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Non-Technical Summary

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Application of Static Secondary Ion Mass Spectrometry to Trace Evidence Analysis

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Abstract

State-of-the-art secondary ion mass spectrometry (SIMS) instrumentation was applied to the characterization of samples representative of trace evidence. The purpose of the study was to assess the efficacy of static SIMS for providing highly specific *chemical* characterization of trace evidence samples. It was found that samples coated with automotive paint and with nail polishes could be distinguished based on their SIMS spectra, provided the data was reduced using multivariate analysis techniques. It was also found that hair samples could be readily characterized in terms of the consumer chemicals present on the surface, namely, soap and softener chemicals. Other studies showed that the drugs of abuse heroin and cocaine could be readily detected on fiber surfaces using SIMS. In order to perform the hair and fiber studies, methods for analyzing hair and fiber samples required development. On the basis of these studies, it was concluded that the technique has the potential for providing a chemical-specific characterization for a variety of trace evidence characterizations. At the present time, limitations of the technique are the high cost of the instrumentation, and the high level of expertise required for routine operation, and more importantly, data interpretation. However, it is projected that cost, operational complexity, and expertise requirements will all decrease in the near future, which should render the technique amenable to a wide variety of characterization efforts.

Keywords: forensic science, trace evidence, surface analysis, coating material, hair

Introduction

State-of-the-art secondary ion mass spectrometry, or SIMS, was applied to the characterization of samples of trace physical evidence, i.e. fingernail polish, paints, fibers, and hair. The purpose of this study was to provide the forensic science community with an alternative nondestructive and highly sensitivity analytical technique capable of generating

specific chemical information about trace samples of forensic interest. Because of the complex environment around us, the variety of commercial products and the advances in manufacturing technologies, forensic laboratories are striving to overcome the limitations of existing microscopic and analytical techniques. This research assesses the efficacy of static SIMS for providing highly specific *chemical* characterization of trace evidence samples and evaluating whether surface analysis is an appropriate forensic methodology.

SIMS can be divided into two operational modes, dynamic and static. Dynamic SIMS has been used in the semiconductor industry for the last 3 decades, mainly for the analysis of bulk metals and bulk semiconductor materials. Static SIMS, on the other hand, provides information about the organic compounds adsorbed to the sample surface, and is the subject of this report. The principle behind SIMS is quite simple, and can be compared to a rock thrown into a pond, whereupon a small amount of water is recoiled (splashed) into the air when the rock impacts the surface. In this simple metaphor, the "pond" represents the sample surface (*e.g.*, a fiber), and the "rock" represents an energetic projectile (Figure 1). The energetic projectiles have kiloelectron volt energies; when they hit the surface, they knock atoms and molecules into the
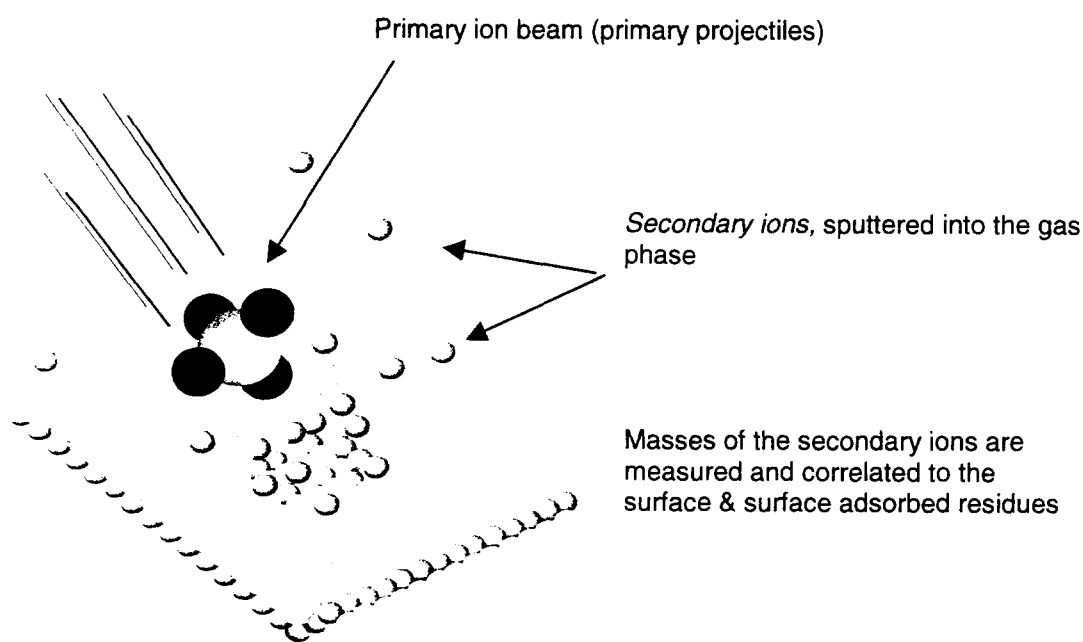

Figure 1. Static SIMS Sputter Process

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gas phase. Some of these atoms and molecules will be charged (*i.e.*, ionized), and are termed "secondary ions". The masses of these secondary ions can be measured using a mass spectrometric detector, similar to the detector used in drug testing. The mass spectra are representative of the sample surface and surface adsorbed residues, which can consist of a wide variety of chemicals, including polymers, pesticides or shampoo constituents.

Identification and comparison of trace samples is challenging because of the limited size of the sample, the limited number of discrete samples available, and the small absolute quantities of analyte compounds present in the samples. These difficulties have resulted in the application of a large number of characterization approaches. Each of these approaches offers distinct advantages over others, but also have definite limitations, including lack of specificity and the consumption or destruction of the sample during testing. Classical visual microscopy is an often-used technique, because a high level of expertise has been developed, and because it is non-destructive. While a great deal of information can be generated using visual examination, the information content from a single sample could be greatly enhanced if chemical information could also be derived from that same sample, i.e. surface contaminants.

Although not applied previously to samples of forensic interest, static SIMS has a number of features that make it an appropriate technique for this application:

- it is capable of performing analysis on samples as small as a single fiber;
- it requires minimal sample preparation, with no mounting media required;
- it provides specific chemical information (molecular and atomic) about the sample;
- it provides fast analyses times (~5 minutes per sample);
- it is capable of very high sensitivity (as low as picogram quantities for some analytes);
- it permits the direct interrogation of a sample surface in a near-nondestructive manner which allows for the sample to be analyzed by other analytical techniques.

For these reasons, the application of SIMS instrumentation represents an approach which could result in greatly enhanced information. Recent advances in SIMS technology at the Idaho National Engineering and Environmental Laboratory (INEEL), and other laboratories, have resulted in improvements that have enhanced the quality of the molecular information obtainable from trace samples. Further, analytical cost has decreased, and operation has been simplified, which suggest that SIMS could find broad applicability in the near-term future.
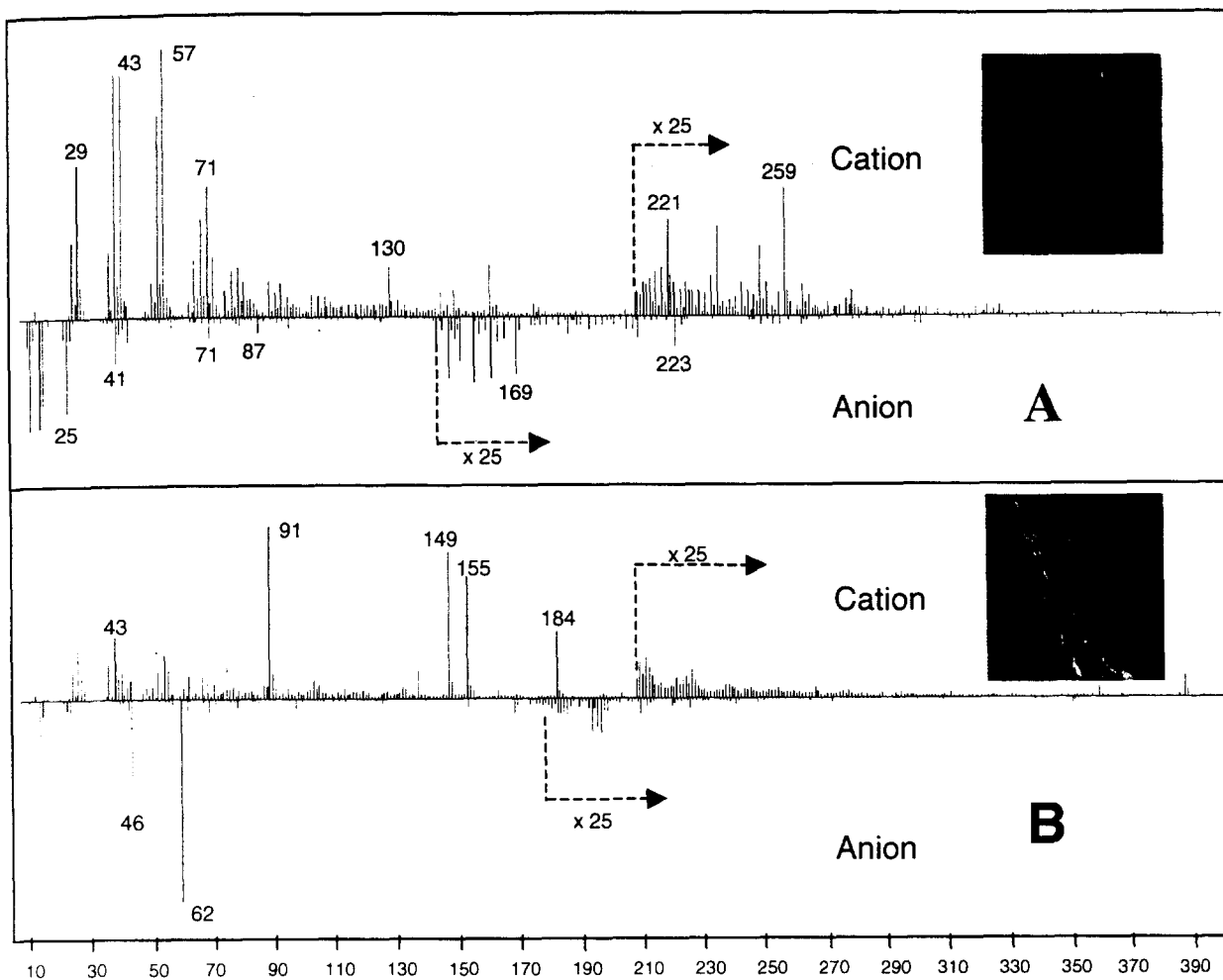
Figure 3. Cation (positive ion) and anion (negative ion) quadrupole SIMS spectra of coatings from different manufacturers. (A) DuPont ChromaPremier® B9708FM-1 Dark Mulberry Metal automotive paint; (B)) L'Oreal® 208 British Red Coat nail polish.

Automotive paints, automotive touch-up paints, aerosol spray paints and fingernail polish samples used in the present study were obtained from local retail suppliers. A number of samples were prepared for each coating and allowed to weather. Samples were analyzed over an 8 to 12 month period after sample preparation. The nominal sample size for the broad beam quadrupole SIMS was 2 x 3 mm; the instrument is capable of analyzing samples as small as 40 microns (.0016 inches) in width to samples slightly less than 0.5 inches in width.

A series of quadrupole SIMS spectra, in which the positive ions are plotted above the mass axis, and negative ions are plotted below were obtained, are seen in Figure 3, along with their

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Areas of Research

Three different areas of research were initiated to evaluate the applicability of SIMS for trace evidence characterization. They included the characterization of nail polish and paint surfaces, characterization of chemicals from consumer products on hair, and characterization of toxins and drugs of abuse on fibers.

Characterization of Nail Polish and Paint Surfaces[1]

Here we describe the application of static SIMS to the characterization and differentiation of coating samples, specifically automotive paints, spray paints and fingernail polishes. The results show that in

Figure 2. Schematic of triple quadrupole secondary ion mass spectrometer (TQ SIMS)

most cases the coatings can be differentiated by manufacturer, and frequently to the specific coating product. The SIMS instrument used in this study was built in-house, and is shown in Figure 2. Secondary positive and negative ions were alternately extracted from the sample target region at 0.2 amu intervals using pulsed secondary ion extraction,[2] which operates by alternating the polarity of the secondary ion extraction lens from positive to negative. This mitigates the sample charge buildup on the sample surface and allows for the simultaneous collection of both positive and negative ion spectra from a single analytical run.
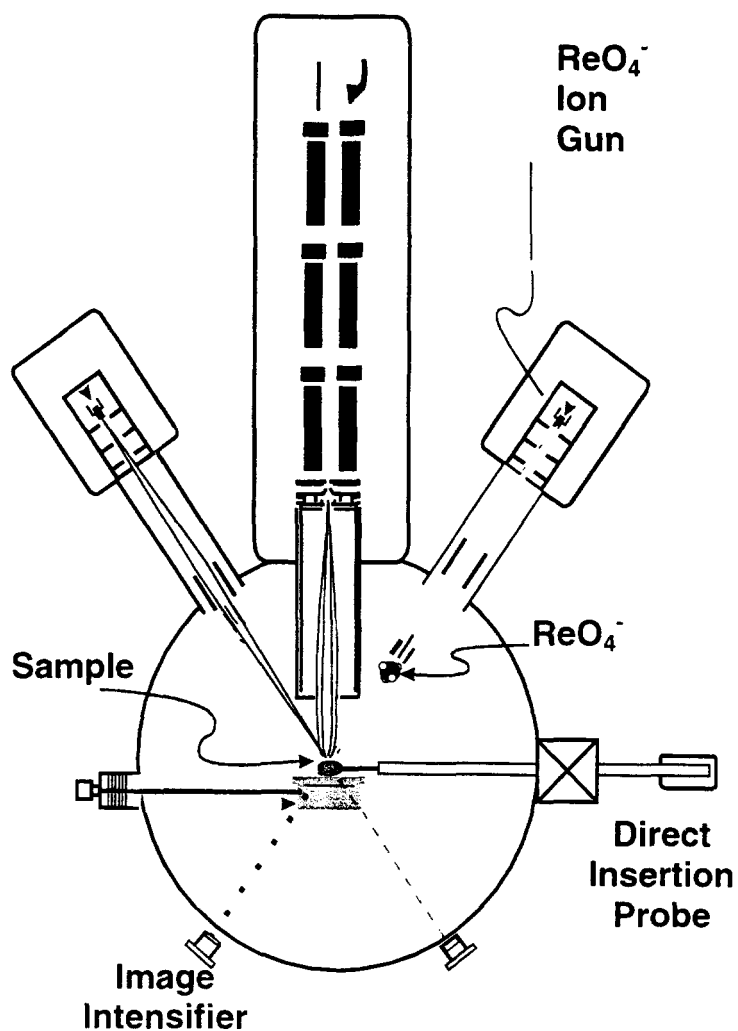
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respective paint schemes. These coatings produce distinctive spectra that can be differentiated from the others. None of the ions observed have been determined to be molecular ions (i.e., derived from intact molecules in the paint).

In other instances, coating distinction was difficult within a product line because of spectral complexity; for this reason and because of the large numbers of spectra generated in this study, multivariate statistical techniques were employed, which allowed the meaningful classification and comparison of spectra. Partial Least Squares (PLS) and Principle Component Analysis (PCA) were applied to quadrupole SIMS data. PCA showed distinct spectral differences between most spectral groups, as seen in Figure 4, and emphasized the reproducibility of the SIMS spectra. When using PLS analysis, reasonably accurate coating identification was achieved with the data. Overall, the PLS model is more than 90% effective in identifying the spectrum of a particular coating, and nearly 100% effective at telling which coating components represented in the PLS models are not present in a spectrum. The level of spectral variation caused by sample bombardment in the SIMS analysis was also investigated using Fourier transform infrared spectroscopy (FT-IR) and quadrupole static SIMS. Changes in the FT-IR spectra were observed and were certainly a result of surface bombardment during SIMS analysis. However, the bulk of the sample is unaltered and may be used for further testing.
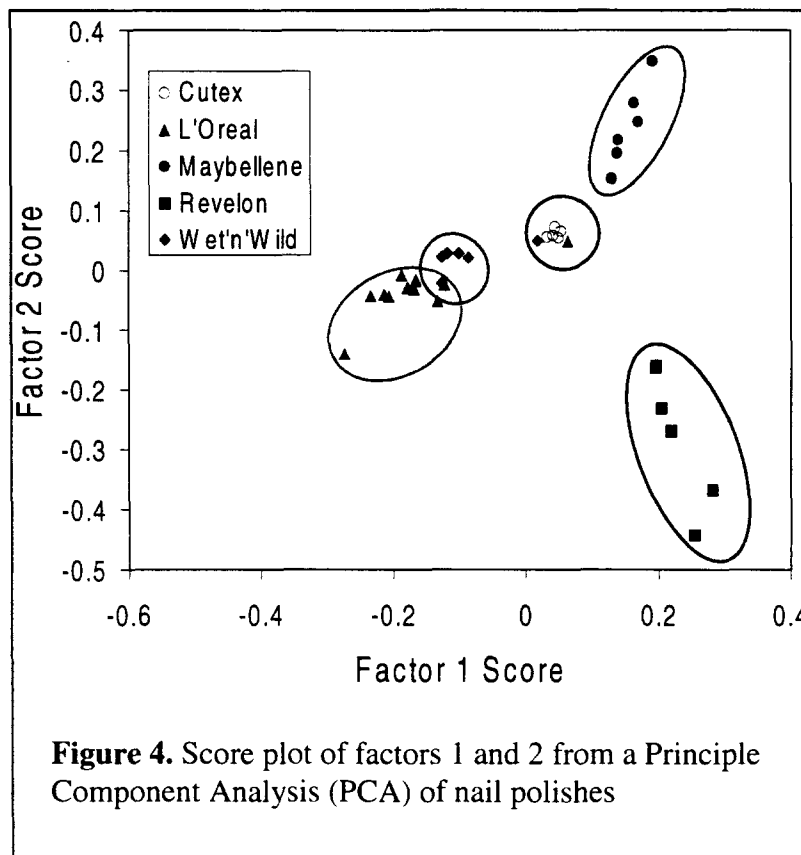

Figure 4. Score plot of factors 1 and 2 from a Principle Component Analysis (PCA) of nail polishes

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Characterization of Chemicals from Consumer Products on Hair[3]

In the second of the studies, hair samples were characterized based on the chemicals constituents on the surface of the hair. The characterization of surface-adsorbed chemicals on hair samples can be important, because these chemicals can be indicative of treatment history, or past environment. A wide variety of chemicals are present in consumer hair care products, such as shampoos and conditioners. Many of these chemical constituents are added because they impart a quality such as softness or luster to hair, and they are frequently designed to be long-lived on hair surfaces. For this reason, identification of surface adsorbed chemicals could be useful in matching unknown hair samples to known exemplars, or for relating a hair sample to a specific environment or location.

Canine hair samples were analyzed as part of a program to assess the efficacy of imaging time-of-flight secondary ion mass spectrometry or ToF SIMS for the characterization of trace samples. The imaging ToF SIMS instrument utilized is a combined ion microprobe / ion microscope instrument capable of generating spectral images such as those seen in Figure 5. The spatial resolution or achievable spot size using the Ga^+ primary ion gun is less than one μm. Typically, an 80 μm x 80 μm, or 120 μm x 120 μm area was mapped by rastering the projectile ion beam, and acquiring a spectrum for each pixel. Total ion images, or individual ion images that were generated after the analysis.
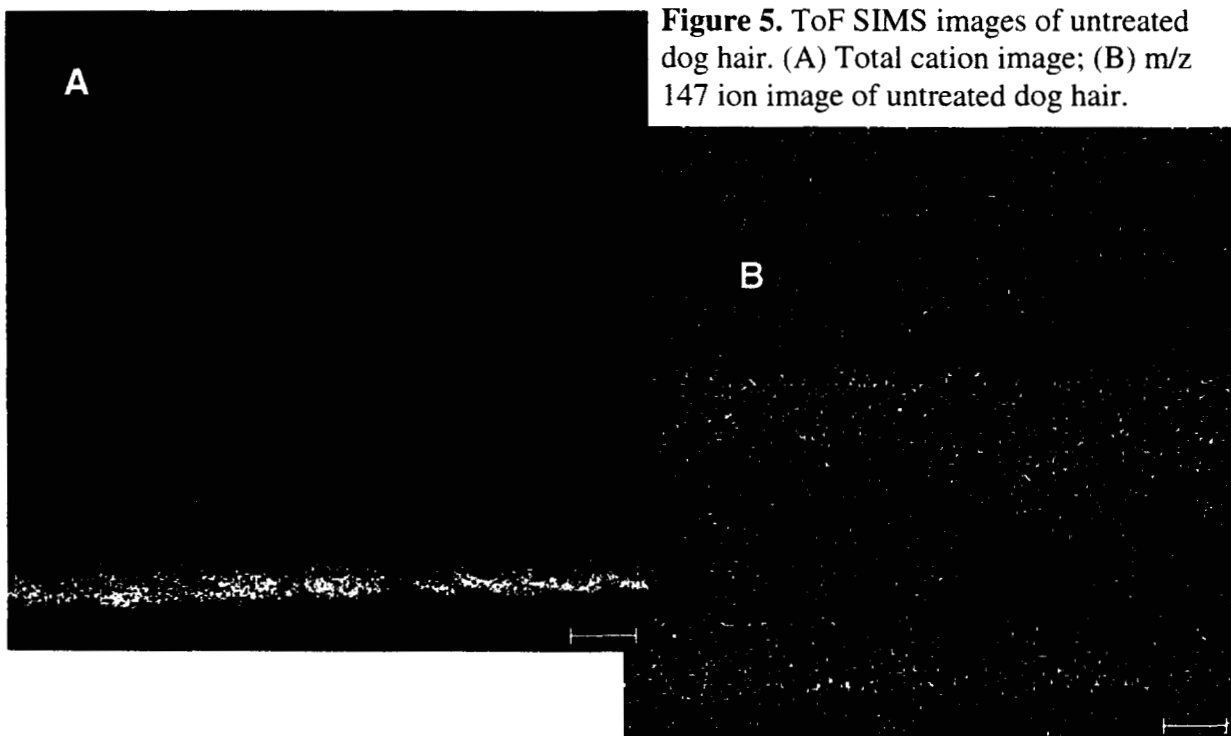

Figure 5. ToF SIMS images of untreated dog hair. (A) Total cation image; (B) m/z 147 ion image of untreated dog hair.

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The hair samples were analyzed as received, and subsequent to treatment with shampoo, and or conditioner products. The imaging SIMS instrument used enabled spectra to be generated only from the hair surface, in a manner which excluded contributions from the support stage. The cation (positive ion) spectra of the untreated hair contained evidence for organic amines and polydimethylsiloxane (PDMS) contaminants, i.e. mass 147 (Figure 5b); these compounds originate from the environment, and are detected with great sensitively using SIMS. When the hair samples were treated with shampoo, the cation (positive ion) spectra showed that the amine-derived ions were removed, but the abundance of the PDMS-derived ions had increased. A series of PDMS-derived ions was also observed in the anion (negative ion) spectra, as was evidence for alkyl-, and ethoxylated alkyl-, sulfate species.

Treatment of the hair samples with conditioner had a dramatic effect on the appearance of the cation (positive ion) spectra. The cation spectra of the unrinsed samples contained abundant ions which corresponded to the cationic surfactants hexadecyltrimethyl ammonium at mass 284 (HTA, also known by the trade name cetrimmonium) and disteryl dimethylammonium at mass 551 (DSDMA, also known by the trade name distearyldimmonium) (Figure 6). When the samples were rinsed in water and re-analyzed, no qualitative changes in the cation spectra could be detected, clearly indicating that water does not efficiently remove them from the hair surfaces. The cation spectrum of the conditioner-treated hair samples contained a variety of other ions which can be readily interpreted. The afore-mentioned PDMS-derived ions are clearly observed. In addition, several even-mass ions are observed which are probably fragment ions from HTA and DSDMA.
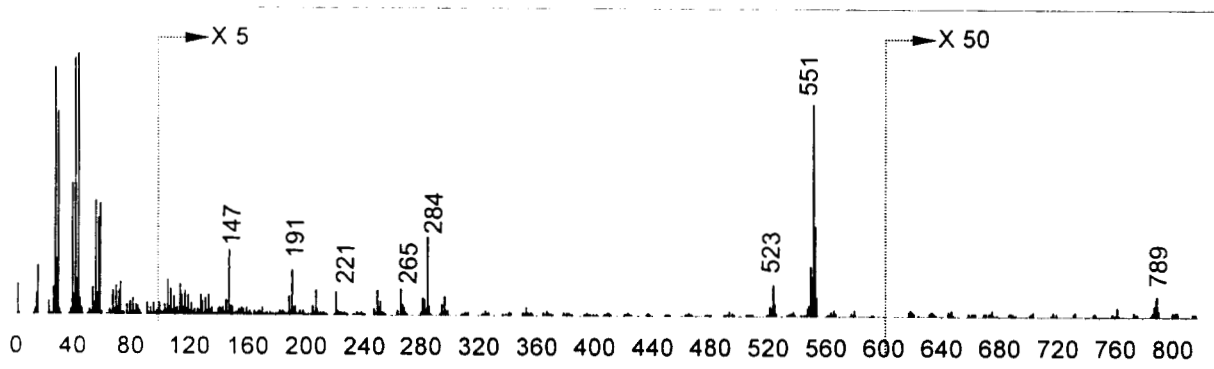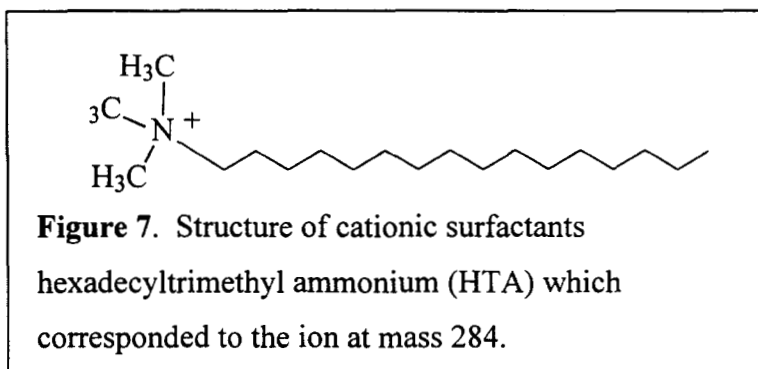

Figure 6. Cation SIMS spectrum acquired from conditioner-treated, rinsed dog hair.

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The identities of the alkylammonium species were confirmed using mass spectrometry/mass spectrometry, or MS^2, using an ion trap SIMS instrument (Figure 7). Subsequent rinsing with hexane removed the PDMS, but did not remove the alkylammonium ions. The results indicate that several components of the hair care products are long lived on hair, and are readily detected using SIMS. Characterization of surface contaminants may be useful for distinguishing different samples.

The SIMS research conducted on relatively uncontrolled hair samples shows that a wealth of chemically specific information can be derived using the technique. A surprising number of surface chemicals can be identified based

Figure 7. Structure of cationic surfactants hexadecyltrimethyl ammonium (HTA) which corresponded to the ion at mass 284.
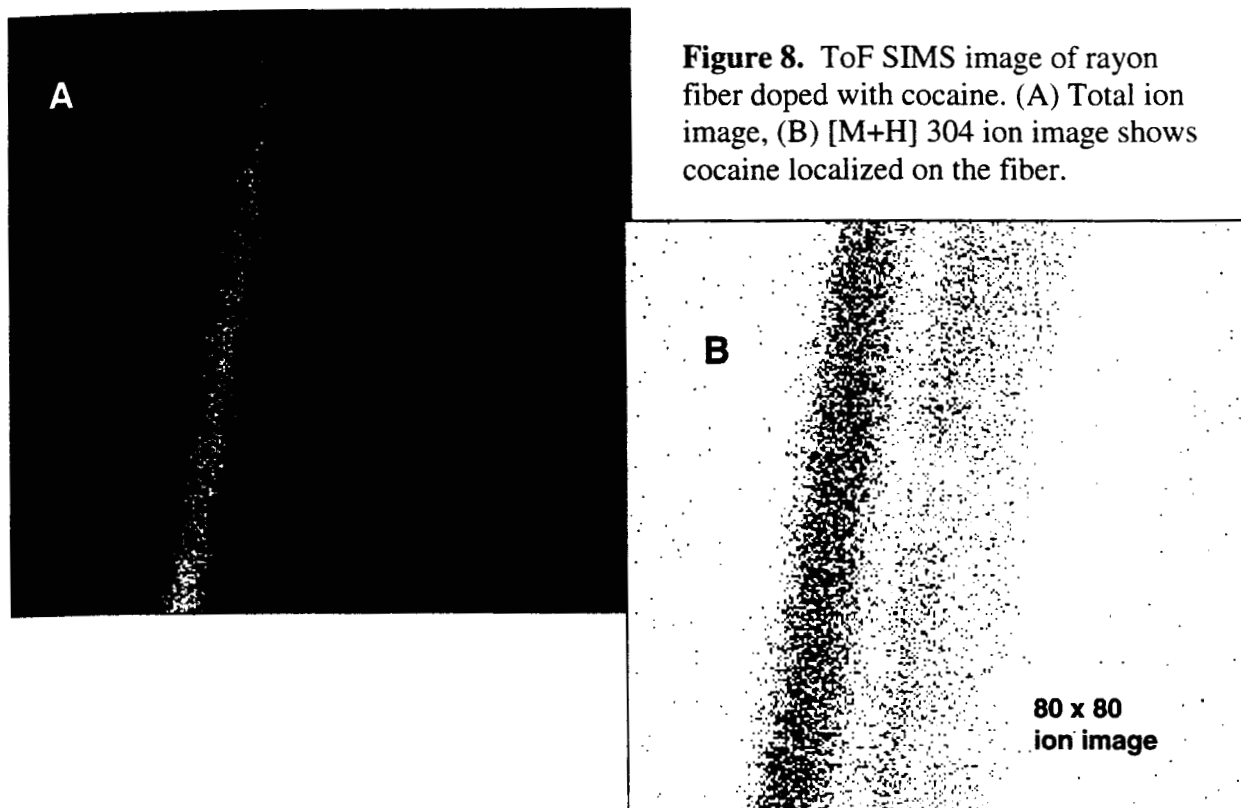
on the mass measured. In many cases, the longevity of these chemicals on hair surfaces may be quite substantial, and hence would constitute a means for sample distinction.

Delectability of Toxins and Drugs on Trace Hair and Fiber Samples

Scoping studies were also performed to assess the detectability of other contaminant compounds on trace fiber and hair samples. Identification of surface adsorbed chemicals could be useful in matching unknown hair or fiber samples to known exemplars, or for relating a hair or fiber sample to a specific environment or location such as clandestine laboratory or industrial setting. It was found in this study that hair and fiber samples exposed to cocaine and heroin were easily analyzed, and the drugs were detected as the protonated molecule in the gas-phase, *e.g.*, [cocaine+H]$^+$ was observed at mass 304 (Figure 8). An additional motivation for this study was that since static SIMS is predominantly a surface technique, it was possible that it might be used to differentiate surface from in vivo contamination. This is an important distinction for assessing the mode of exposure, which is an important forensic question.

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Similarly, the detectability of two organophosphorus compounds was also evaluated, because the variety of toxic compounds that belong to this chemical class. Malathion was chosen because it is a common consumer pesticide, and had been successfully analyzed on large samples

Figure 8. ToF SIMS image of rayon fiber doped with cocaine. (A) Total ion image, (B) [M+H] 304 ion image shows cocaine localized on the fiber.

(plant leaves) using SIMS. The second compound studied, pinacolylmethylphosphonic acid (PMPA), is the principal degradation product of the nerve agent GD (pinacolylmethyl phosphonofluoridate, or Soman). Hence, this compound would be a target analyte in a scenario involving nerve gas, such as may occur in a terrorist attack.

Analysis of hair and fiber samples using an imaging SIMS instrument required solving a focusing problem derived from the fact that the sample was not co-planar with the sample stage, and the fact that the samples were cylindrical. Extraction of secondary ions was studied as a function of substrate potential from samples consisting of insulating dielectric fibers mounted on a metallic substrate. It was determined that ions extracted from the surfaces of the dielectric required a higher potential than those extracted from the surface of the metallic sample stage.

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These results were explained in terms of electrostatic potential distribution in the extraction region and the dielectric properties of the fibers.[4]

Throughout the research, the investigators interfaced with a number of law enforcement entities, for purposes of guidance and review. These included forensic laboratories from the State of Idaho, the State of Wyoming, the Federal Bureau of Investigation, and the Center for Human Toxicology, Utah State University.

Summary

In summary, SIMS has considerable utility for a wide range of challenging characterization problems, in particular those that were the subject of the studies conducted. However, at the present time, the technique is practically unused in the forensic community, for several reasons. First among these is the fact that most SIMS instrumentation is expensive, both in terms of capital expenditure (>$100,000 ranging to $1,000,000), and operation (a skilled operator is required). Secondly, data interpretation can be difficult, as was shown by the need for multivariate methods in the coating differentiation study. Counterbalancing these criticisms is the observation that for many analyses, such as those presented in the analyses of the consumer and illicit chemicals on hair and fiber samples, data interpretation can be straightforward.

Furthermore, as the need for more specific trace sample characterization increases, SIMS and related techniques should find increased utilization, which will be facilitated by the development of small, easy-to-use SIMS instruments, such as small scale quadrupole instruments, as well as ion trap SIMS instruments. These instruments will have markedly lower capital costs, be easier to operate, and in some cases have increased analytical capability.

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