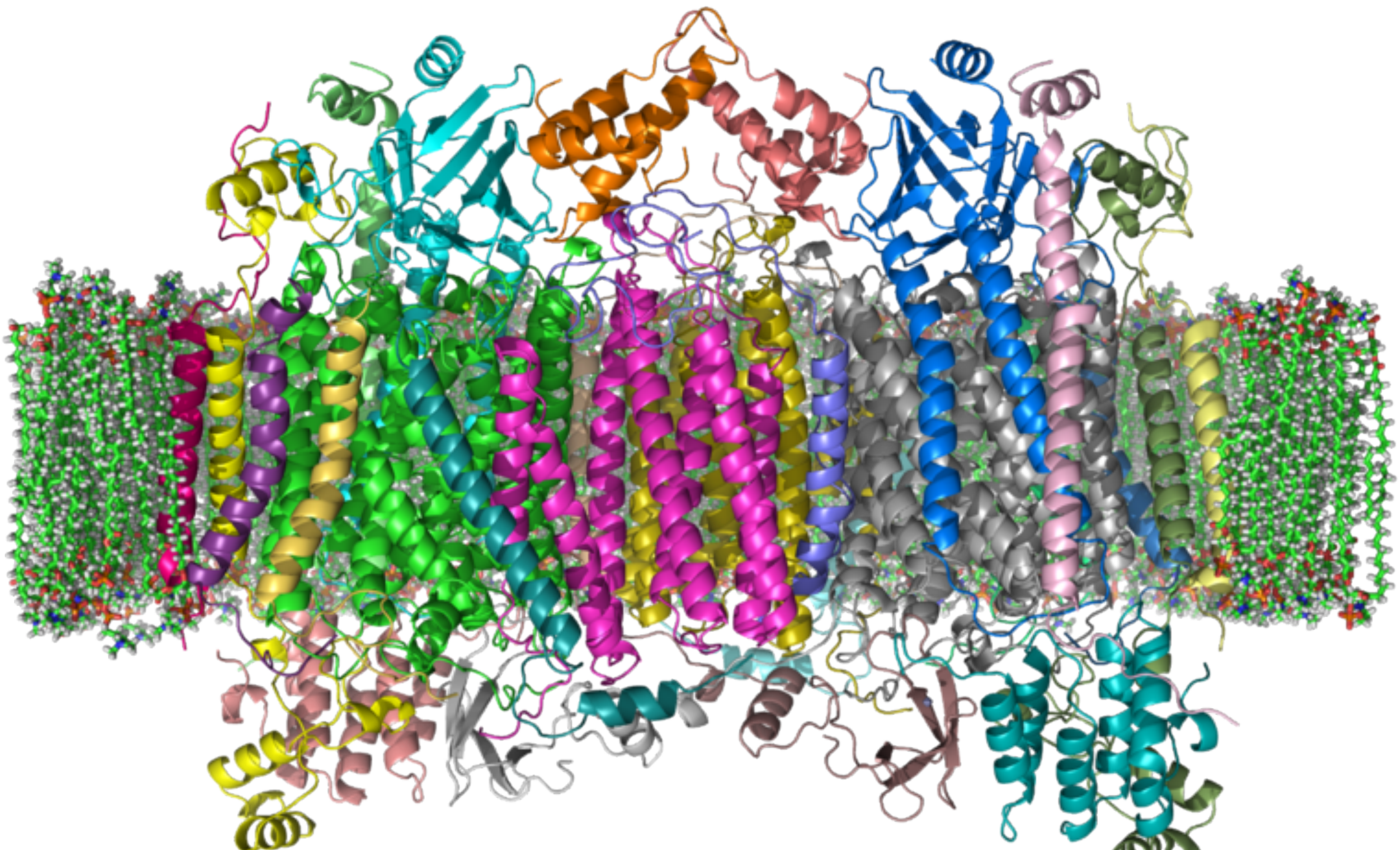
Hydrogen Cyanide, HCN

- 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_2 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.

$$2CH_4 + 2NH_3 + 3O_2 \rightarrow 2HCN + 6H_2O$$

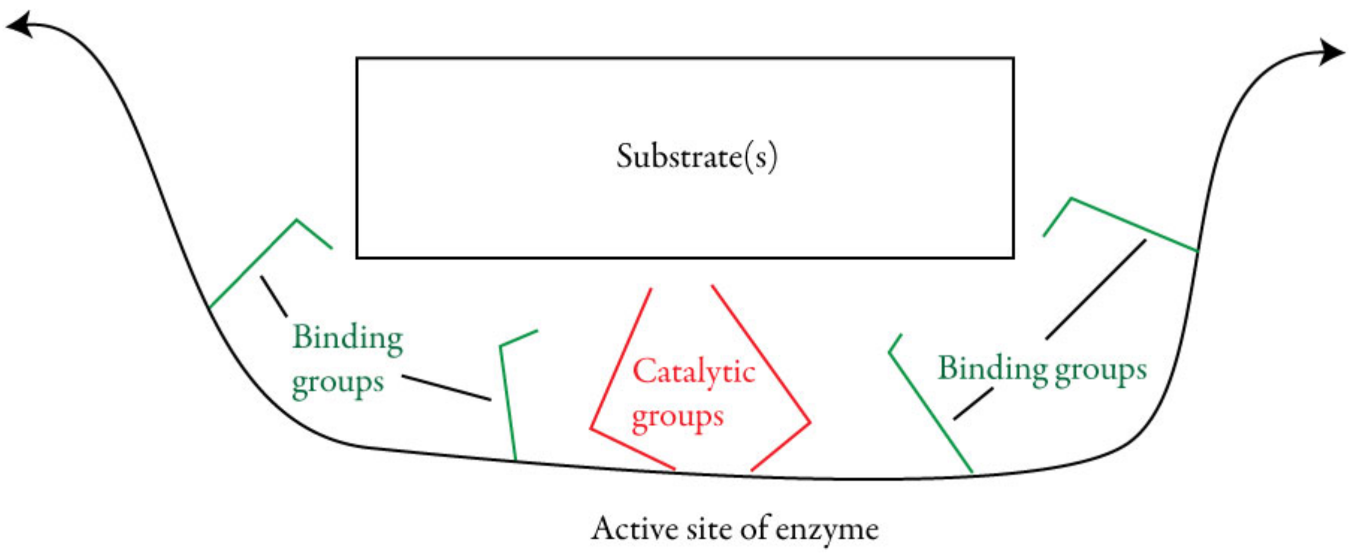
- Converted into sodium cyanide, NaCN, and transported in water solution.

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

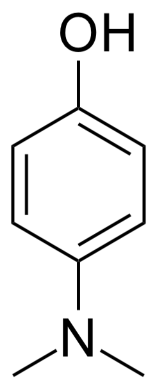
- Very specific due to
  - Substrate shape – “Lock and Key”
  - Positions of binding groups, which attract substrates to the active site.
  - Positions of the catalytic groups that speed the reaction.
- Speed chemical reactions because
  - Provide a different path to products that has more stable intermediates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

One HCN Antidote

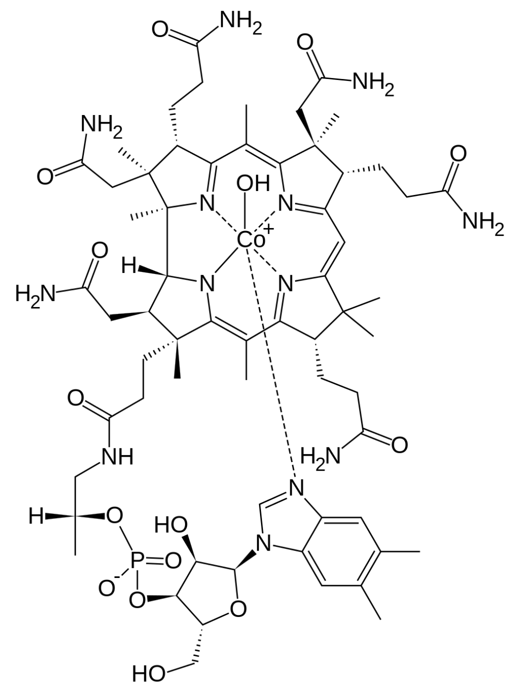
- First - a small inhaled dose of amyl nitrite
  - Nitrites oxidize some of hemoglobin's iron from the Fe^{2+} state to the Fe^{3+} state, converting the hemoglobin into methemoglobin.
  - Cyanide preferentially bonds to methemoglobin rather than the cytochrome oxidase, converting methemoglobin into 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.

Other HCN Antidotes

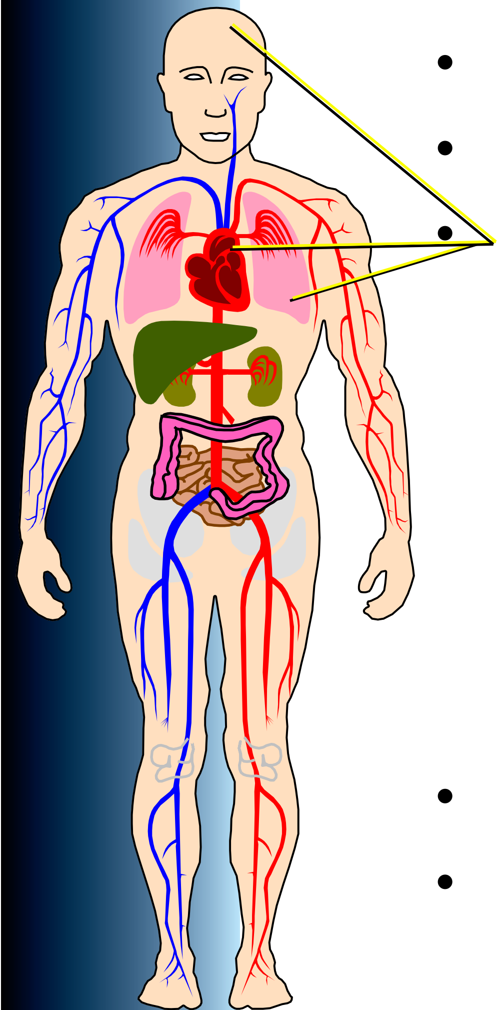
4-dimethylaminophenol



Hydroxocobalamin (vitamin B_{12a}) is newly approved in the US and is available in Cyanokit antidote kits.



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

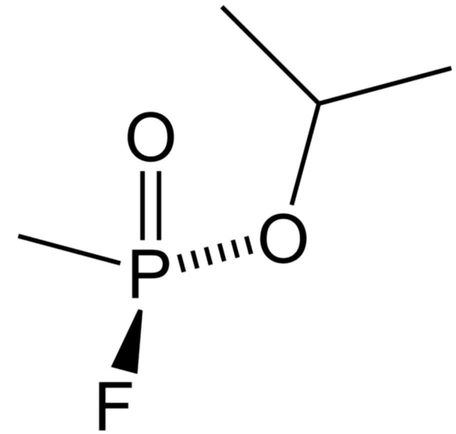
- Cause contraction of pupils, profuse salivation, convulsions, involuntary urination and defecation, and eventual death by asphyxiation as control is lost over respiratory muscles.
- U.S. and the Soviet Union developed and stockpiled large quantities of nerve agents in a chemical arms race that mirrored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

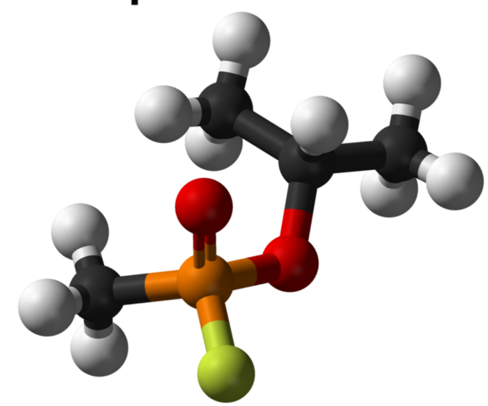
Nerve Agents – Three Series

- 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
- Relatively stable
- Relatively volatile
- Very potent
- Breaks down fairly rapidly in the environment
- Has antidotes
- Adopted as the standard nerve agent for the U.S. in 1948.
- Hard to make



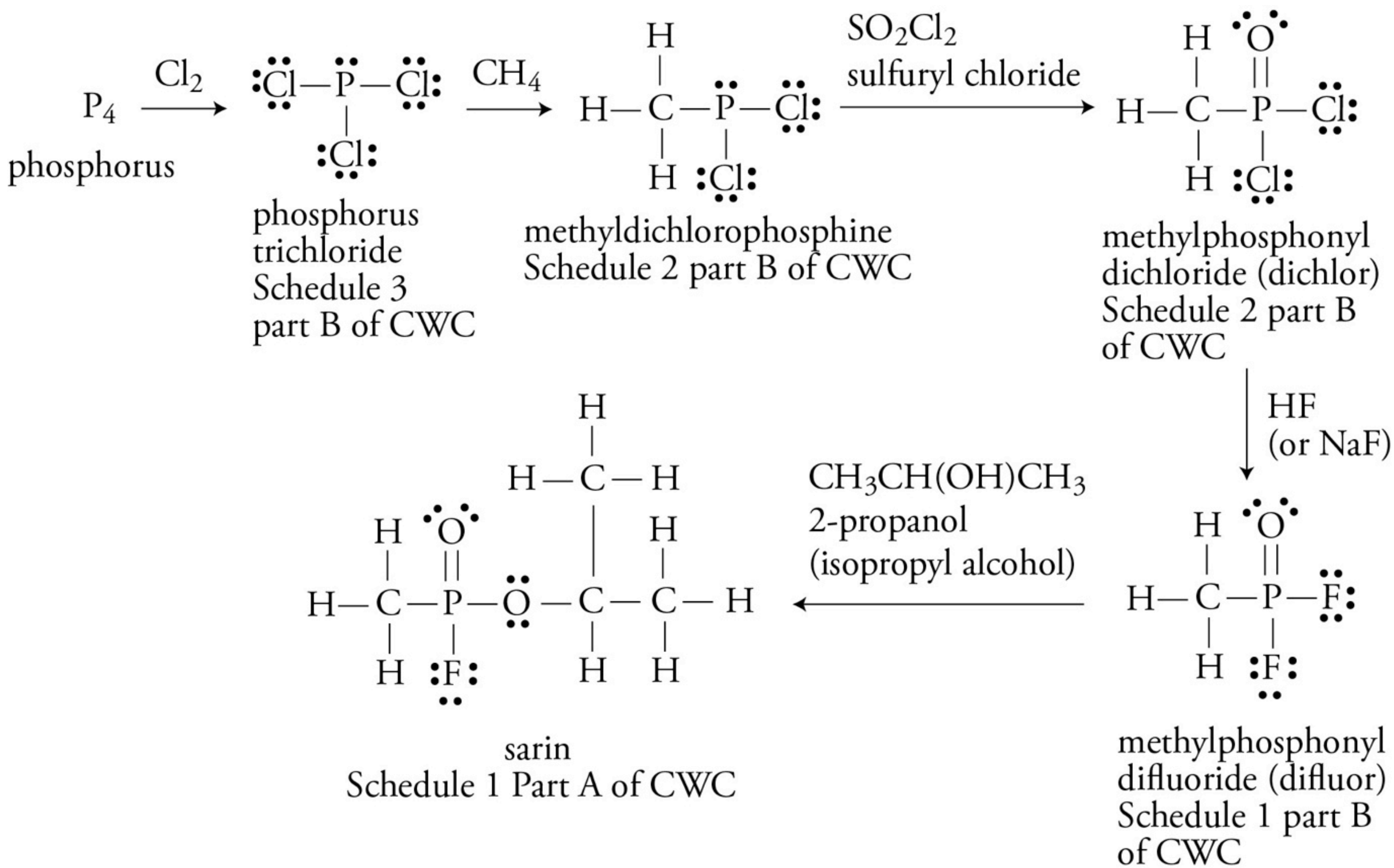


http://chemapps.stolaf.edu/jmol/jmol.php?model=FP%28%3DO%29%28OC%28C%29C%29C

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.
  - 3/20/1995 - Used in the Tokyo Subway attack by Aum Shinrikyo
  - 8/21/2013 – Ghouta, Syria
  - 4/4/2017 – Khan Shaykhun, Syria
  - 4/7/2018 – Douma, Syria

Rough Steps in Production of Sarin



Production of Sarin

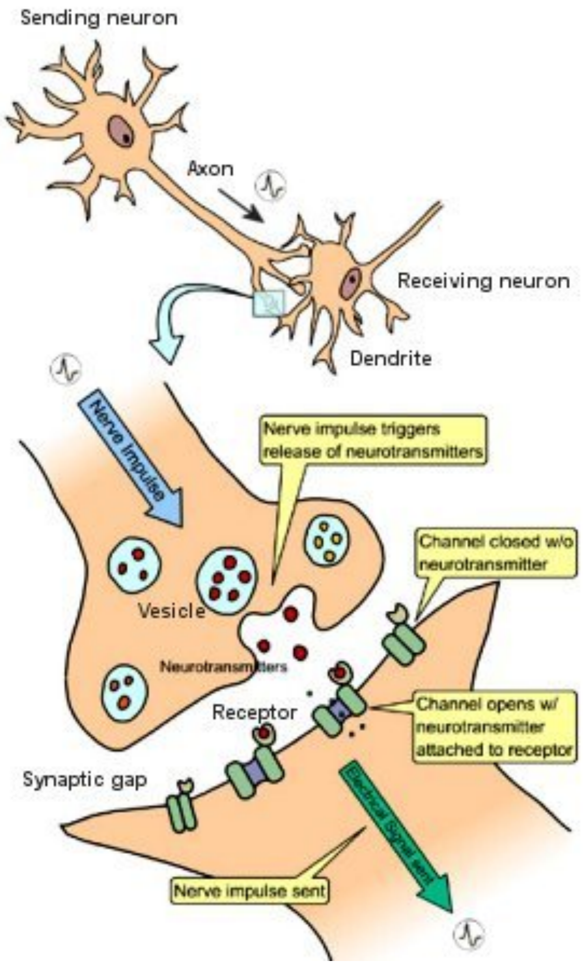
- Most easily prepared from methylphosphonyl difluoride and isopropyl alcohol.

$$CH_3P(O)F_2 + (CH_3)_2CHOH \rightarrow [(CH_3)_2CHO]CH_3P(O)F + HF$$

- 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.
  - Alkylation reaction in which methyl, $-CH_3$, 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

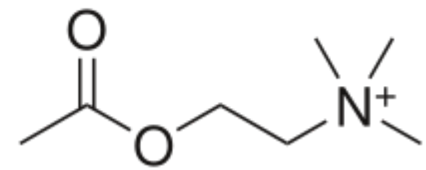
- Neurotransmitters cause nerve cells to fire.

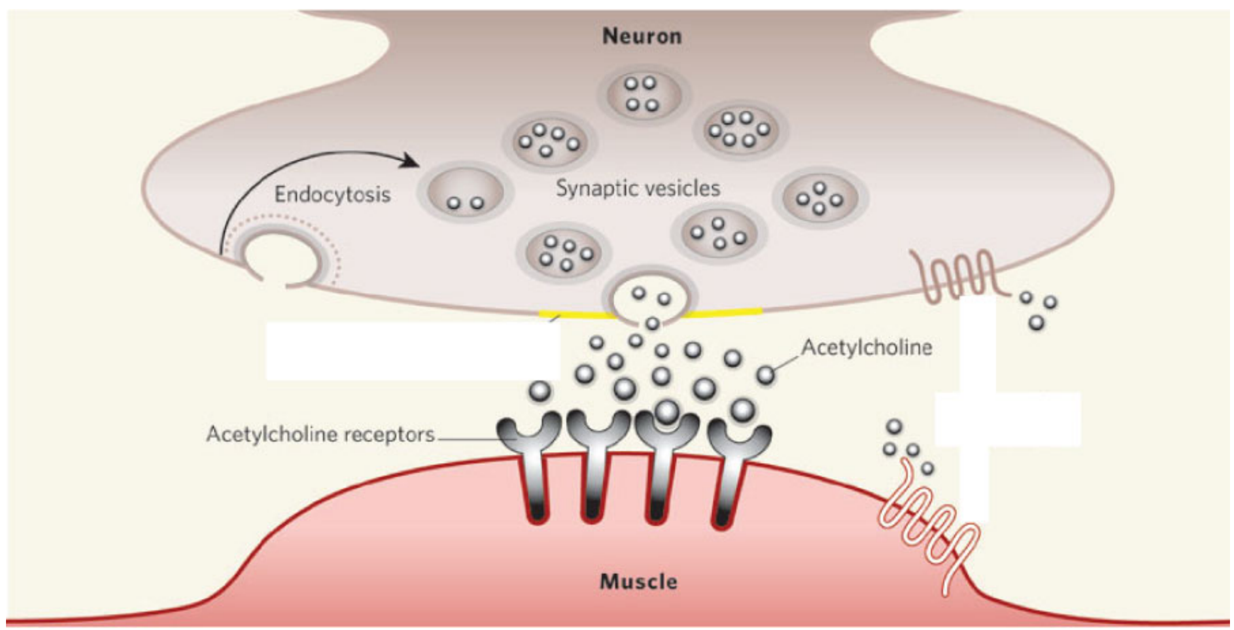


From http://universe-review.ca/R10-16-ANS.htm

Acetylcholine and Muscle Contraction

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

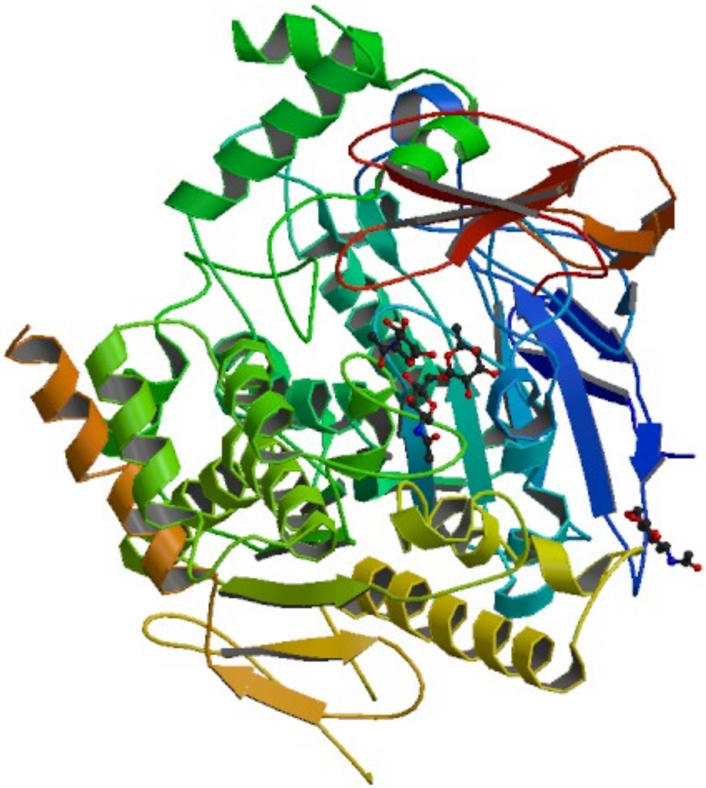




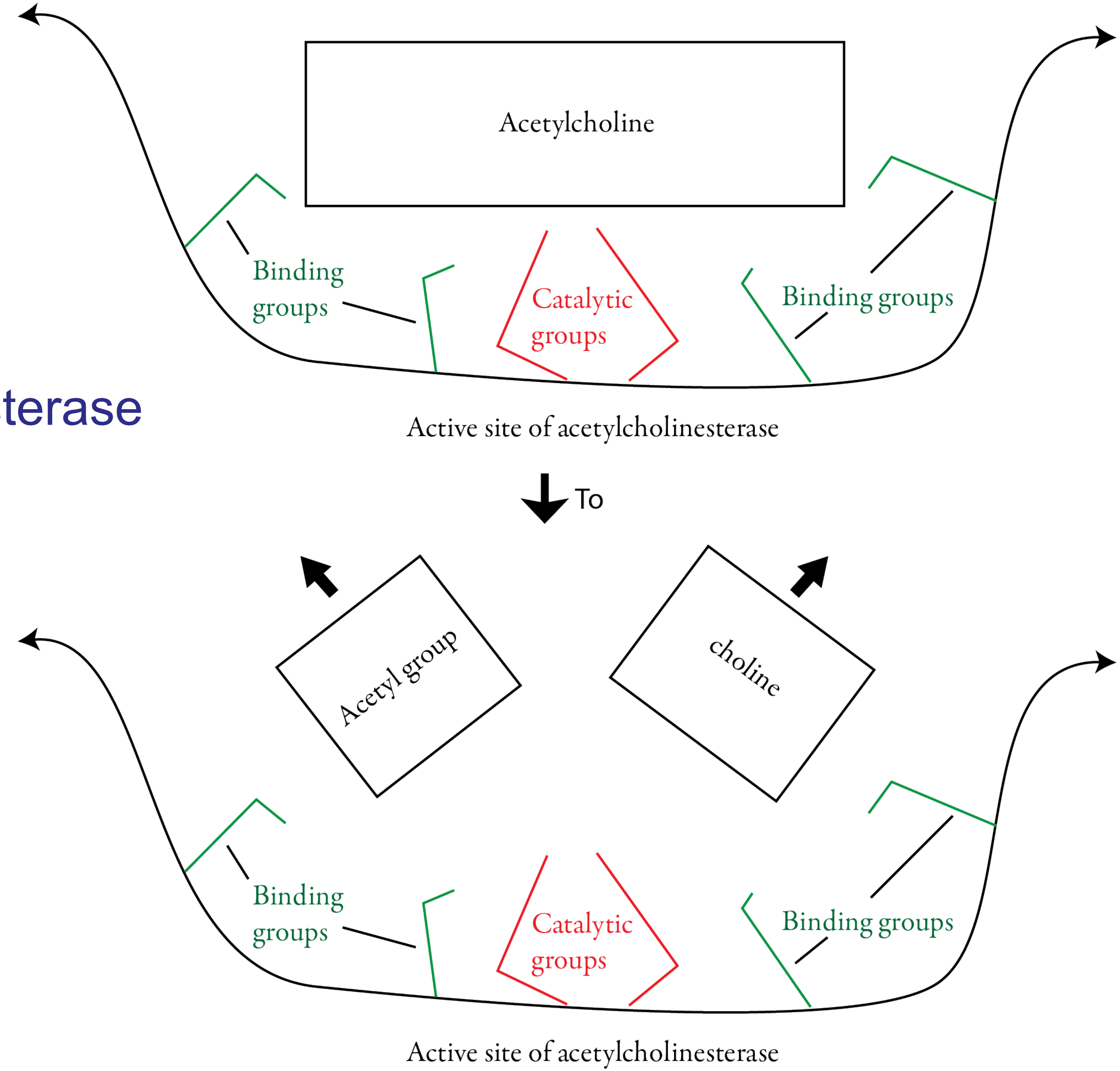
From Nature 436, 473-474 (28 July 2005)

Acetylcholine, Acetylcholinesterase, and Transfer of Nerve Information

- Normally, acetylcholine (ACh) is broken down in the active site of an enzyme, acetylcholinesterase (AChE).
- An enzyme molecule breaks down an acetylcholine molecule in about 80 microseconds.
- Together, ACh and AChE are like an on-off switch for muscles



Acetylcholinesterase



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.

https://preparatorychemistry.com/nerve_agent_sarin_Canvas.html

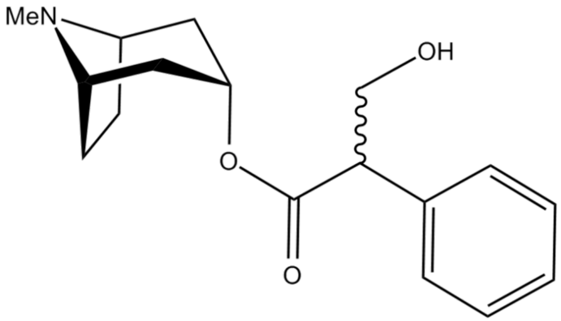
Effects of Nerve Agents

- 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

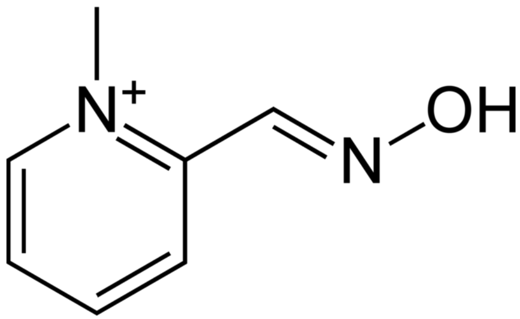
- Low doses lead to inability to think clearly, insomnia, trouble concentrating, and mood swings.
- Continuing exposure to low doses leads to a gradual increase in symptoms.
- It can take up to months for the acetylcholinesterase levels to return to normal.

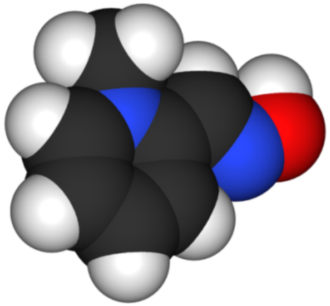
Nerve Agent Antidotes - Atropine



- 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)

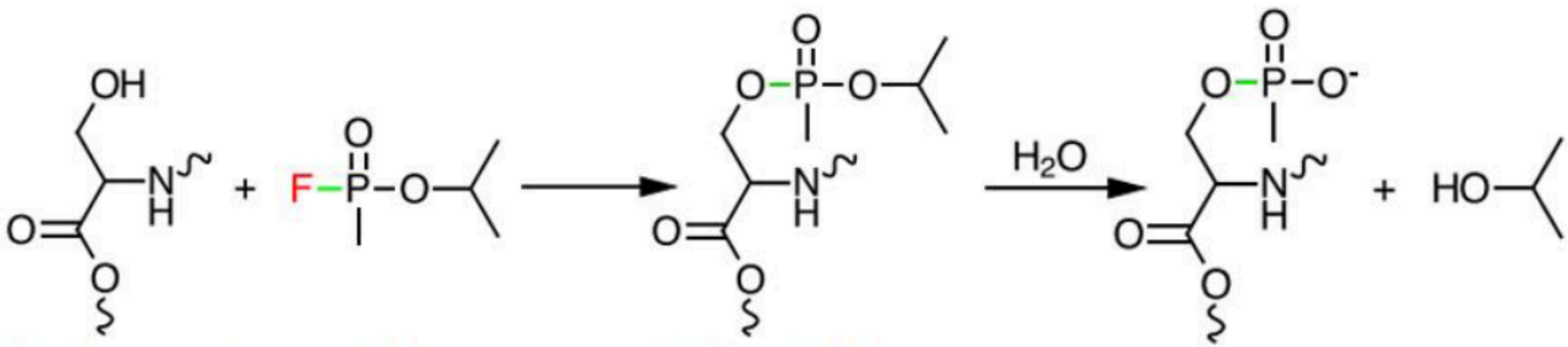




- Pralidoxime (2-pyridine aldoxime methyl chloride,) or 2-PAM
- Removes the nerve agent from the active site of acetylcholinesterase, restoring the enzyme to more normal levels
- Too slow to work well alone
- Works best when administered with atropine, which acts more quickly, giving the slower-acting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

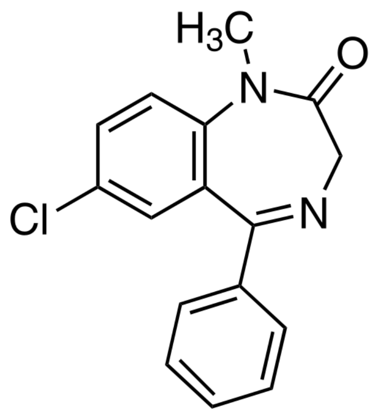
Inhibited and Aged Acetylcholinesterase

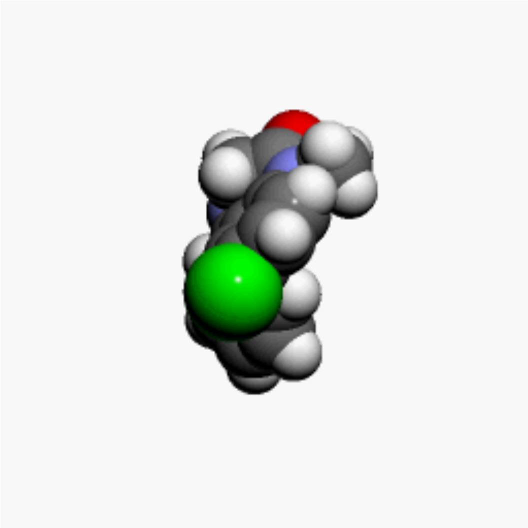
- The attachment of sarin to the active site inhibits the action of the enzyme. The sarin can be removed, so the inhibition is reversible.
- The loss of the isopropyl group from the sarin yields the *aged* form of the enzyme. The sarin cannot be removed in this form, so the inhibition of this enzyme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



Serine in protein | Sarin | inhibited Serine | aged form | Isopropanol

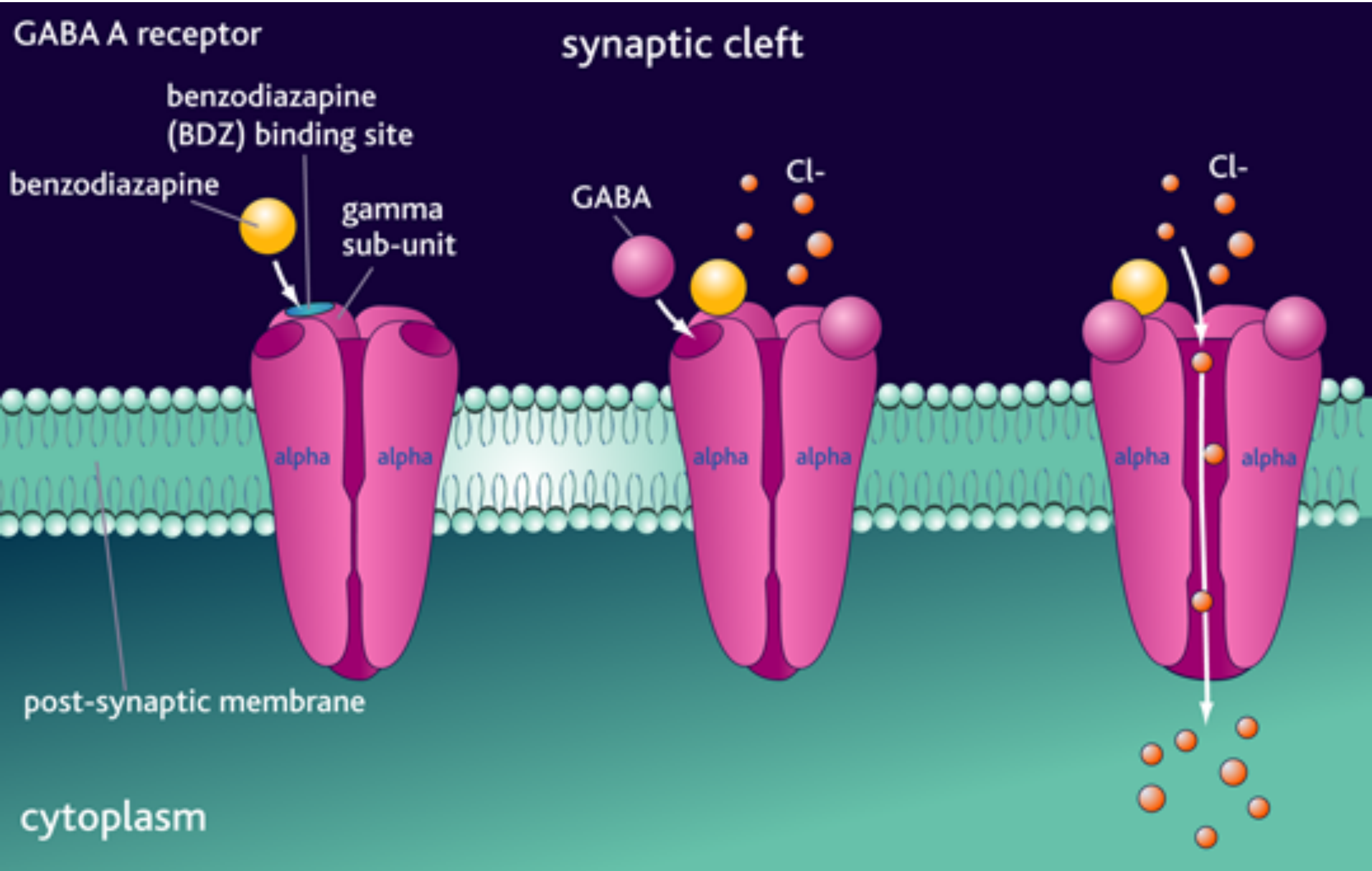
Diazepam (Valium)





- 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^- 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.

Diazepam (Valium)



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.

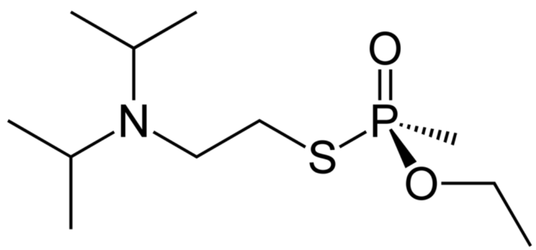
CANA (Convulsive Antidote, Nerve Agent)

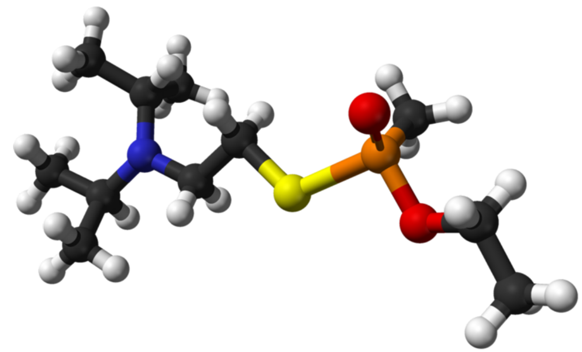
- Contains diazepam (Valium)
- One CANA kit is typically issued to service members, along with three Mark I NAAK kits, when nerve agents are considered a potential hazard.
- Deliver drugs using autoinjectors
- Intended for use in "buddy aid" or "self aid”

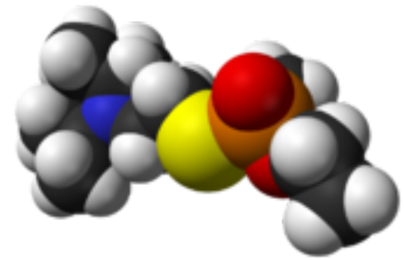
Possible New Antidotes

- Midazolam (Versed) instead of diazepam (Valium)
  - Faster acting
  - Fewer complications
- Different oxime instead of 2-PAM
  - Because 2-PAM is positive, little if any crosses the blood-brain barrier.
  - Developing oximes that are neutral until they pass into the brain where they become positive, which is necessary for their function.

VX



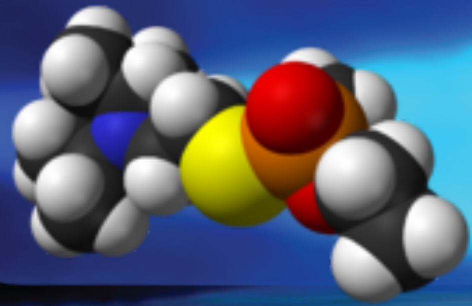




- One of several similar substances that were considered “venomous” and called V-agents.
- First produced in England in 1954
- Odorless liquid with a volatility and viscosity similar to motor oil.

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

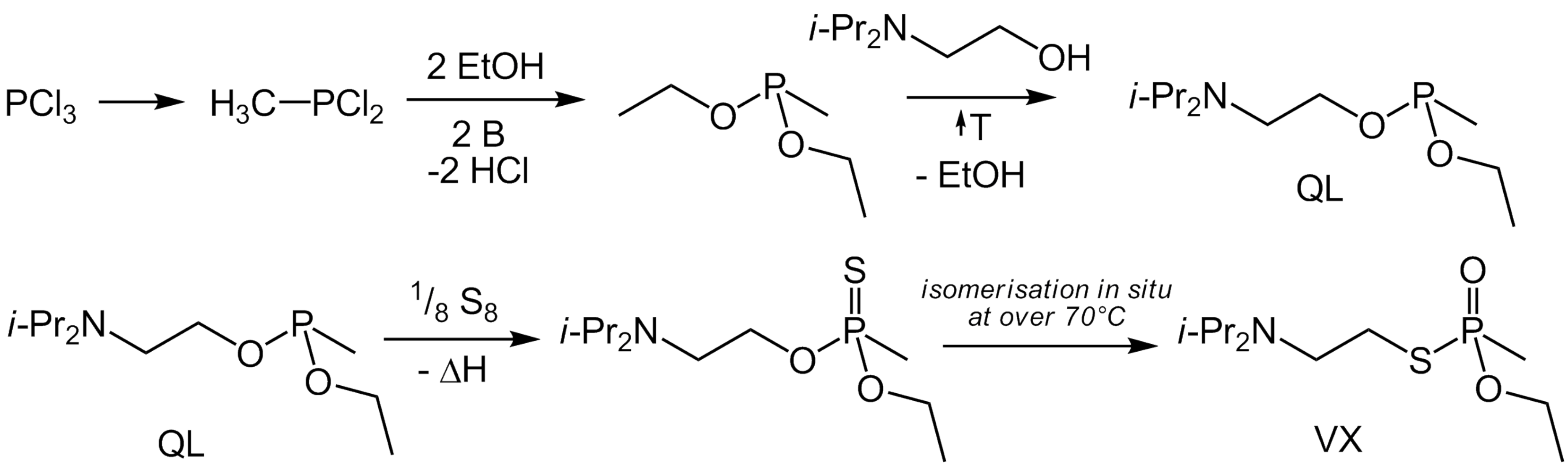
VX



- Three times more toxic that 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 course 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*.
- Used to kill Kim Jong-nam, half brother to North Korean leader Kim Jong-un, 13 February 2017 in the Kuala Kumpur International Airport Malaysia.

Production of VX

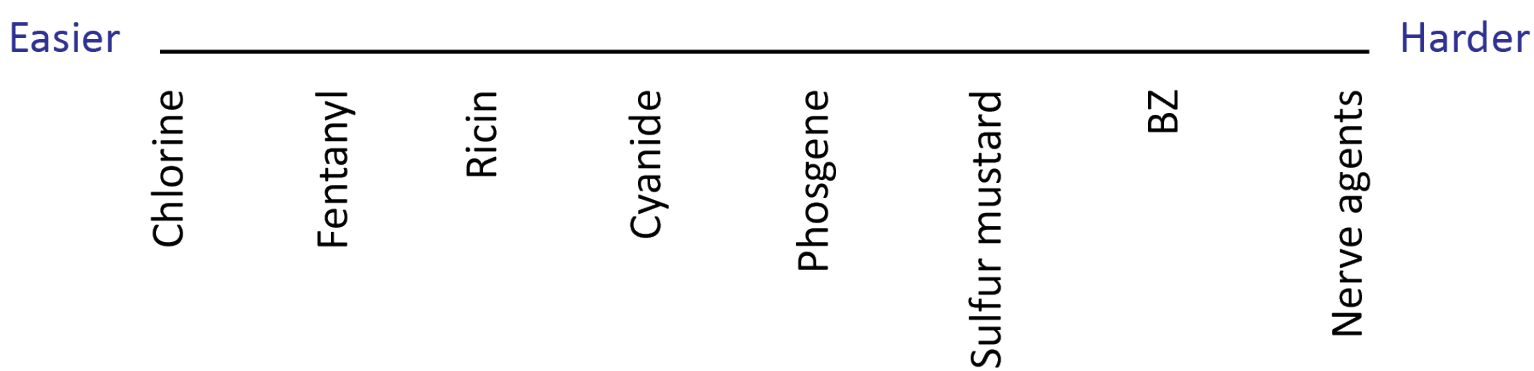
- Phosphorus trichloride (schedule 3, part b) is methylated, forming methyl phosphonous dichloride, which reacts with ethanol to form a diester. This is reacts with N,N-diisopropylaminoethanol (schedule 2, part b) to produce QL (schedule 1, part b), which reacts with sulfur to form VX.
- Has difficult alkylation step but not corrosive HF gas.



Difficulty Obtaining

- This is a very rough ranking of the level of difficulty in obtaining the CW we have discussed.
- It takes into consideration the difficulty in producing them, stealing from production plant, stealing them in transportation, etc.

Difficulty obtaining (not to scale)



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.

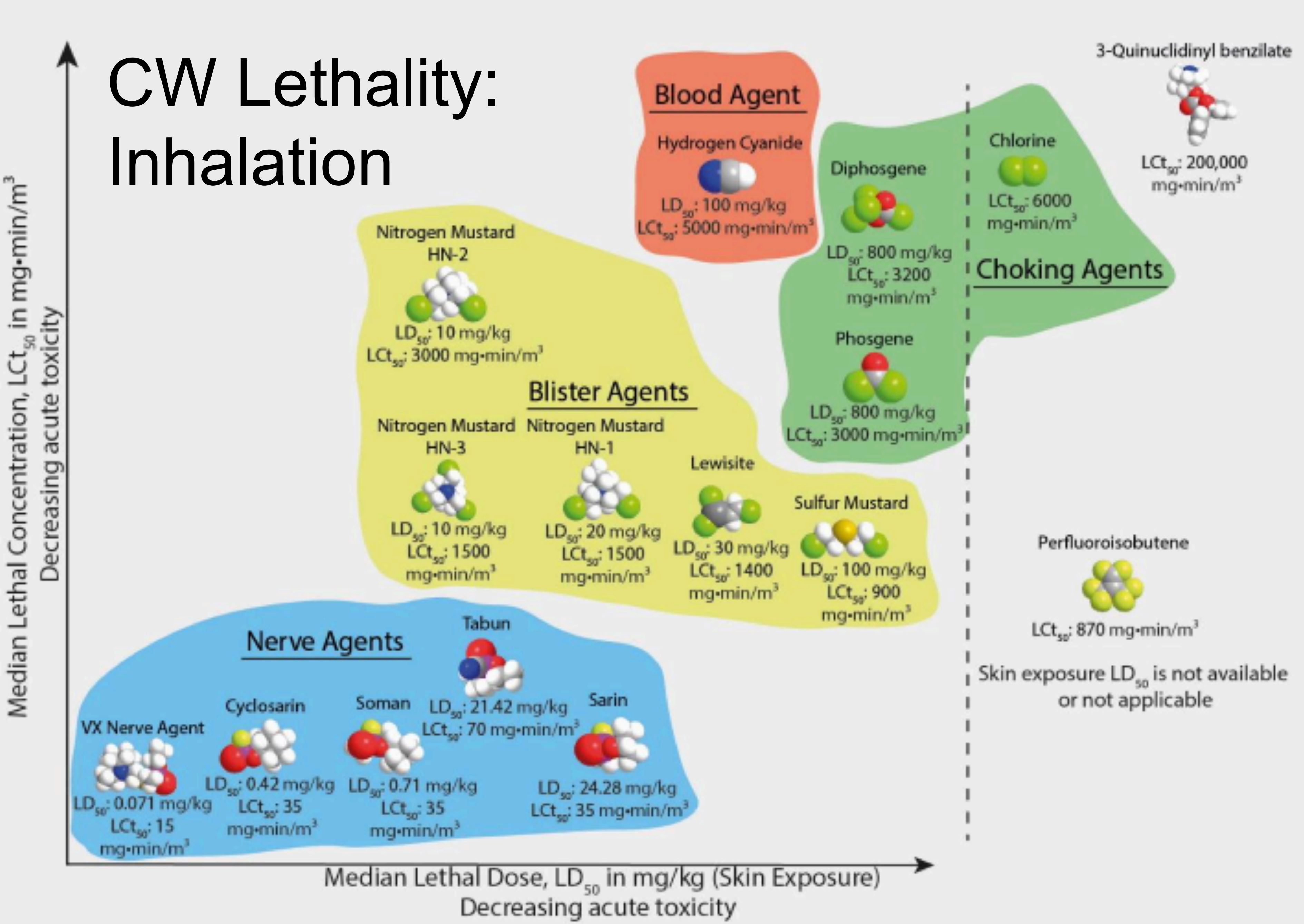
Dosage Units

- 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 = $mg{\bullet}min/m^3$.
- 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 = $mg{\bullet}min/m^3$

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

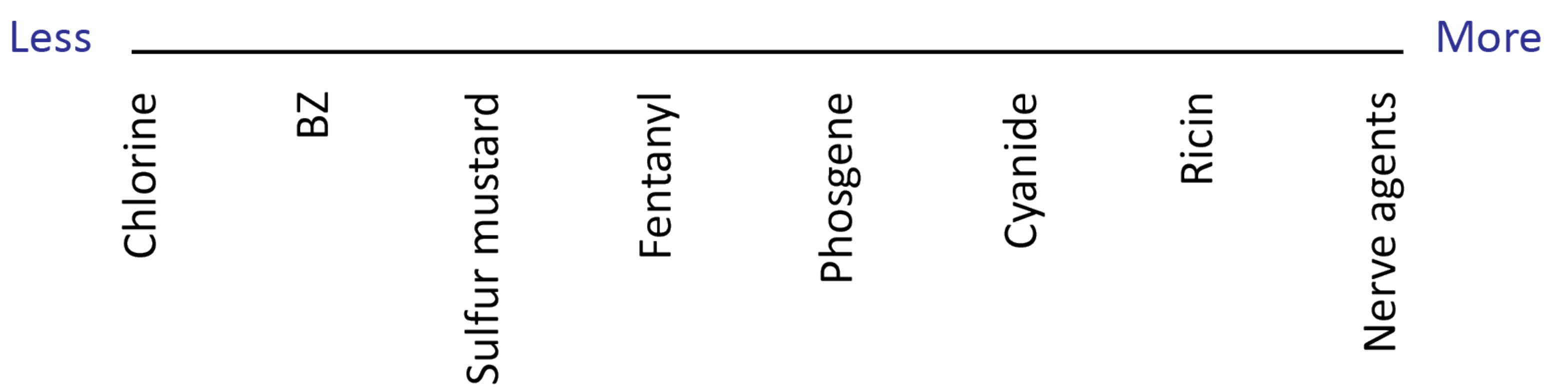


Source: Organisation for the Prohibition of Chemical Weapons (OPCW)

Lethality

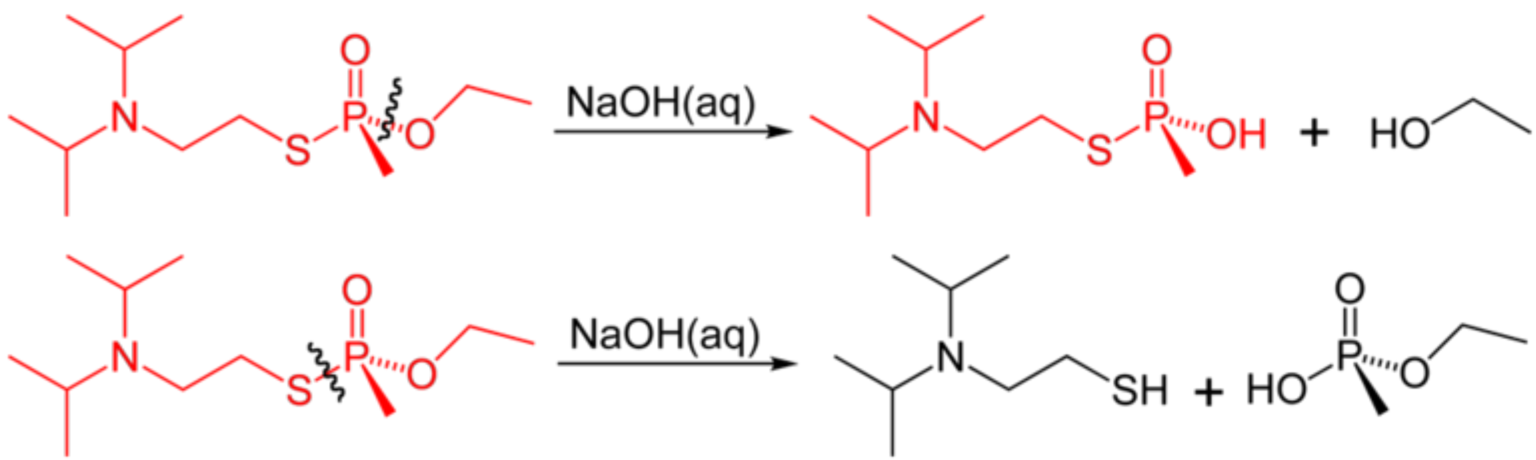
- There are many variables that determine lethality, including mode of dispersal, level of exposure, health of person exposed, etc.
- All of the chemical weapons we have talked about can be lethal, but this scale gives a very rough ranking of the likelihood of them being lethal.

Lethality (not to scale)



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, 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.



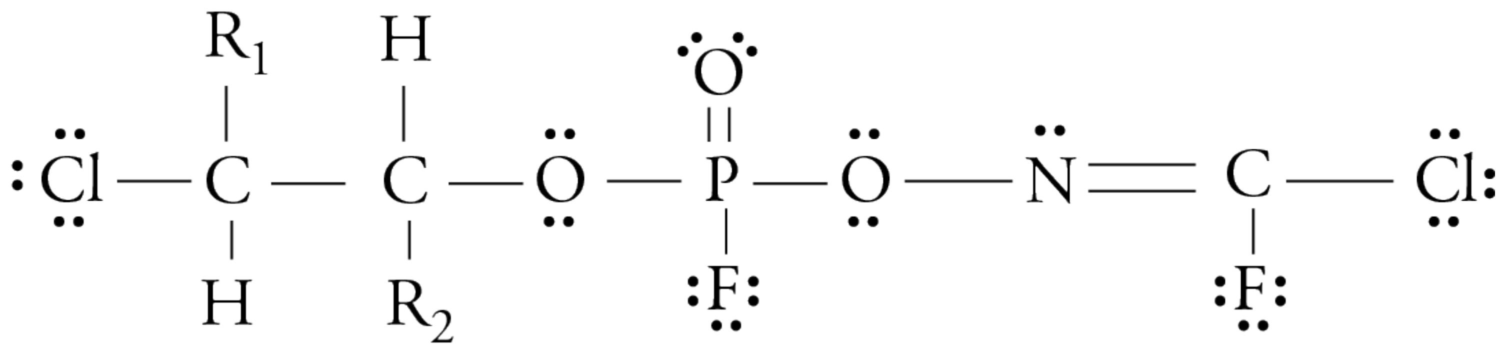
Sarin or VX?

- 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.

Russia's Novichok

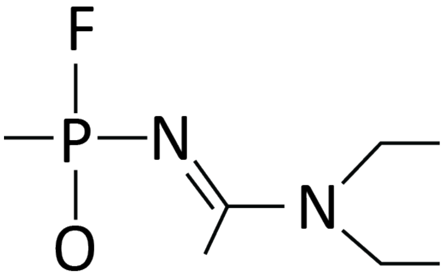
- Alleged Soviet secret program called Foliant
- Novichok (new guy or newcomer) – a category of nerve agents developed in the 1970s and 1980s
- Intent was to develop binary agents that could be made from relatively safe substances similar to normal industrial substances, making it easier to conceal the production
- Allegedly more lethal than VX
- Resistant to treatment
- There have been two proposed structures.

Russia's Novichok (Ellison and Hoenig)

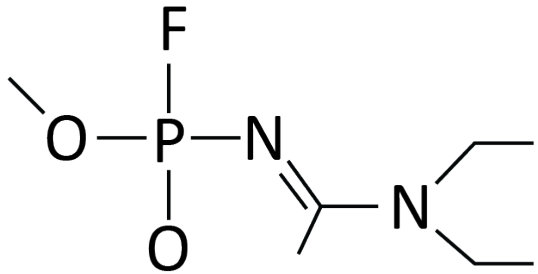


- A230 – R_1=H and R_2=H
- A232 – R_1=H and R_2=CH_3
- A234 – R_1= CH_3 and R_2=CH_3

Russia's Novichok (Mirzayanov)



A-230



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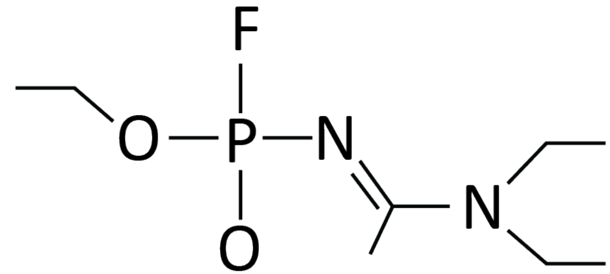
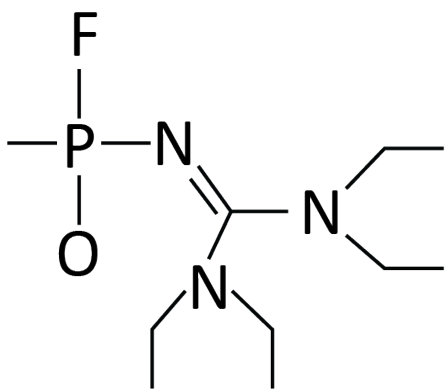


A-234



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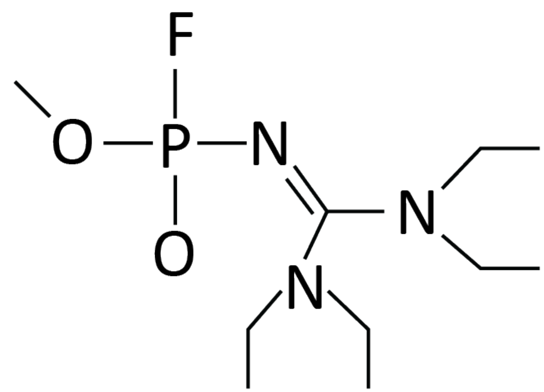


A-262

State Secrets: An Insider's Chronicle of the Russian Chemical Weapons Program by Vil Mirzayanov

Russia's Novichok

- A-234 proposed by Mirzayanov thought to be used in the Salisbury, UK attack on the former Russian military intelligence (GRU) officer Sergei Skripal and his daughter Yulia.
- Czech Republic admitted to making a small quantity of A-230.
- In 2016, Iranian scientists produced five Novichok agents and generated mass spectral data that was added to the OPCW database, which makes identifying Novichoks easier.

Novichok to Schedule 1

- October 2018 - the U.S., Canada, and the Netherlands proposed adding two groups of novichok chemicals, including A-234, to Schedule 1.
- January 14, 2019 - OPCW Executive Council recommended adoption
- April 2019 - Russia submitted its formal objection to the joint proposal, thus preventing the Executive Council's recommendation from becoming final

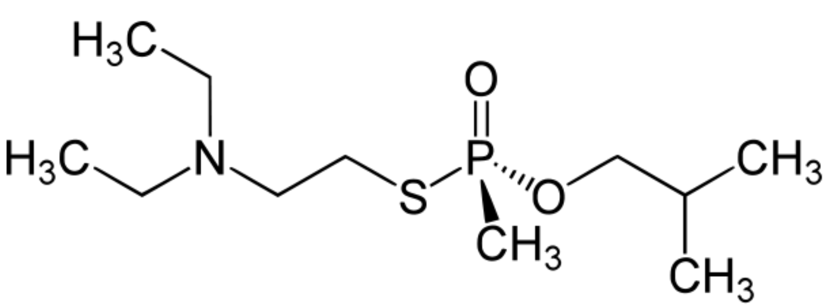
Novichok to Schedule 1

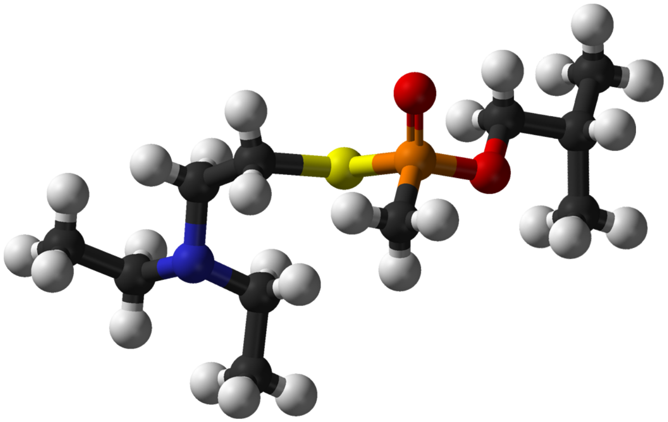
- November 27, 2019 - Twenty-Fourth Session of the Conference of the States Parties to the CWC adopted two decisions to amend for the first time the Annex on Chemicals to the Convention by adding novichoks to Schedule 1
- Will go into effect 180 days after Director-General notifies all States Parties and the United Nations Secretary-General, of the decisions adopted by the Conference

https://www.opcw.org/media-centre/news/2019/11/conference-states-parties-adopts-decisions-amend-chemical-weapons

Russia's VR or Substance-33

- Nerve agent similar to VX.
- Developed in Foliant program as prototype for Novichoks
- Reportedly used to poison banker Ivan Kivelidi and his secretary Zara Ismailova in 1995.





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.

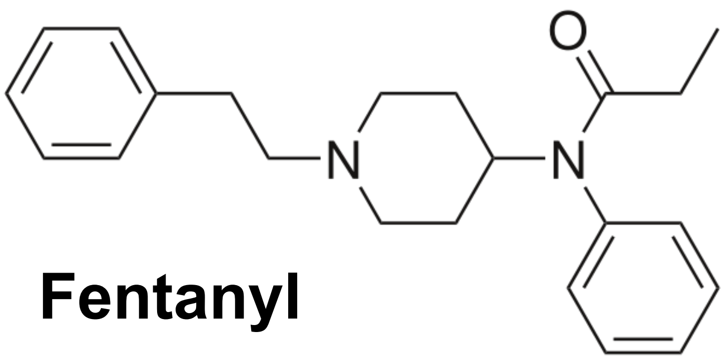
Opiate	Lowest effective dose, ED_{50} mg/kg	LD_{50}, mg/kg	Relative safety index
Meperidine	6.0	29.0	4.8
Alfentanil	0.044	47.5	1,080
Fentanyl	0.011	3.1	277
Sufentanil	0.007	17.9	25,211
Lofentanil	0.0059	0.066	112
Carfentanil	0.0034	3.4	10,000

Moscow Theater Hostage Crisis

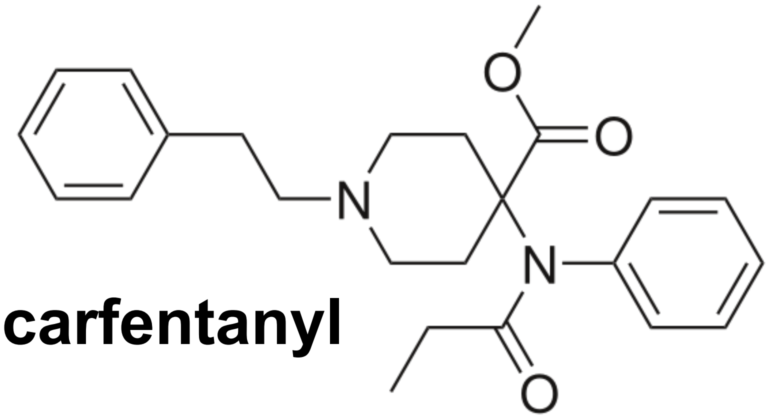
- 23 October 2002 – 40-50 armed Chechens seized a crowded Moscow theater and took 850 hostages
- Claimed allegiance to the Islamist militant separatist movement in Chechnya
- Russian forces pumped a substance thought to be carfentanyl into the building's ventilation system and raided it.
- 39 attackers and at least 129 of the hostages were killed.
- Most of the hostages who died were killed by the toxic substance pumped into the theater to subdue the militants.
- Fatalities are attributed to the weakened condition of the hostages and to lack of adequate medical attention after the attack.

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

Opioids

- The synthetic opioids are thought to bind to the same opioid receptors as natural substances, such as endorphins and enkephalins.
- There are opioid receptors throughout the body that cause a variety of effects, including pain relief, sedation, respiratory depression, constipation, and a strong sense of euphoria.

Opioids and Pain

- There are natural neurons that inhibit the pain response.
- GABA neurons inhibit the neurons that inhibit the pain response, leading to a more free flow of the pain response.
- Opioids inhibit the GABA neurons.
- This diminishes the inhibition of the neurons that inhibit the pain response.
- This leads to greater inhibition of the pain response.

https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4708964/

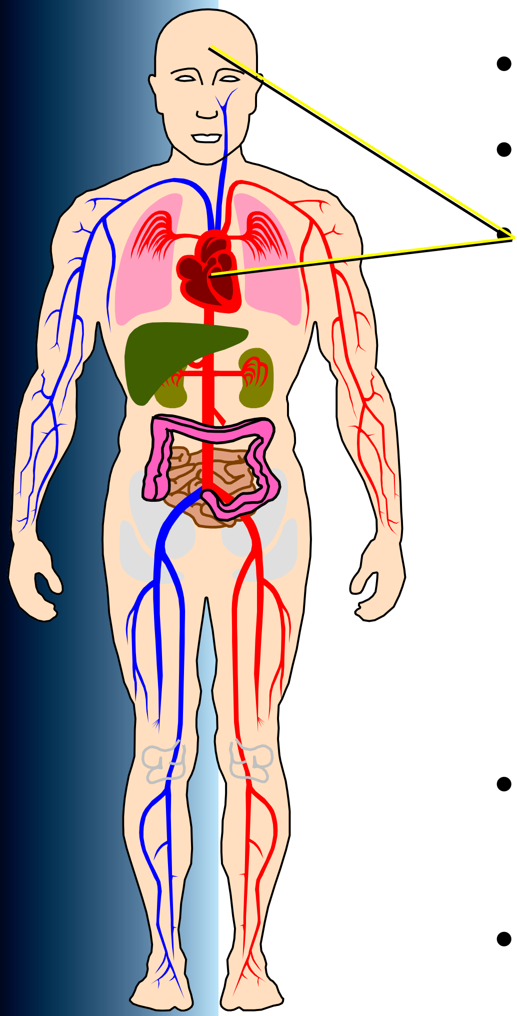
Opioids and the Reward System

- GABA neurons inhibits the release of dopamine (the feel-good chemical).
- The inhibition of the GABA neurons by opioids 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.
- More opioids leads to more inhibition of GABA neurons, which leads to more dopamine, which leads to greater reward.

Opioid Fatalities

- Death can arise from the excess inhibition of the neurons that send signals to the diaphragm muscle telling it to contract, causing one to breathe in.
- The antidote naloxone (Narcan®) competes successfully with opioids for their receptor sites.

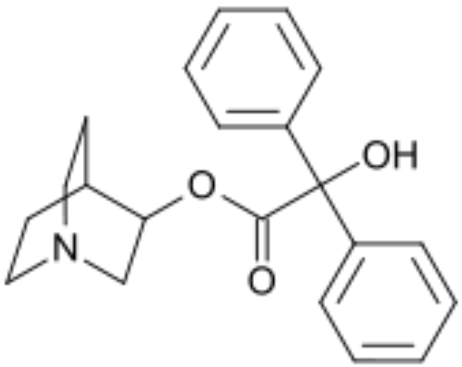
Psychochemical Incapacitants

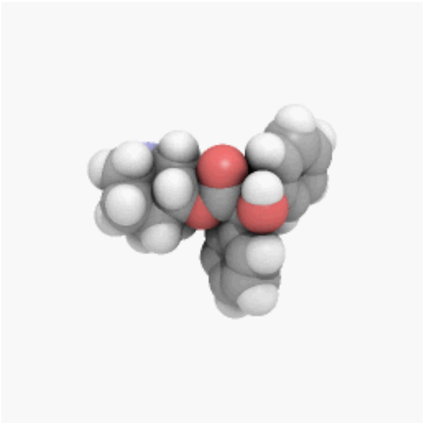


- BZ (3-3-quinuclidinyl benzilate)
- Modes of action: inhalation, ingestion, injection
- Physiological effects
  - Potent anti-cholinergic compound (similar to atropine)
  - Dose <1 mg induces hallucinations and delirium
  - Mild effects within an hour, peak at 8 hours, and decline over next 48-72 hours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

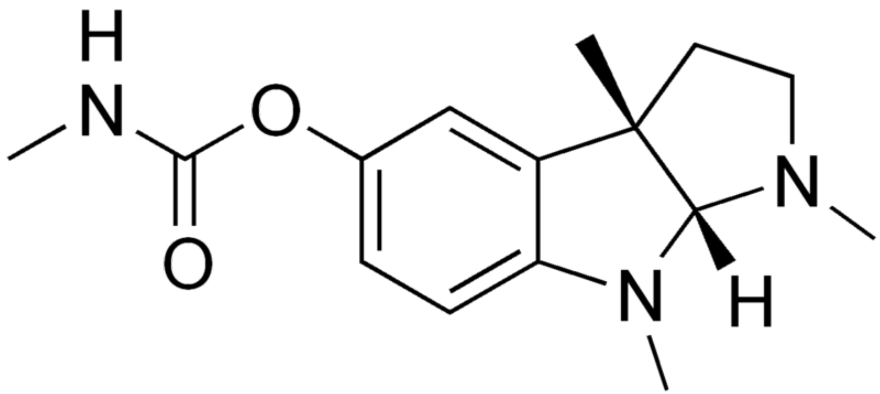
BZ

- **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.

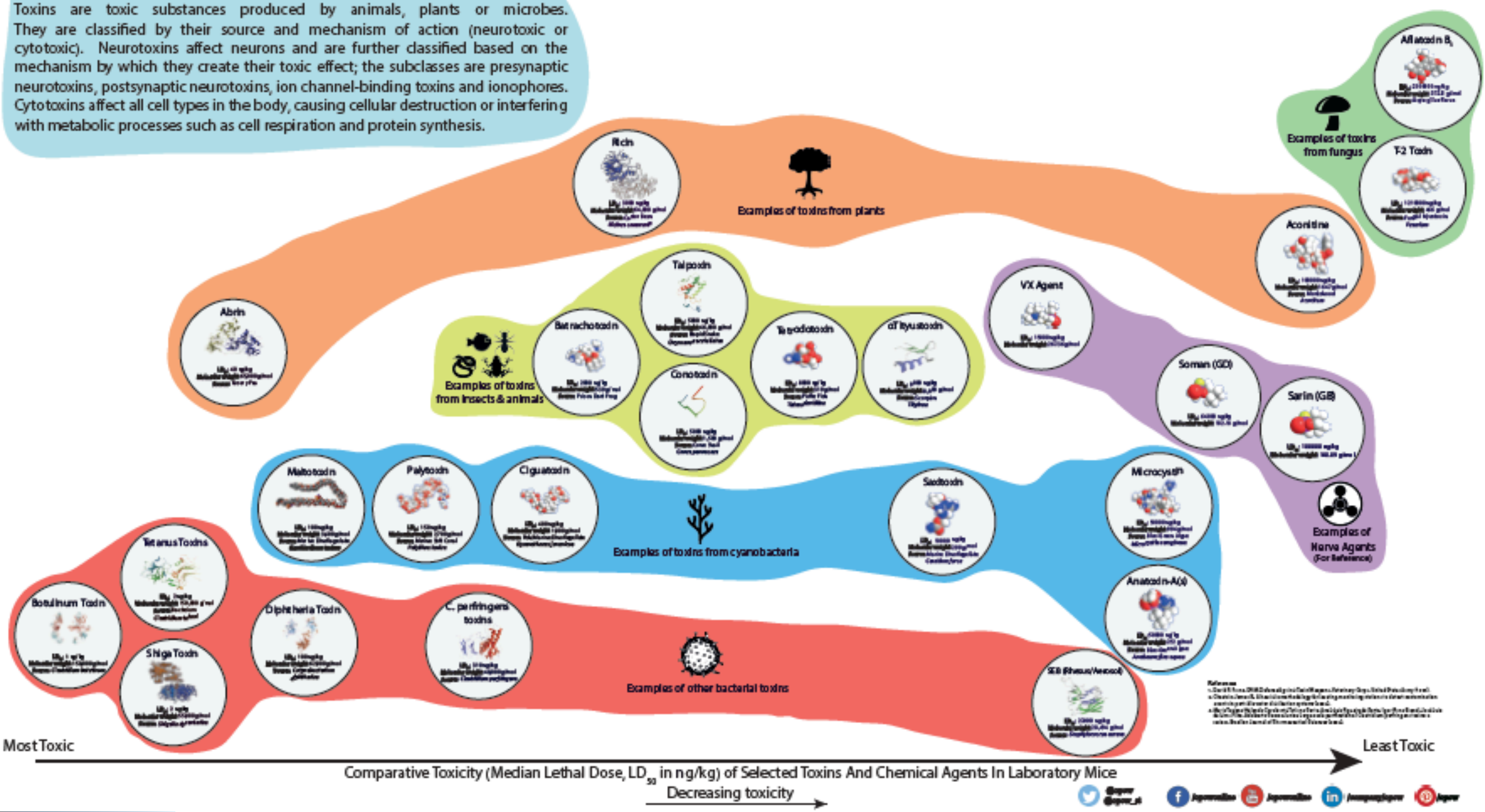
ORGANISATION FOR THE PROHIBITION OF CHEMICAL WEAPONS

Working Together for a World Free of Chemical Weapons

Biological Toxins and their Relative Toxicity

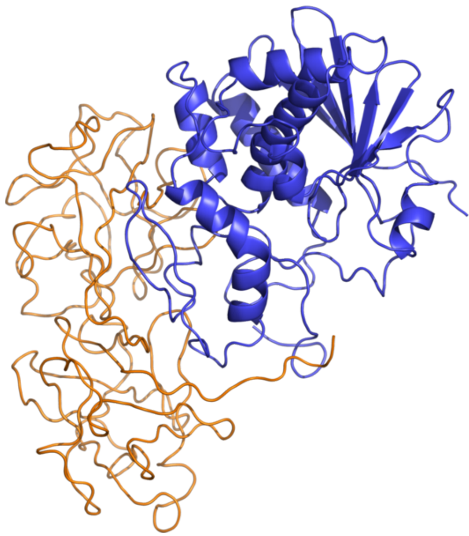
What are Toxins?

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_{50} 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	Chemical Agents
Natural Origin	Human-made
Difficult, small-scale production	Large-scale industrial production
None volatile	Many volatile
Many are more toxic	Less toxic than many toxins
Mostly not dermally active	Can be dermally active
Legitimate medical use	Almost no medical uses
Odorless and tasteless	Noticeable odor or taste
Diverse toxic effects	Fewer types of effects
Many are effective immunogens	Poor immunogens
Aerosol delivery	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 majors 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 - 193 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

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

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

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

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.

Chmical Compound	***Commercial Uses***	***CW Agent***
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)

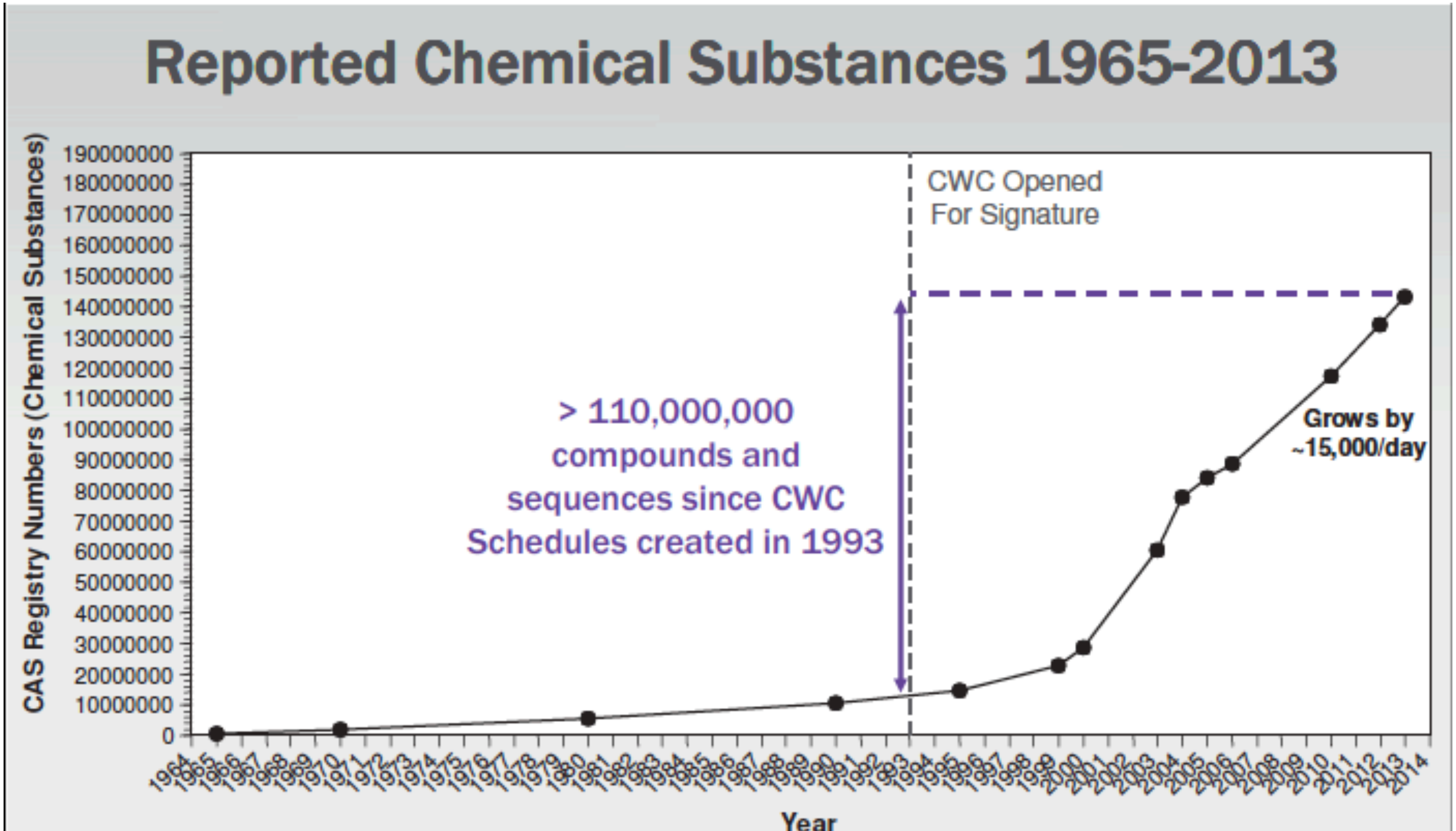
http://www.australiagroup.net/en/participants.html

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

Many New Substances Created



https://www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the_OPCW_2014_2015.pdf

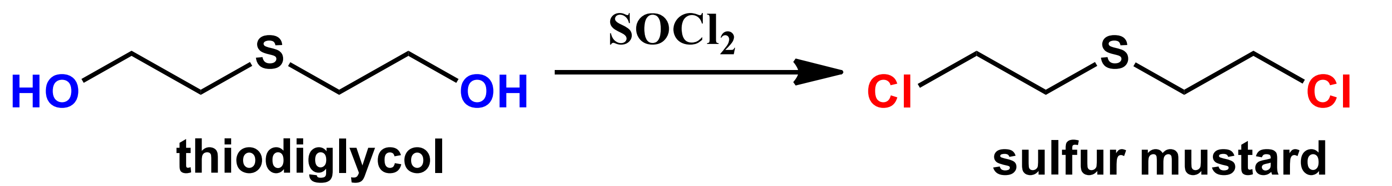
Ways to Circumvent Export Controls on Precursors

- Substitute uncontrolled chemical for controlled one.
- Purchase relatively small quantities from multiple sources
- Produce precursors from simpler, uncontrolled substances.
  - There are at least 9 ways to make sulfur mustard documented in the chemical literature, and some of these involve uncontrolled substances.

http://www.cwc2013.info/RG2013-by-doc/6/AG-precursors.pdf

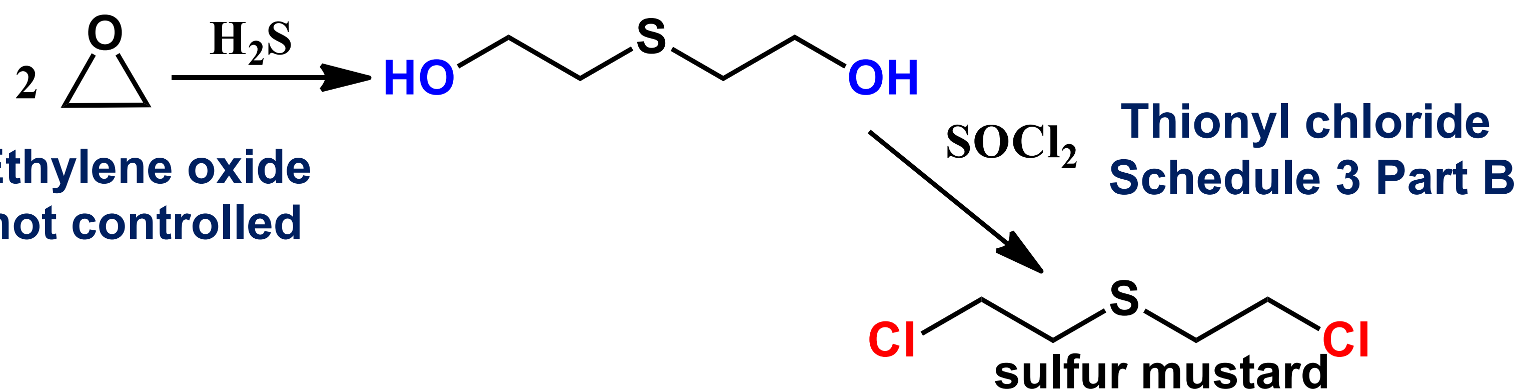
Iraqi Mustard Program

Back-Integration = synthesizing precursor compounds from simpler ones that are not export controlled or are available from domestic sources



↑

Embargo placed on this by Western Countries in early 80's



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

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

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

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

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

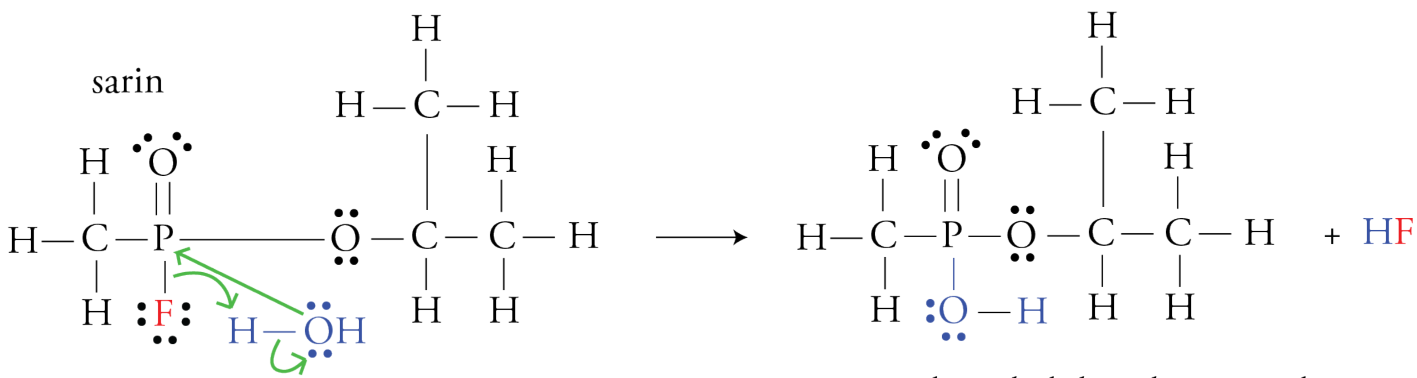
Science for Diplomats 17 March 2015
www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the_OPCW_2014_2015.pdf

Sample Types and Assumed Concentrations

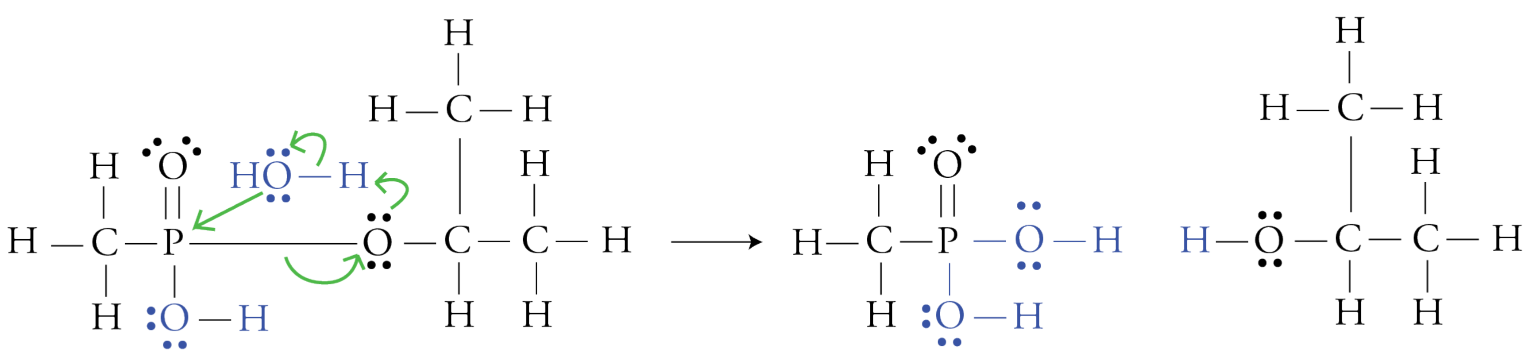
- Environmental samples
  - "Neat" agent from a reactor or bomb
  - Residue from a reaction or waste container
  - Contaminated clothing, hair, soil, water, etc.
  - Concentrations usually expected >1 μg/g (ppm)
  - Survey analysis is possible
- Biomedical samples
  - Urine, blood, plasma, tissue, etc.
  - Intact chemical agent likely not present (degradation/reaction product or metabolite)
  - Concentration levels quite low, < 5 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.



isopropyl methylphosphonic acid
(IMPA)



isopropyl methylphosphonic acid
(IMPA)

methylphosphonic acid
(MPA)

2-propanol
(isopropyl alcohol)

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 organophoshates.

Detection of Sarin Use in Biomedical Samples

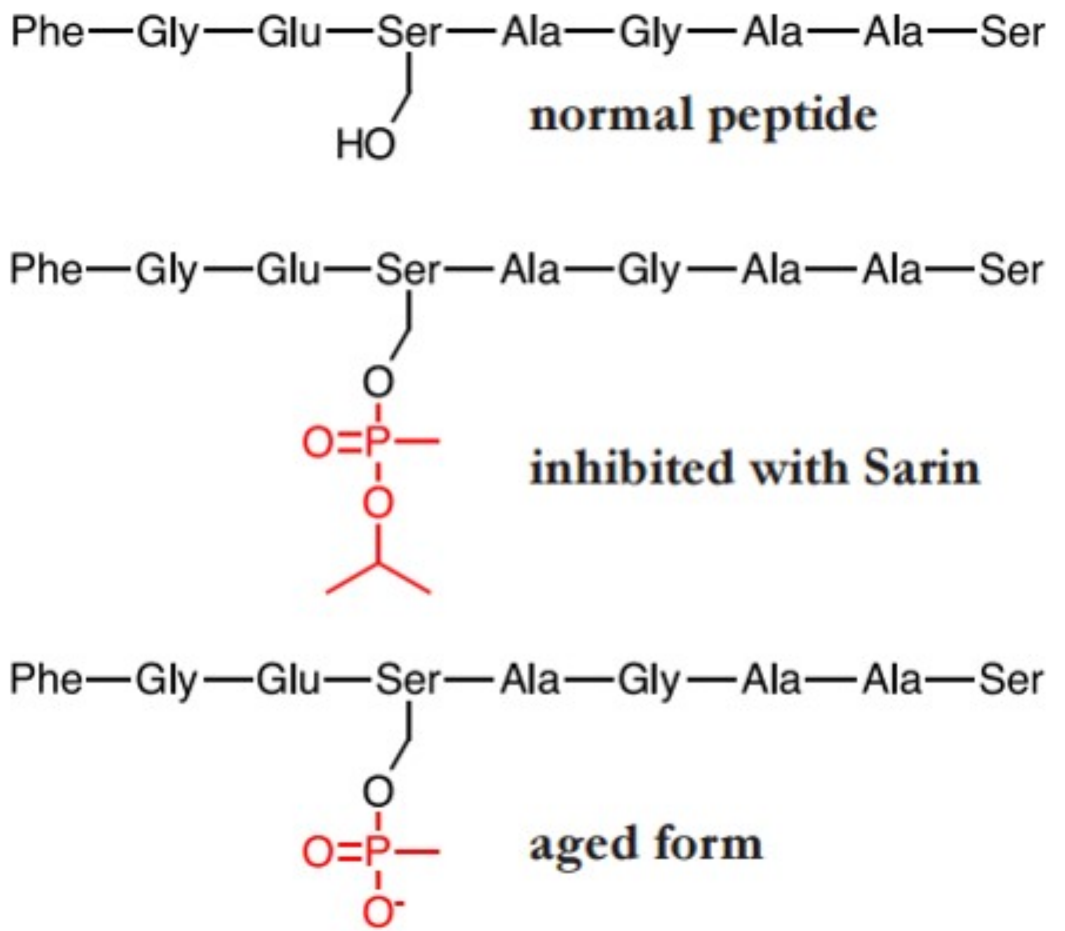
- Urine or blood samples taken from exposed persons are more difficult than environmental samples to analyze because the chemical agent, its adducts, and metabolites degrade and are excreted from the body, giving a limited time window to collect and analyze samples.
- Concentration levels in these samples 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.

Butylcholinesterase (BChE)

- Similar to acetylcholinesterase (AChE).
- Hydrolyzes many different choline-based esters
- In blood serum
- Can be used as a prophylactic countermeasure for nerve agents

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?

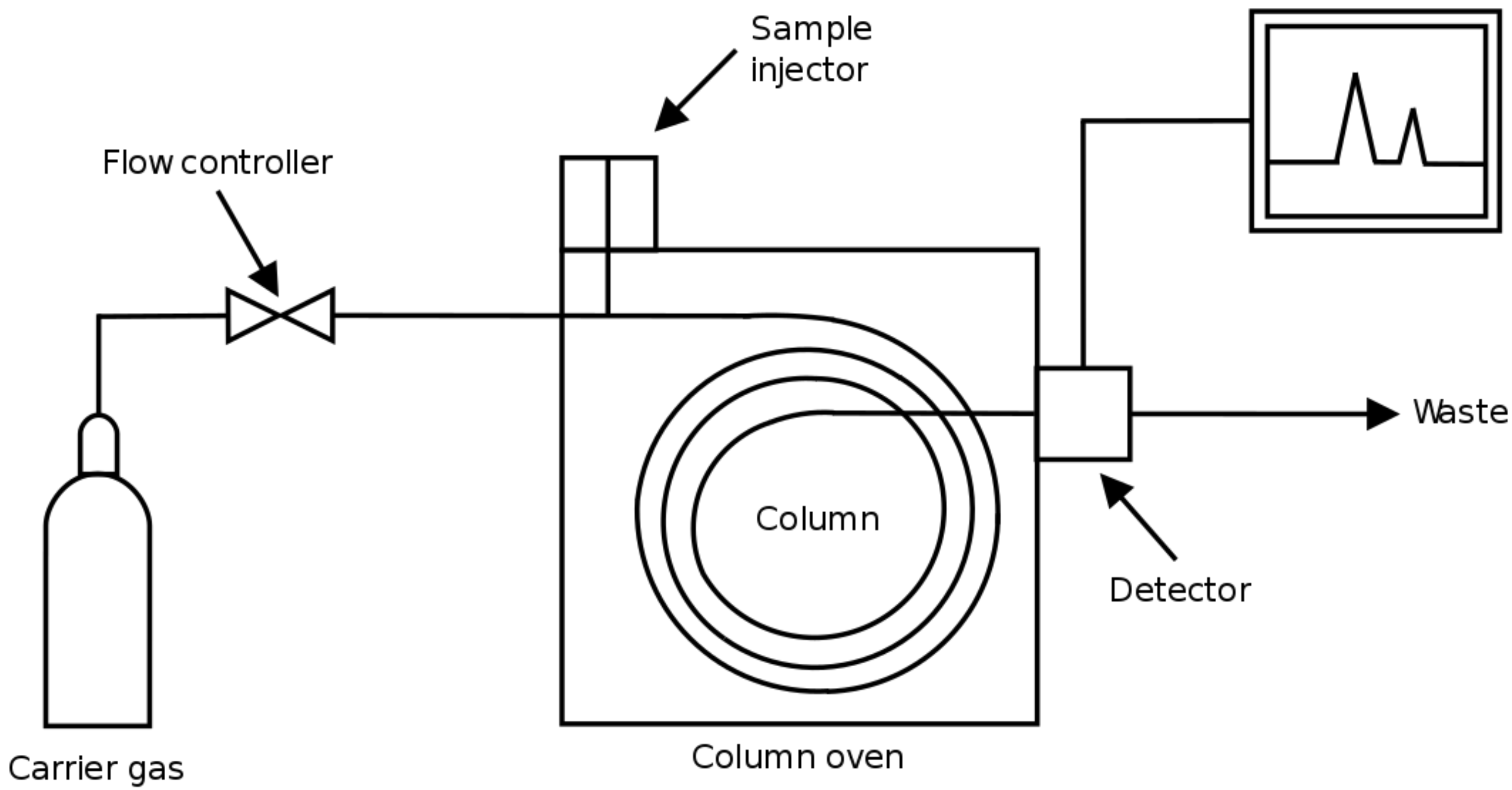
<u>(1) Autosampler</u>:
Injects a small amount (1 µL) of sample into the Gas Chromatograph

<u>(2) Gas Chromatograph</u>:
Separates chemical species and creates a chromatogram of all the species in the sample.

<u>(3) Mass Spectrometer</u>:
Creates a spectrum or "fingerprint" of each compound as it comes from the GC

Science for Diplomats 17 March 2015
www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the_OPCW_2014_2015.pdf

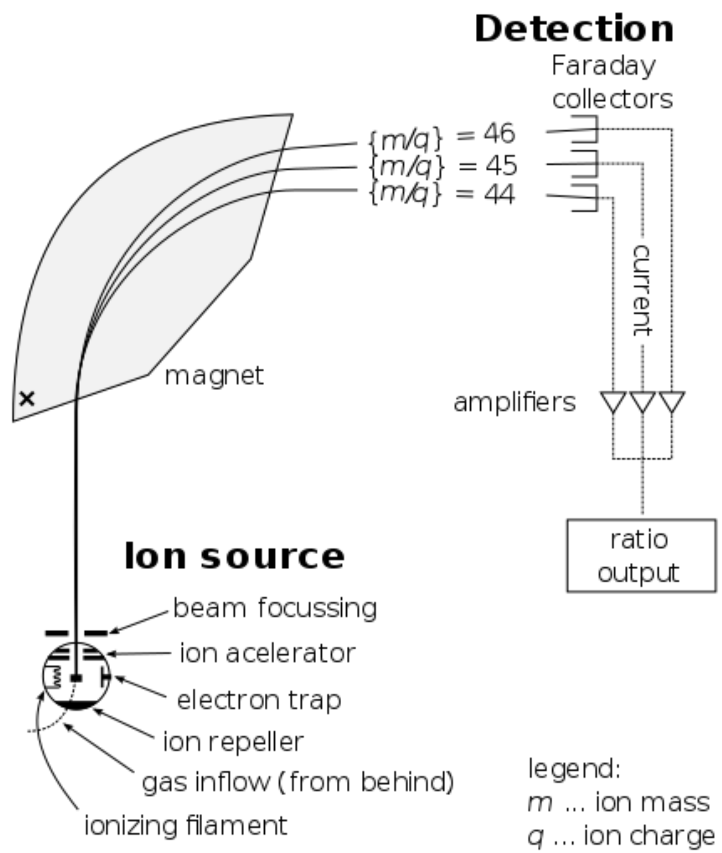
Gas Chromatograph



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 or polymer.
- 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

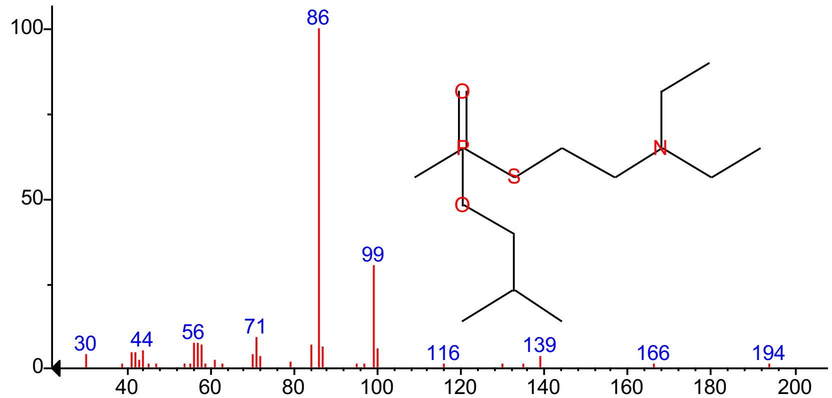
Mass Spectrometer



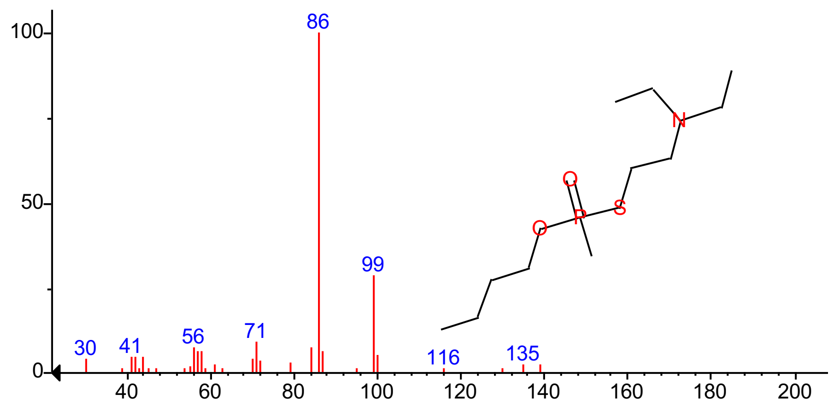
Mass Spectrometer

- 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 Results: Spectra Match to Library



(e-ocad_v16) Isobutyl S-2-diethylaminoethyl methylphosphonothiolate



(e-ocad_v16) Butyl S-2-diethylaminoethyl methylphosphonothiolate

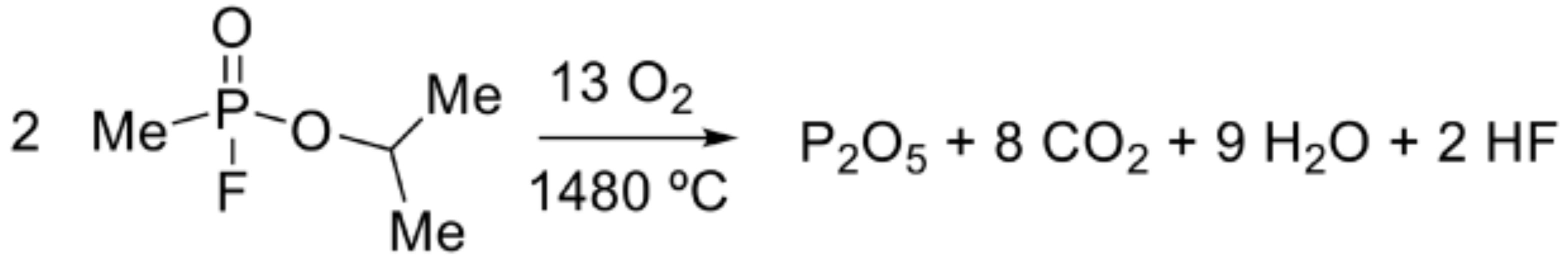
- Small differences in mass spectra indicate different structures
- Both are V-agents

Science for Diplomats 17 March 2015
www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the_OPCW_2014_2015.pdf

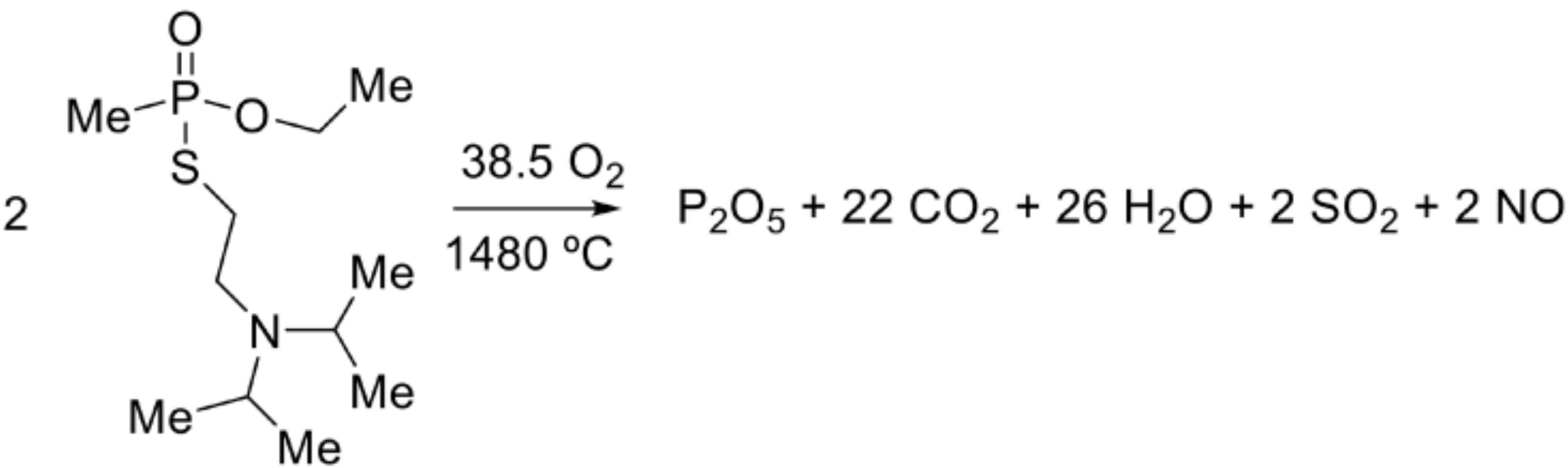
Three Ways of Disposing of Chemical Weapons

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

Incineration of Sarin and VX



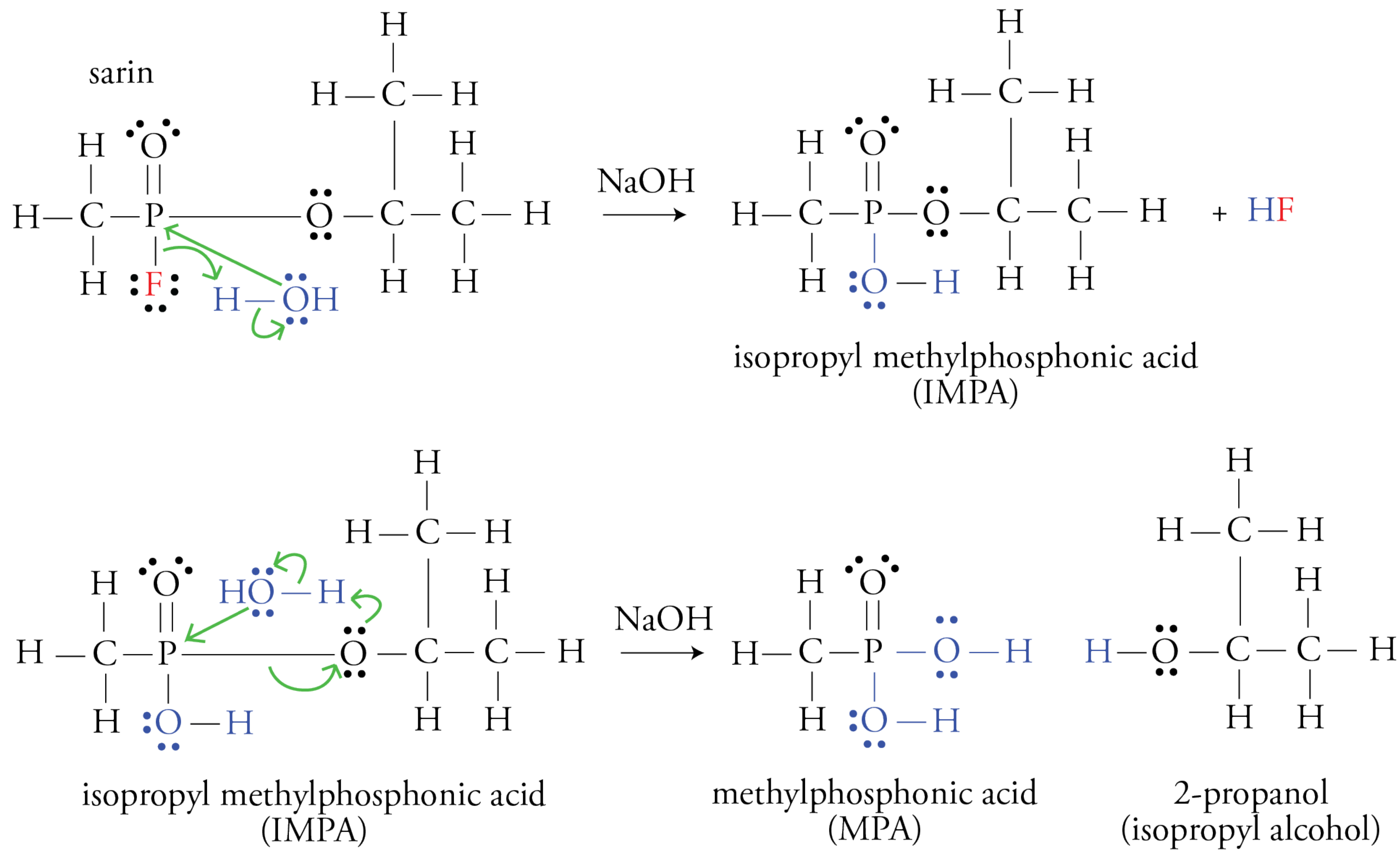
GB (Sarin)



VX

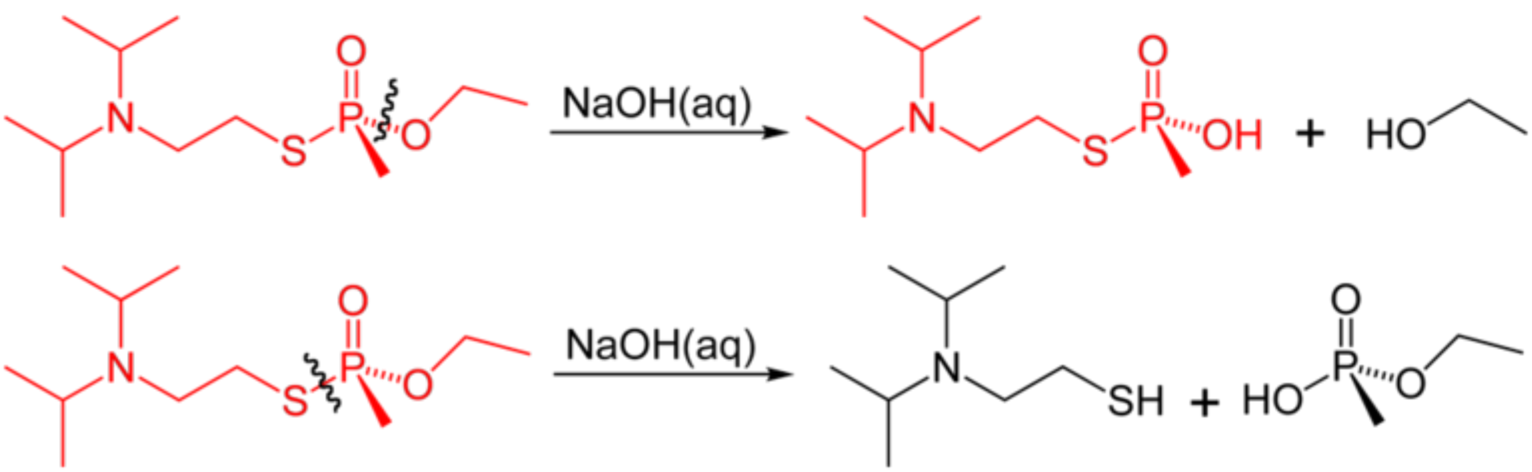
Hydrolysis of Sarin

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.



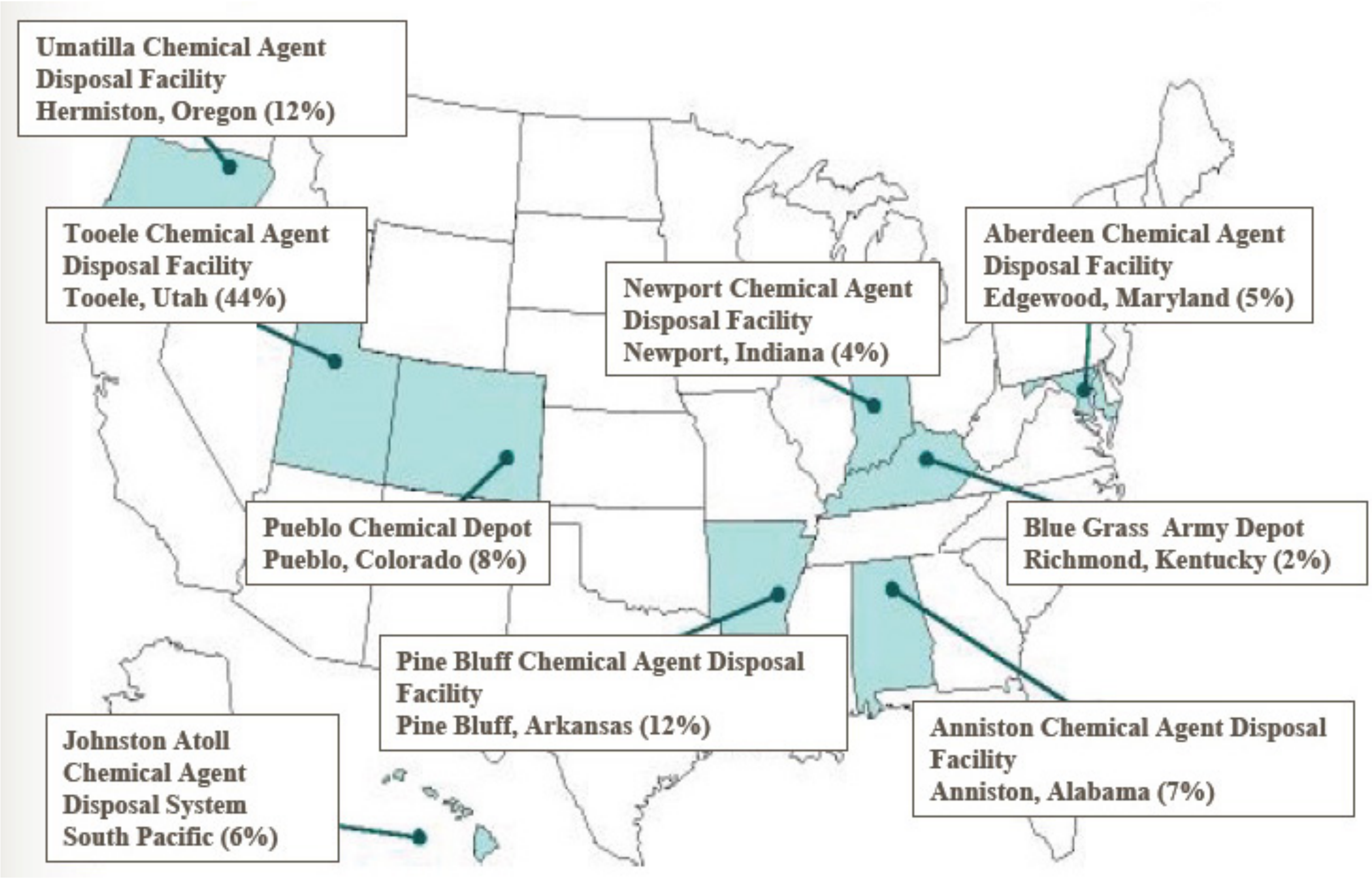
U.S. Army's Chemical Materials Agency (CMA)

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

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

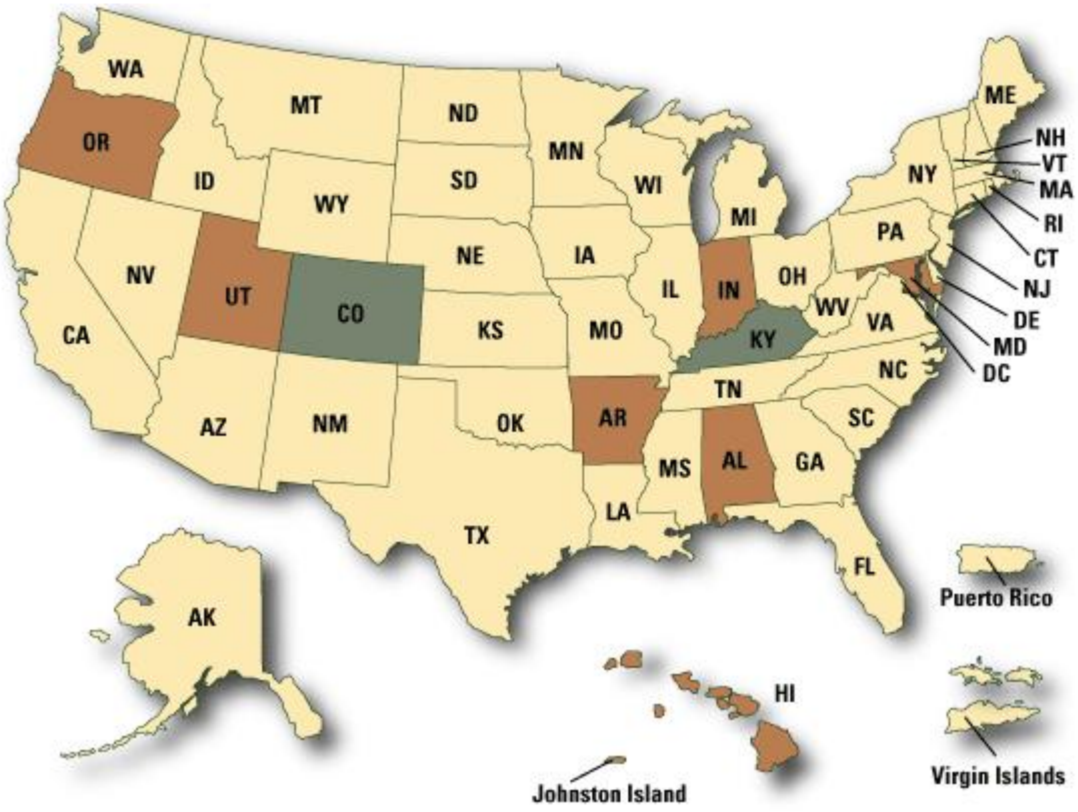
A student fully encapsulated in a protective suit at the Chemical Demilitarization Training Facility at Aberdeen Proving Ground, Md., rolls a simulated waste barrel in the Demilitarization Equipment Room.

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



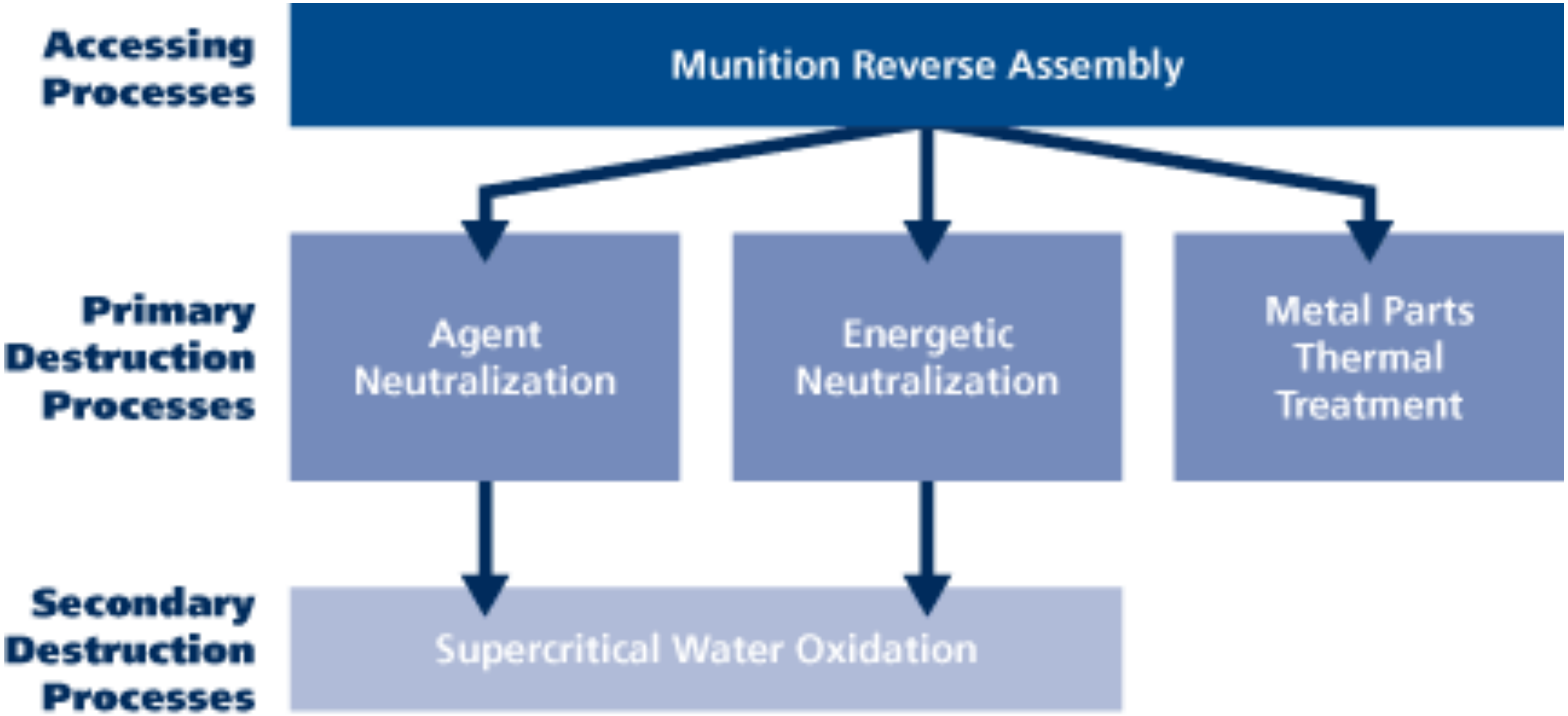
http://www.cma.army.mil/map.aspx

United States Remaining Chemical Weapons

- Blue Grass Army Depot - Richmond, Kentucky
  - 523 tons of nerve agents sarin and VX, and mustard agent in projectiles, warheads and rockets will be destroyed by chemical neutralization followed by supercritical water oxidation.

https://www.cma.army.mil/bluegrass/

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 2,600 tons of mustard agent in approximately 780,000 munitions by neutralization.
  - Started March 2015

https://www.cma.army.mil/pcd/

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)