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Fighting Against the Invisible:

The new weapons against chemical warfare

by Leana Nguyen

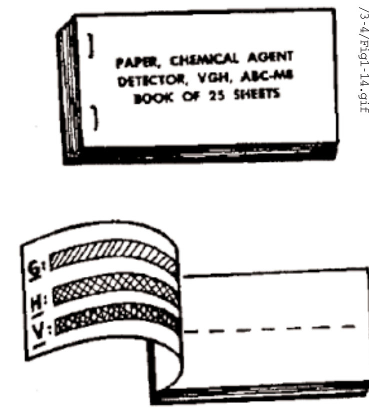
Chemical agents serve as the great “unknown variables” on the battlefield. With the technology of chemical warfare becoming more prevalent, soldiers are experiencing an increase in vulnerability to these difficult to detect dangers that often escape the five senses. The increase in security against terrorism has intensified the need for new detection devices that can quickly identify hazardous compounds. Therefore, scientists are developing new technologies to improve soldiers’ safety. To be useful on the battlefield, though, these tools must meet certain guidelines for mobility and accessibility. The operating mechanisms of these instruments can range from simple applications on special analysis paper to radiation devices, but developments that allow for the detection of specific compounds require more complex methods.

Chemical weaponry has been used since the dawn of war itself. Dated methods include tainted arrows and bullets as well as edible poisons. In an article on the use of poisonous gases (New York Times, April 22, 1915), Will Irwin states that modern chemical warfare began in World War I when the Germans dropped asphyxiating bombs in the second battle of Ypres in Belgium. The toxin did not prove extremely deadly, but it often rendered its victims injured and unable to participate in combat. This effective tactic sparked the race to develop chemical warfare agents. Countries such as Germany, England, and France employed such popular agents as: phosgene, mustard gas, and chlorine gas that decrease pH in the respiratory system and cause skin blistering. Today chemical warfare has come a long way with new compounds like osmium tetroxide which cause skin, respiratory, and eye burning (National Library of Medicine 2007).

According to the Federation of American Scientists, a chemical agent is a substance intended for use in military operations to kill, seriously injure, or incapacitate its victims (American Federation of Scientists 2006). These substances must quickly proliferate to cover a large area and must be reproducible in order for the weapon to be effective. To detect these substances, the technology must respond quickly to minute sample sizes anywhere, anytime in a large area and must give reproducible readings. That is, the device must display the same results even in different environments. The reproducibility of detection allows scientists to confirm or reject results and to find out more about the substance in question in order to develop better detection machinery or to efficiently develop an antidote.

Enzymatic systems

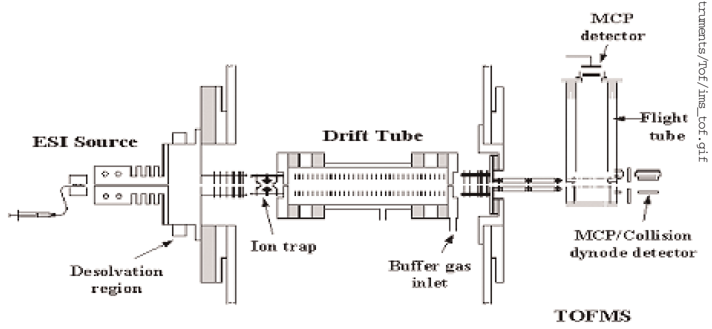
M8/M9 is a special, inexpensive paper that enables users to quickly identify concentrations and possible compounds present. Its name comes from its “model number” (Astrella 2004). This lightweight and highly sensitive tool tests liquid and aerosol agents that cause blistering and nerve damage. This lightweight and highly sensitive tool tests liquid and aerosol agents that cause blistering and nerve damage. The paper contains two dyes and a pH indicator that reacts with a harmful substance to produce a change in color on the paper. This will indicate the type of substance and the degree of contamination. M8/M9 efficiently gives results in thirty seconds. Users simply remove the paper from its packaging and allow the paper to come into contact with the potentially contaminated surface. Soldiers put these sheets into windows or on their uniforms to recognize potential threats when entering unfamiliar environments. However, the high sensitivity of the paper reduces its predictive power because it can sense non-hazardous substances as well, preventing certain analysis of the hazardous chemical. These low cost sheets of paper can range from around $13 for 12 twelve sheets to up to a little over $3,000 for large kits, depending on the specificity and the amount of paper.



http://www.globalsecurity.org/wmd/library/policy/army/fm/3-4/Fig1-14.gif

A booklet of chemical detection paper showing types of agent: nerve or blister

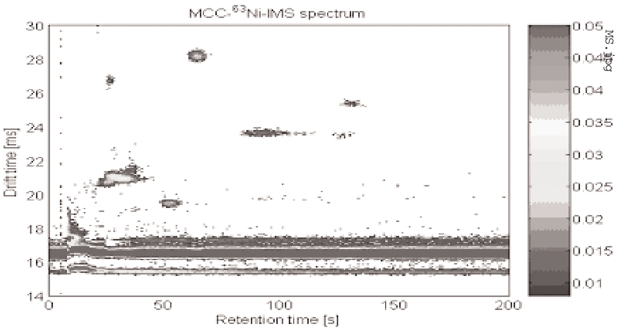
Ion Mobility Spectroscopy



http://www.indiana.edu/~clemmer/Research/ion%20mobility/instruments/Tof/ims_tof.gif

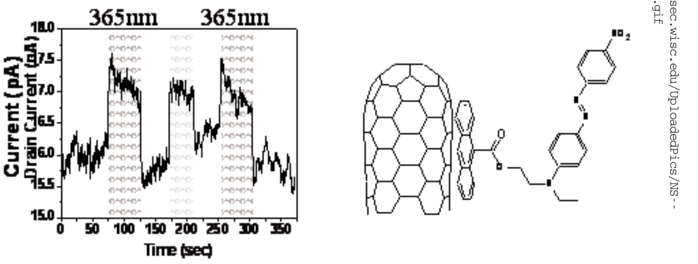
Model of the ion mobility spectroscopy machine

Ion mobility spectroscopy involves "the characterization of chemical substances on the basis of the velocity of gas-phase ions in an electric field"(Eiceman 2005) One such tool that utilizes ion mobility spectroscopy is the Chemical Agent Monitor (CAM), a handheld, battery-operated device that identifies substances that may cause blistering or may attack the nervous or circulatory system. Using molecular ion mobility spectrometry, CAM sucks air into a lined compartment. The lining dries the compartment by absorbing any water vapor present, leaving a pure sample and increasing sensitivity. A weak radioactive source ionizes the air, which causes the agents to form ionized particles. The molecules pass through a charged tube to collide with a plate that detects a pattern of the number of charges for an allotted "time of flight" (see figure below). This pattern depends on the size, shape and mass of the particle, which is then compared to a clean air sample (see graph below). CAM designs a time vs. current graph to indicate the relative concentration of agent present in the air. Another detection tool that uses ion mobility spectroscopy is the single-walled carbon nanotube (SWNT) whose name is indicative of the device's function. The device is one nanometer in diameter and several microns long. A carbon phase with a single layer of atoms makes up its walls. These walls adsorb the accumulation of gas or liquid of the unknown substance onto its surface. In an applicable setting, theses tubes are arranged into a machine that draws air over the transducer to determine the unknown vapor. Each tube responds to specific chemical vapors. Electron charge transfers interact between the variable and single-walled carbon nanotube, changing how readily the wall will allow electrical current to pass. This allowance can be measured to identify the contaminant (Snow 2003). SWNT's ability to detect chemicals at extremely low concentrations makes it highly sensitive as well as accurate. However, this technology can be unfeasible due to the instability of the carbon phase wall.



http://www.isas.de/fileadmin/img/pb2/img/imaging/IMS.jpg

Ion mobility spectroscopy results showing distance (aka concentration) vs time of substance



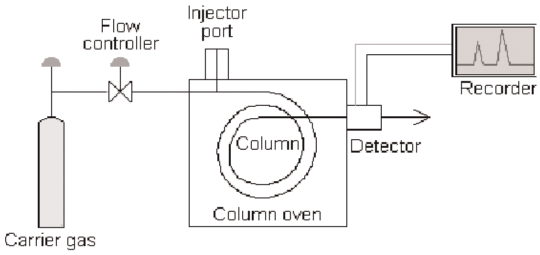
http://www.nsec.wisc.edu/UploadedPics/NS-Presentation1.gif

Carbon nano tube. Displays how chemical attaches to the carbon phase walls.

Other Methods: Infrared Radiation, Flame Photometry, and Surface Acoustic Wave Detection

Infrared radiation technologies such as photo acoustic infrared spectroscopy, passive infrared detection, or filer-based infrared spectroscopy are also commonly used to detect chemical agents in devices that measure point detection and distance detection. These devices detect the vapor forms of chemical agents. Radiation excites the agent's molecules to create infrared patterns with unique "fingerprints" to be matched to each compound. This can be helpful for specific identification; however, if an unknown agent is found, scientists may assume that the new agent is similar to a known agent.

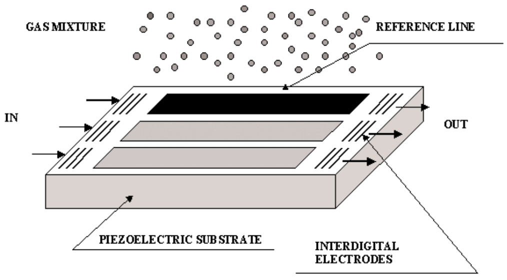
Flame photometry is a more empirical method of identifying and quantifying elements of a compound. This system takes a sample of air and burns it with a hydrogen-rich flame, emitting light of certain wavelengths that produce a characteristic color. Then, specific light detector filters may determine the presence of phosphorous and sulfur since these compounds are commonly found in chemical agents (Hogan 1997). Unfortunately, flame photometry is less accurate when used alone because of its high sensitivity which results in detection of irrelevant substances and false positives. However, when used in combination with gas chromatography (GC), this problem is alleviated as GC will separate compounds, increasing detection accuracy. In GC, a liquid sample is volatilized in a hot injection chamber and then swept with an inert gas (i.e. helium) through a column of high boiling liquid, known as the stationary phase. The high boiling liquid causes the sample component to switch rapidly between gas and liquid phase while traveling down the column, separating the sample into pure elements. A detector at the end of the column records the elements to create a print out (CSU Boulder 2007). (See figure below)



http://teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrm.htm

Basic diagram of a Gas chromatography mechanism

A new form of detection technology specifically senses nerve and blister agents. Recent surface acoustic wave (SAW) apparatuses are battery-operated and portable, making this technology effective and efficient on the battlefield. SAW measures changes in electrical current in response to chemical agents. This equipment can concentrate the sample and adjust the humidity factors for greater accuracy, rendering the device "immune" to variations in temperature and humidity. Each SAW apparatus contains an array of SAW detectors, and each detector is composed of a different polymeric material that creates a thin, chemically sensitive film. In other words, each detector is able to react differentially to the same chemical vapor. The chemicals react with a substrate to produce an electrochemical current that is later transformed to a SAW. When chemical molecules absorb into this film, they influence the speed of the acoustic waves, creating a pattern. A computer retrieves the pattern, rapidly identifying numerous chemicals (Sandia Lab 2000). Further analysis of obtained substances can be extended using mass spectrometry and nuclear magnetic resonance for confirmation of substances.

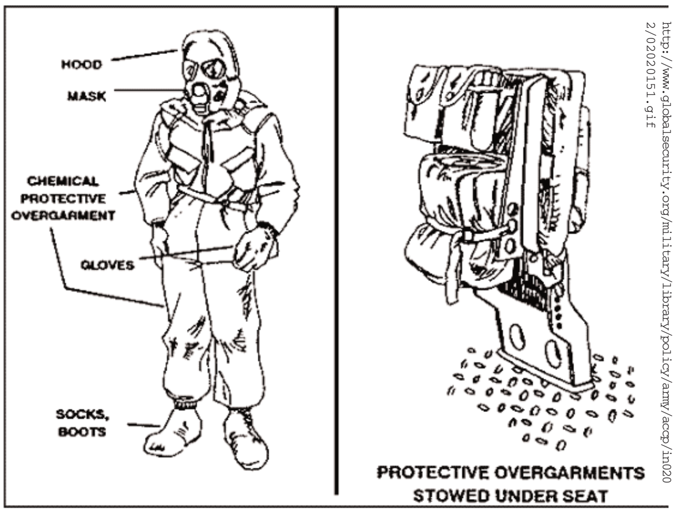


http://www.tms.org/pubs/journals/JOM/0010/Ivanov/fig5.gif

SAW apparatus reaction displaying one film with substrate reacting to a chemical agent

Protective Gear – the First Line of Defense

Still, protective gear serves as the first line of defense against chemical agents. Equipment for this purpose includes: masks, gloves, eye and hearing protection, helmets and footwear. Multiple layers of clothing increase the extent of protection because single-layered material only protects against some specific chemicals. Many materials that protect against chemicals consist of natural rubber, nitrile rubber, butyl rubber, polyvinyl chloride, polyvinyl alcohol, Saranex (TM), and Trellchem (TM) (CCOHS 1999). Other materials include: neoprene, Teflon (TM), Viton (TM), 4H (TM), Barricade (TM), Responder (TM), and Chemrel (TM). However, protection against different chemical threats requires certain materials. Furthermore, most physical protective gear only protects against skin exposure.



http://www.globalsecurity.org/military/library/policy/army/accp/in0202/0202015l.gif

Protective military equipment. Full body suit.

Each material has a different useful property. For example, butyl rubber is a synthetic rubber that is impermeable to air and water and is mainly used for airtight applications. Polyvinyl alcohol is an organic polymer used as a reinforcing sealant that is surprisingly breathable. It creates a flexible water soluble material at certain temperatures and humidity. Saran is made of sandwiching layers of Saran and polyolefins, which create barriers to gas and vapor without being affected by humidity (Dow Chemical company 1995-2007). Nitrile rubber can be found in the common hospital glove. Production of nitrile rubber uses heat and water in an emulsion polymerization system with proportions of acrylonitrile and butadiene. Depending on the proportion of these compounds, the material can vary in oil, fuel, and temperature resistance. Small changes to chemical structure can change various properties (IISRP). Most equipment is hence composed of some form of rubber because of rubber's flexibility and waterproof nature. However, the bulky and restrictive nature of this protective equipment can hinder the immediacy of effectiveness because this gear must first be put on. Additionally, the user may be subject to poor ventilation, limited reusability, and partial loss of the senses.

Protective measures are not limited to only the skin. For example, respiratory protective gear, commonly known as masks, include (from highest to lowest degree of protection): self controlled breathing apparatuses, supplied air respirator, air purifying respirators (which depend largely on face sealing ability), high efficiency particulate air filter (HEPA filter, removes of measurable size particles-.3-.15 micrometers), and a simple surgical mask, which can prevent contamination from entering the user's nasal and/or oral passages (Huebner 2006). It increases use ventilation. In combination with the rubber materials (provided above) these two protective apparatuses can seal the individual from coming into contact with CAs. Therefore respiratory gear serves as another line of defense from entrance of chemical substances to the respiratory system.

http://www.semp.us/_images/biots/Biot171PhotoA.jpg

Resting victims of the Sarin attack in Japan 1995

It is important to note that soldiers are not the only ones who require protection against chemical weaponry since soldiers are not the only victims in war. Civilians are also targeted by chemical attacks and they often do not have access to protective gear. Even still, chemical attacks are usually unpredictable such as the 1995 Japanese subway attack. Providing protection (i.e. masks) to the public might be a step in the right direction, but the immediacy and spontaneity of these attacks would render such a gesture ineffective. Chemical warfare thus poses a threat not just to soldiers on the battlefield but also to civilians in their day-to-day lives.

Chemical detectors are making these difficult-to-detect agents more manageable with increased sensitivity, mobility, and speed. As chemical compounds become more complex and more effective, technologies must adapt in order to detect potential hazards. At the same time, chemical detectors have advanced tremendously as applications of molecular and nano-technology increase due to the extent of research and development of chemical targeting. Technological developments must continue in order to supplant new, unknown, and latent chemical agent detection.

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