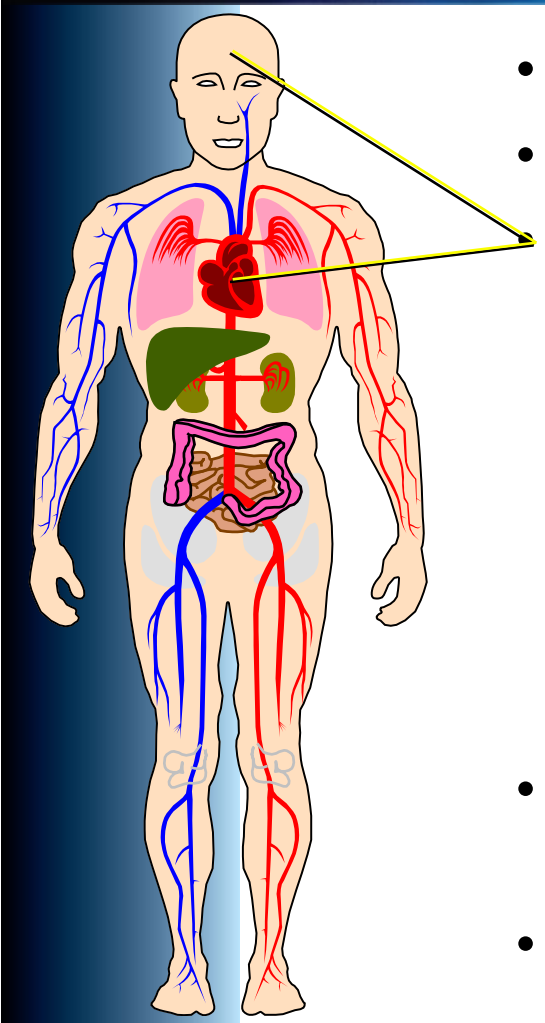
Science and Technology

Chemical Weapons Part 2

By

Mark Bishop

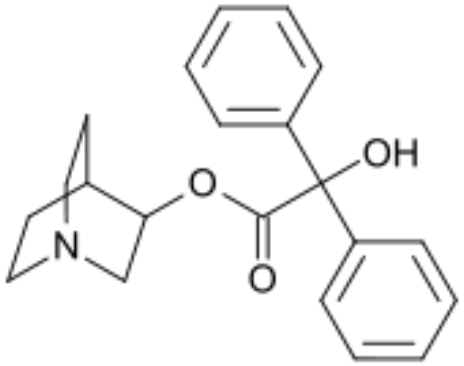
Psychochemical Incapacitants

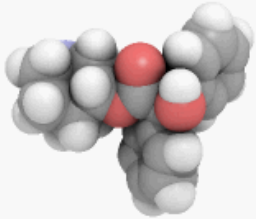


- BZ (3-3-quinuclidinyl benzilate)
- Modes of action: inhalation, ingestion, injection
- Physiological effects
  - Potent anti-cholinergic compound (similar to atropine)
  - Dose <1 mg induces hallucinations and delirium
  - Mild effects within an hour, peak at 8 hours, and decline over next 48-72 hours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

BZ (QNB)

- **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.
- Symptoms are delayed but long-lasting

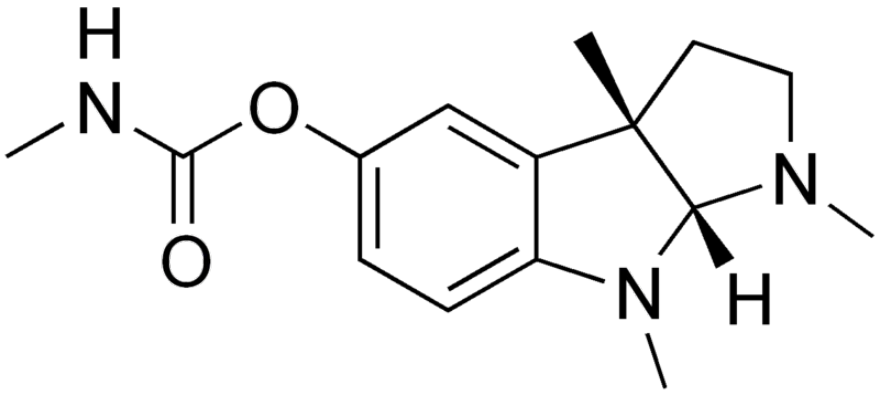




BZ (QNB)

- Crystalline solid
- Can be released into the air as fine particles or as an aerosol created from a solution (BZ dissolved in a solvent)
- Can contaminate water and food
- 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.

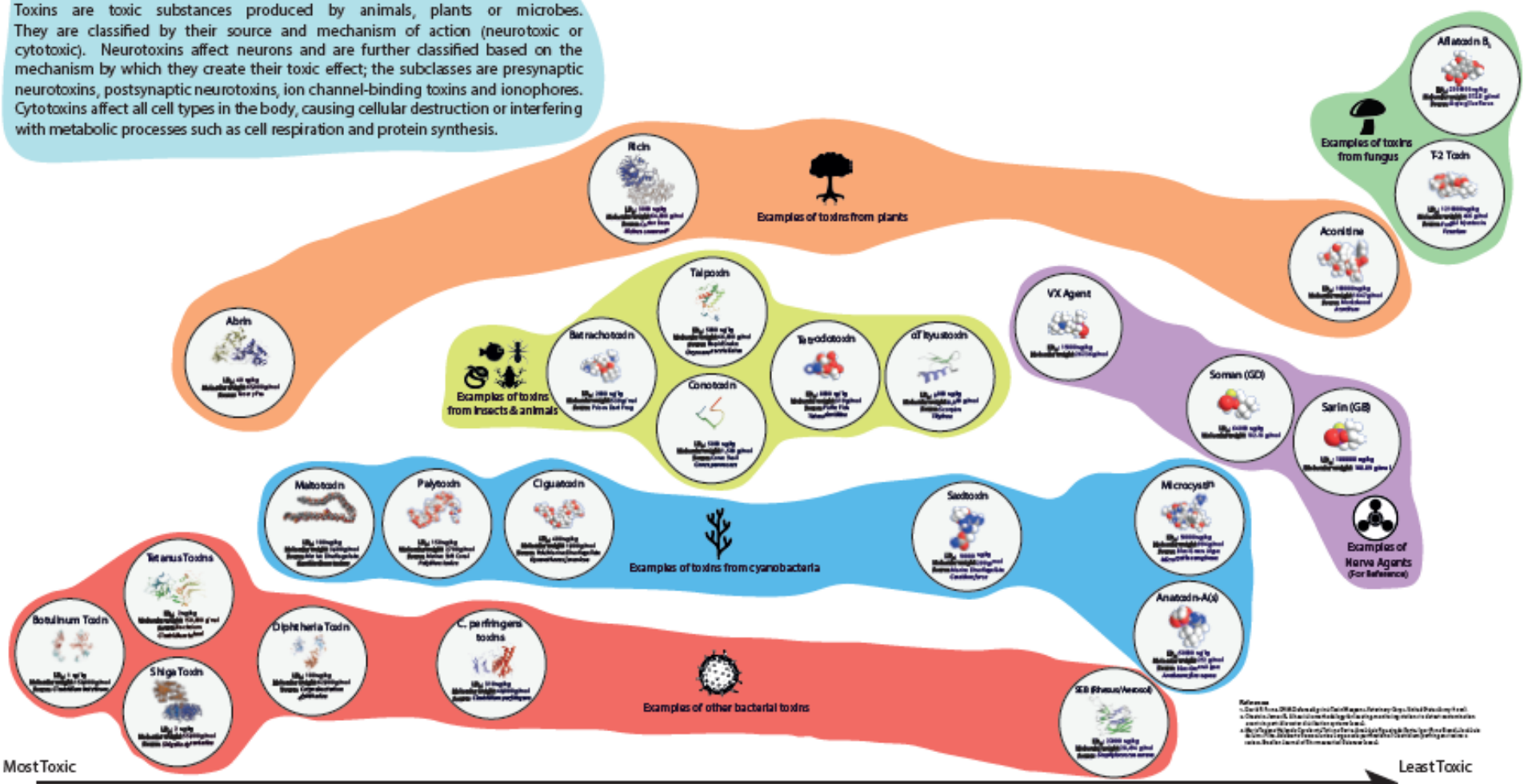
ORGANISATION FOR THE PROHIBITION OF CHEMICAL WEAPONS

Working Together for a World Free of Chemical Weapons

Biological Toxins and their Relative Toxicity

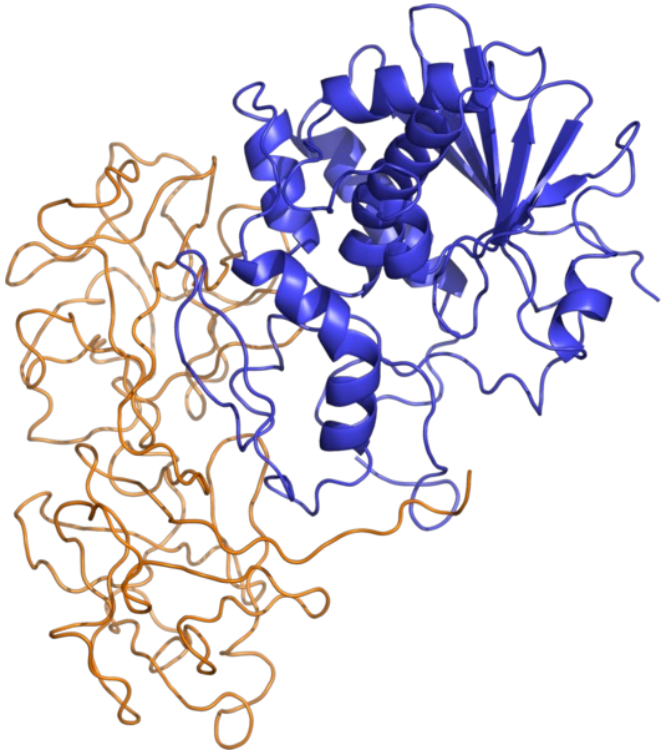
What are Toxins?

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, white powder
- Can be released into the air as a fine powder.
- Can contaminate water and food
- Symptoms arise after a few hours or days
- Can be extracted from castor beans
- Low thermal stability makes it useless in munitions.
- Ricin is listed as a Schedule 1 controlled substance in the CWC.



Ricin

- 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.)

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.

Ricin and the United States

- During World War I, the U.S. investigated ricin for its military potential as a toxic dust and as a coating for bullets and shrapnel.
  - The dust cloud concept could not be adequately developed, and the coated bullet/shrapnel concept would violate the Hague Convention of 1899, "...it is especially prohibited...[t]o employ poison or poisoned arms".
  - World War I ended before the U.S. weaponized ricin.
- During World War II, the US and Canada considered ricin to arm cluster bombs.
  - Conclusion - it was no more economical than using phosgene.
  - Interest in ricin stopped when the U.S. Army Chemical Corps began a program to weaponize sarin.

Ricin and the Soviet Union

- The Soviet Union possessed ricin.
- Georgi Ivanov Markov - Bulgarian dissident writer
  - 1969 - defected from Bulgaria
  - Broadcaster and journalist for the BBC World Service, the US-funded Radio Free Europe, and Germany's Deutsche Welle.
  - Criticized the Bulgarian regime.
  - Died in London when a pellet containing ricin was fired by compressed gas into his leg from an umbrella wielded by someone associated with the Bulgarian secret police.
  - It is believed that the Soviet KGB supplied the ricin pellet.

Ricin as Chemical Weapon

- Ian Davison, a British white supremacist and neo-Nazi, was arrested in 2009 for planning terrorist attacks involving ricin.
- In 2011 the United States government discovered information that terrorist groups were attempting to obtain large amounts of castor beans for weaponized ricin use.

  Eric Schmitt and Thom Shanker (2011-08-13). "Al Qaeda trying to harness toxin for bombs, U.S. officials fear". The New York Times.

- On November 1, 2011, the FBI arrested four North Georgia men and charged them in plots to manufacture ricin from castor beans to assassinate state officials.

http://www.fbi.gov/atlanta/press-releases/2011/north-georgia-men-arrested-charged-in-plots-to-purchase-explosives-silencer-and-to-manufacture-a-biological-toxin

Ricin as Chemical Weapon

- According to a NY Times report, Al-Qaida's Yemeni branch is trying to stockpile the lethal toxin ricin for aerial dispersal in the United States.
  - U.S. insiders said they saw no signs of an impending ricin strike.
  - Yemen's climate is not conducive to ricin retaining its potency

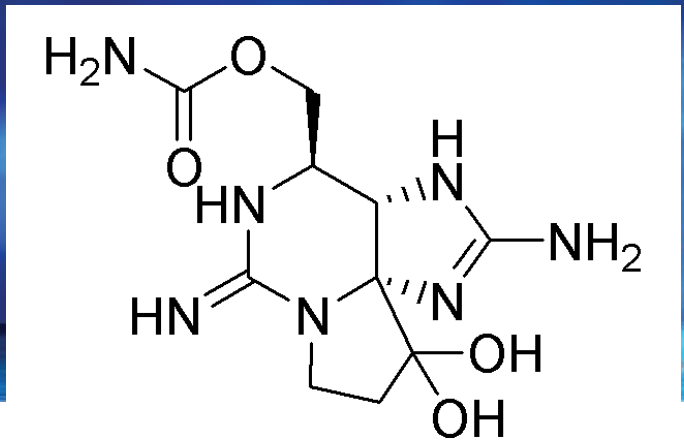
http://www.nytimes.com/2011/08/13/world/middleeast/13terror.html?pagewanted=all&_r=0

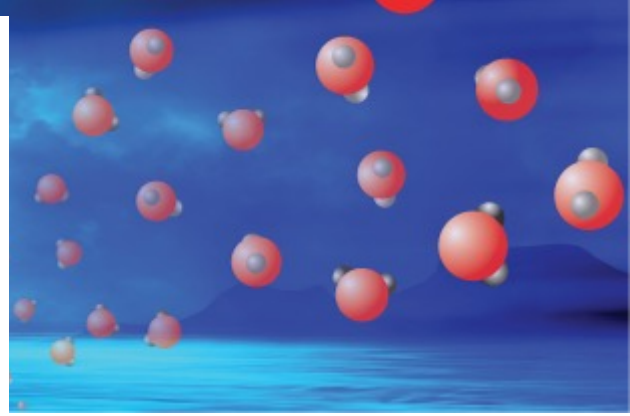
Ricin and ISIS

- Some indications that ISIS has pursued the production of ricin.
- *"The laptop of Muhammed S., a Tunisian chemistry and physics student who joined the Islamic State, contains an eclectic mix of speeches by jihadi leaders, neo-Nazi screeds, and U.S. Army manuals on specific aspects of warfare".*
- *Includes "…instructions for how to obtain the deadly toxin ricin from castor beans."*

http://foreignpolicy.com/2014/09/09/recipes-from-the-islamic-states-laptop-of-doom/

Saxitoxin





- **Saxitoxin** (**STX**) is the most well-known paralytic shellfish toxin (PST)
- STX has been found in at least 12 marine puffer fish species.
- Saxitoxin is a neurotoxin that acts as a selective sodium channel blocker. It acts on the voltage-gated sodium channels of nerve cells, preventing normal cellular function and leading to paralysis.
- Can potentially be produced in a chemical laboratory.
- The oral LD_{50} for humans is 5.7 µg/kg, therefore approximately 0.5 mg of saxitoxin is lethal if ingested and the lethal dose by injection is about one-tenth of the oral dose.

http://en.wikipedia.org/wiki/Saxitoxin

Saxitoxin

- Saxitoxin is about 1,000 times more toxic than the nerve agent sarin.
- The United States military isolated saxitoxin and assigned it the chemical weapon designation TZ.
- U-2 pilot Francis Gary Powers was issued with a hollow silver dollar containing a tiny, saxitoxin-impregnated needle, to be used to commit suicide in case of capture by enemy forces.
- Saxitoxin is listed in Schedule 1 of the CWC.
- Although there are other ways to obtain saxitoxin, it takes 8 tons of clams to extract 1 gram of toxin.

http://en.wikipedia.org/wiki/Saxitoxin

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

U.S. Chemical Warfare Service (CWS)

- Formed in 1918
- Headquartered at Edgewood Arsenal in Maryland
- 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

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.

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.

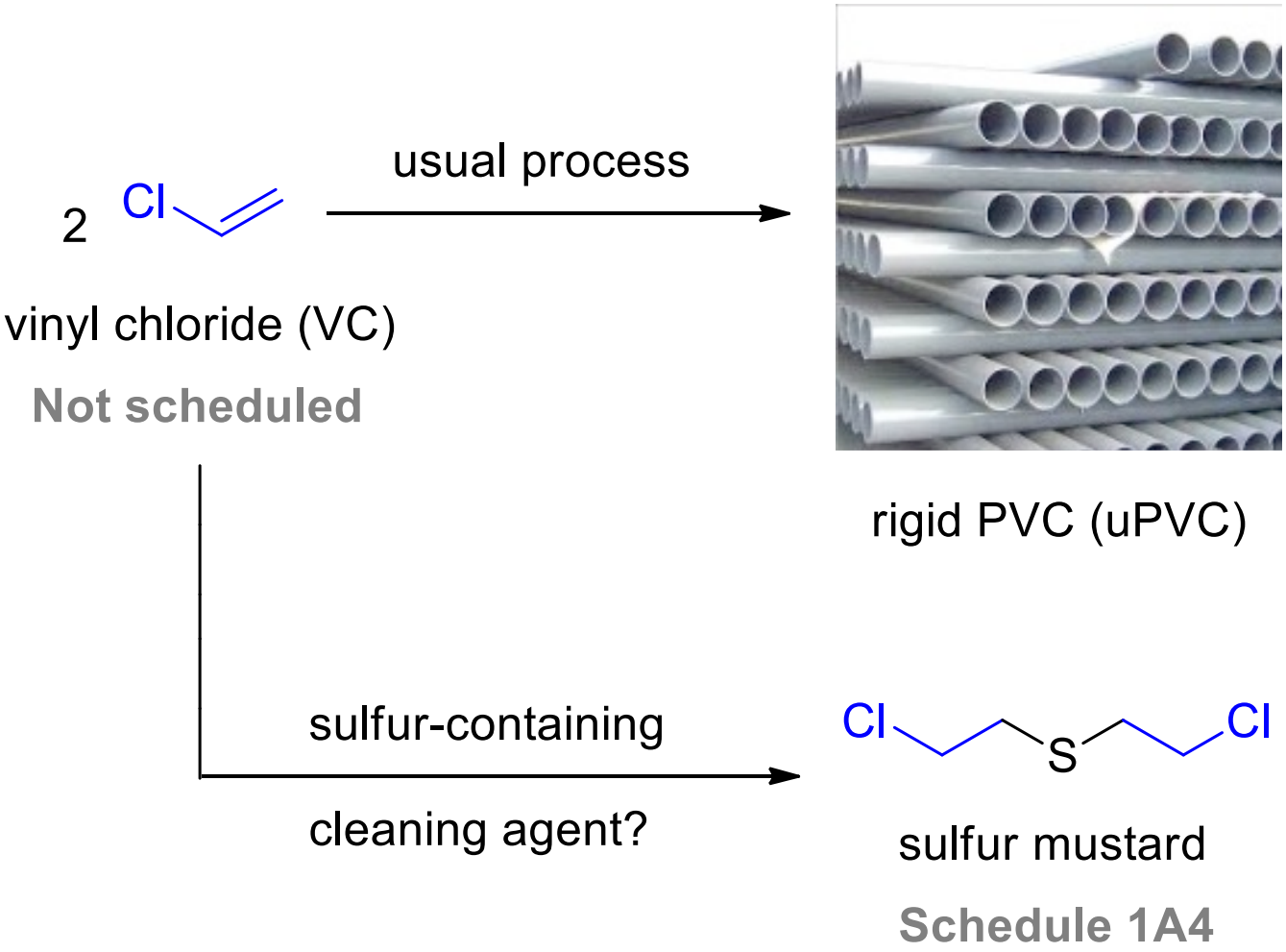
http://www.cwc.gov/index_chemicals_sch1.html

Unintended By-products

- An unintended by-product is a Schedule 1 or 2 chemical formed unintentionally during a sequence of planned chemical reactions.
- An accident involving the formation of the Schedule 1 chemical agent sulfur mustard occurred during cleaning of an industrial plant that manufactured polyvinylchloride (PVC) pipes.

C Curty, J Ducry, S Mogl. Schedule 1 chemicals as captive intermediates or unavoidable by-products in chemical production: technical feasibility assessment based on literature review, LN 2013-01-CC, Spiez Laboratory, Switzerland, 2013

Unintended Schedule 1 Production



- Employees experienced skin blistering, burns and respiratory problems

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

Schedule 1 Captive Intermediate in Production of a Pharmaceutical

- Some Schedule 1 chemicals are intermediates in reactions sequences for making other non-schedule chemicals.
- HN2 can be used to make ketobemidone, a pain-killer for children with cancer who are allergic to morphine.

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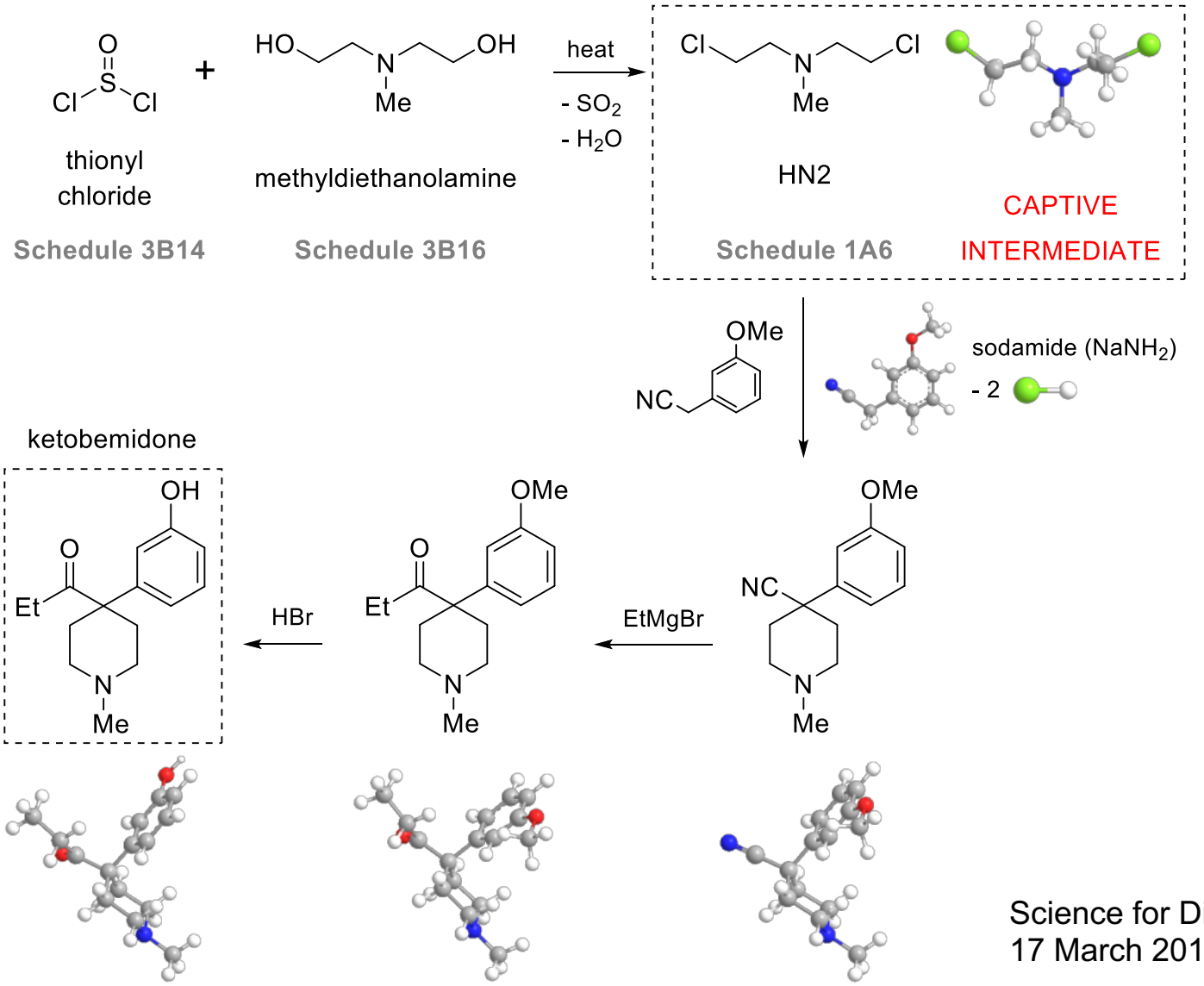
Schedule 1 Captive Intermediate in Production of a Pharmaceutical



Science for Diplomats
17 March 2015

Schedule 1 Captive Intermediate in Production of a Pharmaceutical

- ‘is understood for declaration purposes to include intermediates, by-products, or waste products that are ***produced and consumed*** within a defined chemical manufacturing sequence, where such products are chemically stable and therefore exist for a ***sufficient time*** to make isolation from the manufacturing stream possible, but where, under normal design or operating conditions, isolation does not occur’

Decision of OPCW CSP (C-10/DEC.12 dated 10 November 2005)

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Unintended Schedule 1 Production

- Very few examples of captive use or production as a by-product of Schedule 1 chemicals have been officially reported.
- Alternative synthetic methods can be found to avoid this problem.

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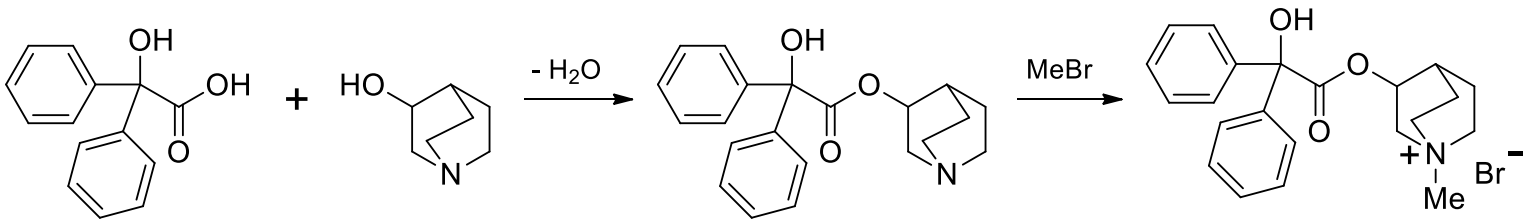
www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the_OPCW_2014_2015.pdf

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

BZ as a Captive Intermediate

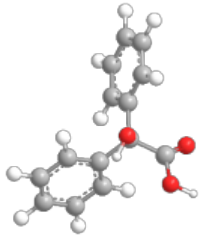


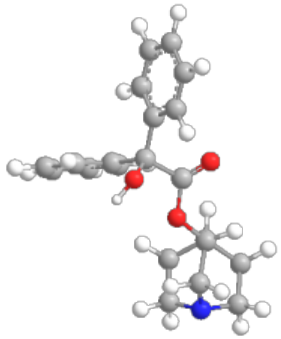
2,2-Diphenyl-2-hydroxyacetic acid

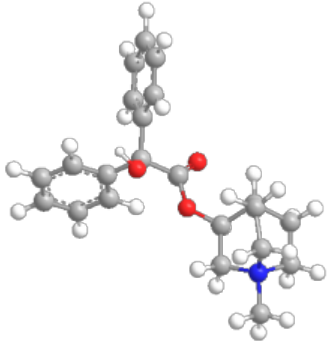
Quinuclidin-3-ol

3-Quinuclidinyl benzilate (BZ)

Clinidium bromide (pharmaceutical)







Schedule 2B8

Schedule 2B9

Schedule 2A3

Not scheduled

Clinidium bromide (Librax®) is used to treat irritable bowel syndrome

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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

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ENVIRONMENTAL SAMPLING

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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
- Report results

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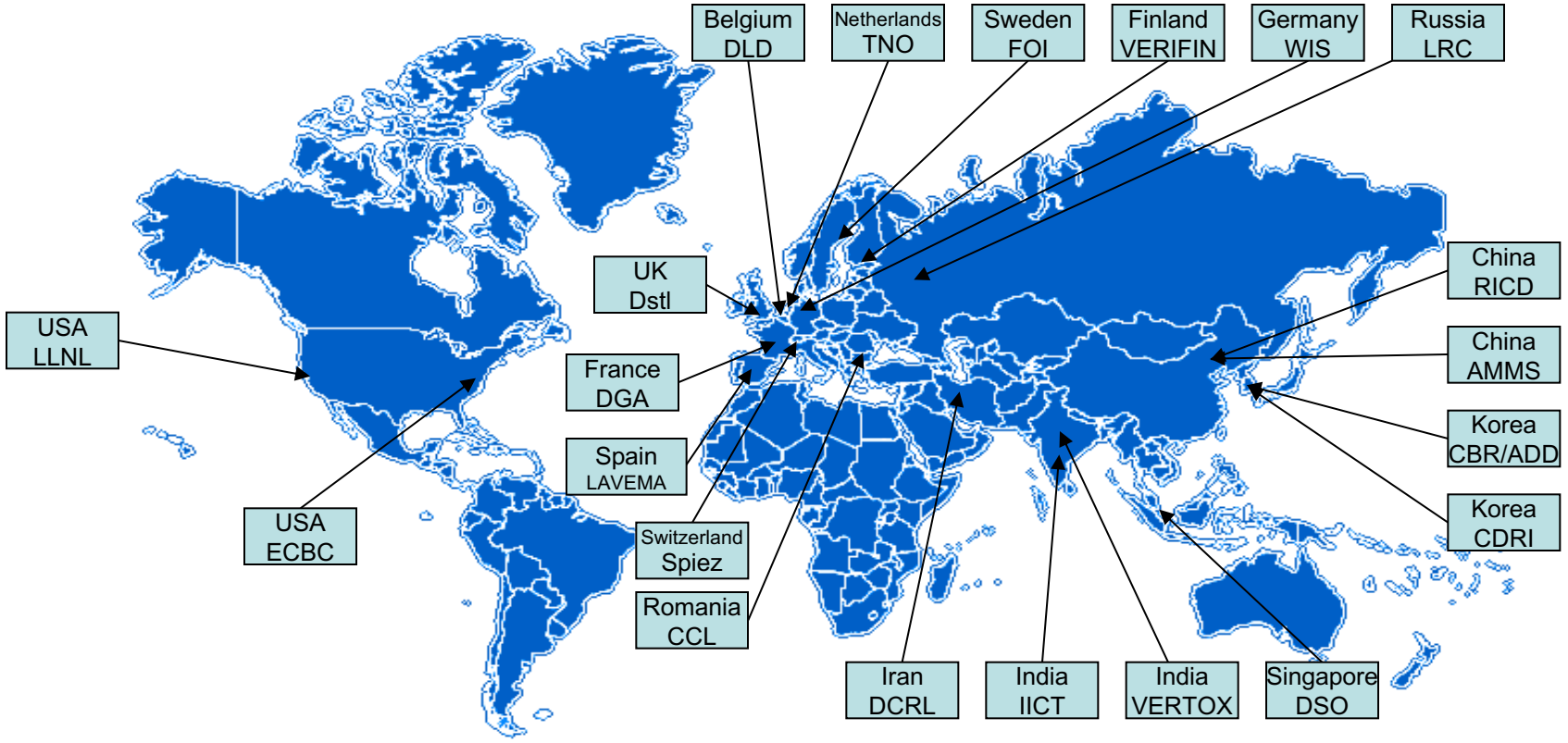
OPCW Designated Laboratories (as of May 2014)



21 Designated Laboratories in 17 countries

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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

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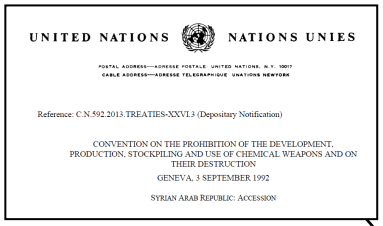
Timeline

UN Mission Team Arrives in Syria

Ghouta incident

US-Russia Framework Agreement and Syria Accession



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Reference: C.N.592.2013.TREATIES-XXVI.3 (Depositary Notification)

CONVENTION ON THE PROHIBITION OF THE DEVELOPMENT, PRODUCTION, STOCKPILING AND USE OF CHEMICAL WEAPONS AND ON THEIR DESTRUCTION
GENEVA, 3 SEPTEMBER 1992

SYRIAN ARAB REPUBLIC: ACCESSION

Interim UNSG report released

Syria CW disclosure

August 2013

18 21 26 - 29 30

September 2013

2 4 8 - 10 14 15 16 19 27 25 - 29

Ghouta

Environmental and biomedical samples collected

Samples received at OPCW Lab

Preliminary results *Sarin!*

Report delivered to UNSG

Additional biomedical samples collected

Samples received at four Designated Labs

Speiz Lab 2013 Annual Report describes testing 49 samples with > 1000 man hours

www.labor-spiez.ch/en/dok/ge/pdf/88_003_e_laborspiez_jahresbericht_2013_web.pdf

Slide courtesy of Jonathan Forman – OPCW Science Policy Adviser and Secretary to the Scientific Advisory Board

Timeline

- 21 August: the attack
- 26, 28, 29 August: Samples collected
- 30 August (late): Samples received at OPCW Laboratory
- 2 & 4 September: Samples dispatch to Designated Laboratories
- 8-10 September: Preliminary summary analysis reports from the 4 labs were received by the UN team
- 13 September: The UN team report was transmitted to the Secretary-General of the United Nations
- Conclusion: Sarin was used in the attack

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Timeline

Destruction of equipment commences

OPCW-UN Joint Mission announced
http://opcw.unmissions.org/

First shipment of chemicals leaves Syria

Destruction plan submitted

Additional disclosures

October 2013

Syria 190th State Party

Functional destruction complete

22/23 CW sites verified

Unfilled munitions destroyed

January 2014

November 2013

December 2013

1 3 4 6 14 16 22 23 31 6 15 6 12 17 7

18/23 sites verified

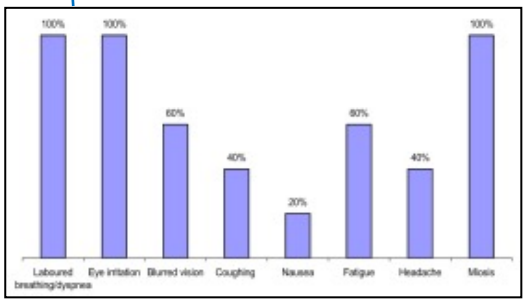
Declaration under CWC Article III

Additional samples sent for analysis

Advance team arrives

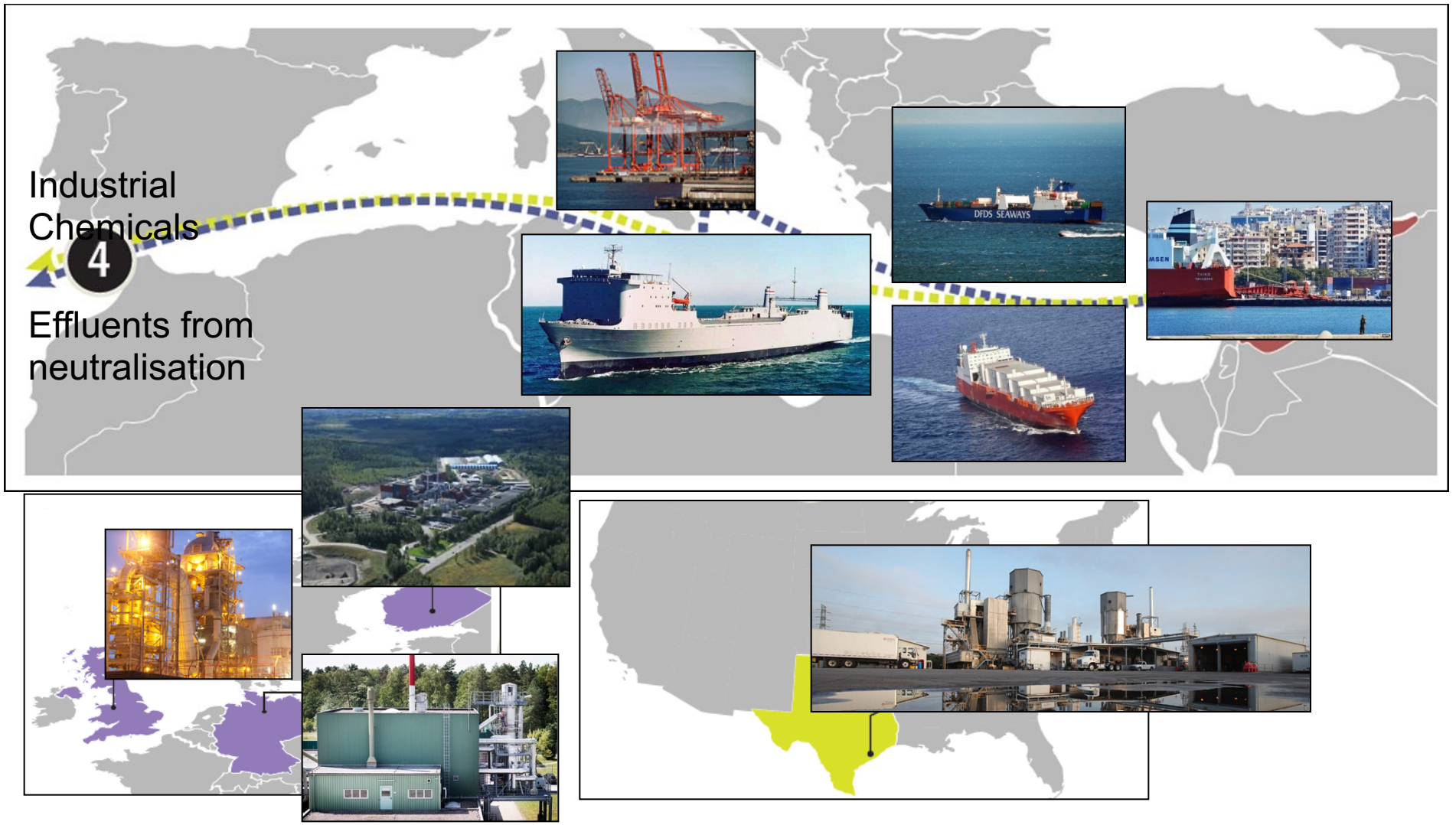
Decision on destruction adopted

Final UNSG Report released



Slide courtesy of Jonathan Forman – OPCW Science Policy Adviser and Secretary to the Scientific Advisory Board

Removal and Destruction of Syrian Chemical Weapons

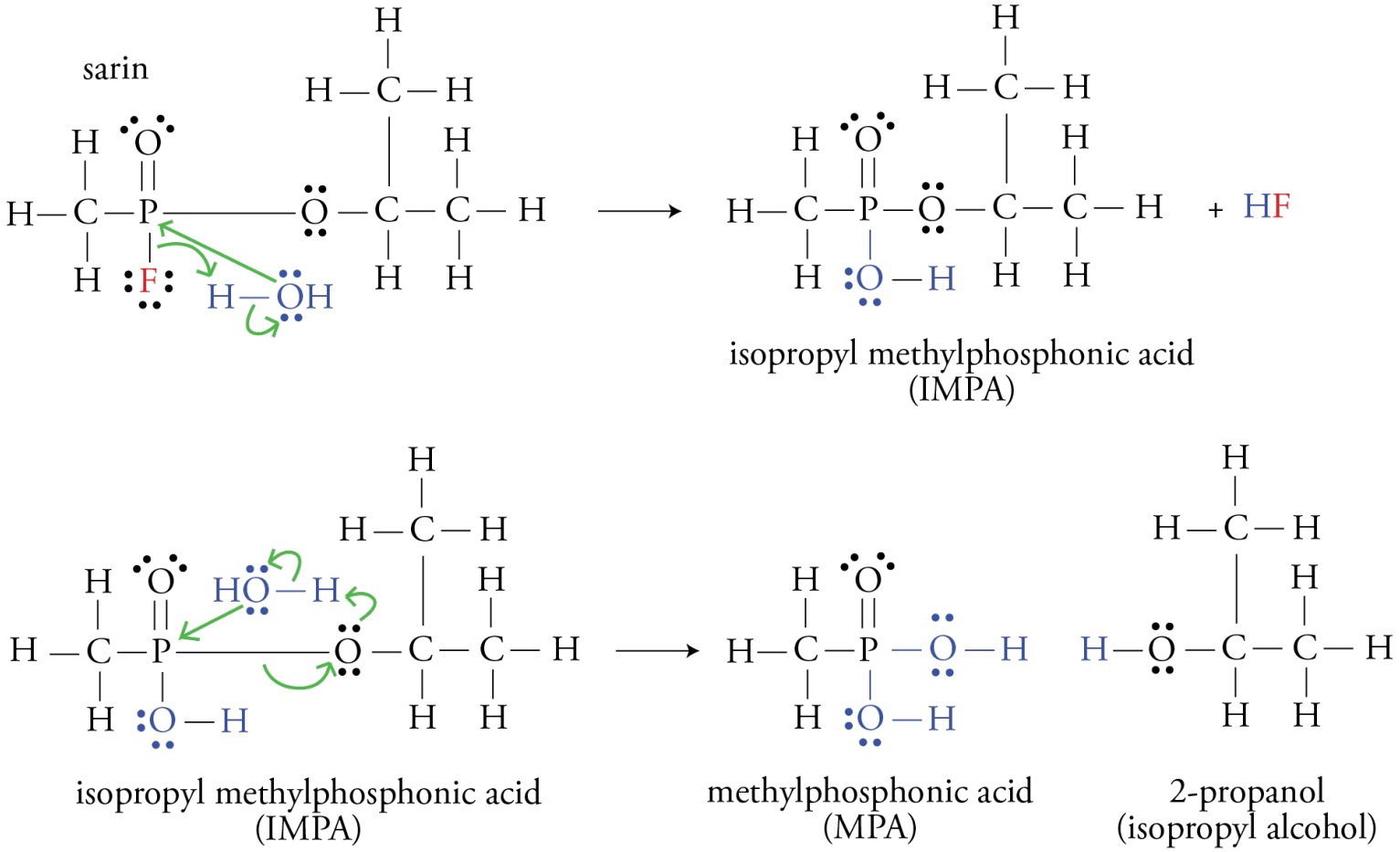


As of 23 June 2014, all declared chemicals had been removed from The Syrian Arab Republic

Slide courtesy of Jonathan Forman – OPCW Science Policy Adviser and Secretary to the Scientific Advisory Board

Hydrolysis of Sarin

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



Detection of Sarin Use

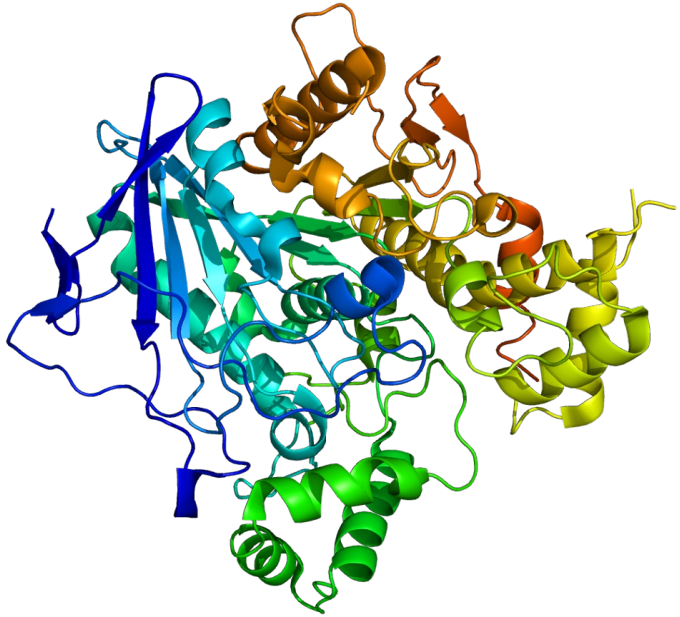
- The product of the first step in the hydrolysis of sarin, isopropyl methylphosphonic acid (IMPA), is a chemical that is not commonly found in nature, so if it is found at the site of a chemical weapons attack, it's an indication of the use of sarin.
- IMPA was detected in 20 of 42 reported environmental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

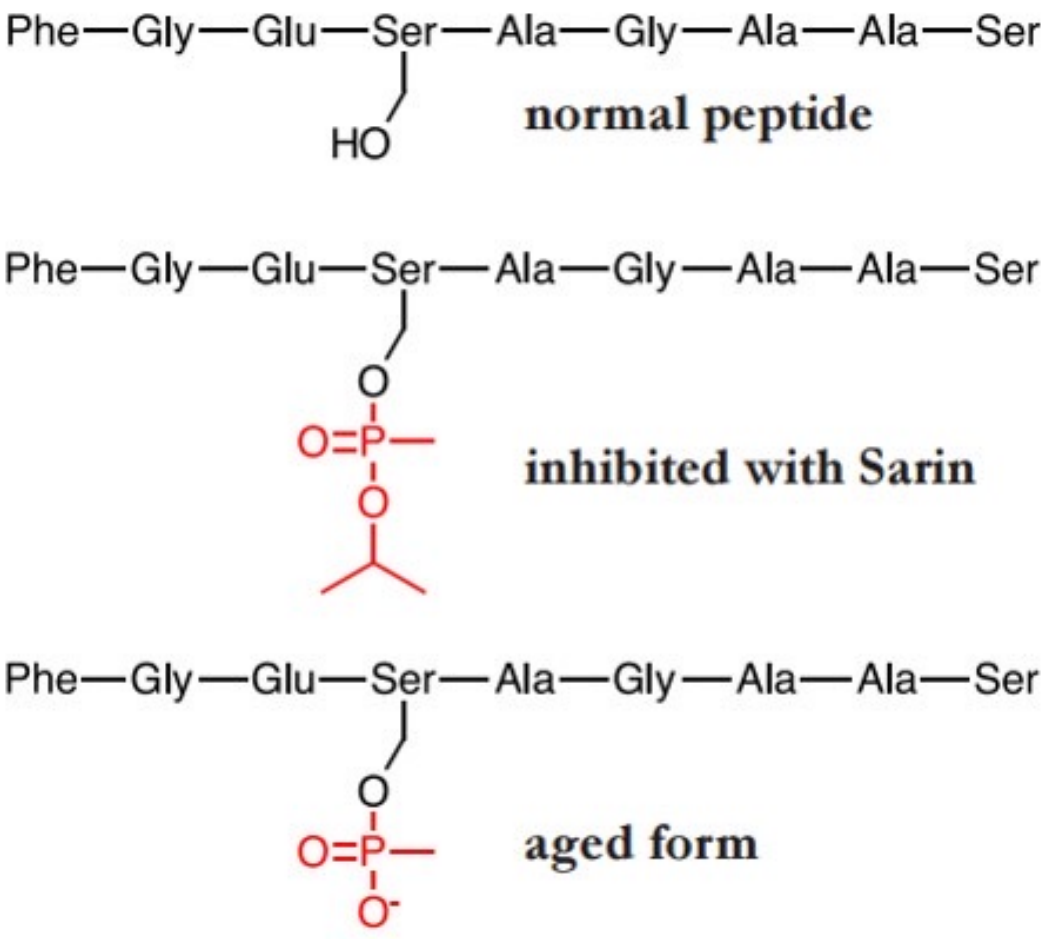
Butylcholinesterase (BChE)

- 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?

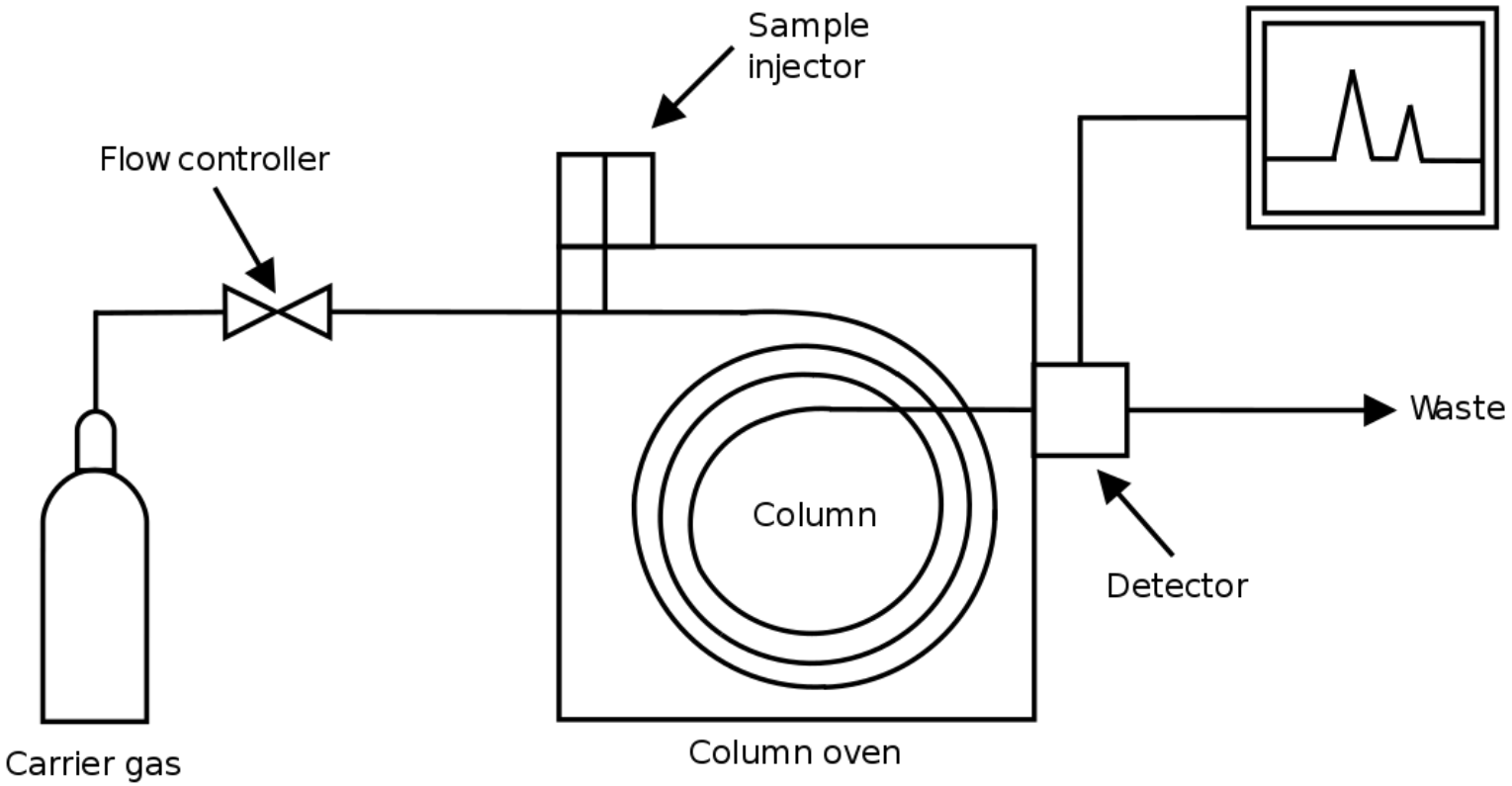
(1) Autosampler:
Injects a small amount (1 µL) of sample into the Gas Chromatograph

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

(3) Mass Spectrometer:
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

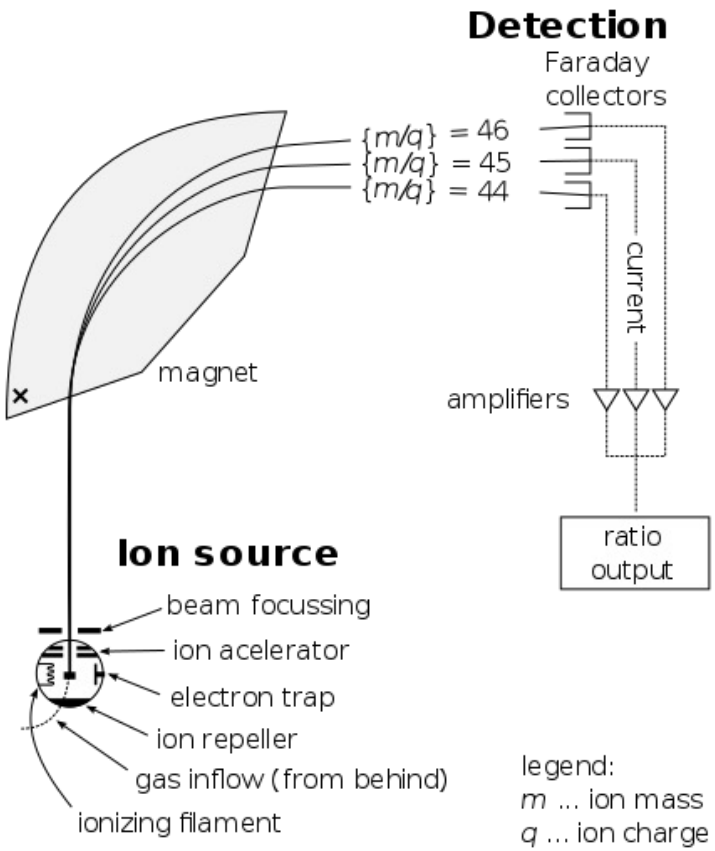
Gas Chromatograph



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

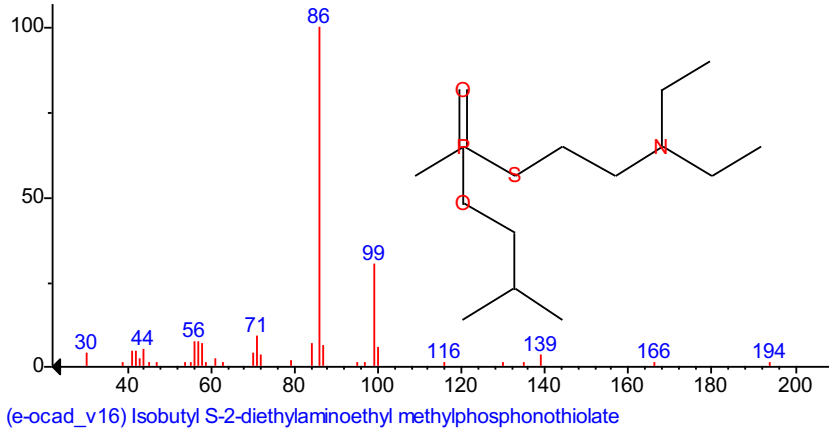
Mass Spectrometer



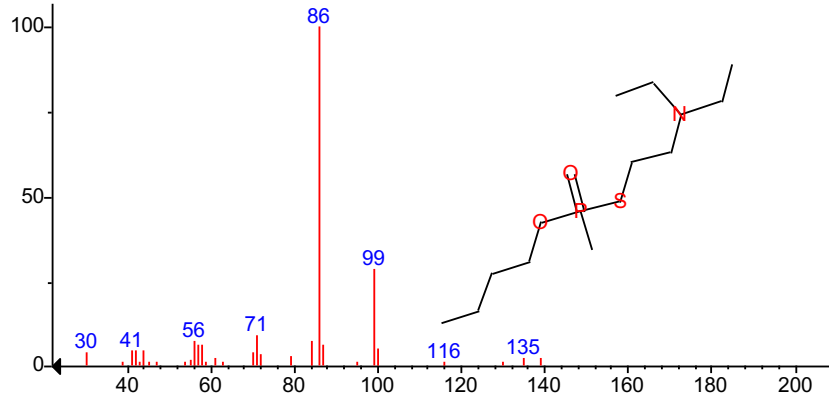
Mass Spectrometer

- Substance 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

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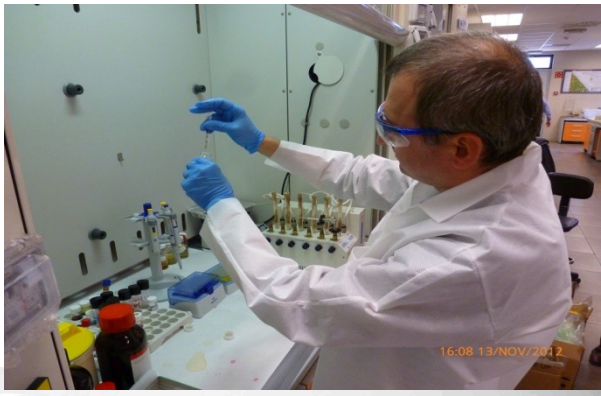
Transportable Agilent GC/MS

- Research grade
- Very low detection limits
- Analysis of wide range of chemicals
- Cons:
  - Bulky equipment
  - Lengthy setup time
  - Sample prep time



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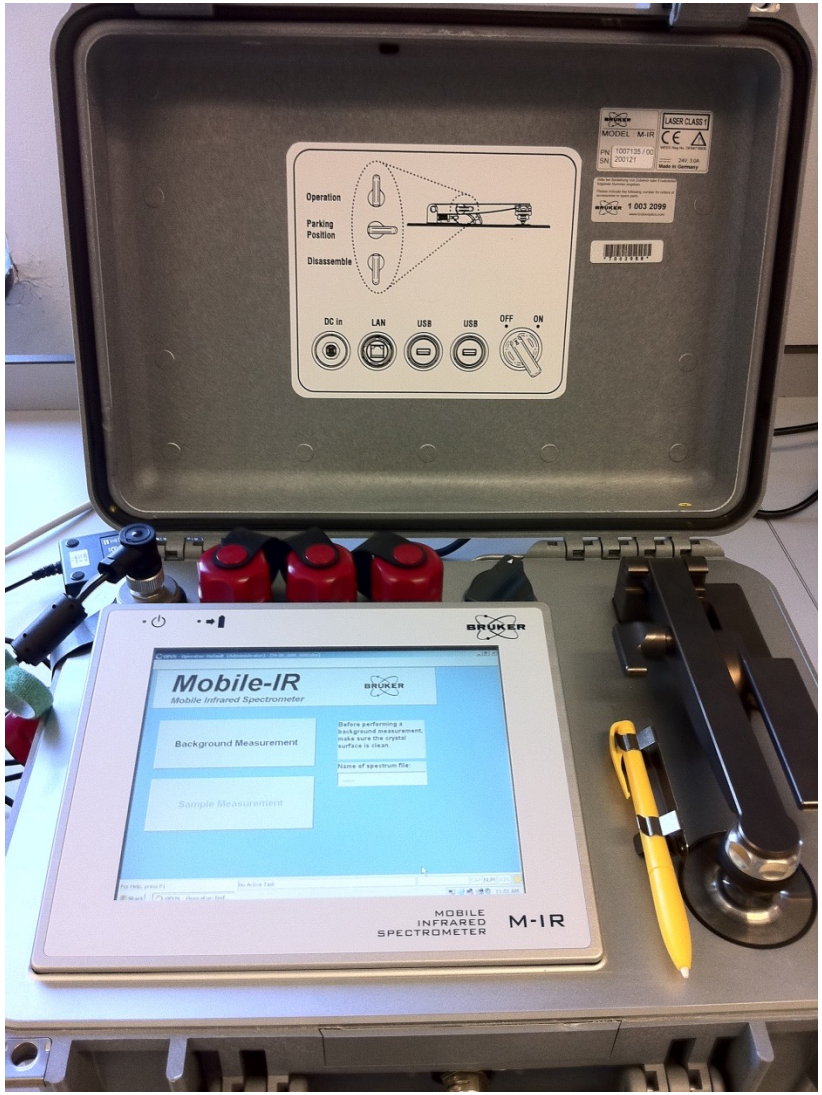
www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the_OPCW_2014_2015.pdf

Bruker Mobile FT-IR

- Attenuated total reflectance fourier transform infrared spectroscopy (ATR FT-IR)
- No sample prep
- Fast analysis
- Portable
- Easy use
- Cons:
  - Not as sensitive as GC/MS
  - Works best with pure chemicals



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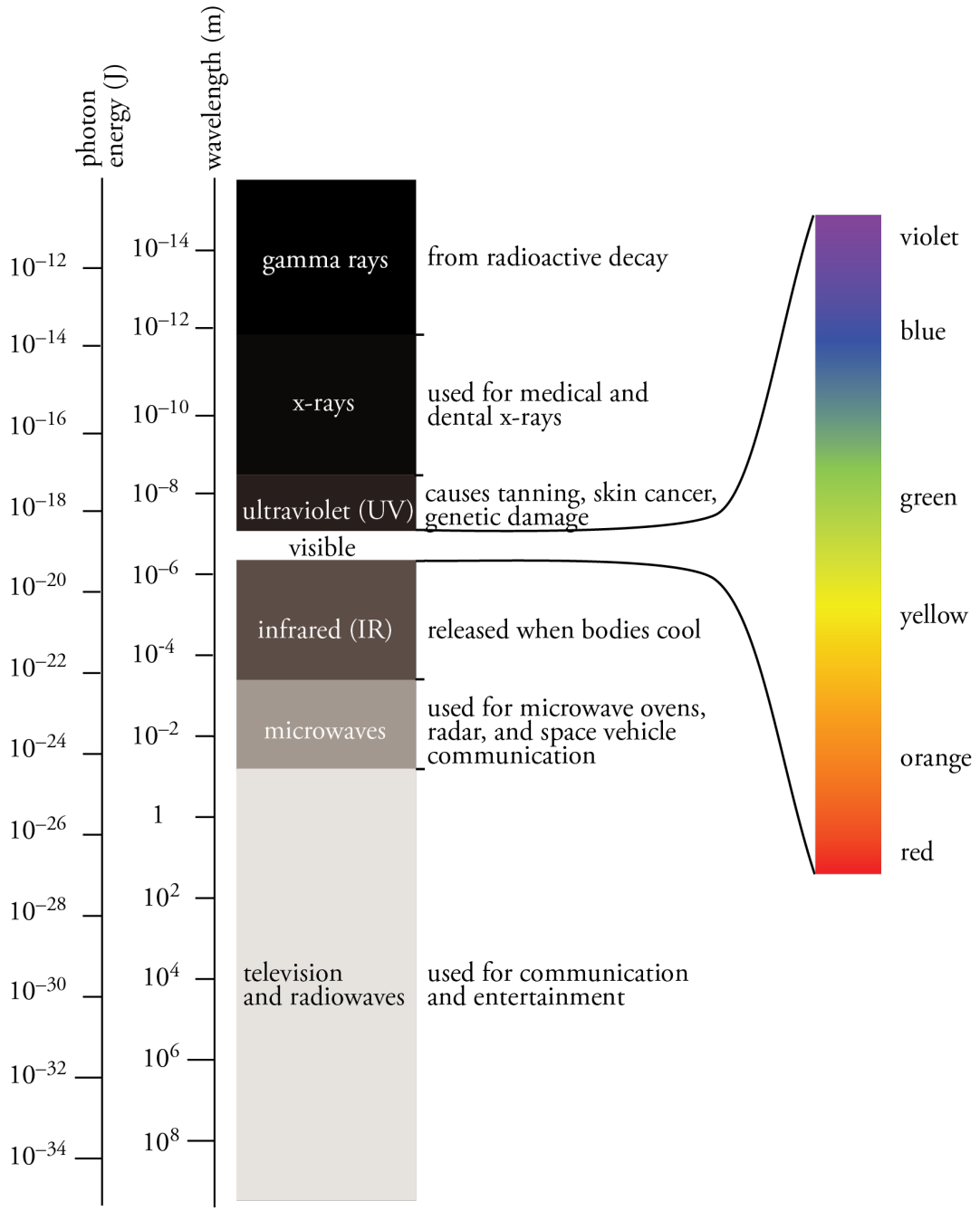
www.opcw.org/fileadmin/OPCW/Science_Technology/Diplomats_Programme/Science_for_Diplomats_at_the_OPCW_2014_2015.pdf

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.

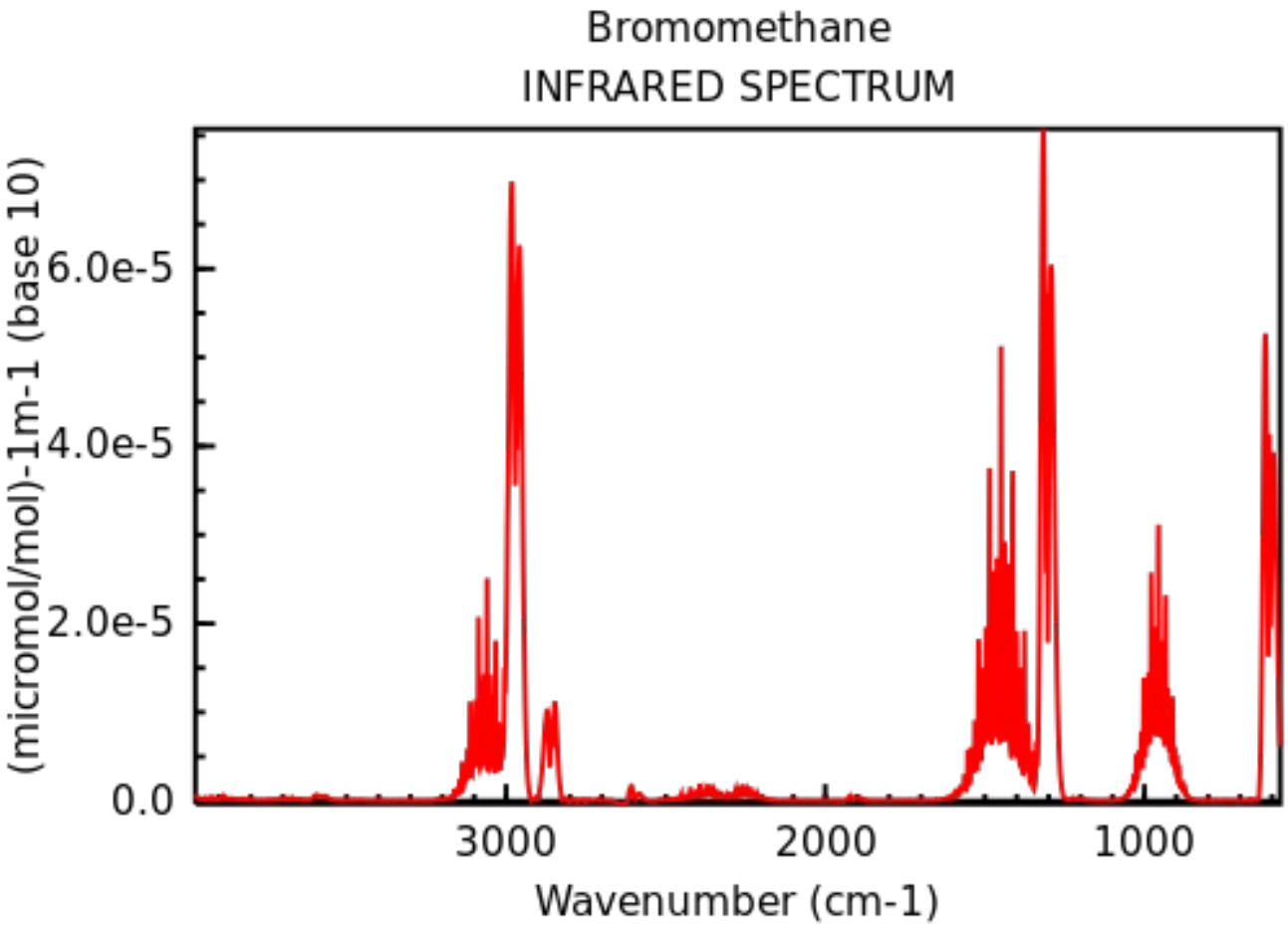


Infrared (IR) Radiation and Vibrations and Rotations

- 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 states 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.

http://www2.ess.ucla.edu/~schauble/MoleculeHTML/CO2_html/CO2_page.html

IR Spectrum


Bromomethane
INFRARED SPECTRUM
(micromol/mol)-1m-1 (base 10)
6.0e-5
4.0e-5
2.0e-5
0.0
3000
2000
1000
Wavenumber (cm-1)
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Greenhouse Gases and Global Warming

- As the Earth cools, it emits infrared (IR) photons.
- When a greenhouse gas molecule absorbs an IR photon, the molecule gets excited to a higher vibrational energy.
- When the molecule returns to a more stable vibrational energy, it emits an IR photon in a random direction.
- Some of the remitted photons return to Earth.

http://www2.ess.ucla.edu/~schauble/MoleculeHTML/CO2_html/CO2_page.html

http://www2.ess.ucla.edu/~schauble/MoleculeHTML/CH4_html/CH4_page.html

Thermo Hand-held FT-IR

- Attenuated total reflectance fourier transform infrared spectroscopy (ATR FT-IR)
- No sample prep
- Fast analysis
- Portable
- Easy use
- Cons:
  - Not as sensitive as GC/MS
  - Works best with pure chemicals

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

Thermo hand-held Raman

- Laser driven Raman Spectroscopy
- Analysis through glass!
- No sample prep
- Fast analysis
- Portable
- Easy use
- Cons:
  - Not as sensitive as GC/MS
  - Works best with pure chemicals

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

Hapsite Mobile GC/MS

- Minimal sample prep
- Relatively fast analysis
- Portable
- Easy use
- Cons:
  - Not as “full-range” as research grade GC/MS
  - Battery change every 3 hours

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

Test Kits for “Problematic” Scheduled Chemicals

- Ricin is a protein that cannot be analyzed by GC/MS
- Saxitoxin, due to its chemical nature, cannot be analyzed by GC/MS
- Test kits similar to pregnancy test kits
- Relatively fast analysis (20 min)
- Portable, easy use
- Cons:
  - Need different kit for Ricin and Saxitoxin
  - Single use kits
  - Kits expire in 2 years

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 Member State Obligations

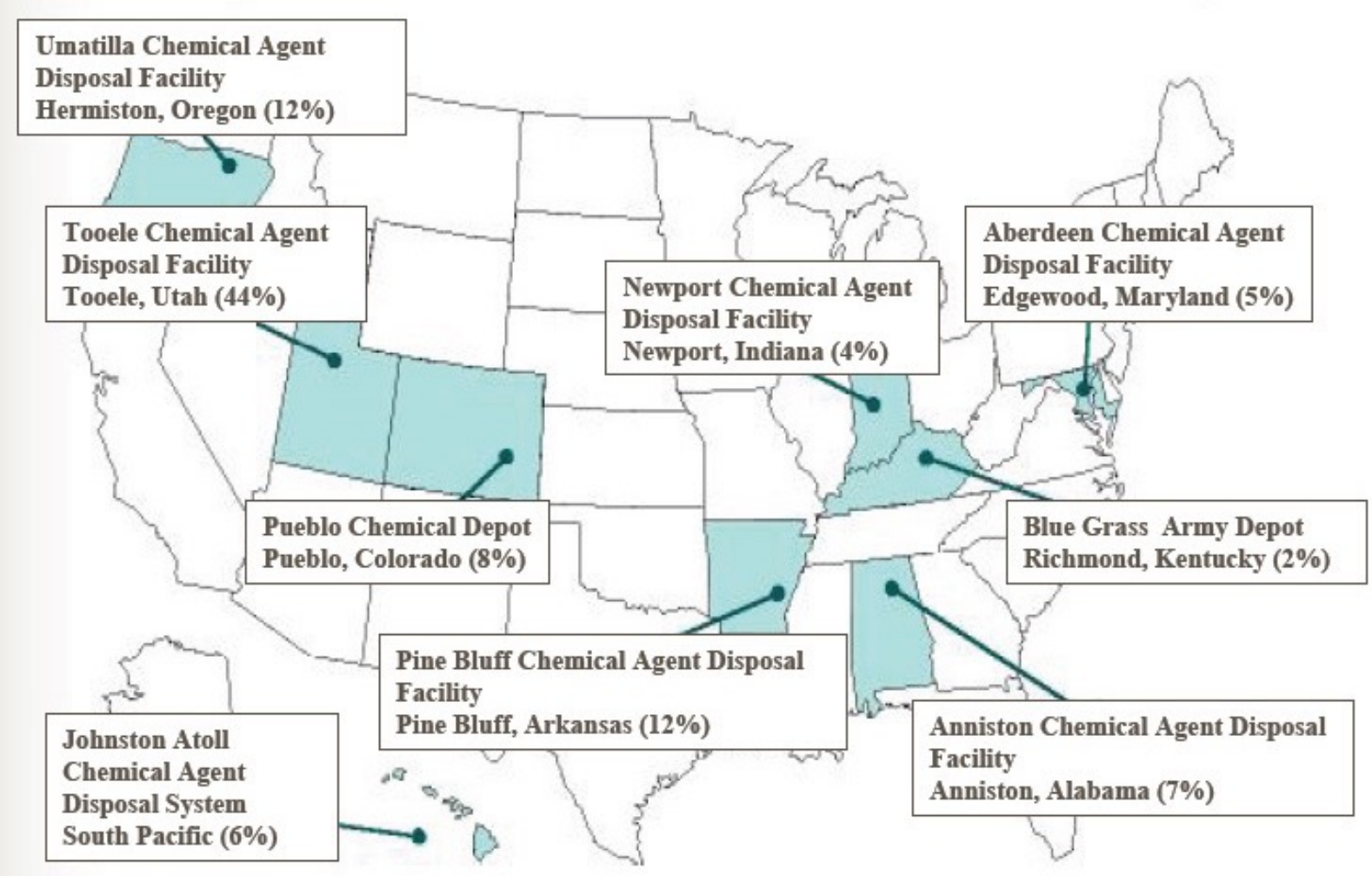
- *Each country that belongs to the OPCW must:*
  - *destroy all chemical weapons it owns or possesses;*
  - *destroy all chemical weapons it may have abandoned in another country; and*
  - *destroy facilities it owns or possesses which were involved in the production of chemical weapons.*

https://www.opcw.org/our-work/demilitarisation/destruction-of-chemical-weapons/

Three Ways of Disposing of Chemical Weapons

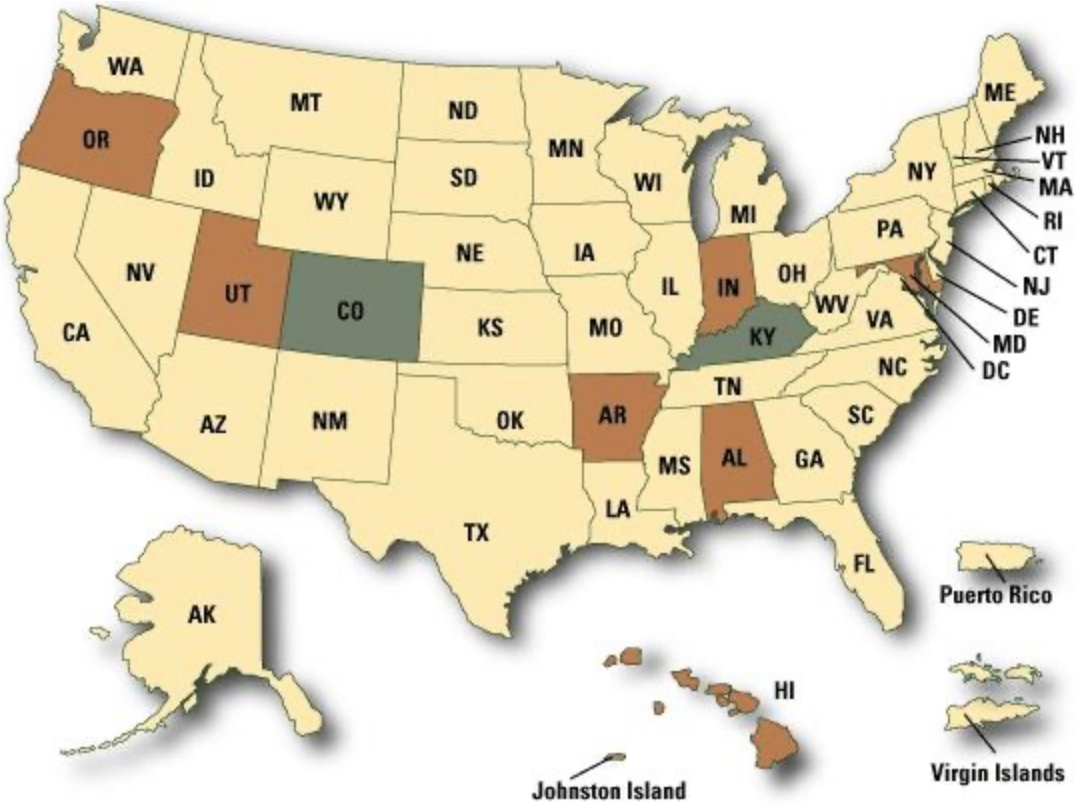
- Ocean dumping (no longer done)
- Incineration
- Hydrolysis (chemical neutralization) followed by various further treatments (now favored)

United States CW Disposal Facilities



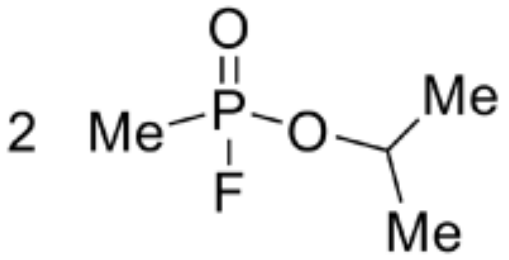
Status of CW Disposal Facilities

Green - States that until recently had Chemical Weapons Stockpiles
Yellow - States and Regions without Chemical Weapons Stockpiles
Brown - States and Regions that had Chemical Weapons Stockpiles



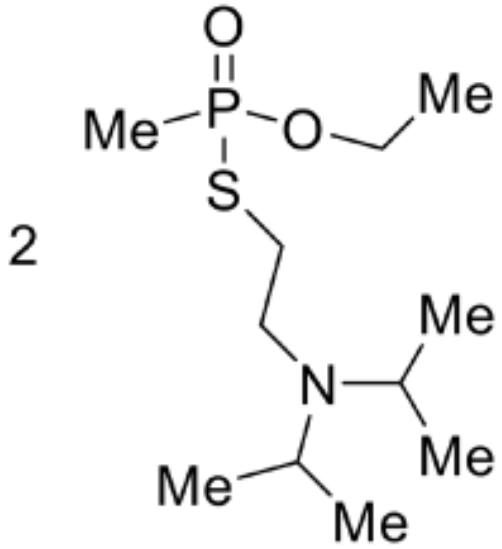
http://www.cma.army.mil/map.aspx

Incineration of Sarin and VX



GB (Sarin)

$$\xrightarrow[1480\ ^{o}C]{13\ O_2} P_2O_5 + 8\ CO_2 + 9\ H_2O + 2\ HF$$

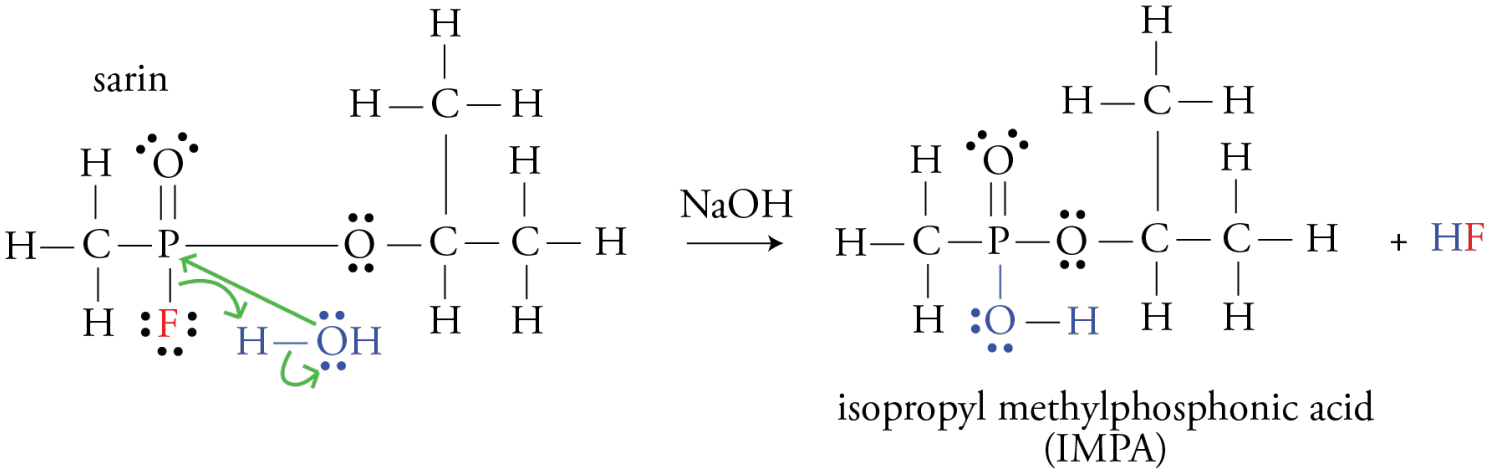


VX

$$\xrightarrow[1480\ ^{o}C]{38.5\ O_2} P_2O_5 + 22\ CO_2 + 26\ H_2O + 2\ SO_2 + 2\ NO$$

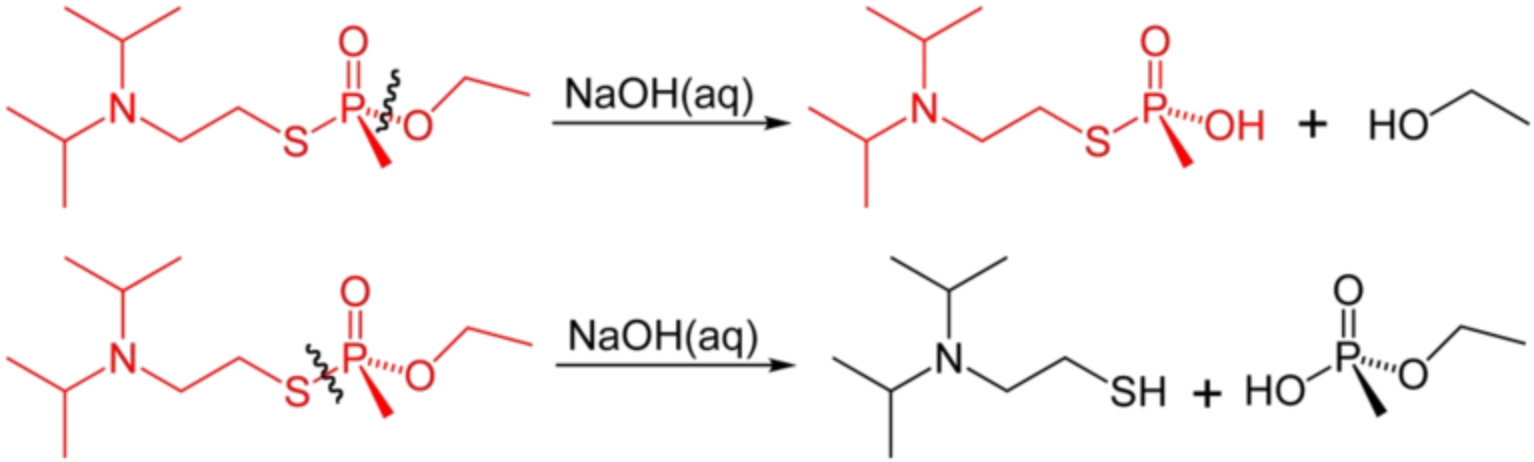
Hydrolysis of Sarin

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.

Destruction of U.S. Chemical Weapons

- Blue Grass Army Depot - Richmond, Kentucky
  - As of 7/7/23, all of the 523.4 tons of nerve agents (sarin and VX) and mustard agent in projectiles, warheads, and rockets were destroyed by hydrolysis followed by supercritical water oxidation.

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

https://www.peoacwa.army.mil/bgcapp/

Large cylindrical containers that prevent any leakage from escaping into the atmosphere are used to move chemical weapons from storage bunkers to processing facilities.

Credit...Kenny Holston/The New York Times

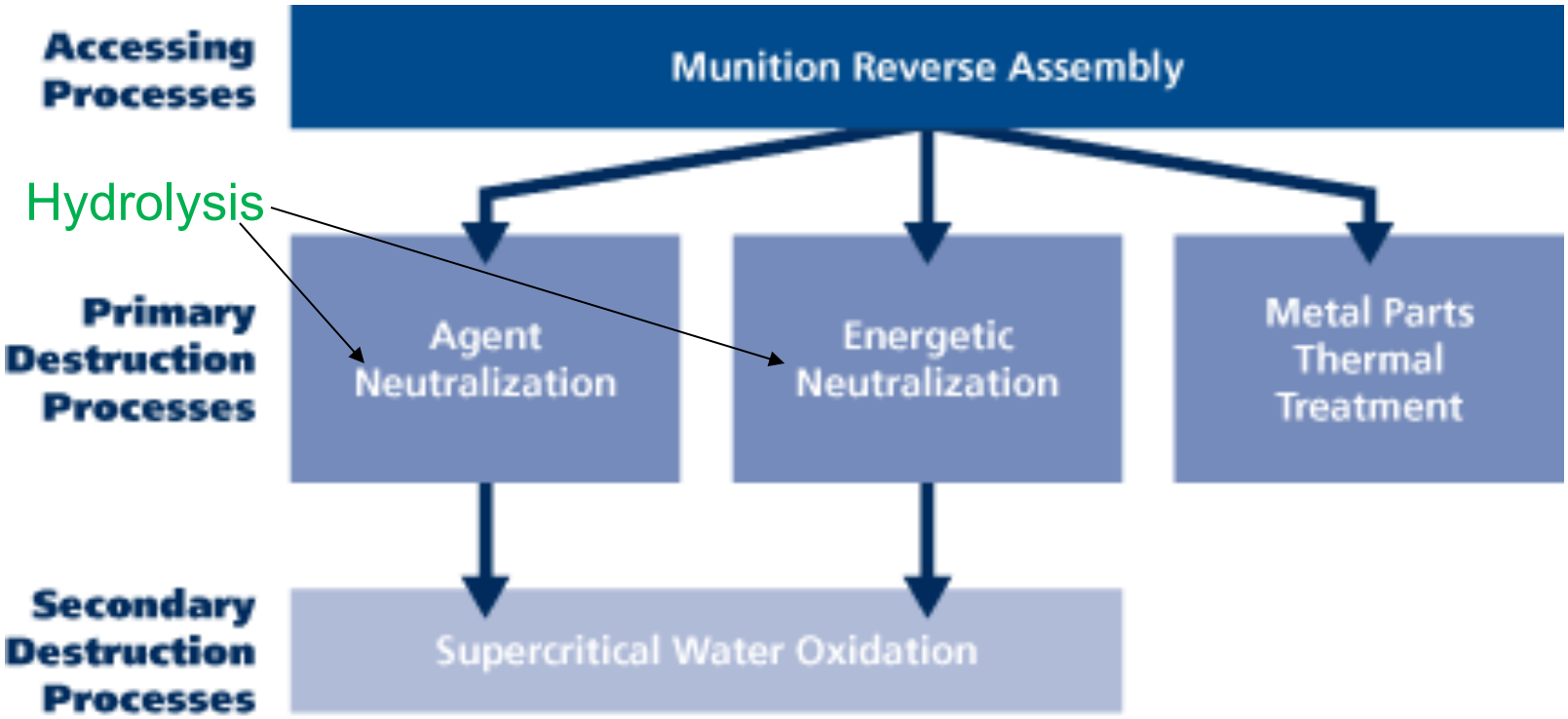
Before processing, chemical munitions, many of them over 50 years old, are X-rayed to determine whether they are leaking.

Credit...Kenny Holston/The New York Times

Among the final munitions to be destroyed at the Blue Grass facility were M55 rockets that contained Sarin, a lethal nerve agent.

Credit...Kenny Holston/The New York Times

Destruction of U.S. Chemical Weapons



Destruction of U.S. Chemical Weapons

- 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/

Destruction of U.S. Chemical Weapons

- Pueblo, Colorado
  - All of the 2613.2 tons of mustard agent in approximately 780,000 munitions was destroyed by neutralization (hydrolysis).
  - Started March 2015, finished 6/22/23

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

https://www.peoacwa.army.mil/pcapp/

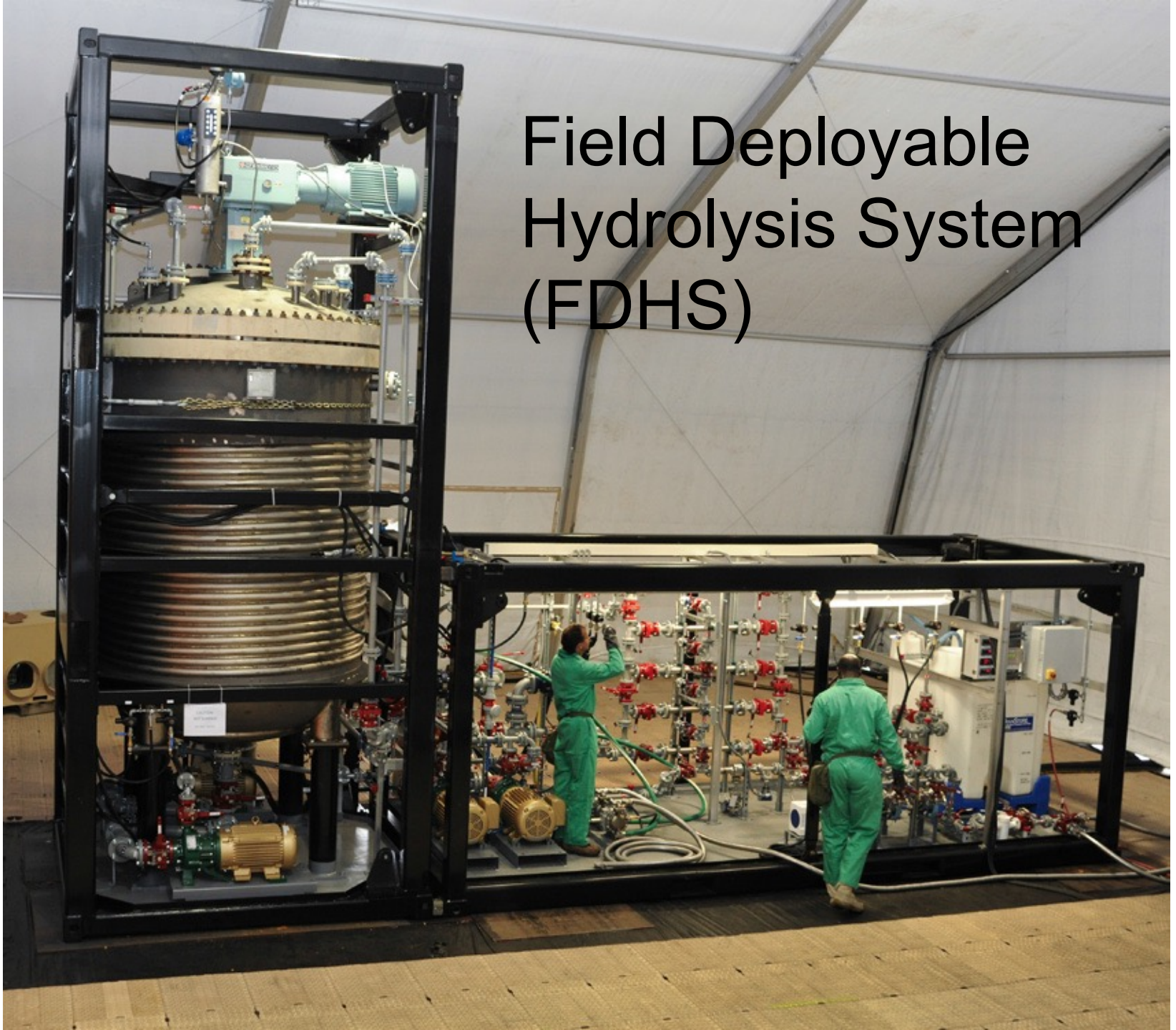
Steps for Neutralization Followed by Biotreatment

- 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)

Common CW Precursors

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

Chemical 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
Phosphorus pentasulfide	insecticides, lubricants, pyrotechnics	VX

Origins of the Australia Group

- *"In early 1984, a United Nations investigation team found that Iraq had used chemical weapons (CW) in the Iran-Iraq war in violation of the 1925 Geneva Protocol, and that at least some of the precursor chemicals and materials for its CW program had been sourced through legitimate trade channels. In response, several countries introduced export controls on certain chemicals that could be used to manufacture CW."*
- *These controls suffered from a lack of uniformity, and it soon became apparent that attempts were being made to circumvent them. This led Australia to propose a meeting of the countries with export controls with the aim of harmonising their national licensing measures and enhancing cooperation.*

https://www.dfat.gov.au/publications/minisite/theaustraliagroupnet/site/en/origins.html

Australia Group

- Established 1985
- *"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."*

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

Australia Group

- The Australia Group lists some chemical weapons precursors that are not listed on CWC Schedules.

  https://www.dfat.gov.au/publications/minisite/theaustraliagroupnet/site/en/precursors.html

- They have a list of dual-use chemical manufacturing facilities and equipment and related technology and software that could be used to make chemical weapons.

  https://www.dfat.gov.au/publications/minisite/theaustraliagroupnet/site/en/dual_chemicals.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)

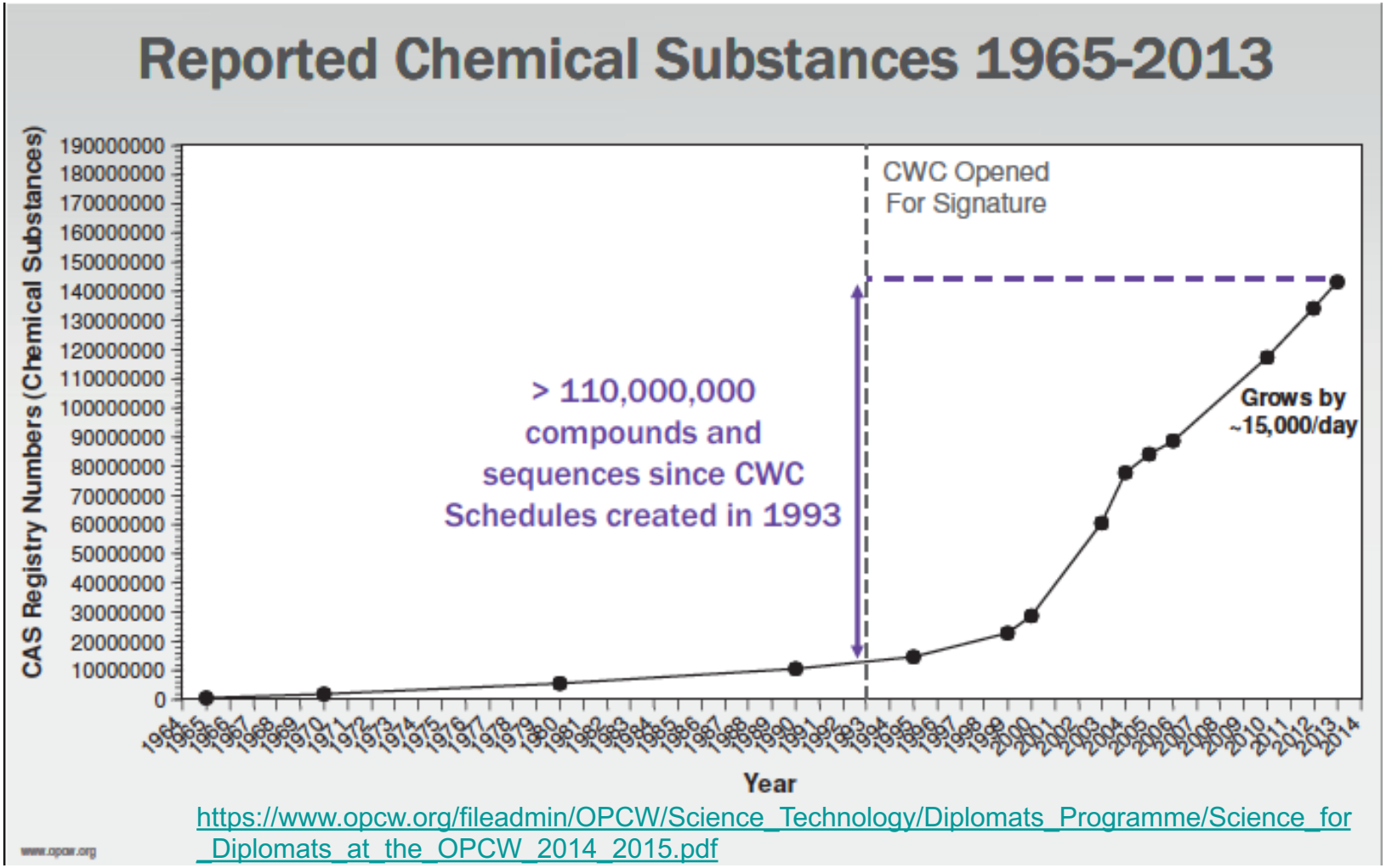
http://www.australiagroup.net/en/participants.html

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

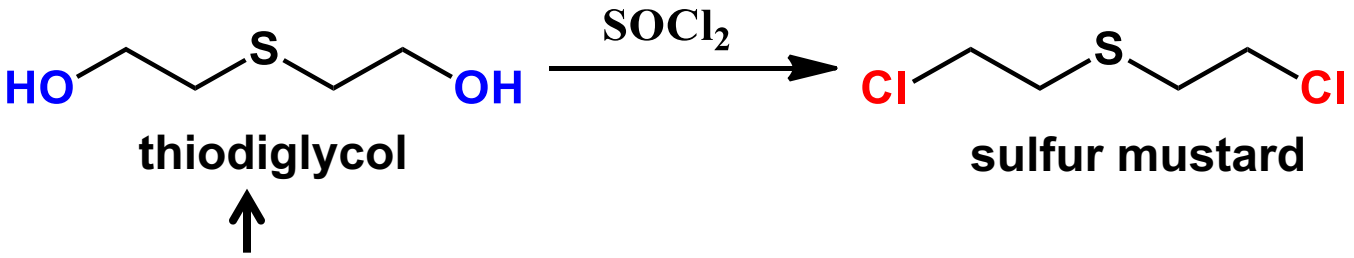
Ways to Circumvent Export Controls on Precursors

- 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.

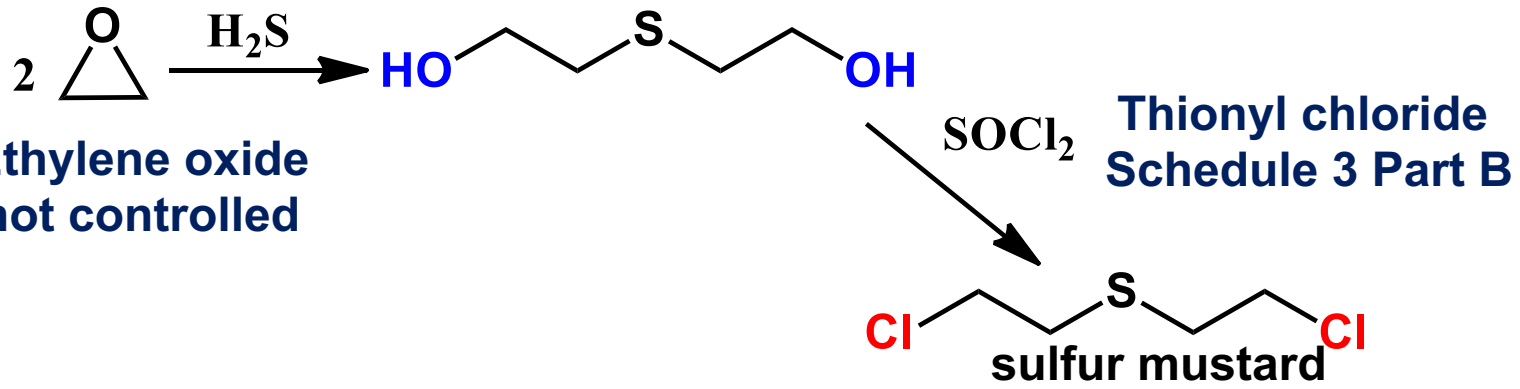
http://www.cwc2013.info/RG2013-by-doc/6/AG-precursors.pdf

Iraqi Sulfur Mustard Program

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

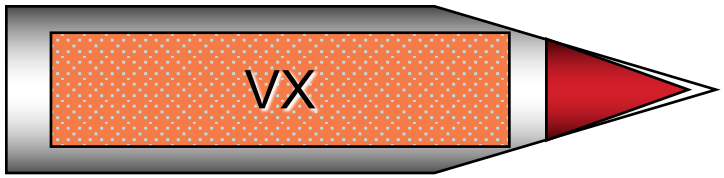


Binary Munitions

- Reactants mixed immediately before firing or mixed in flight
- U.S. 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)

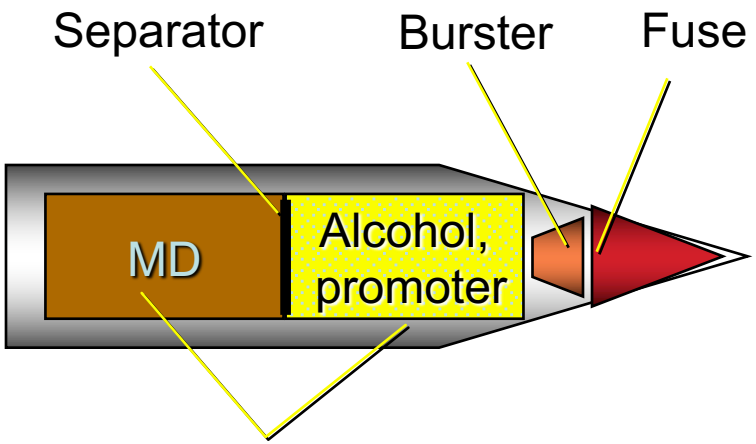
Common CW Munition Types

Unitary Munitions



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

Binary Munitions (sarin)

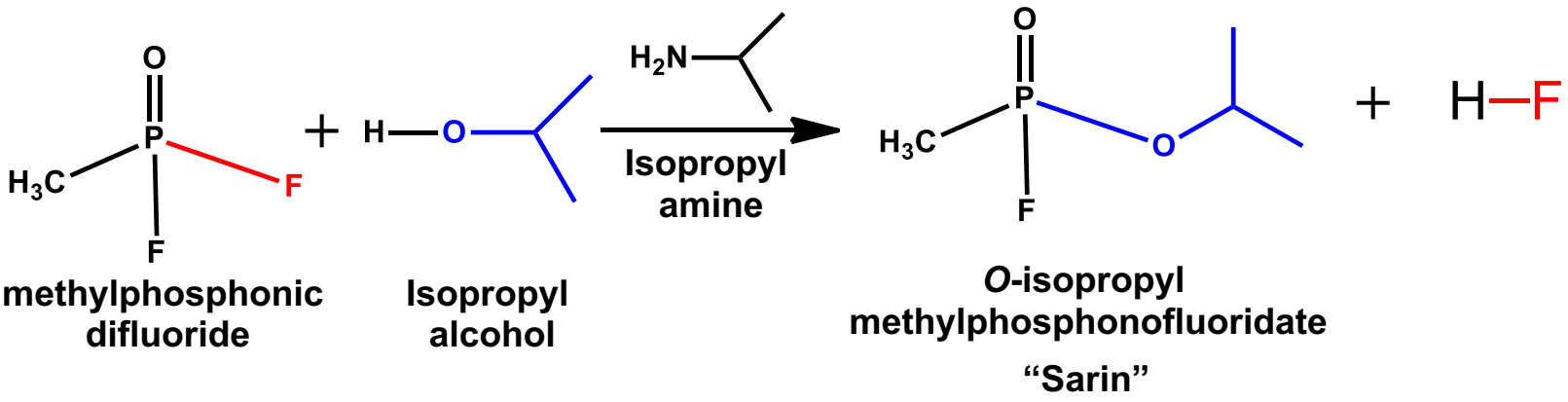


Two non-lethal compounds

- 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 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.



The Story Continues

- On-going allegations of use of chlorine gas and sulphur mustard
- On-going assessments of declarations
- Reports available at: http://www.the-trench.org/cw-in-syria-reports/

Image from bellingcat

Image circulating on social media, August 2015

Slide courtesy of Jonathan Forman – OPCW Science Policy Adviser and Secretary to the Scientific Advisory Board

Joint Investigative Mechanism (JIM)

- Joint Investigative Mechanism (August 2015)
  - "…**to identify** to the greatest extent feasible individuals, entities, groups, or governments who were **perpetrators, organisers, sponsors or otherwise involved in the use of chemicals as weapons**, including chlorine or any other toxic chemical, in the Syrian Arab Republic…"
- First report

http://www.securitycouncilreport.org/atf/cf/%7B65BFCF9B-6D27-4E9C-8CD3-CF6E4FF96FF9%7D/s_2016_142.pdf

Slide courtesy of Jonathan Forman – OPCW Science Policy Adviser and Secretary to the Scientific Advisory Board

OPCW-UN Fact-Finding Missions and Joint Investigation Missions

- Described the investigations and results of eight cases of possible use of chlorine or a chlorine derivative and one related to the use of sulfur mustard in Syria.
- Reported that there were three incidents where there was either a substance “matching the characteristics of chlorine”, “a canister with traces of chlorine or a chlorine-like substance”, “a significant number of people — up to 150 — may have been exposed to chlorine” and a “canister with traces of chlorine”.
- Two cases with a “toxic substance” used.
- They reported one incident where “there was sufficient information to conclude that Islamic State in Iraq and the Levant (ISIL) was the only entity with the ability, capability, motive and means to use sulfur mustard in Marea on 21 August 2015”.
- For the other incidents, they were unable to confirm the use of chemical weapons.

https://www.un.org/ga/search/view_doc.asp?symbol=S/2016/738

OPCW-UN Fact-Finding Missions and Joint investigation missions

https://unoda-web.s3.amazonaws.com/wp-content/uploads/2013/12/report.pdf

http://www.the-trench.org/wp-content/uploads/2016/01/OPCW-FFM-20140616-1st-Chlorine-investigation-report.pdf

http://www.the-trench.org/wp-content/uploads/2016/01/OPCW-FFM-20140910-2nd-Chlorine-investigation-report.pdf

http://www.the-trench.org/wp-content/uploads/2016/01/OPCW-FFM-20141218-3rd-Chlorine-investigation-report.pdf

http://www.the-trench.org/wp-content/uploads/2016/01/OPCW-FFM-20151217-Syria-request-Rev1.pdf

http://www.the-trench.org/wp-content/uploads/2016/01/OPCW-FFM-20151029-Idlib-Governorate.pdf

http://www.the-trench.org/wp-content/uploads/2016/01/OPCW-FFM-20151029-Marea.pdf

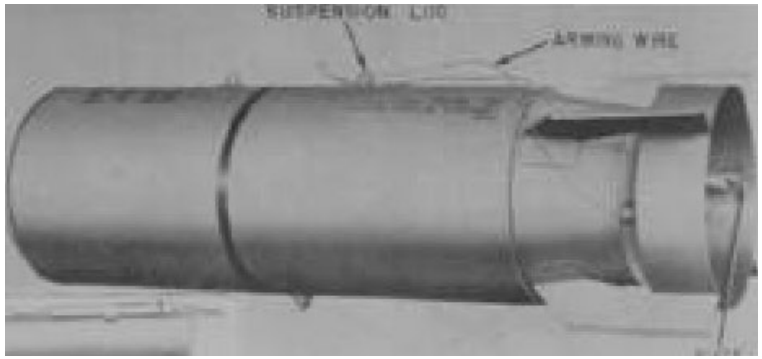
http://www.securitycouncilreport.org/atf/cf/%7B65BFCF9B-6D27-4E9C-8CD3-CF6E4FF96FF9%7D/s_2016_142.pdf

http://www.un.org/en/ga/search/view_doc.asp?symbol=S/2016/530

https://www.un.org/ga/search/view_doc.asp?symbol=S/2016/738

Sarin Weapons

- The sarin made at the Rocky Mountain Arsenal in Colorado was put in M34 cluster bombs and smaller shells, such as the 155mm shell.
- M34 bombs (left below) had 76 sarin-filled bomblets / 1000 pounds overall
- Previously stored at various army depots and in Okinawa
- A stockpile of 155mm shells are on the right.

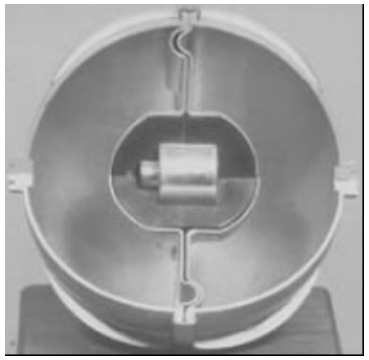


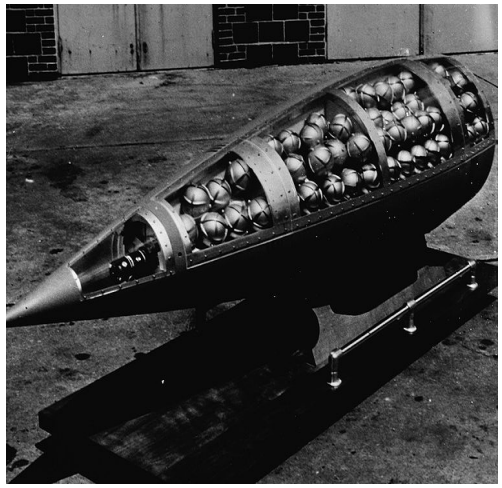
Other Nerve Agent Weapons

- M55 rocket
  - About 478,000 made
  - 6 feet long
  - Range six miles
  - Filled with about five quarts of nerve agent
  - Explosive burster charge to disperse agent
  - Many leaked, causing disposal problems

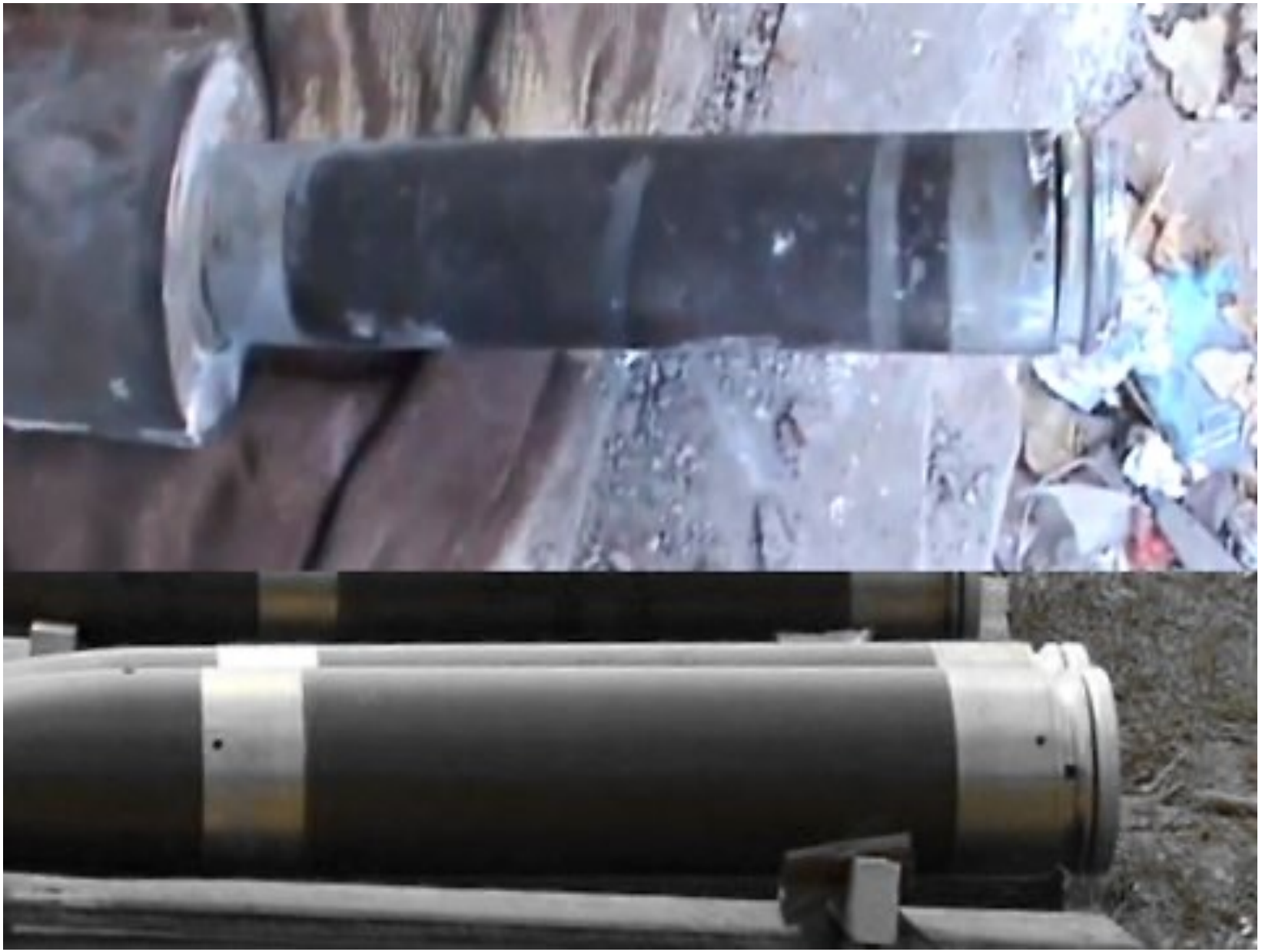
Honest John Rocket

- About 478,000 made
- Contained 356 spherical 4-5 inch bomblets, each with about a pound of nerve agent.
- Range 16 miles
- Designed to break apart over target, releasing the bomblets that detonated on impact, dispersing the nerve agent.





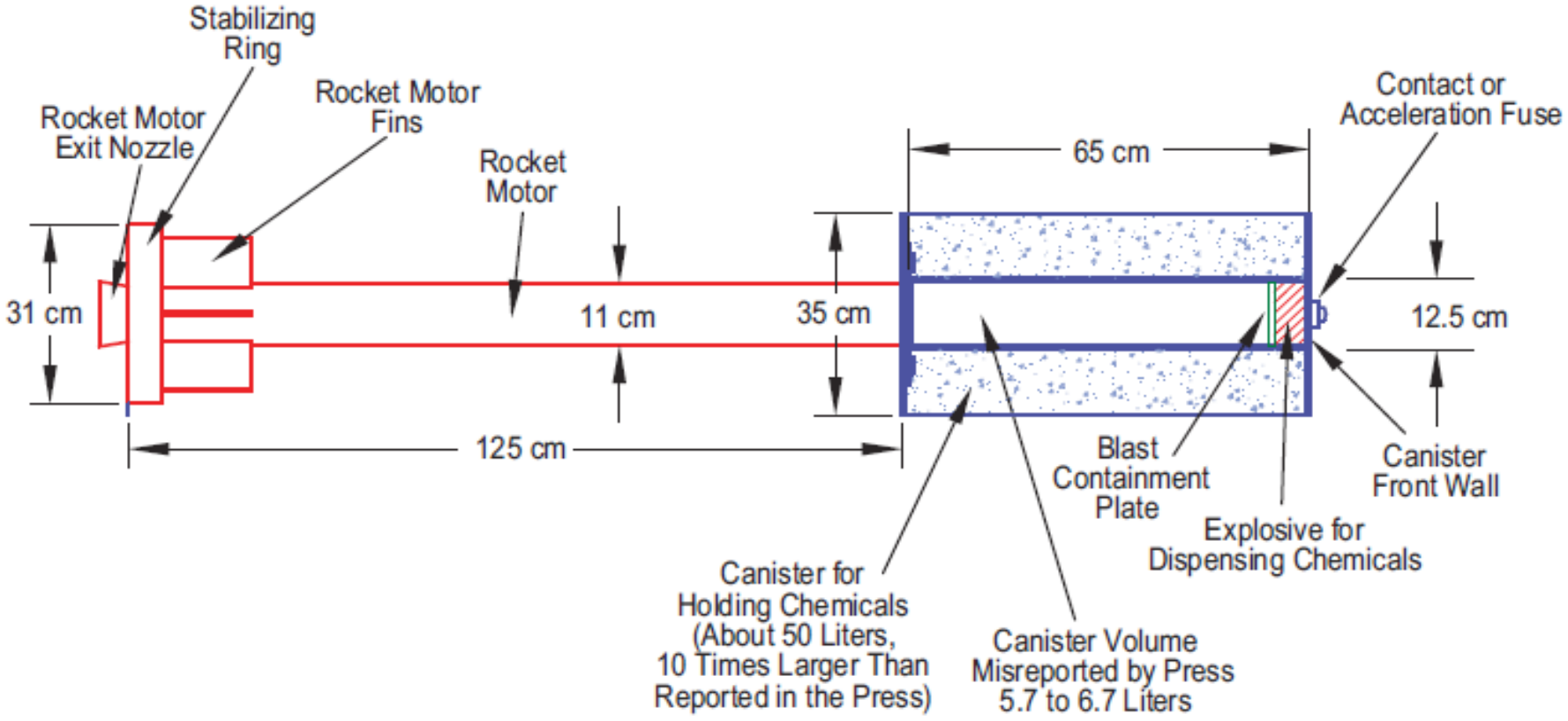
Improvised Rockets in Syria



Improvised Rockets in Syria

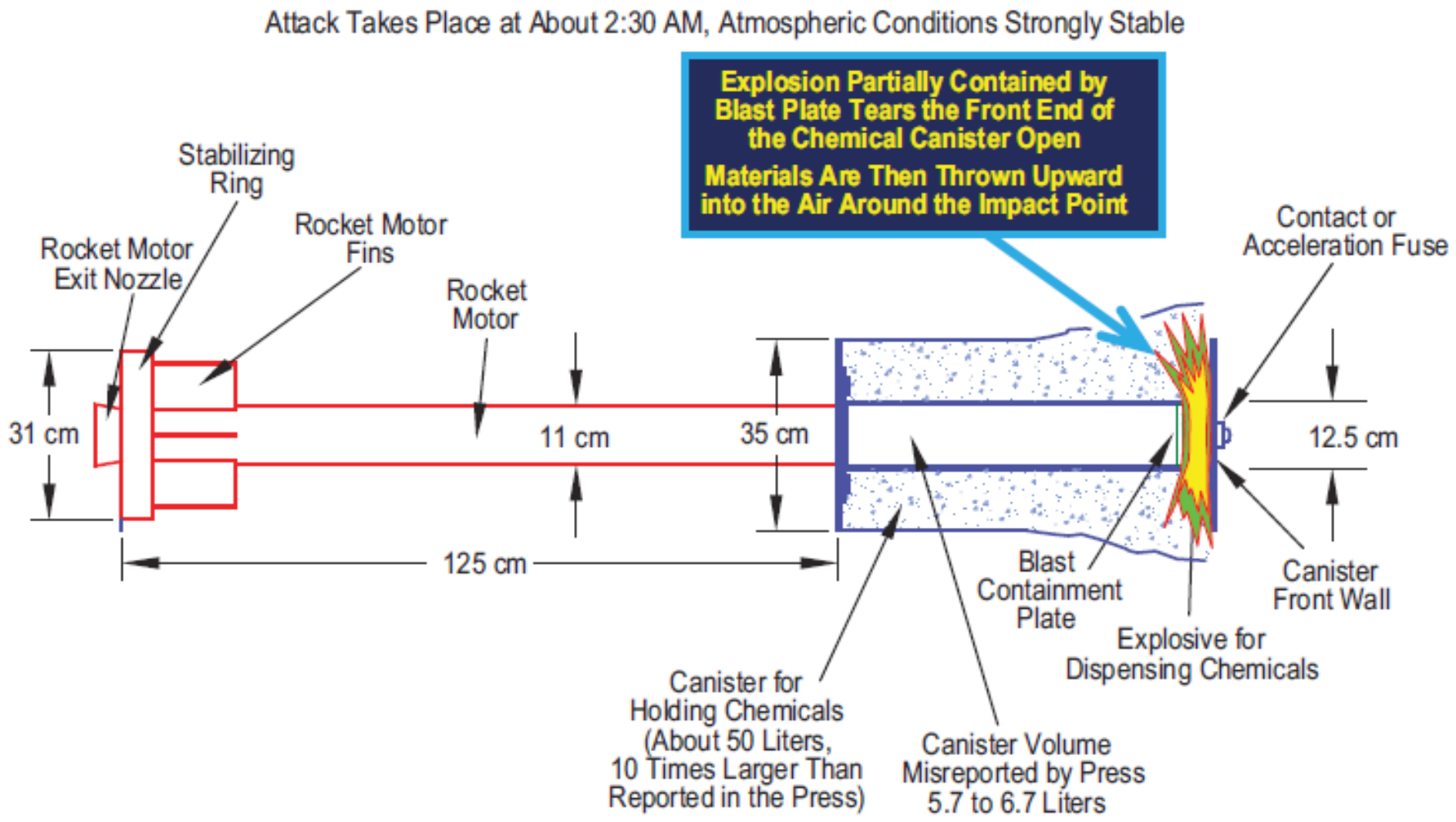
Estimated Dimensions and Payloads of Munitions Used in Sarin Gas Attack on Suburb of Damascus (August 21, 2013)

Attack Takes Place at About 2:30 AM, Atmospheric Conditions Strongly Stable



Improvised Rockets in Syria

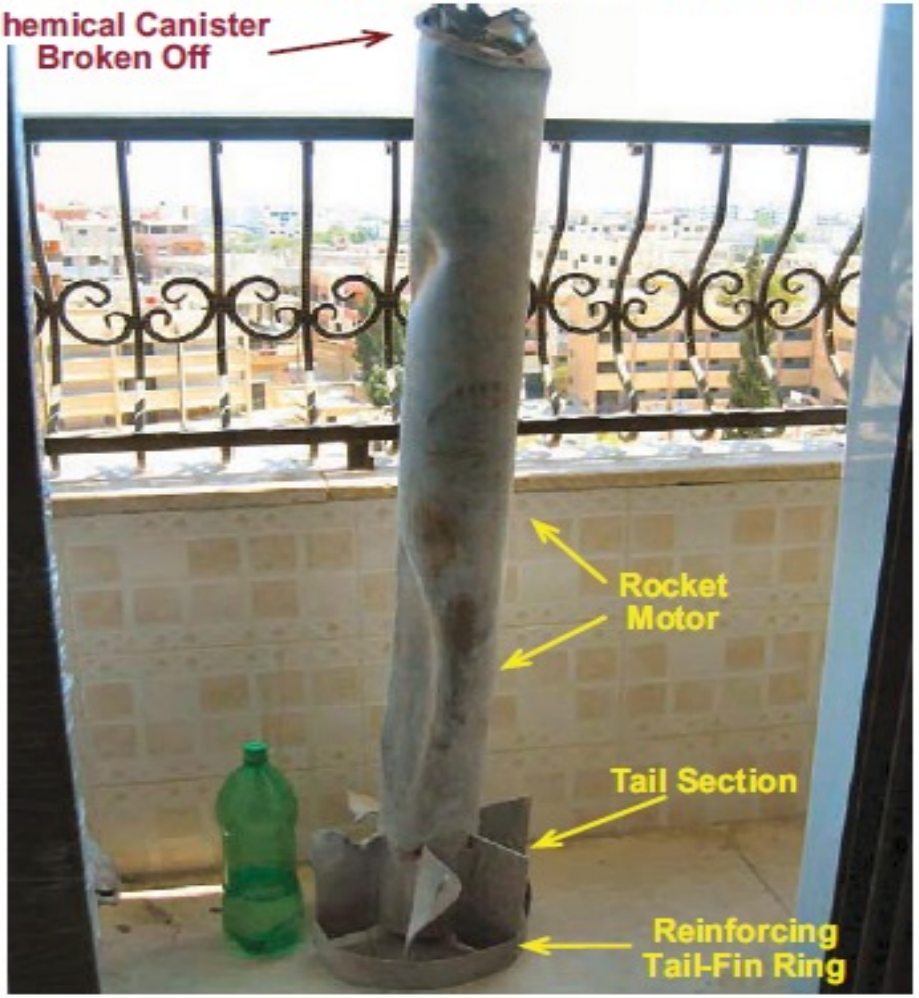
Mechanism for Tearing Open Payload Container Used in Sarin Gas Attack on Suburb of Damascus (August 21, 2013)



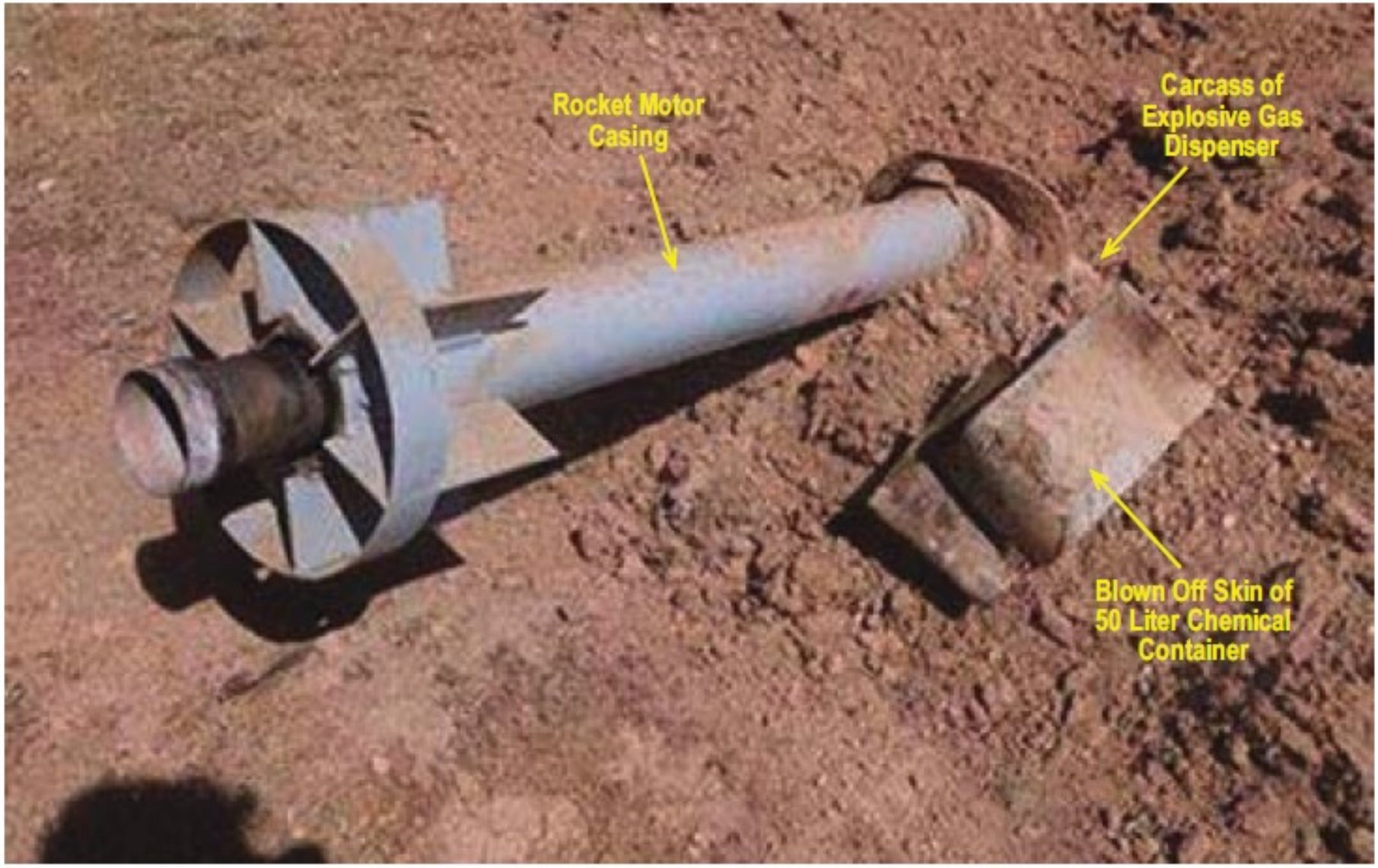
Improvised Rockets in Syria

Munition Used in Sarin Gas Attack on Suburb of Damascus (August 21, 2013)

Attack Takes Place at About 2:30 AM, Atmospheric Conditions Strongly Stable



Improvised Rockets in Syria



Improvised Rockets in Syria