INEL/CON-97-00093
CONF-9705185--

RAPID DETECTION OF CW RESIDUES ON SOIL USING AN ION TRAP SIMS

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ABSTRACT

Technology for the rapid detection and identification of chemical warfare (CW) residues on soil samples is being developed at the Idaho National Engineering and Environmental Laboratory (INEEL). The development effort is being undertaken because of a need for rapid and specific characterization for possibly contaminated soil samples, preferably in the field. Secondary ion mass spectrometry (SIMS) is being pursued for these applications because SIMS combines rapid, specific and sensitive surface analyses with the potential for small instrument size. This latter attribute suggests that field characterization using SIMS is possible, and this avenue is being supported by the Army at the INEEL. This paper describes ongoing development efforts focused on the development of small-scale, transportable SIMS instrumentation, and on the application of the technology to likely contamination scenarios.

INTRODUCTION

A significant problem encountered at unexploded ordinance (UXO) sites is the possibility of a leak from suspect chemical munitions, releasing chemical warfare (CW) compounds into the environment. This problem is substantial because of the high toxicity of the compounds, which represents a safety hazard to remediation personnel working in the area. Consequently, the ability to rapidly detect and identify CW residues at or near remediation sites is highly desirable. However, detection is complicated because the most significant CW compounds readily undergo degradation reactions under environmental conditions, and the degradation products can strongly adsorb to soil surfaces. As a result, thermal desorption and solvent extraction techniques for analysis are frequently ineffective.

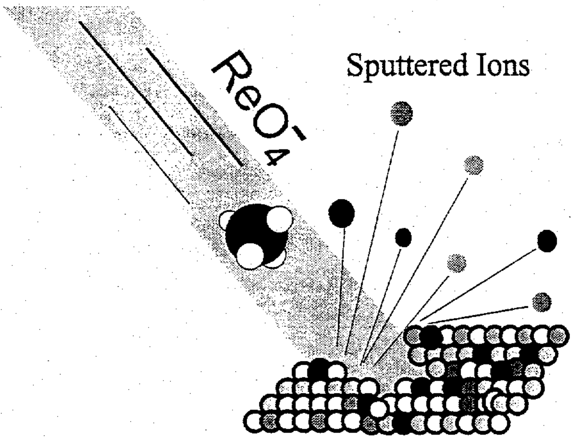

Figure 1. Schematic diagram of a sample surface being bombarded by an energetic particle (5000 electron volt ReO_4^-).

Secondary ion mass spectrometry (SIMS) is a technique which is particularly amenable to the detection of degraded CW compounds, because it interrogates soil surfaces where the CW residues reside. SIMS operates by bombarding the surface of a small (2 - 3 mg) soil sample with an energetic particle beam (Figure 1). This event causes “sputtering” of charged

molecules that are indicative of the identity of the CW residue. Initial demonstrations of this technique showed that approximately 0.1 monolayer of nerve agent and blister agent residues could be detected on soil surfaces. But detection of smaller quantities was hindered by the presence of ubiquitous background chemicals which reside on every surface in the ambient environment; these chemicals served to obfuscate the residue signature.

The chemical background can be ejected from the SIMS analysis using an ion trap mass spectrometer (IT-SIMS), which can also be used for identification of the CW residue by specific fragmentation reactions. This approach has improved the detection limit by two orders of magnitude (0.001 monolayer), and improved the specificity of the analysis. Further, the development of the IT-SIMS has also resulted in instrumentation which is smaller, more rugged, and more transportable. This report will describe progress in the development of the IT-SIMS instrumentation and simulated applications.

INSTRUMENTATION DEVELOPMENT

The development of the IT-SIMS instrumentation has involved major improvements in three areas: a.) the primary bombarding particle; b.) management of surface charging on the sample surface; c.) mass spectrometry/mass spectrometry utilizing an ion trap mass spectrometer. These three areas will be discussed sequentially.

a. Development of the ReO_4^- particle for surface bombardment. Current commercial instrumentation employs an *atomic* primary particle for surface bombardment. However, it has been widely known that *molecular* particles were capable of enhanced surface disruption.(Blaine, 1989; Hand, 1990) The problem with utilizing molecular primary ion guns was that none were in existence which were easy to use. Initial research at the INEEL was focused on employing neutral SF_6° as the primary bombarding particle.(Appelhans, 1989) Successful desorption and detection of organophosphorus compounds from vegetation surfaces validated the notion that improved detection could be achieved using the SF_6° molecular particle gun.(Delmore, 1991) However the SF_6° particle gun had drawbacks which made it incompatible with a small scale instrument, namely that it required an SF_6 cylinder, and a meter-long flight tube (which was needed for autoneutralization of kiloelectron volt SF_6^-).

Subsequent research into ion-emitting ceramics produced a $Ba(ReO_4)_2/Eu_2O_3$ material which would emit an abundant current of ReO_4^- when heated in vacuum.(Delmore, 1995) ReO_4^- was demonstrated to be equal, and in some ways superior to SF_6 for generating secondary ions from bombarded surfaces.(Groenewold, 1997) The technology was refined such that the ceramic was packaged in a rhenium cup one-two mm in diameter. Hence, the primary ion gun was amenable to miniaturization.

b. Development of charge management strategies for sample surfaces. The problem of surface charging largely arises because most insulating surfaces emit many electrons when they are bombarded by energetic particles. This results in the build-up of positive charge on the sample surface, that is deleterious to the emission of both negative and positive secondary ions. Most current commercial instrumentation addresses this problem using a compensating flood of low energy electrons over the sample surface. However, this again adds to the complexity of the instrumentation.

An alternative solution to the problem was to employ the negatively charged ReO_4^- with a pulsed secondary ion extraction technique. Since ReO_4^- is negatively charged, it will to some extent counteract the effect of the departing electrons. Pulsed extraction manages charge by treating the bombarded surface as a capacitor, using a variable alternation of positive ion extraction and negative ion extraction, such that the net charge on the sample surface was null.(Appelhans, 1990) This approach could be utilized in both quadrupole-, and ion trap-based SIMS instruments.

<u>c. Development of transportable, ion trap (IT-) SIMS instruments</u>. The initial SIMS instruments that were developed at the INEEL were constructed using quadrupole mass analyzers; they were bulky and non-transportable, and thus confined to the laboratory. Developments in ion trap mass spectrometry demonstrated facile injection of externally formed ions (i.e., from secondary ion sputtering), and mass spectrometry/mass spectrometry (MS/MS) for improved identification selectivity and detection sensitivity. These improvements motivated the design and fabrication of the initial IT-SIMS instruments at the INEEL, which involved modification of a Finnigan IT-MS with a ReO_4^- primary ion gun and a direct insertion lock (Figure 2). This instrument was used to demonstrate the utility of IT-SIMS/MS, but was not substantially smaller.

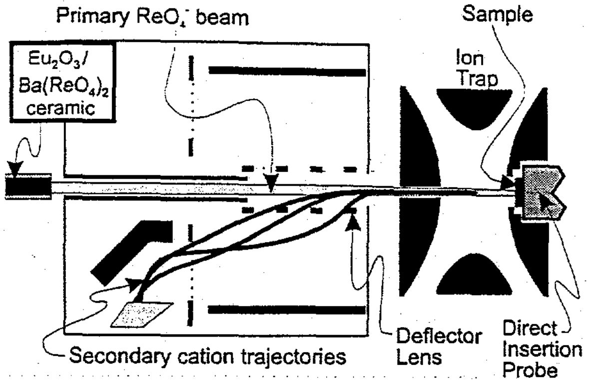

Figure 2. Schematic diagram of IT-SIMS instrument.

This instrument was capable of trapping, and then selectively isolating sputtered secondary ions.(Figure 3) These could be subsequently fragmented using axial radio frequency excitation. The ion signature generated in this fashion was highly diagnostic for contaminant identification, and resulted in improved method detection limits.(Ingram, 1996)

A second generation IT-SIMS instrument was constructed using a Teledyne 3D-Q ion trap mass spectrometer which was fitted with a ReO_4^- primary ion gun, and improved ion detection hardware. This instrument, together with all its pumping, electronics and computer hardware, fit comfortably on a laboratory cart, and was easily transportable within the laboratory setting (Figure 4). The instrument offers more facile mass calibration, improved acquisition software, and easier switching between anion and cation analyses. The latter point is significant because ions of positive and negative polarity are needed for comprehensive characterization of sample surfaces.

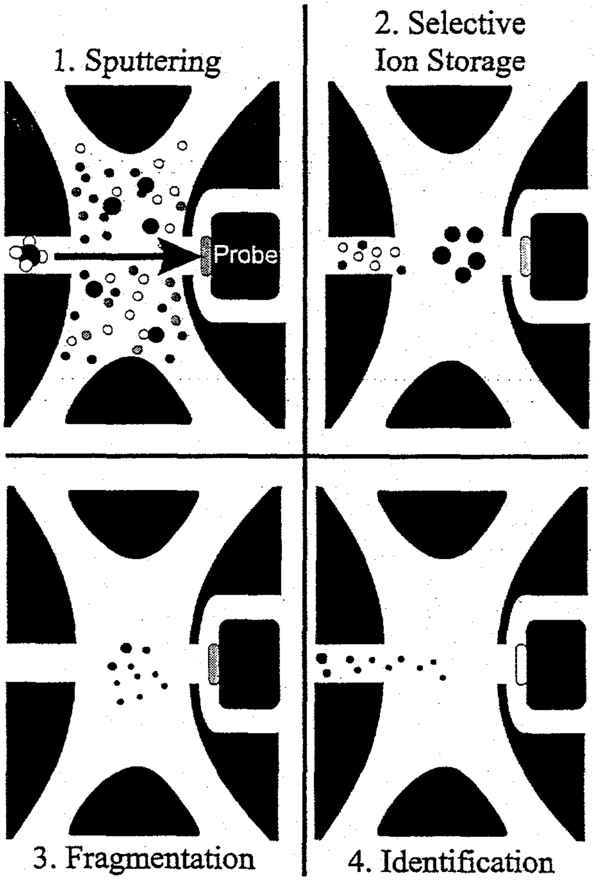

Figure 3. Four-step schematic of IT-SIMS analysis using MS/MS. 1. Contaminant chemicals on the sample are sputtered as ions from the end of the probe, together with ions from the chemical background. 2. Background ions are eliminated from the trap, isolating the contaminant ions. 3. Contaminant ions are excited and fragmented. 4. Fragments are sequentially scanned out of the trap, generating a mass spectrum for identification and quantitation.

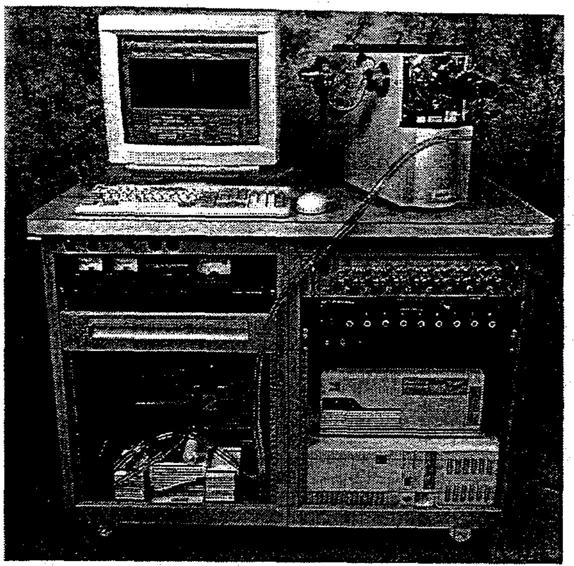

Figure 4. Photograph of the second-generation IT-SIMS instrument, which was based on the Teledyne 3-DQ ion trap.

APPLICATION OF IT-SIMS TO THE CHARACTERIZATION OF CONTAMINATED SOIL SAMPLES.

Blister agents and nerve agents are the two classes of compounds which are of most significance in UXO operations involving CW. For this reason, two examples will be provided which will illustrate the utility of the IT-SIMS for characterizing contaminated soil samples.

Analysis of soil samples contaminated with "one-armed mustard". 2-Chloroethyl ethyl sulfide (one armed mustard, or CEES) was selected as a surrogate for *bis*-(2-chloroethyl)sulfide (mustard) (Figure 5). In these studies, surrogate compounds were used in order to minimize the hazard associated with evaluating the IT-SIMS instrumentation. Soil samples were collected from the Dugway Proving Ground, the Rocky Mountain Arsenal, and the Raritan, NJ site. The soils were exposed to low levels of CEES (as methylene chloride solutions), and hence the exposure to water in these exposures is rather limited. For this reason, hydrolysis of CEES to form hydroxyethyl ethyl sulfide is not occurring to any appreciable extent. The surface concentration on the soil surfaces was calculated at 0.3 monolayers by estimating the molecular area on the surface at 20 Å^2, and corresponds to a mass/mass concentration of about 3 parts per thousand.

The exposed soil samples were attached to the head of a small nail using double-sided tape (the geometric area of the sample on the tape was 7.3 mm^2). The average mass of soil mounted on the sample holder was on the order of 2 - 3 mg. The nail was then attached to the direct insertion probe and evacuated in the insertion lock, then admitted to the IT-SIMS chamber for analysis.

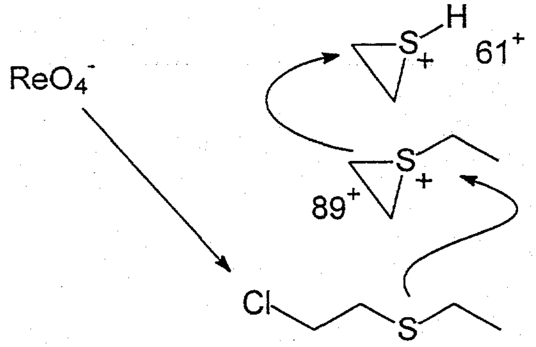

Figure 5. Formation and fragmentation of m/z 89^+ in the SIMS analysis of CEES.

The SIMS spectrum measured for these samples contained an abundant ion at *m/z* 89^+, which corresponds to the ethyl thiiranium ion, and was not present in the analysis of the unexposed sample. This ion arises either by homolytic cleavage of the C-Cl bond, or by elimination of HCl from protonated CEES (which is not observed in the SIMS spectrum; see Figure 6). *M/z* 89^+ was confirmed as the ethyl thiranium ion by MS/MS, which showed elimination of C_2H_4 to form the protonated thiiranium ion at *m/z* 61^+. This is a diagnostic fragmentation reaction for the *m/z* 89^+ signature ion.

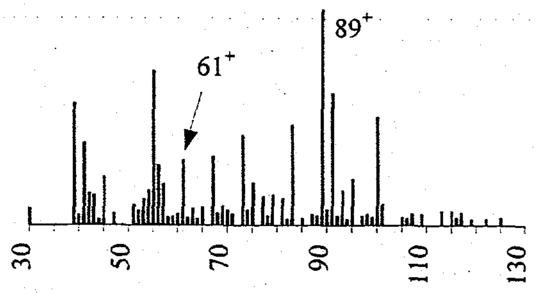

Figure 6. Cation SIMS spectrum of 0.3 monolayer CEES on soil. Other ions in the spectrum are the result of endogenous surface contaminants.

In the presence of water, hydrolysis is prevalent, and the water provides a medium for the reactions of the ethyl thiiranium ion with nucleophiles present in solution. These reactions result in the production of sulfonium condensation ions, which can be remarkably long-lived, and have a high toxicity. These ions constitute part of the contamination signature, and are readily detected using SIMS.(Groenewold, 1995)

<u>IT-SIMS analysis of PMPA on soil</u>. Soil samples exposed to pinacolyl methyl phosphonic acid (PMPA) were generated for the purpose of evaluating IT-SIMS detection. PMPA is an important target compound because it is the primary decomposition product of nerve agent GD, and is typical of nerve agent degradation products (Figure 7). 100 mg of a soil having a surface area of 2 m^2/g (determined using BET method (Adamson, 1990)) was spiked with 50 µl of a standard solution of PMPA and allowed to dry. The amount of PMPA applied to the soil samples was chosen so that a predetermined surface coverage would be achieved. Surface coverage was calculated by assuming that all of the PMPA

was adsorbed to the soil surface, and that the molecular surface area of PMPA with the pinacolyl group oriented normal to the surface is 20 Å^2.(Ingram, 1995) The calculated surface coverages for the PMPA exposures investigated in this work varied from 0.0002 monolayer (0.2 pg/mm^2) to 2 monolayers (2400 pg/mm^2).

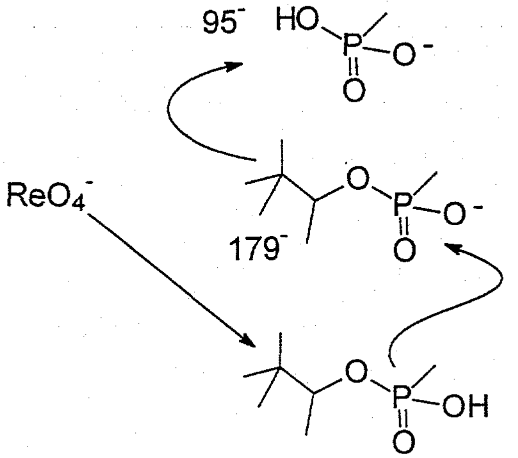

Figure 7. Formation of the PMPA conjugate base (*m/z* 179^-) in the SIMS analysis. Formation of fragment ions.

The anion spectrum of 0.02 monolayers PMPA on soil (Figure 8) contains an ion at *m/z* 179^- (intact PMPA conjugate base), and fragment ions at 95^-, 79^-, and 63^- (Figure 7). However, PMPA cannot be identified on the basis of this spectrum because of the presence of abundant ions at every mass, which arise from other contaminants on the soil surface. MS/MS is the approach that has been adopted to surmount this problem.

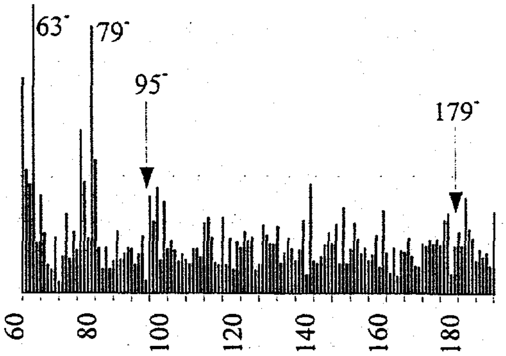

Figure 8. IT-SIMS spectrum of 0.02 monolayers PMPA on soil. Neither 179^- nor 95^- are above the chemical noise, but PMPA is readily identified using MS/MS (see Figure 9). *M/z* 79, 77 and 63 are also part of the PMPA mass spectral signature.

MS/MS using the IT-SIMS permits the distinction of PMPA and the chemical background at lower concentrations. The diagnostic ions at *m/z* 179^- can be isolated through the application of a notched filtered noise field. Subsequently, a frequency component corresponding to *m/z* 179^- is applied to the end caps, which causes excitation of the ion and results in fragmentation to form *m/z* 95^- (Figure 9) This sequence of ion isolation and fragmentation is diagnostic for PMPA, and has also been successfully applied to GB and VX residue chemicals.

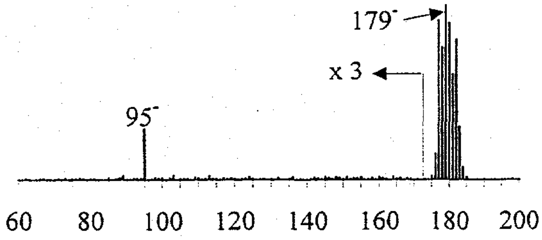

Figure 9. Isolation of the *m/z* 179^- region in the IT-SIMS analysis of 0.02 monolayer PMPA on soil. After isolation, *m/z* 179^- is excited, which results in fragmentation to form 95^- at a high signal-to-noise.

The MS/MS approach significantly lowers the minimum detectable concentration of AMPAs on soil surfaces. The minimum detection limit for PMPA on soil approaches 0.001 monolayer, which is equivalent to 3 ppm (mass/mass) for the soils in this study. In addition, the SIMS response was linear over three orders of magnitude; the data presented in Figure 10 were acquired using no internal standard.

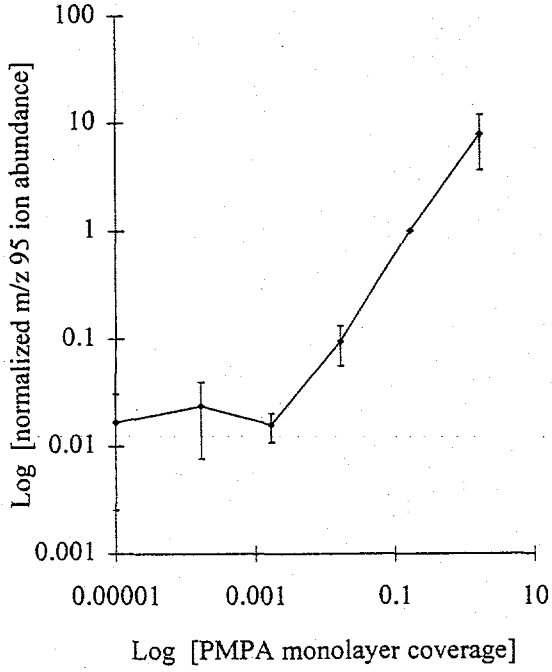

Figure 10. Abundance of m/z 95^- versus surface concentration of PMPA. M/z 95^- was formed from the MS/MS decomposition of 179^-.

SUMMARY AND OUTLOOK

The examples that were presented in this account are indicative of the capability of the IT-SIMS instrumentation, which can be summarized as follows. For compounds which have marginal volatility, and are highly surface adsorptive, IT-SIMS is well suited to rapid and sensitive analyses. Many compounds that are important in the CW realm are in this category. In some cases, sensitivity achievable using SIMS rivals that of extraction-based methods, in spite of the fact that the IT-SIMS approach requires only a few milligrams of sample.

Significant progress has been made in improving IT-SIMS performance and in reducing the size of the instrumentation. A third generation IT-SIMS instrument is currently planned: it will be about half the size of the current instrument, and will have simplified instrument power and pumping. It is expected that this instrument will be trailer-, or van-transportable, which will permit field evaluation of this emerging technique.

ACKNOWLEDGMENTS

This work was supported by the U. S. Army Chemical Materiel Destruction Activity, Non-Stockpile Program, and by the U. S. Department of Energy, Office of Research & Development NN-20. The authors thank Marnie Cortez, Cathy Rae, and Anita Gianotto for assistance during the research.

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