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Analysis of Residual Explosives by Swab Touch Spray Ionization Mass Spectrometry

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Abstract: Swab touch spray ionization mass spectrometry, an ambient ionization technique, has been applied to the analysis of six explosives from various surfaces including glass, metal, Teflon, plastic, human hands and three types of gloves (nitrile, vinyl and latex). A swab, attached to a metallic handle, was used to sample explosives residues and acted as the ion source. The explosives, 1,3,5-trinitro-1,3,5-triazinane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), and 2,2-bis[(nitrooxy)methyl]propane-1,3-diyl dinitrate (PETN) had an absolute limit of detection of 10 ng from all the surfaces except for PETN from the nitrile gloves (limit of detection 100 ng). Sodium perchlorate, 2-Methyl-1,3,5-trinitrobenzene (TNT) and tetra-butylammonium perchlorate had limits of detection of 100 pg, 10 pg, and 1 pg, respectively from all surfaces. This study demonstrates the feasibility of swab touch spray ionization mass spectrometry for detection of a wide array of explosives from a variety of forensically applicable surfaces with disposable, commercial, tamperproof and individually-wrapped conductive swabs without complicated/lengthy sample preparations or extractions.

1 Introduction

Residual and trace explosives analysis by mass spectrometry typically involves the use of a swab or wipe followed by a lengthier sample preparation procedure. [1] Liquid chromatography or gas chromatography coupled to mass spectrometry [2] and ion mobility [3] represent the current state of the art methods in explosives detection. Colorimetric detection methods have been developed but typically suffer from low specificity. [4] Raman spectroscopy methodologies look promising as a good alternative however there can be issues with fluorescence and background mitigation. [5] Bulk detection of explosives is commonly performed by x-ray diffraction as highlighted in a recent review. [6] Radioactive sources (typically ^{63}Ni), are also commonly used, but they represent a major cost burden due to additional administrative oversight to track the sources and routinely test for radiation leakage. [7] A more rapid and simpler test for explosives would be useful in a variety of applications, including airport security and forensic crime scenes. The relatively new field of ambient ionization mass spectrometry pertains to ionization under atmospheric pressure with the stipulation of little to no sample preparation (unlike most electrospray ionization or atmospheric pressure chemical ionization experiments). [8] Desorption electrospray ionization [9] (DESI) and direct analysis in real-time [10] (DART) were the first ambient ionization sources to be reported and many other have followed including low temperature plasma ionization [11] (LTP), paper spray ionization [12] (PS) and swab touch spray ionization. [13] As rapid analysis of explosive residues is desirable, both DESI [14] and DART [15] have been employed for this application. [16] These methods have proven especially useful in the analysis on skin, clothing, and other surfaces; however, both methodologies require specialized equipment. Examples include the DART plasma generator for or the DESI spray setup, of which neither is readily coupled to a portable instrument which would be desirable for *in-situ* analysis [17]. A recent review has detailed the current advances of ambient ionization to the trace detection of explosive residues. [18]

Low temperature plasma ionization has been applied extensively to explosive residues. [19] The low temperature characteristic of the plasma, as well as being safe to the touch, enables residues to be sampled from a variety of surfaces, including human skin without physical damage or sample degradation. [11] This technique has also been used with portable mass spectrometers, where a backpack MS showed promise for *in-situ* measurements for homeland security and defense applications. [20] While LTP is promising, it does require that a specialized ionization source be used and it utilizes high AC potentials which have an extra level of safety concern. [11] By contrast, one of the simplest ambient ionization techniques, PS, uses only a low current DC potential to ionize analyte from a sharply pointed piece of paper wetted with solvent. [21] As shown previously, this allows detection of 2-methyl-1,3,5-trinitrobenzene (TNT), 2,2-bis[(nitrooxy)methyl]propane-1,3-diyl dinitrate (PETN), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) and 1,3,5-trinitro-1,3,5-triazinane (RDX). [22] PS has a low barrier of entrance into a forensic setting as the paper acts as both as the sampling device and the ionization source. While PS shows great promise, the stability of the tip is essential for successful ionization, and this can make swabbing with the paper substrate difficult. [23] If the tip of the paper substrate is damaged during swabbing, subsequent analysis will be adversely affected, although proper training can alleviate this problem. [24]

Swab touch spray ionization, as performed on this experiment, utilizes a rayon swab or an alternative swabbing substrate attached to a conductive handle. [25] Surface analytes are attached to the swab surface by moving the swab over the surface of interest. Solvent is continually applied to the swab's tip after sampling the surface, and a high voltage is applied to the metallic handle to generate a Taylor cone which then leads to ionization of the sample. [25] Similar to paper spray ionization, the swab in swab touch spray ionization acts both as the sampling device and the ionization source. Swab touch spray ionization has the added advantage over PS of being able to perform analysis from an individually-packed, tamperproof swab, rather than a fragile hand-cut paper triangle. [26] Previously we have demonstrated the field-ability of swab touch spray ionization with portable instrumentation for the analysis of organic gunshot residues 1,3-diethyl-1,3-diphenylurea (ethyl centralite) and 1,3-dimethyl-1,3-diphenylurea (methyl centralite).

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[27] Chemical warfare agent simulants have also been analyzed by this methodology. [28] Herein, we demonstrate the feasibility of swab touch spray ionization mass spectrometry for the analysis of six residual explosives from various forensically applicable surfaces.

2 Experimental

2.1 Chemicals and Surfaces Preparation

The explosives TNT, PETN, HMX and RDX were purchased from Cerilliant (Round Rock, Texas), while sodium perchlorate and tetrabutylammonium perchlorate were purchased from Sigma-Aldrich (St. Louis, MO). HPLC grade acetonitrile was purchased from Fisher Scientific (Hampton, NH). Samples were prepared from 1.0 mg/mL stock solutions in acetonitrile. Direct analysis of explosives was performed by depositing 5.0 µL of solution on the swab using a pipette. Lower concentrations for limit of detection studies were prepared by serial dilutions (orders of magnitude) from the stock solutions to provide conservative limits of detection from the surface. This method created a conservative approximate limit of detection that can be expected in the field and is not determined by extrapolation. Surfaces bearing trace explosives were prepared by spotting 1.0 µL of reagent onto each surface. Surfaces included black nitrile exam gloves (Ammex, Seattle, WA), diamond grip latex gloves (Microflex, Reno, NV), anti-static vinyl gloves (OAK Technical, Matteson, IL), glass microscope slides (Gold Seal, Portsmouth, NH), polytetrafluoroethylene (PTFE) plugs (Swagelok, Indianapolis, IN), stainless-steel plugs (Swagelok, Indianapolis, IN), blue polyethylene flat-top screw cap (Fisher Scientific, Hampton, NH) and human hands (those of the authors). Once the sample had been spotted on the surface, it was allowed to dry prior to swabbing with a swab pre-wetted with 20 µL of acetonitrile.

2.2 Swab touch spray ionization

Ionization was performed from rayon medical grade sterile swabs (Copan Diagnostics, Murritea, CA). Each swab was opened by breaking the tamper-proof seal and used only once. Prior to swabbing, the swabs were pre-wetted with 20 µL of acetonitrile. This volume was selected as the swabs remained saturated with solvent during swabbing. To collect samples, the surface was sampled by swabbing using a circular motion (Figure 1). Then swabs were positioned 5-10 mm above the ion transfer capillary of the mass spectrometer. The position was an important variable. If the swab was too close to the inlet, discharge would occur. Conversely, if the swab was too far away, a stable cone would not be produced resulting in an unstable signal or no signal at all. Acetonitrile was added to the positioned swab using a syringe pump (Harvard Apparatus standard infusion only PHD 22/2000 syringe pump, Holliston, MA) connected to a 0.5 mL gastight syringe (Hamilton, Reno, NV) at a flow rate 10–30 mL/min. This flow was varied to maintain a steady spray without over wetting and unnecessarily diluting the sample. A high voltage of +/- 5.5 kV was applied to the aluminum handle, and the generation of a spray could be observed by eye. The flow rate as well as the position were both optimized in order to achieve a steady signal. Efforts have been made previously to achieve robust signal with 3D printed parts and a camera to aid in alignment. [26] Similarly, a rail system has been used to aid in alignment for non-expert users and in-field applications with miniature instrumentation. [29]

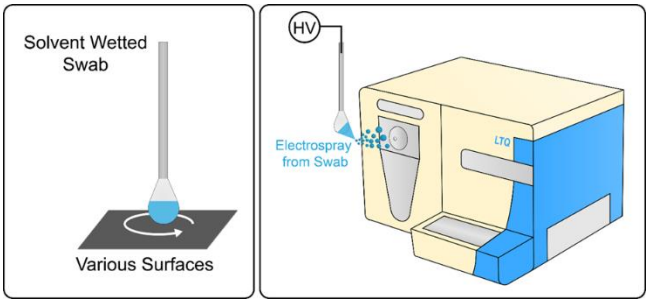

Figure 1: Pictorial representation of swab touch spray ionization source demonstrating sampling (left) and ionization using a commercial ion trap mass spectrometer (right).

2.3 Mass Spectrometry

All mass spectral analyses were performed using a Thermo LTQ Orbitrap XL Hybrid Ion Trap-Orbitrap mass spectrometer (San Jose, CA). Spectra were collected in negative ion mode, except when analyzing tetrabutylammonium perchlorate, which was collected in both positive and negative ion modes. The instrument also served as the supply of the high voltage applied to the metallic shaft of the swab. The entire time from swabbing through the collection of the spectra is ca 2 minutes.

3 Results and Discussion

Direct analysis of 5 µg of TNT using the product ion scan (Figure 2) gave a spectrum rich in fragment ions. The fragmentation of TNT has been previously studied by DESI [14a] and LTP [17] and both the radical anion (*m/z* 227) and deprotonated (*m/z* 226) TNT were observed. Using an isolation width of 3 Th on the LTQ and a peak centered at *m/z* 226.5, both the radical anion and deprotonated TNT were isolated and fragmented. Product ions at *m/z* 210, *m/z* 197, and *m/z* 196 correspond to the loss of OH, the loss of NO, and the loss of HNO, respectively. The product ion mass spectrum recorded for 10 pg of TNT swabbed from a glass surface (Figure S1) gave this as the limit of detection.

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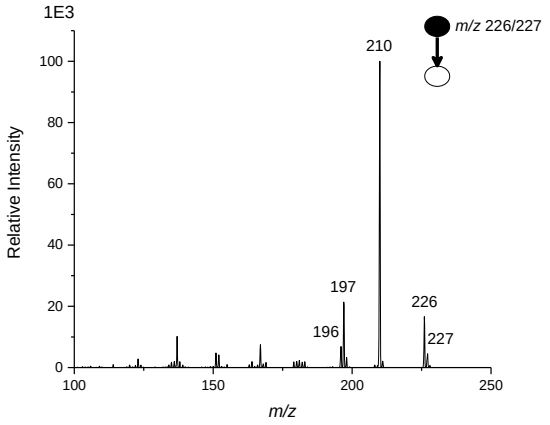

Figure 2: MS/MS product ion scan of TNT using swab touch spray ionization. The ion at *m/z* 226 corresponds to the $[M-H]^-$ species and the ion at *m/z* 227 corresponds to the $[M]^-\cdot$ as expected. Product ions at *m/z* 210, *m/z* 197, and *m/z* 196 correspond to the loss of OH, the loss of NO, and the loss of HNO, respectively**.**

Full scan mass spectra recorded for the direct analysis of 5.0 µg of RDX, HMX, and PETN from a swab are shown in Figure 3. The full scan mass spectra at the limit of detection of 10 ng of RDX, HMX, and PETN swabbed off a glass slide are recorded Figure S2. In agreement with the literature, [19b, 30] RDX was identified by four ions that form adducts with RDX; $[RDX+Cl_{35/37}]^-$ at *m/z* 257 and *m/z* 259, $[RDX+NO_2\text{-}H]^-$ at *m/z* 267 and $[RDX+NO_3]^-$ at *m/z* 284. Similarly, HMX and PETN were identified by the corresponding four adducts. HMX was identified by $[HMX+Cl_{35/37}]^-$ at *m/z* 331 and *m/z* 333, $[HMX+NO_2\text{-}H]^-$ at *m/z* 341 and $[HMX+NO_3]^-$ at *m/z* 358. PETN was identified by $[PETN+Cl_{35/37}]^-$ at *m/z* 351 and *m/z* 353, $[PETN+NO_2\text{-}H]^-$ at *m/z* 361 and $[PETN+NO_3]^-$ at *m/z* 378. PETN had a limit of detection of 10 ng on all surfaces except for the nitrile glove surface, which had a measured limit of 100 ng. These three explosives were identified by their adducts rather than their fragmentation profiles as no measurable fragments are detected on the ion trap mass spectrometer, as is consistent with previous results. [14d]

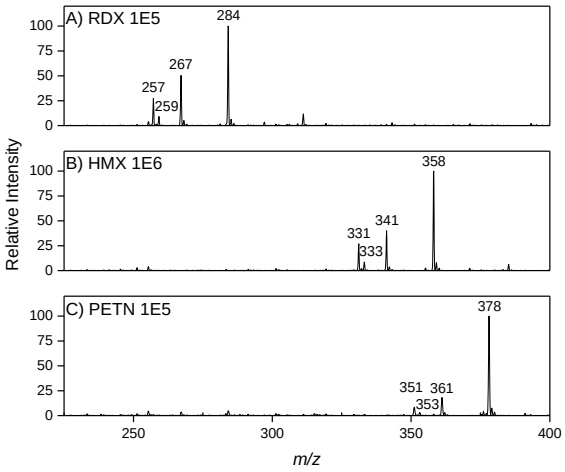

Figure 3: A) Swab touch spray ionization mass spectrum of 5 µg of RDX in negative ion mode. The ions at *m/z* 257 and *m/z* 259 correspond to $[RDX+Cl_{35/37}]^-$ at *m/z* 267 to $[RDX+NO_2\text{-}H]^-$ and at *m/z* 284 to $[RDX+NO_3]^-$. B) Mass spectrum of 5 µg of HMX in negative ion mode. The ions at *m/z* 331 and *m/z* 333 correspond to $[HMX+Cl_{35/37}]^-$ at *m/z* 341 to $[HMX+NO_2\text{-}H]^-$ and at *m/z* 358 to $[HMX+NO_3]^-$. C): Mass spectrum of 5 µg of PETN in negative ion mode. The ions at *m/z* 351 and *m/z* 353 correspond to $[PETN+Cl_{35/37}]^-$ at *m/z* 361 to $[PETN+NO_2\text{-}H]^-$ and at *m/z* 378 to $[PETN+NO_3]^-$.

Explosive perchlorate compounds were also of interest in this study because of their widespread use. [31] The direct analysis of 5.0 µg of tetrabutylammonium perchlorate was analyzed in full scan negative ion mode to look for perchlorate ions, as well as in the positive ion mode to measure tetrabutylammonium (Figure 4). Tetrabutylammonium at *m/z* 242 produced fragments at *m/z* 186, *m/z* 184, *m/z* 142, *m/z* 130 and *m/z* 100 corresponding to tributylammonium, dehydrogenated tributyl ammonium, dehydrogenated methyl dibutylammonium, dibutylammonium and loss of ethane from dehydrated dibutyl ammonium cation. The product ion scan mass spectrum establishing the limit of detection as 1 pg of tetrabutylammonium perchlorate swabbed from a glass surface can be found in Figure S3. Sodium perchlorate was also analyzed (Figure S4) and the characteristic perchlorate peaks were used for identification.

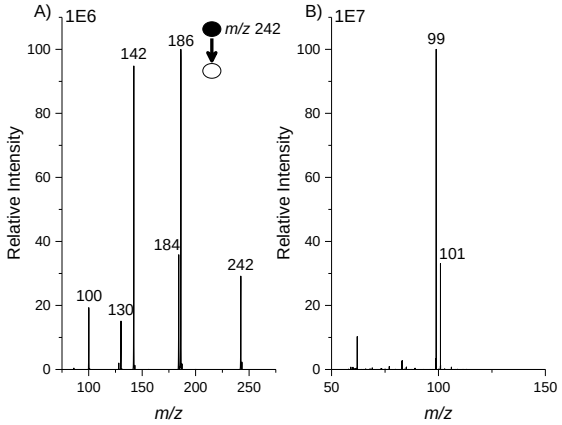

Figure 4: A) Swab touch spray ionization mass spectrometry product ion scan mass spectrum of tetrabutylammonium perchlorate in positive ion mode shows tetrabutylammonium at *m/z* 242 and characteristic fragment ions including those of *m/z* 186, 184, 142, 130, and 100. B) Swab touch spray ionization mass spectrometry full scan mass spectrum in negative ion mode of tetrabutylammonium perchlorate shows the perchlorate ions at *m/z* 99 and *m/z* 101.

In addition to characterizing explosives applied directly to the swab (Figure 2-4) and trace residues on glass (S1-S4), a variety of forensically applicable surfaces were also screened for explosive residues. Identical to the experiments using glass, a known amount was spotted onto the substrate and the sample was allowed to dry. The swab, pre-wetted with 20 µL of acetonitrile, was rastered over the surface in a circular motion to collect the explosives residue. Surfaces and their corresponding limits of detection can be found in Table 1 for each solid surface. Additionally, for screening and forensic purposes, gloves and human hands were swabbed for all explosives and limits of detection for each explosive can be found in Table 2.

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Table 1. Approximate limits of detection for explosives from various surfaces by swab touch spray ionization mass spectrometry.

Explosive	Glass	PTFE	Stainless steel	polyethylene
TNT	10 pg	10 pg	10 pg	10 pg
RDX	10 ng	10 ng	10 ng	10 ng
HMX	10 ng	10 ng	10 ng	10 ng
PETN	10 ng	10 ng	10 ng	10 ng
Sodium perchlorate	100 pg	100 pg	100 pg	100 pg
Tetrabutylammonium perchlorate	1 pg	1 pg	1 pg	1 pg

Analysis from common surfaces for residual amounts of explosives is applicable to forensic and security analyses, from airports to crime scenes. [14d, 20a] The ability to screen people by analyzing human hands is also of great interest in situations such as airports screenings. Similarly, finding gloves near a crime scene that have residual explosives can be traced back to a perpetrator using fingerprints [32] inside the glove or using cameras between the crime scene and the location where the gloves were discovered. Additionally, the successful swabbing of a variety of surfaces shows the robustness of this technique and suggests feasibility across a variety of other surfaces as well. The surfaces studied all gave similar results except that the limit of detection for PETN was an order of magnitude higher for nitrile gloves than other surfaces or other explosives. This is likely a result of chemical selectivity specifically related to PETN and nitrile.

Table 2. Approximate limits of detection for explosives from gloves and human hands by swab touch spray ionization mass spectrometry.

Explosive	Vinyl glove	Nitrile glove	Latex glove	Exposed hand
TNT	10 pg	10 pg	10 pg	10 pg
RDX	10 ng	10 ng	10 ng	10 ng
HMX	10 ng	10 ng	10 ng	10 ng
PETN	10 ng	100 ng	10 ng	10 ng
Sodium perchlorate	100 pg	100 pg	100 pg	100 pg
Tetrabutylammonium perchlorate	1 pg	1 pg	1 pg	1 pg

4 Conclusion

To recapitulate, the analysis of six different explosive residues from a variety of surfaces (glass, stainless steel, polyethylene, PTFE, human hands, nitrile gloves, vinyl gloves and latex gloves) was performed with low absolute limits of detection without the need for complex and time-consuming extraction or sample preparation steps. Limits of detection for RDX, HMX, and PETN were 10 ng from all surfaces, with the exception of PETN on the nitrile gloves. Sodium perchlorate, TNT and tetra-butyl ammonium perchlorate had limits of detection of 100 pg, 10 pg, and 1 pg, respectively from all surfaces examined. The wide breadth of surfaces demonstrates the applicability of swab touch spray ionization for forensic, military and homeland security applications. In addition, as the explosives were detectable from human skin, airport security could employ this technology in conjunction with the current ion mobility systems. With swab touch spray ionization previously being demonstrated using portable mass spectrometers,[27, 29] this technique can be useful for *in-situ* analysis for real time detection of explosive residues.

The advantages of swab touch spray ionization are the ease of use, contained commercial packaging, low entrance barrier, and the fact that your sampling device is also your ionization source. When utilizing PS the paper triangle is the sampling and ionization source; however, swab touch spray does not require the analyst to carefully handle the device to preserve the tip as is needed in PS. Swab touch spray has detection limits comparable to PS [22] while providing a forensically feasible platform. While the detection limits have been shown to be lower for LTP, swab touch spray does not require additional parts such as the plasma generation and AC power supply. [19a]

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Keywords: Mass Spectrometry • Ambient Ionization • Explosives

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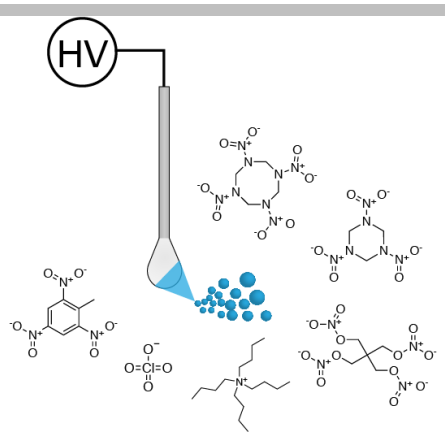
Analysis of Explosive Residues by Swab Touch Spray Ionization Mass Spectrometry



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