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Characterization of Environmental Samples using Ion Trap-Secondary Ion Mass Spectrometry

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Abstract

2-Chloroethyl ethyl sulfide (CEES) is used as a simulant for mustard (HD) in a study to develop secondary ion mass spectrometry (SIMS) for rapid, semi-quantitative detection of mustard on soil. Using SIMS with single-stage mass spectrometry, a signature for CEES can be unequivocally observed only at the highest concentrations (0.1 monolayer and above). Selectivity and sensitivity are markedly improved employing multiple-stage mass spectrometry (MS^n) using an ion trap. $C_2H_5SC_2H_4^+$ from CEES eliminates C_2H_4 and H_2S, which are highly diagnostic. CEES was detected at 0.0012 monolayer on soil. A single analysis could be conducted in under 5 minutes.

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Introduction

The detection of chemical warfare agent residues on environmental surfaces is an important analytical activity because of the potential for proliferation of these weapons, and for environmental monitoring in areas where they are stored. Historically, one of the most widely used agents has been *bis*(2-chloroethyl) sulfide, also known as mustard gas and HD. It was initially used in combat in 1917; by the end of the First World War, more than 16% of all casualties were due to chemicals, in most cases mustard.[2] Manufacture of mustard is continuing to this day; consequently, there are ongoing opportunities for exposure.[3]

Under some conditions, detection of mustard can be challenging. The compound is a semivolatile liquid under ambient conditions, and can strongly adsorb to many surfaces.[3d] These factors can serve to confound many detection approaches; nevertheless several analytical schemes have been successfully adopted. Among these are a variety of chromatographic methods,[3d,4] some of which utilize mass spectrometry as a detector.[3d,5] All of these techniques rely on getting the compound into the gas phase.

An alternative approach is presented in this report, which directly targets strongly sorbed organosulfides. Static secondary ion mass spectrometry (SIMS) can be used to analyze adsorbed contaminants on soil, and has been applied to the detection of organic phosphates[6] and amines[7] in our laboratory. When SIMS is combined with the MS/MS capability of an ion trap mass spectrometer,

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remarkable improvements in detectability have been realized.[8] In this report, the SIMS behavior of the mustard surrogate compound 2-chloroethyl ethyl sulfide (CEES) is explored. It is found that the fragmentation behavior of CEES permits the compound to be distinguished from background, which in turn enables detection at concentrations of one thousandth of a molecular layer. The work builds upon a previous study conducted in our laboratory which showed that SIMS could be used to detect ionic condensation products (organosulfonium ions) originating from CEES degradation.[9]

Experimental

Samples. Soil samples were collected from three sites which have had a history of CW utilization: Dugway Proving Ground (Utah), Rocky Mountain Arsenal (Colorado), and the Raritan Arsenal (New Jersey). The samples were predominantly silicate in nature, with minor contributions from aluminum and iron, as determined using scanning electron microscopy and energy dispersive X-ray analysis. The surface areas of the soils were measured using N_2 adsorption (BET method).[10]

The samples were exposed to CEES, by wetting the soil surface with methylene chloride solutions of the compound, one µl solution to one mg soil. This ratio just wets the soil, but does not leave a lot of standing solution. The monolayer coverage on the soil particles could be calculated using the mass of CEES in the wetting solution, the mass of the soil, the surface area, and assuming 20 $Å^2$ per molecule. This method has been used successfully for generating samples having known surface coverages.[6] The wetted soil samples were allowed to dry, and were then prepared for SIMS analysis by attaching particles to a sample holder using double-sided tape.

Ion Trap SIMS. The instrument used in this study was a Finnigan ITMS instrument equipped with a ReO_4^- primary ion gun.[8,11] This primary particle provides enhanced production of molecular secondary ions, which is advantageous when probing surface adsorbates.[12] The primary ion gun is mounted directly behind one end cap, and produces a beam of ReO_4^- particles which enter the ion trap through a 1 mm hole in the end cap. The particles traverse the ion trap, and impact the sample, which is positioned behind holes in the opposite end cap. The resulting secondary ions drift back into the ion trap, where they are trapped. The primary ion gun was operated at 4.58 keV, at an ion current of 400 picoamperes. Since a typical MS/MS acquisition required approximately 50 seconds, the dose administered to the sample is calculated to be 1.6×10^{13} ions/cm^2. The instrument was operated at a He pressure of 8.5×10^{-5} torr (ion gauge).

In a typical MS experiment, the ion trap was operated at $a_z = 0$, and $q_z = 0.9078$, which corresponds to a low mass cutoff of 40 amu ($\beta = 0.9802$). Ionization time was typically 20 milliseconds, after which the mass spectrum was recorded using a mass selective instability scan with axial modulation.[13] A single "scan" consisted of ten summed spectra.

For MS/MS experiments, the ionization time was typically longer (100 - 1000 milliseconds), during which time a filtered noise field[13] was applied to the end caps, such that *m/z* 89 was isolated. In experiments involving MS^2 of endogenous 89 (likely $C_7H_5^+$), the low mass cutoff was 40 amu, and the frequency range corresponding to the notch required to isolate *m/z* 89 was 166 - 169 kHz at 8.0 V. After forming and isolating the ion, it was then fragmented by applying the same frequency to the end caps at a voltage of 0.65 V. These conditions did not result in efficient fragmentation of the *m/z* 89$^+$ arising from CEES. For this experiment, a low mass cutoff of 25 was used: in this case, *m/z* 89 was isolated and fragmented using an end cap frequency range of 100 to 102 kHz. For isolation, a voltage of 6.0 V was used; for fragmentation, a voltage of 0.6 V was used.

The MS/MS/MS experiments were identical to the MS/MS experiments for CEES-derived *m/z* 89, except that a filtered noise field was added subsequent to the first tickle fragmentation, which had the effect of isolating *m/z* 61 as the daughter ion from *m/z* 89 (149 to 156 kHz, 7.0 V). *M/z* 61 was then tickled at the same frequency, at 1.0 V, which produced fragment ions of only *m/z* 61.

Results and Discussion

A SIMS spectrum containing a wide variety of ions is recorded when soil is analyzed (Figure 1). Most of the ion signal originates from hydrocarbon background. It has been speculated that this originates from pump oil background in instruments, and MS^2 analyses of *m/z* 91 and 89 seems to confirm this: both ions undergo loss of C_2H_2 to form *m/z* 65 and 63, respectively, which is what would be expected from ions having compositions of $C_7H_7^+$ and $C_7H_5^+$. Frequently, *m/z* 95 is the base peak in the spectrum. This ion arises from the reaction of $C_6H_5^+$ with water in the ion trap. This is clearly an efficient gas-phase reaction: very little *m/z* 77 is observed in the spectrum, but when this ion is ejected during ionization, *m/z* 95 practically disappears.

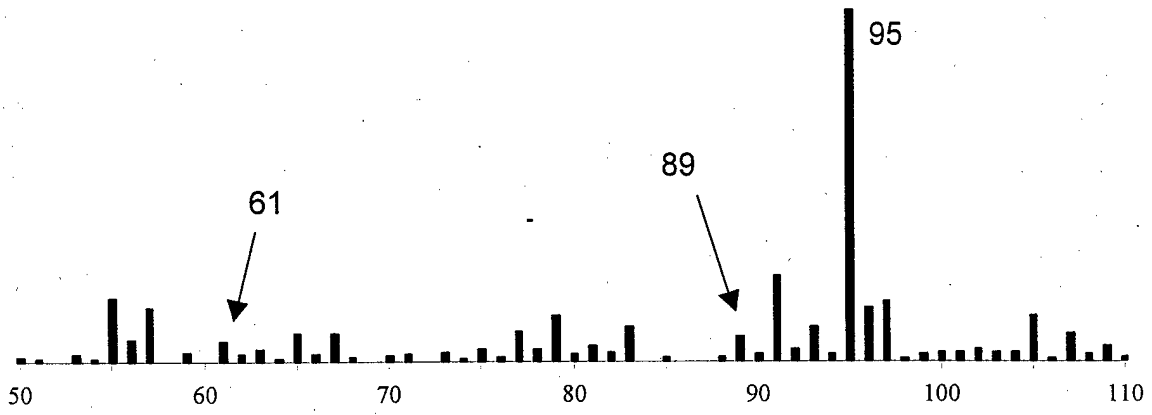
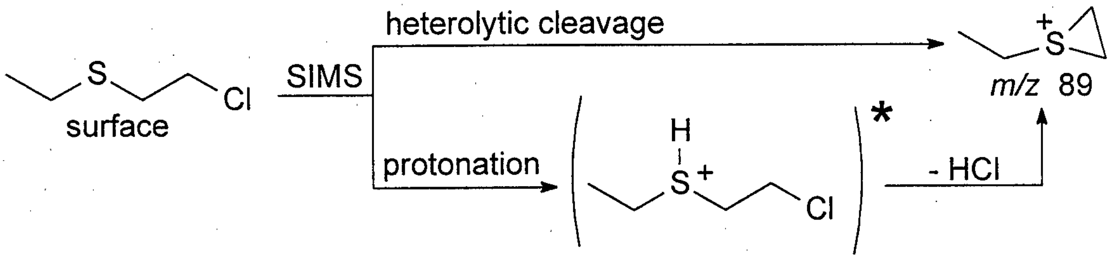


Figure 1. Partial cation SIMS spectrum of 0.03 monolayer CEES on soil, acquired using the ion trap SIMS instrument. Ions at *m/z* 89 and 61 are partially derived from CEES; other ions are background.

When soil samples doped with CEES were analyzed, the spectra collected were similar to the undoped benchmark, but contained an ion at *m/z* 89, which corresponds to $[\text{CEES-Cl}]^+$. Ions corresponding to the protonated, intact molecule were not observed above background. We can envision two mechanisms for the formation of *m/z* 89 upon SIMS activation: 1) heterolytic cleavage of the C-Cl bond, or 2) protonation of CEES to form an unstable cation which rapidly eliminates HCl (Figure 3). We favor the heterolytic cleavage mechanism at this time, since the He bath gas in the ion trap serves to stabilize gas-phase ion species,[14] and stable protonated mustard species have been reported.[15]



Scheme 1. Possible formation mechanisms for *m/z* 89^+, observed in the cation spectrum of CEES on soil.

The identity of *m/z* 89 was proven by MS/MS and MS/MS/MS experiments. *M/z* 89 was isolated using a filtered noise field and then fragmented. Abundant daughter ions were observed at *m/z* 61 and 55, representing the loss of 28 (C_2H_4) and 34 (H_2S) mass units, respectively (Figure 2, Scheme 2). It was noted that these losses were significantly different than those observed from the endogenous *m/z* 89, which only eliminated C_2H_2 to produce *m/z* 63. Further, the elimination of 34 amu is highly diagnostic for a sulfur bearing ion. This reaction must involve substantial rearrangement to produce the $C_4H_7^+$ daughter ion at *m/z* 55; in fact, extensive rearrangement of $C_3H_7S^+$ prior to elimination of H_2S has been observed.[16] The composition of the *m/z* 61 daughter ion was further probed by adding another ion isolation and fragmentation step to the experiment. This showed the elimination of C_2H_2 to form *m/z* 35; this unusual cation is most likely H_3S^+.

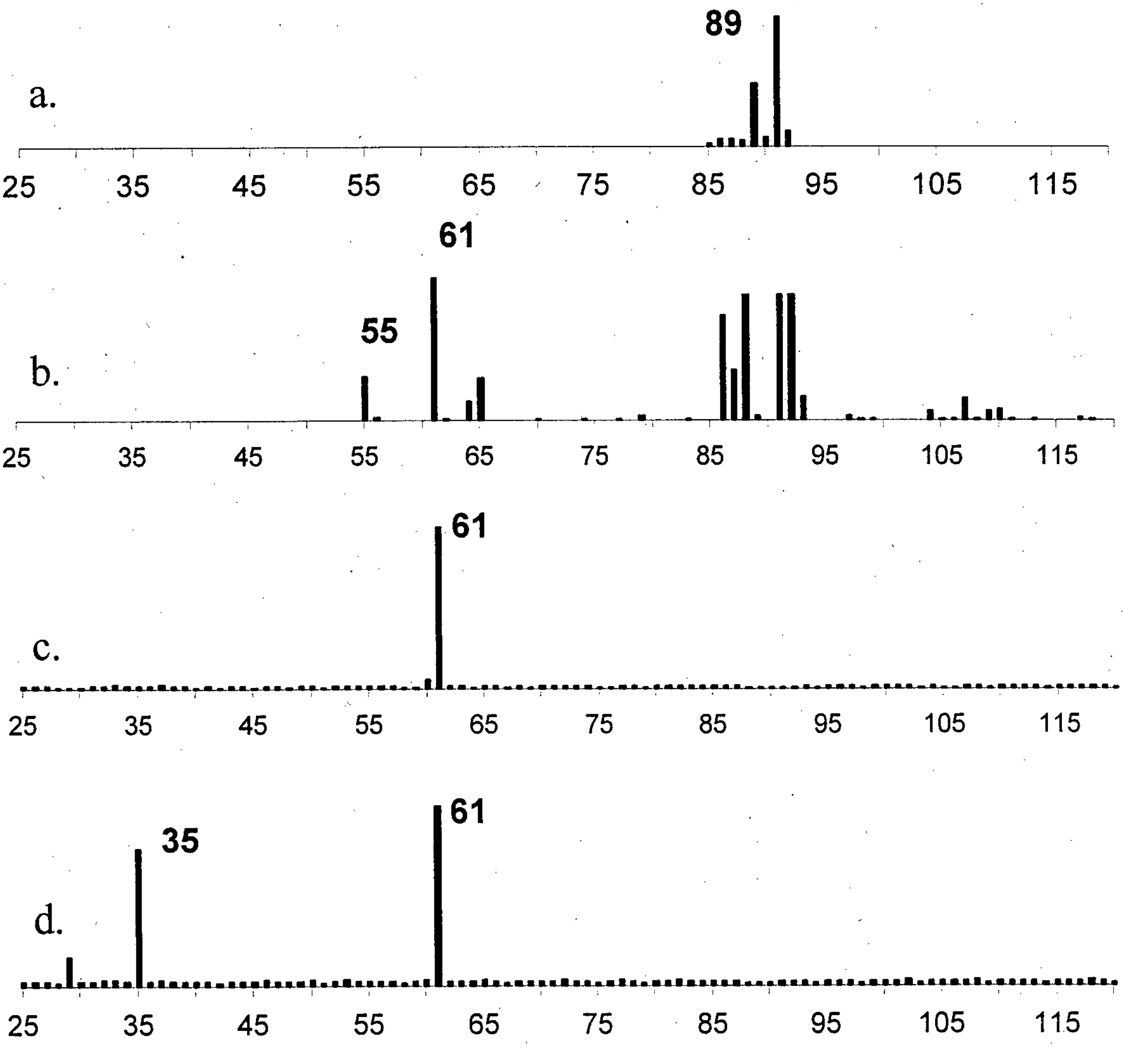
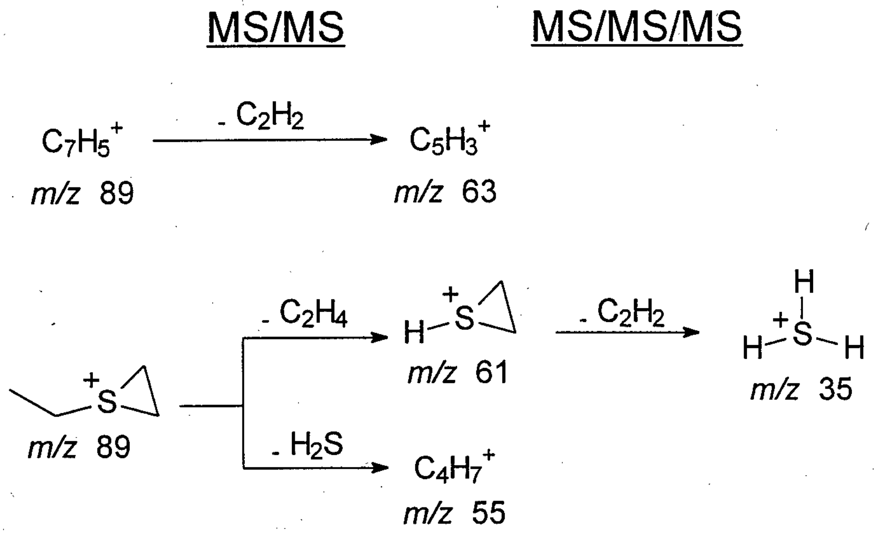


Figure 2. MS^n fragmentation of *m/z* 89 from SIMS analysis of CEES. a, isolation of *m/z* 89 (and 91). b, fragmentation of *m/z* 89 to form 61 and 55. c. Isolation of *m/z* 61. d. Fragmentation of *m/z* 61 to form *m/z* 35.

The structure proposed for *m/z* 89 is the ethyl thiiranium ion, and is consistent with structures proposed for other sulfur bearing species.[17] This ion was most efficiently trapped using a low mass cutoff of 25 amu. This setting also had the effect of discriminating against the fragmentation of $C_7H_5^+$; we rationalize that the elimination of C_2H_2 from $C_7H_5^+$ is energetically more rigorous than the elimination reactions of $C_2H_5SC_2H_4^+$. Lowering the low mass cutoff tends to discriminate against those fragmentations which are energetically more demanding.



Scheme 2. Fragmentation of *m/z* 89. Top, fragmentation of endogenous $C_7H_5^+$. Bottom, fragmentation of ethyl thiiranium$^+$ ($C_2H_5SC_2H_4^+$) formed from CEES.

A sensitive analysis of an adsorbate on soil requires an understanding of the behavior of the adsorbate signal with dose. The abundance of the CEES-derived ions was observed to decrease rapidly upon the initiation of ion bombardment. The decay in secondary ion signal is due to two factors. First, the primary bombardment event causes disappearance of the adsorbate from the surface of the sample, which in turn leads to lower secondary ion abundance. Secondly, operation of the insertion lock leads to a temporary enhancement of emission from the ReO_4^- primary ion gun. Consequently, when sensitivity was evaluated, the abundance of the *m/z* 89 daughter ions were measured over the initial, most sensitive part of the decay curve (first five scans of the analysis). No ion bombardment was performed prior to this.

Sensitivity was assessed by analyzing a series of soil samples that were generated such that the concentration of CEES on the surface of the soil ranged over three decades. The instrument was then set to isolate *m/z* 89, and detect the daughter ions subsequent to fragmentation. The daughter ions could be clearly observed at the lowest concentration studied, which was 0.0012 monolayer (for a 12 m^2/g soil sample, this corresponds to 15 ppm mass/mass). When ion abundance was plotted versus surface concentration (monolayers), a linear relationship was observed from 0.0012 to 0.3 monolayers (Figure 3). Analytical imprecision arising from sample preparation (factors such as fraction of the tape covered by the soil sample) prohibits a high accuracy determination at this time, however.

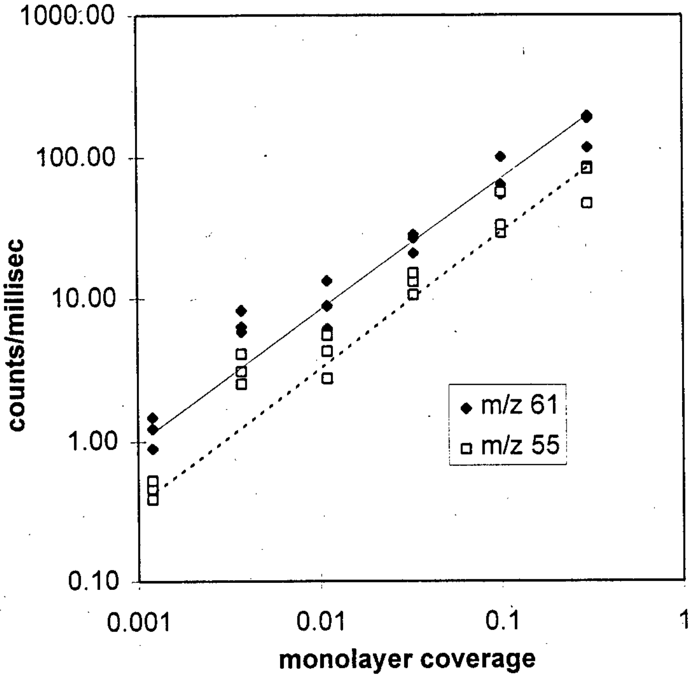


Figure 3. Absolute abundance of the *m/z* 89 daughter ions 61 and 55 versus surface concentration of CEES.

Conclusions

This research demonstrates that organosulfide adsorbates can be easily characterized on soil surfaces using an ion trap SIMS. An MS^2 approach provides the necessary specificity for detection of the analyte ions, which is achieved primarily through the diagnostic loss of H_2S. This elimination is unique compared to other elimination reactions common to endogenous hydrocarbon ions originating from the vacuum system or the environment. The uncorrected abundance of the analyte signal was clearly demonstrated to be proportional to the analyte surface coverage, which makes a semiquantitative assessment of contaminant concentration possible. The secondary ion signal of the adsorbed contaminant is a strong function of the primary ion dose. The analytical implications of this observation are that for the most sensitive detections, the initial portion of the decay curve should be utilized.

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