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Short Communications

Swab touch spray mass spectrometry for rapid analysis of organic gunshot residue from human hand and various surfaces using commercial and fieldable mass spectrometry systems

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ABSTRACT

Organic gunshot residues, specifically methyl centralite (1,3-dimethyl-1,3-diphenylurea) and ethyl centralite (1,3-diethyl-1,3-diphenylurea), are characteristic compounds for which forensic analysts test when determining if an individual has discharged a firearm. These distinctive compounds have long been analyzed by several instrumental techniques, many of which involve extensive sample preparation or have lengthy analysis times. Presented here is an ambient ionization method that requires no sample preparation, offers real-time analysis, and can be paired with a portable ion trap mass spectrometer for *in-situ* analysis. Swab touch spray ionization utilizes a rayon-tipped swab that has an aluminum wire handle which can simply be swabbed over the area of interest. After contacting the hands of the shooter, or other surfaces, the swab simply has solvent applied to the rayon tip and a high voltage applied to the aluminum handle. This process generates ions that the mass spectrometer will use to determine if the organic gunshot residues are present. Mass spectrometry allows for the direct confirmation of organic gunshot residue on suspects hands, confirmed through tandem mass spectrometry. Additional benefits of swab touch spray ionization are that the swabs are commercially available, they are sterile, and they are individually packaged to prevent contamination. The swabs are also forensically feasible because they are sealed prior to delivery by the vendor with a tamper-proof label. Here we have shown that this ambient ionization method allows for the direct swabbing of suspected shooters hands for trace residues and confirm the presence of the two organic gunshot residues investigated.

1. Introduction

Forensic investigation into the possibility of a suspect discharging a firearm in recent years has expanded from elemental inorganic gunshot residue analyses to molecular organic gunshot residue analyses (OGSR) [1]. Protocols have been developed for the collection and analysis of OGSR [1] which focus heavily on the stabilizers present in many ammunition types such as methyl centralite (MC) (1,3-dimethyl-1,3-diphenylurea) and ethyl centralite (EC) (1,3-diethyl-1,3-diphenylurea). These two compounds were selected from the expansive list of OGSRs because they are not commonly used in any other application and would therefore be among the most discriminatory compounds for determining if a person has potentially discharged a firearm [2]. The complementary nature of OGSR analysis adds a level of confirmation to the typical inorganic analysis that is traditionally performed. OGSR has been shown to be detectable on skin hours after discharging a firearm [3]; however, there is degradation over time and improved *in-situ* analysis would greatly benefit the forensic community [4]. A recent comprehensive review identified over 136 compounds to be associated with OGSR [5]; however, this current study will only focus on the detection of MC and EC as a proof of principle.

Currently OGRS analysis has been accomplished by a number of analytical techniques, many of which require lengthy chromatography or extraction techniques [5]. Forensic staples like gas chromatography [6] and ultra-high performance liquid chromatography [7] have demonstrated their capabilities of identifying and determining the presence of OGRS. While these methods are reliable analytical techniques, they suffer from lengthy analysis times and are not amenable to *in-situ* analysis. Similarly, the standard sampling methods for OGSR are various forms of swabs and

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stubs [8,9]. In order for these chromatographic methods to be utilized, an extraction technique, such as a solid phase microextraction [10], has to be performed. Where swabs and stubs are convenient methodologies for sampling, when combined with extraction techniques the number of experimental and sample preparation steps increases, amplifying analysis time and extending the room for operator error and sources of contamination. There have been reports of swabs that have removed the sample preparation steps through the use of TOF-SIMS directly on the swab [11], but the ability of *in-situ* analysis is nonexistent due to the complexity of the instrumental setup.

Ambient ionization mass spectrometry [12], starting with desorption electrospray ionization (DESI) [13] and direct analysis in real-time (DART) [14], changed how mass spectrometry sampling can be performed. Since the onset of ambient ionization, there have been ample forensic advances because of these techniques, as outlined in two recent reviews [15,16]. Two major benefits of ambient ionization as it relates to forensic science are the lack of sample preparation and the ability to form ions in the open environment. DESI mass spectrometry has been shown to be capable of identifying and distinguishing OGSR in a simple and noninvasive method [17,18]. While DESI has advantages over the extraction based techniques spoken above, swab touch spray ionization may be better suited for OGSR analysis [19–21]. Swab touch spray utilizes a rayon-tipped swab to collect the analytes of interest by swabbing the dry swab over the area of interest (i.e. the hands of a suspected shooter, or an article of clothing of the suspected shooter). The swab is constructed with an aluminum handle which allows a high voltage lead to be connected directly to the swab to promote ionization when solvent is applied [20]. The aluminum handle is pertinent to swab touch spray because this is how the high voltage is applied; other handles like wood or plastic are nonconductive. Some of the methods above also utilized swabs, but they either required an extraction method or a more complex method of ionization [5]. These extraction methods or more complex methods of ionization diminish the ability for fast turnaround times of the forensic analysis and further limit the technique's ability to be coupled with a portable instrument. This paper will demonstrate the ease of swab touch spray ionization, its forensic feasibility for organic gunshot residues, and its ability to be coupled to a portable mass spectrometer for *in-situ* analysis.

2. Materials and methods

2.1. Chemicals and supplies

HPLC-grade methanol, methyl centralite (1,3-dimethyl-1,3-diphenyl-urea) and ethyl centralite (1,3-diethyl-1,3-diphenyl-urea) were purchased from Sigma-Aldrich (St. Louis, MO). Anti-static vinyl gloves (OAK Technical, Matteson, IL), Diamond Grip Latex gloves (Microflex, Reno, NV) and Black Nitrile Exam Gloves (Ammex, Seattle, WA) were used in these experiments.

2.2. Swab touch spray source and mass spectrometer

All spectra were recorded in positive ion mode using a Thermo LTQ Orbitrap XL Hybrid Ion Trap-Orbitrap mass spectrometer (San Jose, CA) or a home-built Mini 12 rectilinear ion trap (Purdue University, West Lafayette, IN) [22]. All MS/MS product ion scan mass spectra were generated through collision-induced dissociation (CID). Normalized collision energies from 8 to 15 on the ion trap were used. Medical grade sterile swabs (Copan Diagnostics, Murritea, CA) constructed with aluminum handles and rayon swabs were utilized for all experiments. Each swab was individually packaged with a tamper-proof label and removed from packing only to swab and then was returned to the casing. Each surface (bare hands, gloved surfaces, clothing and spent casings) were swabbed in a circular motion after discharging the firearm. Approximately 20 circular motion passes were performed over the area of interest, for example the top side of the right hand between the thumb and the pointer finger. The swabs were positioned vertically (approximately 8 mm) above the inlet of the mass spectrometer. HPLC-grade methanol was applied to the swab via pipette to ensure that the swab was completely wetted. Then a continual flow of methanol spraying solvent was delivered to the swab by a Harvard Apparatus standard infusion only PHD 22/2000 syringe pump (Holliston, MA) using a Hamilton syringe (Reno, NV) at a varied flow rate (10–30 μl/min) to maintain a steady spray. A high voltage of 5.5 kV was applied to the aluminum handle and the generation of a spray could be visually observed [20].

2.3. Ammunition and firearm

Four different 9 mm handguns, with four different ammunitions were used in this study. Each of the ammunitions were discharged by only one of the four different handguns. Federal Ammunition 9 mm Luger 115 Grain Full Metal Jacket rounds (Anoka, MN) were discharged by a Heckler & Koch VP9 (Newington, NH). Independence 9 mm Luger 124 Grain Full Metal Jacket rounds (Lewiston, ID) were discharged by a Beretta M9 (Accokeek, MD). Winchester 9mm Luger 147 Grain Full Metal Jacket rounds (East Alton, IL) were discharged by a Glock 17 (Smyrna, GA). Federal Ammunition American Eagle 147 Grain Full Metal Jacket Flat Point rounds (Anoka, MN) were discharged by a SIG Sauer P320 (Newington, NH). Different firearms and ammunitions were selected to determine if this could be a universal method. To minimize the confounded variables of shooters, ammunition and firearm the casing of each expended ammunition was swabbed and analyzed for the presence of MC and EC. Each firearm was discharged by one individual and each individual only fired one ammunition and firearm per session at the range. For each experiment, unless otherwise stated, 10 rounds were fired from the handgun and then the shooters hands were immediately swabbed once the weapon was cleared. For all ammunitions where EC and MC could be detected by swab touch spray mass spectrometry after 10 rounds were discharged could also be detected after a discharging of the firearm on both mass spectrometers.

3. Results and discussion

3.1. Swab touch spray of various surfaces

To test the viability of swab touch spray for OGSR analysis the inside of the bottles of MC and EC standards were swabbed and analyzed by the LTQ ion trap (Fig. 1). The MS/MS spectra of both ions correlating to $[MC+H]^+$ (m/z 241) and $[EC+H]^+$ (m/z 269) matched the literature [17,18] and had reproducible and stable spectra with distinctive fragment peaks that were observable through the subsequent experiments.

After these results had demonstrated that swab touch spray is capable of ionizing MC and EC standards, swab touch spray was utilized to analyze OGSR produced from the discharging of a firearm. The researchers shot four different 9mm full metal jacket ammunitions, with varying grains, and tested the ability of the dry swab to extract the OGSR off the right hand of the shooter when swabbed. Four surfaces were tested, an exposed bare hand, a hand covered in a vinyl glove, a nitrile glove, and a latex glove. The variety of gloved surfaces were selected based on the general availability of these to the general public who may try and cover up a crime they committed, as well as to show the robust nature of the swab at extracting the OGSR off of a variety of surfaces. Table 1 describes the ability of the swab to extract the OGSR off the surface.

As seen in Table 1, MC and EC was detected in all four surfaces for the first three ammunitions; however, MC and EC were not detected in the American Eagle 147 Grain full metal jacket flat point ammunition discharged from a SIG Sauer P320. As the composition of the bullets are not public knowledge, the researchers also swabbed the inside of the spent casing to determine if the lack of detection of MC and EC was a result of the swab or the lack of the two compounds found in the ammunitions. There was no signal of MC or EC for the American Eagle casing either, to which the researchers propose that there may not be any MC or EC in this ammunition, or with the increased grain potentially the MC and EC is in a more limited quantity and the quantity transferred to the surface is below the limit of detection of the technique. Each of the three ammunitions that were found to contain MC and EC, a single discharge of the firearm provided enough of both compounds to be detected by swab touch spray mass spectrometry. The lower limit of detection for both MC and EC were lower than 50 ng on the LTQ XL. The researchers checked the inside of the