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Field-portable gas chromatography with transmission quadrupole and cylindrical ion trap mass spectrometric detection: Chromatographic retention index data and ion/molecule interactions for chemical warfare agent identification

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ABSTRACT

Field-portable gas chromatography–mass spectrometry (GC–MS) is well-suited for the reliable identification of dangerous chemicals. The chemical warfare agent (CWA) *O*-ethyl-*S*-2-diisopropylaminoethyl methylphosphonothiolate (VX) and many VX degradation products are challenging GC–MS analytes for a transmission quadrupole detector, as resulting 70 eV electron ionization mass spectra contain little high mass information. Approaches were explored to detect these analytes using two field-portable GC–MS systems having either a transmission quadrupole or a cylindrical ion trap (CIT) detector. Spectral matching alone for the transmission instrument did not unambiguously identify VX and several related analytes, while use of mass spectra and retention index information resulted in accurate identification. Ion/neutral interactions in the CIT produced pseudomolecular ions ($[M+H]^+$) for VX-related compounds and also for other CWA nerve agent compounds. In addition to $[M+H]^+$, protonated dimers ($[2M+H]^+$) were produced in the CIT for phosphonofluoridate compounds such as sarin. The CIT ion/molecule reactions were concentration-dependent, and mass assignment shifts were not unusual with increasing analyte concentrations. For these reasons the CIT detector is potentially problematic for reliable chemical identification by technician-level users under non-laboratory conditions.

1. Introduction

Accurate detection and identification of dangerous chemicals, including chemical warfare agent (CWA) analytes is important to protect military forces and for public safety, and gas chromatography–mass spectrometry (GC–MS) has been used in this role. Following September 11, 2001 expanded market demand for small, rapid GC–MS systems have continued to drive development of innovative GC column heating technologies, and several research and commercial groups have also worked to develop small mass spectrometric detectors [1,2]. Resistive heating of a low thermal mass (LTM) GC column assembly described by Sloan et al. [3] has been the basis for several commercially available GC–MS systems designed for field use [2,4]. This LTM GC assembly is compact, consumes relatively little power, and is capable of high chromatographic performance.

Transmission quadrupole mass spectrometers are commonly used for fieldable GC–MS systems, and are known to provide consistent 70 eV electron ionization (EI) mass spectra for CWA analytes. However the neurotoxic CWA *O*-ethyl-*S*-2-diisopropylaminoethyl methylphosphonothiolate (VX) and a number of VX degradation products yield similar EI fragmentation patterns with this type of detector, with little or no diagnostic high mass information [5–7]. One GC–MS approach that can compensate for this involves the use of GC retention data combined with mass spectral information. The methods of Van den Dool and Kratz [8] allow comparison of linear temperature program GC retention information using a series of reference standards (commonly *n*-alkanes) analyzed with a chosen stationary phase material. The retention characteristics for unknown chemicals analyzed with the same conditions and stationary phase are then related to those of the reference compounds.

Another approach to clearly identify VX and VX-related analytes would be through the use of GC–MS analyses with chemical ionization (CI). As typically carried out, CI is not well-suited for

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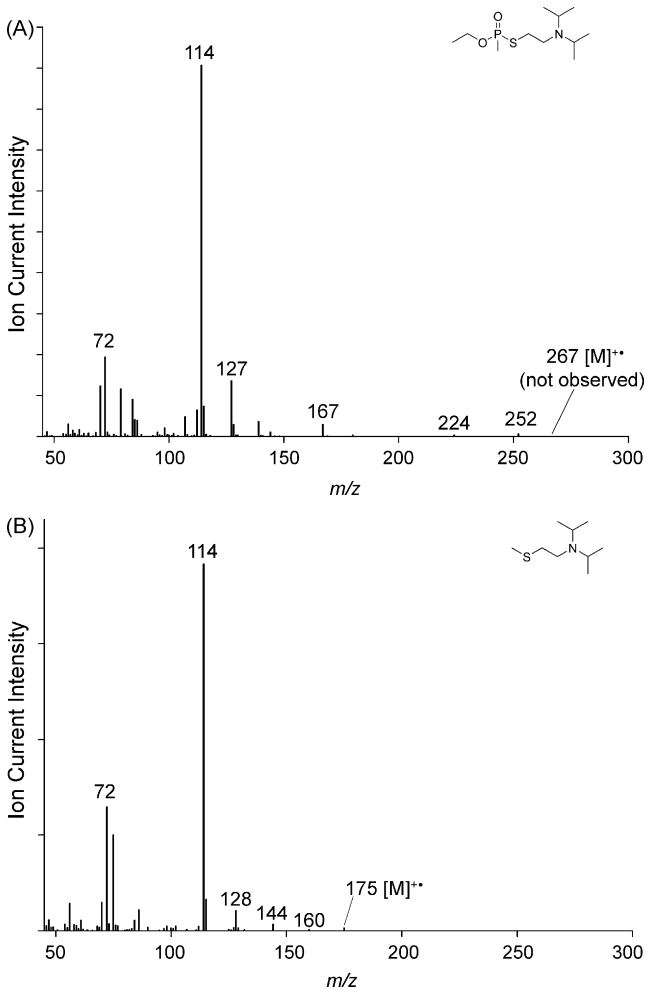

Fig. 1. Transmission quadrupole mass spectra for (A) VX, and for (B) the VX degradation product 2-(diisopropylaminoethyl)methyl sulfide.

a field-portable instrument that must be used to identify a wide range of unknown analytes, as the specific reagent used will limit the applicability of the method. Also, for many unknown analytes CI mass spectra are often not amenable to interpretation by technician-level analysts.

One benefit of using a mass spectrometric detector that relies upon ion storage is that ion/molecule interactions resulting in self-chemical ionization (self-CI) are possible [9–11]. Given time to interact, molecules within an ion trap that escape the EI process uncharged may react with trapped ionic species to create pseudomolecular ions. A pure CI reagent gas is not needed, but the resulting pseudomolecular ions are dependent on the specific chemistry between an analyte and the trapped ions derived from it, and their relative concentrations. Also, space charge effects become a factor in an ion storage mass spectrometer if ion density is not adequately controlled, potentially impacting mass resolution and mass assignment [10].

In this work, three possible strategies were explored for the detection of VX-related analytes and other CWA nerve agent compounds in the field during defensive military training exercises using two types of GC–MS systems with either a transmission quadrupole or a cylindrical ion trap (CIT) [1] detector. Spectral matching alone, and spectral matching in combination with retention index information were used with the transmission quadrupole, while the third approach used the CIT to produce pseudomolecular ions through self-CI to attempt nerve agent identification.

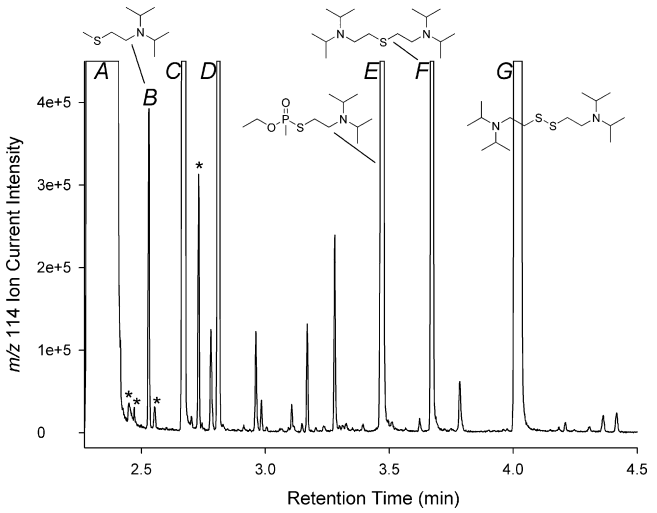

Fig. 2. Extracted ion chromatogram for *m*/*z* 114, degraded VX sampled by SPME and analyzed using van-mounted GC–MS system with transmission quadrupole mass spectrometric detection. A base peak of *m*/*z* 114 was observed in mass spectra of all GC peaks in this chromatogram, except for the four marked with a single asterisk. Around 20 analytes with *m*/*z* 114 as the most intense mass spectral peak are represented in the chromatogram, and for each of these the relative ion current intensity for mass spectral peaks greater than *m*/*z* 127 was <10%. Identities of labeled peaks: (A) 2-diisopropylaminoethanethiol; (B) 2-(diisopropylaminoethyl)methyl sulfide; (C) 2-(diisopropylaminoethyl)ethyl sulfide; (D) 2-(diisopropylaminoethyl)isopropyl sulfide; (E) VX; ***F***, bis(diisopropylaminoethyl)sulfide; (G) bis(diisopropylaminoethyl)disulfide.

2. Experimental

A field-portable GC–MS system with a miniature CIT mass spectrometric detector (model 450, ICX-Griffin, West Lafayette, IN) was used with ultra high purity He carrier gas to obtain mass spectra from liquid injections with varied concentrations of CWA analytes dissolved in solvent. Retention index comparisons to identify VX and VX-related degradation products were obtained from a van-mounted Agilent Technologies (Wilmington, DE) 5975 transmission quadrupole mass spectrometer combined with a 6890 GC system using high purity H_2 carrier gas generated electrolytically on-site.

Both GC–MS systems used LTM GC column heating for fast analysis, with identically manufactured open tubular columns (Agilent Technologies) having DB-5 stationary phase with 25 μm film thickness, 30 m length, and 0.25 mm I.D. For both instruments the initial column temperature was held at 40 °C for 0.5 min. Following the initial temperature hold time the built-in LTM GC system of the Griffin instrument raised the column temperature 40 °C min^{-1} to 300 °C, with no hold time at the terminal temperature. The retrofit LTM GC module of the Agilent instrument heated at 75 °C min^{-1} to 300 °C, with 2 min terminal temperature hold time. The injector temperature was 250 °C for each instrument and both were operated in splitless injection mode, with 22.5% split flow applied to the Griffin instrument at 0.5 min, and 50 ml min^{-1} purge flow at 0.75 min for the Agilent instrument. The GC transfer lines for the Griffin system were maintained at 200 °C while the corresponding temperature was 250 °C for the Agilent system.

The ion source and quadrupole assembly of the Agilent system were maintained at 230 and 150 °C respectively, and this instrument relied on standard 70 eV electron ionization (EI). The temperature of the CIT was held at 150 °C during analyses, and the voltage bias between the EI filament and the trap entrance was 13.8 eV. In this instrument the RF trapping field imparts additional energy to the electrons produced at the filament, providing ionization with molecular energy deposition similar to

Table 1
Comparison of observed retention index (RI) values for VX and VX-related degradation products observed in Fig. 2 and the corresponding literature values (where available). In Fig. 2 GC peak labels identify the respective analytes.

Analyte		Observed RI[a]	Reference RI
A	2-(Diisopropylamino)ethanethiol	1151.7	1113.5 ± 0.4[b]
B	2-(Diisopropylaminoethyl)methyl sulfide	1233.9	1205.1 ± 0.6[c]
C	2-(Diisopropylaminoethyl)ethyl sulfide	1298.6	1277.6 ± 0.4[b]
D	2-(Diisopropylaminoethyl)isopropyl sulfide	1366.0	Not available
E	*O*-Ethyl-*S*-2-diisopropylaminoethyl methylphosphonothiolate (VX)	1730.7	1705.0 ± 1.0[b]
F	Bis(diisopropylaminoethyl)sulfide	1861.4	1836.1 ± 0.5[b]
G	Bis(diisopropylaminoethyl)disulfide	2107.1	2057.9 ± 0.5[b]

[a] Using LTM GC module and column temperature programming at 75 °C min^{-1}.
[b] Ref. [4], DB-5 type stationary phase, column temperature programming at 10 °C min^{-1}.
[c] Analysis of synthetic 2-(diisopropylaminoethyl)methyl sulfide standard, completed following GC temperature program used in Ref. [4] with DB-5 column (30 m, 0.25 mm I.D., 0.25 μm d_f).

that seen with 70 eV conditions. For CIT analyses the manufacturer's standard feedback-controlled ionization time control (automated level control or ALC) was used to manage the number of trapped ions, with possible ionization times ranging from 0.050 to 150 ms. The scan ranges included ions from m/z 50 to 425 for the CIT, and from m/z 45 to 450 for the transmission quadrupole.

The CWA nerve agent compounds *O*-isopropyl methylphosphonofluoridate (sarin or GB), *O*-pinacolyl methylphosphonofluoridate (soman, or GD), cyclohexyl methylphosphonofluoridate (GF), and *O*-ethyl *S*-2-diisopropylaminoethyl methyl phosphonothiolate (VX) were obtained from and used at Defence R&D Canada-Suffield (DRDC Suffield, Ralston, Alberta Canada). These chemicals were handled only by licensed personnel under controlled conditions at DRDC Suffield. The purities of the CWA analytes were verified by GC–MS to be 96%, 98%, 92%, and 75% respectively for GB, GD, GF, and VX. Commercially available *n*-alkane hydrocarbons ranging from C_8 to C_{21} were used as obtained from a commercial source (Aldrich, Milwaukee, WI). The VX degradation product 2-(diisopropylaminoethyl)methyl sulfide was synthesized by reacting 2-(diisopropylamino)ethyl chloride hydrochloride (97% purity, Aldrich) with 2 equiv. of sodium thiomethoxide (>90% purity, Aldrich) in acetonitrile for several hours. The desired end product was extracted into pentanes followed by removal of solvent under a steady stream of Ar at 45 °C. The purity of this compound was shown to be >99% by gas chromatographic methods, and its identity was verified by ^{1}H and ^{13}C NMR. Analyses by GC–MS (transmission quadrupole detector) operated under both EI and CI (NH_3) conditions per the general approach described by D'Agostino et al. [5] also confirmed the identity of this analyte.

Each CWA compound was gravimetrically measured and volumetrically diluted in methylene chloride, and a mixture containing each CWA analyte was serially diluted to provide five mixtures with concentrations (ng/μl) from: 1.2 to 121 for GB, 1.2 to 117 for GD, 1.3 to 133 for GF, and 1.1 to 111 for VX. Known amounts of CWA

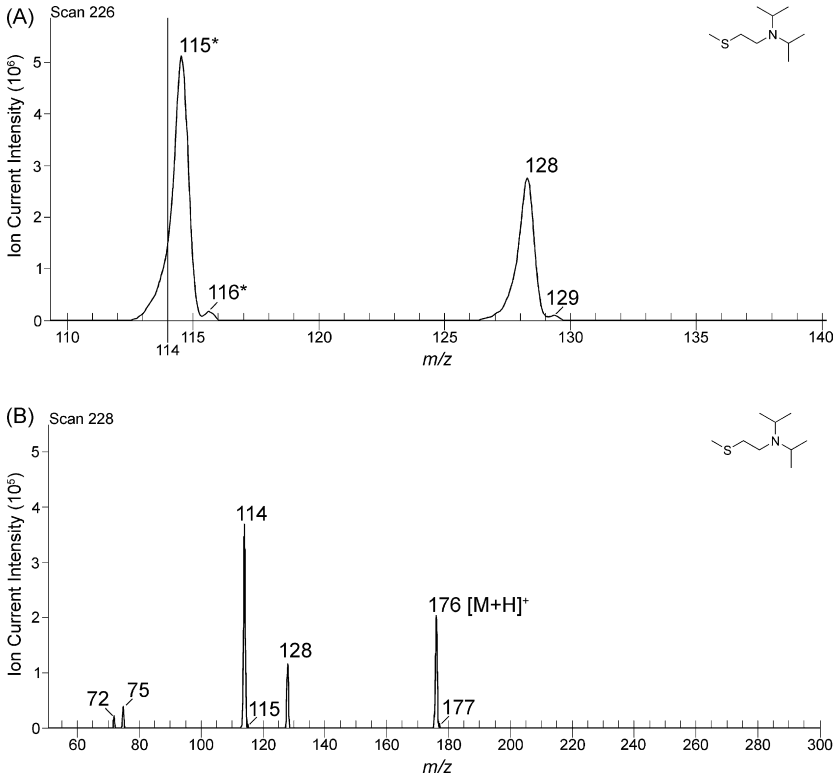

Fig. 3. GC–MS analysis of VX degradation product 2-(diisopropylaminoethyl)methyl sulfide, CIT detector (100 ng injected). (A) Mass spectrum from apex of the chromatographic peak (scan 226); (B) mass spectrum following decrease in analyte concentration (scan 228, from the trailing edge of the GC–MS peak). The peak m/z label values shown were assigned by the CIT GC–MS data system. * denotes inappropriate mass assignment

Table 2
Tabular CIT mass spectra for G-series nerve agents analyzed, as observed with varied CWA analyte masses injected for analysis.

Analyte/molecular mass (u)	Mass injected (ng)	m/z[a] observed (relative intensity)	m/z[b], NIST base peak
GB/140	1.5	99(100), 125(21), 141(15)[c]	99
	15	141(100)[c], 99(87), 125(13), 281(15)[d]	
	36	141(100)[c], 281(63)[d], 99(34)	
	73	281(100)[d], 141(60)[c,e]	
	145	281(100)[d], 141(24)[c,e], 183(12)[e]	
GD/182	1.4	99(100), 126(42), 82(34), 85(26), 69(19), 83(17)	126
	14	99(100), 126(51), 85(40), 82(22), 183(19)[c], 69(16)	
	35	99(100), 85(79), 183(68)[c], 126(41), 69(33), 281(33), 197(31), 82(17), 365(12)[d], 224(12)	
	70	365(100)[d], 183(60)[c,e], 281(46), 85(43), 197(16)	
	140	365(100)[d,e], 281(22)[e], 85(18)[e], 183(15)[c,e]	
GF/180	1.6	99(100), 67(15), 181(4)[c]	99
	16	99(100), 181(40)[c], 67(18), 361(2)[d]	
	40	99(100), 361(55)[d], 181(89)[c], 67(12), 279(12)	
	80	361(100)[d,e], 181(34)[c,e], 99(18)[e]	
	160	361(100)[d,e], 181(26)[c,e], 99(11)[e]	

[a] Mass spectrum associated with apex of a given GC peak, the first diastereomer peak was used for GD; m/z intensities ≥10% base peak are listed for all peaks except $[M+H]^+$ and $[2M+H]^+$, for which intensities ≥1% of the base peak are listed.
[b] Mass spectrum found in 2008 Mass Spectral Library, U.S. National Institute of Standards and Technology.
[c] $[M+H]^+$.
[d] $[2M+H]^+$.
[e] Mass assignment shift observed, the relative intensity values shown in these cases were obtained by summing all ion current produced by ions of a given m/z value (e.g., including +1 or in some cases +2 m/z ion current).

compounds were introduced to the CIT GC–MS system through 1.2 μl injections, and the mass spectra at each concentration were observed. Liquid injection (1 μl volume, 100 ng total analyte) analysis of 2-(diisopropylaminoethyl)methyl sulfide was also completed using the CIT GC–MS system.

A sample of heat-degraded VX was analyzed using the van-mounted GC–MS system, with 20 mg of VX placed onto a small piece of fibrous ceiling tile backing material in a 40 mL headspace vial, which was then sealed and kept at 70 °C in a hot block heater under a fume hood during sampling. Sampling was completed by solid phase microextraction (SPME) using a commercially available SPME fiber (65 μm PDMS/DVB coating thickness, Supelco, Bellefonte PA), with the sample duration of 1 min. Repeated heating/cooling cycles over several days generated numerous VX degradation compounds in this sample.

3. Results and discussion

3.1. Transmission quadrupole mass spectra and retention index values

Fig. 1 demonstrates the lack of ions with high m/z values for VX and many VX-related analytes when a transmission quadrupole is used with 70 eV EI for analysis of a SPME sample obtained from heated VX material. Small signals for $[M-CH_3]^+$ and $[M-C_3H_7]^+$ are observed in the mass spectrum of VX (Fig 1A), and $[M]^{+\bullet}$ and $[M-CH_3]^+$ ions are noted in the mass spectrum of the VX degradation product 2-(diisopropylaminoethyl)methyl sulfide (Fig. 1B). However, the very low ion current intensity for all of these high m/z value ions makes it difficult to differentiate their presence from background noise. Fig. 2 shows a section of the m/z 114 extracted ion chromatogram for the analysis that provided the mass spectra of Fig. 1. Ion current for m/z 114 dominates the mass spectra for many of these peaks. As with Fig. 1 analytes, for each of the numerous GC peaks in this figure where the m/z 114 ion current produced the base peak, very little high mass ion current was seen.

Due to the highly similar mass spectra for most of the GC peaks seen in Fig. 2, transmission quadrupole MS data alone were not adequate for the identification of agents such as VX and many of its degradation products by field technicians. These chemicals normally require CI for identification based solely on mass spectral data [5]. Mass spectral data combined with calculated and reference retention index (RI) values (Table 1) allowed technicians to differentiate between VX and VX-related degradation products in the field within minutes after completing GC–MS analyses. While useful to guide analyte identification, the RI values obtained with rapid column temperature ramping rates (that allowed complete GC–MS analyses in <5 min) were consistently higher by as much as 3.9% from the literature values obtained with slower standard GC column temperature ramping of 10 °C min^{-1}. Final confirmation for the identities of these compounds was obtained by comparing calculated values to those from previous work by the authors using the same fast column heating rates.

3.2. CIT mass spectra and self-CI

Self-CI leading to the production of $[M+H]^+$ was observed with CIT analyses of VX, and VX degradation products having the diisopropylamine functional group. Fig. 3 shows CIT mass spectra for the VX degradation product 2-(diisopropylaminoethyl)methyl sulfide with m/z 114 and 115 ions displaying concentration-dependent mass assignment shifts (Fig. 3A). When observed, mass assignment shifting was more prominent for low mass ions, and as in Fig. 3A less noticeable for higher m/z value ions. This observation is consistent with space charging as the cause of mass assignment shifts as the CIT will have lower ion density after the smaller m/z value ions are initially lost through resonance ejection. Concentration-dependent spectral changes were frequently observed for CIT analyses in spite of the use of ALC for feedback-controlled ionization time management. Mass assignment shifting for the m/z 114 ion signal was observed starting with injections of 66 ng VX, while all m/z values less than that of the pseudomolecular ion $[M+H]^+$ were subject to incorrect mass assignment with CIT analysis of the highest VX concentration.

Mass spectral data produced by the CIT system for the three G-series nerve agents analyzed at five concentrations are listed in Table 2. The ion corresponding to $[M+H]^+$ was seen with analysis of all G agent compounds, except in the case of the lowest concentration GD sample. The respective protonated dimer compound was also observed for each G agent analyte injected at higher concentrations. The mass spectra for GB shown in Fig. 4A and B and the relative ion current intensities produced with varied GB concentra-

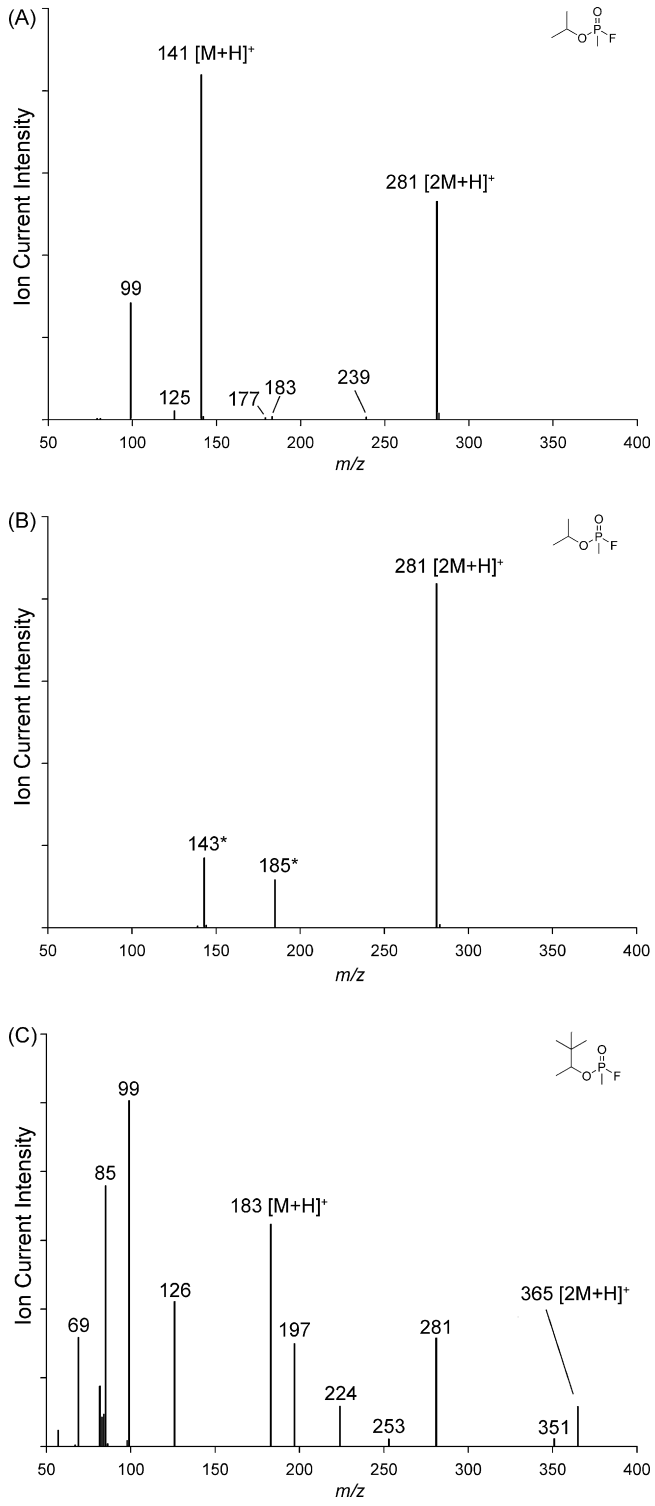

Fig. 4. CIT mass spectra from analysis of liquid injections, with several CWA concentrations; (A) GB (36 ng), (B) GB (145 ng), and (C) GD (35 ng). Each mass spectrum represents the apex of a chromatographic peak, the first diastereomer peak was used for GD. The peak *m*/*z* label values were assigned by the CIT GC–MS data system. * denotes inappropriate mass assignment

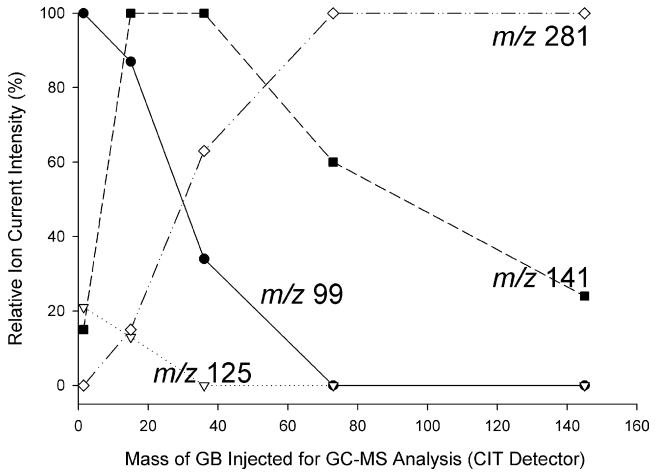

Fig. 5. Relative ion current intensities with varied mass of GB injected for GC–MS analysis (CIT detector), from Table 2 GB data. As in Table 2, all values have been corrected for mistaken instrumental mass assignments.

tions (Fig. 5) provide an example of the concentration-dependent changes observed for mass spectra of all the phosphonofluoridate compounds analyzed. Similar ion/molecule interactions were noted for each G-series nerve agent analyzed (Table 2, also Fig. 4C as an example for GD analysis). Evidence was seen for the initial formation of $[M+H]^+$ followed by increasing relative intensity for $[2M+H]^+$ as the concentration of each G agent in solvent injected for analysis was increased.

Similarly, an increase in $[2M+H]^+$ and eventual decrease in intensity of $[M+H]^+$ with increased mass of diethylmethylphosphonate analyzed using an ion trap mass spectrometer was observed by Méchin et al. [12]. In our data, the protonated GB dimer (*m*/*z* 281) was not seen in the CIT mass spectrum corresponding to the lowest mass of GB injected (1.5 ng), but signal for this ion was observed with all higher GB concentrations analyzed.

Fig. 6 shows a proposed formation mechanism for the protonated GB dimer consistent with the relative ion intensities of $[M+H]^+$ and $[2M+H]^+$ seen in Fig. 5. Initial formation of $[M+H]^+$ is proposed to proceed through protonation of the phosphoryl oxygen, which produces an electrophile susceptible to nucleophilic attack. Interaction between $[M+H]^+$ and neutral GB will then lead to the formation of a covalently bonded adduct with several resonance stabilization forms. Low concentrations of GB in the CIT were observed to predominantly form $[M+H]^+$, but as increasing concentrations of GB were analyzed, this provided higher levels of both Fig. 6 reagents (neutral GB and $[M+H]^+$) in the CIT, favoring formation of the dimer under this mechanism. Evidence that the protonated GB dimer observed was formed by a covalent bond comes from AM1 semi-empirical calculations (Spartan software, Wavefunction Inc., Irvine, CA). Considering the covalent and hydrogen bonded dimer structures, both were calculated to be energy minima, with the covalent dimer calculated to be more stable by 60 kJ/mol.

The effects of varied analyte injection concentration noted in Table 2 and Figs. 4 and 5 were also seen within extracted ion chromatograms for a single chromatographic peak as mass spectra were collected during periods of varied analyte concentration within the CIT. For example, with the injection of 73 ng GB, scans from the apex of the chromatographic peak for GB (representing the highest instantaneous analyte concentration in the CIT) showed an apparent drop in *m*/*z* 141 ion current for $[M+H]^+$ to zero as ion current for $[2M+H]^+$ dominated. As shown in Table 2 which displays data adjusted for incorrect mass assignments, this is partially due to the mass assignment shifting for $[M+H]^+$ ion current which is then counted as *m*/*z* 142 or even *m*/*z* 143 ion current (see Fig. 4B). Similar mass assignment shifting was consistently seen for other classes of analytes (e.g., hydrocarbons) when relatively high analyte concentrations were introduced for GC–MS analyses with the CIT detector.

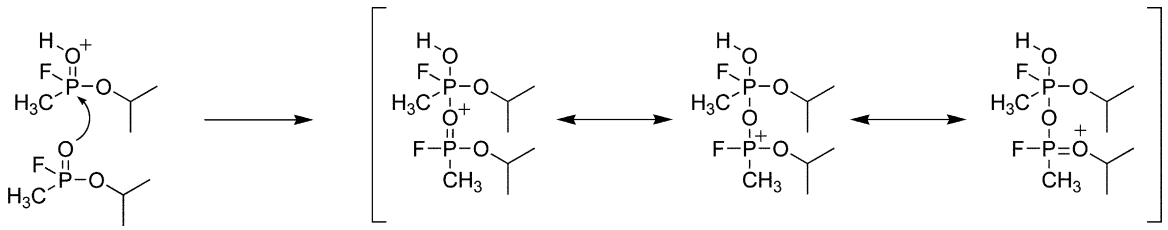

Fig. 6. Proposed dimerization mechanism for GB from interaction between the neutral compound and $[M+H]^+$.

4. Conclusion

During military chemical defense exercises, three possible strategies using two field-portable GC–MS systems were explored for the detection of VX and VX-related analytes. The 70 eV El mass spectra collected using a quadrupole mass filter instrument were shown to be insufficient alone for the identification of analytes such as VX by technicians, for which CI would normally be required. Transmission quadrupole data for VX-related compounds could be useful for near real-time identification of VX and VX-related degradation products when GC retention information is considered by comparing observed RI values in unknown samples to the literature. Additional work in this area is necessary to verify the effects of rapid temperature programming on expected RI values for analytes of interest if fast GC temperature programming is to be routinely used in the field. The CIT mass spectrometric detector demonstrated a capability for self-CI, producing pseudomolecular ions for VX, and VX-related and other CWA nerve agent compounds. However, CIT ion/molecule interactions produced concentration-dependent mass spectra, and mass assignment shifts related to space charging were also concentration-dependent. These phenomena increase the complexity for the interpretation of CIT mass spectral data and will potentially challenge technician-level field operators.

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