FEATURE

Safety, security and dual-use chemicals

Many chemicals that are commonly used in laboratories and industries can be harmful if not handled properly. Chemical safety best practices are designed to protect people from accidentally being exposed to hazardous chemicals. On the other hand, chemical security best practices are designed to protect people from someone deliberately exposing others to hazardous chemicals. Many chemical safety best practices overlap with chemical security best practices, but there are important differences, as will be discussed in this article.

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INTRODUCTION

Many chemicals that are commonly used in laboratories and industries can be harmful if not handled properly. Chemical safety best practices are designed to protect people from accidentally being exposed to hazardous chemicals. On the other hand, chemical security best practices are designed to protect people from someone deliberately exposing others to hazardous chemicals. Many chemical safety best practices overlap with chemical security best practices, but there are important differences, as will be discussed in this article.

The term "dual-use chemical" is applied to a substance that can be used for both beneficial and harmful purposes. A number of dual-use chemicals are regulated as chemical weapons (CWs) because they have a history of being used as such. Note that while most chemists consider all explosive weapons as chemicals, the regulatory concept of chemical weapons is considered as "any toxic chemical or its precursor that can cause death, injury, temporary incapacitation or sensory irritation through its chemical action"[1] (not due to explosive force as in conventional or nuclear weapons). The distinction between chemical and biological weapons is also sometimes a gray area. According to the Chemical Weapons Convention, the use of live organisms, such as smallpox, is termed a biological weapon; whereas the use of toxins derived from living organisms, such as ricin, are considered chemical weapons.[1]

This article provides a brief history on the use of chemicals in warfare, some of the international regulations concerning them, and an overview of chemical security and its relationship with chemical safety. We then give some modern examples where the dual-use nature of certain chemicals was exploited by terrorists. The purpose of this paper is to raise the awareness of chemical security issues among chemists and chemical safety professionals.

BRIEF HISTORY OF CHEMICAL WEAPONS[2–4]

The use of chemicals as weapons has a long history involving many nations and reaching back thousands of years. The Greek epics by Homer; the Iliad and the Odyssey, describe how both sides in the Trojan War used poisoned arrows thousands of years ago. The Chinese used arsenical smoke around 1000 BC, and in about 600 BC, Athenians are said to have poisoned the wells of the Spartans. The Spartans retaliated by tossing burning sulfur over the city walls of Athens.

In the 15th century Leonardo de Vinci proposed a machine that fired shells filled with sulfur, arsenic and verdigris (copper acetate). The Taino Indians of Hispaniola hurled lighted gourds filled with ground hot peppers and ashes at the Spanish conquistadors to create a blinding smoke screen before launching attacks. In 1672 during the siege of Groningen, the Bishop of Munster used explosives and incendiaries containing the alkaloid belladonna (deadly nightshade) to produce deadly fumes.

In some cases, prominent scientists were involved in developing them and/or advocating their use. Ironically, it was a Professor of Chemistry at Edinburgh University and British Secretary of Science, Lyon Playfair, who advocated the use of poison gas (cacodyl cyanide) in 1854 against the Russians in the Crimean war. The British Ordinance Department rejected the idea as a bad mode of warfare, but Playfair's response was later used in the 20th century to justify broader adoption of chemical warfare. In 1862 during the US Civil War, John Doughty, a New York schoolteacher, proposed using liquid chlorine in artillery shells. Half a century later, both

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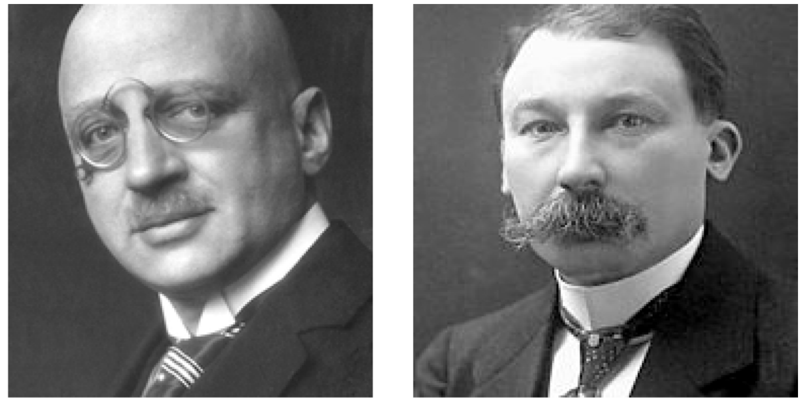
sides in World War I (WWI) used the idea.

WORLD WAR I: THE WAR OF THE CHEMISTS

The first use of chemical weapons during WWI was by the French, when they fired ethyl bromoacetate (tear gas, originally used as a sedative and flame retardant) against the Germans in August 1914. The Allies continued to experiment with other chemical irritants like iodoform (originally an antiseptic) and sulfur dioxide (a preservative used in winemaking). Germany quickly followed suit. In 1914 Carl Duisberg (CEO, Bayer AG) and Hermann Walter Nernst (1920 Nobel Prize for chemistry) developed artillery shells filled with shrapnel, trinitrotoluene (TNT) and the irritant dianisidine chlorosulphonate. In 1915 Germany used the Tappen shell (by Prof. von Tappen, with explosives and the irritant xylyl bromide) on the Eastern Front against the Russians.

Large scale attacks using poison gas made its debut at the second battle of Ypres in 1915, when chlorine gas was used against British, French, Belgium and Canadian troops. Fritz Jakob Haber (1918 Nobel Prize for chemistry) directed German field operations, and first proposed using chlorine gas cylinders as weapons. Haber's French counterpart was Francois Auguste Victor Gringard (1912 Nobel Prize for chemistry). Haber and Gringard were rivals, but with very different backgrounds and personalities (Figure 1).



Germany
Fritz J. Haber
1868-1936
Nobel Prize 1918

France
F. A. Victor Gringard
1871-1935
Nobel Prize 1912

Figure 1.

FRITZ HABER[4–7]

Fritz Haber has been described at the "father of chemical warfare". His chemical gas warfare team included future Nobel laureates James Franck, Gustav Hertz, and Otto Hahn. In addition to their work with poison gases they also developed various types of gas masks and absorbent filters. Haber downplayed the use of gas warfare stating, "Poison gas caused fewer deaths than bullets." He was in the trenches when chlorine gas was first used in April 1915 at the second battle of Ypres, Belgium when about 5,700 cylinders of chlorine gas blanketed the battlefield, resulting in 5,000 casualties, including Germans. (Note: Adolph Hitler was gassed at the third battle of Ypres in 1917).

Haber and his brother-in-law, Carl Bosch (1931 Nobel Prize for chemistry), developed the Haber-Bosch process for synthesizing ammonia from atmospheric nitrogen and hydrogen (nitrogen fixation). The process was a milestone in the production of fertilizer, explosives, feedstuffs, and became the standard for mass production of ammonia. Most of the world's food production still relies on this process today to produce fertilizer. In 1918, Fritz Haber was awarded the Nobel Prize in chemistry for the Haber process.

Haber also formulated the Haber Rule ($C \times t = k$), which expressed the relationship between the concentration of poison gas (C) and the length of time (t) the gas must be breathed to produce death or toxic effects. He noted that exposure to low concentrations for long periods often resulted in the same effects as exposure at high concentration for short periods. The Rule is still used today as an approximation.

In the 1920s, scientists working with Haber at the German chemistry company I. G. Farben developed the cyanide gas formulation Zyklon A, originally used as an insecticide and grain fumigant, and later reformulated as Zyklon B for use in Nazi gas chambers in WW II. In the late 30s and early 40s Gerhard Schrader, also a chemist at I. G. Farben, specializing in developing new insecticides to combat world hunger, discovered the nerve agents sarin, tabun, and cyclosarin. Schrader is often called the "father of nerve agents".

The Nazi Party's anti-Semitic policies led Haber to resign in 1933 as head (since 1911) of the Kaiser-Wilhelm Institute (now The Haber Institute of the Max Plank Society). Haber once said, "During peace time a scientist belongs to the World, but during war time he belongs to his country." This was an example of the ethical dilemmas facing chemists at that time. Like his close friend Albert Einstein, Haber left Germany and moved to England in 1933. While in England Noble laureate Ernest Rutherford refused to shake hands with him, because of his involvement in poison gas warfare.

VICTOR GRIGNARD[8–11]

François Auguste Victor Grignard was born in Cherbourg France in 1871, became a professor at the University of Nancy in 1910, and in 1919 moved to the University of Lyon where he was chair of the chemistry department. Grignard is most noted for the reaction

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