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Rapid Screening for Chemical Weapons Infiltration in Drinking Water

There is widespread recognition of the need for early warning system (EWS) capabilities to provide timely and accurate information with which to make informed decisions in response to adverse events (Gullick et al, 2003 and 2004). The problem has been amplified recently by the heightened risks and threats posed by potential terrorist activities (Mays, 2004). As a result of the attacks on September 11, significant progress has been made in the areas of vulnerability assessments (USEPA, 2002; ASDWA 2002) and preparedness planning.

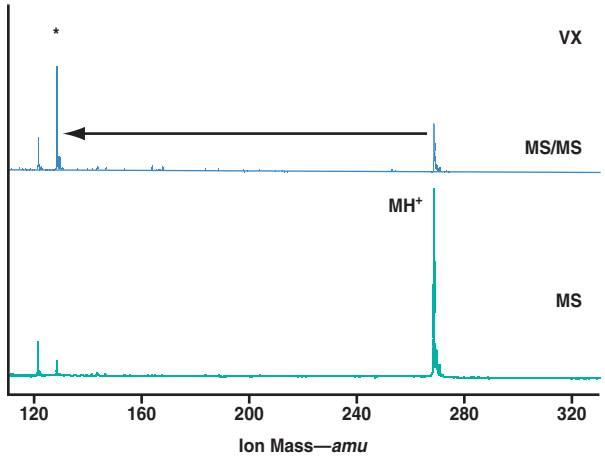
An effective early warning monitoring system must satisfy several requirements. Guidelines have been published by the International Life Sciences Institute for EWS monitoring equipment (ILSI, 1999). The guidelines recommend that such equipment have the following functions:

- rapid response time,
- automated analysis,
- specific identification of a wide range of contaminants,
- low false-negative and false-positive rates at required concentrations, and
- high sampling rate.

A new screening technology based on photoionization/mass spectrometry (PI/MS) has been developed for monitoring chemical weapons, related compounds (e.g., precursors, decomposition products), and other suspect compounds (e.g., pesticides, drugs). The PI source is the crucial advance that makes it possible to conduct high-speed, high-throughput analysis of complex mixtures at the requisite sensitivity for threat detection. The instrumentation meets all of the preceding requirements.

The sidebar on the last page describes the fundamentals of PI/MS analysis, which is being used by a growing number of municipalities and government facilities to help safeguard public drinking water. In the following sections the strategy being taken by the city of Houston, Texas, to develop an early warning capability based on the PI/MS screening technology is reviewed.

FIGURE 1 PI/MS spectrum of VX and the resulting MS/MS spectrum from selective fragmentation of the VX parent ion



M—molecular ion, MH^+—protonated molecule for molecule M, MS—mass spectrometry, PI—photoionization

The VX parent ion is MH^+, which results when the initially formed molecular photoion M^+ reacts with the surrounding solvent (typically either nascent H_2O or an organic solvent such as CH_3OH).

** Fragment ion*

DEPLOYMENT BY WATER UTILITIES

Because online monitors are currently not capable of detecting chemical weapons agents at subacute levels, the city of Houston collects samples and takes them to a central laboratory for analysis. These samples are then loaded onto the PI/MS instrument for rapid screening. The PI/MS analyzer may be operated in an online continuous-monitoring mode, but the manufacturer wants to gain additional experience in the field using the current sampling mode before it develops an online sampling option.

The PI/MS at Houston currently screens for the factory-loaded chemical weapons compounds as well as new ones, such as atrazine and dursban, added by plant personnel. The instrument's screening library can be expanded routinely for both standard and nonstandard compounds. This provides an additional tool for identifying compounds that are not routinely monitored in drinking water samples. The PI/MS analyzer is used for screening distribution water and raw water samples from all the city's plants. The instrument is also used as a quick screening method to test water from all components

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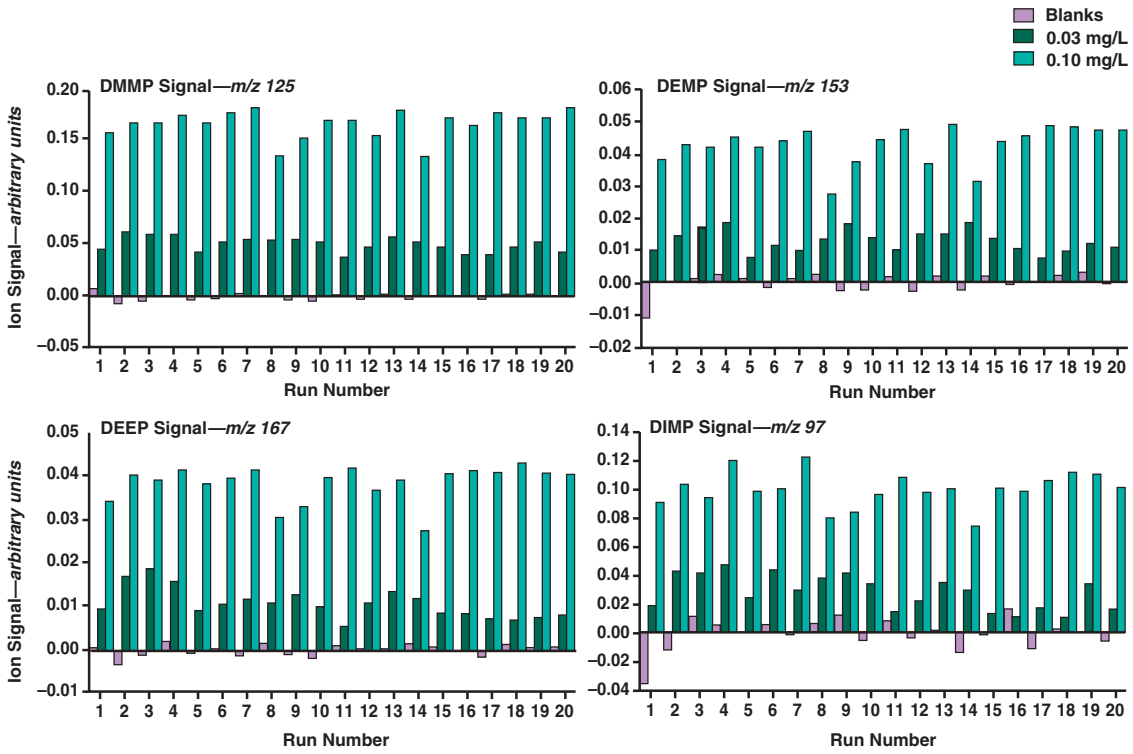
FIGURE 2 Results of recording 20 runs each for specific concentrations of a chemical weapons stimulant mixture in water



DEEP—diethyl ethylphosphonate, DEMP—diethyl methylphosphonate, DIMP—diisopropyl methyl phosphonate, DMMP—dimethyl methyl phosphonate, m/z—mass-to-charge ratio
Signal levels were obtained after subtracting the mean background signal at each of the signature ion masses.

of the system. The instrument baseline is calibrated each day (about a 5–10-min procedure) before screening for samples.

The high-throughput capabilities become important in the event of an emergency or heightened security concern in which a greatly increased number of samples may need to be quickly screened. The short sampling times and automated analysis are also advantageous for maximizing staff resources.

THREAT SCENARIOS

Little information is available regarding the toxicity of chemical weapons compounds in water because the majority of studies have been concerned with inhalation of vapors or absorption through the skin (Somani, 2001). The Department of Defense Tri-Services guidelines for safe levels of these chemicals in drinking water for seven-day exposures (Tri-Services, 1999) are shown in Table 1. It is assumed that acute exposure leading to illness or impairment would occur at five times these safe levels. The calculated acute concentration levels in the last column of Table 1 represent daily consumption levels of 0.66 gpd (2.5 L/d) of source water and a two-day exposure period (i.e., 1.3-gal [5-L] consumption).

Chemical weapons contamination of drinking water is a viable threat. A population of one million people used about 100 mgd (379 ML/d), most of which goes to nonconsumptive use. The amount of a chemical weapon that must be added to this daily volume to reach an acute level of 0.5 mg/L (Table 1) is about 200 kg or about the equivalent of a 55-gal drum. This is a plausible scenario with the potential to impair 1 million people after one to two days of exposure. Other threat scenarios include contamination of source water (pretreated), for which a greater contamination volume would be required because of the greater source volume, and contamination in the distribution system where lower quantities of chemical weapons are needed to reach acute concentrations. This latter scenario may be the most serious because high concentrations with minimal degradation can reach end users.

PERFORMANCE

An effective EWS system must be able to detect subacute concentrations at a response time that is much shorter than the relevant exposure time. The PI/MS instrumentation was tested at chemical weapons surety labs on several occasions. From these tests, the MS and MS/MS spectral libraries were developed and the mean detection limits (MDLs) determined. The MDLs are based on the US Environmental Protection Agency (USEPA) method 1 and are expressed as the concentration at which the signal level is 3σ above the background distribution. Essentially all the chemical weapons agents tested on the PI/MS analyzer (VX, GA, GB, GD, GF, HD,

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TABLE 1 Toxic and safe levels of chemical weapons in drinking water

Compound	Tri-Services Water Quality Standards* *mg/L*	Assumed Acute Concentrations for Short-term Exposure† *mg/L*
GA (Tabun)	0.140	4.9
GB (Sarin)	0.028	0.98
GD (Soman)	0.012	0.42
VX	0.015	0.52
Sulfur mustard	0.140	4.9
Lewisite (As fraction)	0.080	2.8

*Data are from Tri-Services (1999); 1.3-gpd (5-L/d) consumption, seven-day exposure.
†Deleterious effects are assumed at five times the recommended Tri-Services (1999) guidelines for 0.66-gpd (2.5-L/d) consumption and two-day exposure.

TABLE 2 False-negative and false-positive rates for various threshold levels and concentrations for the chemical weapons stimulant mixture in water

Threshold *mg/L*	Concentration *mg/L*	Result	DIMP %	DMMP *%*	DEMP *%*	DEEP *%*
3σ	0	FP	0	0	0	0
	0.03	FN	55	0	10	0
	0.10	FN	0	0	0	0
0.03	0	FP	0	0	0	0
	0.03	FN	45	45	50	55
	0.10	FN	0	0	0	0
0.10	0	FP	0	0	0	0
	0.03	FN	100	100	100	100
	0.10	FN	45	30	40	30
3σ MDL			0.033	0.006	0.021	0.011

DMMP—dimethyl methylphosphonate, DEMP—diethyl methylphosphonate, DEEP—diethyl ethylphosphonate , and DIMP—diisopropyl methyl phosphonate
Values in bold correspond to recommended settings.

HN-1, HN-3, CR, CS, BZ) had MDL values in the 0.05- to 0.5-mg/L range, which meets the short-term acute concentration levels assumed in Table 1.

To obtain false-negative (FN) and false-positive (FP) rates at the required threshold levels for an alarm, analyses were conducted on a mixture of four chemical weapons surrogates—dimethyl methylphosphonate (DMMP), diethyl methylphosphonate (DEMP), diethyl ethylphosphonate (DEEP), and diisopropyl methyl phosphonate (DIMP)—in concentrations of 0, 0.03, and 0.10 mg/L. These were sampled 20 times each on a 50-second-per-sample cycle time. Thus, the 60 total analyses, consisting of 240 measured intensities, were completed in 50 minutes. Uncontaminated water standards were run first to set the alarm thresholds. Generally eight blank measurements are sufficient, and the instrument automatically computes the standard deviation σ for the background at all ion masses corresponding to the CW spectral library and any other compounds selected for screening. The user then sets the alarm threshold from a choice of values ranging from 1–6σ above the background level. The recommended level is 3σ, which corresponds to the USEPA MDL level explained earlier.[2]

The results of the FN/FP analyses are shown in Figure 2. The plotted signals represent the measured intensity minus the mean of the background (blank) intensity for each compound ion mass. (Thus, the plotted signals for the 0-mg/L blank samples represent the distribution of the background from the mean.) From these data it is clear that the 0.03-mg/L signal level is distinctly detectable from the background level for all the compounds.

Table 2 summarizes the FN, FP, and 3σ MDL results for the chemical weapons simulant mixtures in water. The 3σ MDL values ranged from 0.006 mg/L for DMMP to 0.033 for DIMP. The FN and FP results show the expected trends. For all of the alarm thresholds chosen (i.e., 3σ, 0.03 mg/L, and 0.10 mg/L), the FP rate, which depends on the threshold and concentration, was 0%. If the alarm threshold is set above the compound concentration, a high FN rate will occur. For thresholds set equal to the compound concentration, the FN will be about 50% (Table 2). For the 3σ or 0.03-mg/L thresholds, the FN was 0% for all chemical weapons stimulant compounds at 0.10 mg/L concentration. This concentration is below the acute concentrations for chemical weapons agents shown in Table 1. If the chemical weapons stimulant results are representative of actual agents, which has been the case thus far in actual chemical weapons agent testing, then the PI/MS analyzer meets the low FN and FP requirements that must be met for a screening technology to be designated as effective for chemical weapons in water. The PI/MS instrument at Houston exhibits a low FP rate; when positives do occur they are easily resolved by repeating the measurements or by inspecting the mass spectrum.

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FOOTNOTES

[1]By definition the 3σ MDL corresponds to a false-positive value of 0.15% (the fractional area of a Gaussian distribution 3σ removed from the mean).
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FUNDAMENTALS OF PI/MS

The fundamentals of photoionization/mass spectrometry (PI/MS) have been reviewed elsewhere (Syage et al, 2000; Syage and Evans, 2001). The main characteristics that differentiate PI from other ionizers and that make it suitable for rapid and accurate analyses of mixtures are: (1) ionization of a wide range of compounds, (2) predominant parent-ion signal with minimal fragmentation, (3) minimal susceptibility to ion suppression, and (4) minimal ionization of common matrixes, such as air and most solvents.

Other ionizers are not suitable for direct analysis of complex mixtures without using on-line separation such as gas chromatography (GC) or liquid chromatography (LC) because of their susceptibility to either extensive ion fragmentation or ion suppression. PI, on the other hand, significantly minimizes these deficiencies, yet ionizes a broad range of compounds including nearly all major chemical weapons compounds and other hazardous threats.

The ion mass analyzer is based on quadrupole ion trap, time-of-flight (QitTof) MS, which is a powerful yet simple device. The main characteristics that differentiate it from other MS systems include (1) spectral recording of all ions simultaneously, (2) full mass spectral acquisitions at high speeds (e.g., 60 Hz), and (3) capability to conduct confirmatory MS/MS analysis, whereby parent ions can be selectively fragmented to deduce the chemical structure and characterize the compound. An example of MS/MS characterization is shown in Figure 1 for the compound VX. The primary parent-ion signal is at a mass of 268 and the characteristic fragment ion that is used to characterize the detected compound is at mass 128.

The analyzer has an integrated autosampler for injecting sample on a 45–50-second cycle time. There are several key benefits to this configuration versus GC/MS and LC/MS, including high-speed, high-throughput analysis, minimal or no sample preparation, low operating costs as a result of minimal consumables, and ease of operation. These benefits meet the requirements of an early warning system.

The instrument is preloaded with a chemical weapons database that includes VX, GA, GB, GD, GF, HD, HN-1, and HN-3, an important feature because many chemical weapons standards are unobtainable. Many other compounds have been shown to be detectable and can be added to the database, such as the riot agents CR and CS, the hallucinogen BZ, chemical weapons starting materials such as DF and QL, and chemical weapons decomposition products such as YL and VX-disulfide. The screening results are recorded in a spreadsheet-compatible file for quick review. A visual indicator of the results of each sample is also available as a software option.

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