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Initial evaluation of inlet thermal desorption GC–MS analysis for organic gunshot residue collected from the hands of known shooters

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ABSTRACT

The discharge of a firearm produces a wealth of physical and chemical evidence. Traditional forensic analysis has focused on inorganic particulates formed from the primer, referred to as gunshot residue (GSR). The last few years have seen interest in expanding the list of target compounds to include organic constituents of firearm discharge residue (OGSR). To facilitate adoption by the forensic community, new assays ideally should exploit instrumentation commonly found in forensic laboratories such as gas chromatography/mass spectrometry (GC/MS). Here, a commercially available thermal separation probe that fits directly into the injection port was evaluated as a means of sample introduction for GC/MS operated in a selected ion monitoring mode. A statistical approach utilizing bivariate plots linked retention time to ion ratio data to afford a probabilistic interpretation of the results. A total of 27 authentic shooter swabs were collected after firing of 1–5 rounds and were analyzed in halves or triplicates. Ethyl centralite was detected in 81% of the samples; diphenylamine in 56%, and 2-nitrodiphenylamine in 14%. Dimethyl and dibutyl phthalates were detected in a majority of the swabs but also in many of the hand swab blanks. The use of surrogate standards provided a measure of recovery and reproducibility for retention times and ion ratios.

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1. Introduction

Once a firearm is discharged, vapors and particles escape from the weapon in a radial expulsion known as a plume. The plume is a complex heterogeneous mixture referred to as firearm discharge residue (FDR) and is comprised of inorganic particulates (GSR), organic condensates, and particles of unburnt and partially burnt propellant (OGSR collectively). This mixture is deposited on proximate surfaces (Fig. 1) including the hands, chest, and face of the individual firing the weapon.

Many variables dictate the amount of residue deposited including ammunition and weapon used and environmental conditions. In a recent study it was estimated that deposition amounts for OGSR compounds on the hands of shooters ranged from 90 to 178 ng total [1]. Thus, it becomes essential to collect as much residue as possible over a large surface area (the hands) while concentrating what is collected in a relatively small area. Doing so facilitates the use of different strategies for sample preparation and extraction. Various methods have been used for sampling FDR including adhesive tapes, stubs, glues, swabbing, and vacuum

lifts [2–5]. Adhesive tapes and stubs are the most common and are typically used for collecting GSR particulates. Recent research has investigated the capability to utilize the same stub for collection of both GSR and OGSR compounds [5]. Swabbing is the second most common technique for FDR sampling and is used for the collection of both inorganic and organic residues. Frequently, the swab is dipped in a suitable solvent prior to sampling to facilitate transfer of residues to the surface of the swab.

Current forensic methods of FDR detection focus on the inorganic particulates (GSR) originating from compounds found in the primer. Analysis using scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) is a technically sound and vetted method detailed in an ASTM Method [6]. SEM-EDX identifies GSR based on spherical morphology and inorganic composition. There is no issue with this methodology per se; however, the combination of organic and inorganic data would increase the value of any positive findings. The primary limitations of SEM/EDS include long analysis times as well as the cost and complexity of instrumentation. Particulate GSR evidence is prone to secondary transfer, meaning it can be transferred by physical activity or hand washing. Loss due to secondary transfer makes data interpretation more difficult as time passes. In addition, ammunition manufacturers have begun producing lead free

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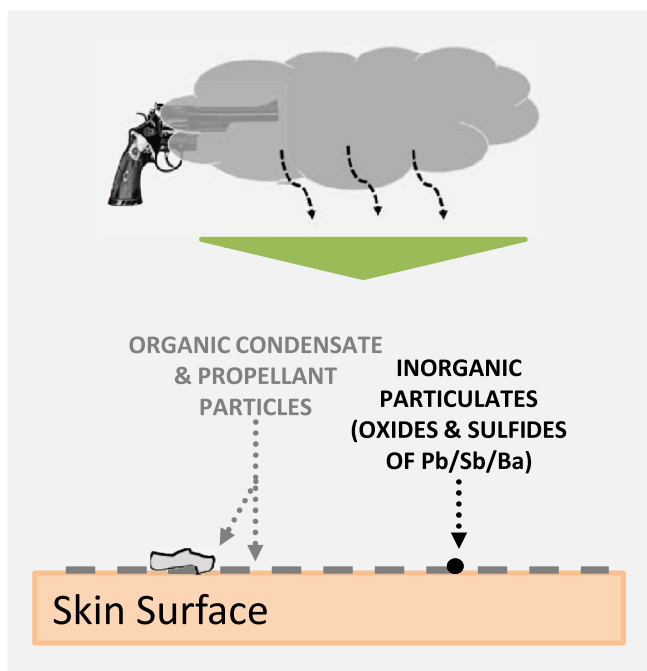


Fig. 1. Deposition of firearm discharge residue including GSR and OGSR on the surface of the skin.

ammunition (LFA) by replacing of lead with other metals such as copper, aluminum, and zinc, which results in changes in the composition of traditional GSR particulates [7]. Although the ASTM method now includes additional elements found in LFA the absence of a traditional GSR inorganic component (Pb, Ba, Sb) could lead to false negatives or inconclusive results. Finally, the GSR particulates make up a fraction of the discharge residue, leaving other potential chemical evidence unexamined. At the least, methods targeting organic constituents could serve as strong supporting evidence for the presence of FDR and could aid in addressing the limitations associated with GSR merely by itself.

Nitrocellulose (NC) and nitroglycerine (NG) are the main energetic components in small arms propellants. Although these two explosive components decompose upon discharge of a firearm, decomposition also occurs during storage. The decomposition, which particularly occurs in moist air or under hot conditions, forms nitric and nitrous acids which will further degrade the propellant. Ancillary compounds are added to propellants to function as stabilizers, plasticizers, flash suppressants, and deterrents. These include compounds such as ethyl centralite (EC), methyl centralite (MC), dimethyl phthalate (DMP), and diphenylamine (DPA) [1,2,8–15]. Nitration products of DPA including *n*-nitrosodiphenylamine (N-NDPA), and 2-, and 4-nitrodiphenylamine (2-NDPA and 4-NDPA), formed as the energetic materials degrade have also been studied [1,2,8–15]. Reviews by Dalby et al. [2] and Taudte et al. [15] and work done by Weyermann [16] include more extensive lists of compounds that may contribute to OGSR. These lists include compounds such as carbazole, camphor, akardite, and cresol [2,15,16]. These compounds have been the focus of much research as was the case with this work.

Although methods utilizing liquid chromatography and mass spectrometry (LC/MS) and gas chromatography-mass spectrometry (GC/MS) have been applied to hand swabs, the methodology has not yet found widespread application in forensic laboratories [15]. Solvent extraction of the swabs are generally multi-step processes that include drying and reconstitution in small volumes. Extractions are time consuming, destructive, and risk the introduction of contamination. Prepared with proper care, these extracts

clearly can be used in conjunction with electrospray (ESI) and atmospheric pressure ionization (APCI) mass spectrometers coupled to mass spectrometers such as exact mass time of flight or triple quadrupole systems. ESI/MS systems are often available in toxicology sections but developing and validating methods on working instruments can be a challenge in a casework laboratory. Conversely, GC/MS instruments are ubiquitous in forensic laboratories, but limitations such as the small amount of FDR present, swabbing efficiency, and extraction efficiency tend to drive concentrations below detection limits for successful characterization of OGSR recovered by solvent extraction from swabs.

Solvent-less methods have also been examined for sample introduction for GC/MS in the context of OGSR. These methods rely on thermal desorption of compounds from the swab or other sample such as unburnt and partially burnt gunpowder particles, firearm barrels, and spent cartridge casings [11,14,16–20]. In passive thermal desorption, the vapors are introduced directly into the GC inlet without additional pre-concentration. Alternatively, the vapors can be re-concentrated on a solid phase such as in SPME or variants such as stir bar, micro-drop, or planar surface sorption.

The use of passive thermal desorption (TD) to introduce OGSR samples into an instrument has been demonstrated previously in our laboratory. Ion mobility spectrometry (IMS) has been shown to be useful for differentiating known shooters from non-shooters when used as a screening test [8,9,21–23]. With IMS, sampling media is directly inserted into the thermal desorber without any preparation or pre-treatment. Direct heat is applied to the swab, releasing volatile organic compounds (VOCs) from the sampling matrix into the ionization region of the instrument as a function of vapor pressure. The temperature is optimized to afford rapid desorption without inducing degradation of the sample media.

In this project, TD was directly coupled with gas chromatography mass spectrometry (GC/MS) using a commercially available specialized injection port fitting called a thermal separation probe (TSP). The probe assembly takes the place of the top nut of the injection port and the sample holder fits down into the inlet liner. Thus, the injection port acts as the thermal desorber. Volatilized compounds are swept into the column via carrier gas and concentrated on the head of the column which is maintained as close to room temperature as possible.

The TSP has been applied to FDR analysis before although not as a passive sample introduction system as described in this paper. Tarifa et al. [24] and Fan et al. [25] described pre-concentration methods in which vapors from samples, collected on cotton swabs, were trapped onto glass fiber filters coated with PDMS contained within a capillary. The capillary was then inserted into the TSP holder and desorbed onto the column. This method, called capillary microextraction of volatiles (CMV) was used along with LIBS spectroscopy to characterize swabs recovered from police officers and non-shooters [24]. A combination of passive and active headspace methods were used to pre-concentrate the organics on the glass/PDMS filters which were in turn thermally desorbed using the TSP and characterized by GC/MS (or GC- μ ECD). The authors estimated detection limits for target compounds (NG, 2,4-DNT, and DPA) in the headspace to be in the range of \sim 3 to 9 ng and when the method was applied to authentic shooting samples, NG and DPA were detected in 5 of the 9 known shooter samples.

The goal of this research was to evaluate the feasibility and performance characteristics of thermal desorption as a means of sample introduction for analysis of organic gunshot residue with GC-MS directly from hand swabs without prior extraction or pre-concentration. The advantage of this approach is that there is literally no sample preparation – swabs are loaded into a quartz micro-tube, placed in the TSP, and desorbed in the injection port. The challenge is detecting compounds from hand swabs at forensically-relevant amounts (1–3 shots). Here, selected ion

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