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Direct Sampling of Chemical Weapons in Water by Photoionization Mass Spectrometry

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The vulnerability of water supplies to toxic contamination calls for fast and effective means for screening water samples for multiple threats. We describe the use of photoionization (PI) mass spectrometry (MS) for high-speed, high-throughput screening and molecular identification of chemical weapons (CW) threats and other hazardous compounds. The screening technology can detect a wide range of compounds at subacute concentrations with no sample preparation and a sampling cycle time of ~45 s. The technology was tested with CW agents VX, GA, GB, GD, GF, HD, HN1, and HN3, in addition to riot agents and precursors. All are sensitively detected and give simple PI mass spectra dominated by the parent ion. The target application of the PI MS method is as a routine, real-time early warning system for CW agents and other hazardous compounds in air and in water. In this work, we also present comprehensive measurements for water analysis and report on the system detection limits, linearity, quantitation accuracy, and false positive (FP) and false negative rates for concentrations at subacute levels. The latter data are presented in the form of receiver operating characteristic curves of the form of detection probability P_D versus FP probability P_{FP}. These measurements were made using the CW surrogate compounds, DMMP, DEMP, DEEP, and DIMP. Method detection limits (3σ) obtained using a capillary injection method yielded 1, 6, 3, and 2 ng/mL, respectively. These results were obtained using 1-μL injections of water samples without any preparation, corresponding to mass detection limits of 1, 6, 3, and 2 pg, respectively. The linear range was about 3−4 decades and the dynamic range about 4−5 decades. The relative standard deviations were generally <10% at CW subacute concentrations levels.

Increased terrorist activity is driving the need for early warning systems (EWS) that can routinely provide fast and accurate detection of hazardous compounds dispersed in media such as air, water, and food. Chemical weapons (CW) agents are a lethal class of compounds that threaten primarily military operations. However, there is a growing awareness that CW agents can pose a civilian threat as well. There is a increasing effort in developing portable and fast methods to detect CW agents in air, water, and soil. Smith, Hook, and co-workers compared various field-portable mass spectrometer (MS) systems for gas-phase CW detection.[1] These investigators have also been developing solid-phase microextraction (SPME) to sample air and soil for CWs,[2,3] while Lakso and Ng have demonstrated SPME for analysis in water.[4] Groenewold et al. have developed ion trap MS methods for screening for CWs in soil and on concrete.[5,6] Finally, we mention the use of capillary electrophoresis by Nasser et al. for detection of CWs and their decomposition products in water.[7,8]

A particular vulnerability is contamination of water supplies due to their easy access and rapid distribution to a broad population base.[9−12] Another application that requires high throughput is site inspection, such as compliance monitoring of the Chemical Weapons Convention (CWC) treaty.[13] The validated method of detection is gas chromatography/mass spectrometry (GC/MS) by a method that takes ~1 h/run. This analysis rate is inadequate to sample the large number of samples that are prepared from swipes, soil samples, etc. What is needed is a high-throughput screener that can make positive determinations for the presence of targeted compounds and then confirm their presence by GC/MS. We describe an analyzer technology based on photoionization mass spectrometry that offers high-speed, high-throughput screening and molecular identification of CW threats and other hazardous compounds.

Photoionization (PI) is becoming widely adopted in analytical MS owing to favorable properties relative to other available ionization sources. PI MS can (i) extend the range of compounds that can be ionized, (ii) reduce ion suppression, and (iii) reduce

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ion fragmentation.[14] The introduction of compact, sensitive PI sources for commercial analytical MS instruments at atmospheric pressure (e.g., atmospheric pressure photoionization, APPI)[15−19] and subatmospheric pressure (e.g., low-pressure photoionization, LPPI)[20−23] has opened up new applications and areas of research.

In this work, we have investigated the potential for PI and in particular LPPI MS to be used as a fast screening method for detection of chemical weapons in air, water, and soil extracts. The main characteristics that differentiate PI from other ionizers and make it uniquely suitable for rapid and accurate analyses of mixtures are as follows: (1) ionization of a wide range of compounds; (2) predominant parent ion signal with minimal fragmentation; (3) minimal susceptibility to ion suppression; (4) minimal ionization of common matrixes, such as air and most solvents.

These properties enable for many applications the analysis of mixtures without the need for chromatographic separation. The most widely used ionizers on today's MS systems are not suitable for analyzing mixtures, which largely explains the use of on-line chromatographic separation of samples before entering the ionizer and MS. These ionizers include electron ionization (EI), electrospray ionization (ESI), and chemical ionization (CI) including atmospheric pressure CI (APCI). EI and CI are low-pressure methods used primarily with GC/MS. ESI and APCI are atmospheric-pressure methods used primarily with LC/MS. The reason these ionizers are not suitable for direct analysis of mixtures has to do with their susceptibility to either extensive ion fragmentation or ion suppression. PI, on the other hand, greatly minimizes these deficiencies, yet ionizes a broad range of compounds including nearly all major CW compounds and other hazardous threats.[12]

The LPPI source is coupled to a quadrupole ion trap, time-of-flight (QitTof) MS analyzer, which provides (i) complete ion mass acquisitions, (ii) high repetition rates, and (iii) MS/MS confirmatory analysis. The LPPI source contains a heated injector that can accommodate syringe injections and capillary infusion sample introduction. An air sampling inlet may also be routinely adapted to the injector. The instrument has an integrated autosampler for injecting liquid samples on a 45−50-s 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 due to minimal consumables, and ease of operation. This makes the CW analyzer well suited to the requirements of an EWS and for high-throughput screening.

In the following, we present PI mass spectra of CW standards, report on the method detection limits (MDL), and present detectability in dirty samples such as soil extracts. We then report on a statistically comprehensive set of measurements of CW surrogate compounds in order to provide detailed data on the instruments MDL, linearity, dynamic range, and reproducibility. For a screening instrument, the sensitivity and specificity are important properties as they determine the probability of detection P_D and the probability of false positives P_{FP} rates for relevant CW concentrations. We present these data in the form of receiver operator characteristic (ROC) curves of the form P_D versus P_{FP}.

EXPERIMENTAL SECTION

Apparatus. The experimental results were recorded on a Syagen Radiance Pro LPPI, QitTof MS system. Details of this instrument have been presented before.[12,23] Here we give a brief description of the general operation before focusing on the sampling methods that are unique to this work.

Ionization in the LPPI source takes place at about 1−4 Torr. The ions are focused into the ion trap using einsel lenses. The milliTorr buffer gas in the ion trap is provided by the sample and is air for headspace sampling and vaporized solvent for liquid sampling. The trapped ions are then injected into a reflectron TOFMS at a rate of 60 Hz. The reflectron TOFMS has a total drift length of ~1.2 m and operated in this work with a resolution of ~1500 ($m/\Delta m$ fwhm).

Sample Injection. Sample introduction is done by syringe injection using an autosampler. Generally samples are collected in 2- or 4-mL vials and loaded into a 54-vial tray. The autosampler as presently configured holds 4 trays enabling 216 samples to be analyzed at a time. Other sample formats include 96- and 384-well microtiter plates permitting up to 1536 samples to be analyzed at a time. Two methods have been developed for injecting sample into the analyzer. The conventional method involves injecting sample by syringe directly into the low-pressure PI source as shown in Figure 1A. The syringe pierces a septum that is the interface between atmosphere and the low-pressure region. In a more recent configuration currently under testing, the sample is injected onto a capillary line (31-cm-long, 75-μm-i.d., deactivated silica) that flows directly into the LPPI source as shown in Figure 1B. The capillary is interfaced to the LPPI source through a metal tube that is inserted through the septum. The metal sheath and capillary position is adjusted to optimize performance with regard to signal level and reduction of background signal. For both sample injection methods, 1 μL of sample is injected. The total injection cycle time by either method is ~50 s. The syringe loading conditions for each method are as follows:

(1) Syringe Injection. The autosampler is programmed to draw ~1 μL of methanol wash (in addition to the ~1 μL of methanol that resides in the dead volume of the syringe needle), followed by 1 μL of sample, and then 6 μL of air. The injection into the LPPI injector reverses this order. The air and sample mixture assists the volatilization process after exiting the syringe into the hot source. The final methanol slug also mixes with this volume, but tends to provide a final rinse of the syringe to improve the injection efficiency of the sample.

(2) Capillary Injection. The syringe is loaded with 8 μL of methanol, followed by 1 μL of sample and then 1 μL of methanol. Injection onto the capillary reverses this order. The final 8-μL

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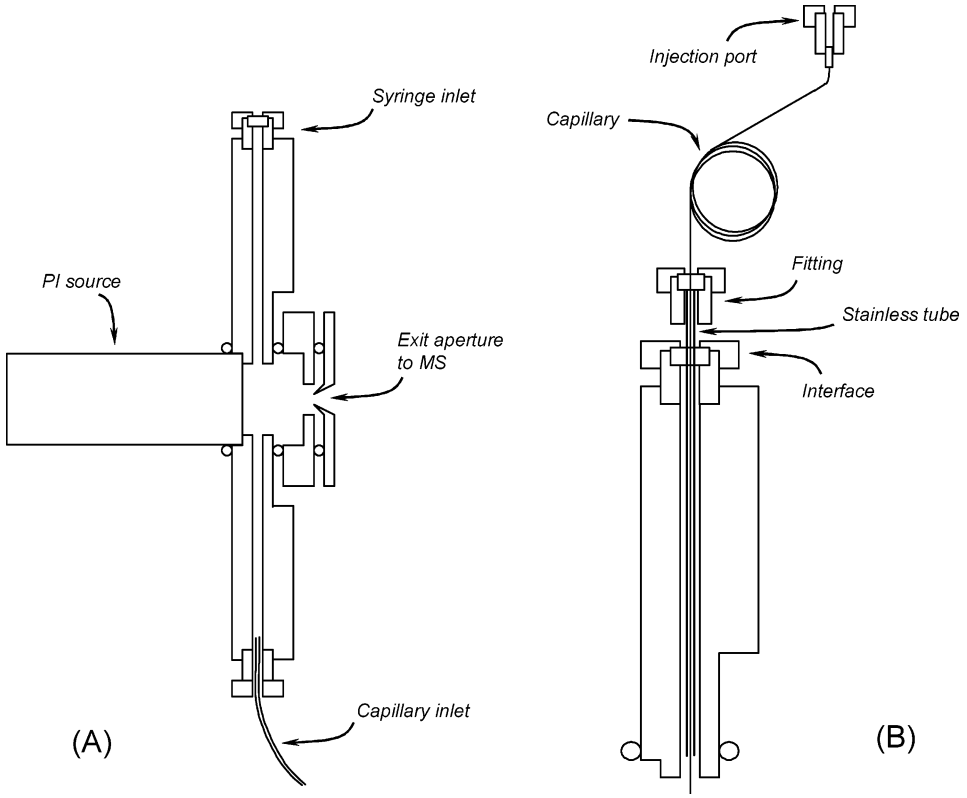

Figure 1. Schematic drawings of the LPPI source showing configuration for (A) direct syringe injection and (B) capillary injection. The latter method uses the injection port of a six-way valve for convenience. The valve is not actually switched.

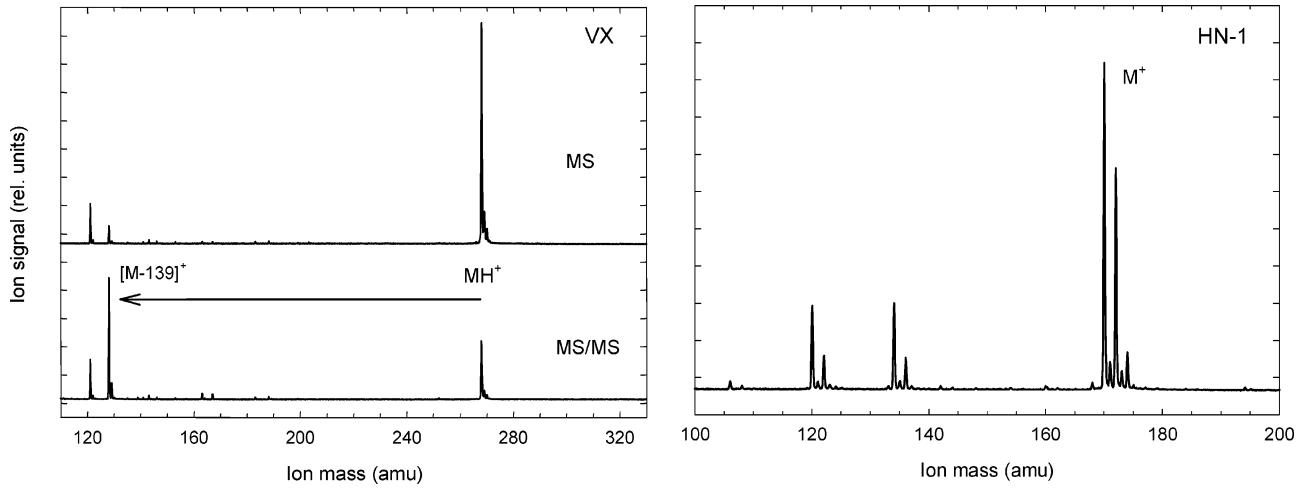

Figure 2. PI MS signatures for VX (left) and HN1 (right). The VX spectrum also shows selective ion fragmentation (MS/MS) to give definitive fragment signature peaks. (The MH^+ ion signal arises by formation of M^+ followed by hydrogen abstraction from the i-PrOH solvent used to introduce the sample.) The HN1 spectrum shows the isotope distribution for two chlorines.

methanol injection effectively elutes all sample compounds through the capillary.

Sample Preparation. All samples were made with HPLC-grade water; however, essentially identical results were obtained when using tap or purified drinking water. In actual practice, water samples can be collected and analyzed without any sample preparation. Also there are no carrier gases or special reagents required. The only consumable is the solvent in the wash stations. After each sample injection, the syringe is washed 3−5 times with 10 μL of methanol, so total consumption equates to less than 50 mL per 1000 sample analyses.

RESULTS AND DISCUSSION

The basic mechanism of photoionization is

$$M + h\nu \rightarrow M^+ + e^- \quad (1)$$

However, in protic solvents, the predominant ion observed by APPI is typically $[M + H]^+$ (henceforth MH^+) due to a hydrogen abstraction reaction with solvent S according to the reaction[23]

$$M^+ + S \rightarrow MH^+ + S(-H) \quad (2)$$

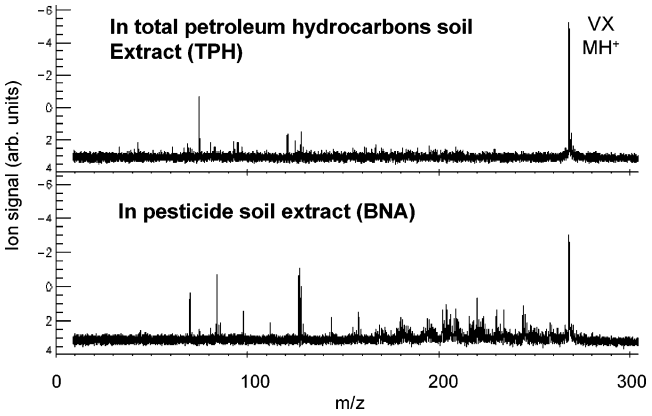

Figure 3. Direct sampling of soil extract contaminated with high levels of TPH and BNA and low levels of VX.

CW Agent Tests. Chemical agent measurements were conducted at the Edgewood Chemical and Biological Center (ECBC) in Aberdeen, MD. On these occasions, MS and MS/MS spectral libraries were developed and MDLs determined for the nerve agents VX, GA, GB, GD, and GF, blister agents HD, HN1, HN3, riot agents CR and CS, and the hallucinogen BZ. The PI mass spectra gave predominately parent ion signal with minimal fragmentation. Figure 2 shows representative spectra for VX and HN3. The predominant ion is either M^+ or MH^+ depending on the thermochemistry for the hydrogen abstraction reaction.[23] The spectra for the mustards (HD, HN1, HN3), which contain two chlorine atoms, show the characteristic 9:6:1 isotope distribution (Figure 2).

The MDLs are based on the EPA method and are expressed as the concentration for which the signal level is 3σ above the background distribution. Measurements were made for all the CW agents listed above. Standard samples were diluted in HPLC water. Though the MDLs for the individual agents are not cleared for public disclosure, it can be stated that the MDL values are in the 0.07−0.7 mg/L range, which meets the short-term acute concentration levels determined elsewhere.[11,12]

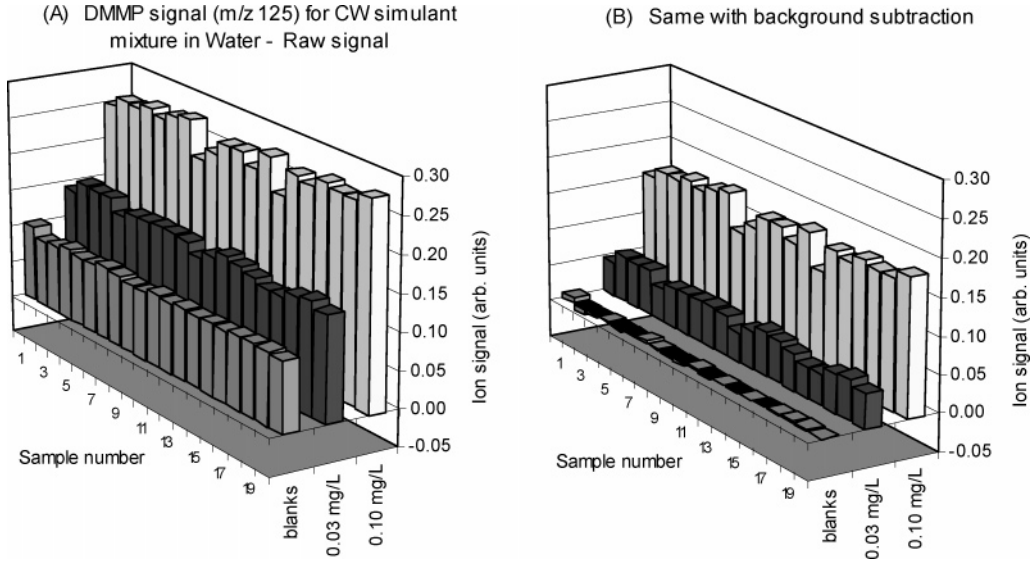

Figure 4. DMMP results for 20 analyses at concentrations 0, 0.03, and 0.10 mg/L of a CW stimulant mixture containing DMMP, DEMP, DEEP, and DIMP in water (for the 1-μL injections, corresponding to 0-, 30-, and 100-pg injections). (A) Raw signal levels, showing evidence of background intensity at *m*/*z* 125. (B) Signal levels after subtracting the mean background signal at *m*/*z* 125. Results obtained by syringe injection.

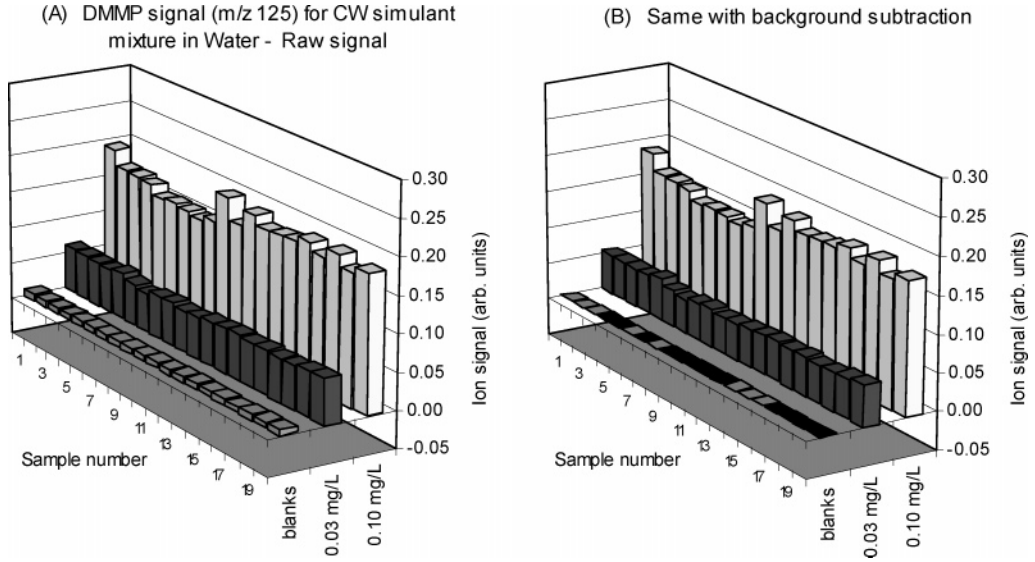

Figure 5. Same as Figure 4 except results obtained by capillary injection.

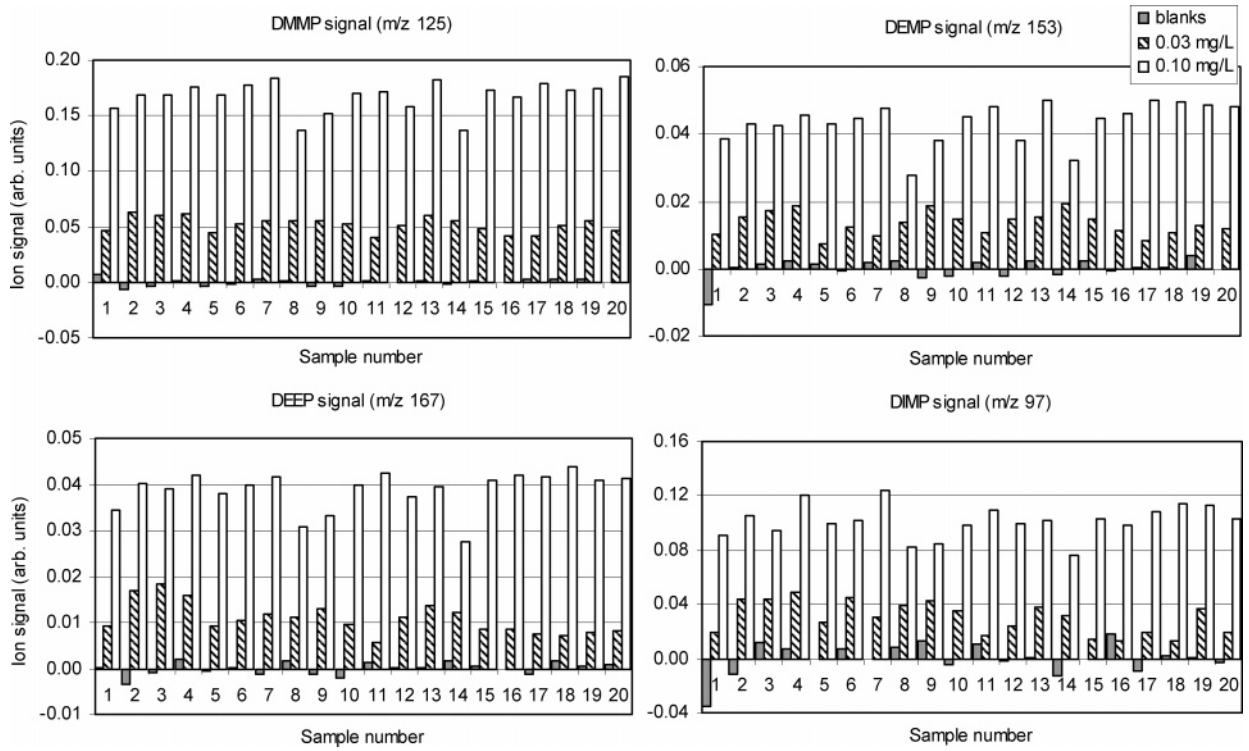

Figure 6. Syringe injection results. Measurements for 20 analyses each for concentrations 0, 0.03, and 0.10 mg/L of a CW stimulant mixture containing DMMP, DEMP, DEEP, and DIMP in water (for the 1-μL injections, these correspond to 0-, 30-, and 100-pg injections). Signal levels are after subtracting the mean background signal at each of the signature ion masses.

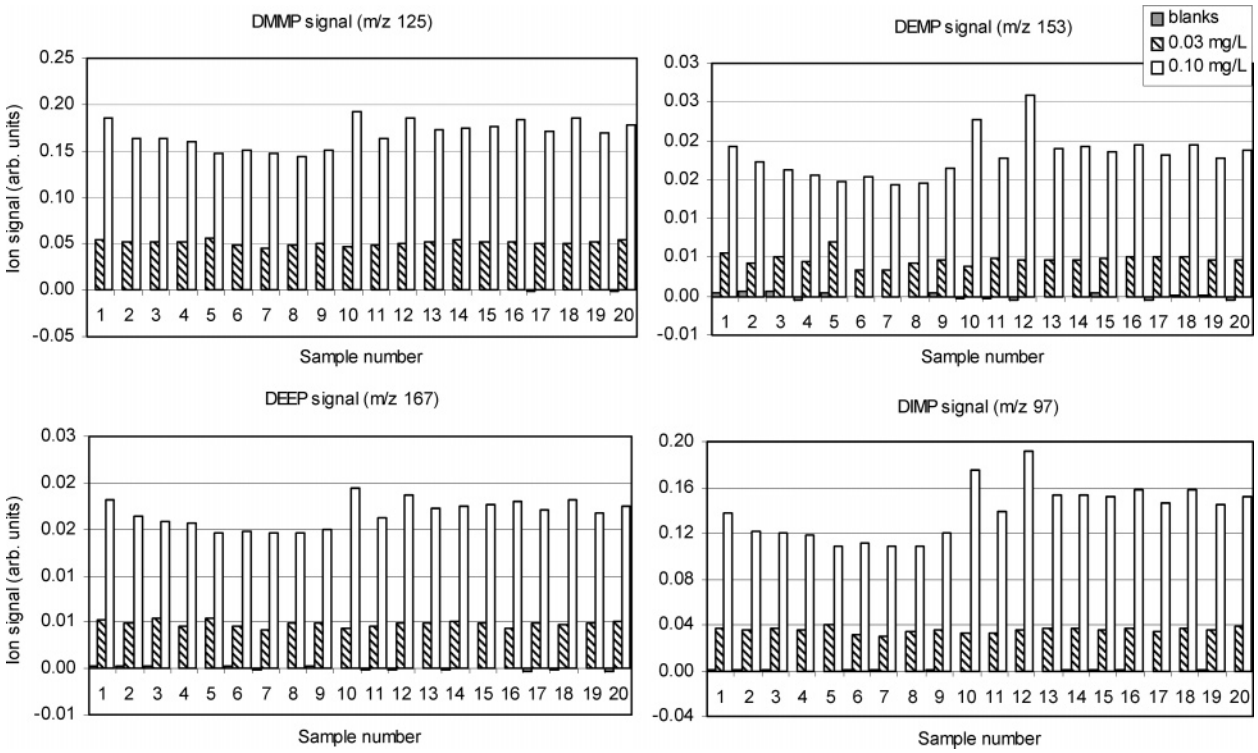

Figure 7. Capillary injection. Measurements for 20 analyses each for concentrations 0, 0.03, and 0.10 mg/L of a CW stimulant mixture containing DMMP, DEMP, DEEP, and DIMP in water (for the 1-μL injections, these correspond to 0-, 30-, and 100-pg injections). Signal levels are after subtracting the mean background signal at each of the signature ion masses.

The detectability of chemical agents, other agents, and decomposition products in dirty samples was also conducted in order to assess the adequacy of direct PI MS screening for detecting evidence of CW agents in complex matrixes. A particularly challenging application is the detection of low levels of CW in extracted samples, such as soil. In this test, dilute samples of CW agents were mixed with extracts of soil heavily contaminated with total petroleum hydrocarbon (TPH) or pesticide base neutral

Table 1. Intensities, RSDs, and MDLs

conc (mg/L)	m/z	DIMP 97	DMMP 125	DEMP 153	DEEP 167
	(A) Syringe Injection				
0	stdevp	0.0112	0.0032	0.0030	0.0014
0.03	average	0.0301	0.0519	0.0134	0.0108
	RSD (%)	39	13	26	30
0.1	average	0.1015	0.1677	0.0436	0.0388
	RSD (%)	12	8	13	11
3σ MDL (mg/L)		0.033	0.006	0.021	0.011
	(B) Capillary Injection				
0	stdevp	0.0008	0.0005	0.0004	0.0002
0.03	average	0.0354	0.0514	0.0047	0.0048
	RSD (%)	7	5	16	7
0.1	average	0.1388	0.1684	0.0180	0.0167
	RSD (%)	17	8	15	9
3σ MDL (mg/L)		0.002	0.001	0.006	0.003

Table 2. P_D and P_{FP} Values for Various Threshold Levels and Concentrations for the CW Stimulant Mixture in Water

		P_D							
		DIMP		DMMP		DEMP		DEEP	
threshold (mg/L)	conc (mg/L)	0.03	0.10	0.03	0.10	0.03	0.10	0.03	0.10
		(A) Syringe Injection							
	P_{FP}								
0	0.5	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
3σ	0	0.45	1.00	1.00	1.00	0.90	1.00	1.00	1.00
0.03	0	0.55	1.00	0.55	1.00	0.50	1.00	0.45	1.00
0.1	0	0.00	0.55	0.00	0.70	0.00	0.60	0.00	0.70
		(B) Capillary Injection							
0	0.5	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
3σ	0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.03	0	0.65	1.00	0.60	1.00	0.50	1.00	0.55	1.00
0.1	0	0.00	0.55	0.00	0.55	0.00	0.50	0.00	0.55

acid (BNA) mixture (provided to us by ECBC). The compounds VX, GA, HN1, HN3, CR, EMPTA, and VX-disulfide were diluted in the extracts to final concentrations ranging from 0.8 to 26 ppm (molar ratio). The total TPH and pesticide BNA concentrations were estimated to be ~1000 ppm. The results for VX are shown in Figure 3. In all cases, the parent ion signal was clearly distinguishable from the background matrix material. The MDLs, though not measured, would probably have a limit of ~100 ppb (molar ratio).

Accuracy Tests. We analyzed a mixture of four CW surrogates [dimethyl methylphosphonate (DMMP); diethyl methylphosphonate (DEMP); diethyl ethylphosphonate (DEEP); diisopropyl methyl phosphonate (DIMP); ethylmethyl phosphothionate (EMPTA)] in concentrations of 0, 0.03, and 0.10 mg/L in water. For the 1-μL injections used in this work, these correspond to injected masses of 0, 30, and 100 pg of each compound, respectively. These sample concentrations were analyzed 20 times each on a 50 s/sample cycle time. These tests were run by both direct syringe injection and by injection onto a capillary. The results by these two sample introduction methods are given in Figures 4 and 5, respectively, for the compound DMMP detected at its parent ion mass of m/z 125 (MH^+ ion). In each figure, the data are plotted as raw values and with background subtraction by the average of the blank sample intensities. Two observations are worth noting: (i) the intensities for concentrations 0.03 and 0.10 mg/L are distinctly detectable from the blank (0 mg/L) samples, and (ii) much lower background levels were observed by the capillary injection method than by the syringe injection method.

Figures 6 and 7 show results for all the CW surrogate compounds for the syringe injection and the capillary injection method, respectively. These plots include the background subtraction at each of the compound signature ion masses. Again, it is evident that the capillary injection method gives more uniform results than the syringe injection method.

Table 1 tabulates the mean intensities, the reproducibility of the measurements as denoted by the relative standard deviation (RSD) and the MDL by the two sample introduction methods. The capillary injection method produces lower MDL levels compared to syringe injection due to the greatly reduced background signal (as seen in Figures 4 and 6 vs 5 and 7, respectively). Still, each method of sample injection gives MDL levels that are significantly below the acute concentrations for actual CW agents

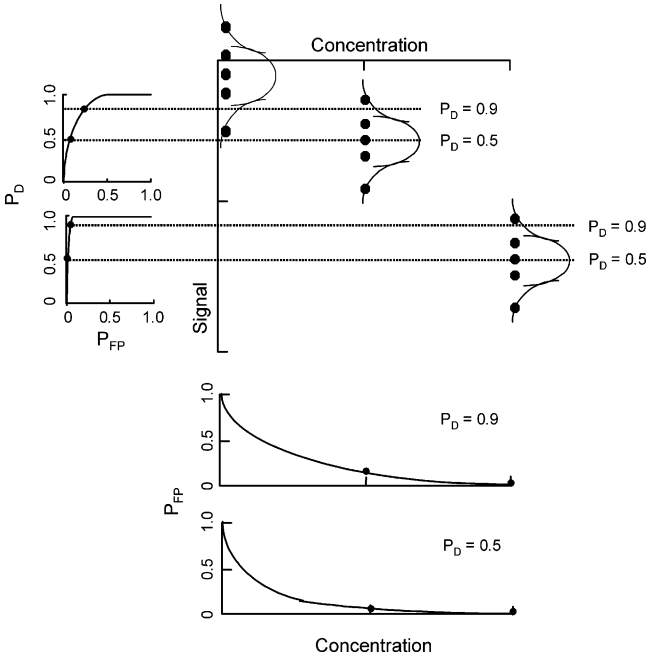

Figure 8. Relationship between ROC curves and linearity plots.

determined elsewhere (e.g., 500 ng/mL for VX for 5-L water consumption).[12] For the capillary injection method, each of the compounds had detection limits less than 10 pg (i.e., 10 ng/mL) with DMMP being at 1 pg.

The RSD values are also much better by the capillary injection method than by the syringe injection method. The measured values in Table 1 do not benefit from normalization to an internal calibrant. As is evident in Figures 6 and 7, the signal variation is due to absolute intensity variations of the total ion signal. In fact, the relative intensities of the four CW surrogate compounds from sample to sample vary by a much smaller factor. This indicates that the use of a calibrant signal to normalize the target signal intensities would lead to significantly improved RSD values. Still the unnormalized RSD values are quite adequate for screening at these low concentrations.

Table 2 summarizes the probability of detection P_D and the probability of a false positive P_{FP} as a function of the threshold setting for CW surrogate concentrations of 0.03 and 0.10 mg/L in water. The P_D and P_{FP} results show the expected trends. For

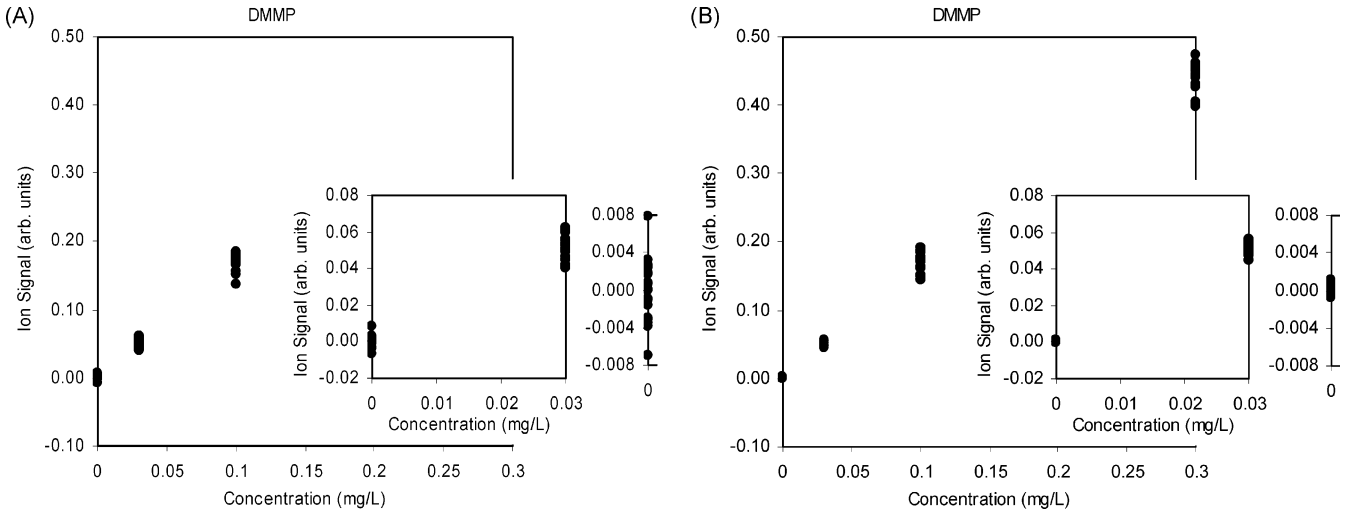

Figure 9. Linearity curves for DMMP in the CW surrogate mixture. The 20 measurements were made for each concentration. (A) Syringe injection (measurements were not made at 0.3 mg/L) and (B) capillary injection.

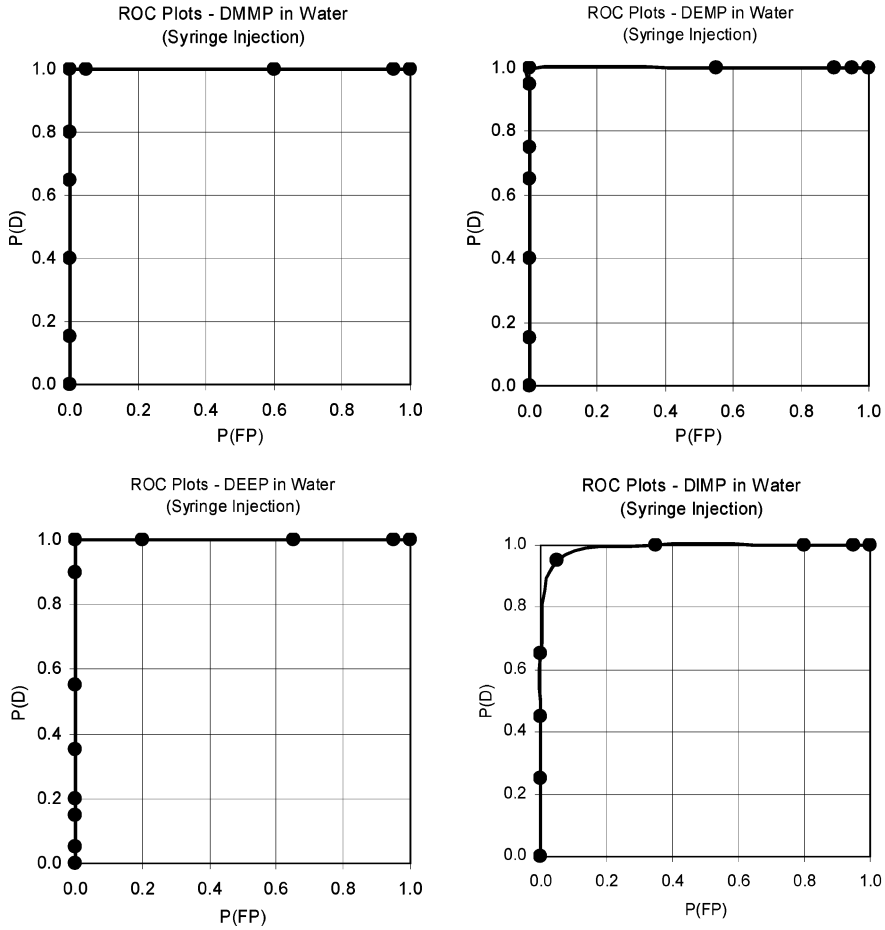

Figure 10. ROC curves plotted as a function of P_D vs P_{FP} for concentrations of CW surrogates of 0.03 mg/L in water. Results are for syringe injection.

all alarm thresholds chosen (i.e., 3σ, 0.03 mg/L, and 0.10 mg/L), the P_{FP} was 0%. The P_D rate depends on the threshold and concentration. Clearly, if the alarm threshold is set above the compound concentration, a low P_D will occur. For thresholds set equal to the compound concentration, then P_D will be ~50% (Table 2). For 3σ thresholds, the P_D was 100% for all CW surrogate compounds at 0.10 mg/L concentration. This concentration is below the acute concentrations for CW agents cited above and reported elsewhere.[12] If the CW surrogate results are representative of actual agents, which has been our experience thus far in real CW agent testing, then the PI MS analyzer meets the high P_D and low P_{FP} requirements for an effective screening technology for CWs in water. In operation at various localities, the PI MS instrument exhibits a very low false positive rate, and when positives do occur, they are easily resolved by repeating the measurements or by inspecting the mass spectra.[11,12]

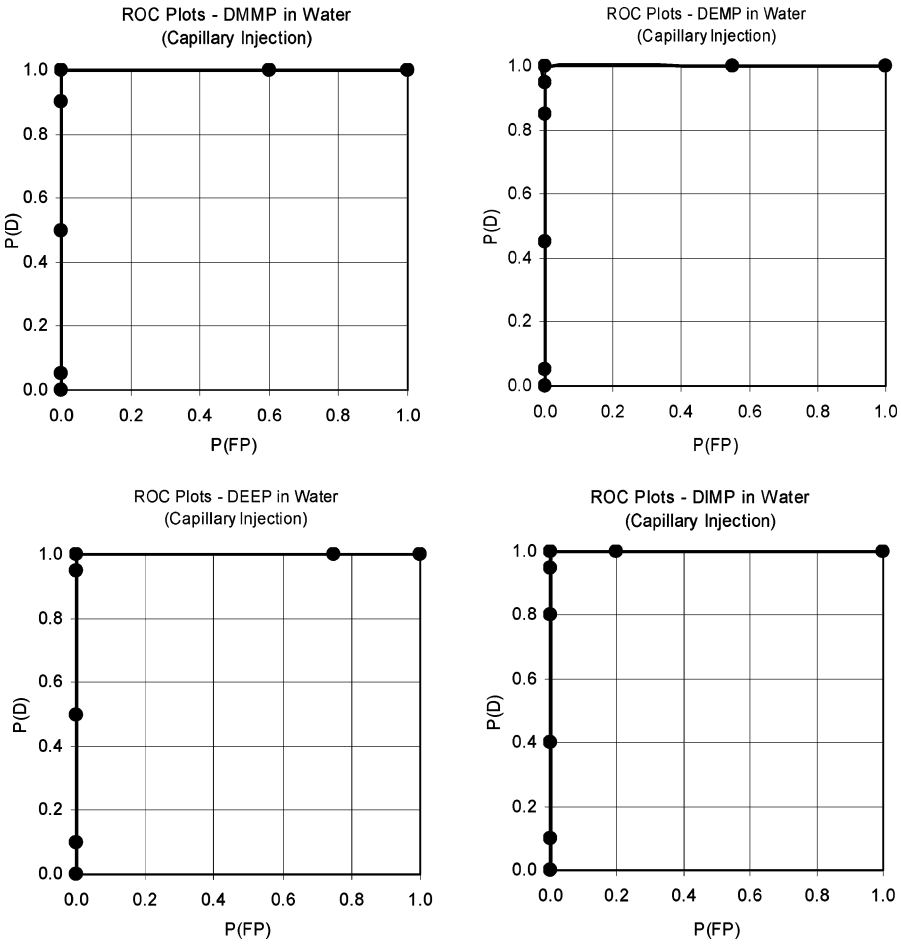

Figure 11. Same as Figure 10 except results are for capillary injection.

ROC Curves. Sensitivity and specificity are the features of merit for screening devices. Sensitivity is related to the limit of detection and the probability of detection for a required concentration. Specificity is related to how immune the measurement is to other factors that can give a false positive signal. The sensitivity and specificity of a detector may be expressed many different ways, but a particularly convenient way is by plotting the probability of detection P_D versus the probability of false positive P_{FP} for some required detection concentration. This type of signal detection analysis was advanced during World War II for the analysis of radar images where it was necessary for radar receiver operators to make judgments on whether a blip was due to enemy or friendly objects, or just noise. Consequently the analysis is known as "receiver operator characteristics" or ROC.

Figure 8 illustrates the relationship between linearity plots (multiple measurements at a series of concentrations) and generation of ROC curves from these data. Two methods that we employ for determining ROC curves are the following: (1) Fit Gaussian functions to the data for each concentration and then integrate P_D and P_{FP} for a variable threshold value for each relevant concentration. (2) If the data set is large enough, one can determine the actual P_D and P_{FP} values for an incrementally changing threshold value.

In this work, we employed the latter method. We accomplished this by listing all the intensities for a given data set comprising standard sample at some concentration and blanks in a spreadsheet. A logic (if, then) statement then compared a given threshold to the intensity array and assigned a 0 for less than and a 1 for greater than. Depending on whether the sample was a standard or a blank dictates whether there was a true positive or negative or a false positive or negative. The threshold value was incremented from zero to greater than the highest value to get a mapping of P_d versus P_{FP} for the ROC curves.

The linearity plots for DMMP in water are given in Figure 9 for the syringe injection and capillary injection methods of sampling. The insets to the plots are blowups of the lower concentration data including the distribution of intensities for the blank samples. As noted above, the background signal variation is much less for the capillary injection method than for the syringe injection method, and this trend is clearly seen in Figure 9. As we show, this leads to improved ROC curves for the capillary injection method.

ROC curves in the form of P_D versus P_{FP} are plotted in Figures 10−12 for DMMP, DEMP, DEEP, and DIMP in water. The detected ions in all cases were the parent MH^+ ion, except for DIMP, for which the parent ion undergoes a well-known rearrangement. Consequently, we used the prominent m/z 97 fragment ion as the signature ion. The ROC curves for the four CW surrogate compounds for a concentration of 0.03 mg/L are compared for syringe injection versus capillary injection in Figures 10 and 11. Ideal ROC curves are obtained for capillary injection for all four compounds (Figure 11). For syringe injection only, the DIMP curve is nonideal, but nonetheless excellent (Figure 10). At higher concentration (0.10 mg/L), ideal ROC curves were

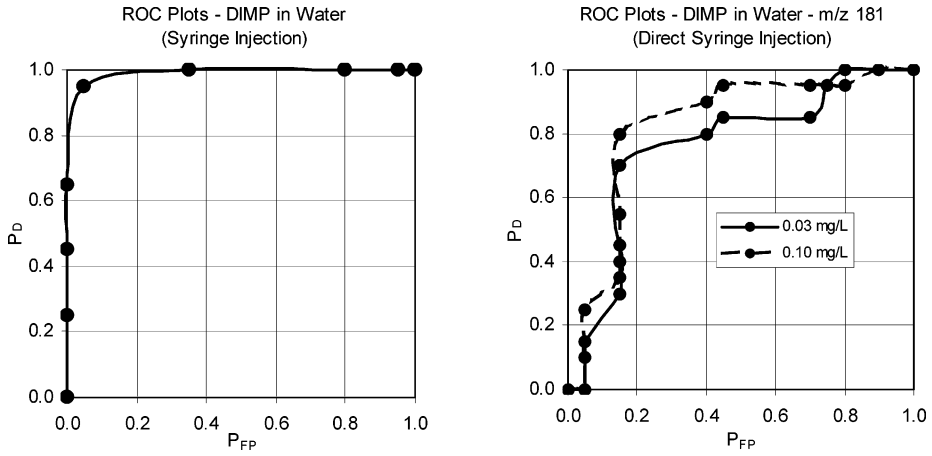

Figure 12. ROC curves for DIMP in water for detection of signal at *m*/*z* 97 (left plot) and at *m*/*z* 181 (right plot). Results are for direct syringe injection.

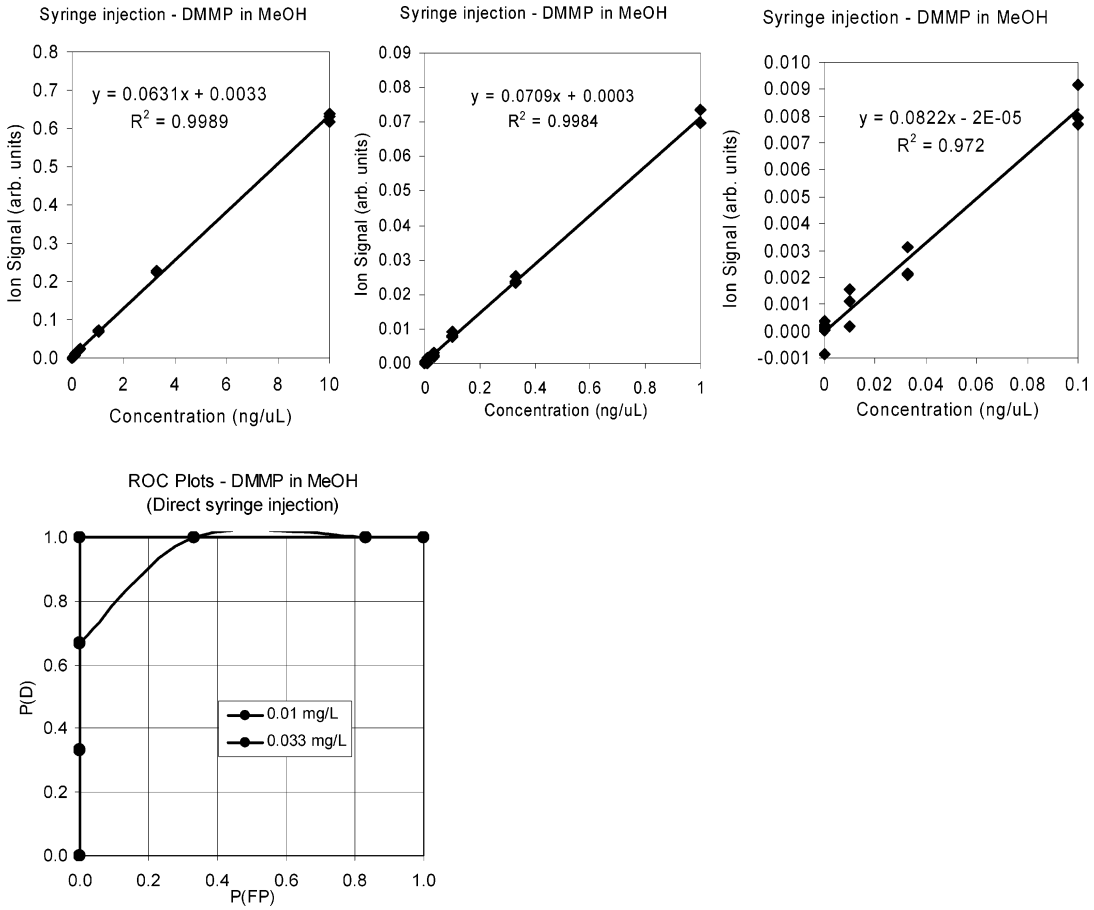

Figure 13. Linearity plots and ROC curves for DMMP in methanol and detecting signal at *m*/*z* 125.

obtained for all compounds by both sampling methods. The excellent ROCs at concentrations well below the short-term acute concentrations for CW contamination in water attest to the effectiveness of the reported PI MS instrument for high-speed, high-throughput screening.

As noted above, DIMP gave the poorest results. This compound does not yield a significant parent ion MH^+ at m/z 181, and the detected ion at m/z 97, though strong, is compromised by significant chemical background. The m/z 181 signal, however, is perceptible and we generated ROC curves for 0.03 and 0.10 mg/L concentrations, which are shown in Figure 12. These measurements were done by syringe injection. The result for m/z 97 is also shown for comparison. For screening purposes, the m/z 97 ion signal gives much more reliable results.

Finally, we show the linearity plots and ROC curves for DMMP in methanol at concentrations of 0.01 and 0.033 mg/L. Only six measurements were made for the blank samples and three measurements each for the 0.01 and 0.033 mg/L. This number is sufficient to obtain qualitative ROC curves as shown in in Figure 13. Ideal behavior is observed at 0.033 mg/L and less than ideal at 0.01 mg/L. It should be noted that these analyses correspond to injected masses of 33 pg and 10 pg.

We now discuss some other attributes of ROC curves. Each point on a ROC curve corresponds to a different threshold level for triggering a positive event. The ideal operating point on the ROC curve is the top left corner corresponding to a $P_D = 1$ and $P_{FP} = 0$. Achieving the optimum set of conditions requires properly setting the threshold level. The procedure used here is to first calibrate the instrument with a standard, uncontaminated water sample to measure the natural levels. Generally, 20 measurements are made (~15 min). From these measurements, threshold levels for all target ion signals are determined. The user has a choice of threshold levels, but the recommended setting is at 3σ of the background variation corresponding to a P_{FP} rate of 0.15%. [By definition the 3σ threshold level would correspond to a false positive probability of 0.15% (the fractional area of a Gaussian distribution 3σ removed from the mean).]

SUMMARY AND CONCLUSIONS

The increased threats to the public, whether real or perceived, due to lethal materials require prompt and automated means to detect to warn. In this paper, we described a method based on photoionization mass spectrometry to rapidly screen water samples for the presence of chemical weapons. This instrumentation can be expanded to other threat compounds. Furthermore the instrumentation can be adopted for air monitoring as well. As opposed to APPI, the LPPI method used here minimizes the ion competition that can occur at high pressures due to ion−molecule reactions. Consequently, no chromatographic sample separation or even sample preparation is required, which greatly simplifies the screening of water, making it a truly routine analysis.

This work has established detection limits for CW and CW surrogates that are substantially below the short-term acute levels in water, making it an effective early warning system for public water utilities as well as government facilities, such as those of the DOD. Sample introduction is by syringe injection making it easy to collect and analyze samples. This technology can also be routinely adapted for on-line monitoring using a continuous sampling line.

The PI MS instrumentation for CW analysis, while not inexpensive, has a low operating cost for the following reasons: (i) it requires a relatively nontechnical person, (ii) sample preparation is minimal, (iii) the analysis times are short, reducing the manpower burden on a per sample basis, and (iv) there are minimal consumables (no gases or solvent flows) that would add recurring costs. The cost per sample in consumables is a few cents.

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