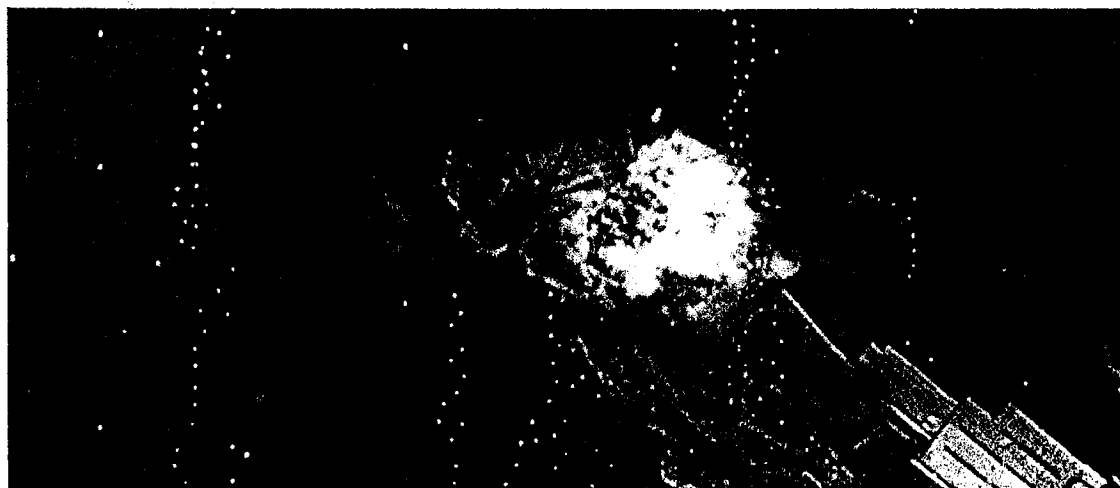


Denmark Group Meeting  
27 August ~~16~~, 2002  
Tyson A. Miller

## Chemical Weapons



"Chemical weapons work. They are undergoing revolutionary developments which make them, and a new generation of biological substances as well, practical and very lethal participants in those human affairs which are ultimately resolved with blood and iron. Be ignorant and be damned, and condemn your children as well."

- James A.F. Compton

# What constitutes a Chemical Weapon?

2

## Properties of a useful chemical weapon

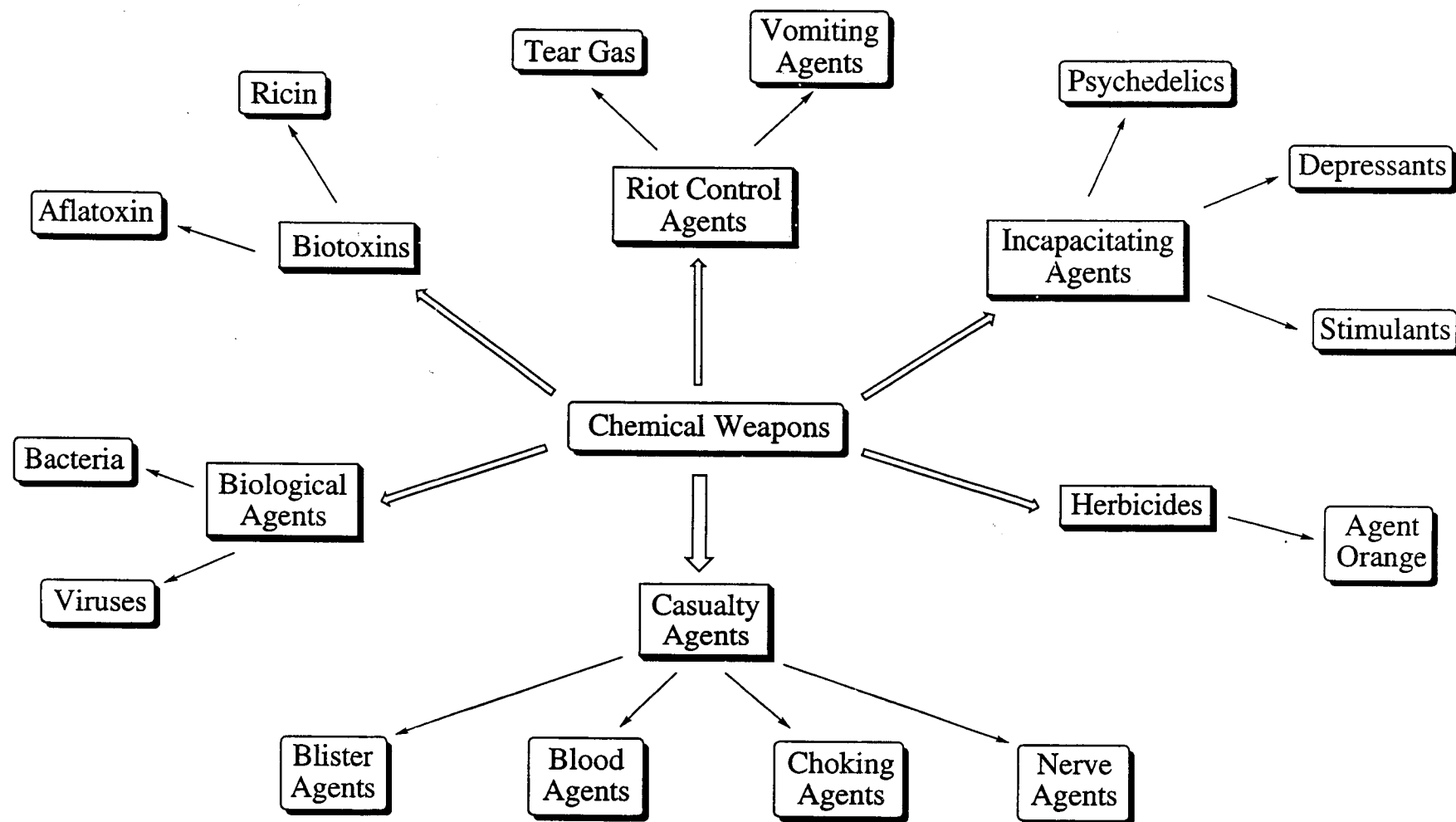
- Environmental persistence
- Chemical reactivity with enemy leading to symptoms or injury that stops enemy
- Non-reactivity with location of deployment
- Physical properties for deployment
- Ease of deployment
- Stability of storage
- Target specificity (chemical stays where you put it and doesn't come back to find you!)
- Low flammability (flash point)
- Ease and low cost of production
- Safe handling

## Purposes for a chemical weapon

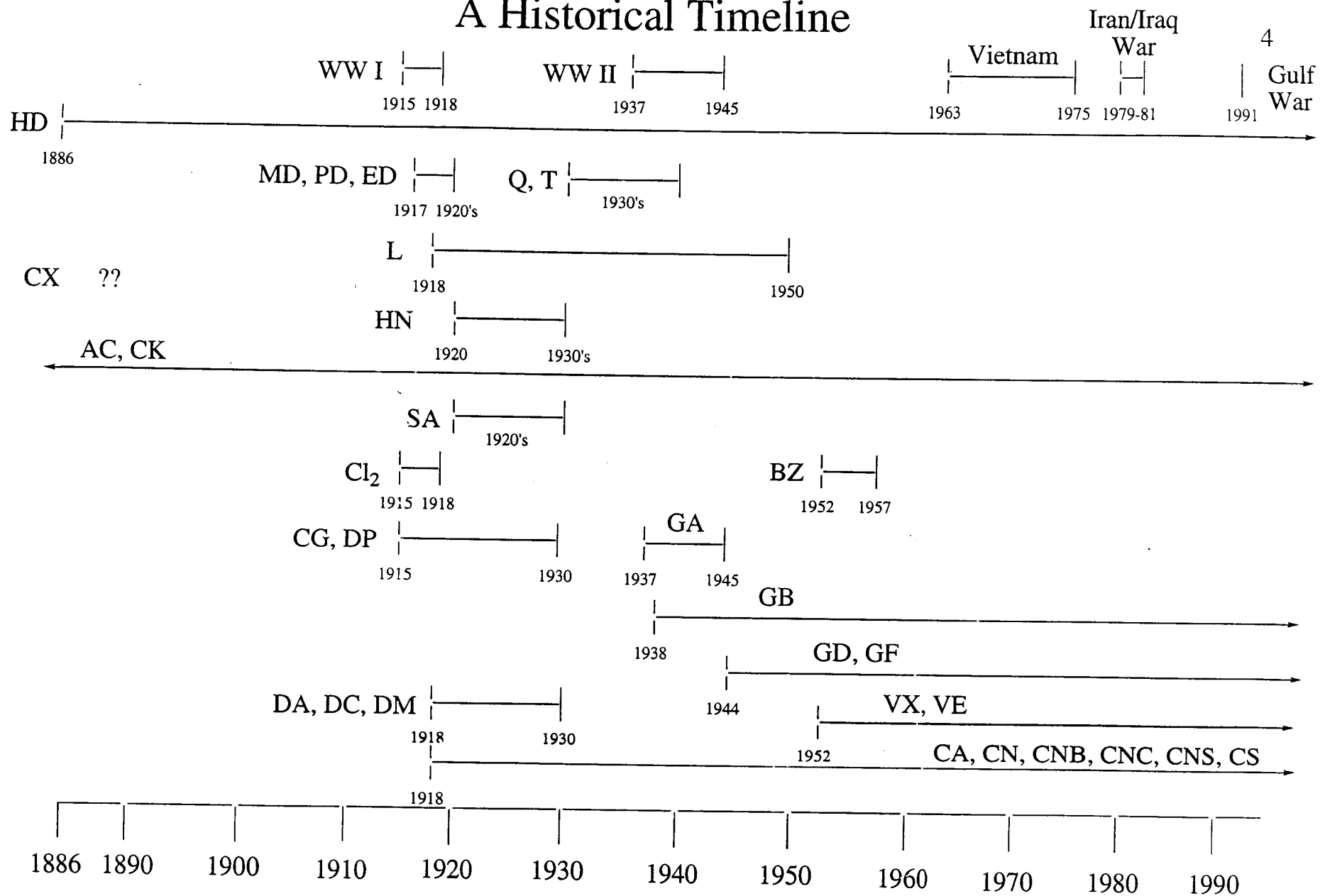
- To cause casualties (injury or death)
- To decrease and opponent's effectiveness
- To restrict and channel the use of terrain
- To delay and opponent's advance
- To contaminate avenues of approach
- To attack hardened targets
- To deny the use of structures
- To deny the use of materials or equipment
- To attack an opponent's reserves
- To attack an opponent's fire support (artillery)
- To attack opponent's logistical train (supply and maintenance)

# What are the types of Chemical Weapons?

3



# A Historical Timeline



Code names standardized by Tripartite Pact (U.S., Britain, Canada) or NATO

G - German, D - Vomiting, C - Tear or Chlorine, V - Nerve, H - Mustard, HN - Nitrogen Mustard

# Blister Agents

5

## Mustards

- HD - distilled mustard

## Arsenicals

- MD - methyldichloroarsine
- PD - phenyldichloroarsine
- ED - ethyldichloroarsine
- L - Lewisite (dichloro (2-chlorovinyl) arsine)

## Nitrogen Mustards

- HN-1 - 2,2-dichlorotriethylamine
- HN-2 - 2,2-dichloro-N-methyldiethylamine
- HN-3 - 2,2,2-trichlorotriethylamine

## Oximes

- CX - phosgene oxime

## Other Agents

- T
- Q - sesquimustard

## Mixes

- HL - mustard-lewisite mix: 63% L and 37% HD, by weight
- HT - mustard-T mix: 60% HD and 40% T, by weight

- Used to restrict terrain, slow movements, hamper use of materials and installations

- Targets: eyes, lungs, skin

- Distinctive odors to no odor

- Long persistence in normal weather

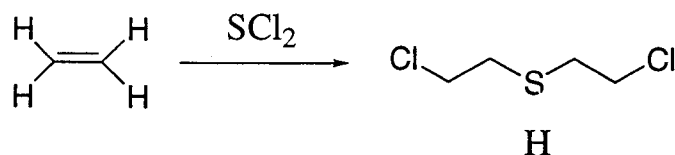
- Little or no pain at time of exposure, except L and CX

- Painful to fatal, depending on length and extent of exposure

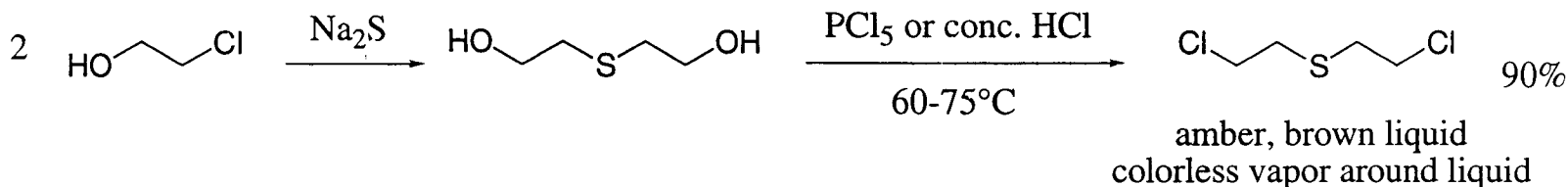
- Protection from blister agents is difficult

# Distilled Mustard

6



Levinstein Process      30-50%  
+ other side products, then distilled - HD



## Physical Properties

mp - 14.45°C; bp - 217°C (decomp. at 149°C); flash point - 105°C (flammable!!)  
hydrolysis in 17 minutes in dist. water at RT°C, 2 hrs. in salt water >> HCl + thiodiglycol  
stable in steel or aluminum cannisters, not corrosive  
lasts several days under temperate climate  
vapor density - 5.4 X air; vapor pressure - 0.072 torr at 20°C  
low and slow rate of detoxification - effects cumulative

- known as dye by-product in 1880's - treating warts and killing pests
  - 1st used on July 12th, 1917 near Ypres, France on British troops (annoyed one day, dead the next!)
  - 16.5% of all British casualties were due to HD
  - permanent damage: conjunctivitis, laryngitis, chronic bronchitis, heart conditions
  - also used by British, French, Spanish, and Japanese
  - plants opened in Britain, France, Germany, USSR, and US
  - except for one time during WWII, HD use stopped after WWI until Iran/Iraq war
- (S.S. John Harvey destroyed by German air raid in Italian Adriatic Sea in 1943; had munitions with 100 tons of HD made by Levinstein process, had hydrogen and ethane gas, all hands + 1000 Italian civilians died)

Meyer, V. *Ber.* **1886** 19 3260.

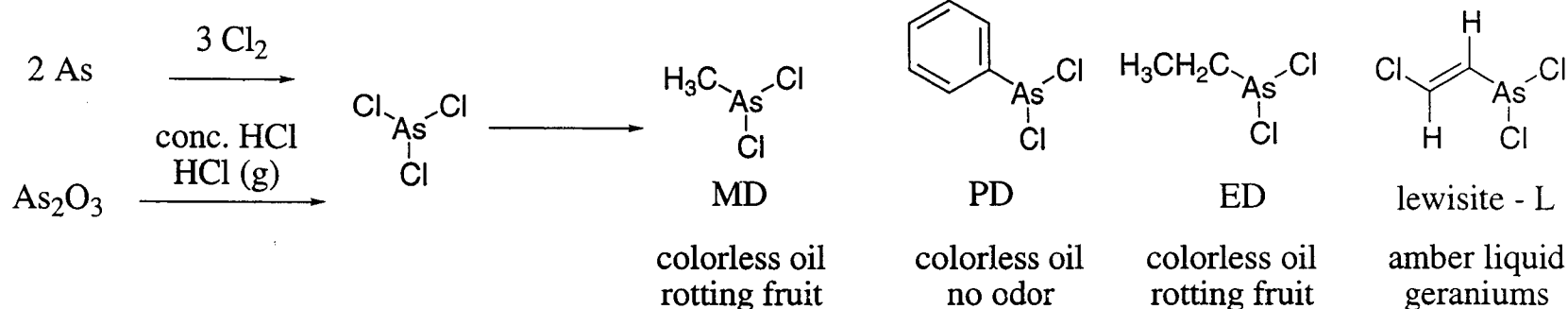
Mann, F.G.; Pope, W.J. *JCS* **1922** 121 594.

Gomberg, M. *JACS* **1919** 41 1414.

Compton, James A.F. Military Chemical and Biological Agents. The Telford Press: Caldwell, N.J., **1987**.

# Arsenicals

7



## Physical Properties

mp -  $-65$  -  $-18^\circ\text{C}$ , bp -  $133$  -  $252^\circ\text{C}$ ; non-flammable  
 low solubility in water, MD, PD, ED - rapid hydrolysis; L - very slow hydrolysis  
 stable in steel, ED, L - destroys rubber, plastics, masks, and brass  
 MD, PD, ED - low persistence (1 hour max.); L - 1 day.  
 vapor density - 6 X air; vapor pressure - MD - 7.76 torr at  $20^\circ\text{C}$ ; accumulative toxin

from  $\text{AsCl}_3$   
acetylene,  
and  $\text{AlCl}_3$

- immediate destruction of lung tissue >> dry land drowning
- destroys eyes, leads to blindness
- destruction of RBC, T-cells, and cytochrome oxidase
- arsenic displacement of calcium in bone marrow and tissue
- MD, PD, ED hydrolyzes too rapidly under many conditions; L short-lived
- L still stockpiled, but development stopped after nerve agents were discovered
- good for airplane aerosols, was a complement to HD in military arsenals to 1950's

Smith, R.C. *Ind. Chem. Eng.* **1919** 11 109.

Schenk, P.W. *Handbook of Prep. Inorg. Chem.*, Vol. 1 **1963** 596.

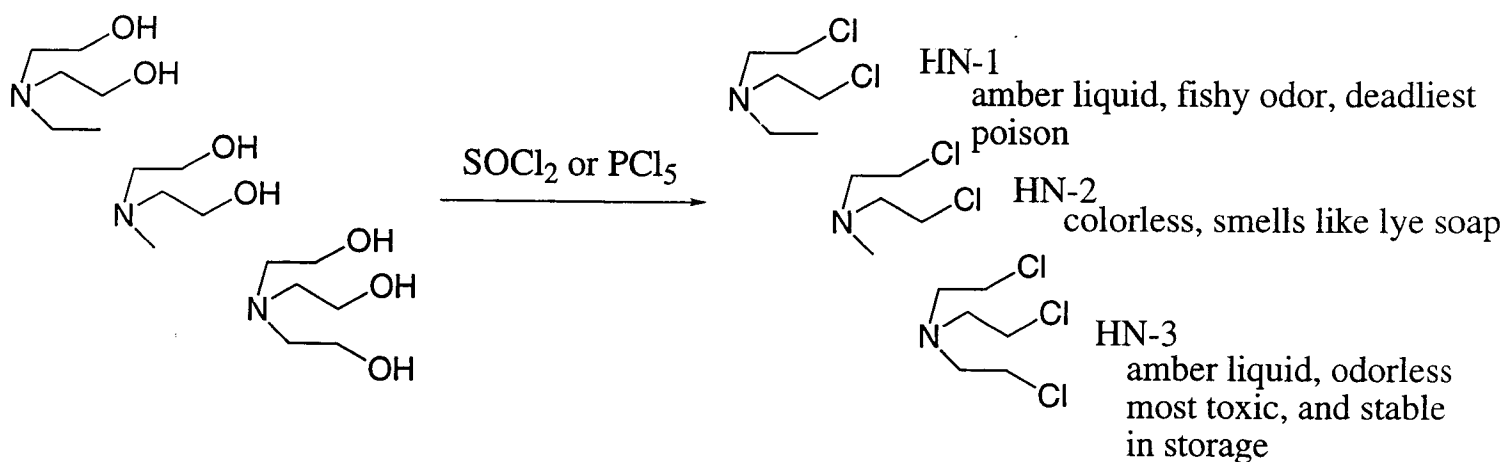
Gibson, C.S.; Johnson, J.D.A. *JCS* **1931** 754.

Lewis, W.L.; Steigler, H.W. *JACS* **1925** 47 2546.

Compton, James A.F. *Military Chemical and Biological Agents*. The Telford Press: Caldwell, N.J., **1987**.

# Nitrogen Mustards

8



## Physical Properties

mp -  $-64$  -  $-4^\circ\text{C}$ ; bp -  $75$  -  $256^\circ\text{C}$  (all with decomp.); non-flammable  
 very slow hydrolysis, HN-1, 2 - polymerizes in long storage in munitions  
 lasts up to 1 day in moderate climate, weeks in winter; cumulative toxin  
 vapor density -  $5.4$ - $7.1$  X air; vapor pressure - very low; fairly persistent

- can kill tumors if directly injected into them
- destruction of lung tissue >> bronchial damage
- destroys eyes, leads to blindness
- destruction of immune system
- lesions made in GI tract
- developed by accident by German and Czech drug companies
- doesn't do as much damage as HD, good persistent agent for contamination of supplies.

Prelog, Stepan. *Coll. Czech. Chem. Comm.* **1935** 7 93.

Ward, Jr., K. *JACS* **1935** 57 914.

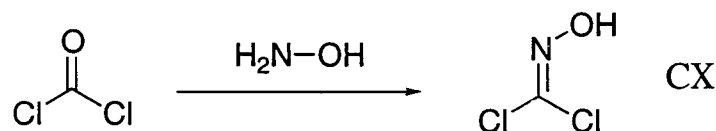
Hanby, W.E.; Rydon, H.N. *JCS* **1947** 513.

Compton, James A.F. Military Chemical and Biological Agents. The Telford Press: Caldwell, N.J., 1987.



# Phosgene Oxime

9



white solid when pure  
when melted burned or dissolved -  
emits a clear musty, pepperish vapor

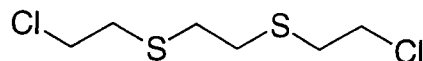
## Physical Properties

mp - 40°C; bp - 54°C (with decomp.); non-flammable  
no hydrolysis data, detoxification rate not studied  
stable in steel containers when dry, corrosive when mixed with water  
highly toxic, acts immediately

- attacks whatever tissue it comes in contact with (skin, muscle, nerves) with great pain
- sores are wheals, hard masses form where CX accumulates under scabs, then re-enters through adjacent tissue
- healing takes from a week to a year
- originated in the Soviet Union as a by-product for cockroach insecticide research
- lethal dose information not known to the West
- solid form lasts for days and weeks in temperate weather, almost indefinitely in cold weather
- compound is not mentioned in standard chemical or pharmaceutical texts, mentioned in passing in chemical warfare literature, samples taken in Laos in the 1980's

# Other Agents and Mixes (Obsolete)

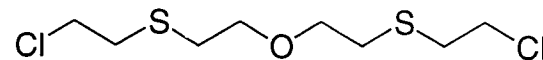
10



Q

pale amber solid with no odor

- Created in mid 1930's at British Porton Down to have the asphyxiation qualities of phosgene (CG) and delayed systemic damage of HD
- Used in solution with many organic solvents as an aerosol

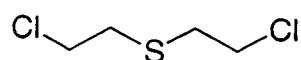


T

dark oily liquid with no odor

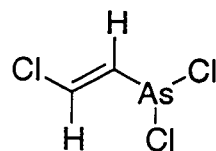
- Created in mid 1930's at British Porton Down as an HD thickener for use in aerial sprays or in warm climates
- 2 HD groups tied with an oxygen atom

HL



HD

37-50% by weight

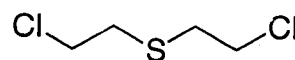


L

50-63% by weight

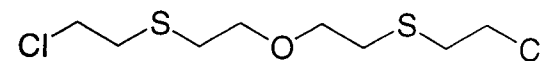
- combined to make a dark brown oily liquid with a strong musky, garlic odor
- devised for low-freezing mixture use in cold weather or high altitude aerial sprays
- lasts 1-1.5 days under temperate conds.; 1 week in cold
- dry-land drowning imminent with permanent damage to lungs, endocrine system, eyes, bone marrow, and red blood cells, accumulative toxin

HT



HD

60% by weight



T

40% by weight

- combined to give a clear yellow pale amber liquid with twice the persistency of HD alone
- designed for absorption instead of inhalation
- same pathology as HD
- rendered obsolete after nerve agents arrived, but still in existence in military stockpiles

# Comparison of Blister Agents

11

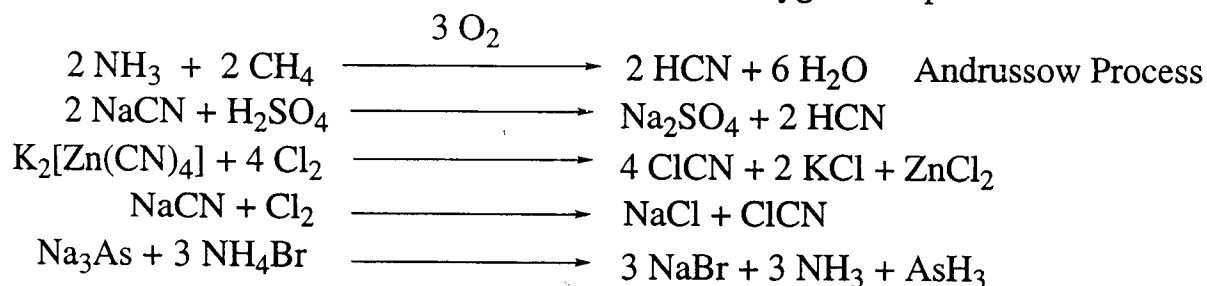
agent	rate of action	state at 68°F	odor	volatility (mg/m <sup>3</sup> )	LCt <sub>50</sub> (mg-min/m <sup>3</sup> )	ICt <sub>50</sub> (mg-min/m <sup>3</sup> )	vapor density (x air)	vapor pressure (mm Hg)
HD	delayed, hours to days	colorless to pale yellow liquid	raw garlic	610 at 68°F	1500 inhal; 10,000 skin	200 eye; 2000 skin	5.4	0.072 at 68°F
MD	rapid	colorless liquid	none when pure	74,900 at 68°F	3,000	25 inhal	5.5	7.76 at 68°F
PD	immediate eye; to 1 hr skin	colorless liquid	none when pure	390 at 77°F	2600 inhal	16 vomit; 1800 blist	7.7	0.033 at 77°F
ED	immediate irritation; blistering delayed	colorless liquid	none when pure	20,000 at 68°F	3000 inhal	5-10 inhal	6.0	2.09 at 68°F
L	rapid	dark oily liquid	may resemble geraniums	4480 at 68°F	1200 inhal 100,000 skin	300 eye; 1500 skin	7.1	0.394 at 68°F
HN1	delayed: 12 or more hours (blistering)	dark liquid	fishy or musty	1520 at 68°F	1500 inhal; 20,000 skin	200 eye 9000 skin	5.9	0.24 at 77°F
HN2	delayed: 12 or more hours (blistering)	dark liquid	soapy to fruity	3580 at 77°F	3000 inhal	100 eye	5.4	0.29 at 68°F
HN3	delayed, hours to days	dark liquid	none when pure	121 at 77°F	1500 inhal; 10,000 skin	200 eye; 10,000 skin	7.1	0.0109 at 77°F
CX	instantaneous	colorless solid if pure	like tear gas	none	unknown	any expos	none	none

# Blood Agents

11

- AC - hydrogen cyanide
- CK - cyanogen chloride
- SA - arsine

- cyanide based agents bind the iron atom on heme, preventing cytochrome oxidase from performing oxygen/carbon dioxide exchange from cells
- arsine oxidizes cytochrome oxidase and incorporates the iron-oxygen complexes into molecules the body can't use



- problem is that AC, SA agents have low flash points and are highly volatile.
- CK is non-flammable, but less effective
- munitions are aerial sprays and non-thermal rocket delivery

agent	rate of action	state at 68°F	odor	volatility (mg/m <sup>3</sup> )	LCt <sub>50</sub> (mg-min/m <sup>3</sup> )	ICt <sub>50</sub> (mg-min/m <sup>3</sup> )	vapor density (x air)	vapor pressure (mm Hg)
AC	rapid	colorless gas or liquid	bitter almonds	1,080,000 at 77°F	2000 to 4500 in open; 300 ppm inclosed areas	150 ppm	0.93	742 at 77°F
CK	rapid	colorless gas	very faint odor of bitter almonds	2,600,000 at 55°F	11,000	7000	2.1	1000 at 77°F
SA	delayed: 2 hours to 11 days	colorless gas	mild garlic	30,900,000 at 32°F	5000	2500	2.69	11,100 at 68°F

Andrussow, L. *Angew. Chem.* 1935 48 593.

Schenk, P.W. *Handbook of Prep. Inorg. Chem.*, Vol. 1 1963 593.

Glemser, O. *Handbook of Prep. Inorg. Chem.*, Vol. 1. 1963 658.

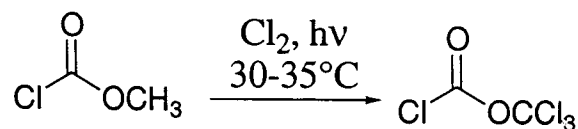
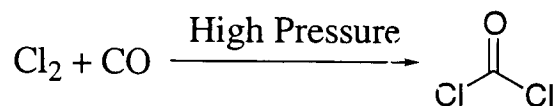
Compton, James A.F. *Military Chemical and Biological Agents*. The Telford Press: Caldwell, N.J., 1987.

# Choking Agents

13

- Cl<sub>2</sub> - chlorine
- CG - phosgene
- DP - diposgene

Cl<sub>2</sub> smells like conc. bleach  
CG, DP - smells like new mown hay, or green corn



- choking agents injure a person in the respiratory tract (nose, throat, lungs)
- membranes swell, lungs fill with fluid, death from dry-land drowning
- persistency erratic (gases), but effective within minutes
- CG accounted for 80% of chemical deaths in WW I
- Cl<sub>2</sub> was first chemical battlefield agent used in WW I (April 22, 1915 at Langemarck, near Ypres, 23rd and 26th German Army corps did an experiment with 6,000 cylinders . . . .
- IG Farbin, German dye and chemical works donated research on CG to Kaiser Wilhelm Inst. in Spring of 1915. It was used as pesticide originally. In December 1915, the British at Ypres were hit with CG and thought it was a nuisance impurity in a failed chlorine attack. Two days later mass casualties occurred from pulmonary edema.
- all must be stored in glass containers, metals are promptly etched and destroyed

agent	rate of action	state at 68°F	odor	volatility (mg/m <sup>3</sup> )	LCt <sub>50</sub> (mg-min/m <sup>3</sup> )	ICT <sub>50</sub> (mg-min/m <sup>3</sup> )	vapor density (x air)	vapor pressure (mm Hg)
chlorine	immediate	yellow gas	like bleach	19,369,000 at 68°F	19,000	1800	2.4	4992 at 68°F
GG	immediate to 3 hours, depending on concentration	colorless gas	new-mown hay; green corn	4,300,000 at 45°F	3200	1600	3.4	1.173 at 68°F
DP	immediate to 3 hours, depending on concentration	colorless gas	new-mown hay; green corn	45,000 at 68°F	3200	1600	6.8	4.2 at 68°F

Kurita, K.; Iwakura, Y. *Org. Syn. Coll. Vol. VI*. 1980 715.

Compton, James A.F. *Military Chemical and Biological Agents*. The Telford Press: Caldwell, N.J., 1987.

# Nerve Agents

14

## Wehrmacht Agents (G-Series)

- GA - tabun
- GB - sarin
- GD - soman
- GF - cyclohexyl sarin

## V-Series

- VX
- VR-55
- VE

- Fortunately, these have never been used in battle, but if they ever are, here's what you can expect to happen . . .

- difficulty in breathing
- drooling and excessive sweating
- vomiting, cramps, involuntary defecation and urination
- twitching, jerking, and staggering
- headache, confusion, drowsiness, convulsion, and coma
- dimness of vision and pinpointing of the pupils
- death from complete nervous system failure

- Despite "The Rock", there is no blistering and melting of the skin, though absorption through the skin is rapid, and death occurs within 2 minutes.  
- There is no "GC", as it was an old medical code for gonorrhea. (no joke!)  
These agents were too serious for bad humor; therefore, it was not used.

- These nerve agents act by destroying all cholinesterase inhibitors in the body. This leads to a massive presence of acetylcholine in all synaptic clefts, which causes nervous system collapse.

- Vapors cause death within 10 mins.; absorption causes death in 2 mins.



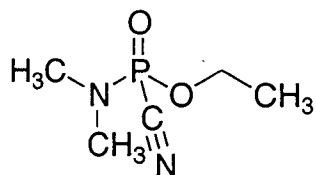
<http://filmstills3.net/firms.com/rockthe1/rockt07.jpg>

Compton, James A.F. Military Chemical and Biological Agents. The Telford Press: Caldwell, N.J., 1987.

# 1937 - GA - Tabun

15

(dimethylphosphoramidocyanidic acid)



dark amber liquid  
colorless vapor  
when pure, no odor  
when oxidized, rotting fruit  
to bitter almond smell

GA is least vapor hazard of  
the G-series agents, but has  
greater persistence than GB  
or GD.

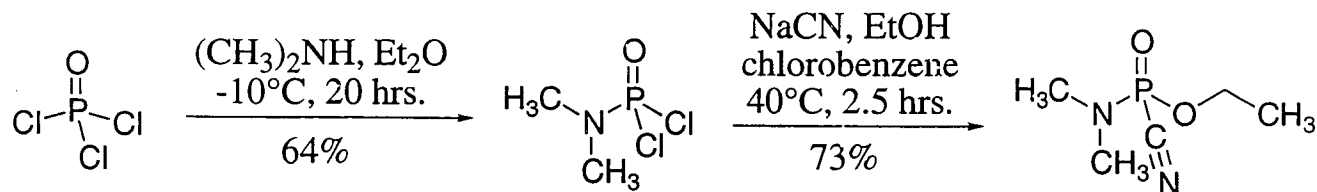
Designed to be delivered via  
artillery munitions or aerial spray.  
Low flash point (172°C); no  
explosive hazard.

- Dr. Gerhard Schrader was a researcher at I.G. Farben since 1902, working on pesticides, and insecticides based on fluorine-containing compounds
- During testing, a drop of GA was spilled onto a lab bench. Within minutes, Dr. Schrader and his assistant were experiencing contracted pupils, difficulty breathing, and dizziness. He said they were "lucky to escape with their lives."
- Tabun was abandoned as a pesticide, but the Reichs ordinance of 1935 mandated that studies of all toxic substances (or anything else of military significance) be under government report. Dr. Schrader was sent to the Wehrmacht chemical lab at Berlin-Spandau. Tests were continued under Col. Rüdiger, and the production of tabun was moved to a secret facility at Dyhernfurth-am-Oder near Breslau in Silesia.
- It took from 1940-1942 to get operational, as certain intermediates were so corrosive that all reactions were run in quartz or silver-lined vessels. Final production units were enclosed in double glass walls with pressurized air circulating between walls.
- Despite rubber/cloth/rubber clothing and masks, a workforce of 3,000 had 300 accidents, with 10 deaths. Examples:
  - Four pipe fitters had liquid GA drain onto them and die before rubber suits could be removed
  - One worker had 2 liters of GA pour down the neck of his rubber suit and died within 2 minutes
  - Seven workers were hit in the face with a stream of GA of such force that the liquid was forced behind their masks. Only two survived, with huge resuscitation efforts.
- 12,000 tons of GA would be produced, only to be hydrolyzed by alkalies and dumped into the Oder river to prevent capture. However, the Soviets took over the plant.
- In the West, postwar testing was done at Porton Down (UK) and Edgewood Arsenal (US). Production was shelved in the 1950's in favor of GB.

# 1937 - GA - Tabun

(dimethylphosphoramidocyanidic acid)

16



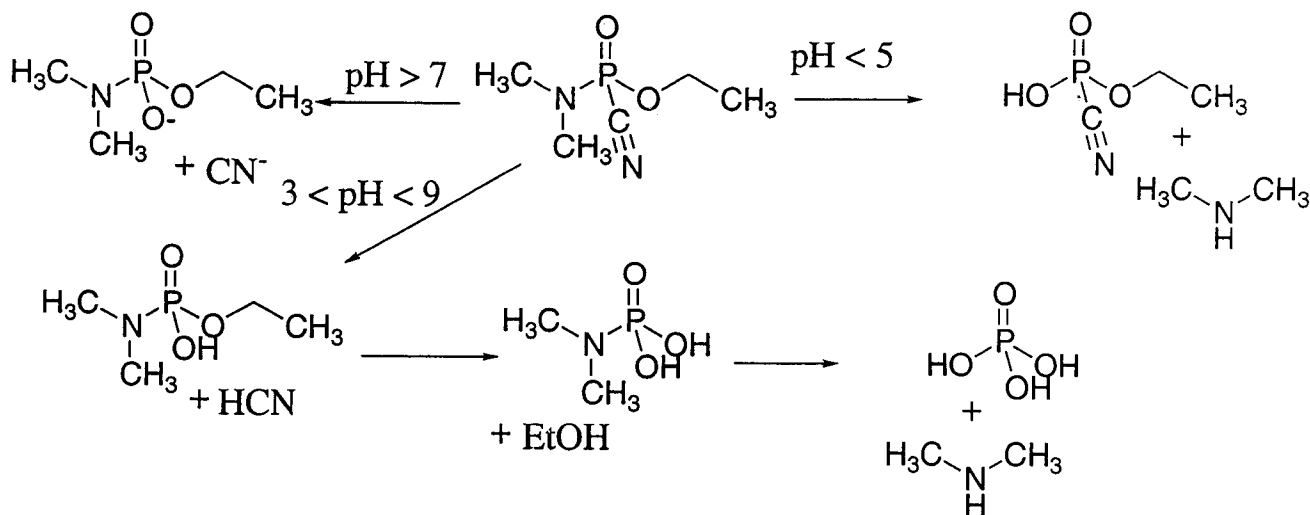
mp - -50°C  
 bp - 246°C  
 vapor pressure - 0.07 torr at 20°C  
 density - 1.077 g/ml  
 aqueous solubility - 72 g/L

## GA Hydrolysis Rates in Sea Water

T (°C)	sea water t <sub>1/2</sub> (min)	k <sub>obsd</sub> , calc. (hr <sup>-1</sup> )
15	475	0.088
20	267	0.156
25	175	0.238

## GA Hydrolysis Rate Constants

T (°C)	pH	k <sub>obsd</sub> (hr <sup>-1</sup> )
25	5.00	0.39
20	5.10	0.07
20	7.20	0.17
20	8.60	0.28
25	8.50	0.26
25	8.75	0.33
25	9.00	0.50
25	9.00	0.42
35	9.00	1.44
25	9.50	1.26
35	9.50	4.21



Holmstedt, B. *Acta. Physiol. Scand.*; *Supp.* 90 **1951** 25 26.

Larsson, L. *Acta. Chem. Scand.* **1953** 7 306.

Larsson, L. *Acta. Chem. Scand.* **1958** 12 783.

<http://www.mitretek.org/home.nsf/EnvironmentEnergy/Tabun>

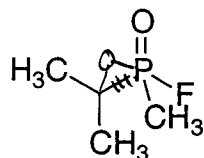
Compton, James A.F. Military Chemical and Biological Agents. The Telford Press: Caldwell, N.J., 1987.



# 1938 - GB - Sarin

17

(methylphosphonofluoridic acid, (1-methylester) ester)



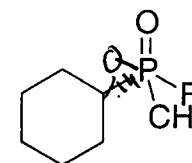
colorless liquid  
colorless vapor  
when pure, no odor  
when impure, rotting  
fruit smell

Internal assimilation  
is much higher with GB  
due to the F, methyl,  
and i-propyl groups.  
But, also increased  
environmental dissipation.  
Hence, less persistent.

GB is the most toxic  
and volatile of the  
G-series agents. It is  
delivered by artillery or  
spray and is not flammable

- Dr. Gerhard Schrader developed the second of these G-series nerve agents in 1938.
- The name is compiled from the individuals involved in its creation: Schrader, Ambrose, Rüdiger, and van der Linde.
- Tests in 1939 showed that GB worked ten times faster than GA.
- While the GA plant in Silesia was under construction, a complex known as "Building 144" was used for small scale GB production. Another facility was built for GB production just in time for the Soviet forces to take it over in 1945.
- When prototype munitions were captured in the Ruhr, the Western Allies realized the advances that the Germans had made in nerve agent production. NATO quickly adopted GB as the nerve agent of standard, as it remains today.

- The British version of GB is GF or cyclohexyl sarin.
- It offered no advantage in lethality over GB.
- GF was an attempt to make a naturally thick G agent without sacrificing volatility. Instead, the cyclohexyl ring tended to eliminate to form a benzene ring while in munitions. This led to a less effective agent in munitions which tended to explode on impact.



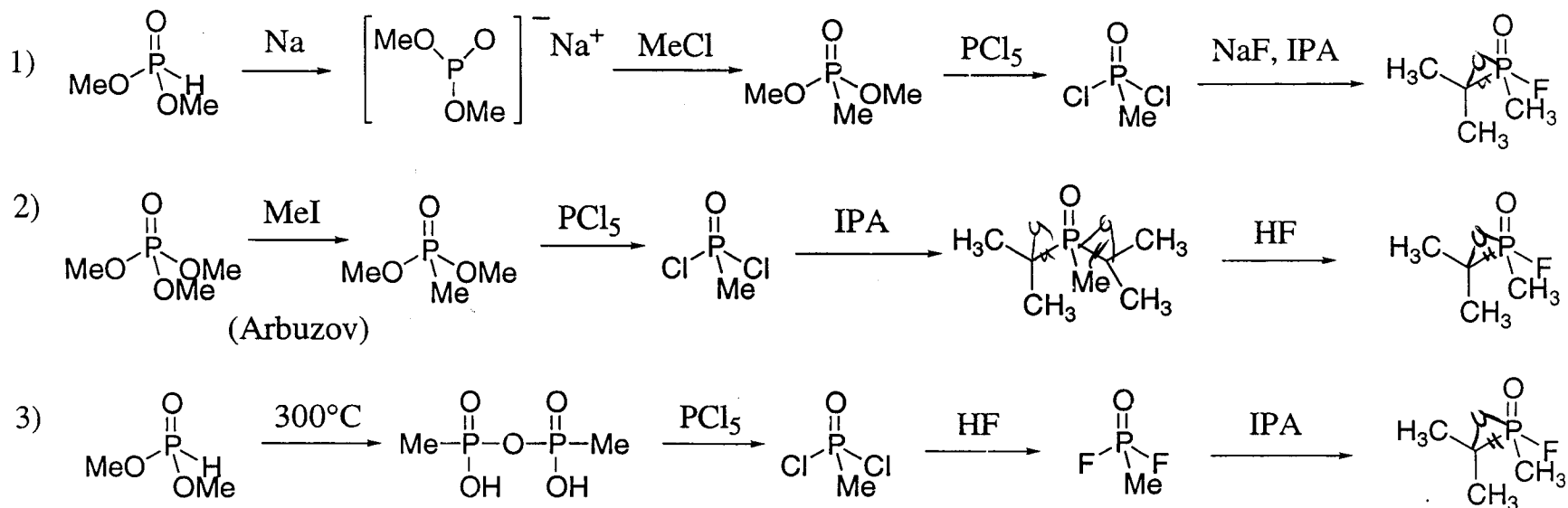
GF  
colorless liquid  
colorless vapor  
when pure, no odor  
when impure, rotting  
fruit smell

# 1938 - GB - Sarin

18

(methylphosphonofluoridic acid, (1-methylester) ester)

There are many ways to make GB. Here are three.



mp - -57°C  
bp - 147°C  
vapor pressure - 1.48 torr at 20°C  
density - 1.11 g/mL  
miscible in water

## GB Hydrolysis Rate Constants

T (°C)	k <sub>OH</sub> (L mole <sup>-1</sup> sec <sup>-1</sup> )	k <sub>w</sub> (sec <sup>-1</sup> )
0.3	4.67	1.7 x 10 <sup>-5</sup>
25	23.7	5 x 10 <sup>-5</sup>
25	25.80	-
35	42.40	-
42.5	63.7	5 x 10 <sup>-5</sup>

## GB Hydrolysis Rate Constants

T (°C)	pH	k <sub>obsd</sub> (hr <sup>-1</sup> )
23	4.5-5.0	0.00334
25	7.4	0.0324
25	9	0.84
25	9	1.2

Saunders, B.C. Some Aspects of the Chemistry and Toxic Action of Organic Compounds Containing Phosphorus and Fluorine. Cambridge University Press: Cambridge, 1957.

Larsson, L. *Acta. Chem. Scand.* **1953** 7 306.

Larsson, L. *Acta. Chem. Scand.* **1958** 12 783.

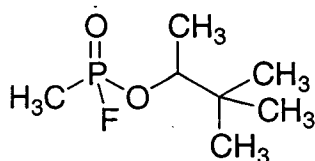
<http://www.mitretrek.org/home.nsf/HomelandSecurity/Sarin>

Compton, James A.F. Military Chemical and Biological Agents. The Telford Press: Caldwell, N.J., 1987.

# 1944 - GD - Soman

19

(methylphosphonofluoridic acid, 1,2,2-trimethylpropyl ester)



colorless liquid  
colorless vapor has a fruit odor  
when pure, camphor-  
like odor when impure

- Soman was never used in combat but was stockpiled primarily by the Soviet Union.
- The Falkenhagen archives, where GB production and GD testing occurred, were kept in a mine shaft complex about 10 miles east of Berlin in 1945. In March of that year, everything was captured by Soviet intelligence. All information, equipment, and everything else was sent to the Karpov Institute in Moscow. By the end of 1946, Soviet production of GD was in full swing.
- There are theories as to where the name came from. In Greek, soman means "to sleep." In Latin, it means "to bludgeon."
- GD is more volatile than GA, but less than GB. GD is more persistent than GB, but less than GA.

## GD Hydrolysis Rate Constants

mp - -80°C, bp - 190°C  
vapor pressure - 0.92 torr at 20°C  
density - 1.01 g/mL  
aqueous solubility - 34 g/L

T (°C)	pH	k (hr <sup>-1</sup> )
ambient	2	0.231
ambient	4.5-5.0	0.00182
25	7	0.0050
25	7	0.078
25	7.4	0.3
25	9	0.324
25	9	0.49
25	9.6	1.97
25	9.8	2.13
25	10.3	6.34
25	10.6	14.7
25	10.7	19.4



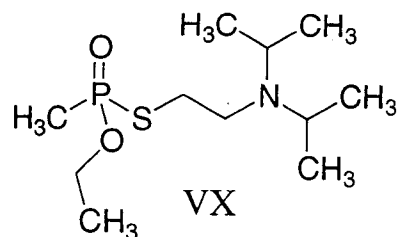
<http://www.mitretek.org/home.nsf/HomelandSecurity/Sarin>

Compton, James A.F. Military Chemical and Biological Agents. The Telford Press: Caldwell, N.J., 1987.

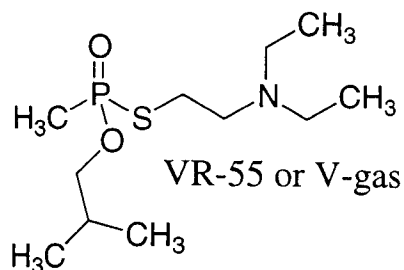
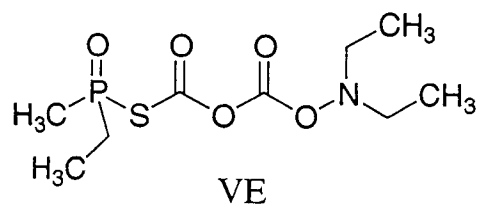
# 1956 - VX

20

(methylphosphonothioic acid, S-[2-[bis(1-methylethyl)amino]ethyl]-O-ethyl ester)



odorless pale amber  
liquid similar in look  
to 20-weight motor oil  
colorless vapor



similar in properties to  
the original VX-gas

- Dr. Ranaji Ghosh at Imperial Chemical Industries (ICI) discovered an organophosphate/sulfur compound that was immediately toxic to mammals as well as insects. The formula and samples were sent to the British at Porton Down.
- The British were committed to either GA or GB, and passed on the formula to Canada and the U.S. Canada declined, and the U.S. took it under study, refining the original formula VE to what is now coded VX.
- Somewhere between ICI and Porton, Soviet military intelligence got a hold of the formula and proceeded to develop their own version by 1995 called VR-55.
- Porton Down worked on some VX production technology until the British ordered a halt to chemical weapons production. All work came to the U.S.
- By 1960, there was a small plant in Newport, Indiana producing about 1300 lbs. a year of VX, until 1968 after the Skull Valley incident. (20 lbs. of VX leaked from an aerial spray tank and drifted over the boundaries of the Dugway, UT proving grounds, killing 6000 sheep.
- Also, an improperly stored cannister of VX leaked in Okinawa in the summer of 1969. After that, President Nixon issued an executive order in Nov. 1969 halting the development and production of all chemical weapons in the U.S.
- Only 1 mg on the skin kills a human.



<http://www.chem.ox.ac.uk/mom/vx/VX.htm>

<http://www.mitretrek.org/home.nsf/HomelandSecurity/vx#propvx>

Compton, James A.F. Military Chemical and Biological Agents. The Telford Press: Caldwell, N.J., 1987.

# 1956 - VX

21

(methylphosphonothioic acid, S-[2-[bis(1-methylethyl)amino]ethyl]-O-ethyl ester)

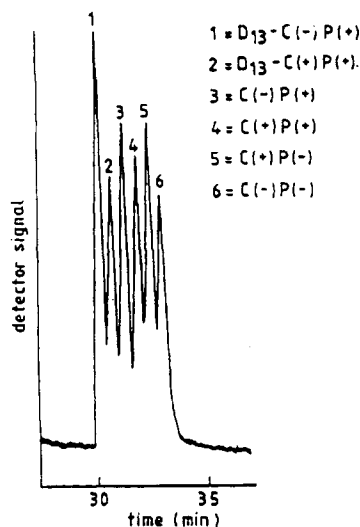
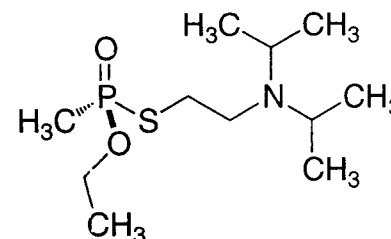
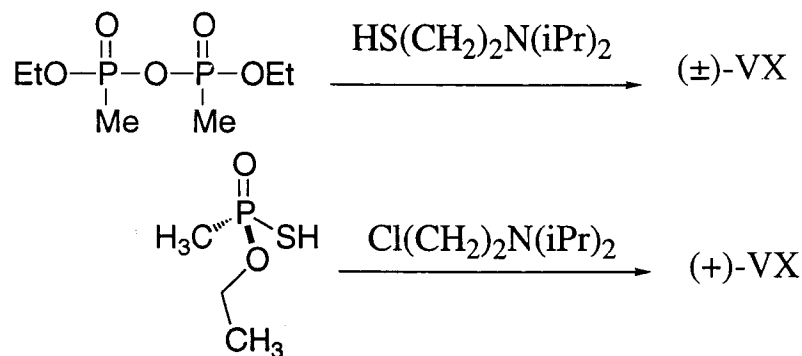


Figure 2. Gas chromatographic resolution of the four stereoisomers of C(±)P(±)-soman and of D<sub>13</sub>-C(±)P(+)-soman on a 50-m, wide-bore column coated with Chirasil Val.<sup>27</sup>

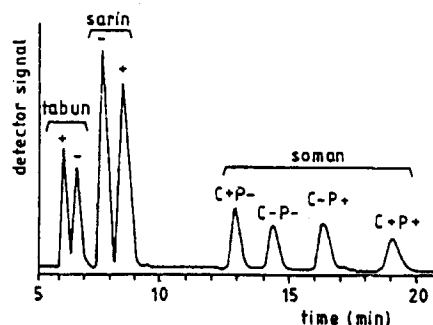


Figure 4. Gas chromatogram obtained after injection of (±)-tabun, (±)-sarin, and C(±)P(±)-soman on an 11-m, wide-bore column coated with bis[(1R)-3-((heptafluorobutyl)camphorato)]nickel(II) in OV-101.<sup>30</sup>

Table I  
Stereoselectivity in Anticholinesterase Activity and Acute Lethality of Nerve Agent Stereoisomers

nerve agent stereoisomer	rate constant for inhibition of AChE, <sup>a</sup> M <sup>-1</sup> min <sup>-1</sup> (25 °C)	LD <sub>50</sub> (mouse), μg/kg	ref
C(+)-P(-)-soman	2.8 × 10 <sup>8</sup>	99 <sup>b</sup>	13
C(-)-P(-)-soman	1.8 × 10 <sup>8</sup>	38 <sup>b</sup>	13
C(+)-P(+)-soman	<5 × 10 <sup>8</sup>	>5000 <sup>b</sup>	13
C(-)-P(+)-soman	<5 × 10 <sup>8</sup>	>2000 <sup>b</sup>	13
C(±)-P(±)-soman		156 <sup>b</sup>	13
(-)-sarin	1.4 × 10 <sup>7</sup>	41 <sup>c</sup>	34, 35
(+)-sarin	<3 × 10 <sup>8</sup> <sup>d</sup>	34	34
(±)-sarin		83 <sup>c</sup>	35
(-)-tabun	2.3 × 10 <sup>6</sup>	119 <sup>c</sup>	30
(+)-tabun	3.7 × 10 <sup>6</sup>	837 <sup>c</sup>	30
(±)-tabun		208 <sup>c</sup>	30
(-)-VX	4 × 10 <sup>8</sup>	12.6 <sup>c</sup>	35, 19
(+)-VX	2 × 10 <sup>8</sup>	165 <sup>c</sup>	36, 19
(±)-VX		20.1 <sup>c</sup>	35

<sup>a</sup>Rate constants for soman and tabun isomers were measured with AChE from electric eel at pH 7.5, whereas those for sarin and VX enantiomers were obtained with AChE from bovine erythrocytes at pH 7.7. <sup>b</sup>Subcutaneous administration. <sup>c</sup>Intravenous administration. <sup>d</sup>Estimated from an experiment with optically enriched (+)-sarin (64% ee).<sup>34</sup>

Benschop, H.P.; DeJong, L.P.A. *Acc. Chem. Res.* **1988** *21* 368.

Compton, James A.F. Military Chemical and Biological Agents. The Telford Press: Caldwell, N.J., 1987.

# Nerve Agents

22

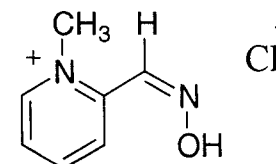
<i>agent</i>	<i>rate of action</i>	<i>state at 68°F</i>	<i>odor</i>	<i>volatility (mg/m<sup>3</sup>)</i>	<i>LCT<sub>50</sub></i>	<i>ICt<sub>50</sub></i> (mg-min/m <sup>3</sup> )	<i>vapor density (x air)</i>	<i>vapor pressure (mm Hg)</i>
GA	very rapid	colorless liquid	faintly fruity; none when pure	610 at 77°F	400	300	5.63	0.07 at 77°F
GB	very rapid	colorless liquid	almost none when pure	22,000 at 77°F	100	75	4.86	2.9 at 77°F
GD	very rapid	colorless liquid	fruity; camphor odor when pure	3900 at 77°F	100	35	6.33	0.4 at 77°F
VX	rapid	colorless or pale amber liquid	odorless when pure	10.5 at 77°F	100	50	9.2	0.0007 at 77°F

Compton, James A.F. Military Chemical and Biological Agents. The Telford Press: Caldwell, N.J., 1987.

# Decontamination

23

- In general, bases ( $\text{NaOH}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{KHCO}_3$ ) help to neutralize most agents.
- Sodium hypochlorite is very effective against the nerve agents, including VX.
- If exposed to a nerve agent, four things must be done to survive:
  - a) assisted ventilation (breathing), b) parasympathetic blockage (atropine directly to the heart)
  - c) decontamination of skin and surface, d) enzyme reactivation (2-PAM-chloride removes the agent from your cholinesterases)



**Table I. Decontaminants Composed of Hypochlorites**

decontaminant	composition	applications
bleach	2-6 wt % $\text{NaOCl}$ in water	skin and equipment
HTH (high test hypochlorite)	$\text{Ca}(\text{OCl})\text{Cl} + \text{Ca}(\text{OCl})_2$ as a solid powder or a 7% aqueous slurry	equipment and terrain
STB (super tropical bleach)	$\text{Ca}(\text{OCl})_2 + \text{CaO}$ as a solid powder or as 7, 13, 40, and 70 wt % aqueous slurries	equipment and terrain
Dutch powder	$\text{Ca}(\text{OCl})_2 + \text{MgO}$	skin and equipment
ASH (activated solution of hypochlorite)	0.5% $\text{Ca}(\text{OCl})_2 + 0.5\%$ sodium dihydrogen phosphate buffer + 0.05% detergent in water	skin and equipment
SLASH (self-limiting activated solution of hypochlorite)	0.5% $\text{Ca}(\text{OCl})_2 + 1.0\%$ sodium citrate + 0.2% citrate acid + 0.05% detergent in water	skin and equipment

**Table II. Field Decontamination Equipment and Systems**

item name	description	decontaminants	applications
ABC-M11, decontaminating apparatus, portable	a fire extinguisher-like device to spray DS2; Comes with mounting bracket for attaching to vehicles	1.5 qt (1.3 L) DS2	vehicle and equipment
ABC-M12A1, decontamination apparatus, power-driven, skid-mounted	includes pump, tank, personnel shower units, and M2 water heater	water, foam, deicing liquid, DS2, or STB	washing, deicing, and showering
M258A1, decon kit, personal	consists of foil-packaged pairs of towelettes in a plastic carrying case	I. water, phenol, $\text{NaOH}$ , ethanol, and ammonia II. water, ethanol, chloramine-B, and $\text{ZnCl}_2$	skin and individual equipment
M280, decon kit, individual equipment	consists of 20 foil-packaged pairs of towelettes in a plastic carrying case	I. water, phenol, $\text{NaOH}$ , ethanol, and ammonia II. water, ethanol, chloramine-B, and $\text{ZnCl}_2$	individual equipment
M291, skin decon kit	consists of 6 foil-packaged nonwoven fiber pads filled with XE-555 resins	2.8 g of XE-555 resins of a total water content of 25 wt %	skin
M13, decon apparatus, portable	self-contained device with a disposable 14-liter DS2 container; can be mounted to the standard fuel can which mounts on vehicles and equipment	DS2	vehicle and equipment
M17, transportable, lightweight, decon system	draws water from any natural source within 30-ft distance and less than 9-ft below pump level; delivers water at pressures up to 689 kPa and temperatures up to 120 °C; includes hoses, cleaning jets, personnel showers, and collapsible rubberized fabric tank	water	equipment, vehicle, and personnel

## Conclusions

24

- There are multiple types of chemical weapons available that do varying degrees of damage
- Access to knowledge for the synthesis of all types of chemical weapons is easy and prevalent (scary!)
- Education of the public is the key to lowering hysteria with regard to weapons of mass destruction



# R107 CONTROL AGENTS

## EMITTING AGENTS



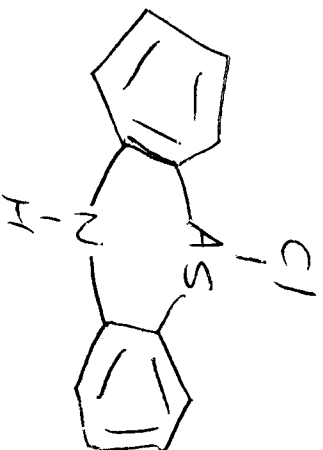
DA

DIPHENYL CHLOROARSINE



DC

DIPHENYL CYANOARSINE



DM

(ADAMSITE)

DIPHENYL AMINO CHLOROARSINE

EFFECTS WHEN OFT IN 0.5-1 HR.  
AS - CUMULATIVE TOXIN  
BANNED BY NATO MEMBERS

riot control agents: vomiting

comparative data

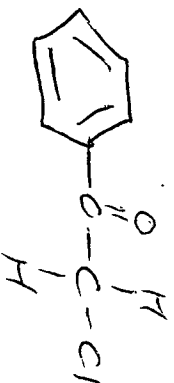
agent	rate of action	state at 68°F	odor	volatility (mg/m <sup>3</sup> )	LCT <sub>50</sub> (mg-min/m <sup>3</sup> )	ICT <sub>50</sub> (mg-min/m <sup>3</sup> )	vapor density (x air)	vapor pressure (mm Hg)
DA	very rapid	white to brown crystalline solid	none	48 at 113°F	15,000	12	very little of own	0.0036 at 113°F
DC	very rapid	white to brown crystalline solid	none	insignificant	15,000	8-22	very little of own	insignificant
DM	very rapid	white to brown crystalline solid	bitter almond-garlic mixture	2.8 at 68°F	10,000	20-30	very little of own	0.0002 at 68°F

# R107 CONTROL AGENTS

## TRIAL AGENTS



CA  
BROMOBENZENE  
ACETONITRILE



CN  
CHLOROBENZENE  
(USED BY POLICE)

MAIN  
COMPONENT  
OF

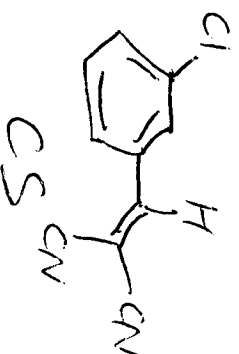
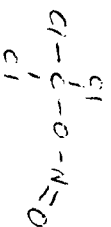
METHYL

CHLOROFORM  
CHLOROACETONITRILE

CNB - 10% CN  
45% CCl<sub>4</sub>  
(EUMMALES)  
45% BENZENE

CNC - 30% CN  
70% CHCl<sub>3</sub>

CNS 23% CN  
38.5% CHCl<sub>3</sub>  
38.5% CHLOROPHOSPHINE



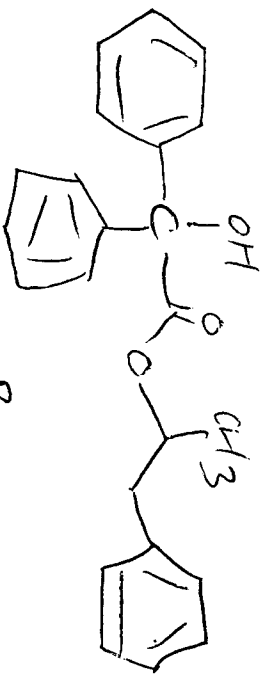
CS  
CN

O-CHLOROBENZYLIDENE MALONONITRILE  
(TRIAL GAS), (PERMAN GAS)

riot control agents: tear agents      comparative data

agent	rate of action	state at 68°F	odor	volatility (mg/m <sup>3</sup> )	L <sub>C</sub> t <sub>50</sub> (mg-min/m <sup>3</sup> )	I <sub>C</sub> t <sub>50</sub> (mg-min/m <sup>3</sup> )	vapor density (x air)	vapor pressure (mm Hg)
CA	instantaneous	usually in liquid solution	rotten fruit	115 at 68°F	8000	30	6.7	0.011 at 68°F
CN	instantaneous	solid	apple blossoms	343 at 68°F	14,000	80	5.3	0.0041 at 68°F
CNB	instantaneous	liquid	benzene	varies	11,000	80	aprox 4.0	variable. mostly solvent
CNC	instantaneous	liquid	chloroform	varies	11,000	80	4.4	127 at 68°F
CNS	instantaneous	liquid	flypaper	610,000 at 68°F (due to solvent)	11,400	60	aprox 5.0	78 at 68°F
CS	instantaneous	colorless solid	pepperish	0.71 at 77°F	61,000	10-20	varies with burn agent	varies with burn

# INCAPACITATING AGENTS



BZ (Buzzi)

3-QUINUCLIDINYL BROMATE

Ro 2-3308 (LA Roche)

~~CNS~~ CNS DEPRESSANT PARALYZING  
CRYSTALLINE SOLID + E<sub>30</sub> ON RETRONE

# BIO TOXINS

## BOTULINUS TOXIN

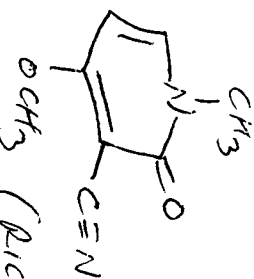
8 TOXINS - PROTEINS

(A, B, C, D, E, F, G)

(COSTRIBUVA BOTULINUM)

USAO TO BT BTX

## RICININE



(RICINUS COMMUNIS)

NATURAL SOURCES LARICIA  
FROM SYNTHETIC

(OT-IR MOY BAZU)

(ASTON)

BEAN

BEAN

## TRICOTHECENE MYCOTOXINS

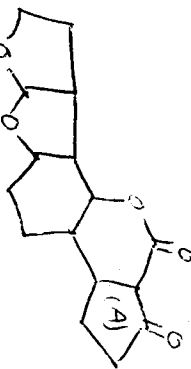
T-2

FUSARIUM

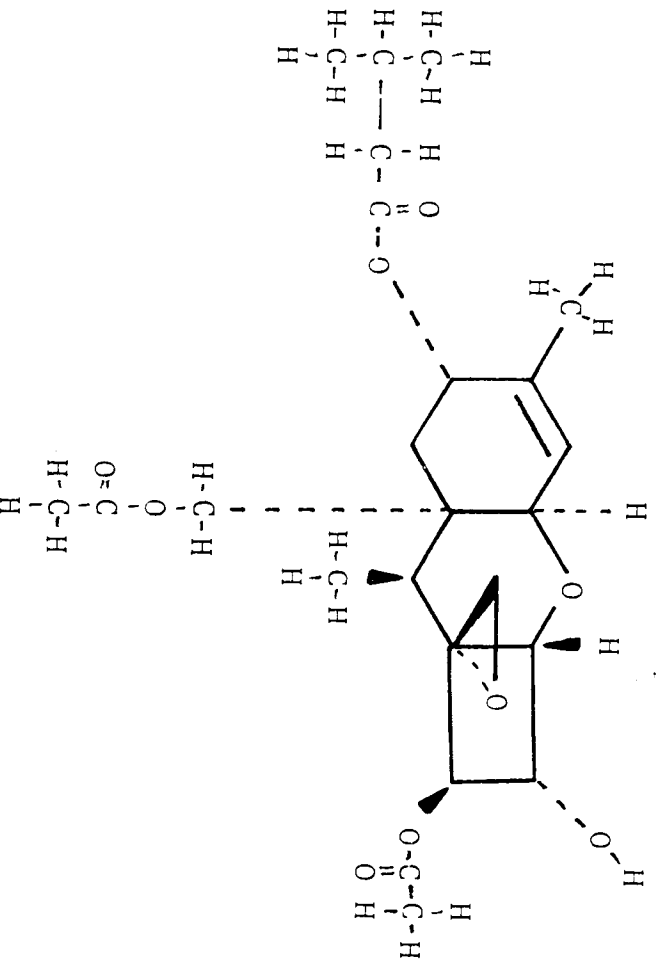
NIVALTUM

NIVME

## AFLATOXINS



T-2                      12,13-epoxytricothec-9-ene-3,4,8,15-tetrol 4,15-diacetate 8-(3-methylbutanoate)



*description*

Tricothecene mycotoxin isolated from *fusarium tricinctum*. Soluble in methanol, ethanol.

*effects*

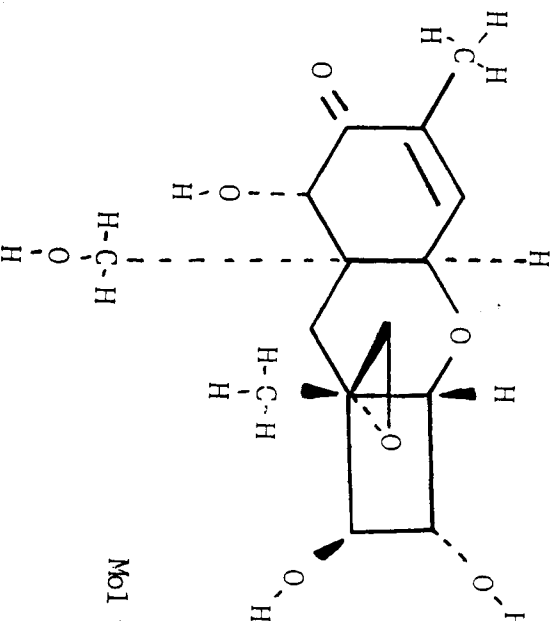
Caustic skin irritant and hemorrhagic, causing tissue necrosis on contact. Also causes blisters, nausea and dizziness, vomiting and diarrhea. Untreated, it may lead to death. Its systemic toxicity is proportional to dosage.

*detection*

(CHROMATOPOGRAPHY)

# NIVALENOL

12,13-epoxy-3,4,7,15-tetrahydroxytrichotec-  
9-en-8-one



Mol wt 312.33

## description

Tricothecene mycotoxin isolated from *fusarium nivale*. Soluble in methanol, ethanol, and other polar organic liquids. Slightly soluble in water.

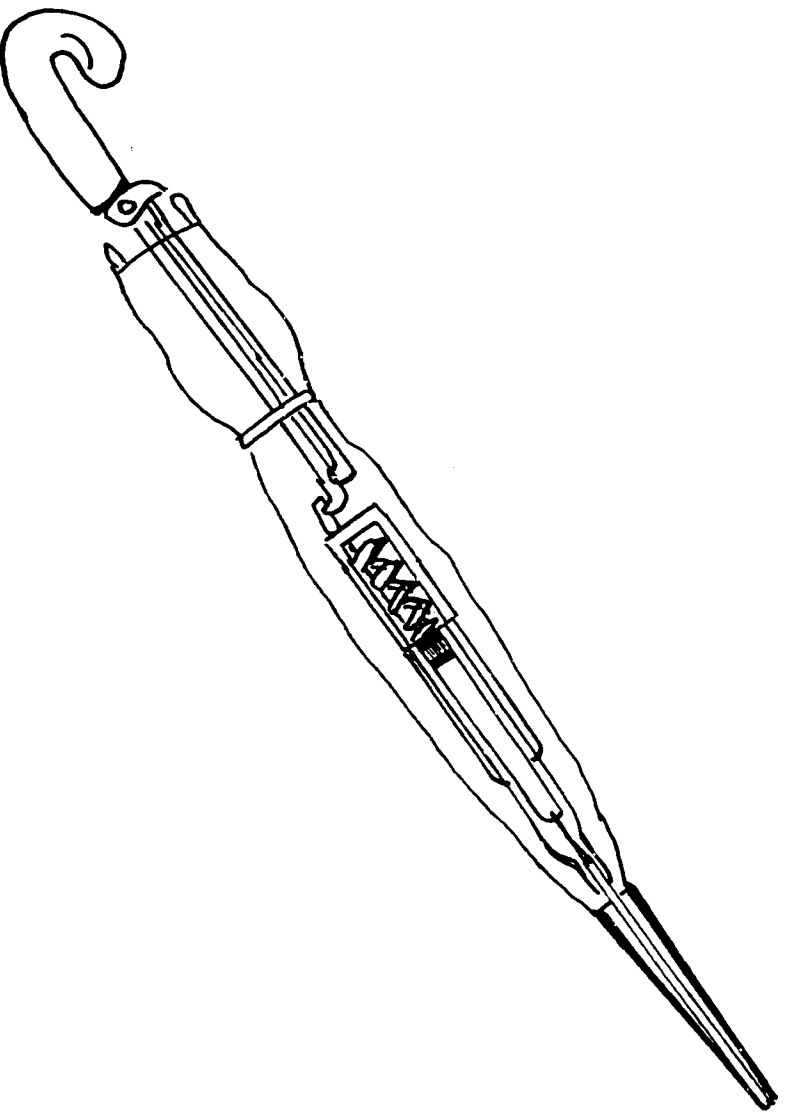
## effects

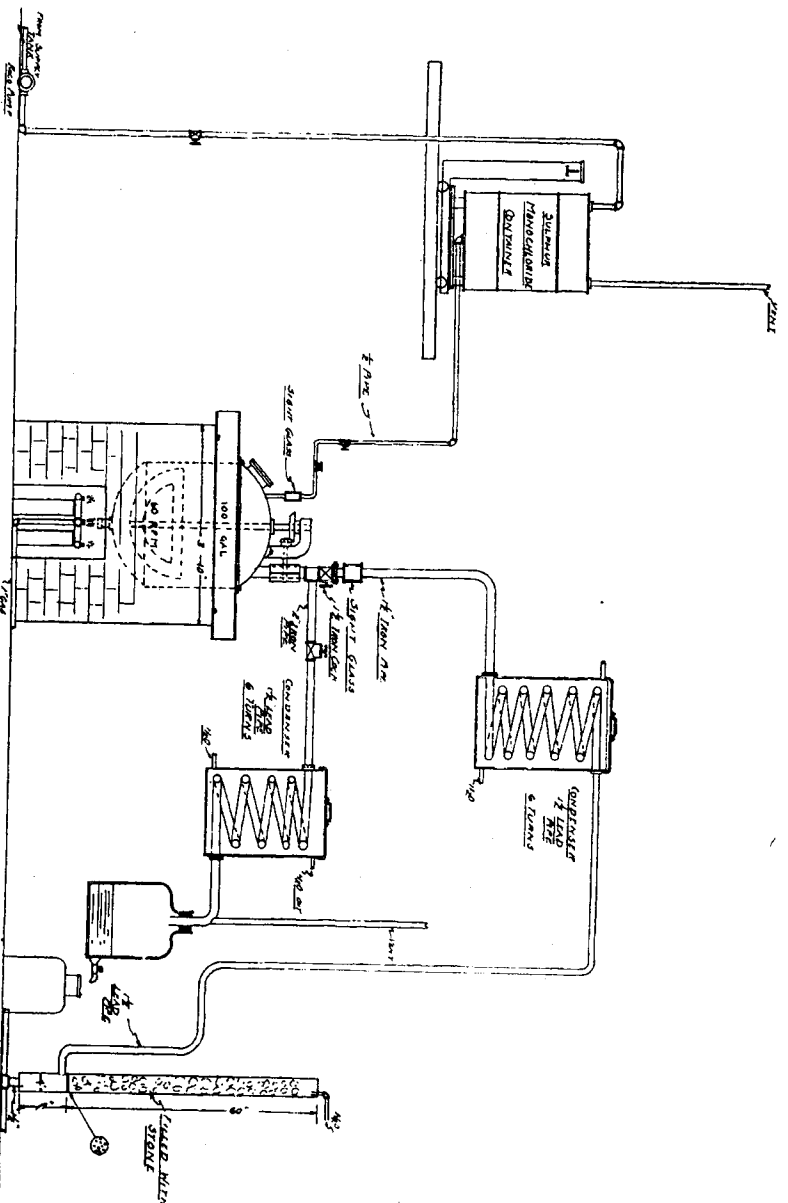
An extremely strong hemorrhagic substance. Causes immediate tissue necrosis. Also causes blisters, nausea and dizziness, vomiting and diarrhea. Untreated, it may lead to death. Its systemic toxicity is proportional to dosage.



Soviet embassy protested against one of its citizens being dissected and filed a sharp series of protests with the US State Department. As a coroner's jury looked on the autopsy was finally performed. A platinum-iridium alloy ball was removed. The ball was kept by the American friends while the victim, Boris Korczak, was sent to his final resting place aboard an otherwise empty Aeroflot plane.

A number of people have died from these mysterious ricin filled metal balls. A number of people, from the British labor leader Hugh Gaitskell to the Algerian statesman Houari Boumédiénne have died from ricin-like symptoms.





APPARATUS FOR MANUFACTURE OF ARSENIC TRICHLORIDE

trace of arsenic trioxide. If opened when too hot, the sulfur residue is liable to take fire.

The charge of arsenic trioxide was divided into two parts in order to use agitation during as much of the process as possible. The first charge required about 1 1/2 hrs. to complete and the second charge about 3 hrs. The total time of operation was between 7 1/2 and 8 hrs.

Based on the amount of sulfur chloride used the yield was 93 per cent of product averaging 99 per cent pure.

The first distillate which was always colored was decolorized by redistilling with a small amount of arsenic trioxide.

This investigation was started under the Bureau of Mines at the American University Experiment Station and was continued under the Research Division of the Chemical Warfare Service.

SMALL SCALE MANUFACTURING SECTION  
RESEARCH DIVISION, C. W. S., U. S. A.  
AMERICAN UNIVERSITY EXPERIMENT STATION  
WASHINGTON, D. C.

## ORIGINAL PAPERS

### THE DETERMINATION OF CADMIUM BY THE HYDROGEN SULFIDE METHOD

By EDWARD SCHRAMM

Received August 12, 1918

#### I—INTRODUCTION

In the course of some cooperative work on the determination of small quantities of cadmium in brass it was found that varying results were obtained by several laboratories. A diversity of methods is in current use, most of which do not appear to have been tried out on materials of known composition.<sup>1</sup> The present work was accordingly undertaken with a view to developing a convenient and reliable procedure for this determination, and to ascertaining what degree of

<sup>1</sup> Two methods have been described in considerable detail in the second edition of Price and Meade, "Technical Analysis of Brass," pp. 229-233.

accuracy is to be expected. To accomplish these aims, analyses were made of brasses with cadmium additions and of salt mixtures of known composition. The hydrogen sulfide precipitation was chiefly employed for the necessary separations, and accordingly the work became primarily a study of the most suitable conditions for separating a small amount of cadmium from other metals by this method.

Structural brasses may contain, besides the principal constituents, copper and zinc, one per cent or more of tin, and varying quantities of lead, iron, manganese, arsenic, and other metals, which may have been added intentionally or introduced accidentally as impurities in the copper or zinc. Very little has been published on the determination of cadmium in brass, but its determination in spelter has been the subject of a