CHAPTER 1

Introduction

By definition, weapons of mass destruction (WMD) cause massive destruction and a large number of casualties. The use of a WMD involves deployment of chemical, biological, or radiological weapons. Chemical weapons have been used throughout history, and their development continues throughout the world. Recently, chemical weapons have been used against civilians, while abandoned chemical weapons cause casualties to innocents unless properly disposed of. Sensitive and reliable detectors are desperately needed to provide advance warning of chemical agent exposure to reduce potential casualties. Many governments strongly support research and development of technologies aimed at building improved detectors.

1.1 HISTORICAL OVERVIEW

Historically, humankind has used poisonous chemicals to disable or kill insects, fish, or other animals for various purposes. Chemical warfare agents are poisonous chemicals that can rapidly cause death or disability to the enemy. The deployment of chemical weapons is the use of poisonous compounds in time of war with the intention to kill or incapacitate large numbers of the enemy. In World War I, tear gases, phosgene, chlorine, mustard gases, and other respiratory impairment agents were used. For example, German soldiers deployed chlorine gas on April 22, 1915, resulting in the deaths of more than 5,000 Allied troops. The overall casualty toll from chemical weapons during WWI is estimated at 100,000 deaths and 900,000 injuries.

Many countries voted against the use of chemicals as weapons and signed the "Protocol for the Prohibition of the Use in War of Asphyxiating, Poisonous or Other Gas, and of Bacteriological Methods of Warfare" in 1925 at Geneva. Meanwhile, however, the development of poisonous chemicals to kill, incapacitate, or irritate enemy soldiers continued. During World War II, nerve agents such as tabun and sarin were developed and stockpiled by the Germans; tens of thousands of concentration camp victims were killed with chemical gases.

The Japanese also used chemical weapons during WWII. The Japanese Imperial Army injured and killed close to 100,000 people during the war using chemical and biological weapons. An estimated two million chemical warfare munitions and approximately 100 tons of toxic chemicals were abandoned in China alone when Japan surrendered. These abandoned chemical munitions continue to inflict casualties. As recently as August 4, 2003, mustard gas leaking from an abandoned Japanese chemical weapons plant in northeast China killed at least 1 civilian and injured 35 others. Abandoned chemical weapons in China have caused an estimated 2,000 deaths since WWII.

Development of chemical weapons continued after WWII. In 1952, scientists from the U.K. discovered a nerve agent more toxic than the G-agents, called VX. VX is a sulfonated organophosphorous compound that is substantially more toxic than the G series of nerve agents. In contrast to the G agents, VX is a persistent agent with extremely low volatility (10.5 mg/m^3 at 25°C). Because of its toxicity and persistency, VX is considered the most dangeous CWA. During the Vietnam War, chemicals used by the U.S. to defoliate vegetation are said to have caused deaths after contact with the chemicals. Other incidents of casualties caused by chemical weapons include the use of mustard and nerve agents during the war between Iraq and Iran in the 1980s. Iraqi soldiers used nerve agents against Iraqi civilians in 1988, resulting in the deaths of about 5,000 people. Chemical weapons have been used in recent terrorist attacks. The Sarin deployment by the Aum Shinrikyo in the Tokyo subway system in 1995 that killed more than ten people and injured thousands was a vivid example of the disastrous effects of even a small-scale release of chemical agents.

As history has demonstrated, the use of chemical warfare agents (CWAs) has caused a significant number of casualties. To minimize these numbers as a result of a chemical agent attack or accidental release of such chemicals, a general understanding of CWA behaviors by soldiers and the general public is extremely important. Knowledge will lessen the degree of anxiety that may lead to panic and ensuing catastrophe in the event that an incident occurs. Well-informed individuals would know the proper protection and evacuation procedures to minimize exposure and prevent the spread of contamination.

1.2 CHEMICAL WARFARE AGENTS

There are several classes of CWAs designed for different purposes with the intent to harass, disable, or kill people en mass. CWA characteristics follow:

- Toxicity
- Stability
- Can be easily made in mass production
- Can be disseminated in sufficient concentration in the field to produce desired effect

- Transportability
- Little or no corrosive action on storage containers
- Ability to minimize effectiveness of enemy's protective equipment
- Known mechanism of action, protection measures, and method of treatment
- Difficulty of detection before onset of physiological or psychological effects in targeted people
- Colorless, odorless, and nonirritating, yet toxic on exposure

Not all known CWAs possess all of the above characteristics, although the "ideal" agent would. Chemical warfare compounds are grouped according to their intended uses and effects on the human body. The best known lethal agents include nerve, blister, choking, and blood agents.

1.2.1 Nerve Agents

Nerve agents cause an increase in acetylcholine throughout the body. Acetylcholine is the substance that interferes with the functioning of the enzyme cholinesterase. Thus, nerve agents are also known as cholinesterase inhibitors or anticholinesterase agents. Acetylcholine plays the vital role of controlling the skeletal muscles, autonomic ganglia, and many structures of the central nervous system. Nerve agents produce symptoms such as respiratory difficulty, drooling and excessive sweating, nausea, vomiting, and cramps. Nerve agents are extremely toxic. Death can occur within minutes when a sufficient dosage enters the body through the respiratory system. Symptoms develop more slowly after skin exposure. Although a lethal dose may occur in 1 to 2 min of exposure, death may be delayed for 1 to 2 hr. Nerve agents include the G-agents (fluorine- or cyanide-containing organophosphates tabun [GA], sarin [GB], soman [GD], and cyclosarin [GF]) and V-agents (sulfur-containing organophosphorus compounds VX and Vx).

1.2.2 Blister Agents

Blister agents are used with the intention to injure or inflict casualties, often with the intent of slowing down troop movements. These agents affect the eyes and lungs of large numbers, who then require medical attention from other personnel. Exposure to high concentrations will cause eventual death. Mustard gas (HD) is one of the common blister agents that include the nitrogen mustards and Lewisite.

1.2.3 Choking Agents

These agents cause inflammation and swelling in the respiratory tract. The secretion of excess fluid in response to the irritation leads to coughing; when coughing becomes inadequate to the task of ridding the lungs of fluid, the person begins to choke. Death occurs when the person literally "drowns" in his own body fluid. Choking agents include phosgene (CG) and diphosgene (DP). Phosgene caused more than 80% of the CWA fatalities in WWI.

1.2.4 Blood Agents

Blood agents enter the body mainly via respiration. They prevent the normal use of oxygen by the blood cells and cause damage to tissues. These agents include hydrogen cyanide (AC), cyanogen chloride (CK), and arsine (SA).

1.2.5 Other Types of Agents

Incapacitating agents produce physiological or mental effects that may persist for several hours or days after exposure. Such effects hinder the enemy's effectiveness in battle, but do not seriously endanger their lives. Except in very high doses, an individual will recover from exposure to this type of agent.

Vomiting compounds (which, when heated, vaporize and condense to form aerosols) cause great discomfort to victims, thereby rendering them less effective in fighting. Included in this class of compounds are diphenylchlorarsine (DA), adamsite (DM), and diphenylcyanoarsine (DC). Excepting high-dosage cases, victims will recover in several hours.

Tear-producing compounds cause weeping and skin irritation. They cause transient injury and are widely used for riot control. Becasue of their fast acting and nonlethality, tear gases are commonly used in training of students to measure their ability in donning protective gears in the event of a CWA attack. Principal tearing compounds include chloroacetophenone (CN); chloroacetophenone in chloroform (CNC); chloroacetophenone, chloropicrin, and chloroform (CNS); chloroacetophenone, benzene, and carbon tetrachloride (CNB); bromobenzylcyanide (CA); and *O*-chlorobenzylidene malononitrile (CS).

Other types of less toxic CWAs are grouped according to their intended uses, such as riot control agents, training agents, smoke screen and signal chemicals, and defoliants. This book focuses on those chemical agents that adversely affect humans in particular. Most modern detection devices aim to detect nerve, blood, blister, and choking agents because of their high toxicity and lethality.

1.3 TOXIC INDUSTRIAL COMPOUNDS

Unlike CWAs that are manufactured explicitly to kill or incapacitate, thousands of chemicals used in modern industry run the gamut from mildly to extremely toxic. Some of these were considered CWAs in the past. For example, AC and CK were once classified as blood agents and phosgene was the choking agent CG. Because they are being used by manufacturers in many applications, they were removed from the more restrictive list of controlled CWAs to facilitate regular transportation in railway tanker cars or via tanker trucks over roadways. Thus, these compounds are now listed as highly toxic industrial compounds (TICs).

TICs are easily accessible in large quantities by potential terrorists. While detection of these compounds was not considered very important in early phases of developing CWA detection devices, they are now receiving much attention. Homeland Defense has added TICs to detector requirements.

1.4 CWA AND TIC DETECTION

Numerous methods, techniques, and instruments have been developed for the detection of CWAs and TICs. After the September 11 incident, aggressive efforts have focused on obtaining better detectors for diverse scenarios.

1.4.1 Historical Overview

During World War I, mustard gas and other chemicals such as chlorine gas were used on the battlefield. Detectors based on color changes resulting from reactions between decomposed mustard and appropriate reagents were developed. However, all detectors developed during the war, including the most common one of using trained soldiers to sniff the air for the characteristic garlicky odor of mustard gas, were not sensitive enough or fast enough to prevent casualties.

After WWI, efforts to build detectors that could rapidly detect chemical agents, especially mustard gas, led to development of standardized colorimetric detector kits, such as the M4 Mustard Agent Vapor Detector Kit, M5 Liquid Detector Paint, and M9 Chemical Agent Detector Kit. The M9 used a hand pump to sample air through a tube containing adsorbent and colorimetric reagent; detection was based on the change in color of the reagent.

Historically, developing detection techniques almost always lagged behind development of the chemical agents themselves. After the discovery of nerve agents by German scientists during World War II, the science of detection techniques faced even greater challenges because of these agents' high toxicity. The first fast-action field detector kit for nerve agents, the M9A2 Chemical Agent Detector Kit, was standardized in 1952.

Automatic CWA detectors developed in the United States in the 1960s and 1970s included the M43 and the M43A1 alarms, which were devoted to detect nerve agents. Technology for automatic detection of mustard vapor was not developed. Subsequently, the ability to detect mustard blister agents has become a necessity. Although not as lethal as nerve agents, HD is a carcinogen and the average person can generally detect its odor at very low concentrations. Because it is a carcinogen, there is no safe exposure level above the arbitrarily set allowable airborne exposure limit (AEL). The AEL of HD is currently set at $0.003 mg/m^3$ or less over an 8-hour exposure period. Much effort has been expended since the 1970s to advance HD detection. Most high-quality modern detectors are required to detect both nerve and blister agents.

1.4.2 Detection Requirements and Detector Development

While detection techniques for mustard gas and nerve agents are far from perfect at present, requirements to detect TICs as well pose even greater challenges to the developers. Because TICs are numerous with equally diverse properties, detecting them alongside blister and nerve agents is very complex. Minimum requirements for a high-quality CWA and TIC detector are most, if not all, nerve and blister agents, and some TIC compounds.

CWA and TIC detectors used in the field would be subject to diverse environmental conditions. The instrument needs to operate at a wide range of temperature and humidity levels. To provide adequate advance warning, detection sensitivity needs to be well below immediate danger to life and health (IDLH) concentration levels. This means that the combined dosage effect from the detectable concentration level and the time required for the detection must be sufficiently low to allow an individual sufficient time to protect herself once alerted. The detector should be able to detect these compounds with specificity. Detection must not be affected by coexisting substances in the atmosphere that could cause false-positive or false-negative responses. Of course, the ideal detector would use no consumables and work forever, and thus needs no additional supplies and provides noninterrupted protection. Unfortunately, the ideal detector does not exist now and will not exist in the future. Most sensors that have been mass-produced are designed for use in specific environments to detect one or two compounds.

Advances in analytical chemistry, microtechnologies, and computer software have made more techniques available for CWA and TIC detection. Detectors have become smaller, more sensitive, more reliable, and with more functions. Modern computer technologies have permitted more sophisticated data processing to enable fine-tuning of detection algorithms. Further miniaturization of detectors that are more sensitive, with lower false-alarm rates, and high tolerance to varied environment conditions summarizes the current focus of development.

The United States needs to improve and expand the uses of sensors in preventing terrorism and to minimize the impact should an incident occur. Besides point sampling devices, sensors to help provide sensitive and rapid detection and advance warning of toxic vapor at fixed sites such as subways, buildings, financial centers, and airports are of utmost importance. These sensors need to be operable around the clock. For example, sensors installed in the ventilation system could be coupled with a rapid shutdown procedure. Portable sensors to allow assessment from a remote or on-site point can be used to map the potential extent of the chemical cloud cover to aid authorities in organizing the movement of people. Current sensors have limited capabilities and must be improved.

To develop robust sensors, a multidisciplinary systems approach should be taken. Experimentalists, statisticians, engineers, and data analysts should collaborate from the beginning of a concept to the fielding of the final product. Statistically designed experimentation helps in reducing the need for exhaustive testing during development to produce a field-worthy sensor. Actual and potential interference must be identified and dealt with either through hardware design, multiple sensor types, multivariate techniques, or through sophisticated software development. Developing new, integrated multiple-source databases to create libraries for quick identification and to permit access to different methodologies is necessary. Manufacturers have already created many libraries. There is a need for consolidation to avoid redundancies. Researchers of diverse technologies need to collaborate and to share their expertise rather than limiting their applications to their own fields. A multisensor system is needed to provide the broadest detection capability possible.

Once developed, detectors and sensors must be thoroughly tested according to rigorous criteria. Sensor calibration and potential drifts in detection algorithm caused by operating environment conditions such as variations in humidity, temperature, and/or atmospheric pressure need to be addressed and corrected. As technologies evolve, more stringent requirements are being developed and applied to testing and evaluation of detection devices. Consequently, a number of different subsystems are needed to support development of these more sensitive instruments. Systems for reliable sample collection, sample processing, and presentation of chemical vapor to sensors are essential. Standardization of proven methodologies is needed. Systematic quality assurance for sensor evaluations can only be achieved through the use of standardized methodologies that have been proven successful. For example, mere testing for detection sensitivity using uncontrolled conditions has proven to be insufficient. Many devices perform differently under variable conditions. Temperature, relative humidity, moisture contents, and other substances in the atmosphere can affect detector performance. This is especially true during an incident. Many substances could influence the detection algorithm, resulting in false alarms in the absence of the CWAs (false positive) or their opposite in the presence of CWAs (false negative). Therefore, we must recognize that in any attempt to simulate real-world situations in the laboratory, many artifacts could arise. Care must be taken to recognize these possibilities and be receptive to make changes to eliminate all such artifacts.

Individual manufacturers may test newly developed detectors with CWA simulants and some TICs. Since CWAs are strictly controlled, their detectors cannot be tested with actual CWAs except in very few laboratories. The results from simulants cannot and should not be construed the same as with CWAs. In view of the many restrictions on the use of CWAs, the federal government offers the opportunity for developers to conduct laboratory, field, and wind tunnel tests through Test Service Agreements (TSA). A well-defined and very demanding set of test standards, including minimum detection levels, initiated by the Department of Defense, has been in place for the last 15 years. These standards include plans and methodologies for testing under conditions simulating real-world scenarios where possible. Evaluation criteria for detectors tested in government facilities follow:

- Accuracy of detected agent concentrations and dosages
- Consistency of exposure response times for repeated exposures at specific agent concentration levels
- Magnitudes of any interactions and effects of humidity, temperature, agent type, agent concentration, dynamic profile, and chemical interferent type and concentration
- Assessment of potential for false-positive and false-negative situations
- Probability of detection and identification of each agent (class and type) or simulant as a function of agent or simulant concentration
- Probability of a false alarm and estimate of mean time between false alarms

The U.S. government supports research of chemical sensors mainly through the Department of Defense, National Science Foundation, and the Department of Energy.

Sensor development is also heavily supported by private industry. Most of the current technological advances have had little real impact on improving emergency preparedness. Emergency preparedness requires that sensors be reasonably inexpensive so that they can be widely deployable and networked. More importantly, sensors must be reliable with good sensitivity and specificity toward detection of the targeted substances. Development of sensors that can detect and identify the release of toxic materials must continue. Effective responses to the specific agent involved in a chemical attack can only be achieved through the right choice of sensors for the job. Proper detection equipment is crucial for effective consequential management including orderly evacuation to minimize casualties. Therefore, a program with sustained funding to focus and coordinate research and development on sensors and sensor networks together with an emphasis on fielding the system is needed.