

Characterization of VX on Concrete Using Ion Trap Secondary Ionization Mass Spectrometry

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The nerve agent VX (O-ethyl S-2-diisopropylaminoethyl methyl phosphonothiolate) was analyzed on the surface of concrete samples using an ion trap secondary ion mass spectrometer (IT-SIMS). It was found that VX could be detected down to an absolute quantity of 5 ng on a concrete chip, or to a surface coverage of 0.0004 monolayers on crushed concrete. To achieve these levels of detection, the m/z 268 \rightarrow 128 ion fragmentation was measured using MS², where m/z 268 corresponds to $[VX + H]^+$, and 128 corresponds to a diisopropylvinylammonium isomer, that is formed by the elimination of the phosphonothiolate moiety. Detection at these levels was accomplished by analyzing samples that had been recently exposed to VX, i.e., within an hour. When the VX-exposed concrete samples were aged, the SIMS signature for intact VX had disappeared, which signaled the degradation of the compound on the concrete surface. The VX signature was replaced by ions which are interpreted in terms of VX degradation products, which appear to be somewhat long lived on the concrete surface. These compounds include ethylmethylphosphonic acid (EMPA), diisopropyl taurine (DIPT), diisopropylaminoethanethiol (DESH), *bis*(diisopropylaminoethane)disulfide [(DES)₂], and a particularly tenacious compound that may correspond to diisopropylvinylamine (DIVA), or an isomer thereof. It was found that the thiolamine-derived degradation products DIPT, DESH, and (DES)₂ were removed with isopropyl alcohol extraction. However, the DIVA-related degradation product was observed to strongly adhere to the concrete surface for longer than one week. Although quantitation was not possible in this set of experiments, the results clearly show the rapid degradation of VX on concrete, as well as the surface sensitivity of the IT-SIMS for intact VX and its adsorptive degradation products. (J Am Soc Mass Spectrom 2000, 11, 69–77) © 2000 American Society for Mass Spectrometry

The environmental fate of the chemical warfare agent VX (O-ethyl S-2-diisopropylaminoethyl methyl phosphonothiolate) is a topic of acute interest, because the compound is extremely toxic [1–3] and can be persistent in the environment [4]. The degradation of VX, either in the environment, or subjected to decontamination processes [5–10], has been studied extensively, yet much less work has been done to understand the behavior of the compound on surfaces. This is a significant shortcoming, because the compound is highly surface adsorptive as a consequence of its molecular size, and the presence of reactive functional groups [11]. For this reason, VX detec-

tion was the subject of a recent analytical investigation that utilized an ion trap secondary ion mass spectrometer (IT-SIMS) [12]. In this earlier study, it was found that the compound could be readily detected on soil particles (which were predominantly silicate); ions observed were the intact protonated cation $[VX + H]^+$, and a highly abundant diisopropylvinylammonium (or isomer) fragment ion at m/z 128. By monitoring the collision-induced $[VX + H]^+ \rightarrow m/z$ 128 reaction in the ion trap, detection to 0.002 monolayer was demonstrated on soil particles. Furthermore, by repeatedly analyzing exposed silicate particles over a period of several months, it was observed that VX was relatively stable. In these earlier experiments, the particles were stored at 5 °C in between analyses.

Surface adsorbed molecules like VX are detected in the IT-SIMS in the following manner. The surface of the

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solid sample is bombarded with energetic, polyatomic projectiles, which “sputter” adsorbed molecules into the gas phase. Some fraction of the sputtered molecules will be ionized, and these can be trapped in the thermal He bath gas that is present inside the ion trap. Once trapped, the analyte ions, as well as “background”-derived ions, can be scanned out of the trap by mass and detected, thus generating a mass spectrum (MS^1). Improved specificity and sensitivity can be achieved using MS^2 , which is accomplished in the IT-SIMS by isolating the ion of interest on the basis of mass, collisionally inducing fragmentation reactions, and finally scanning out and detecting the fragment ions. This approach eliminates the background signal from the fragment ion region of the mass spectrum. Using these techniques, a variety of highly surface adsorptive compounds have been detected on naturally occurring surfaces, notably organosulfides [13, 14], organophosphates [15–18], organoamines [19, 20], organometallic compounds [21], and inorganic species [22, 23].

In the present study, concrete samples that had been exposed to VX were interrogated using an IT-SIMS. The study was prompted by the fact that conventional extraction/GC/MS analyses were encountering difficulty in achieving a mass balance after a very short period of time. This difficulty probably stems from the fact that VX and its degradation products can obstinately resist extraction [24]. However, the tendency of these compounds to strongly adsorb to the surface suggests that the IT-SIMS approach may be able to provide qualitative information which would assist in reconciling the mass balance. The approach may also be capable of providing a more thorough sample characterization than current Chemical Weapons Convention analytical protocols, which are based on extraction/GC/MS.

Experimental

Sample Generation

Caution: VX is a highly lethal compound capable of killing or injuring at extremely minute doses. The compound should only be handled in approved chemical warfare surety laboratories by trained agent chemists. All sample preparation and analyses were performed at the chemistry laboratory of the U. S. Army West Desert Test Center (WDTC), Dugway Proving Ground, Dugway, UT; this lab is equipped with appropriate engineering and administrative controls for handling chemical warfare agents.

A concrete sample was collected from the runway of the Salt Lake City International Airport, and was analyzed subsequent to washing with an alkylsulfonate soap, distilled water rinse, and finally heating to dryness. Because SIMS sensitivity is a function of surface coverage, the surface area of the concrete was measured, and found to be $4.0 \text{ m}^2/\text{g}$ using N_2 adsorption (BET method) [25].

The VX used in the study was the property of the U. S. Army, and was an analytical reference standard. The compound was received and used as either a neat, or a $\mu\text{g}/\mu\text{L}$ (isopropanol) standard solution. The primary stan-

dard solution was used for serial dilutions. For a given surface coverage, the objective was to dilute the primary standard so that the number of μL of standard solution was roughly equal to the number of milligrams of the sample. Crushed, weighed concrete samples ($\sim 50 \text{ mg}$) were covered with a volume of the secondary standard solution, which contained a mass of VX equivalent to 0.04, 0.004, or 0.0004 monolayers, respectively. The mass of VX corresponding to monolayer coverage was estimated by assuming that the molecular area of the compound was equivalent to 79 \AA^2 , which is the area of a circle having a radius equal to half the length of the molecule on the surface (estimated at 5.0 \AA). This radius estimate assumed that the molecule laid flat on the surface, and was generated using molecular mechanics calculations (Cerius², Molecular Simulations, San Diego, CA). If the molecule exists on the surface in an upright fashion, or is coiled, then the monolayer coverages will be somewhat less than the values used in this study. This approach for the preparation of coated samples has, in the past, resulted in self-consistent data, viz., the abundance of secondary ions stops increasing with increasing adsorbate mass when the estimated surface concentration exceeds one monolayer.

The concrete samples were analyzed as soon as they appeared to be dry (ambient temperature, requiring about 2 h), whereupon approximately 1 mg of particles were attached to a sample holder (the head of a #18 nail) using double-sided tape. The sample holder was then attached to the probe for analysis. SIMS analysis showed only ions derived from the VX-spiked concrete, and not from the tape. Therefore, we conclude that the concrete particles are efficiently covering the tape surface.

A second type of VX-exposed concrete samples were also prepared for analysis. Concrete chips (irregularly shaped, $\sim 2\text{--}4 \text{ mm}$ across) were spiked with $0.01 \mu\text{L}$ neat VX, and the compound (a viscous liquid) was allowed to disperse/soak into the concrete sample. As before, the chip was mounted on a nail head using tape, and analyzed.

When the analyses were complete, samples were immersed in bleach solution, to neutralize the residual VX. The waste from the decontamination procedure was then treated as hazardous waste and disposed of appropriately.

Concrete particles exposed to DESH were also analyzed. The DESH hydrochloride salt (TCI Chemicals, Tokyo, Japan) was dissolved as a $1.84 \mu\text{g}/\mu\text{L}$ isopropanol solution (with a trace of H_2O added as a co-solvent). This solution was then applied to concrete samples to generate a 0.5 monolayer surface concentration (the molecular area used for this estimate was 38 \AA^2).

A surrogate compound for the degradation product DESH was also analyzed. Dimethylaminoethanethiol (DMAET, as the hydrochloride, Aldrich, Milwaukee, WI) was dissolved in methanol, and applied to soil and concrete samples such that the concentration was equivalent to 0.1 monolayers. The molecular area used for this calculation was 24 \AA^2 . In a second set of experiments, the methanolic solution was applied to the head of a small nail and allowed to dry.

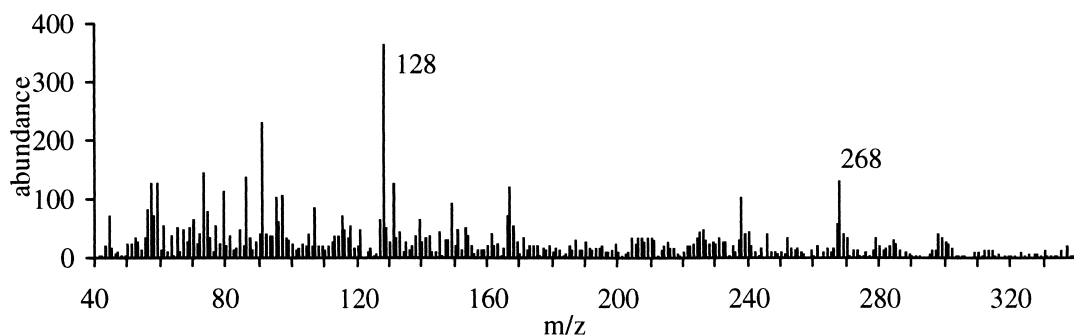


Figure 1. Cation SIMS spectrum (MS^1) of 0.004 monolayer VX on crushed concrete.

IT-SIMS

Two separate IT-SIMS instruments were used in this study, one located at the WDTC, and one at the INEEL. The WDTC instrument was a Teledyne Discovery 2 ion trap mass spectrometer (Mountain View, CA) modified for SIMS, and was used for all of the VX experiments. The physical layout of the IT-SIMS instrument involved placement of the vacuum housing in a chemical warfare agent surety hood, where all agent-contaminated manipulations were performed. The vacuum housing was connected to the power supplies and computer by elongated cables. Two mechanical pumps which pumped the turbo and the insertion lock were also located outside the hood, but were vented back into the hood using Tygon tubing.

The Teledyne-based IT-SIMS has not been described previously in the literature, but is very similar in design and operation to an IT-SIMS instrument based on a Finnigan ion trap, that is described in detail in [21]. Briefly, the instrument is equipped with a ReO_4^- primary ion gun, an offset dynode/multichannel plate detector system, and an insertion lock for introducing the sample using the direct insertion probe. The ReO_4^- primary particle provides enhanced production of molecular secondary ions compared to atomic projectiles [22, 26, 27]. This is advantageous when probing surface adsorbates. The ReO_4^- beam is directed through the ion

trap along the main axis of the device, passing through a hole in one end cap, and striking the sample holder, which is located behind a 1-mm diameter hole in the opposite end cap. The ReO_4^- ion gun was operated at 4.5 keV, at a primary ion current of 30 pA (measured using a Faraday cup probe). The ReO_4^- beam is gated to impact the sample only during the initial period of the IT-SIMS analysis sequence. By varying the length of the ionization period, the dynamic range of the instrument may be varied over three orders of magnitude. Secondary ions sputtered from the sample surface are focused into the ion trap by a small, cylindrical, electrostatic lens. The electrostatic potential of the sample holder is not controlled; instead, the potential of the sample holder floats at the ambient (and variable) potential of this region of the ion trap [28]. Upon entering the trap, the secondary ions undergo collisions with the He bath gas (3×10^{-5} torr), and lose sufficient kinetic energy such that they are trapped by the oscillating rf field.

One particularly advantageous attribute of the ion trap is that by applying a filtered noise field to the end caps during the ion formation period, all ions except those within a selected narrow mass range are kept out of the trap [29]. This makes it possible to populate the trap with only the ions of interest, thereby greatly improving the signal to noise, and lowering the minimum detection limit.

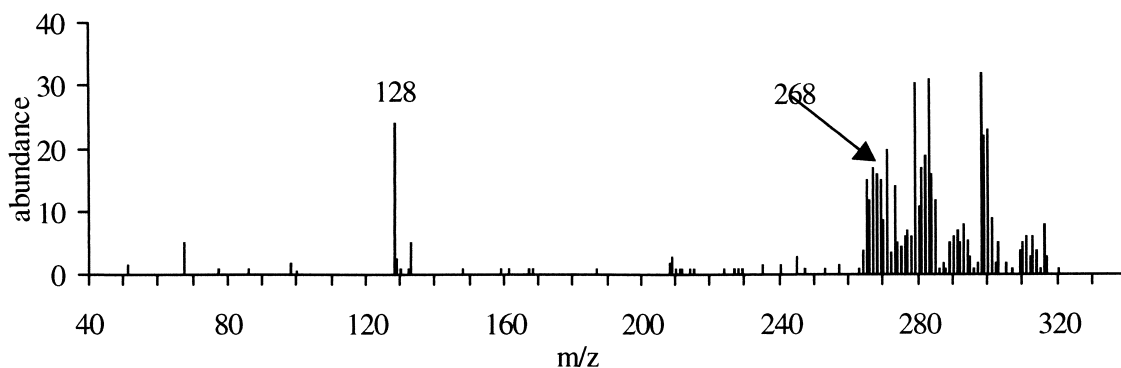


Figure 2. Cation SIMS spectrum (MS^2) of 0.0004 monolayer VX on crushed concrete. Parent ion is $[VX + H]^+$ at m/z 268, and is surrounded by other abundant ions derived from the chemical background on the concrete surface. Ions at $< m/z$ 265 were ejected from the trap during ion formation using the filtered noise field. The MS^2 fragment ion is m/z 128.

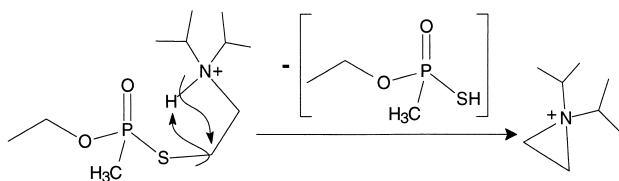


Figure 3. Primary fragmentation reaction of $[VX + H]^+$, producing a diisopropylaziridinium (or isomer) at m/z 128. The mechanism involving transfer of the amino proton was suggested by D-labeling results, see [12].

Once trapped, the ions can be mass selectively ejected from the ion trap to the detector (MS^1), which is located off axis on the same side of the ion trap as the ReO_4^- primary ion gun. Alternatively, the ions can be collisionally dissociated through collisions with He, by applying a high frequency oscillating field to the end caps (MS^2). The ionic fragments are then mass selectively ejected to the detector.

In a typical MS^1 experiment, the ion trap was operated at base rf amplitude corresponding to a low mass cutoff of 40 u. Ionization time was typically 250 ms, after which the mass spectrum was recorded. A single "scan" consisted of 10 summed spectra. A normal analysis would consist of about 30 scans.

The primary ion dose for a typical analysis can be calculated at about 1.5×10^{12} ions/cm², by using the ionization time and scan acquisition information above, the area irradiated (8×10^{-3} cm²), and the primary ion current (30 pA). At this dose, the surface of the sample is not considered to have been seriously perturbed [30].

The second IT-SIMS instrument used was based on a Varian ion trap mass spectrometer modified for SIMS, which is located at the INEEL, and was used for all the DMAET experiments. Like the WDTC instrument, it has not been specifically described in the literature, but is very similar to the WDTC instrument in terms of components, layout, and function.

Results and Discussion

Initial experiments were focused on recording the SIMS spectrum of VX on concrete. VX was applied to crushed concrete as a dilute solution, which wetted the entire

sample, and resulted in a uniform distribution of VX on the surface. In this case, the surface concentration can be calculated. The dilute solutions, as well as neat VX (0.01 μ L), were also applied to small concrete chips. In these samples, the compound could be observed to spread out on the surface, and the VX distribution on the concrete chip was certainly inhomogeneous.

When the 0.004 monolayer crushed concrete (VX solution exposed) was analyzed *shortly after spiking*, the positive ion spectra were nearly identical to those recorded for VX on silicate (soil) particles [12]. The spectrum contained abundant ions at m/z 268, 128, and 86, and lower abundance ions at m/z 167 and 139 (Figure 1). These ions are the result of intact VX on the sample surface, and are not the result of surface decomposition prior to bombardment. This is an important distinction, because the disappearance of m/z 268 signals the disappearance of intact VX on the concrete surface. In subsequent experiments, a crushed concrete sample spiked at the 0.0004 monolayer level was analyzed; in the MS^1 spectrum, the ion signature for intact VX could not be distinguished from background, but the $[VX + H]^+ \rightarrow m/z$ 128 fragmentation reaction could be readily detected using MS^2 (Figures 2 and 3), which clearly reveals the presence of the intact compound on the surface. This surface concentration corresponds to about 0.9 ppm on a mass/mass basis.

VX was also successfully analyzed on the surface of small concrete chips that were spiked directly with dilute solutions of VX. When 10 ng was spiked onto a chip surface, $[VX + H]^+$ could be observed at an abundance just above background in the MS^1 spectrum. 5 ng could be observed with reasonable signal/noise using MS^2 (Figure 4). This quantity, which could not be distinguished from background using MS^1 , is probably within a factor of 2 or 3 of the minimum detectable quantity on this surface.

When the chips that were spiked with 0.01 μ L VX were analyzed after standing at ambient temperature for 1 day or longer, no evidence for VX was observed (Figure 5a). This conclusion is based primarily on the absence of a significant m/z 268 in the SIMS spectrum. Instead, the spectrum contained evidence consistent with the presence of several distinct degradation prod-

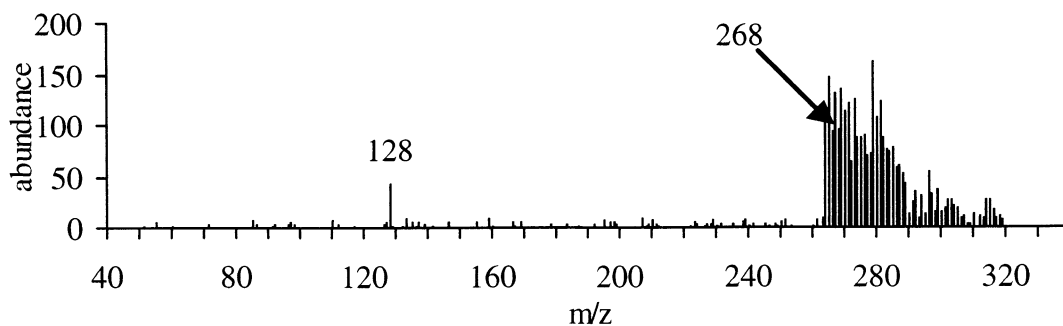


Figure 4. Cation SIMS spectrum (MS^2) of 5 ng VX on a concrete chip. Parent ion is m/z 268, $[VX + H]^+$, fragment ion is m/z 128.

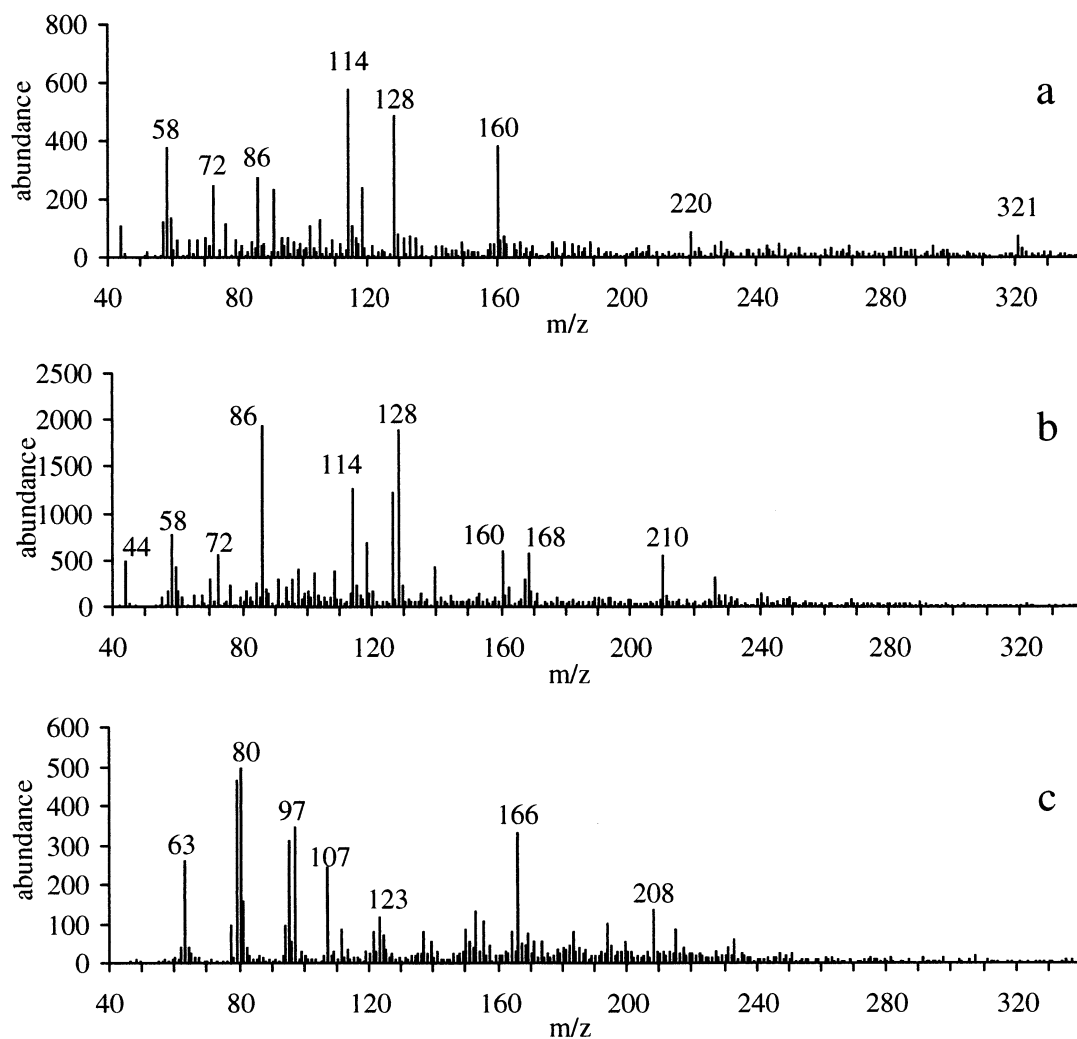


Figure 5. SIMS spectra (MS^1) of 0.01 μL VX on a concrete chip, after standing for 5.5 days. (a) Cation spectrum containing evidence for DIVA (m/z 128), DESH (m/z 160), and $(\text{DES})_2$ (m/z 321). (b) Cation spectrum, containing evidence for DIVA, DESH, and DIPT (m/z 210). (c) Anion spectrum, containing evidence for DIPT (m/z 208) and EMPA (m/z 123).

ucts, which have been identified in solution phase degradation studies [5–7, 31]. The most significant of these is diisopropylaminoethanethiol (DESH), which arises from cleavage of the P–S bond. Consistent with the structure of DESH, abundant ions were observed at m/z 160, 118, and 114. m/z 160 corresponds to $[\text{DESH} - \text{H}]^+$, which formally corresponds to the net loss of a hydride. A mechanism involving loss of a hydride is unlikely; a more plausible explanation is protonation followed by facile elimination of H_2 . The mechanism for formation of this ion has not been established, but the tendency for its formation is identical to that observed in the analysis of the DESH, and the model compound DMAET (see below). In the case of the $[\text{DESH} - \text{H}]^+$ ion, we hypothesize that the structure corresponds to N,N -diisopropyl thioazetidinium (m/z 160, Figure 6), which is consistent with two prominent ionic fragmentation reactions, viz., loss of C_3H_6 , and loss of $\text{CH}_2=\text{S}$ (the latter possibly via a retro [2 + 2] mechanism).

These parent ion–fragment ion relationships were verified using MS^2 .

Lower abundance ions at m/z 321 and 220 are consistent with the presence of a second degradation product on the surface, which is likely *bis*(N,N -diisopropylaminoethyl)disulfide $[(\text{DES})_2]$. The intact, protonated molecule gives rise to m/z 321, and the principal fragment ion arises via loss of diisopropylamine (Figure 7). m/z 220 is the salient fragment ion in the MS^2 analysis of $[(\text{DES})_2 + \text{H}]^+$. $(\text{DES})_2$ is certainly formed on the surface prior to SIMS bombardment; it was detected in an isopropanol extract using GC/MS. We have considered the possibility that this compound could be the ionic precursor to m/z 160, previously attributed to DESH. In experiments where lower quantities of VX was applied to concrete, ions corresponding to $[\text{DESH} - \text{H}]^+$ were observed, but the $[\text{disulfide} + \text{H}]^+$ was not. Analogous results were achieved when low surface concentrations of DESH and DMAET were

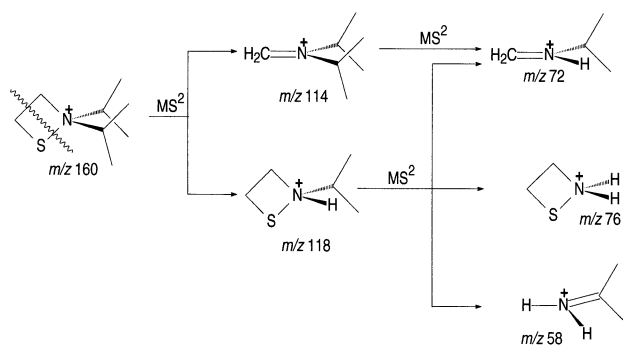


Figure 6. Ionic fragmentation pathways of $[\text{DESH} - \text{H}]^+$, identified using MS^2 . The retro $[2 + 2]$ fragmentation is denoted by the sawtooth line in m/z 160.

analyzed. These observations suggest that $(\text{DES})_2$ is at best a minor contributor to the ion at m/z 160.

A third degradation product likely accounts for the abundant secondary cations at m/z 128, 86, and 44. The compound is almost certainly a diisopropylvinylamine (DIVA) isomer, where m/z 128 corresponds to the intact, ionized degradation product, and 86 and 44 arise from the losses of one and two C_3H_6 molecules, respectively (Figure 8). The relationship of these fragment ions to m/z 128 was verified using MS^2 . Formation of this compound would involve cleavage of the S–C bond in the VX molecule, and although this has not been identified as a dominant degradation mechanism, it has been reported in the literature [31]. It may be that this compound exists as an ammonium ion on the surface of the concrete; we hypothesize that this may be the case, because the m/z 128 does not disappear upon extraction with isopropanol, which might be expected if the compound were present in a nonionic form. It should be noted that m/z 128, 86, and 44 are also part of the cation SIMS signature of intact VX; however, in the absence of a significant $[\text{VX} + \text{H}]^+$, these do not indicate the presence of the intact agent on the surface.

The ion observed at m/z 139 is rationalized in terms of a phosphonothioate degradation product, also arising from S–C bond cleavage. This ion, which is also observed in the spectrum of intact VX, may have a structure similar to that depicted in Figure 8.

Ions consistent with the presence of two other degradation products could be observed in some (but not all) of the spectra of exposed concrete. These degradation products arise from the oxidative cleavage of the VX P–S bond. These compounds are diisopropyl taurine (DIPT) and ethylmethylphosphonic acid (EMPA). DIPT

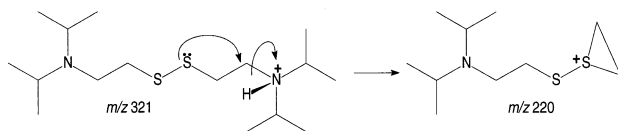


Figure 7. Proposed structure for protonated bis(*N,N*-diisopropylaminoethyl)disulfide $[(\text{DES})_2 + \text{H}]^+$ (m/z 321), and fragment ion at m/z 220.

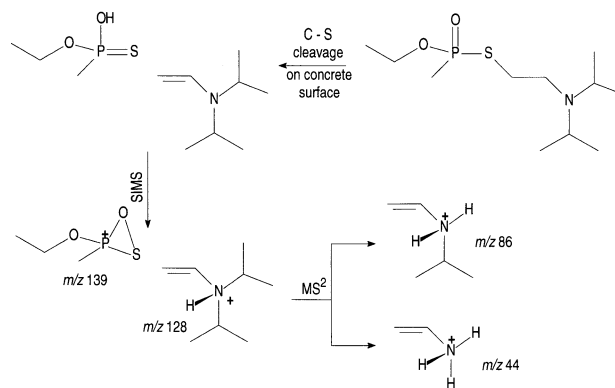


Figure 8. Schematic representation of C–S bond cleavage of VX on the concrete surface, prior to SIMS analysis. Secondary cations observed at m/z 139 and 128 are consistent with phosphonothioate and DIVA degradation products formed in this process. Neither surface nor ion structures have been rigorously established; best estimates have been presented. Formation of m/z 86 and 44 from 128 was verified using MS^2 .

can be observed in the cation spectrum as the protonated molecule $[\text{DIPT} + \text{H}]^+$ at m/z 210, which undergoes sequential eliminations of two C_3H_6 to form 168 and 126 (Figures 5b and 9). Intact DIPT could also be readily observed in the anion spectrum as $[\text{DIPT} - \text{H}]^-$ at m/z 208, with fragment ions at m/z 166, 124 (losses of one and two C_3H_6) and 80 (SO_3^-) (Figure 5c). The second degradation product, EMPA, is observed as the conjugate base $[\text{EMPA} - \text{H}]^-$, and is accompanied by signif-

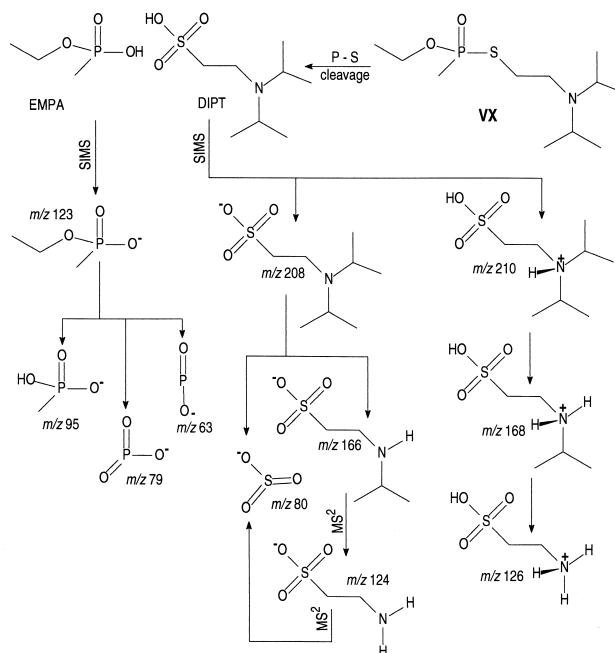


Figure 9. Schematic representation of P–S bond cleavage of VX, with oxidation, on the concrete surface, prior to SIMS analysis. Secondary anions observed at m/z 123 and 208 are attributed to this, as is m/z 210 in the cation spectrum. Ion fragmentation reactions account for the remainder of the abundant ions observed.

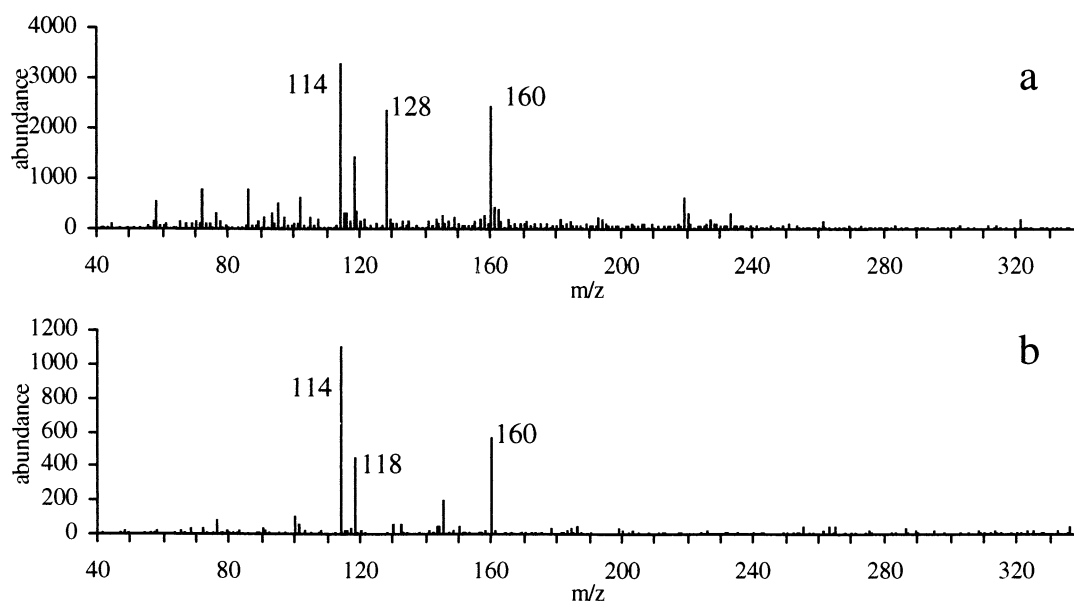


Figure 10. Cation SIMS spectra of 0.5 monolayer DESH on concrete particles. (a) MS¹. (b) MS² spectrum, m/z 160 isolated and tickled to form m/z 118 and 114.

icant fragment ions at m/z 95, 79, and 63 [32]. Two abundant ions observed in the anion spectrum have not yet been satisfactorily explained, viz., m/z 107 and 97. m/z 97 may correspond to HSO_4^- , and was observed in benchmark analyses of unexposed concrete. m/z 107 may correspond to a vinylsulfonate-type compound, perhaps derived from DIPT.

Analysis of DESH and Dimethylaminoethanethiol (DMAET): The cation SIMS spectrum of DESH confirmed the tendency of the compound to form $[\text{DESH} - \text{H}]^+$, m/z 160 (Figure 10). In addition, abundant ions were observed at m/z 114, and 118, which were shown to be derived from $[\text{DESH} - \text{H}]^+$ by MS²: this behavior was identical to that observed in the VX-exposed samples. An abundant ion at m/z 128 was also observed, however, this could not be produced by CID of m/z 160 (or of the low abundance m/z 162, $[\text{DESH} + \text{H}]^+$). We hypothesize that the m/z 128 ion is formed by surface decompositions, which may be aided by the bombardment process.

The tendency of the 1,4-thioamine compounds to form $[\text{M} - \text{H}]^+$ cations was further investigated by analyzing dimethylaminoethane thiol (DMAET). The cation SIMS spectrum of multiple monolayers of DMAET on steel (Figure 11) contained three abundant ions which were derived from DMAET (a variety of other ions are also detected, which are believed to be primarily phthalate derived, and are common to steel surfaces). The three DMAET-derived ions, observed at m/z 209, 164, and 104, to a large degree reflect the behavior of the DESH formed from VX on concrete surfaces. The best explanation for the formation of m/z 209 is the disulfide dimerization of DMAET, resulting in *bis*(*N,N*-diimethylaminoethyl)disulfide [analogous to $(\text{DES})_2$], which is observed as the intact protonated molecule when probed using SIMS. Whether this occurs in the condensed phase, or upon SIMS bombardment, has not been identified. However, because DESH forms a similar compound without the aid of ion bombardment, it seems likely that at least some of the disulfide

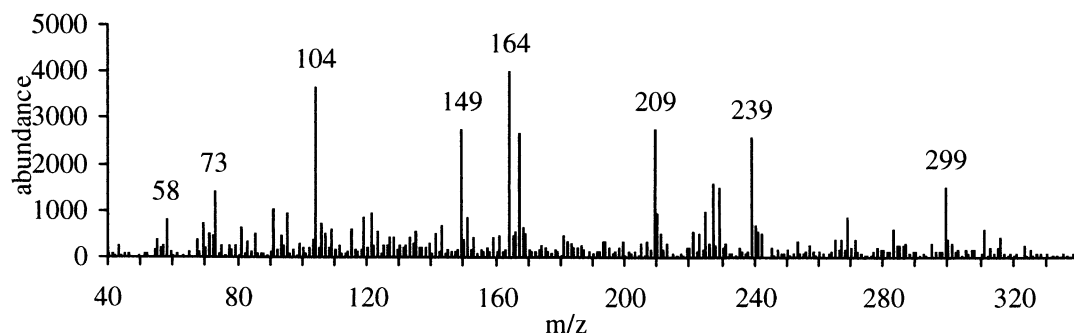


Figure 11. Cation SIMS spectrum of multiple monolayers of DMAET on steel. Ions at m/z 209, 164, and 104 are derived from DMAET, and are not observed in abundance on the surface of untreated steel. Other ions in the spectrum are derived from the chemical background on the steel surface.

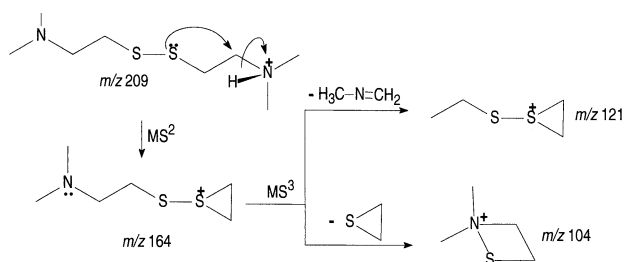


Figure 12. Schematic diagram of the MS^2 and MS^3 fragmentation reactions of the protonated *bis*(*N,N*-dimethylaminoethyl)disulfide (m/z 209) observed in the cation SIMS spectrum of DMAET on steel.

dimer is being formed in the condensed phase prior to analysis.

Using MS^2 , m/z 164 was identified as a fragment ion of the protonated *bis*(*N,N*-dimethylaminoethyl)disulfide. This would represent the loss of dimethylamine, which may be anchimerically assisted by the S lone pairs (Figure 12), and is directly analogous to the formation of the m/z 220 ion observed from $(DES)_2$. An MS^3 experiment showed that m/z 164 fragmented to m/z 104; the loss of 60 u likely is accounted for by C_2H_4S .

Although m/z 104 is formed from the ionic fragmentation of the disulfide dimer, it is also formed directly from the SIMS bombardment of DMAET, resulting in $[DMAET - H]^+$. This conclusion is supported by an experiment in which the surface concentration of DMAET was limited to 0.1 monolayer: in this case, an abundant m/z 104 was observed, but the abundance of m/z 209 and 164 were not above the chemical background. In contrast to the behavior of most amine adsorbates, little $[M + H]^+$ was observed [20]. Multiple stage mass spectrometry experiments were used to interrogate the m/z 104 ion, to determine whether there was structural similarity with the m/z 160 ion derived from DESH. Three significant fragmentation reactions of m/z 104 were observed, forming m/z 76, 71, and 58. m/z 76 and 58 are consistent with retro $[2 + 2]$ fragmentations, starting from a parent possessing a *N,N*-dimethyl thioazetidinium structure (m/z 104, Figures 12 and 13). Formation of m/z 71 requires the elimination of a HS radical, and the mechanism and ion structure are open for conjecture. Because the ion resulting from C_2H_4 elimination constituted the best evidence for the

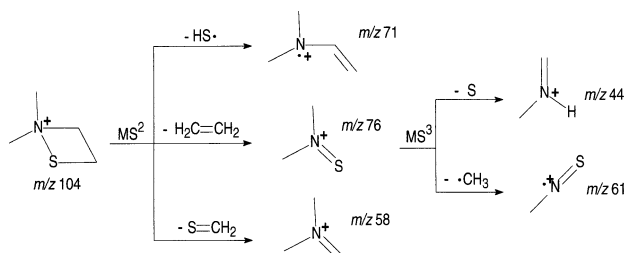


Figure 13. Schematic diagram of MS^2 and MS^3 fragmentation reactions of m/z 104 derived from DMAET.

thioazetidinium structure, it was subjected to MS^3 : this experiment showed two fragment ions, at m/z 61 and 44. Both ions can be readily rationalized in terms of neutral S and CH_3 losses.

Conclusions

The results of this study show clearly that the majority of VX on the surface of concrete degrades within one day, forming DESH, DIPT, and EMPA via cleavage of the P–S bond, and a DIVA isomer via cleavage of the S–C bond. DESH can further react to form *bis*(*N,N*-diisopropylaminoethyl)disulfide, $(DES)_2$. This behavior is vastly different from that of VX on soil particles at 4 °C, where the compound was observed to be stable for several months. The SIMS spectra are consistent with VX degradation pathways known to occur in solution.

The degradation products and intact VX can be readily observed using the IT-SIMS instrument. With the instrument set up for MS^2 of m/z 268, VX was detected at 4×10^{-4} monolayers on the concrete, which corresponded to 0.9 ppm mass/mass. These attributes, coupled with minimal sample preparation and analysis time (<10 min/analysis) requirements, highlight the applicability of the IT-SIMS approach for following complex adsorbate chemistry on real-world surfaces. The limitations of the approach are that the adsorbate molecules must readily form ions (not problematic in the case of VX), and that the technique is currently semiquantitative (which requires a priori knowledge of the surface area of the solid and the response of the target compound). Nevertheless, the approach provides an easy method for the identification of strongly adsorbed agent and degradation products on sample surfaces where conventional extraction/analysis methodologies do not work.

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