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TASK FORCE* ON SCIENTIFIC ASPECTS OF THE DESTRUCTION 
OF CHEMICAL WARFARE AGENTS1 

SOME PROBLEMS IN THE DESTRUCTION OF 
CHEMICAL MUNITIONS, AND RECOMMENDATIONS 
TOWARD THEIR AMELIORATION 

(Technical Report) 

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1The Task Force has official status as a subcommittee of the Organic Chemistry Division. 

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Some problems in the destruction of chemical munitions, and recommendations toward their amelioration (Technical Report)

SYNOPSIS

These recommendations are offered primarily to national authorities with responsibility to destroy chemical munitions and the chemical warfare (CW) agents they contain. They probably also will be of interest to citizens who are in one way or another concerned with this question. The problems and pertinent recommendations are as follows:

A. Problems of Science and Technology

(1) How long do chemical warfare agents linger in the environment, and what happens to them? Recommendation: Investigation of rates and products of degradation of chemical warfare agents in the environment and under relevant controlled conditions should be undertaken.

(2) The problem of recovered old munitions: what they are, and what is in them? Recommendation: Efforts should be made to discover and develop additional useful methods for non-intrusive identification of the contents of recovered old munitions.

(3) The problem of gelled or crusty materials in containers of "mustard". Recommendation: The chemistry of gelled or crusty HD ("mustard") should be thoroughly studied.

(4) The problem of ascertaining how much chemical warfare agent may remain after being subjected to a destruction process. Recommendation: Research to discover and develop superior analytical methods for detection and quantitative determination of any CW agent surviving destruction processes should be undertaken, insofar as methods now known are less than fully satisfactory.

(5) The problem of monitoring of air spaces and gas streams during storage and destruction of chemical warfare agents. Recommendation: Further research toward, and development of sensitive, definitive methods and equipment for rapid monitoring of air spaces and gas streams should be undertaken.

(6) The problem of inadequacy of knowledge about the fundamental chemistry of chemical warfare agents. Recommendation: Rigorous research for systematic expansion of knowledge of the fundamental chemistry of chemical warfare agents, as relevant to their destruction, should be conducted.

(7) The problem of disposal of scrubber or neutralization brines. Recommendation: Scientific questions raised by possible ocean discharge of refined brines resulting from destruction of chemical warfare agents should be investigated.

(8) The possibility of combining destruction of a chemical warfare agent by "neutralization" with follow-up degradation of the intermediate products by wet air or supercritical water oxidation. Recommendation: The feasibility of combining "neutralization" with ensuing wet air or supercritical water oxidation into an integrated process should be studied, with special attention to engineering concerns.

B. Problems of Information and Communication

(1) The problem that the lay public is not adequately informed about technological aspects of the destruction of chemical weapons. Recommendation: Chemists are urged to communicate with their fellow citizens by writing articles in language intelligible to laymen, by giving public talks, and by participating in radio and television broadcasts.

(2) The problem that some studies of the properties and chemical reactions of CW agents, relevant to their destruction, which were militarily secret during the Cold War, have not been made publicly available. Recommendation: The chemists who did those studies or department heads who have custody of their reports are urged to make them available to all scientists of the world in one of three ways: preferably, by publication in peer-reviewed scientific journals; alternatively, as publicly available reports; or (for minor studies of good quality) by submission to the Technical Secretariat of the Organization for the Prohibition of Chemical Weapons, for inclusion in a data bank.

(3) Problems of locating existing publications. Recommendation: A comprehensive bibliography of published or publicly available reports concerning properties and chemical behavior of CW agents relevant to their destruction, to be available to all persons in all countries on payment of a modest charge, should be prepared.
INTRODUCTION

The original poison gases of World War I were literally gases (notably chlorine, phosgene and hydrogen cyanide). Although the dreadful "mustard" agent, also of World War I, is a liquid of low volatility, it was often called "mustard gas". Modern chemical warfare agents, of chemical structures shown below, are all liquids but nevertheless are sometimes called "poison gases".

All these agents have systematic names, but they are usually referred to by the indicated special names or military code designations. HD and L are vesicants (blister agents), while GA, GB, GD and VX are lethal nerve agents that disorganize a victim's nervous system.

Not many years ago most discussion of the destruction of chemical weapons dealt with political problems. Moral considerations were often invoked.

Now there is wide political agreement, evidenced by the Chemical Weapons Convention, that the world's stockpiled chemical weapons must be destroyed. A related problem is that thousands if not millions of abandoned or discarded chemical munitions lie buried in the earth or sunk beneath water at uncertain locations. They are unearthed now and then by accident, or caught in the nets of fishermen. Efforts are often made to find and destroy those close to human activities.

Attention now turns to technological aspects of the problem. How does one safely destroy stockpiles of chemical weapons that measure in thousands of tons? How does one go about destruction of a rusty old shell, of uncertain contents, dug up on an old battlefield or storage dump? And how can one destroy chemical weapons of whatever type in a safe and environmentally acceptable manner without enormous expenditures that may be beyond the capability of some nations?

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**Principal Modern Chemical Warfare Agents**

2 IUPAC names for the six agents are as follows: for HD, bis(2-chloroethyl) sulfide; for L, dichloro[(E)-2-chloroethenyllarsine; for GB, propan-2-yl methylphosphonofluoridate; for GD, 1,2,2-trimethylpropyl methylphosphonofluoridate; for VX, S-2-(dipropan-2-ylamino)ethyl O-ethyl methylphosphonothioate; for GA, ethyl NN-dimethyl-phosphorimidocyanidate.

Many chemists and engineers have worked on these problems. Much has been learned of the properties and chemistry of chemical warfare (CW) agents as relevant to their destruction, and some good technologies for destruction of chemical munitions and agents have been developed. Nevertheless, progress in destruction of chemical weapons has been slow, in part because of fierce citizen opposition to incineration. Only small fractions of the major stockpiles of Russia and the United States, which are of the order of magnitude of 30,000 tons each, have yet been destroyed despite government decisions years ago to destroy them.\(^4\) The efforts of national authorities to develop destruction plans more acceptable to the citizenry have been impeded by limitations of scientific knowledge. There is an insufficiency of knowledge: about the fundamental chemical properties of CW agents, about technologies that might be used to destroy them, and about the consequences of minor releases of CW agents into the environment.

Further problems concern destruction of old or abandoned (non-stockpile) chemical munitions that have been buried for years in the earth or sunk in lakes, estuaries or the sea. Some of them were fired in battles or in training and did not explode as planned. Others were lost on old military bases, buried, or dumped into the sea. Such means of disposal were common practice in earlier years. Because many countries were locations of battles in twentieth century wars, or of bases where military forces gathered in preparation for action, the problem of ‘non-stockpile’ chemical weapon destruction faces many more nations than the small number of countries that have declared stockpiles of chemical munitions.

The ‘non-stockpile’ chemical munitions are sometimes brought to the surface by accident, other times in campaigns to find and destroy them. In either case, they present special problems. They are usually heavily corroded on the exterior, without legible markings, and their origins as well as their contents are usually unknown. A special difficulty is identification of their contents: high explosives, water,\(^5\) or toxic chemicals; if the latter, what CW agent? Also, while ‘stockpile’ munitions exist in substantial number at storage sites, only a few ‘non-stockpile’ items may require destruction at a given site at one time. Therefore, while building major installations to destroy ‘stockpile’ munitions may be justified, mobile systems are needed to deal with those ‘non-stockpile’ munitions that cannot be transported. That may imply use of different technologies for destruction of munitions of the two categories.

Some valuable studies of technologies now available for chemical munitions destruction, notably by committees of the U.S. National Research Council relative to the U.S. problem, have been made and published. Those and other studies have given some attention to gaps in scientific knowledge. Chemical defense scientists have identified others in informal conversations, but there has been little formal attention to the whole problem in international perspective.

The IUPAC Task Force on Scientific Aspects of the Destruction of Chemical Warfare Agents, which is studying the general problem, met in Rome, Italy, September 6-9, 1994. The Task Force now offers some recommendations, relating mostly to general problems, discussed and approved in that meeting.

A. Problems of Science and Technology
1. How long do chemical warfare agents linger in the environment, and what is their fate?

Communities in the vicinity of sites where CW agents are stored or where their destruction is planned are, naturally, concerned that their immediate and long-term health not be jeopardized by minor releases of CW agents that might occur due to accident or incompleteness of destruction.

Military organizations have long made estimates of the persistence of CW agents as practical guides to

\(^4\) In contrast, substantial hoards of chemical weapons that were in the possession of Iraq were safely and effectively destroyed by a United Nations team. It was free of some of the constraints that restrict and often retard destruction work in other countries.

\(^5\) For testing purposes, munitions were sometimes filled with water.
decisions under battlefield conditions. It is important to know how long an area in which an agent has been released remains dangerous to an unprotected soldier. Persistence estimates emphasize effects that would impair the performance of soldiers, with little attention to long term effects on health. Persistence is recognized to depend on weather (especially wind and rain), on the condition of exposed surfaces, and of course on the identity of an agent.

For purposes of estimating long term effects on health, especially of civilians who may be in the vicinity of minor releases, more exact information is needed. If low persistence were due only to high volatility, a chemically resistant substance conceivably might exist for months or years in the atmosphere, in water bodies that it had contacted, or in solid materials. On the other hand, if CW agents were degraded rapidly in the environment, civilian worries over long term health effects would have little justification. Knowledge of degradation rates will facilitate rational decision making by persons responsible for destruction of CW agents and will be welcomed by civilians.

Several sectors of the environment need attention. In air, photolysis of CW agents by sunlight, oxidation by oxidants (e.g., hydroxyl radical, ozone) generated by solar radiation, and hydrolysis by reaction with water vapor are plausible. In water droplets in the air (in clouds, fog, rain), photolysis and oxidation may occur, much as in the gas phase, but also hydrolysis that may be accelerated by dissolved impurities (such as acids responsible for acid rain). In water bodies (lakes, rivers, the ocean), hydrolysis is probable — possibly accelerated by dissolved substances such as pollutants and sea salts. Additionally, at or near the surface of the sunlit ocean, reductive cleavage by hydrated electrons is probable.

On solid surfaces, photolysis is conceivable, as is hydrolysis if the surface is wet with water and thermolysis if the surface is hot (e.g., in bright sunshine). However, the paint on a painted surface may dissolve CW agents and protect them from degradation. In the soil, hydrolysis is probable, possibly catalyzed by minerals or humic materials. If appropriate microorganisms were present and conditions (nutrients, oxygen pressure) were favorable, biodegradation of CW agents might occur in several media: in water, in the soil, on solid surfaces, on vegetation, and within plant tissues.

Some of these possibilities have been investigated, in some cases admirably, so as to measure quantitatively rates of degradation under well-defined conditions. Rough estimates have been made in other cases. Summaries of knowledge of natural degradation processes have been published. They give principal attention to degradation (especially hydrolysis) in water and in soils. Actual hydrolysis rate constants have been reported in some cases, specifically for HD, GB, GD and VX.

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Environmental decay of CW agents in the gas phase has received less study. Other sorts of carbon compounds have however been given significant attention. Especially important is degradation by reaction of the aggressive hydroxyl radical (HO\(^+\)), of which an authority\(^{15}\) has said: "Since OH radicals are the primary attacking species initiating the atmospheric transformation of a wide variety of organic and inorganic compounds, the OH rate coefficients are important physico-chemical parameters for any serious quantitative discussion of the atmospheric behavior of these compounds". Hydroxyl radicals are generated in the atmosphere by the action of photons from the sun on ozone and water.\(^{16}\)

Rate constants for numerous gas phase reactions of hydroxyl radicals have been estimated.\(^{16,17}\) From the second order rate constants and knowledge of the steady state concentration of hydroxyl radicals in the troposphere on sunny days (1.5 \(\times\) \(10^6\) molecule cm\(^{-3}\)),\(^{18}\) one can reckon pseudo-first-order rate constants and the half-lives of substances in respect to reactions with HO\(^+\). The half-lives vary hugely, depending on molecular identity. For example, about 2 hours at 25°C for 1,3-butadiene versus 110 days for trichloromethane.

Among the few organic phosphorus compounds whose reactivity with hydroxyl radical has been measured is triethyl phosphate;\(^{19}\) for it, \(k_2\) at 296 K is 5.5 \(\times\) \(10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). From that value\(^{20}\) and the steady state HO\(^+\) concentration, one reckons the half life on a sunny day to be 2.32 hours. In view of some structural similarity between triethyl phosphate and nerve agents GA, GB, GD and VX, that datum suggests that they may have similarly short half-lives. If so, an accidental release at Johnston Atoll would be reduced to about 3% of the initial amount in one full day of sunshine, to about 0.1% in two days, and to about a millionth of the original amount in four days. Depending on trans-Pacific wind velocities, it seems possible that hydroxyl radical reactions alone would destroy a release of nerve agent before it got to inhabited shores. Other heretofore neglected atmospheric reactions, of sort sketched in general terms above, could only increase the rate of their destruction.

Citizens properly would not be satisfied with this calculation based on triethyl phosphate reactivity because it involves an assumption that triethyl phosphate reactivity is similar to that of the nerve agents. Needed are data concerning the agents themselves.

Data on the reaction of hydroxyl radical with diethyl sulfide\(^{21}\) (\(k_2 = 1.5 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) at 255-370 K (-18 to 97°C) indicate that, on a sunny day, its half-life in the troposphere is 8.33 hours. The reaction with diethyl sulfide is slower than with triethyl phosphate, but nevertheless traces in the air would be reduced to less than 1% of the original amount in five days of sunshine. Whether the chlorine atoms of HD would accelerate or retard reaction with hydroxyl radical is unclear. Data based on a good experimental study of HD itself are needed.
Attention above is focussed on degradation by hydroxyl radical, which is generally the most aggressive of the oxidants present in the atmosphere on sunny days. Two others also significant are ozone and (at night) the nitrate radical (NO₃⁻).

Among other conceivable natural degradation possibilities, reaction with hydrated electrons at the surface of a sunny sea may be less familiar than the others. Hydrated electrons are formed by photo-ejection of electrons from chloride ions in ocean water: Cl⁻ + hv \rightarrow \text{Cl}^* + \text{e}_{aq}^-

Hydrated electrons are non-persistent and highly reactive; in the absence of organic substances, their steady-state concentration near the surface of the ocean exposed to strong sunlight has been estimated to be about 1 \times 10^{-17} \text{ moles/liter}.^{22} Although rate data^{23} on reactions of many organic compounds with the hydrated electron have been obtained, few concern analogs of CW agents, and to our knowledge none the agents proper. The fastest conceivable degradation by this route can be estimated from the exceedingly high reactivity of nitrobenzene.^{23} The estimated half-life of nitrobenzene dissolved in ocean-surface water is about 38 days, each of twelve hours of sunshine. Even if CW agents were as reactive as nitrobenzene, this mechanism would be a minor contributor to agent degradation.

Products of environmental degradation reactions should be determined, and their toxicities evaluated. Certainly degradation to a product nearly as toxic as the CW agent would be unwelcome; whatever the products are, their toxicities should be known.

**Recommendation:** Investigation of rates and products of degradation of CW agents in the environment and under relevant controlled conditions should be undertaken.

2. The problem of recovered old munitions: what are they, and what is in them?

Many old chemical munitions, dating from World War I or II, still lie buried in the ground or sunk under water. They are occasionally recovered from old battlefields, or on old military posts, or from harbors or lakes, even in countries that did not themselves possess CW agents. As found, they are usually highly corroded and uncertain as to origin or contents.

Such munitions must be destroyed, for the sake of safety. Is a recovered munition of high explosive or chemical type? If the latter, what CW agent does it contain? It is desirable to get answers to these questions without opening the munitions. Determining their contents and how they were constructed is difficult; at many sites even the national origin of a corroded old shell is uncertain. Rarely can one read the identification number of an item and look it up on a list.

One method employed in such work is X-ray photography, analogous to medical practice, which reveals the inner structure of a munition. It also can reveal a liquid filling, which may be a chemical agent, or water.\(^5\) (Not all chemical agents are liquid at temperatures that may prevail in the field; HD has freezing point 14.4°C.) Also used is neutron activation analysis,\(^24\) which is useful to determine the presence of

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certain characteristic elements. Thus, the presence of phosphorus may indicate a nerve agent. Neutron activation analysis does however have some limitations. It is slow, requiring from one minute to half an hour, depending on what elements are present and in what amount; it does not determine the quantities of substances present in munitions; and in general it does not identify them uniquely. Invasive analysis is sometimes employed: drilling a small hole and taking a sample for chemical analysis. Drilling a hole may however enable a lethal agent to be released, or cause detonation of the munition.

Thus there are practical methods for examining recovered munitions and assessing their contents, but they are less than fully satisfactory.

**Recommendation:** Efforts should be made to discover and develop additional useful methods for non-intrusive identification of the contents of recovered old munitions.

The problem is difficult because the wall of a munition is usually steel several millimeters thick. Visible, ultraviolet and infrared radiation, familiarly used for chemical analysis, are blocked by it. Neutrons, X-rays, neutrons and sound can however penetrate it. Below, some possibilities that seem worthy of investigation are suggested. Alternatively, an ingenious scientist may think of some other possibility, and try it. The goal is sufficiently important to warrant “long-shot” efforts. Furthermore, a workable technique would find application elsewhere in modern society.

Optimally, the equipment required to employ a new analytical method would be sufficiently low in weight and volume to be man portable. Next best would be equipment light and compact enough for installation in a mobile laboratory that could be driven to a site in the field.\(^2^5\)

**X-Ray possibilities.** In chemical analysis, X-ray absorption and fluorescence spectrometry\(^2^6,2^7,2^8,2^9\) find significant application. X-Ray fluorescence spectrometry is the more often used; an unknown substance is irradiated with X-rays, causing excitation of inner-shell atomic electrons to higher levels, from which they return with fluorescent emission of X-rays of characteristic wave length. This method of qualitative analysis seems however inapplicable to the non-intrusive examination of recovered munitions, for the X-rays of fluorescent emission from the elements that predominate in CW agents are probably too "soft" to penetrate munition walls.

X-Ray absorption spectrometry is analogous in principle to common visible, ultraviolet and infrared spectrometry. It can tell what elements are present in a sample, but is seldom used.

One might think that differences of refractive index of CW agents under X-radiation might be the basis of a method of non-invasive analysis. That seems however unlikely, for the X-ray refractive indices of all substances approximate unity.

**Sonic possibilities.** Ultrasonic examination of recovered munitions is serviceable in two ways: to determine their internal structure, and to identify their contents.\(^3^0\) The former is analogous to ultrasonic

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\(^{25}\) The U.S. Army is developing PINS equipment that can be shipped by air.


medical imaging. Indications of the contents of old munitions come from acoustic impedance and velocity measurements, but they tell whether a munition is empty, filled with liquid or filled with solid, rather than revealing specific chemical identities. There are perhaps further opportunities in acoustics.

3. The problem of gelled or crusty materials in containers of "mustard"

HD ("mustard") is one of the oldest CW agents. It was used extensively in World War I and is a major item in stockpiles of CW agents manufactured subsequently. In HD munitions long buried in the ground or sunk at sea, and in tanks that have held HD in storage for decades, the HD has become partly or even mostly gelled or crusty. The extent of gelling or solidification depends on what process was used to manufacture the HD and on how long the HD resided in its container. Such old containers often contain also gases that escape when the container is punctured or opened, sometimes spraying a mist of HD onto nearby persons and equipment.

The gelled or solidified HD does not easily drain from opened containers. The amount of HD remaining in such old containers has been said to be as high as 78% of the original weight. People who have worked at destruction of old HD have used such colorful language as "you can only get it out with a corkscrew" (or with a spoon). Inasmuch as the gelled or solidified HD that remains in a container is wet with liquid HD, a container with such material in it is hazardous. An attraction of incineration for destruction of CW agents is that such gelled or crusty HD can be removed by pyrolysis cum combustion in a suitable furnace. The solid or semi-solid material is nevertheless troublesome in furnace operation. If chemical reactions are chosen to destroy HD, the intractability of the residual material is a big problem.

A difficulty is that the chemical structure of the gelled or crusty material is not known. It is generally assumed to be polymeric, often to be a poly(sulfonium salt), but there are indications also of a poly(ethylene sulfide) backbone. Dithiane (1,4-dithiacyclohexane) and 1,2-dichloro-ethane are formed when HD is pyrolyzed. Structures of "mustard" pyrolysis products identified by Fuson et al., and of one presumed sulfonium salt intermediate, are presented in Scheme I.

If "mustard" were made by the Levinstein process, even when new it was contaminated by extra sulfur; the gelled or crusty material derived from it, years later, may also contain that sulfur, in elemental or chemically combined form. Another complication is that the "mustard", before being placed in a munition, may have had a thickener added to it, to improve agent dispersion. Thickeners, if present, may have had some role in formation of the gelled or crusty material, and presumably are incorporated in it. The chemical nature of a thickener, if incorporated, should be determined. It is possible that hydrogen chloride (HCl), generated by plausible reactions on long standing, reacted with iron of the container to form dihydrogen (H₂) and iron salts; the iron may also be chemically combined in the gelled or solid material.

The gases associated with old "mustard" were stated in a U.S. Army report to be HCl, ethene, vinyl chloride and hydrogen sulfide. Dihydrogen was not mentioned. That report lacks experimental detail; the situation should be re-examined.

31 A German report mentions, as a step in draining old chemical munitions, "removal of pastyous fillings using special tools, such as spatulas"; H. Martens, transcript (in English) of presentation at SIPRI conference, Munster, Germany; October, 1993.

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Desirable would be a chemical treatment that would destroy, or at least dissolve, the gelled or crusty material. Possibly it could be dissolved in dimethyl sulfoxide, N,N-dimethylformamide, N-methyl-2-pyrollidone or hexamethylphosphoric triamide (phosphoric tris(dimethylamide)), solvents that are useful to dissolve polyamides and other commercial polymers. If it is a polysulfonium salt, one would expect from the known chemistry of sulfonium salts\textsuperscript{34,36} that it would be attacked and degraded by nucleophiles or bases. A polymer of poly(ethylene sulfide) type should, in principle, be degraded by reaction with a strong base or with an alkylating agent that delivers a short alkyl group while releasing a nucleofuge of significant nucleophilicity.

Finding a chemical treatment that would degrade or dissolve the gelled or crusty material would be greatly aided by knowledge of its chemical structure. Knowing the chemical composition of the gases will also assist understanding the chemistry of the aging of "mustard".

**Recommendation:** The chemistry of gelled or crusty HD ("mustard") should be thoroughly studied.

It is therefore recommended that research be undertaken to determine the structure of the gelled or solidified material and what chemical reactions it undergoes, as well as the composition of the gases and the chemistry of the aging process. For structure determination, proton and carbon-13 NMR, infrared and photoelectron spectroscopy (ESCA), and X-ray methodologies should be useful. Those physical techniques should be supplemented by organic chemical experiments with attention especially to identification of products and determination of yields. As more is learned about the chemistry of the gelled or solidified material, attention should turn increasingly to finding reactions that will degrade it to form soluble or volatile products.

An allied problem is determination of the chemical nature of "mustard" on the surface of soil as a result of spills, diffused within it in consequence of underground explosion of munitions, or leaked onto the floor of the sea from munitions discarded by ocean dumping. "Mustard" in such situations can persist for years, owing largely to its low solubility in water. Has such "mustard" undergone partial change into gelled or

solid material of presumably polymeric character? Have perhaps other types of chemical change occurred in those environments? Knowing the chemical nature of such "mustard" deposits will importantly facilitate decontamination of such sites.

4. The problem of ascertaining how much chemical warfare agent may remain after being subjected to a destruction process

Knowing how completely a CW agent is destroyed by a destruction process is important. In order to know, one must perform chemical analysis of the products formed. The analysis should enable both detection and quantitative determination of the agent, accurately even at extremely low concentration levels and in different matrices. Although methods that meet this standard are known for some CW agents in specific situations, it is not clear that the standard is met for all the major CW agents and all the situations in which the agents might exist.

**Recommendation:** Research to discover and develop superior analytical methods for detection and quantitative determination of any CW agent surviving destruction processes should be undertaken, insofar as methods now known are less than fully satisfactory.

Classical and modern analytical chemistry offer a vast range of analytical methodologies. Which should be utilized depends on what CW agent is involved and on the character of the product mixture. Some destruction processes involve reaction of the agent with a chemical (such as sodium hydroxide) in water solution; in such a case, traces of agent must be sought in the aqueous mixture at the supposed end of the process. Whatever the character of the product mixture, gaseous, liquid, a slurry of solid and liquid, or solid, a method of analysis appropriate to the system and the specific CW agent is necessary. Some methods may be attractive to determine a given agent under ideal conditions, but not applicable in respect to the chemical conditions in which the agent needs to be determined. A suitable method should enable both detection and quantitative determination of the agent, accurately even at extremely low concentration levels.

Analytical methods for two somewhat different purposes are needed. One is to ascertain the adequacy of destruction technologies. Do they effectively destroy CW agents, reducing agent concentrations low enough to meet legal requirements, or lower? The other is for process control, to assess whether a selected destruction technology consistently reduces agent concentration to acceptable levels during routine operation.

Although an analytical method to verify the adequacy of a technology need not, in general, be especially fast, quick response is desirable for routine monitoring of continuous processes. Optimum is a method that can operate in real time, with instantaneous response. Somewhat less preferred for process control is a method involving analysis of aliquots, for it obliges assumption that "snapshot" analyses on aliquots are representative of process behavior during intervals between sampling. If a technology involves batch operation, there is less requirement for speed, although an expeditious method is preferred.

For either purpose, an analytical method must be adequately sensitive and specific. It must perform well under conditions such as involved in actual agent destruction work, in particular being undisturbed by interferences from impurities. In that connection, one must know in testing analytical methods what impurities may be present in the samples or streams to be analyzed. If impurity contents are not reliably on record, they should be determined. For stockpile munitions, noteworthy impurities may be by-products of agent manufacture, inhibitors meant to prolong agent life, thickeners, and decomposition products. For agents from recovered old munitions, metal salts resulting from corrosion of metal containers are probable impurities; others may be extremely diverse, depending on the provenance of munitions and the conditions in which they existed until recovered. Nevertheless, prominent possibilities can be recognized (e.g., gelled material in old "mustard") and taken into account in judging the adequacy of analytical methods.

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Inasmuch as a product mixture is likely to contain, if any, very little of a surviving CW agent, the problem resembles that faced by biochemists who seek to determine, say, the concentration of a single amino acid at perhaps millimolar concentration in the fluid of a cell. Biochemical analyses that meet such requirements sometimes involve converting the biochemical of interest into a fluorescent derivative of characteristic chromatographic behavior. For example, nanogram amounts of $\alpha$-amino acids can be determined by converting them to fluorescent derivatives by treatment with 5-(dimethylamino)naphthalene-1-sulfonyl chloride ("dansyl chloride"), separation of the dansyl derivatives by chromatography, and quantitative fluorescence spectrophotometry.\textsuperscript{37}

The worth of analytical methods employed should be confirmed by subjecting samples to analysis by independent methods. A selected independent method should involve not only a different physical or chemical principle, but also different treatments (if any) of the sample before actual analysis.

5. The problem of monitoring of air spaces and gas streams during storage and destruction of chemical warfare agents

The highest priority in storage and destruction of CW agents is protection of human beings from exposure to them. In view of the constant possibility of a leak or spill of an agent, or that a destruction operation will be incomplete, it is desirable to have means for the immediate detection of any escape of CW agent, even at the trace level, within buildings for storage or destruction, or into the external atmosphere. Several detection systems have been developed, but they are less than ideal. Needed is a superior continuous, real-time monitoring system able to detect CW agents in the gas phase at very low concentrations, determining both the presence and the specific identity of the detected agent, with rare false alarms.

Recommendation: Further research toward, and development of sensitive, definitive methods and equipment for rapid monitoring of air spaces and gas streams should be undertaken.

Methods for detection and identification of CW agents are of obvious military importance. Much attention has been given to real-time detection of agents at militarily significant concentrations. Most of the systems developed, although they work in real time, respond however to a broad range of chemicals rather than to a specific chemical agent. One system for example is based on the use of flame photometry; it will detect organic compounds of sulfur and, whilst it responds rapidly to HD, may generate false alarms in response to other sulfur compounds. (Sulfur compounds are ubiquitous, being for example abundant in foods.) A more selective technique uses ion mobility spectroscopy for rapid detection of chemical agents. It is however also subject to false alarms. Neither method can currently provide reliable detection at levels required for occupational health monitoring purposes.

Highly selective, low-level detection methods that involve the taking of samples are available. Since sampling is followed by time-consuming separation and concentration procedures, these are not "real-time" methods. The best of these techniques still requires 4 to 8 minutes to detect the presence of CW agent vapor at occupational health level concentrations and even longer for identification of the specific agent.

Monitoring technologies that give false positive alarms may have unfortunate consequences: creating needless anxiety among neighbors of a destruction plant, generating indifference among plant workers whose experience may be that an alarm is nothing to worry about (the crying "wolf!" phenomenon), in general undermining confidence in the monitoring system.

Desired is a real time monitoring system, that is, one that responds instantaneously on the time scale of human nervous response. Spectroscopic methods merit careful study, but have forseeable limitations. Ultraviolet-visible spectroscopy in favorable cases has high sensitivity, accompanied however by low specificity. An infrared spectrum has "finger print" characteristics that should enable false positives to be avoided. Whether the sensitivity of infrared spectroscopy would be sufficient is unclear; if that is marginally a problem, arrangements to enable long path lengths to be examined would increase the probability of meaningful responses. A combination of ultraviolet and infrared methods might in a favorable case provide an excellent analysis.

Diligent efforts to develop an accurate, sensitive real time monitoring system will, if successful, solve not only important needs in regard to CW agents. An excellent system will doubtless find many applications in civilian life.

6. The problem of inadequacy of knowledge about the fundamental chemistry of chemical warfare agents

Since 1915 chemists have studied the chemistry and physical properties of CW agents. Many studies were however made before powerful modern experimental techniques became available. Chemists working on destruction of CW agents are often frustrated by gaps in fundamental knowledge of agent chemistry. Knowledge of chemistry relevant to the arsenical agents needs especially to be expanded.

**Recommendation:** Rigorous research for systematic expansion of knowledge of the fundamental chemistry of chemical warfare agents, as relevant to their destruction, should be conducted.

Most research on chemical warfare agents has been done for an applied purpose: synthesis, medical treatment, detection, decontamination, or destruction. Some of that research was performed in "quick and dirty" fashion, that is, without special care in definition of experimental conditions and with a rough-and-ready evaluation if its outcome; thus, was there residual toxicity after a decontamination technique had been applied to field-quality agent?

Fortunately, some studies were thorough in definition of experimental materials and conditions, and in characterization of experimental results. Among them were careful kinetic determinations of hydrolysis rate constants and/or products, studies of the thermolysis of agents under controlled conditions, with characterization of thermolysis products, and investigations of rates and products of reactions with conceivable antidotes to CW agents. Inasmuch as studies of thorough character were mostly done after World War II, few of them are recorded in early books. Some more recent reviews summarize information of the desired sort, insofar as available and consistent with scope.

Numerous determinations of physical properties of CW agents have been made by military organizations. Chiefly measured were properties directly related to use in military offense or defense. Those determinations varied in quality. While many such measurements are pertinent to destruction of agents, others that scientists would desire are missing.

In order that the recommended research should fill in lacunae of existing knowledge, an early stage should be organization of what is known, in outline or review article form. For that purpose, the comprehensive annotated bibliography whose construction is urged in a parallel recommendation should be useful. The recommended outline might well be organized with use of computer technology and made available to interested laboratories or libraries in electronic form.

Inasmuch as there exists no clear demarcation between the fundamental and the more specialized chemistry of any substance, determination of missing information of the following sorts is recommended:

1) Physical properties
   a) freezing point, vapor pressure as function of temperature, thermodynamic values associated with changes of state
   b) spectra: infrared, visible and ultraviolet absorption spectra; NMR spectra for major constituent nuclides
   c) ionization potentials; electron affinities
   d) solubility data for several representative solvents, such as: water, toluene or other aromatic hydrocarbon, ethanol, dimethyl sulfoxide
   e) spectra of radical ions, if readily formed: visible-ultraviolet and ESR spectra

2) Rates and products of hydrolysis reactions
   Choice of solvent for hydrolysis studies should depend on agent solubility. In all cases hydrolysis should be studied at neutral pH in water or, if water solubility is forbiddingly low, in a mixture of water and cosolvent with cosolvent concentration as low as possible. Rates and products of hydrolysis at high and low pH should also be determined.

3) Thermolysis reactions, with attention to rates as well as products formed at various temperatures.

4) Rates and products of reactions with prominent electrophiles and nucleophiles.

5) Hydrogenation and hydrogenolysis reactions, at least with Pt or Pd catalysis.

6) The redox chemistry of agents, including determination of redox potentials and description of oxidation and reduction reactions in terms of reagents involved and products formed.

Why should the chemistry of CW agents, rogue substances that are about to be outlawed, be studied? First, although CW agents are outlawed, they are still very much present in the world despite the determined efforts of major nations to destroy them. Some responsible scientists doubt that their destruction can be completed before the deadline set by the Chemical Weapons Convention. Further knowledge of the fundamental chemistry of the agents, which would result from the recommended research, will advance efforts to destroy all chemical munitions.

Second, the data obtained will be contributions to general knowledge and may have value for civilian purposes unrelated to chemical warfare. To illustrate: during World War II there was much attention to agents known as "nitrogen mustards", which were 2-chloroethyl amines in contrast to the usual "mustard" with its 2-chloroethyl sulfide functionality. Biomedical studies indicated that the "nitrogen mustards" are antineoplastic (anti-cancer) agents; from those indications cyclophosphamide, a drug effective for control or eradication of cancer, was developed.

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Another illustration concerns careful kinetic studies of "mustard" hydrolysis carried out by several chemists during World War II. The observed first-order kinetics for reactions with nucleophiles was discerned to be due to rate-determining initial formation of a cyclic sulfonium ion, which then rapidly reacted with nucleophiles present. Those studies were a paradigm for physical organic chemists during the 1950's and 1960's as they studied neighboring group participation in solvolysis reactions.  

7. The problem of disposal of scrubber or neutralization brines

Two prominent technological alternatives, incineration and "neutralization" with sodium hydroxide, both generate — in different ways — brines that contain sodium chloride and other salts dissolved in water. Many of those salts are normal constituents of sea salt. It is therefore conceivable that, when a CW agent destruction plant were near the ocean, discharge of those brines directly into the ocean would not abuse the environment or harm marine life. A difficulty, however, is that the brines often contain small amounts of salts of lead, mercury and other "heavy" metals. Before such brines could responsibly be discharged into the sea, methods to reduce concentrations of the "heavy" metal constituents to a level consistent with environmental regulations would need to be developed. Furthermore, possible environmental impacts of the remaining salts, freed of heavy metals, would need to be evaluated by oceanographers.

Recommendation: Scientific questions raised by possible ocean discharge of refined brines resulting from destruction of chemical warfare agents should be investigated.

When CW agents are incinerated, besides carbon dioxide and water, several acidic products are formed. From the most common CW agents, depending on what elements they contain, the acidic products include HF, HCl, and oxides of nitrogen, phosphorus, sulfur and arsenic. These acidic by-products are generally removed in "scrubbers", in which the flue gases contact water solutions of NaOH or sodium carbonate, with which they react to form salts, such as sodium chloride from HCl and sodium sulfate from SO₃. When large amounts of a CW agent are incinerated, large amounts of such salts are formed, initially in water solutions called "scrubber brines". The constituents of scrubber brine salts from the U.S. Army CW agent incineration plant on Johnston Atoll in the Pacific Ocean are listed in Table I.  

**Table I**

"Mustard" Incineration Scrubber Salts

<table>
<thead>
<tr>
<th>Salt</th>
<th>Percent</th>
<th>Metal</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>44.3</td>
<td>Mercury</td>
<td>1.03</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>23.6</td>
<td>Cadmium</td>
<td>1.60</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>5.9</td>
<td>Copper</td>
<td>5.30</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>15.7</td>
<td>Zinc</td>
<td>3.50</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>11.9</td>
<td>Lead</td>
<td>5.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.2</td>
<td>Manganese</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Silver</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Molybdenum</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Potassium</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Soluble iron</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Insoluble iron</td>
<td>2315</td>
</tr>
</tbody>
</table>

Scrubber brines may be disposed of by discharge into the ocean or land burial of the solid salts from evaporation of them. Discharge is cheaper for an incineration plant near the ocean. Either method of disposal is however complicated by the presence of small amounts of toxic salts of lead, mercury or other "heavy metals" in the scrubber brines. Ocean discharge has therefore been avoided because of potential danger of the "heavy metals" to marine life. Even land burial may be complicated; in the United States the presence of "heavy metal" salts obliges land burial to be in special hazardous waste "landfills", at high cost.

Destruction of CW agents by reaction with NaOH or by other "neutralization" reactions generally forms organic compounds much less toxic than CW agents but, according to some national regulations, unsuitable for discharge into the ocean. The initial neutralization reaction may therefore be followed by another process, such as biodegradation or wet air oxidation, to make the products suitable for discharge. Water solutions of products from the follow-up process generally contain the same salts as do the scrubber brines; disposal problems are therefore similar.

As mentioned, ocean discharge of brines from CW agent destruction is attractive for its simplicity and, in many cases, low cost. Ocean discharge cannot however be recommended before a scientific problem and a question have been satisfactorily answered. The problem is discovery and development of an inexpensive way to remove lead, mercury and other "heavy metal" salts from the brines. The question, relevant if that problem were solved, is whether the remaining salts would unacceptably disturb the oceans. It seems unlikely that they would, for most of the ions from the salts are normally present in sea water. Satisfactory answers can however come only from well-qualified biological and physical oceanographers.

8. The possibility of combining destruction of a chemical warfare agent by "neutralization" with follow-up degradation of the intermediate products by wet air or supercritical water oxidation

Laboratory studies have indicated that several CW agents are destroyed by reaction with aqueous sodium hydroxide, alone or in conjunction with hydrogen peroxide, sodium hypochlorite or other oxidant, forming products of greatly reduced toxicity. In many cases the products formed must be further degraded, for safety and to meet legal requirements. It has generally been assumed that "neutralization" and follow-up degradation would be conducted as separate processes, one after the other. Conceptually, it seems possible that "neutralization" and follow-up degradation by wet air or supercritical water oxidation could be combined into a single process.

**Recommendation:** The feasibility of combining "neutralization" with ensuing wet air or supercritical water oxidation into an integrated process should be studied, with special attention to engineering concerns.

"Wet air oxidation" is a general term for oxidation (for example, by air, dioxygen, or hydrogen peroxide) of organic contaminants at low concentrations in water at temperatures around 250-300°C. Water at such temperatures develops very high pressure, which must be contained. To minimize corrosion, wet air oxidation is preferably conducted on alkaline solutions.

This technology is widely used for purification of waters contaminated with low concentrations of dissolved or suspended organic wastes. Increasing reaction temperature as high as 250-300°C has two prominent advantages: fatty impurities become more soluble in water, and oxidation reactions become

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48 Incineration of arsenical agents results in substantial concentrations of arsenite salts in the scrubber brines. In German practice, the arsenites are oxidized in the brines to arsenates, which upon addition of iron(III) salts form an easily removed precipitate of iron(III) arsenate.


50 The word "organic" is used in the chemist's sense, referring to compounds of carbon.
Recommendations on destruction of chemical munitions

faster. Utilization of wet air oxidation for destruction of chemical warfare agents was discussed in a report of a U.S. National Research Council committee. 51

Supercritical water oxidation is similar, but is conducted at temperatures above the critical point of water (374°C; very high pressure), where liquid and gaseous water do not co-exist; rather, the water exists as "supercritical fluid", which has properties as a solvent that are quite different from familiar properties of liquid water. Oxidation of organic contaminants of water is much faster at, say, 450°C than 250°C, and forms more highly oxidized products. On the other hand, engineering problems, especially the blockage of pipes by solids, and corrosion, are more severe at the higher temperatures and pressures. Supercritical water oxidation is under intensive study in pilot plants and is beginning to be used for practical purposes.

If follow-up degradation following "neutralization" were conducted as a separate process, it would mostly be necessary that "neutralization" effect virtually complete destruction of the agent. The products of "neutralization" would need to be conveyed to the follow-up process, possibly with intervening storage. If "neutralization" and wet air or supercritical water oxidation were integrated, 52 completion of destruction of agent during "neutralization" would be less essential, for the conditions of the second process would either insure completion of "neutralization" or would oxidize the agent directly to products of very low toxicity. Both speed and simplification of operations would be achieved if the two could be satisfactorily integrated.

B. Problems of Information and Communication

1. The problem that the lay public is not adequately informed about technological aspects of the destruction of chemical weapons

**Recommendation:** Chemists are urged to communicate with their fellow citizens by writing articles in language intelligible to laymen, by giving public talks, and by participating in radio and television broadcasts.

Besides the general desirability of informing the public about technological issues, a better public understanding of technological aspects of the destruction of chemical weapons might speed actual destruction. In both Russia and the United States, public protests of CW agent destruction plants have caused years of delay in agent destruction. Some technologists believe the public protests to stem from misconceptions about CW agents and destruction technologies. If that is truly the case, provision of valid information to the public should diminish protests against processes considered by technologists to be effective and safe. At the minimum, members of the public who are deeply interested in the destruction of chemical munitions will appreciate receiving reliable information.

2. The problem that some studies of the properties and chemical reactions of CW agents, relevant to their destruction, which were militarily secret during the Cold War, have not been made publicly available

**Recommendation:** The chemists who did those studies or department heads who have custody of their reports are urged to make them available to all scientists of the world in one of three ways: preferably, by publication in peer-reviewed scientific journals; alternatively, as publicly available reports; or (for minor studies of good quality) by submission to the Technical Secretariat of the Organization for the Prohibition of Chemical Weapons, for inclusion in a data bank.


52 Integration might involve a continuous flow system, in which a liquid stream would flow directly from the "neutralization" reactor into the wet air or supercritical water oxidation reactor. Conceptually simpler would be combination of the two stages in a single reactor.

Reasons for delays in publication are various. During Cold War years, much information was classified as militarily secret. Now, in an era of peace, keeping such data secret can no longer be justified. Moreover, why should a manager skeptical of peace not assist a potential enemy to destroy his weapons? Another reason is procrastination; work is required to assemble data for publication from old records and to refresh one's mind as to why certain experiments were performed and what inferences were drawn from them. The data are of such potential value in assisting mankind to get rid of extremely dangerous materials that scientists should feel an ethical imperative to publish all such data, insofar as of publishable quality.

Some data are doubtless too fragmentary to constitute a proper research report or journal paper. If they are of good quality, they are nevertheless valuable. When contributed to the Organization for the Prohibition of Chemical Weapons, for inclusion in a broadly accessible data bank, in which they would be combined with data from other sources, they are likely to be useful to scientists working on chemical munitions destruction problems.

3. Problems of locating existing publications

Although reports of much useful CW agent research are still kept secret, others are now available, but often as government agency reports not abstracted by Chemical Abstracts. As a result many of those reports are extremely difficult for a chemist to discover, making them effectively unavailable.

Recommendation: A comprehensive bibliography of published or publicly available reports concerning properties and chemical behavior of CW agents relevant to their destruction, to be available to all persons in all countries on payment of a modest charge, should be prepared.

Compilation of the recommended bibliography will be a major task, requiring dedicated full-time work. The project must receive adequate financial support as well as willing cooperation by numerous military and other organizations that have published reports.

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