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Static secondary ionization mass spectrometry and mass spectrometry/mass spectrometry (MS^2) characterization of the chemical warfare agent HD on soil particle surfaces

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Abstract

Detection of the blister agent HD [bis(2-chloroethyl)sulfide] or distilled mustard directly on the surface of soil particles using ion trap secondary ion mass spectrometry in the static mode is demonstrated. HD by its very nature is adsorptive; this attribute makes detection of surface adsorbed HD by gas-phase approaches difficult, but renders the compound amenable to surface detection. Two different ion trap (IT) mass spectrometers, modified to perform secondary ionization mass spectrometry using a ReO_4^- primary ion beam, were employed in the present study. Sputtered ions were trapped in the gas phase in the IT, where they could be scanned out (MS^1), or isolated and fragmented (MS^2). The intact HD molecular ion was not observed, however an abundant ion corresponding to $[HD - Cl]^+$ was formed, as were lower mass fragment ions, and ions derived from the chemical background. Ab initio calculations were used to propose structures of the fragment ions. At 0.5 monolayers surface coverage, $[HD - Cl]^+$ and lower mass HD fragment ions were significantly more abundant than the background. At lower concentrations, however, the HD secondary ion signal became masked by the background. Sensitivity and selectivity were significantly improved in the MS^2 mode of operation. MS^2 of $[HD - Cl]^+$ resulted in production of analytically diagnostic $C_2H_4SH^+$ and other S- and Cl-bearing fragment ions. HD was detected at 0.07 monolayers using the MS^2 approach, which corresponds to 108 ppm on a mass/mass basis. (Int J Mass Spectrom 208 (2001) 135–145) © 2001 Elsevier Science B.V.

Key words: Secondary ion mass spectrometry; Blister agent; Distilled mustard; Chemical agent; Surface analysis

1. Introduction

Bis(2-chloroethyl)sulfide, also known as distilled mustard or HD, is a chemical warfare agent (CWA) that was developed prior to the First World War, and

became the blister agent by which all others have been judged [1]. It was considered to be the most effective chemical agent used in World War I, because it could be readily aerosolized, and was persistent on contact with enemy personnel. Dermal contact with HD caused blistering and lachrymation followed by pulmonary edema, which resulted in a slow death due to “dry land drowning.” For these reasons, the Chemical

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Weapons Convention bans the use and production of HD, and mandates the destruction of HD stockpiles [2,3]. HD, however, continues to be of interest because of use by Iraq against Iran and the Kurdish population in northern Iraq [4–7], along with the existence of stockpiles throughout the world.

HD displays variable behavior in the environment. It can remain intact on surfaces, undergo polymerization, or hydrolysis. In any case, it has been noted that the surface and surface-agent interactions have a major influence on degradation processes [8,9]. HD and its degradation products are persistent on environmental and anthropogenic surfaces. Consequently, there is ongoing interest in direct surface analysis for HD and its degradation products, without subjecting samples to thermal or liquid extraction techniques, which could bias characterization results.

Early analytical efforts focused on structural analysis and identification using low and high resolution electron- and chemical ionization (CI) mass spectrometry (MS) [10]. This work showed an abundant $[\text{HD}]^+$ ion for HD using electron ionization, and abundant $[\text{HD} + \text{H}]^+$ and $[\text{HD} - \text{Cl}]^+$ ions using methane and isobutane CI, respectively. Later work confirmed the salient CI fragmentation chemistry of HD, in which the most abundant fragment ion $[\text{HD} - \text{Cl}]^+$ is formed by loss of HCl from the base peak $[\text{HD} + \text{H}]^+$ [11]. However, the main problem to be overcome in an analytical scheme is not the spectral identification, but separation of the chemical agent from the environmental matrix. To achieve this, HD and its degradation products have been effectively extracted from soils, environmental samples, and charcoal canisters using sequential extractions with hexane/methylene chloride, or methylene chloride and water. Subsequently, the extracted compounds were detected (with or without derivatization) using gas chromatography (GC), GC/MS, or GC-MS² [12,13]. Picogram limits of detection could be achieved using these techniques [14–16].

Derivatization can be avoided by using liquid chromatography techniques, in tandem with atmospheric pressure chemical ionization mass spectrometry, electrospray mass spectrometry and flame photometric detection. These techniques are capable

of detecting chemical agents at the ppm to ppb ($\mu\text{g/L}$) level. Like the GC based techniques, multiple extractions and filtration are required prior to analysis to separate the analytes from the sample matrix [17,18]. Solid adsorbents and adsorbent resins have also been used to isolate and concentrate HD from air and H₂O samples. Subsequent chromatographic analysis resulted in detection well into the ppb concentration range [19].

Because of the toxicity of HD and related compounds, rapid analysis is desirable for some applications. This requirement, and the fact that some compound/surface combinations resist extraction or thermal desorption, would suggest a detection approach that does not utilize these extraction schemes. One such approach is NMR spectroscopy (¹H and ³¹P¹H), which has been used to detect HD on solid samples at concentrations in the low ppm range [20]. An alternative approach is secondary ion mass spectrometry (SIMS), which was employed in the present study because it enables the direct interrogation of surface adsorbed chemicals. SIMS has been employed for the detection of a variety of highly surface-adsorptive compounds on naturally occurring surfaces, notably tri-*n*-butyl phosphate [21,22], nitrogen based mustards [23], alkylmethylphosphonates [24,25], the nerve agent VX (methylphosphonothioic acid, S-[2-[bis(1-methylethyl)amino]ethyl] O-ethyl ester) [26,27], and the HD surrogate, 2-chloroethylethyl sulfide [28,29].

Separation of the compound from the matrix is accomplished in SIMS by bombarding the sample surface with an energetic projectile, which sputters adsorbed molecules into the gas phase. In the present study, the polyatomic projectile ReO_4^- is utilized [30,31], which has been demonstrated to be superior to atomic projectiles for “sputtering” intact adsorbates from the surface into the gas phase [32]. Some fraction of the sputtered molecules will be ionized, and these ions are trapped in the thermal He bath gas that is present in the ion trap’s mass analyzer (IT-SIMS). Once trapped, the analyte ions, as well as “background” ions can be sequentially scanned out of the trap by mass and detected, thus generating a mass spectrum (MS¹). 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. In most cases, this approach eliminates the background signal from the fragment ion region of the mass spectrum, and significantly improves the signal to noise ratio of the ions of interest.

In the present study, the utilization of the IT-SIMS for the detection of HD on soil particles is reported, and demonstrated to be complementary to gas phase detection techniques. The results show that the detection of small quantities of HD is highly amenable to the IT-SIMS approach. Although SIMS of environmental samples is not a high precision technique, detection can be accomplished at a fraction of the time relative to conventional analytical methods that require multiple extractions. As a result of utilizing MS^2 at low monolayer coverage, the fragment ion chemistry of $[HD - Cl]^+$ is also explored using both experimental and computational methods.

2. Experimental

2.1. Sample preparation

Caution: HD is an extremely hazardous chemical compound capable of causing severe injury at low doses. All sample preparation was performed at the U.S. Army West Desert Test Center (WDTC) chemistry laboratory, Dugway Proving Ground, Dugway, UT. The WDTC facility is equipped with appropriate administrative and engineering controls for handling blister agents.

Clean soil samples obtained from the Edison, NJ, area near the former Raritan Army Depot, were used in the present study. This material was chosen because it has been characterized previously during the course of earlier studies and has routinely been utilized in adsorbate research at this laboratory. The soil sample was predominantly silica in nature, with minor contributions from aluminum and iron, as determined using scanning electron microscopy and energy-dispersive x-ray analysis. The soil was sieved

and the surface area of the $0.0049 < \chi < 0.0098$ in. mesh fraction was determined to be $2.2 \text{ m}^2/\text{g}$ using N_2 adsorption (BET method).[33]

The HD used in this study was the property of the U.S. Army and was an analytical reference standard prepared from stock solutions of Chemical Agent Standard Analytical Reference Material (CASARM) grade HD. HD exposed soil samples were prepared at surface concentrations ranging from 0.5 to 0.036 monolayers, by covering ~ 100 mg of soil with $\sim 100\text{--}200 \mu\text{L}$ of a HD/isopropyl alcohol solution, and then allowing the solvent to evaporate. The mass of HD corresponding to monolayer coverage was estimated by assuming that the molecular area of the compounds was equivalent to $\sim 28 \text{ \AA}^2$, which is the area of a circle having a radius equal to half the length of the molecule (estimated at 3 \AA) on the surface. This estimate assumes that the molecule lays flat on the surface of the soil. If the molecule exists on the surface in an upright fashion, or was coiled, then the monolayer coverage will be somewhat less than the values calculated. 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 [25].

The HD exposed soil samples were allowed to dry under ambient conditions for a minimum of 2 h after spiking. Samples were prepared for analysis by attaching ~ 3 mg of soil to a sample holder (the head of a no. 18 nail) using double-sided tape (3M, St. Paul, MN) or self-assembly adhesive (3M, St. Paul, MN). The sample holder was then attached to the direct insertion probe and inserted into the vacuum chamber for analysis. SIMS analysis showed only ions derived from the HD-exposed soil, and not from the tape or adhesive. Therefore, we conclude that the soil particles are efficiently covering the tape surface.

2.2. Ion trap secondary ion mass spectrometry

The IT-SIMS instruments used in this research were based on modified ion traps available from commercial vendors: the first IT-SIMS was based on

a Teledyne Discovery 2 instrument (Mountain View, CA), and the second IT-SIMS was based on a Varian Saturn 2000 instrument (Walnut Creek, CA).[23,27] Both IT-SIMS instruments are similar in design and operation to the Finnigan based IT-SIMS instrument that is described in detail in [34].

Both instruments were equipped with a ReO_4^- primary ion gun [30,31] operating at 4.5–5.0 keV and mounted coaxial with the ion trap. The ReO_4^- beam enters the ion trap through an aperture in the endcap, passes along the main axis of the ion trap, and strikes the sample located behind the opposite endcap. The ReO_4^- ion guns were operated at a primary ion current of approximately 200 pA, which were measured using a Faraday cup. The ReO_4^- primary ion beams were gated to impact the sample only during the ionization period of the SIMS analysis sequence. A typical ionization period was 100 ms. By varying the length of the ionization period, the dynamic range of the instruments was varied over three orders of magnitude.

For both instruments, single analysis consisted of ~50–300 summed spectra. The primary ion dose for a typical analysis ranged from about $(1-5) \times 10^{10}$ ions/cm²; this value was calculated by using the ionization time, scan acquisition and beam current. Since the dose does not exceed 10^{12} – 10^{13} ions/cm² (referred to as the static SIMS limit), the surface of the sample is not considered to have been seriously perturbed [35]. Secondary ions sputtered from the sample surface were focused into the ion trap by a small cylindrical electrostatic lens. The electrostatic lens was also used for sample charge compensation utilizing “self charge stabilizing optics” [36]. Those secondary ions that lose sufficient kinetic energy within the ion trap as a result of collisions with the He bath gas, are trapped by the oscillating rf field. The nominal pressure in the system was 3×10^{-5} Torr (1 Torr = 133.3 Pa) of helium (uncorrected). The actual pressure inside the ion trap was estimated at 1×10^{-3} Torr. In a typical MS¹ experiment, the IT-SIMS was operated at base rf amplitude corresponding to a low mass cutoff of ~35 u. Once trapped, ions were mass selectively ejected from the ion trap (MS¹); alternatively, selected ions were mass isolated (vide

infra) and then dissociated through collisions with He bath gas (MS²). Ions were mass selectively ejected out of the ion trap onto an off-axis “venetian blind” dynode/electron multiplier assembly located between the primary ion gun and the ion trap. A diagram of the instrument has been previously published in [23,29].

The two instruments employed did not share the same sample insertion mechanism, vacuum configuration or ion isolation/excitation method. The Teledyne Discovery 2-based IT-SIMS was located in a surety laboratory at the WDTC. The vacuum housing/ion trap system was placed inside a CWA surety hood, where all chemical agent manipulations were performed. Samples were inserted into this instrument through a two-stage manual insertion lock with a direct insertion probe. Power supplies, electronics, computer, and mechanical backing pumps were located outside the hood, and were connected to the vacuum housing by means of elongated cables and hoses. The two mechanical backing pumps, which pumped the turbo and insertion lock, were vented back into the surety hood. The modified Teledyne Discovery 2-based instrument performed ion isolation using a filtered noise field applied to the endcaps during the ionization period; this served to eject all ions except those within the preselected mass window from the IT [37]. Ion excitation was performed using the same technique, except that the field was applied subsequent to the ionization period (after ion isolation).

The Varian Saturn 2000-based IT-SIMS was incorporated into a customized motor home, and represents the most recent generation of IT-SIMS instrumentation. This instrument was configured to allow field samples to be analyzed onsite. The instrument was equipped with an automated sample introduction system that did not require a manual sample insertion. Samples were attached to sample holders, which were placed under vacuum in a custom sample introduction chamber and then pneumatically inserted into the high vacuum chamber of the instrument. The instrument was pumped by two turbopumps: one for the vacuum housing and one for the sample introduction chamber. The turbopumps were backed by diaphragm pumps vented to external carbon filters. Ion isolation was

accomplished in this instrument using a selected ion storage field [37].

2.3. MINICAMS sample screening

Samples analyzed with the Varian Saturn 2000-based IT-SIMS instrument were screened prior to IT-SIMS analysis using Dugway Proving Ground Method WDC-CL-044R [38], which utilizes a MINICAMS series 3000 (CMS Field Product Group, Birmingham, AL) continuous air monitoring system. The Series 3000 MINICAMS is an automated GC system equipped with a flame photometric detector and solid phase preconcentrator, which achieves detection limits below TWA values for chemical agents in air. (TWA is defined as the Surgeons General's 8 h time-weighted-average for exposure to chemical agents. This is the chemical agent concentration that personnel can be exposed to over an 8 h period with no clinically observable effects.) The instrument was calibrated at 1 TWA HD (0.003 mg/m^3) and tested at 2 TWA ($\pm 25\%$) prior to sample analysis. After initial calibration, three samples of clean laboratory air were analyzed to ensure that no sample carryover was observed. At this time the HD-spiked soil samples, which were allowed to equilibrate inside a large polypropylene bag for 8 h, were analyzed. The minimum detection limit for HD specified in manufacturer literature is 0.0006 mg/m^3 .

2.4. Computational methods

Computations were performed using the General Atomic and Molecular Electronic Structure System (GAMESS) [39] program at the restricted Hartree-Fock (RHF) level of theory. The RHF calculations utilized the 6-311G basis set. All minima were located under C_1 symmetry. Vibrational frequencies were calculated for all stationary points to identify them as minima (zero imaginary frequencies). To include correlation contributions, single point energies were calculated with the Møller-Plesset second order perturbation theory (MP2) [40] at the RHF optimized geometries. Reported energies are corrected for the zero point energy and from absolute zero to 298.15 K

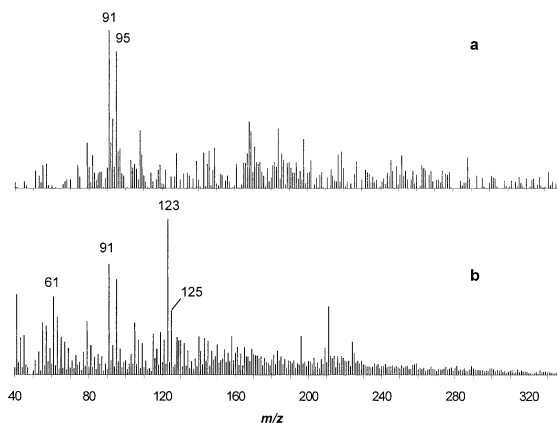


Fig. 1. (a) Cation IT-SIMS spectra of aluminosilicate soil particles not exposed to HD solution and (b) soil exposed to HD resulting in 0.5 monolayers coverage HD.

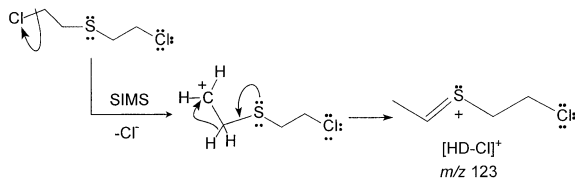
(using RHF vibrational frequencies). The enthalpies obtained from an RHF geometry/MP2 energy scheme showed good agreement with experiment results for a variety of the systems [41].

3. Results and discussion

3.1. SIMS behavior

Soil particles spiked at 0.5 monolayers of HD were initially analyzed using the Teledyne Discovery 2-based IT-SIMS. Although the cation SIMS spectrum of “clean” soil contains a variety of endogenous background ions [Fig. 1(a)], HD on the surface was clearly observable at a surface concentration of 0.5 monolayers [Fig. 1(b)]. The background signal is derived from organic adsorbates that are present on virtually every surface. However, the abundant ions at m/z 123 and m/z 61 were not observed in the spectrum of unexposed soil and are attributable to HD.

Ions observed at m/z 123 and 125 correspond to $[\text{HD} - \text{Cl}]^+$ that arise from the elimination of Cl^- from the intact HD molecule (^{35}Cl and ^{37}Cl , respectively). This behavior is analogous to that of 2-chloroethylethyl sulfide (2-chloroethylethyl sulfide: CEES, a HD simulant), which also undergoes cleavage of C–Cl during the SIMS event [28]. $[\text{HD} - \text{Cl}]^+$



Scheme 1. Postulated formation mechanism of m/z 123 observed in the cation spectrum of HD on soil.

is most likely formed from direct elimination of Cl^- upon SIMS bombardment (Scheme 1). Two alternative mechanisms were considered: (1) initial formation of $[\text{HD} + \text{H}]^+$ followed by loss of HCl , and (2) initial formation of HD^+ followed by loss of Cl^- . However, neither $[\text{HD} + \text{H}]^+$ nor HD^+ were observed in the SIMS spectrum, which does not support their involvement. In consideration of mechanism (1), the IT-SIMS is clearly capable of generating and stabilizing abundant protonated cations and $[\text{HD} + \text{H}]^+$ is the dominant ion in the Cl mass spectrum of HD [10]. Consequently, if $[\text{HD} + \text{H}]^+$ were formed, then it should be observable. Considering mechanism (2), static SIMS using the ReO_4^- projectile does not routinely produce abundant radical ions, however, an abundant HD^+ is observed in the EI spectrum [10]. Again, if HD^+ were formed, it should be readily observable. We speculate that a heterolytic cleavage of Cl^- with a hydride shift forms a carbosulfonium structure $[\text{HD} - \text{Cl}]^+$, which is more stable than its alternatives (e.g. 2-chloroethylthiiranium). This conclusion was supported by ab initio calculations (vide infra).

In addition to the ions observed at m/z 123 and 125, an abundant ion was observed at m/z 61, which is indicative of a sulfur-containing surface adsorbate. The composition of the ion observed at m/z 61, formed from CEES was previously probed using MS^3 , and found to eliminated C_2H_2 to form an ion at m/z 35 (H_3S^+), consistent with the composition of the parent ion $\text{C}_2\text{H}_5\text{S}^+$ [28]. Taken together, these ions are highly indicative of the presence of HD on the surface. When lower surface concentrations of HD were analyzed, however, the abundance of the HD-derived ions was comparable to that of the background, which obfuscated the HD SIMS signature.

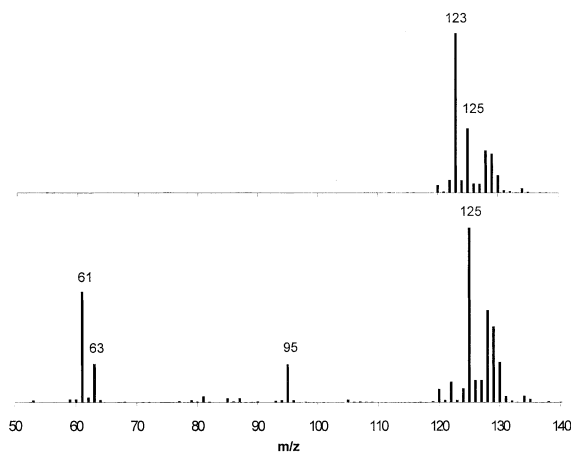
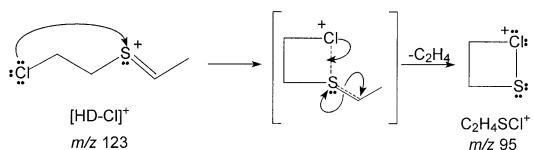


Fig. 2. Cation IT-SIMS MS^2 analysis of m/z 123 sputtered from soil particles exposed to 0.5 monolayer HD. Top, isolation of m/z 122–130. Bottom, tickle of m/z 123 with subsequent fragmentation.

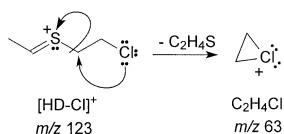
This fact required using MS^2 analysis for compound identification.

MS^2 was accomplished by isolation of $[\text{HD} - \text{Cl}]^+$ followed by fragmentation to form the m/z 95, 63, and 61 product ions (Fig. 2). The m/z 95 ion corresponded to $\text{C}_2\text{H}_4\text{S}^+$ and was formed by the loss of C_2H_4 . The best mechanistic possibility would involve attack of the Cl lone pair on the positive sulfur atom, forming a four-membered heterocyclic cation which could then eliminate the C_2H_4 moiety as a possible carbene (Scheme 2). The composition of the resulting $\text{C}_2\text{H}_4\text{S}^+$ was supported by MS^2 analysis, which resulted in the formation of $\text{C}_2\text{H}_3\text{S}^+$ (m/z 59) by elimination of HCl .

The formation of the m/z 63 ion from $[\text{HD} - \text{Cl}]^+$ likely occurs by Cl lone pair attack on the proximate α -carbon, resulting in the formation of $\text{C}_2\text{H}_4\text{Cl}^+$, and eliminating neutral thioacetaldehyde (Scheme 3). This elimination reaction was verified by MS^2 of the ^{37}Cl isotopic ion at m/z 125: the fragment ion was observed



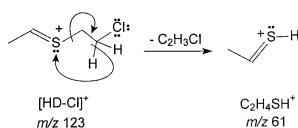
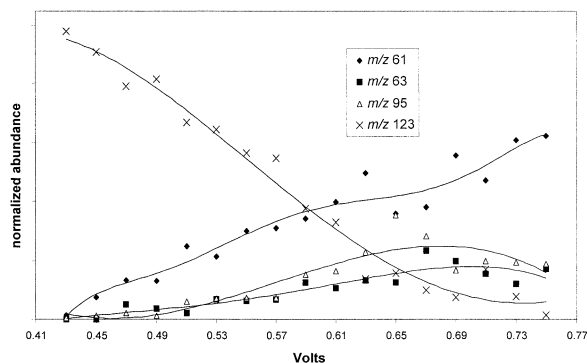
Scheme 2. Proposed formation of $\text{C}_2\text{H}_4\text{S}^+$ from $[\text{HD} - \text{Cl}]^+$.

Scheme 3. Proposed formation of $\text{C}_2\text{H}_4\text{Cl}^+$ from $[\text{HD} - \text{Cl}]^+$.

at m/z 65, which corresponds to the mass of $\text{C}_2\text{H}_4^{37}\text{Cl}^+$.

The most abundant fragment ion in the MS^2 spectrum of $[\text{HD} - \text{Cl}]^+$ was observed at m/z 61, which we believe corresponds to protonated thioacetaldehyde. The fragment ion arises by way of the elimination of vinyl chloride, and may involve a β -hydride transfer from the departing neutral to the ion (Scheme 4).

Relative ion abundances are strongly influenced by collision induced dissociation, or tickle voltage (V_{tickle}). Consequently, this parameter was systematically varied so that the observation of the m/z 61, 63, and 95 fragment ions was optimized (Fig. 3) using the Varian Saturn 2000-based IT-SIMS instrument. No fragmentation was observed until the V_{tickle} was increased to 0.45 V, whereupon the m/z 61 ion was observed. Further increases in V_{tickle} resulted in the slight appearance of the m/z 63 and 95 ions at 0.47 V. As the V_{tickle} was increased, the fractional abundance of the m/z 123 ion continued to decrease, the m/z 61 ion continued to increase, and the m/z 95 and 63 ions slowly peaked at approximately 0.67 V. The results suggest that the lowest energy fragmentation pathway is the elimination of vinyl chloride to produce the protonated thioacetaldehyde (m/z 61), and indicates that a V_{tickle} in excess of 0.47 V is required in order to observe the less abundant fragment ions. A V_{tickle} value of 0.58 V was adopted for the routine MS^2 analysis of HD using the Varian Saturn 2000-based system; at this voltage, $[\text{HD} - \text{Cl}]^+$ is efficiently

Scheme 4. Proposed formation of $\text{C}_2\text{H}_4\text{SH}^+$ from $[\text{HD} - \text{Cl}]^+$.Fig. 3. Plot of normalized abundance vs. tickle voltage (volts) for isolated $[\text{HD} - \text{Cl}]^+$ (m/z 123), and three fragment ions.

converted to fragment ions, and ion losses due to ejection from the IT are minimized.

The MS^2 behaviour of $[\text{HD} - \text{Cl}]^+$ enabled the ion observed at m/z 123 to be distinguished from the chemical background observed at that mass. This conclusion was reached by performing MS^2 of the m/z 123 ion produced from unexposed soil, which showed elimination of 28 mass units to form the m/z 95 ion. However, the ion did not eliminate $\text{C}_2\text{H}_4\text{S}$ or $\text{C}_2\text{H}_3\text{Cl}$. Further, the ion observed at m/z 95, derived from the background, did not eliminate HCl.

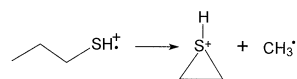
3.2. Comparative results

Because of the highly adsorptive nature of HD, the compound would certainly be partitioned between the gas phase and the surfaces in any exposed environment. Hence, one objective of the present study was to evaluate whether the IT-SIMS analysis could provide information complementary to that generated using an analysis of the gas-phase environment. 100 mg soil samples were exposed to HD such that a range of concentrations were generated (from 0.5 monolayers to 0.036 monolayers). The headspace of these samples was then analyzed using DPG Method CL-044R [38]. The 100 mg samples at 0.5 monolayers indicated the presence of HD at concentrations well below the action level (1 TWA). HD was not detected in the headspace of any of the other samples. These results are directly influenced by the small sample size and large bag volumes.

The HD-exposed samples were subsequently analyzed using IT-SIMS in the MS² mode, monitoring the 123 → 61 transition (within 1 h of sample screening and within 10 h of sample preparation). HD was detected on all Raritan soil samples down to, but not including the 0.036 monolayer surface concentration. The lowest surface concentration at which HD was detected was 0.07 monolayer, which corresponded to 108 ppm (mass/mass) for a 2.21 m² g⁻¹ soil sample. In these experiments, the MS¹ abundance of [HD - Cl]⁺ was indistinguishable from the background, but the MS² fragmentation was above the detection criteria (defined as a S/N ratio of 3:1, where the noise was measured by analyzing three replicate blank soil samples).

Typically, the precision in measuring ion abundances in static SIMS analyses of environmental samples is on the order of 30% (1σ), and this value increases to 50 to 100% as the surface concentration decreases. That was the case in the present experiments, however, the number of samples analyzed at the 0.07 monolayer surface concentration was not sufficient to enable rigorous calculation of a standard deviation. These results were very similar to the precision achieved in the analyses of CEES [29] and tri-*n*-butyl phosphate [22] on soil particles, in which it was possible to generate linear calibration plots of secondary ion abundance versus monolayer surface concentration. These results would suggest that the approach could be utilized for a quantitative measurement; however, the term “semiquantitative” is a better description, i.e., the correct order of magnitude can be readily deduced, but accuracy beyond this is not routine, principally as the result of substantial variability that can be encountered when analyzing soil samples of only 3 mg.

Despite the limitations in precision, the results demonstrated that for small samples, a surface detection approach can be more effective than one that relies on detecting molecules in the gas phase. Clearly, there are many scenarios where characterization of the atmospheric environment is the most important analytical objective; however, even in these cases, consideration of the surface contamination can



Scheme 5. *n*-propanethiol ion fragmentation.

provide complementary knowledge of the exposure area.

3.3. Computational results

The observation of the secondary, HD-derived ions, and assignment of their composition, provoked extensive discussion regarding ion structure. We sought to gain additional insight into the thermodynamics of the possible ion structures by performing RHF calculations, which resulted in enthalpy of formation values for possible isomers. Certainly, these thermodynamic results cannot be blindly extrapolated to the present system, because the reaction kinetics and barrier heights are not taken into account. However, in the SIMS event, secondary ions are formed having a wide range of internal energies, which implies that a significant fraction would be sufficiently activated to traverse isomerization barriers encountered in C_xH_yS⁺ systems. Furthermore, the long lifetimes of ions in the IT-SIMS (milliseconds) provide sufficient time for the formation of kinetically slow, but thermodynamically favored products. Hence, while caution must be exercised in application of the calculated structures to the present system, they may well be suggestive of probable isomers.

The initial task was to test the validity of the RHF optimization and RHF/MP2 energy scheme for these systems, which was accomplished by comparing benchmark calculations to values cited in the literature. The ion (CH₃)₃S⁺ was calculated to compare bond lengths. The experimental literature values for the C–S bond lengths are 1.79–1.81 Å [42]. The calculated C–S bond lengths are in good agreement at 1.87 Å, a difference of roughly 4%. To evaluate the RHF method for ΔH_{Rxn} accuracy, the reaction enthalpy was calculated for elimination of CH₃ from ionized *n*-propanethiol (Scheme 5) and was in excellent agreement with the experimental value, which

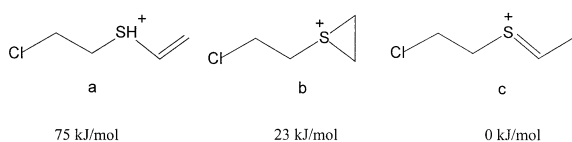


Fig. 4. Possible sulfonium ion structures for $[\text{HD} - \text{Cl}]^+$; (a) vinyl sulfonium structure; (b) thiiranium structure; and (c) carbosulfonium structure. ΔH_{Rxn} values are relative to structure C.

was estimated as endothermic by 125 kJ mol^{-1} [43]. The RHF computational scheme used in the present study resulted in a calculated reaction enthalpy of 122 kJ mol^{-1} .

All computational attempts to locate a carbon-centered cation for $[\text{HD} - \text{Cl}]^+$ were unsuccessful, which is not unexpected since the primary carbocation, formed from simple C–Cl cleavage would be expected to be unstable. Three possible structures having improved stability were envisioned (Fig. 4). If the sulfur abstracts a proton from the vicinal carbon, a vinyl sulfonium compound is formed [Fig. 4(a)]. If the sulfur attacks the nascent primary carbocation, a thiirane structure is formed [Fig. 4(b)]. The last possibility is the carbocation abstracting a hydride from the vicinal carbon, leading to a carbosulfonium structure, containing a carbon–sulfur double bond [Fig. 4(c)]. It was found the carbosulfonium structure [Fig. 4(c)] was the most stable of the three structures, lying 23 kJ mol^{-1} below the ΔH_{Rxn} of the thiirane and 75 kJ mol^{-1} below the vinyl sulfonium [Fig. 4(a)] structure. If the barriers separating these compounds are relatively low, the carbosulfonium structure will be generated. Calculated potential energy surfaces are beyond the scope of this article, but a more detailed computational study of these reactions is currently underway.

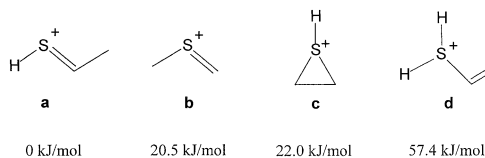


Fig. 5. Possible structures for m/z 61; (a) protonated thioacetaldehyde; (b) methyl carbosulfonium; (c) protonated thiirane; and (d) protonated vinyl mercaptan. ΔH_{Rxn} values are relative to structure A.

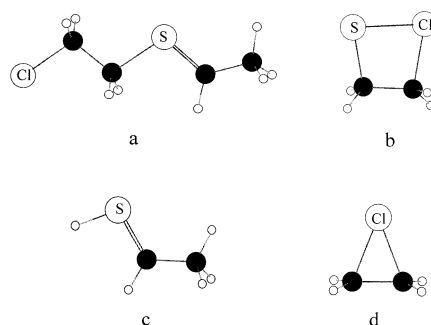


Fig. 6. Calculated fragment cations. Important geometric parameters: (a) $\text{S} = \text{C} = 1.67 \text{ \AA}$, $\text{S}-\text{C} = 1.93 \text{ \AA}$, $\text{C}-\text{S}-\text{C} = 105^\circ$; (b) $\text{S}-\text{Cl} = 2.30 \text{ \AA}$, $\text{S}-\text{C} = 1.91 \text{ \AA}$, $\text{C}-\text{S}-\text{Cl} = 78^\circ$, $\text{S}-\text{Cl}-\text{C} = 75^\circ$; (c) $\text{S} = \text{C} = 1.68 \text{ \AA}$, $\text{C}-\text{C} = 1.47 \text{ \AA}$, $\text{S}-\text{H} = 1.37 \text{ \AA}$, $\text{C}-\text{S}-\text{H} = 100^\circ$; (d) $\text{Cl}-\text{C} = 2.01 \text{ \AA}$, $\text{C}-\text{C} = 1.44 \text{ \AA}$, $\text{C}-\text{Cl}-\text{C} = 42^\circ$, $\text{C}-\text{C}-\text{Cl} = 69^\circ$.

Nibbering et al. [43] suggested four possible ion structures for the ion observed at m/z 61 in the spectrum (see Fig. 5). The protonated thioacetaldehyde structure [Fig. 5(a)] is the most stable. Calculated energies listed in Fig. 5 are with respect to the thioaldehyde structure. Protonated vinyl mercaptan [Fig. 5(d)] is unlikely since it is 57 kJ mol^{-1} higher in energy. The methyl carbosulfonium [Fig. 5(b)] and the protonated thiirane [Fig. 5(c)] are close enough in energy to be energetically feasible; however, the methyl carbosulfonium [Fig. 5(b)] is very unlikely, if starting from $[\text{HD} - \text{Cl}]^+$, because of the number of bonds that would have to be broken. Protonated thiirane [Fig. 5(c)] could be formed if the ion observed at m/z 123 has the thiirane structure previously discussed in Fig. 4(b). However, if starting from the vinyl sulfonium ion [Fig. 4(a)], the most likely structure for the m/z 61 ion is obviously the protonated thioacetaldehyde structure [Fig. 5(a)].

The calculated structures for the four major fragment ions are illustrated in Fig. 6, and the calculated enthalpies for the ionic fragmentation reactions (Schemes 2–4) are listed in Table 1. Schemes 2 and 4 are both in the range of estimated reaction enthalpies for the fragmentation of thiol radical cations listed in [43]. The large disparity between reaction enthalpies can be explained by ring strain. The large reaction enthalpy for scheme 3 is likely due to the product ion being a very strained three-membered ring, $\text{C}_2\text{H}_4\text{Cl}^+$.

Table 1
Reaction enthalpies

Scheme no.	ΔH_{Rxn} (kJ mol ⁻¹)
2	236
3	821
4	91

The C–Cl–C would prefer to be closer to the angle in an unstrained bent molecule such as (CH₃)₂S, where C–S–C = 105°. The C–Cl–C angle is very strained, though, at 42°. Scheme 2 is significantly higher in reaction enthalpy than scheme 4, also likely due to the strained sulfur and chlorine atoms in the product, a four-membered ring (C₂H₄SCI⁺). Instead of the ideal angle of 105°, the C–S–Cl angle is 78°, and the S–Cl–C angle is 75°. In contrast, the product of scheme 4 does not have a strained ring as a product.

4. Conclusions

The results of this research demonstrate that adsorbed HD can be easily characterized on soil surfaces using ion trap SIMS, and that surface analysis for the presence of HD on particle surfaces is a valuable complement to gas-phase analyses. Detection can also be accomplished at a fraction of the time relative to conventional analytical methods that include extraction steps. Detection using SIMS was based on the collision-induced fragmentation behavior of the [HD – Cl]⁺ ion, which is produced instead of the protonated molecule (as in chemical ionization). MS² of [HD – Cl]⁺ results in production of S- and Cl-bearing fragment ions that are diagnostic for HD, and distinguish the ion from the chemical background that is present on naturally occurring surfaces such as soil particles. Using a MS² approach to discriminate against the chemical background, detection of 0.07 monolayers (equivalent to 108 ppm on a mass/mass basis) was achieved with no wet chemical separation or sample cleanup. Although superior detection limits for HD are obtainable using extraction-based methods, the sensitivity, and speed of the IT-SIMS analysis are attractive for on-site or environmental screening

applications. The IT-SIMS approach is also appealing because of the sensitivity of the technique for the detection of polymeric sulfonium ions, which are formed under hydrolyzing conditions, and cannot be detected using gas-phase approaches [28]. These results highlight the applicability of the IT-SIMS approach for detection of strongly adsorbed chemical species on solid environmental surfaces, where toxicity and sample size are problematic.

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