

Chemical Warfare Agents and Toxic Industrial Chemicals

CWAs are chemicals that are intended for use in warfare or terrorist activities with the intention to kill, seriously injure, or incapacitate people through physiological effects upon exposure. These chemicals produce disabling effects that severely reduce the ability to fight. When CWAs enter or contact the human body, they attack various organs and prevent them from functioning normally. CWA classifications, defined in [Chapter 1](#), include nerve, blister, choking, blood, incapacitating, and vomiting agents. Nerve, blister, and blood agents are considered the most noxious or dangerous because a very small dose may cause death.

TICs are chemicals toxic to humans that are widely used in manufacturing or primary material processing (mining and refining). To qualify as a TIC, the chemical must have an LCt_{50} value of less than 100,000 mg-min/m³, and be produced at a level of more than 30 tons per year at a single production facility. LCt_{50} means 50% of the exposed population would die when that dosage (concentration multiplied by exposure time) is ingested by an average-sized individual. A number of chemicals (more than 90), including many household-cleaning agents (e.g., ammonia and chloride in bleach), are considered TICs. Several of the TICs, such as hydrogen cyanide, cyanogen chloride, and phosgene, were once classified as chemical agents by the military, and were used in CW attacks during the world wars. TICs are ranked as being high-, medium-, or low-hazard TICs based on the combination of their toxicity level, amount being produced, and relative volatility.

Improper handling and accidents or intentional use on civilian targets by terrorists can lead to disasters. (Toxic chemical leaks and spills around the world are reported on the Environmental Protection Agency [EPA] website at <http://yosemite.epa.gov/oswer/ceppoweb.nsf/content/ap-chsa.htm>.)

One example of such disasters, based on the EPA Office of Solid Waste and Emergency Response, July 1993 (EPA-560-K-93-001 Series 8, No. 3), is the release of 30,000 to 50,000 pounds of hydrogen fluoride (HF) and isobutane at a Texas

petroleum refinery due to a construction accident at an alkylation unit. The chemical vapors migrated to an adjacent residential area. Eighty-five square blocks and approximately 4000 residents were evacuated. Although no fatalities were reported, more than 1000 residents sought treatment at three local hospitals.

2.1 CHEMICAL, PHYSICAL, AND TOXICOLOGICAL PROPERTIES

Toxicity of chemicals can be expressed in terms of IDLH (immediate danger to life and health) level, LC₅₀, REL (recommended exposure limit) and PEL (permissible exposure limit), and AEL (acceptable exposure limit), among others. Physical and chemical properties have direct influence on the behavior of a compound. For example, a vapor or liquid with high vapor pressure would create a respiratory inhalation hazard as the primary threat. Solids or low-volatility liquids may not produce a sufficiently concentrated vapor to act as an inhalation threat. Their primary threat would be through direct contact. Specific hazards will dictate respective detection and evaluation methodologies.

2.1.1 Molecular Formula

A molecular formula shows the molecular composition of a substance. It provides the actual number of atoms of each element in a molecule of the compound. The formula of sarin, for example, is C₄H₁₀FO₂P. This formula shows that one sarin molecule contains 4 carbon atoms, 10 hydrogen atoms, 1 fluorine atom, 2 oxygen atoms, and 1 phosphorus atom. The formulas for CWAs and some of the most hazardous TICs are included in this chapter's tables.

2.1.2 Molecular Structure Formula

A molecular structure formula differs from a molecular formula in that it indicates the relative connectivity or arrangement of the atoms in a molecule. For example, the molecular structure of sarin with the molecular formula of C₄H₁₀FO₂P is shown Figure 2.1:

The structural formula shows how atoms are grouped and bonded to form the sarin molecule. This formula provides clues for predicting the substance's behavior.

Organic compounds with the same molecular formula, but different structures, are called isomers. Isomers' properties may be very different. For example, ethanol and dimethyl ether have the same molecular formula, C₂H₆O. Ethanol is a colorless

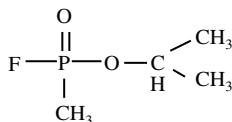


Figure 2.1 Structure of GB.



a. Ethanol



b. Dimethyl ether

Figure 2.2 Structures of (a) ethanol and (b) dimethyl ether.

liquid; its structural formula is shown in Figure 2.2a. Dimethyl ether is a colorless gas; its structural formula is shown in Figure 2.2b.

Compounds with different formulas may have similar physical/chemical behaviors when their molecules are in the same function group. For instance, both hydrogen cyanide (H-CN) and cyanogen chloride (CN-Cl) contain the “cyanide (CN)” function group. Therefore, they act similarly to produce similar effects upon contacting blood cells.

2.1.3 Molecular Weight

Molecular weight (MW) is the weight of a molecule expressed in atomic mass units (amu), and calculated from the molecular formula of a substance. It is the sum of the atomic weights of the atoms that comprise the molecule. High-molecular-weight substances tend to be solids. Low-molecular-weight substances tend to be gases. MW also indicates the relative persistency of a compound. Heavier molecules usually have lower rate of evaporation and, thus, greater persistency.

2.1.4 Relative Vapor Density

Relative vapor density is the ratio between the density of a gas or vapor (D_g) and the density of air (D_a) at the same temperature and pressure conditions:

$$VD = \frac{D_g}{D_a} \quad (2.1)$$

Vapor density of a chemical is directly proportional to its MW. The average MW of air is 29 amu. At 25°C and 1 atmospheric pressure, average air density is 1.19 kg/m³. The vapor density of air is referred to as being 1 for the calculation of relative vapor density of other vapors. Any chemical with MW >29 amu would have a vapor density >1 under the same temperature and pressure conditions, according to the Ideal Gas Law. Hence, the vapor is heavier than air and it will tend to stay in or flow to low places. Vapor of chemicals with MW <29 amu have a vapor density of <1. These vapors would tend to migrate to higher places and will be easily diluted by air currents. The vapor densities of all CWAs and TICs, except for a few chemicals such as hydrogen cyanide, carbon monoxide, diborane, and ammonia, are >1.

2.1.5 Vapor Pressure

Vapor pressure (VP) is the pressure generated by the vapor of a substance that is at equilibrium with its liquid and/or solid state in an enclosed space. In other words, if there is only one chemical in a closed container, and the evaporation/condensation between the vapor and the liquid/solid has been established, the pressure on the wall of the container will be generated by that chemical only. Vapor pressure determines the saturated concentration of a given vapor in air (volatility) and the chemical's persistency. A chemical with VP lower than the ambient air pressure evaporates gradually at a certain rate (such as water evaporation at room temperature). Lower VP indicates lower volatility, and hence, higher persistency. A chemical is gaseous when its VP is equal or greater than the atmospheric pressure (e.g., oxygen and nitrogen in the air, or water vapor when water is heated to its boiling point). Nerve and blister agents have VPs of <1 atmospheric pressure (760 mmHg), while most of the high-hazard TICs have VPs of >1 atmospheric pressure.

2.1.6 Volatility

When the vapor of a chemical is at equilibrium with its solid or liquid phase, the total weight of the chemical vapor found in terms of milligrams (mg) in a cubic meter (m^3) volume of air at a specified temperature represents its volatility. Its units are normally expressed as mg/m^3 at a specific temperature. Volatility (V) represents the maximum amount of a chemical that a cubic meter air can hold at the specified temperature. For example, the volatility of water at 20°C is 23,010 mg/m^3 . This means that at that temperature, 1 cubic meter air contains 23.01 g of water when the air is saturated.

In an open space, the chemical vapor will continually be diluted by air and diffuse away. The vapor–solid or vapor–liquid equilibrium can never be reached. Thus, concentration of a compound is at its maximum near the interface. V is directly related to temperature. At a higher temperature, a compound will have relatively higher volatility. This is best illustrated by the different amounts of water that air can contain at different temperatures. During the summer, humidity (water content in the air) can be much higher than during the winter. V is one of the most important physical properties of an agent or TIC that one should know when dealing with detection device development, vapor generation, and equipment evaluations.

V plays an important role in determining deployment and detection effectiveness. The V of all CWAs and some TICs is higher or much higher than their respective IDLH concentration levels. This suggests that the chemicals can easily reach dangerous vapor concentrations in the surrounding air.

For chemicals of similar toxicity, higher-volatility compounds are considered more dangerous than lower-volatility ones. That is because highly volatile substances enter the air more easily and will produce higher vapor concentrations. Methods designed to detect chemical vapors must treat volatility as a first consideration. Methods required for detection of chemicals with very low volatility as opposed to those with higher volatility may be different. Similarly, a thorough understanding of the compound's volatility is a must for proper vapor generation, sample collection,

safe handling, and effective protection or deployment of these types of chemicals. Its importance cannot be over-emphasized.

V is inversely related to the persistency of a chemical. A chemical with high persistency, and thus lower volatility, will be found on the surface of an object long after the initial encounter. Residues of persistent blister agents and VX enter the human body through absorption on contact with unprotected skin. Their persistency enhances their effectiveness. The vapor concentration of highly persistent chemicals in the air is likely to be quite low. Such low concentration availability makes detection of these chemicals in the atmosphere more difficult. A detection instrument must be able to identify the targeted compound in highly diluted states; that is, the device must segregate a minute amount of material in an ocean of potentially interfering substances. Therefore, surface-sampling techniques should be used to supplement vapor detection techniques when detection of such chemicals is desired.

2.1.7 Concentration

Concentration refers to the amount of a substance contained in a volume of liquid or vapor. Since detection of toxic chemical vapors is our primary objective, our attention will be focused on those dealing with vapor concentrations. Vapor concentration is usually expressed in terms of number of milligrams per cubic meter (mg/m^3). Some practitioners may use different terms such as microgram per liter ($\mu\text{g}/\text{l}$), parts per million (ppm) or parts per billion (ppb), or percentage (for high concentrations). When concentration is expressed using parts per million or billion, temperature and pressure must be specified. Milligrams per cubic meter or micrograms per liter denotes that the value is the actual vapor concentration that contains the same amount of the substance in a fixed volume no matter what the temperature and atmospheric pressure are, while the actual amount of an agent in vapor varies with temperature and pressure when the concentration is expressed as parts per million or billion. More details on concentration units and conversion among them are provided in [Chapter 4](#).

2.2 TOXIC PROPERTIES

Toxicity together with the volatility of a compound dictates the effectiveness of a CWA or TIC when deployed. Common terms used to gauge the relative toxicity of a CWA or a TIC are IDLH level, LCt_{50} , ICt_{50} , TWA (time-weight average), and AEL.

2.2.1 IDLH Level

IDLH level is the concentration of a chemical in the air that would cause immediate or delayed permanent adverse health effects after 30 min of unprotected exposure. At IDLH level, an exposed person may have 30 min to escape the contaminated environment without loss of life or irreversible health effects. The IDLH

level was established by the National Institute for Occupational Safety and Health (NIOSH) as respirator selection criteria in the mid-1970s.

The purpose for establishing the IDLH level is to determine a concentration that permits sufficient time for a person to escape safely or to seek protection without incurring serious injury or irreversible health effects. In determining IDLH levels, the ability of a person to escape or seek protection was considered together with severe eye or respiratory irritation and other deleterious effects (e.g., disorientation or lack of coordination) that could prevent a timely escape. The IDLH level is the concentration at which the dosage received during a 30-min exposure without physical protection would cause minimal adverse health effects. However, the 30-min period is *not* meant to imply that people should stay in that contaminated environment any longer than necessary. In fact, every effort should be made to evacuate the locale immediately.

IDLH levels vary widely among diverse compounds. A lower value means that the compound is more dangerous and has greater toxicological effects. The volatility of all CWAs and most TICs is, unfortunately, much higher than respective determined IDLH level. This means that the vapor concentration in the air can easily reach the dangerous level.

The establishment of IDLH levels does not mean that exposure to lower levels of CWAs or most TICs is safe. Exposure to chemicals at concentrations much lower than the IDLH level for a long period will also be dangerous or even fatal. Although exposures to lower concentrations for a short period may not cause immediately observable effects or symptoms, toxicity effects may be cumulative. While some toxic substances (such as HCN) can be gradually detoxified naturally by human organs, many of them cause irreversible effects. The latter type of compound is commonly called “refractory.” Soman (or GD) and other refractory compounds must be handled with special care to avoid any exposure.

2.2.2 LC_{t50}

LC_{t50} represents the lethal (L) concentration (C) that will cause death to 50% of the exposed population for a period of exposure time (t). It is a function of vapor concentration ($C = \text{mg}/\text{m}^3$) and exposure duration (t in minutes).

LC_{t50} values are established for both inhalation and percutaneous exposures. Inhalation dosage is exposure through the respiratory tracts. Percutaneous exposures occur through skin contact. For most chemicals of interest here, the inhalation LC_{t50} dosage is lower than that of the percutaneous exposure because the body absorbs the chemical vapor much faster and more effectively through the respiratory tract than through skin permeation. Thus, it is most important to protect the airway immediately to minimize inhalation dosage. Once the airway has been protected, it is necessary then to eliminate contaminated clothing and remove residue contamination as soon as possible. In general, absorption through the skin is somewhat limited to exposed skin initially, and then later the chemical penetrates clothing.

Dosage is a function of concentration and exposure time. For example, if 100 people exposed to air containing 100 mg/m³ of a chemical that has an LC_{t50} value

Table 2.1 Concentrations and Exposure Time to Reach LC_{t50} of Sarin via Inhalation

| Concentration of Sarin in Air (mg/m ³) | Exposure Time for Person at Rest (min) ^a | Exposure Time for Mildly Active Person (min) ^b |
|--|---|---|
| 200 | 0.5 | 0.35 |
| 100 | 1 | 0.7 |
| 50 | 2 | 1.4 |
| 5 | 40 | 14 |

^a LC_{t50} is 100 mg-min/m³ for person at rest.

^b LC_{t50} is 70 mg-min/m³ for mildly active person.

of 100 mg-min/m³ without protection, about 50 people would be killed with 1 min of exposure. Fifty people will be killed with 4 min of exposure when the concentration is 25 mg/m³. Table 2.1 shows exposure times for sarin to reach LC_{t50} at various concentrations.

A few factors may affect LC_{t50}. Respiration rate is one of them. The respiration rate is slower when an individual is resting than when active; a smaller dosage will be breathed in during the same period of time and at the same concentration level when a person is at rest. A resting individual will also have slower blood circulation due to a lower pulse rate. Lower breathing and pulse rates mean lower dosage ingested over a given time period and at a given concentration. Therefore, the LC_{t50} value is generally higher for a person at rest (e.g., 100 mg-min/m³ for GB) than for an active person (e.g., 70 mg-min/m³ for GB).

Similar to LC_{t50}, the concentration that incapacitates 50% of the exposed population multiplied by the exposure time is defined as IC_{t50}. The IC_{t50} value is lower than the LC_{t50} because it is the dosage that will cause incapacitation of an individual to perform normal functions effectively rather than to cause death. For example, if exposure to a chemical compound causes coughing, vomiting, hallucinating, or any uncontrolled bodily functions, it will have diminished the effectiveness of an individual to perform normal functions. If the individual were a soldier, he or she would be spending time dealing with symptoms instead of fighting.

Given that people ingest lower doses when at rest, one of the most important keys to surviving a chemical attack is to remain calm.

2.2.3 TWA

The concentration of toxic chemicals may vary during the period of exposure. TWA reflects the exposure level over a period time. For example, assume that a person is exposed to a chemical at a concentration of 0.1 ppm for 6 hr and at a concentration of 0.2 ppm for 2 hr. The TWA over the 8-hr period is calculated as

$$\text{TWA} = (0.1 \text{ ppm} \times 6 \text{ hr} + 0.2 \text{ ppm} \times 2 \text{ hr}) / 8 \text{ hr} = 0.15 \text{ ppm} \quad (2.2)$$

Three common terms are based on TWA. REL, or recommended exposure limit, is maximum TWA concentrations for up to a 10-hr workday during a 40-hr

workweek. PEL, or permissible exposure limit, is the TWA concentration that must not be exceeded during any 8-hr workday of a 40-hr workweek. STEL, or short-term exposure limit, is designed for a 15-min TWA exposure that should not be exceeded at any time during a workday.

2.2.4 Other Terms

Other terms that may be used include LC_{50} (lethal concentration for 50% of population), IC_{50} (incapacitation concentration for 50% of population), and LD_{50} (lethal dosage for 50% of population). These terms will be explained when they are used.

2.3 COMMON CWAs

Included here are nerve agents, blister agents, choking agents, and blood agents, among others. The important agents in each group, their common names, symbols, and symptoms upon exposure are summarized in Table 2.2. Each type of agent is briefly reviewed below.

2.3.1 Nerve Agents

Nerve agents, including the G- and the V-agents, attack the nervous system by disrupting the normal transmission of nerve impulses. Since muscle functions depend on nerve signals, interrupting signal transmission produces neurologic disorders, followed by paralysis, cardiovascular, or respiration failure. Lungs and eyes could

Table 2.2 Common Agents and Symptoms After Exposure

| Group | Common Agents | Common Symptoms After Exposure |
|----------------|--|--|
| Nerve agents | GA (tabun), GB (sarin), GD (soman), GF (cyclosarin), and VX | Runny nose, tightness of chest, dimness of vision and myosis, breathing difficulty, drooling and excessive sweating, nausea/vomiting, involuntary defecation and urination, twitching, jerking and staggering, headache, confusion, drowsiness, convulsions, coma, and eventually, death. Death is caused by respiratory arrest, as all respiratory muscles contract |
| Blister agents | Distilled mustard (HD), nitrogen mustards (HN-1, HN-2, HN-3), lewisite (L) | Reddening of skin that develops into inflammation and/or blister |
| Choking agents | Phosgene (CG), diphosgene (DP) | Sneezing, pain in chest, painful swallowing, choking, breathing difficulty, and tightness in chest |
| Blood agents | Hydrogen cyanide (AC), cyanogen chloride (CK) | Convulsions, rapid deep breathing, and bradycardia followed by shallow breathing and eventual cessation of breathing. CK has choking and strong irritation effects |

rapidly absorb nerve agent vapor, resulting in deadly effect in <1 min. Reaching lethal dosage occurs rapidly after exposure to liquid nerve agents as well.

Nerve agents cause an increase in acetylcholine throughout the body. Acetylcholine interferes with the vital enzyme, cholinesterase. Thus, nerve agents are also known as cholinesterase inhibitors. Acetylcholine and cholinesterase play a vital role in controlling nerve signal transmission to skeletal muscles, autonomic ganglia, and many central nervous system structures. Symptoms include difficulties in breathing, drooling and excessive sweating, nausea, vomiting, and cramps, among others. Nerve agents are extremely toxic. Death can occur within minutes when a sufficient dose enters the body through the respiratory route. Exposure symptoms appear more slowly from skin exposures. Although a lethal dose may be reached in 1 to 2 min of exposure, death may be delayed for 1 to 2 hr.

G-agents such as tabun (GA), sarin (GB), soman (GD), and cyclosarin (GF) are fluorine- or cyanide-containing organophosphates, and V-agents (VX and Vx) are sulfur-containing organophosphorus compounds. They are colorless liquids at 20°C, with or without odors. The MWs of the nerve agents are >29 amu; therefore, their vapors are heavier than air (relative vapor density >1). Among the nerve agents, GB has the highest VP, and VX the lowest. VP of the nerve agents decreases in the following order:



The toxicity of VX is the highest among the nerve agents with an IDLH level of 0.002 ppm. It is about 10 times more toxic than GB and GA. GD is the most toxic agent among the G-agents. The IDLH level for nerve agents decreases in the following order:



Table 2.3 provides toxicity data for nerve agents, including IDLH, LC_{t50}, and IC_{t50}. IDLH levels are listed as ppm. However, these indicators can be calculated as milligrams per cubic meter, as discussed in Chapter 3.

2.3.1.1 Tabun

The first nerve agent, tabun, also known as GA, was discovered by German scientists who had developed the fluorine-containing compound as a pesticide. The effect of nerve agents on human beings was first noticed when workers were observed to experience pupil contraction and shortness of breath when exposed to tabun vapor.

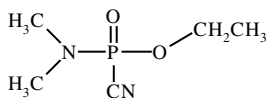
GA, with the structure formula shown in Figure 2.3 — chemically known as ethyl N,N-dimethylphosphoramidocyanidate — is a colorless to brownish liquid. Its vapor is also colorless. GA may have a faintly fruity odor when not pure. It is about 30 times as toxic as phosgene, which was used in WWI. Like other G-agents, it enters the body primarily through the respiratory tract. GA is approximately 20 times more persistent than GB, but not as stable in storage. At 20°C, its volatility is 328 mg/m³, which increases to 858 mg/m³ when temperature changes to 30°C.

Table 2.3 Properties of Common Nerve Agents

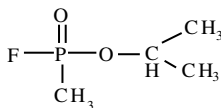
| Agent | Molecular Formula | CAS # | MW (amu) | Vapor Pressure (mmHg at 20°C) | Volatility (mg/m ³ at 20°C) | Vapor Density | Odor | IDLH (ppm) | LCt ₅₀ (mg-min/m ³) ^a | ICt ₅₀ (mg-min/m ³) ^a |
|-------|--|------------|----------|-------------------------------|--|---------------|----------------|------------|---|---|
| GA | C ₅ H ₁₁ N ₂ O ₂ P | 77-81-6 | 162.13 | 0.037 | 328 | 5.63 | Faintly fruity | 0.03 | 400 (Resting) | 300 (Resting) |
| GB | C ₄ H ₁₀ FO ₂ P | 107-44-8 | 140.10 | 2.10 | 16,091 | 4.86 | None | 0.03 | 100 (Resting) | 75 (Resting) |
| GD | C ₇ H ₁₆ FO ₂ P | 96-64-0 | 182.12 | 0.40 (25°C) | 3,900 (25°C) | 6.33 | Camphor | 0.008 | 70 (Mild activity) | In GA and GB range |
| GF | C ₇ H ₁₄ FO ₂ P | 329-99-7 | 180.2 | 0.044 | 438 | 6.2 | None | 0.03 | — | — |
| VX | C ₁₁ H ₂₆ NO ₂ PS | 50782-69-9 | 267.38 | 0.0007 | 10.5 (25°C) | 9.2 | None | 0.002 | 100 | 50 (Resting) |

^a For respiration exposure.

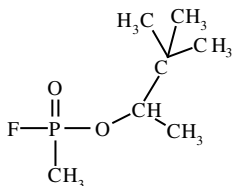
CAS #, Chemical Abstracts Service registry number; IDLH, immediate danger to life and health; MW, molecular weight.



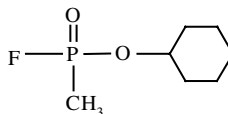
GA: Ethyl N, N-dimethylphosphoramidocyanidate



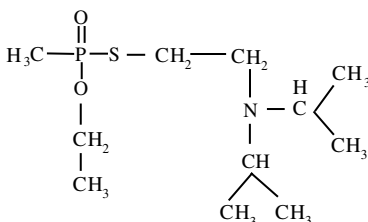
GB: Isopropyl methylphosphonofluoridate



GD: Pinacolyl methyl phosphonofluoridate



GF: O-Cyclohexyl-methylfluorophosphonate



VX: O-ethyl-S-(2-isopropylaminoethyl)methyl phosphonothiolate

Figure 2.3 Structure and chemical names of nerve agents.

2.3.1.2 Sarin

The second nerve agent, sarin, also known as GB, was discovered in 1938. Its structure formula is given as [Figure 2.2](#) together with its chemical name. GB is a potent organophosphate with an IDLH level similar to GA at 0.03 ppm. It is a colorless liquid at ambient temperatures with almost no odor in its pure state. Its volatility at 20°C is 16,091 mg/m³, which is much higher than that of GA (328 mg/m³). GB molecules contain a fluorine atom (–F) instead of a –CN group, as in GA molecules.

2.3.1.3 Soman and Cyclosarin

Subsequent to the discoveries of GA and GB, soman, also known as GD, was discovered in 1944. Details of the discovery were uncovered by the Soviets, who subsequently produced and stockpiled soman. GD molecules may penetrate the central nervous system within minutes, which makes GD the most toxic of the G-agents. GD is also a colorless liquid at ambient temperature that evaporates to colorless vapor with

a fruity odor. Its IDLH level is 0.008 ppm, which is much lower than other G-agents. Soman volatility of 3900 mg/m³ at 25°C is also much higher than that of GA. Since it permanently binds to receptors in the body, it is considered a refractory agent. Similar to GB, the GD molecule also contains a fluorine atom (–F).

Cyclosarin, or GF, is another G-agent that contains a fluorine atom. Its IDLH level is 0.03 ppm, similar to GA. GF volatility (438 mg/m³) is higher than that of GA, but much lower than that of GB and GD.

The abovementioned chemicals are G-agents whose molecules contain phosphorous and either a fluorine (–F) or cyanide (–CN) function group. Molecules of the other group of nerve agents, V-agents, contain both sulfur and phosphorous atoms.

2.3.1.4 VX and Vx

VX, or S-[2-[bis(1-methylamino)ethyl]-O-ethyl methylphosphonothiolate, is one of a group of organophosphate esters derived from substituted 2-aminoethanethiols. Soviet scientists developed a slightly different compound — S-[(diethylamino)ethyl]-O-ethyl isobutylphosphonothiolate — with the same molecular formula as VX, known as V-gas or Vx. These compounds were discovered in the 1950s. They are more toxic than the G-class compounds. They have much lower volatility, and thus are more persistent but less effective in causing respiratory exposure casualties than G-agents. Except for direct exposure to an active aerosol shortly after dissemination, the primary hazard from this class of nerve agents is through contact with contaminated surfaces after aerosols have settled.

2.3.2 Blister Agents

Blister agents blister the skin and produce chemical burns to any exposed part of the body. Eyes, mucous membranes, and lungs are especially sensitive. Unlike nerve agents, which can kill exposed people rapidly, blister agents are primarily intended to injure rather than kill. Injured people require attention by responders, and thus tie up more resources than dead people. Large-scale severe injuries or slow deaths are strategically more effective in defeating the enemy soldiers' efficiency.

Blister agents include arsenicals and mustards. Lewisite (L) is the most important arsenical. Mustards include sulfur mustard (HD) and nitrogen mustards (HN-1, HN-2, and HN-3); of these, HD and HN-3 are the most common.

Figure 2.4 provides the structures and chemical names of selected blister agents and Table 2.4 lists the chemical and physical properties of blister agents. All blister agents are liquids at 20°C, with characteristic odors. The mustards are colorless to amber-colored, and lewisite ranges from a clear to brown liquid. HD, HN-3, and L are lower in VP than HN-1 and HN-2. The vapor density of each of the blister agents is heavier than air.

Blister agents are less toxic than nerve agents. There are no IDLH levels established for them due to potential carcinogenic properties of these compounds. LC_{t50} and IC_{t50} levels are also listed in Table 2.4.

Mustards may penetrate exposed skin in 1 or 2 min, but symptoms may not be noticeable for 2 hr and up to 48 hr later. Unlike mustards, lewisite causes immediate

Table 2.4 Properties of Common Blister Agents

| Agent | Molecular Formula | CAS # | Molecular Weight | Vapor Pressure (mmHg) ^a | Volatility (mg/m ³) ^a | Vapor Density | Odor | LC ₅₀ (mg-min/m ³) | | IC ₅₀ (mg-min/m ³) | |
|-------|--|----------|------------------|------------------------------------|--|---------------|-----------------------------------|---|--------------|---|-----------------------|
| | | | | | | | | Respiration | Percutaneous | Respiration | Percutaneous |
| HD | C ₄ H ₉ Cl ₂ S | 505-60-2 | 159.08 | 0.072 | 610 | 5.4 | Garlic | 1500 | 10,000 | 150 | 2000 |
| HN-1 | C ₆ H ₁₃ Cl ₂ N | 538-07-8 | 170.08 | 0.24 | 1520 | 5.9 | Faintly fishy or musty | 1500 | 20,000 | — | 9000 |
| HN-2 | C ₅ H ₁₁ Cl ₂ N | 51-75-2 | 156.07 | 0.29 | 3580 (25°C) | 5.4 | Fruity odor in high concentration | 3000 | — | — | Between HN-1 and HN-3 |
| HN-3 | C ₆ H ₁₂ Cl ₃ N | 555-77-1 | 204.54 | 0.0109 (25°C) | 121 (25°C) | 7.1 | None | 1500 | 10,000 | — | 2500 |
| L | C ₂ H ₂ AsCl ₂ | 541-25-3 | 207.35 | 0.087 | 4480 | 7.1 | Geranium | 1400 | 100,000 | — | >1500 |

^a At 20°C.

CAS #, Chemical Abstracts Service registry number.

garlic-like odor, is more stable, and has slightly greater blistering power than H. Moist skin absorbs mustard more readily than dry skin. Thus, mustard used in hot and humid weather will result in a higher casualty rate. Eyes are extremely susceptible to mustard exposures. Very low levels of exposure to mustard gas will cause “red-eye” conjunctivitis. High-level exposure results in strong lung irritation and overall disabling effects. The detoxification rate is very slow. Due to sensitization, repeated exposures are cumulative. Mustard is also found to be a carcinogenic compound. Consequently, there is no exposure concentration level value considered as safe for human health.

2.3.2.3 Nitrogen Mustards

Nitrogen mustards (HN) are compounds derived from ammonia by replacing hydrogen atoms with various organic groups. The central atom is nitrogen. Included in this group are 2,2-Dichlorotriethylamine (HN-1), 2,2'-Dichloro-N-methyldiethylamine (HN-2), and 2,2',2''-trichlorotriethylamine (HN-3). Physiologic effects of nitrogen mustards are similar to those of HD. HN compounds are also useful in treating certain cancers.

HN-1 is a colorless liquid with a faint, fishy or musty odor. It is used as a delayed-action agent; damage to skin begins to appear 12 or more hr after exposure. However, HD may act more quickly on the eyes than HD. The body does not detoxify HN-1, and it is a refractory agent.

HN-2 may appear as a dark liquid with a fruity odor at high concentrations and a soft soap odor at low concentrations. Its toxicity is somewhat higher than HN-1. HN-2 has the highest blistering power of all nitrogen mustards when in vapor form. Skin effects for this compound are delayed, and it is highly unstable.

HN-3, a liquid with no odor in its pure form, is the most common nitrogen mustard and its blistering power is similar to that of HD. It is used as a delayed-action casualty agent — most symptoms may be delayed for 4 to 6 hr. The body does not detoxify HN-3; therefore, it accumulates in the body. Unlike HN-2, HN-3 is stable in storage.

2.3.2.4 Mustard-T Mixture

Mustard-T (HT) is a mixture of 60% HD with 40% T (Bis-[2(2-chloroethylthio)ethyl] ether, $(\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2)_2\text{O}$). HT contains sulfur and chlorine similar to the HD structure. It is a yellowish liquid having an odor similar to that of HD. HT possesses a stronger blistering effect than HD. It is more stable and has a lower freezing point than HD.

2.3.2.5 Mustard-Lewisite Mixture

Mustard-lewisite mixture (HL) is a variable mixture of HD and L. The mixture ratio varies according to weather conditions during an operation. L is added to the HD to increase volatility and to lower the freezing point of HD to permit cold-weather application.

2.3.2.6 Phosgene Oxime

Phosgene oxime (CX) may appear as a colorless, low-melting-point crystalline solid or as a liquid. It has a high VP and decomposes slowly at normal temperatures. CX is readily soluble in water, and possesses a disagreeable and penetrating odor. Upon contact with the skin, it produces immediate pain resembling a bee sting. It causes violent irritation to mucous membranes of the eyes and nose. Rapid reaction with the skin makes it difficult for effective decontamination. Flushing with large amounts of water immediately upon exposure proves to be the most effective way to quickly remove excess agent from the skin.

2.3.3 Blood Agents

Blood agents, which enter the body primarily through the respiratory tract, prevent the normal utilization of oxygen by blood cells. Included are hydrogen cyanide (AC), cyanogen chloride (CK), and arsine (SA). Figure 2.5 shows blood agent structures, and Table 2.5 shows properties.

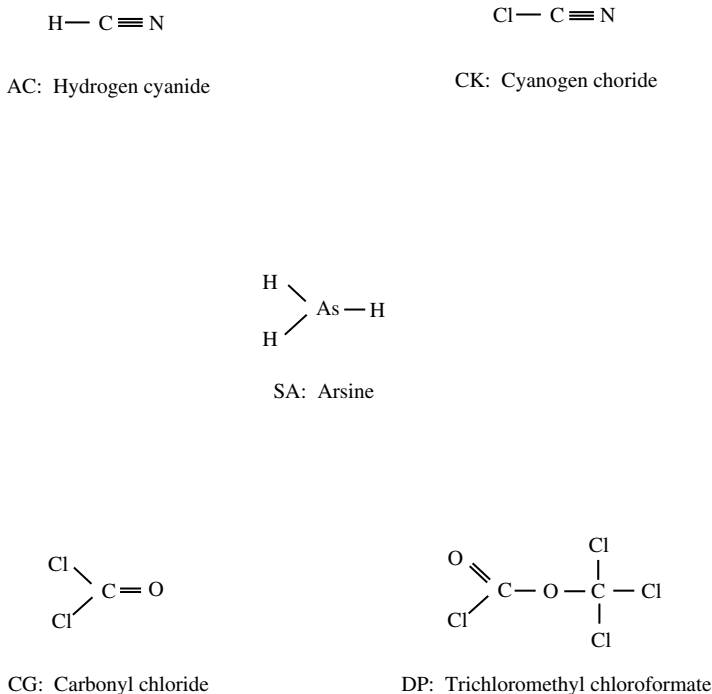


Figure 2.5 Structure and chemical names of blood and choking agents.

Table 2.5 Properties of Common Blood and Choking Agents

| Agent | Molecular Formula | CAS # | Molecular Weight | Vapor Pressure (mmHg) ^a | Volatility (mg/m ³) ^a | Vapor Density | Odor | LC _{t50} (mg-min/m ³) | IC _{t50} (mg-min/m ³) |
|-------|---|-----------|------------------|------------------------------------|--|---------------|---|--|--|
| AC | HCN | 74-90-8 | 27.03 | 612 | 1,080,000 (25°C) | 0.99 | Similar to bitter almonds | 2000 to 4500 ^b | Varies with concentration |
| CK | CNCl | 506-77-4 | 61.48 | 1010 | Gas | 2.2 | Pungent, biting | 11,000 | 7000 |
| SA | AsH ₃ | 7784-42-1 | 77.93 | 11,100 | 30,900,000 (0°C) | 2.69 | Mild, garlic like | 5000 | 2500 |
| CG | COCl ₂ | 75-44-5 | 98.92 | 1173 | 4,300,000 (7.6°C) | 3.4 | Similar to new-mown hay, grass, or green corn | 3200 | 1600 |
| DP | C ₂ Cl ₄ O ₂ | 503-38-8 | 197.85 | 4.2 | 45,000 | 6.8 | New-mown hay, grain, or green corn | 3000 (Resting) | 1600 (Resting) |

^a At 20°C.

^b LC_{t50} and IC_{t50} vary with concentration because of the high detoxification rate at which the body decomposes HCN to nontoxic compounds. At a concentration of 200 mg/m³, the LC_{t50} is 2000. At 150 mg/m³, the LC_{t50} is 4500.

CAS #, Chemical Abstracts Service registry number.

2.3.3.1 Hydrogen Cyanide and Cyanogen Chloride

AC and CK are colorless liquids with distinctive odors. The vapor density of AC is slightly less than that of air while that of CK is heavier. AC is more toxic than CK due to higher cyanide content, as indicated by respective IDLH levels and LCt₅₀ values.

AC inhibits the cytochrome oxidase enzyme reaction, which directs oxygen utilization in the bloodstream. Upon exposure, the breathing rate increases, which in turn leads to inhalation of a larger dose. At high concentrations, exposed individuals could be killed in less than 15 sec. Because the body can detoxify AC quickly, its LCt₅₀ varies according to exposure concentration. The LCt₅₀ of 2000 mg-min/m³ in Table 2.5 represents the concentration of AC at 200 mg/m³. CK affects the oxygen utilization function similar to AC. In contrast to AC, CK causes breathing to slow down because of its strong irritation and choking effects.

2.3.3.2 Arsenic Trihydride

AsH₃, also known as SA, damages the liver and kidneys. Light exposure causes headache and uneasiness. Higher-dose exposure causes chills, nausea, and vomiting. Severe exposure damages blood cells, leading to anemia and eventual death. SA has the highest VP and volatility and is the most rapidly dispersing chemical agent of the three common blood agents.

2.3.4 Choking Agents

Choking agents (Figure 2.5 and Table 2.5) target the respiratory tract and lungs. After entering the airway, the choking agent decomposes into hydrochloric acid and oxygen-free radicals, which irritate the respiratory tract, and cause membrane swelling. This swelling triggers the secretion of copious amounts of fluid, which in turn causes excessive coughing to clear the airway. Despite the coughing, the lungs may fill with fluid, and thus victims “choke,” while literally drowning in their own body fluid. Death occurs when dosage is high enough. The effects of choking agents may be immediate or delayed depending on exposure concentration.

These agents include phosgene (CG) and diphosgene (DP). In World War I, phosphene accounted for more than 80% of CWA fatalities. A gas at room temperature, phosgene boils at 7.6°C. Diphosgene, with much higher boiling point (127°C), is a colorless liquid at room temperature with new mown hay odor similar to that of phosgene. Both agents have similar IDLH and LCt₅₀ values.

2.3.5 Other CWAs

Other chemical compounds are sometimes grouped according to their intended use, such as incapacitating agents and riot control agents.

Incapacitating agents produce physiologic or mental effects that may persist for several hours or days after an exposure. Such effects make people less effective fighters, but do not seriously endanger their lives, unless subjected to very high doses.

Compounds that cause vomiting are normally solids that are vaporized and condensed to form aerosols, including diphenylchloroarsine (DA), adamsite (DM), diphenylcyanoarsine (DC). Unless subjected to high-dose exposure, victims will recover in several hours.

Tear-producing compounds cause copious tears and irritation of the skin, and are widely used for training and riot control. The principal tearing compounds include chloroacetophenone (CN); chloroacetophenone in chloroform (CNC); chloroacetophenone, chloropicrin, and chloroform mixture (CNS); chloroacetophenone, benzene, and carbon tetrachloride mixture (CNB); bromobenzylcyanide (CA); and O-chlorobenzylidene malononitrile (CS).

The well-known "tear gas" consists of CS, CS1, and CS2. CS1 is comprised of CS mixed with silica aerogels and CS2 is the mixture of CS and silicone treated silica aerogels. CS in its pure form has a pepper-like odor, and produces immediate effects even in low concentrations. Maximum effects are reached in 20 to 60 sec and duration is 5 to 10 min after the individual is removed from the contaminated area.

2.4 TOXIC INDUSTRIAL COMPOUNDS

Toxic industrial compounds or chemicals (TICs) have received more attention in recent years mainly because of the fear of terrorist acts. Although they are much less deadly than conventional CWAs, terrorists can easily gain access to large quantities of TICs.

More than 90 chemicals are considered TICs, and they are grouped as high, medium, and low hazards based on the combination of toxicity, volatility, and amount being produced, stored, and transported annually. Each TIC is ranked according to a hazard index (HI). The HI is the product of four factors, numerically ranked between 1 and 5 according to the ranking scheme in Table 2.6.

$$\text{HI} = \text{toxicity} \times \text{state} \times \text{distribution} \times \text{producers} \quad (2.3)$$

Table 2.6 Hazard Index Parameters

| Toxicity (IDLH in ppm) | State (Vapor Pressure in mmHg) | | Distribution ^a | | | Number of Producers | |
|------------------------------|--------------------------------------|------------------------|---------------------------|-------|-------|------------------------|---|
| | Index | Index | Index | Index | Index | Index | |
| <1 | 5 | Gas | 5 | 5/6 | 5 | >100 | 5 |
| 1 to 10 | 4 | Liquid: >400 | 4 | 4 | 4 | 50 to 99 | 4 |
| 11 to 100 | 3 | Liquid: 100 to <400 | 3 | 3 | 3 | 25 to 49 | 3 |
| 101 to 500 | 2 | Liquid: 10 to <100 | 2 | 2 | 2 | 5 to 24 | 2 |
| >500 | 1 | Liquid: <10 | 1 | 1 | 1 | <5 | 1 |

^a Number of continents in which production occurs.

IDLH, immediate danger to life and health.

Source: U.S. Department of the Army. Appendix D of JCAD Performance Specification Revision B, 13 August 1999.

Chemicals with an HI value of ≥ 90 are listed in the “high” hazard group, those with an HI value between 36 and 89 are listed as “medium” hazards and those with an HI value < 36 are considered “low” hazards.

2.4.1 High-Hazard TICs

High-hazard TICs (Table 2.7) are widely produced, stored, or transported chemicals with high toxicity that are easily vaporized. This group contains mainly inorganic chemicals except the two small molecular organic chemicals (formaldehyde and ethylene oxide). Some of the TICs in this group, such as chlorine, hydrogen cyanide, cyanogen chloride, and phosgene were once considered as CWAs by the military. Most of the chemicals in this group exist as gaseous compounds at room temperature as designated by “G” in the volatility column in Table 2.7. Volatility values range from 3.7 ppm to 800 ppm. Sulfuric acid has relatively low volatility but is an extremely strong acid; thus, it is considered a high-level contact hazard.

2.4.2 Medium-Hazard TICs

High-hazard TICs are highly toxic, produced in large quantities, and vaporize easily. TICs that may be ranked high in one or two of these characteristics, but low in the rest, are grouped as medium hazards. Table 2.8 lists properties of selected medium-hazard TICs.

The IDLH of the TICs in this group ranges from 1 ppm to 1200 ppm. Clearly, the volatility of each TIC in this group is higher than respective IDLH level. Vapor pressures are mostly lower than the compounds listed in the high-hazard group.

2.4.3 Low-Hazard TICs

Low-hazard TICs include compounds that have relatively low toxicity, VP, or volatility, and relatively small quantities are being produced, stored, or transported (Table 2.9). The threat from deployment of these TICs is considered much less likely than those listed as high or medium hazards. Nevertheless, their existence could still become threats to the public.

Table 2.7 Properties of High-Hazard TICs

| Chemical | Formula | MW | Volatility | Odor | IDLH ^a | Effects |
|------------------------|---------------------------------|-------|------------|---|-------------------|---|
| Ammonia | NH ₃ | 17 | G | Pungent, suffocating odor | 300 | Eyes, skin, respiratory system |
| Boron trichloride | BCl ₃ | 117.2 | G | Pungent | — | Corrosion in eyes, skin, and respiratory system |
| Boron trifluoride | BF ₃ | 67.8 | G | Pungent, suffocating odor | 25 | Eyes, skin, respiratory system, kidneys |
| Carbon disulfide | CS ₂ | 76.1 | 390,000 | Sweet ether-like odor | 500 | Central nervous system, peripheral nervous system, cardiovascular system, eyes, kidneys, liver, skin, reproductive system |
| Chlorine | Cl ₂ | 70.91 | 19,369,000 | Pungent, irritating odor | 10 | Eyes, skin, respiratory system |
| Diborane | B ₂ H ₆ | 27.7 | G | Repulsive, sweet odor | 15 | Respiratory system, central nervous system, liver, kidneys |
| Ethylene oxide | C ₂ H ₄ O | 44.1 | G | Ether-like odor | Ca [800] | Eyes, skin, respiratory system, liver, central nervous system, blood, kidneys, reproductive system |
| Fluorine | F ₂ | 38.0 | G | Pungent, irritating odor | 25 | Eyes, skin, respiratory system, liver, kidneys |
| Formaldehyde | HCHO | 30 | G | Pungent, suffocating odor | Ca [20] | Eyes, respiratory system |
| Hydrogen bromide | HBr | 80.9 | G | Sharp, irritating odor | 30 | Eyes, skin, respiratory system |
| Hydrogen chloride | HCl | 36.5 | G | Pungent, irritating odor | 50 | Eyes, skin, respiratory system |
| Hydrogen fluoride | HF | 20.0 | G | Strong, irritating odor | 30 | Eyes, skin, respiratory system, bones |
| Hydrogen sulfide | H ₂ S | 34.1 | G | Strong odor of rotten eggs | 100 | Eyes, respiratory system, central nervous system |
| Nitric acid (fuming) | HNO ₃ | 63.0 | 63,000 | Acrid, suffocating odor | 25 | Eyes, skin, respiratory system, teeth |
| Phosphorus trichloride | PCl ₃ | 137.4 | 130,000 | Odor like hydrochloric acid | 25 | Eyes, skin, respiratory system |
| Sulfur dioxide | SO ₂ | 64.1 | G | Characteristic irritating, pungent odor | 100 | Eyes, skin, respiratory system |
| Sulfuric acid | H ₂ SO ₄ | 98.1 | 1.3 | Odorless | 3.7 | Eyes, skin, respiratory system, teeth |
| Tungsten hexafluoride | WF ₆ | 297.9 | G | Odorless | NE ^b | Eyes, skin and mucous membranes |

^a The notation Ca appears in this column for all substances that the National Institute for Occupational Safety and Health considers to be potential occupational carcinogens. However, IDLH values that were originally determined in the Standards Completion Program or were recently revised are shown in brackets following the Ca designations.

^b Not established.

IDLH, immediate danger to life and health; G, gas; MW, molecular weight.

Table 2.8 Properties of Selected Medium-Hazard Chemicals

| Chemical | Structure/ Formula | MW | Odor | IDLH | Effects |
|---------------------|---|-------|---|----------|---|
| Acetone cyanohydrin | $\text{CH}_3\text{C}(\text{OH})\text{CNCH}_3$ | 85.1 | Faint odor of bitter almond | N.D. | Eyes, skin, respiratory system, central nervous system, cardiovascular system, liver, kidneys, gastrointestinal tract |
| Acrolein | $\text{CH}_2=\text{CHCHO}$ | 56.1 | Piercing, disagreeable odor | 2 | Eyes, skin, respiratory system, heart |
| Acrylonitrile | $\text{CH}_2=\text{CHCN}$ | 53.1 | Unpleasant odor | Ca [85] | Eyes, skin, cardiovascular system, liver, kidneys, central nervous system |
| Allyl alcohol | $\text{CH}_2=\text{CHCH}_2\text{OH}$ | 58.1 | Pungent, mustard-like odor | 20 | Eyes, skin, respiratory system |
| Boron tribromide | BBr_3 | 250.5 | Sharp, irritating odor | N.D. | Eyes, skin, respiratory system |
| Carbon monoxide | CO | 28.0 | Odorless | 1200 | Cardiovascular system, lungs, blood, central nervous system |
| Ethylene dibromide | $\text{BrCH}_2\text{CH}_2\text{Br}$ | 187.9 | Sweet odor | Ca [100] | Eyes, skin, respiratory system, liver, kidneys, reproductive system |
| Hydrogen selenide | H_2Se | 81.0 | Resembling decayed horse radish | 1 | Eyes, respiratory system, liver |
| Methyl bromide | CH_3Br | 95.0 | Chloroform-like odor at high concentrations | Ca [250] | Eyes, skin, respiratory system, central nervous system |
| Methyl hydrazine | CH_3NHNH_2 | 46.1 | Ammonia-like odor | Ca [20] | Eyes, skin, respiratory system, central nervous system, liver, blood, cardiovascular system |
| Methyl isocyanate | CH_3NCO | 57.1 | Sharp, pungent odor | 3 | Eyes, skin, respiratory system |

(continued)

Table 2.8 Properties of Selected Medium-Hazard Chemicals (Continued)

| Chemical | Structure/ Formula | MW | Odor | IDLH | Effects |
|--------------------------------------|--|-------|---|-----------------|---|
| Methyl mercaptan | CH ₃ SH | 48.1 | Disagreeable odor like garlic or rotten cabbage | 150 | Eyes, skin, respiratory system, central nervous system, blood |
| Nitrogen dioxide | NO ₂ | 46.0 | Pungent, acrid odor | 20 | Eyes, respiratory system, cardiovascular system |
| Phosphine | PH ₃ | 34 | Fish- or garlic-like odor | 50 | Respiratory system |
| Phosphorus oxychloride | POCl ₃ | 153.3 | Pungent and musty odor | N.D. | Eyes, skin, respiratory system, central nervous system, kidneys |
| Selenium hexafluoride | SeF ₆ | 193.0 | Pungent | 2 | Respiratory system |
| Stibine | SbH ₃ | 124.8 | Disagreeable odor like hydrogen sulfide | 5 | Blood, liver, kidneys, respiratory system |
| Sulfuryl fluoride | SO ₂ F ₂ | 102.1 | Odorless | 200 | Eyes, skin, respiratory system, central nervous system, kidneys |
| Tellurium hexafluoride | TeF ₆ | 241.6 | Repulsive odor | 1 | Respiratory system |
| n-Octyl mercaptan | CH ₃ (CH ₂) ₇ SH | 146.3 | Mild odor | NE ^a | Eyes, skin, respiratory system, blood, central nervous system |
| Other TICs in medium-hazard category | Allylamine, allyl chlorocarbonate, carbonyl sulfide, chloroacetone, chloroacetonitrile, chlorosulfonic acid, diketene, 1,2-dimethylhydrazine, methanesulfonyl chloride, methyl chloroformate, methyl chlorosilane, phosphorus pentafluoride, silicon tetrafluoride, sulfur trioxide, sulfuryl chloride, titanium tetrachloride, trichloroacetyl chloride, trifluoroacetyl chloride | | | | |

^a Not established.

IDLH, immediate danger to life and health.

Table 2.9 Low-Hazard TICs

| Chemical Name | Chemical Name |
|-----------------------------------|---------------------------|
| Allyl isothiocyanate | Hexachlorocyclopentadiene |
| Arsenic trichloride | Hydrogen iodide |
| Bromine | Iron pentacarbonyl |
| Bromine chloride | Isobutyl chloroformate |
| Bromine pentafluoride | Isopropyl chloroformate |
| Bromine trifluoride | Isopropyl isocyanate |
| Carbonyl fluoride | n-Butyl chloroformate |
| Chlorine pentafluoride | n-Butyl isocyanate |
| Chlorine trifluoride | Nitric oxide |
| Chloroacetaldehyde | n-Propyl chloroformate |
| Chloroacetyl chloride | Parathion |
| Crotonaldehyde | Perchloromethyl mercaptan |
| Dimethyl sulfate | sec-Butyl chloroformate |
| Diphenylmethane-4,4'-diisocyanate | tert-Butyl isocyanate |
| Ethyl chloroformate | Tetraethyl lead |
| Ethyl chlorothioformate | Tetraethyl pyroposphate |
| Ethyl phosphonic dichloride | Tetramethyl lead |
| Ethyl phosphonothioic dichloride | Toluene 2,4-diisocyanate |
| Ethyleneimine | Toluene 2,6-diisocyanate |