CERTIFIED REFERENCE MATERIALS

See **QUALITY ASSURANCE: Reference Materials; Production of Reference Materials**

CHARGE COUPLED DEVICES

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CHEMICAL OXYGEN DEMAND

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CHEMICAL WARFARE AGENTS

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Introduction

Chemical warfare agents are a group of toxic chemicals that have been defined in the Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and their Destruction (commonly referred to as the Chemical Weapons Convention or CWC) as 'any chemical which through its chemical effect on life processes can cause death, temporary incapacitation or permanent harm to humans or animals...'. Poisonous or toxic compounds have been utilized in an effort to gain military superiority throughout history but it is only during the past century that chemical warfare agents have been produced and used on a large scale. Tear gas grenades were used in 1914 by the French at the outbreak of the First World War, but it was not until the Germans first used chlorine near Ypres in 1915 that the world entered the modern era of chemical warfare. Other chemical warfare agents such as phosgene and mustard were weaponized during the First World War and were used by both sides throughout the conflict.

The use and development of chemical warfare agents continued following the First World War despite the signing of the 1925 Geneva Protocol, which bans the first use of chemical weapons. Mustard was used by the Italians against the Abyssinians (Ethiopia) during the 1936–37 war and just prior to the Second World War, the Germans discovered and produced the first nerve agent, tabun. Tabun was weaponized by the Germans but neither side made use of their chemical weapons stocks. More effective nerve agents, such as VX, were developed in the 1950s, mustard was used in the Yemen War (1963–67) and allegations of chemical warfare agent use were reported in South East Asian conflicts. Nerve and mustard agents were used by Iraq in the 1980s war between Iran and Iraq, and were considered a real threat to United Nations armed forces during their action against Iraq (1990–91). More recently, sarin and mustard were collected in 1992 from a site where chemical weapons were thought to have been previously used against the population of a Kurdish village. Most recently, sarin was released by the Aum Shinrikyo cult in the Tokyo underground transit system (1995) resulting in thousands seeking medical attention and 12 deaths.

After considerable effort the CWC was opened to signature in 1993, with the treaty coming into force on April 29, 1997. More than 160 States Parties have ratified the CWC and agreed not to develop, produce, stockpile, transfer, or use chemical weapons and agreed to destroy their own chemical weapons

and production facilities. A strong, compliance monitoring regime involving site inspections was built into the CWC to ensure that the treaty remains verifiable. The Organisation for the Prohibition of Chemical Weapons, or OPCW, based in The Hague, has responsibility for implementation of the treaty. Routine OPCW inspections have or will take place at declared sites, including small-scale production, storage and destruction sites, and challenge inspections will take place at sites suspected of noncompliance. Proliferation of chemical weapons and their use will hopefully decrease over the coming years as the CWC proceeds toward its goal of worldwide chemical weapons destruction.

Concerns over possible terrorist use, continued interest by the defense community and the requirements of a verifiable CWC, have driven the development and application of analytical methods for the detection, characterization, and confirmation of chemical warfare agents. Analytical techniques play an important role in this process as sampling and analysis will be conducted to ensure treaty compliance, to investigate allegations of use, and to verify the use of these weapons for forensic purposes.

Chemical Warfare Agent Categories

Chemical warfare agents have been classified into nerve, blister, choking, vomiting, blood, tear, and incapacitating agent categories based on their effect on humans. The most significant chemical warfare agents in terms of military capacity and past use are the nerve and blister agents. For these reasons the analysis of these compounds will be emphasized over the other groups. The choking, blood, and vomiting agents are for the most part obsolete chemical agents that were employed during the First World War. The tear agents were used during the Vietnam War but their primary use, because of their inability to produce high casualties, remains in riot control and for the training of military personnel in chemical defense. Incapacitating agents have been included in the CWC as the United States did develop an agent in this category.

The compounds listed in **Table 1** represent the most common chemical warfare agents, by category with their Chemical Abstracts registry numbers, and is not intended to be exhaustive. It has been estimated that more than 10 000 compounds are controlled

Table 1 Common chemical warfare agents

Full name (trivial name(s))	*CA no.*
Nerve (react irreversibly with cholinesterase which results in acetylcholine accumulation, continual stimulation of the body's nervous system, and eventual death)	
1-Methylethyl methylphosphonofluoridate (sarin, GB)	107-44-8
1,2,2-Trimethylpropyl methylphosphonofluoridate (soman, GD)	96-64-0
Cyclohexyl methylphosphonofluoridate (GF)	329-99-7
Ethyl dimethylphosphoramidocyanidate (tabun, GA)	77-81-6
O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate (VX)	50782-69-9
Blister (affect the lungs, eyes, and produces skin blistering)	
Bis(2-chloroethyl)sulfide (mustard, H)	505-60-2
Bis(2-chloroethylthio)ethane (sesquimustard, Q)	3563-36-8
Bis(2-chloroethylthioethyl)ether (T)	63918-89-8
Tris(2-chloroethyl)amine (HN-3)	555-77-1
(2-Chloroethenyl)arsonous dichloride (lewisite, L)	541-25-3
Choking (effects respiratory tract and lungs)	
Chlorine	7782-50-5
Carbonic dichloride (phosgene, CG)	75-44-5
Vomiting (causes acute pain, nausea, and vomiting in victims)	
Diphenylarsinous chloride (DA)	712-48-1
10-Chloro-5,10-dihydrophenarsazine (adamsite, DM)	578-94-9
Diphenylarsinous cyanide (DC)	23525-22-6
Blood (prevents transfer of oxygen to the body's tissues)	
Hydrogen cyanide (HCN, AC)	74-90-8
Tear (causes tearing and irritation of the skin)	
[(2-Chlorophenyl)methylene]propanedinitrile (CS)	2698-41-1
2-Chloro-1-phenylethanone (CN)	532-27-4
Dibenz[b,f][1,4]oxazepin (CR)	257-07-8
Incapacitating (prevents normal activity by producing mental or physiological effects)	
3-Quinuclidinyl benzilate (BZ)	6581-06-2

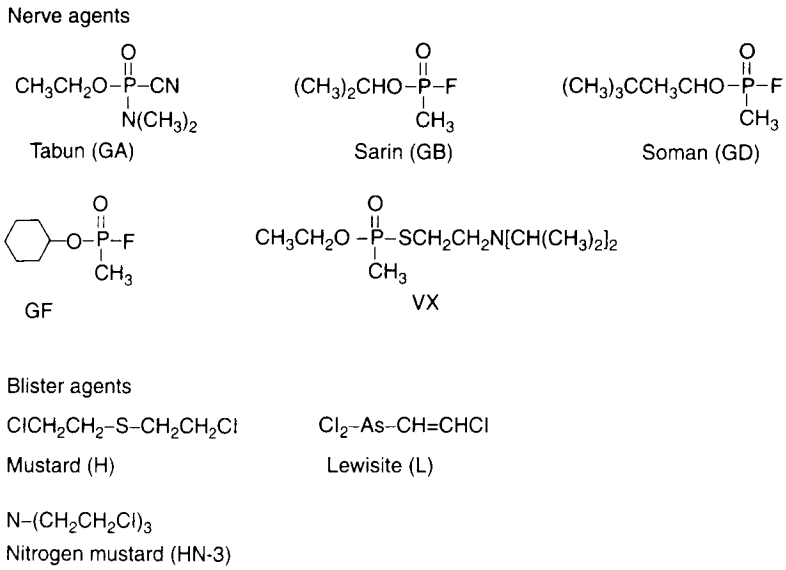

Figure 1 Structures of common chemical warfare agents.

under the CWC, although in practical terms the actual number of chemical warfare agents, precursors, and degradation products that are contained in the OPCW database is in the hundreds. The structures of some common nerve and blister chemical warfare agents are illustrated in Figure 1.

Sample Handling

Samples contaminated with chemical warfare agents generally fall into one of the following general categories: (1) munitions or munition fragments (e.g., neat liquid or artillery shell casing) or (2) environmental (e.g., soil, water, vegetation, or air samples), man-made materials (e.g., painted surfaces or rubber), and biological media (e.g., blood or urine). The ease of analysis depends on the amount of sample preparation required to obtain a suitable sample or extract for chromatographic analysis. In the simplest case where neat liquids can be obtained the sample typically only requires dilution with a suitable solvent prior to analysis. Aqueous samples may be analyzed directly or following solvent extraction with an organic solvent, while biological fluids typically require extensive sample handling and/or derivatization prior to analysis. Soil and other solid samples generally require, at a minimum, solvent extraction and concentration prior to analysis.

Soil may be collected following chemical warfare agent contamination and is one of the more commonly analyzed media. Extraction of chemical warfare agents from soil samples may be accomplished using a number of solvents (e.g., hexane, dichloromethane, or water), with dichloromethane being the most commonly employed extraction solvent for chemical warfare agent determinations. A small portion of soil sample (e.g., 2 g) would typically be ultrasonically extracted with dichloromethane (e.g., 4 ml) in screw-capped glass vial or culture tube for $\sim$10 min. The fines may be removed from the dichloromethane extract by centrifugation or filtration prior to concentration (if necessary) and analysis by gas chromatography–mass spectrometry (GC–MS) or another analytical technique. The sample handling procedures developed for contaminated soils can usually be extended to other solid samples with minor modifications to extraction solvent, volume, or vessel.

Identification Methods

Chemical warfare agents have often been referred to as warfare gases and, in the military, the phrase 'gas, gas, gas' has become synonymous with attack by chemical warfare agents. In fact, many chemical warfare agents exist as liquids at ambient temperatures but have varying degrees of volatility and pose a significant vapor hazard as well as a liquid contact hazard. This physical characteristic has made the analysis of chemical warfare agents amenable to the analytical techniques commonly employed for most environmental analyses, namely GC with a variety of detectors including MS. Synthetic or relatively pure samples are typically characterized by nuclear magnetic resonance (NMR) or Fourier transform infrared (FTIR) spectroscopy. Liquid chromatography–mass spectrometry (LC–MS) has been

used with increasing regularity for the detection and confirmation of chemical warfare agents and their nonvolatile degradation products in aqueous samples and extracts. Thin-layer chromatography (TLC) methods have been thoroughly investigated but have been largely superseded by GC and LC.

The OPCW inspectorate, an important end user of analytical techniques for chemical warfare agents, requires the use of two or more spectrometric techniques and the availability of authentic reference standards for the unambiguous identification of these controlled compounds. For this reason, the combined use of GC–FTIR has received increased attention as newer technologies have led to detection limits approaching those routinely reported during GC–MS analysis. For analyses involving low levels of chemical warfare agents in the presence of high levels of interfering chemical background, tandem mass spectrometry (MS/MS) is often employed.

Chromatography

Samples contaminated with chemical warfare agents typically contain multiple components that are best characterized following chromatographic separation. TLC was routinely employed for the detection of chemical warfare agents but with the advent of GC this technology has been used less frequently for analytical applications. Work continues in the area of two-dimensional overpressured TLC with applications being reported for nerve agents. TLC methods have also been proposed for rapid field analyses, but at present this technique sees most application in support of synthetic programs for the isolation of pure materials or as a quick screening procedure.

Capillary column GC remains the most frequently employed analytical separation method for the screening of samples contaminated with chemical warfare agents. Separation of chemical warfare agents may be achieved with many of the commercially available fused silica columns coated with polysiloxane or other films and retention index data relative to *n*-alkanes and alkyl bis(trifluoromethyl)phosphine sulfides (M-series) have been reported for many chemical warfare agents and related compounds. In general, the best separations have been achieved with a moderately polar film such as (86%)-dimethyl–(14%)-cyanopropylphenyl–polysiloxane. Chiral stationary phases have been developed for the resolution of stereoisomers of several chiral nerve agents, most notably soman. The use of multiple columns of differing polarity during one analysis has also been successfully employed during chemical warfare agent analysis and the term 'retention spectrometry' was coined to describe this technique.

Most of the GC detectors commonly applied to pesticide residue analysis have also been applied to the screening of samples for chemical warfare agents with detection limits typically being in the nanogram to picogram range. Flame ionization detection (FID) is routinely used for preliminary analyses as this technique provides a good indication of the complexity of a sample extract. **Figure 2** illustrates typical GC–FID chromatographic separations obtained for three different munitions-grade mustard formulations, HT, HS, and HQ. Mustard comprised 54%, 74%, and 82% of the volatile organic content in HT, HS, and HQ, respectively, based on peak area measurements. The longer chain blister agents, sesquimustard (Q) and bis[(2-chloroethylthio)ethyl]ether (T) were significant in all three samples along with a number of other related compounds that may provide synthetic procedure or source information.

The need for higher specificity and sensitivity has led to the application of element-specific detectors

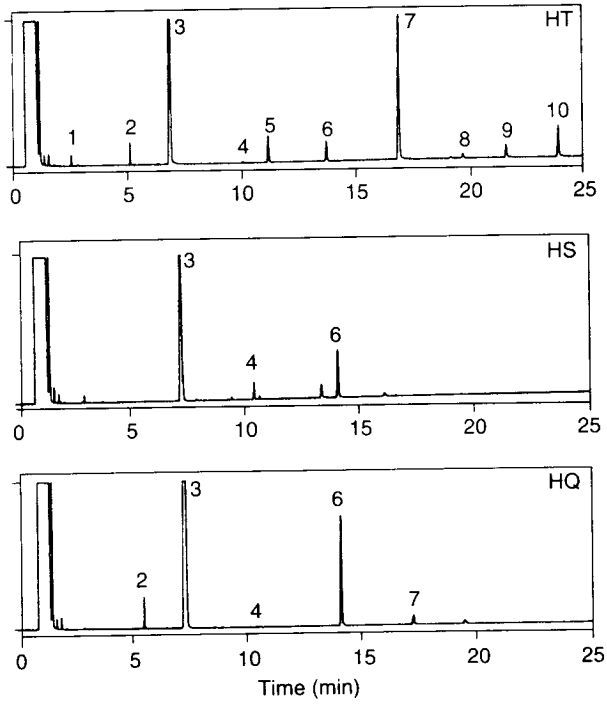

Figure 2 Capillary column GC-FID chromatograms of three munitions-grade mustard samples: HT (top), HS (middle), and HQ (bottom). Identified compounds include: (1) 1,4-thioxane, (2) 1,4-dithiane, (3) mustard (H), (4) bis(2-chloroethyl)disulfide, (5) 2-chloroethyl (2-chloroethoxy)ethyl sulfide, (6) sesquimustard (Q), (7) bis(2-chloroethylthioethyl)ether (T), (8) 1,14-dichloro-3,9-dithia-6,12-dioxatetradecane, (9) 1,14-dichloro-3,6,12-trithia-9-oxatetradecane, and (10) 1,16-dichloro-3,9,15-trithia-6,12-dioxaheptadecane. (GC conditions: 15 m × 0.32 mm ID J&W DB-1; 50 °C (2 min) 10 °C min^{-1} 280 °C (5 min).)

such as flame photometric detection, thermionic detection, atomic emission, and electron capture detection. The simultaneous use of FID with one or more element specific detectors has also been demonstrated during dual- or tri-channel GC analysis using conventional and thermal desorption sample introduction. While data obtained with these detectors may provide strong collaborative evidence for the presence of chemical warfare agents, they cannot be used for full confirmation. Use of GC with one or more spectrometric technique such as MS is required to confirm the presence of chemical warfare agents.

LC–ESI-MS is being used increasingly, as electrospray mass spectrometric data may be used to directly identify chemical warfare agents, degradation products, and related compounds in collected aqueous samples or extracts. Both the nerve and blister agents undergo hydrolysis in the environment and methods are required under the CWC for retrospective detection and confirmation of these compounds. These compounds are significant as they would not be routinely detected in environmental samples and their identification strongly suggests the prior presence of chemical warfare agents. The degradation products of the chemical warfare agents, in particular the nerve agents, are nonvolatile hydrolysis products that must be derivatized prior to GC analysis. A variety of derivatization reagents, leading to the formation of pentfluorobenzyl, methyl, *tert*-butyldimethylsilyl, and trimethylsilyl ethers (or esters), have been investigated to allow GC analysis of, in particular, the organophosphorus acids related to the nerve agents (e.g., alkyl methylphosphonic acids and methylphosphonic acid).

Mass Spectrometry

Mass spectrometry is the method of choice for the detection and characterization of chemical warfare agents, their precursors, degradation products, and related compounds. Extensive use has been made of GC–MS and the mass spectra of numerous chemical warfare agents and related compounds have been published, with the most common chemical warfare agent mass spectra being available in the OPCW, commercial, or defense community databases.

Most of these data were obtained under electron impact (EI) ionization conditions. However, many of the chemical warfare agents, in particular the organophosphorus nerve agents and the longer chain blister agents related to mustard, such as T, do not provide molecular ion information under EI-MS. This hinders confirmation of these chemical warfare agents and makes identification of novel chemical warfare agents or related impurities difficult.

Considerable effort has been devoted to the use of chemical ionization (CI) as a complementary ionization technique. This milder form of ionization generally affords molecular ion information for the chemical warfare agents and has been used extensively for the identification of related compounds or impurities in chemical warfare agent munitions samples and environmental sample extracts. The identity of these related compounds is important because the origin of samples, synthetic process information, or degree of degradation (weathering) information may aid OPCW or other investigations.

Isobutane, ethylene, and methane gases were initially demonstrated as suitable CI gases for the acquisition of organophosphorus nerve agent CI-MS data. The efficacy of ammonia CI-MS for organophosphorus nerve agents and related compounds has been demonstrated and many laboratories now employ this complementary confirmation technique. Ammonia CI not only offers abundant molecular ion data but also affords a high degree of specificity as less basic sample components are not ionized by the ammonium ion. Additional data may be obtained through the use of deuterated ammonia CI, as this technique provides useful hydrogen/deuterium exchange data that indicates the presence of exchangeable hydrogen(s) in CI fragmentation ions. Finally, for full confirmation, the acquired EI and CI mass spectrometric data should be compared to authentic reference data obtained under identical experimental conditions.

Figure 3 illustrates EI and ammonia CI data obtained for VX and a significant VX degradation product, bis[2-(diisopropylamino)ethyl] disulfide. The acquired EI data for both compounds, as well as other VX related compounds, are remarkably similar. Both compounds lack a molecular ion and contain a base ion at m/z 114 due to $(CH_2N(iPr)_2)^+$ and additional ions related to the $-SC_2H_4N(iPr)_2$ substituent. Under ammonia CI conditions, mass spectra containing pseudomolecular and CI fragmentation ions were acquired, with these data being used to confirm molecular mass and differentiate VX related compounds that exhibit similar EI data.

Capillary column GC–MS/MS offers the analyst the potential for highly specific, sensitive detection of chemical warfare agents as this technique significantly reduces the chemical noise associated with complex biological or environmental sample extracts. The specificity of product scanning with moderate sector resolution, as well as the specificity of ammonia CI, was demonstrated with a hybrid tandem mass spectrometer during analysis of painted panel samples circulated during an international round robin verification exercise.

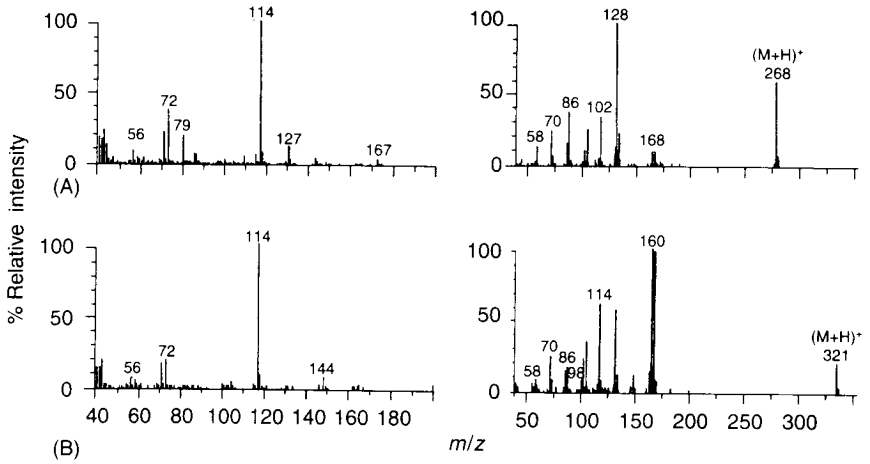

Figure 3 EI (left) and ammonia CI (right) mass spectrometric data obtained for (A) VX and (B) bis[2-(diisopropylamino)ethyl] disulfide.

The painted panel extract was contaminated with numerous hydrocarbons and only two of the three longer chain blister agents, sesquimustard (Q) and bis(2-chloroethylthioethyl)ether (T), could be identified during capillary column GC–MS (EI) analysis (**Figure 4A**). The arrow indicates the chromatographic retention time of the third blister agent, 2-chloroethyl (2-chloroethoxy)ethyl sulfide (O). The specificity of ammonia CI (**Figure 4B**) was clearly demonstrated during this analysis. All three longer chain blister agents were determined in the presence of high levels of interfering hydrocarbons, as the hydrocarbons were not sufficiently basic to ionize. Similarly, it was possible to use the resolution of hybrid MS/MS to discriminate between ions at *m/z* 123 arising from the longer chain blister agents from those ions at *m/z* 123 arising from the hydrocarbon background. The resultant GC–MS/MS chromatogram (**Figure 4C**), where only *m/z* 123 ions due to the blister agents were transmitted into the collisional activated dissociation cell, was virtually free of chemical noise and all three components were detected. The three longer chain blister agents were well resolved with the J&W DB-1701 capillary column, with all three components exhibiting similar product spectra during GC–MS/MS analysis.

Both the nerve and blister agents undergo hydrolysis in the environment and methods are required for retrospective detection and confirmation of these hydrolysis products. Hydrolysis products are significant as they are generally compounds that would not be routinely detected in environmental samples and their presence strongly suggests the prior presence of chemical warfare agents. The degradation products of the chemical warfare agents, in particular the nerve agents, are nonvolatile hydrolysis products that must be derivatized prior to GC analysis. Alternatively, aqueous samples or extracts may be analyzed by LC–MS, negating the need for additional sample handling steps and derivatization.

Use of thermospray MS and more recently the atmospheric pressure ionization (API) (e.g., electrospray (ESI), ionspray, and atmospheric pressure CI) techniques have enabled the direct mass spectrometric analysis of the hydrolysis products of chemical warfare agents. Both techniques may be interfaced to liquid chromatography for component separation, with thermospray having been largely superceded by API for most LC–MS applications. LC–ESI-MS methods have been used for the direct analysis of chemical warfare agent hydrolysis products in a number of studies and have recently been demonstrated for the analysis of nerve agents. These new methods complement existing GC–MS methods for the analysis of chemical warfare agents and their hydrolysis products and LC–ESI-MS methods will replace some GC–MS methods used for the analysis of contaminated aqueous samples or extracts.

Mustard and longer chain blister agents hydrolyze to their corresponding diols, with thiodiglycol being the product formed following hydrolysis of mustard. **Figure 5A** illustrates a typical LC–ESI-MS chromatogram obtained for the aqueous extract of a soil sample taken from a former mustard storage site. The soil sample extract contained thiodiglycol (**Figure 5B**) and 6-oxa-3,9-dithia-1,11-undecanediol (**Figure 5C**), the hydrolysis products of blister agents mustard and bis(2-chloroethylthioethyl)ether, respectively. ESI-MS data for both compounds contained protonated molecular ions that could be used to confirm molecular mass and characteristic lower mass product ions.

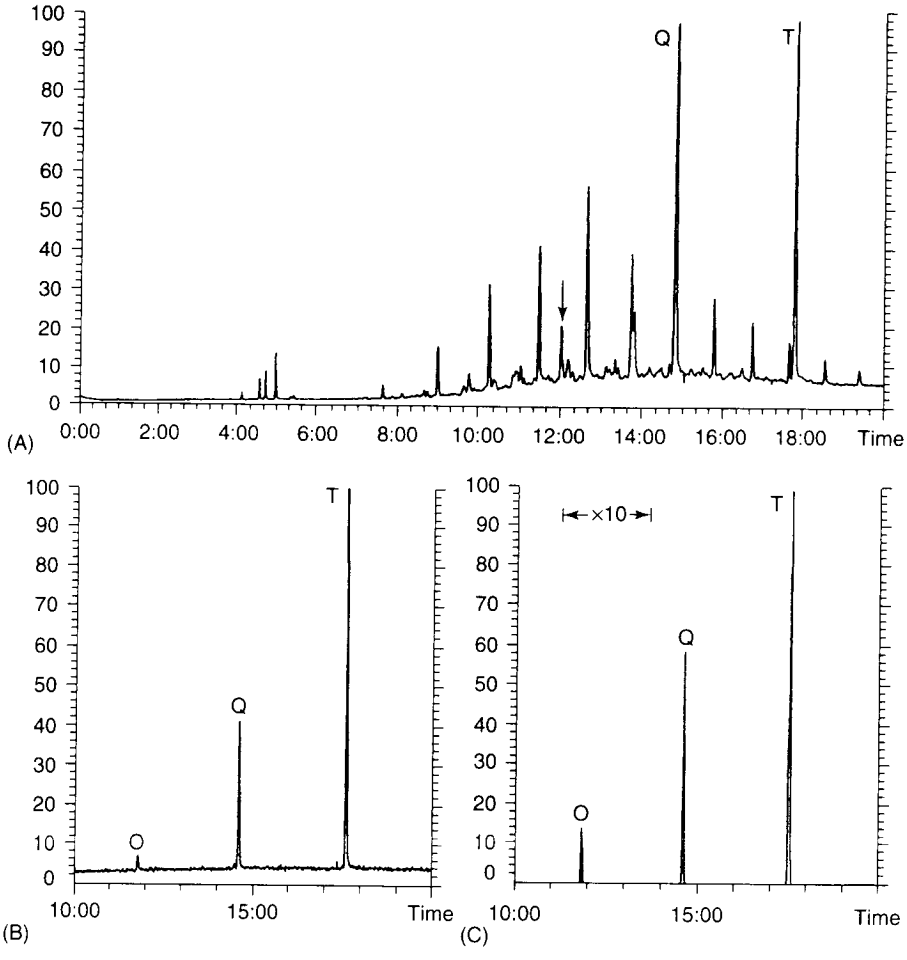

Figure 4 Capillary column (A) GC–MS (EI); (B) GC–MS (ammonia CI); and (C) GC–MS/MS (EI) chromatograms obtained during analysis of international round robin painted panel extracts. Sequimustard (Q) and bis(2-chloroethylthioethyl)ether (T) were detected during EI analysis. The downward arrow in (A) indicates the retention time of 2-chloroethyl (2-chloroethoxy)ethyl sulfide (O). This compound was masked by the sample matrix during EI analysis and was only detected following (B) ammonia CI and (C) MS/MS analysis. (GC conditions: 15 m × 0.32 mm ID J&W DB-1701, 40°C (2 min) 10°C min^{-1} 280°C (5 min), *x*-axis: time (min).)

Figure 6 illustrates the LC–ESI-MS chromatogram for a complex munitions-grade tabun sample. Tabun and a number of related compounds were identified based on their acquired ESI-MS data. The mass spectra contained $(M+H)^-$, $(M+H+ACN)^+$ ions and/or protonated dimers that could be used to confirm the molecular mass of each compound. Structural information was provided by inducing product ion formation in either the ESI interface or the quadrupole collisional cell of a MS/MS instrument. Product ions due to alkene loss from the alkoxy substituents, and the acetonitrile adduct associated with these product ions, were generally observed. Figure 7 illustrates typical ESI-MS data obtained for tabun and three other nerve agents.

Considerable effort has been expended on the development of field portable MS and GC–MS instruments, as this technique holds the greatest promise for the confirmation of chemical warfare agents under field situations. The OPCW has available field portable GC–MS instrumentation that may be taken onsite to confirm the presence of chemical warfare agents. An atmospheric pressure MS/MS has also been developed and evaluated for real-time detection of nerve agents in air. Alternatively, air samples may be collected on solid-phase microextraction fibers or on Tenax tubes that may be thermally desorbed into an onsite GC–MS instrument. Secondary ion mass spectrometry has been used for the detection of chemical warfare agents and their hydrolysis products on leaves, soil, and concrete, offering a new option for the detection of these compounds on adsorptive surfaces. Finally, rapid separation and detection of chemical warfare agents has recently been

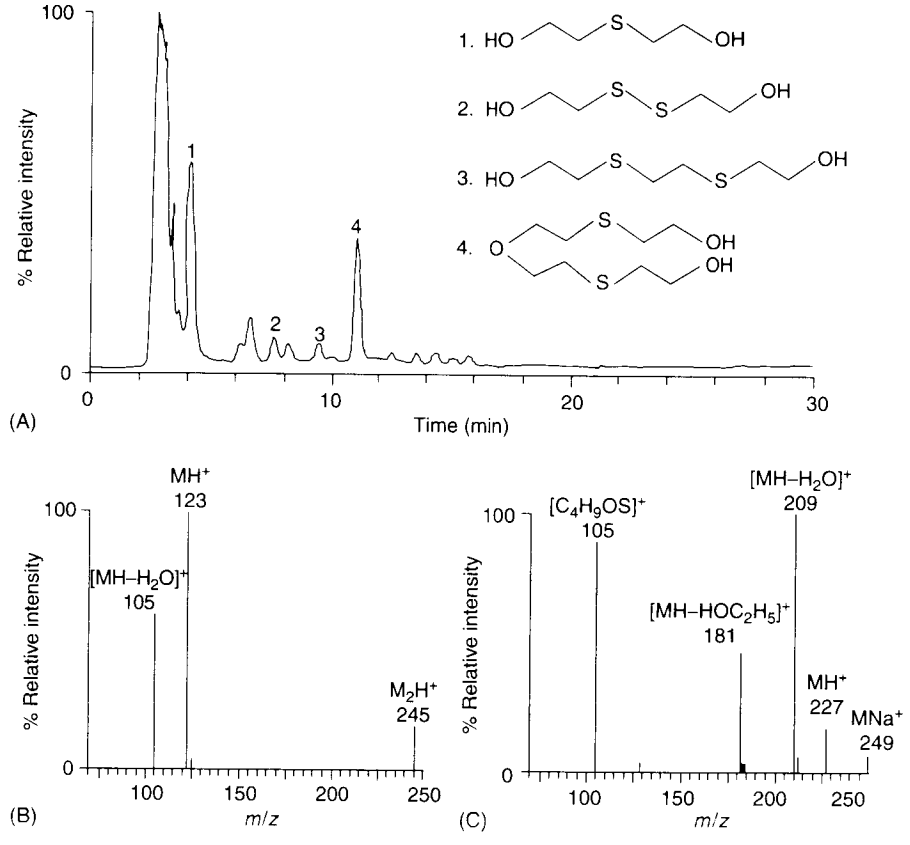

Figure 5 (A) Packed capillary LC–ESI-MS chromatogram obtained for the water extract of a soil sample obtained from a former mustard site. ESI-MS data obtained for (B) thiodiglycol (sampling cone voltage: 20 V) and (C) 6-oxa-3,9-dithia-1,11-undecanediol (sampling cone voltage: 30 V). (LC conditions: 150 mm × 0.32 mm ID C_{18}, acetonitrile/water gradient.).

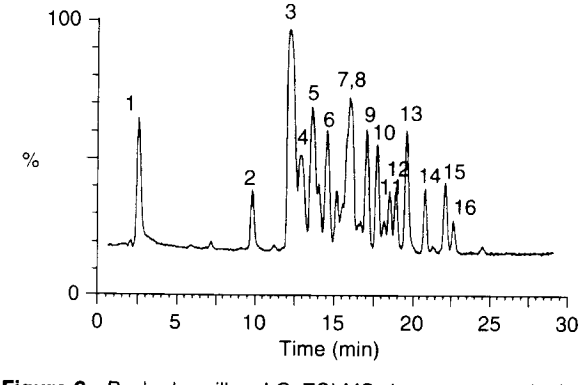

Figure 6 Packed capillary LC–ESI-MS chromatogram obtained for 0.1 mg ml^{-1} munitions-grade tabun sample. Tabun (peak number 4) and 15 related organophosphorus compounds were identified by ESI-MS. (LC conditions: 150 mm × 0.32 mm ID C_{18}, acetonitrile/water gradient.)

demonstrated with ESI-ion mobility spectrometry (IMS)–MS. IMS is commonly employed in military devices for rapid field detection and this approach could be lead to the development of instrumentation for the analysis of aqueous samples.

Other Techniques

NMR is an important technique for the structural analysis and characterization of chemical warfare agents, particularly for the authentication of reference materials or unknown chemical warfare agents and related compounds. The presence of heteronuclei such as ^{31}P and ^{19}F in the nerve agents leads to diagnostic splitting patterns and coupling constants due to ^{1}H–^{31}P and ^{1}H–^{19}F spin–spin coupling. The utility of NMR for analysis of complex sample mixtures or for trace analysis is somewhat limited. Specific heteronuclear experiments such as ^{31}P NMR may be used to identify organophosphorus nerve agents in complex matrices. Characteristic chemical shifts of compounds containing a phosphorus–carbon bond and splittings due to phosphorus–fluorine spin–spin coupling can be used to screen for the presence of nerve agents (**Table 2**). However, ^{31}P chemical shifts are sensitive to temperature, concentration, and solvent and the identification must be supported with additional spectrometric data such as MS. Two-dimensional correlation experiments have been used to help in structural elucidation of

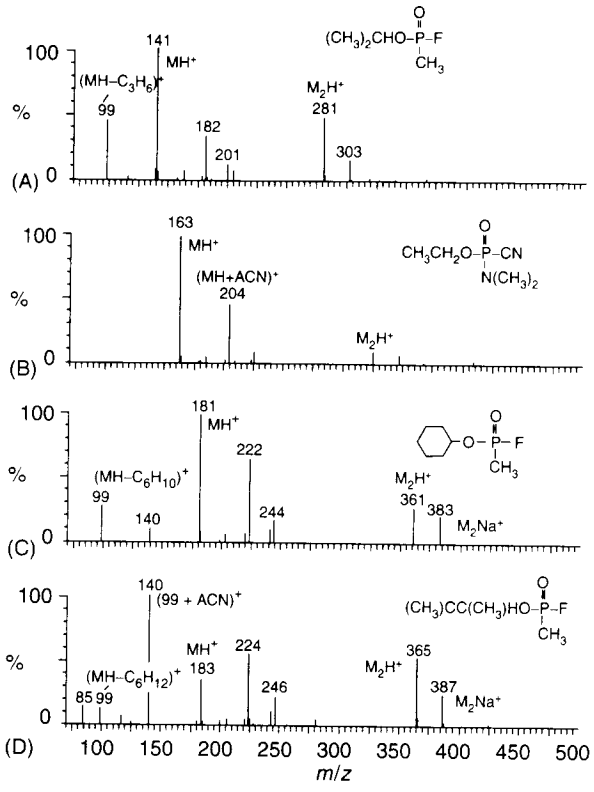

Figure 7 ESI-MS data obtained for (A) sarin (GB); (B) tabun (GA); (C) cyclohexyl methylphosphonofluoridate (GF), and (D) soman (GD) with a sampling cone voltage of 20 V.

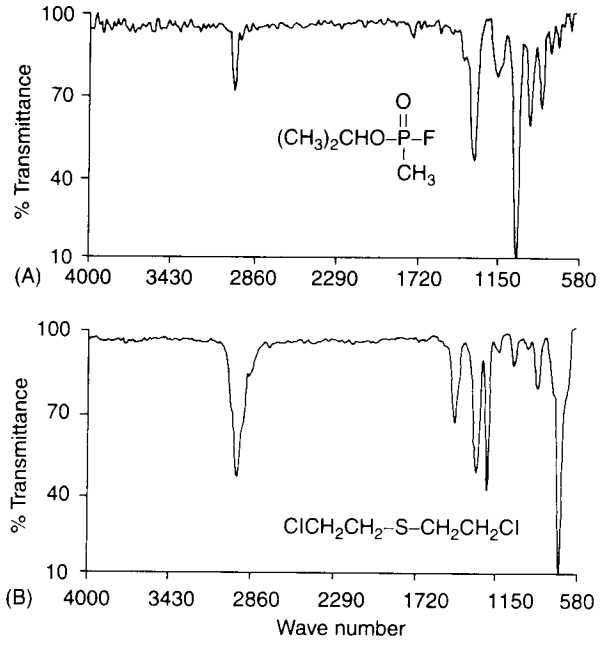

Figure 8 Vapor phase FTIR spectra obtained for (A) sarin (GB) and (B) mustard (H) during capillary column GC–FTIR analysis.

Table 2 Phosphorus-31 chemical shifts of nerve agents in deuterochloroform

Nerve agent	$\delta^{31}P$ *(ppm)*[a]	J_{PF} *(Hz)*[b]
VX	53.9	–
Soman (two isomers)	29.1	1047
	28.1	1047
GF	28.5	1047
Sarin	28.4	1046
Tabun	−9.8	–

[a] Chemical shift relative to an internal reference standard of triethyl phosphate, −1 ppm.
[b] Spin–spin (^{31}P–^{19}F) coupling constants.

unknowns in contaminated samples, making NMR a valuable technique to be used alongside other spectrometric techniques.

Condensed phase infrared (IR) data exist for many chemical warfare agents and related compounds as this technique was routinely used prior to the advent of GC–MS. Capillary column GC–FTIR offers considerably more promise for the identification and characterization of chemical warfare agents in multiple component sample extracts and has been utilized as a complementary confirmation technique. Sensitivity is generally poorer than that obtained by MS but may be improved by using large volume (e.g., 50 µl) injections with peak compression onto an uncoated precolumn with lightpipe technology or through the use of cryodeposition.

Figures 8A and 8B illustrates the FTIR vapor phase data obtained for sarin and mustard, respectively. Sarin exhibits characteristic absorption bands at 2991, 1313, 1018, 924, and 843 cm^{-1} due to C–H, P–F or P=O, P–O–C, P–CH_3, and P–F, respectively. Mustard contains bands at 2969 and 717 cm^{-1} that can be assigned to C–H and C–Cl, respectively. The spectra for other chemical warfare agents differ sufficiently such that library searching may be routinely employed for tentative identification.

Military Detection

A variety of detection devices and other chemical warfare agent defense equipment have been developed for specific military applications. Most of the effort in this area resulted from the perceived threat during the Cold War era and although this threat has decreased dramatically, interest in chemical detection equipment persists because of worldwide chemical weapons proliferation. During the 1990–91 Iraq War chemical detection equipment was deployed into the

Persian Gulf and similar equipment has been used to support the United Nations Special Commission during the destruction of Iraqi chemical weapons. Equipment of this type has been used by the OPCW and could potentially be utilized again by the United Nations in peacekeeping or intervention roles where the threat of chemical weapons use exists. **Table 3** lists examples of chemical detection equipment by country and indicates the principle of detection and capabilities of each system.

Table 3 Selected military chemical warfare agent detection devices

Country	*Device name and capabilities*
Canada	Chemical Agent Detection System (CADS II) – Early warning system that controls a network of Chemical Agent Monitors (see UK) for the real time detection of nerve and blister agents
China	Chemical Warfare Agent Identification Kit, M-75 – Wet chemistry detection of nerve, blister, choking, vomiting, and blood agents
Denmark	INNOVA 1312 Multi-Gas Monitor – Photoacoustic detection of nerve, blister, choking, and blood agents
Finland	Chemical Agent Detection System, M90 – Alarm for the ion mobility spectrometric detection of nerve and blister agents
France	PROENGIN Portable Chemical Contamination Monitor AP2C – Hand-held flame photometric detection of nerve and blister agents – Also designs for fixed sites (AP2C-V and ADLIF)
Germany	MM-1 Mobile Mass Spectrometer – Quadrupole mass spectrometric detection of chemical warfare agents Rapid Alarm and Identification Device – 1 (RAID-1) – Ion mobility spectrometric detection of nerve and blister agents
Hungary	Chemical Agent Sensor GVJ-2 – Ion mobility spectrometric detection of nerve and blister agents Remote Chemical Agent Sensor VTB-1 – Field deployable laser radar for the detection of chemical warfare agents
Romania	Nerve Agent Alarm ASTN-2 – Nerve agent detector based on optical and acoustic signals
Switzerland	IMS 2000 CW Agent Detector – Ion mobility spectrometric detection of nerve and blister agents
CIS (formerly USSR)	Automatic Nerve Agent Detector Alarm, Model GSP-11 – Enzyme inhibition for the detection of nerve agents
UK	Chemical Agent Monitor (CAM), GID-2/GID-3 Detectors – Ion mobility spectrometry based monitor for the detection of nerve and blister agents NAIAD – Nerve agent immobilized enzyme detector and alarm
USA	ICAD Miniature Chemical Agent Detector – Personal detector based on electrochemical principals for the detection of nerve, blister, blood, and choking agents MINICAMS – Gas chromatographic detection of nerve and blister agents M21 Remote Sensing Chemical Agent Alarm (RSCAAL) – Passive infrared detection of chemical warfare agents Chemical Agent Detection Kit, M256A1 – Wet chemistry detection of nerve, blister, choking, and blood agents SAW MINICAD MK II – Surface acoustic wave detection of nerve and blister agents

Safety and Disposal

Chemical warfare agents are extremely hazardous and lethal compounds. They can only be used in designated laboratories by personnel trained in safe-handling and decontamination procedures and with immediate access to medical support. Safety and standard operating procedures must be developed and approved before any chemical warfare agents are handled. Chemical warfare agents can only be used in laboratory chemical hoods with a minimum face velocity of 100 linear feet per minute equipped with emission control devices that limit exhaust concentration to below 0.0001 mg m^{-3}. Personnel handling chemical warfare agents should wear rubber gloves, lab coats, and full faceshields and keep a respirator (gas mask) within easy reach. Sufficient decontaminant to destroy all chemical warfare agents being handled must be on hand before commencing operations.

Blister and nerve agents can be destroyed using saturated methanolic solutions of sodium or potassium hydroxide. Decontaminated chemical warfare agents must be disposed of in an environmentally approved method according to local legislation.

See also: **Gas Chromatography**: Overview; Fourier Transform Infrared Spectroscopy. **Liquid Chromatography**: Overview. **Mass Spectrometry**: Overview; Ionization Methods Overview; Gas Analysis. **Nuclear Magnetic Resonance Spectroscopy**: Overview.

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CHEMICALLY MODIFIED ELECTRODES

See **SENSORS: Chemically Modified Electrodes**

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