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Short Communications

Identification of polymers and organic gunshot residue in evidence from 3D-printed firearms using DART-mass spectrometry: A feasibility study

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ABSTRACT

Rapid advances in 3D-printing technology have created an emerging class of firearms. As the movement to self-manufacture firearms with 3D-printing grows, it is reasonable to assume that they will be increasingly used in crimes. Here, we test-fired gun barrels made with acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), polyethylene terephthalate (PETG), chlorinated polyethylene (CPE), and nylon. The resulting cartridge cases, bullets, and gunshot residue (GSR) were examined by direct analysis in real time – mass spectrometry (DART-MS). High-resolution mass spectra detected polymer from the gun barrel on bullets and cartridge casings for a 0.38 special caliber gun and, to a lesser extent, for a 0.22 caliber 3D-printed gun. Particles of plastic were identified in some GSR samples collected from clothing used as a backstop for test-fires. DART-MS also readily detected signature organic GSR compounds, including methyl centralite, ethyl centralite, diphenylamine, and nitrocellulose, on recovered bullets, cartridge cases, and in extracts of SEM stubs used to collect GSR from the clothing. Overall, this study demonstrates that analysis of firearm trace evidence using DART-MS deserves more attention, and that the technique may be particularly useful for investigating crimes involving 3D-printed guns.

1. Introduction

Rapid advances in 3D-printing technology have created an emerging class of firearms that we know almost nothing about, forensically speaking. As the movement to self-manufacture firearms with 3D-printing technology grows, and as 3D guns themselves become more functional and reliable, it is reasonable to assume that they will be used increasingly in crimes, especially by individuals who may have less access to traditional guns. Printed plastic guns and bullets are also of concern to public safety because they can potentially go undetected by metal detectors into high security areas, and to criminal justice because they do not bear traceable serial numbers. As the use of 3D-printed guns in crimes grows, criminal justice practitioners will need proven new forensic methods to analyze the particular types of evidence that these guns deposit at crime scenes.

The notion that making a 3D-printed gun is complicated and that the resulting weapon is inefficient is changing. The barrier to the proliferation of do-it-yourself 3D-printed guns has been functionality, but specially-designed bullets and other inventive features have made them one step closer to being widely available to the general public. Already 3D-printed guns have been shown to withstand repeated firing and have been found at crime scenes [1–3]. Incidents involving 3D-printed guns can be expected to grow as the technology improves, costs decline, and as superior gun blueprints are posted on the Internet. Blueprints for 3D-printed guns first appeared online around 2013 and continue to surface on the internet. The 3D-printable file for the world's first 3D-printed gun, the so-called "Liberator" 3D-printed gun, was downloaded 100,000 times in two days from the high-tech gunsmithing group Defense Distributed Company [1]. The company removed the files from the website at the request of the U.S. State Department. Whereas such blueprints are often removed or the web-address blocked, many have been leaked to sites like Pirate Bay where they continue to exist and can potentially be downloaded and stored offline. Effectively, once initially released, such digital files persist indefinitely through download sites and offline storage media [1]. Moreover, the increased public debate over individual access to firearms can be expected to further increase interest in 3D-printed guns. A report on the security implications of 3D-printed firearms found that law enforcement agencies in many countries are concerned about the ease of access to 3D-printed firearms, which can be created in complete privacy and are difficult to detect with current security measures [1]. Despite the need for the forensic science community to properly address

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this emerging class of firearms and the threats it poses, to our knowledge there have been no publications on trace chemical evidence from 3D-printed guns.

DART-MS is a powerful analytical technique that is currently used in many federal, state and private laboratories for forensic applications, including the identification of drugs of abuse, trace evidence analysis, and sexual assault investigations [4–9]. DART is a versatile atmospheric pressure ion source allowing the analysis of materials in open air under ambient conditions [7]. Desorbed ions are carried by the gas stream into the sampling orifice of a mass spectrometer. When coupled with a high-resolution mass spectrometer, the system can determine the chemical composition of a sample in its native form, and produce accurate mass spectra with little or no sample preparation. Because so little sample is needed, it can be considered a pseudo-non-destructive technique, allowing the sample to be preserved or used for other analyses.

DART-MS has been used to identify trace particles of explosives in fingerprints [10]. The technique can measure nitrated propellants and burn stabilizers such as nitroglycerin and dinitrotoluene, in negative-ion mode, and centralites and phthalates in positive-mode [11]. In addition, DART-MS can provide “fingerprint” mass spectra for the identification of polymers, their additives, and other materials, and is used at NASA for the identification of spaceflight-related contaminants, including industrial polymers [12–14]. However, DART-MS has not been sufficiently applied to GSR and other trace evidence from firearms, in part, because fundamental studies are lacking.

GSR is produced from the combustion of the primer and propellant, and is composed of combustion products, unburned and partially burned propellant, primer particles, as well as lubricants and metal from the cartridge and weapon [15]. Inorganic GSR often includes heavy metals such as lead (Pb), barium (Ba), and antimony (Sb) from the primer, trace metals from metallic parts, and nitrates and nitrites [15]. Organic gunshot residue (OGSR) may contain nitroglycerine, dinitrotoluene, phthalates, ethyl centralite, and diphenylamine, among other compounds [16,17]. Some crime laboratories are moving away from traditional (inorganic) GSR testing due to budget constraints, sample backlogs, and concerns regarding interpretation, such as potential environmental sources of particles resembling inorganic primer [18,19]. In addition, “lead-free” contamination has introduced the potential for false negatives with some GSR tests, such as primer GSR analysis by conventional SEM/EDX protocols [20]. Recently, several new methods have focused attention on OGSR [20]. Advantages of targeting OGSR for analysis include condensates that stick to the skin and are not prone to secondary transfer, multiple target compounds with options for chemical analysis, and low background which improves limits of detection [20]. However, these techniques are often tedious and time-consuming. A relatively new technique that has the capability to detect and identify a wide-range of compounds in GSR is direct analysis in real time (DART) mass spectrometry.

In this study, we fired a gun with barrels made from different polymers and sought to determine whether DART-MS can be used to readily detect and identify traces of polymer and organic GSR compounds on the bullets, cartridge cases, and in GSR collected from clothing.

2. Material and methods

2.1. Experiments and firearm construction and test-firing

A summary of the experiments and the compounds detected by DART-MS is given in Table 1. The study was conducted in two phases (Fig. 1). In phase I, we constructed a crude firearm with a machined polymer barrel (0.359″ ID, 2″ OD) for proof-of-concept. The 0.38 special caliber gun consisted of an ABS or Nylon 6/6 polymer for the barrel, a 6061 aluminum cap, and a tool steel roll pin. We successfully fired the ABS gun several times and collected GSR, cartridge cases, and the 0.38 special caliber bullets. However, the Nylon gun broke apart when fired, allowing for only one viable test shot. Because we successfully detected polymer and OGSR compounds on recovered bullets, cartridge cases, and SEM stubs, we proceeded to construct a fully functional 3D-printed firearm for additional testing.

In phase 2, we repeated the study using a 3D-printed 0.22 caliber firearm generated from “Washbear” blueprint files obtained online and printed using an Ultimaker 2^+ printer with accompanying CURA software. Firearm components were printed in PLA polymer, except the cylinders, which were interchangeable and consisted of four separate polymers: ABS, PLA, PETG, and CPE. For visual simplicity, the four polymers obtained consisted of different colors, with white, orange, green, and blue corresponding to ABS, PLA, PETG, and CPE respectively. The firing pin was machined from a 1/8″ steel drill bit blank using a dremel tool. Polymers were obtained from commercial providers: Ultimaker and MatterHackers.

In both phases of the study GSR was collected from a cotton shirt situated ∼0.3 m from the gun using a standard carbon-adhesive GSR stub (Ted Pella Inc.12.7 mm SEM pin stub). Spent cartridges, bullets and GSR stubs were wrapped in aluminum foil and shipped to JEOL USA, Inc. for DART-MS analysis.

2.2. AccuTOF-DART analysis of cartridge cases, bullets, and GSR stubs

We used an AccuTOF-DART 4G (JEOL USA, Inc., Peabody, MA) time-of-flight mass spectrometer (TOF-MS) for high-resolution mass measurements (resolving power ≈ 10,000, FWHM definition)

Table 1
Summary of experiments carried out and compounds detected.

Firearm	Barrel Polymer	DART Mass Spectrometry				SEM
		Cartridge Scraping[1]	Bullet Scraping[1]	GSR on SEM stub[2]		
				Positive Ion Mode	Negative Ion Mode	
Phase I 0.38 Caliber Machined Barrel	ABS	ABS and OGSR[3]	ABS	OGSR[3]	Not measured	Not measured
	Nylon	Nylon and OGSR[3]	Nylon			
Phase II 0.22 Caliber 3D-Printed Firearm	ABS	Barrel Polymer and OGSR[3]	ABS	OGSR[3]	Nitro-glycerine	Yes
	PLA		PLA			
	PETG		Polymer not detected			
	CPE					

[1] Measured directly; positive ion mode.
[2] Methanol extract; OGSR and nitroglycerine peaks were not detected on a blank SEM stub wash.
[3] Organic GSR compounds detected include methyl centralite, ethyl centralite, monomethyl phthalate, and diphenylamine.

Fig. 1. Phase I test-fire of ABS polymer barrel (left). Fully 3D-printed gun and interchangeable cylinders composed of blue CPE, white ABS, orange PLA, and green PETG (center). Phase II test-fire of 3D-printed gun (right).

of cartridge cases, bullets, and GSR stubs (Fig. 2). A melting point (glass capillary) tube was used to scrape the bullet and cartridge cases and then the tube was placed in the DART beam near the sampling inlet orifice of the AccuTOF mass spectrometer. For GSR collected from clothing, we deposited approximately 50 μL of methanol onto the center of the GSR stub using a pipette, and then immediately withdrew the methanol back into the pipette for transfer into a glass sample vial. The 50 μL volume was sufficient to cover the entire surface of the stub without overflow. Approximately 1–3 μL of the methanol were deposited onto the sealed end of a glass melting point tube for analysis in the DART gas stream. A mass spectrum of polyethylene glycol (PEG), with an average molecular weight of 600 g/mol, was used as a reference standard for the mass calibration. The atmospheric pressure interface was operated with the atmospheric pressure interface potentials set to: Orifice 1 = 20 V, Orifice 2 = 5 V, and Ring Lens = 5 V. At these potentials, little to no collision-induced dissociation (CID) occurs and the resulting mass spectra are dominated by protonated molecules ($[M + H]^+$). The RF ion guide voltage was set to 600 V to allow the detection of ions greater than m/z 60. The DART-SVP ion source (IonSense Inc., Saugus, MA) was operated with a helium gas heater temperature of 300 °C and exit grid voltage of 250 V. TSS Unity software (Shrader Analytical, Detroit, MI) and Mass Spec Tools software (RBC Software, available from http://www.shop.

Fig. 2. Categories of trace evidence analyzed in this study. Bullet fired from a gun with a black ABS barrel showing a polymer smear mark and scrape marks from the melting point tube used for DART-MS analysis (left). Cartridge case from the same gun (middle, left shell) showing external black polymer residue, unlike a cartridge case from a traditional gun (middle, right shell). Adhesive stub used to collect GSR and occasionally polymer (colored) fragments from a cotton t-shirt (right).

mass-spec-software.com/) were used for data processing, data interpretation and report generation. Polymers were identified with Mass Mountaineer by matching the DART mass spectra against spectra in a previously compiled custom database that contained DART mass spectra of common polymers, including the polymers used to construct the 3D-printed firearm components. A summary of the DART experiments carried out is given in Table 1.

2.3. Scanning electron microscopy and energy dispersive spectroscopy of GSR stubs

We used a JSM-IT300LV SEM (JEOL USA, Inc., Peabody, MA) with an Oxford Aztec EDS system with dual X-Max^N 80 mm^2 silicon drift detectors to analyze the GSR stubs. The SEM was set to 20 kV using the backscatter electron detector for image collection. EDS maps and spectra were then collected.

2.4. Differential scanning calorimetry (DSC) of common 3D-print polymers

DSC analysis was performed on a TA Instruments Q2000. Approximately 5 mg of each polymer was analyzed from 0 °C to 250 °C followed by 250 °C to 0 °C with a ramp rate of 30 °C min^{-1}. Each sample was run in three replicate cycles.

3. Results and discussion

Table 1 provides a summary of the major compounds detected by DART-MS. We discuss the results for polymers and OGSR separately below.

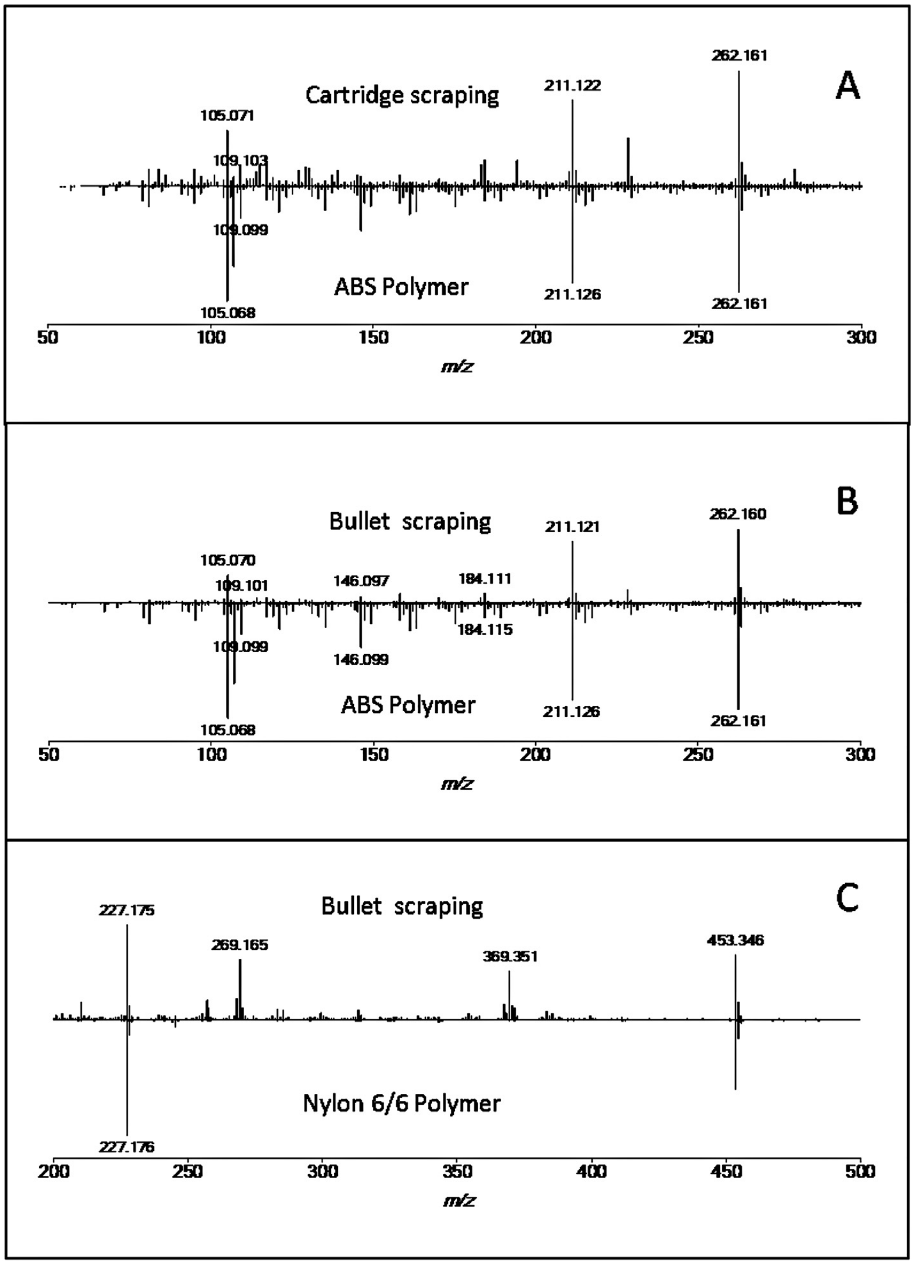

Fig. 3. DART-TOF high-resolution mass spectra for cartridge case (A) and bullet (B, C) scrapings. Major peaks were compared to the DART polymer database and correctly identified the polymer used in the barrel. The peaks at *m*/*z* 269.165 and *m*/*z* 369.351 in Fig. 3C correspond to protonated ethyl centralite and $[M + H - H_2O]^+$ for cholesterol (from handling).

3.1. Detection and identification of polymers

Bullet and cartridge cases from the 0.38 special caliber gun gave accurate-mass spectra clearly indicating the presence of the polymer used in the gun barrel, as shown by the *m*/*z* values for major peaks in both the sample and database spectra (Fig. 3). Evidence from the gun with the ABS barrel showed all three major spectral peaks (*m*/*z* 105.06, 211.12, and 262.16) for the ABS polymer represented in the library spectrum. The nylon 6/6 samples showed both major peaks (*m*/*z* 227.18 and 452.34), as well as a peak at *m*/*z* 269.165 corresponding to protonated ethyl centralite. A peak at *m*/*z* 369.351 is assigned as $C_{27}H_{45}^{+}$ which is commonly associated in DART mass spectra with $[M + H - H_2O]^+$ from cholesterol (fingerprints resulting from handling).

Detecting polymer in the trace evidence from the 0.22 caliber 3D-printed gun was more challenging, perhaps because of the less powerful cartridge used. Another factor that may play a role in how much material is transferred to the bullet and cartridge casing is how tight the cartridge fits in the barrel. Nevertheless, some of the stubs had particles that looked like plastic under a microscope. When those particles were picked out and analyzed by DART-MS, clear spectra were obtained that matched the plastic from the gun.

SEM/EDS analysis of GSR stubs collected in phase II of the study showed small (micron-sized) spherical particles with high levels of Pb and Ba, presumably inorganic GSR condensates, on larger particles (flakes) that had high levels of C and O, presumably partially burnt or unburnt propellant and/or primer (Fig. 4). However, using SEM/EDS to distinguish between OGSR and polymer from the 3D-printed gun is problematic given that both are organic and can have a range of particle sizes and morphologies. CPE contains chlorine that may not be present in typical OGSR, and there may be some morphological differences between OGSR and polymer fragments to key in on, but this requires further investigation and is beyond the scope of this paper. Polymer was not detected in the GSR stub solvent washes; instead, those spectra were dominated by the compounds typical of OGSR discussed earlier. This would likely be the case even if the solvent dissolved small amounts of polymer particles.

DSC was used to characterize common 3D-printer polymers. The DSC melting/crystallizing curves (transition temperatures) were able to distinguish between the types of plastic and were independent of the plastic's color (Supplemental Fig. 1). A thermal desorption-pyrolysis attachment is commercially available for the DART mass spectrometer, which would make it possible to obtain both thermal desorption profiles and mass spectra on a single sample. This approach may lower the mass spectral background and permit separation of the 3D-printed gun evidence polymer from the GSR stub base polymer. In addition, creating a searchable DART-pyrolysis library spectrum will be useful to identify signature additives such as plasticizers that might aid in identifying specific brands of polymer used.

3.2. Organic GSR by DART-MS

A SEM stub that was not exposed to GSR was extracted with 50 μL of methanol following the same procedure used for the stubs used to sample GSR. Methanol was chosen because it is effective in extracting compounds associated with organic GSR, but it does not dissolve the black adhesive material attached to the SEM stub. In both phases of the study, DART-MS readily detected ethyl centralite, methyl centralite and diphenylamine, commonly found in firearm propellants, on the bullet and cartridge case, as well as in the solvent wash of the GSR stub (Fig. 5). In contrast, the blank stub showed trace phthalates and a peak at *m*/*z* 217.107 corresponding to the elemental composition $C_{10}H_{17}O_5$. The compound responsible for this peak is not assigned, but the peak was not observed in the stub exposed to GSR. Because positive-ion DART operates by proton transfer, DART is particularly sensitive to compounds with high proton affinities, such as ethyl centralite and diphenylamine that are observed in organic GSR, but it is less sensitive to the background peaks observed in the blank. Both scraping of the material firearm evidence and solvent washes of the GSR stubs were

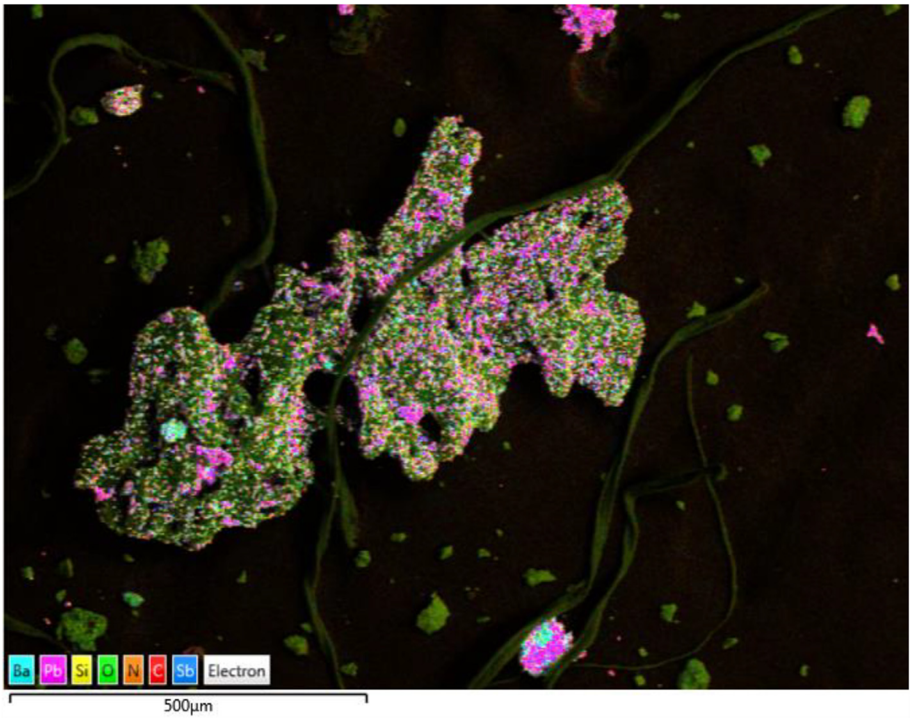

Fig. 4. SEM/EDS image showing the distribution of heavy metals (Pb, Ba, and Sb) in GSR from a 3D-printed gun.

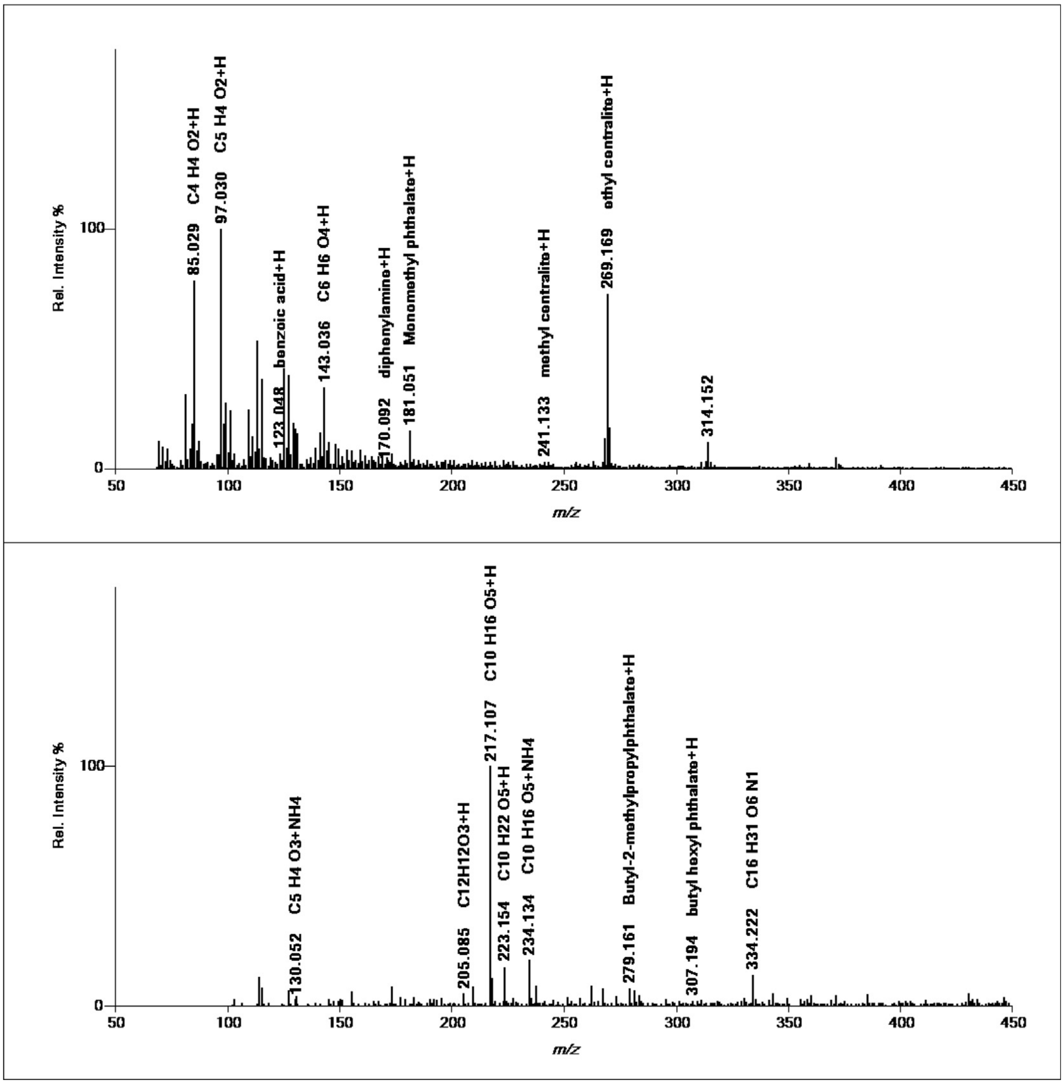

Fig. 5. (A) DART mass spectra of a methanol wash of a GSR stub showing compounds characteristic of OGSR. (B) DART mass spectrum of a methanol wash of a blank GSR stub. The peaks observed in A corresponding to characteristic GSR compounds such as ethyl centralite and diphenylamine are not detected in the blank stub (A). Furthermore, the background peaks in the blank stub (B) are not detected above the chemical noise level in the stub used to sample GSR (A).

effective in detecting ethyl centralite as shown in Fig. 3 and Fig. 5A. The presence of both M^+ and MH^+ for diphenylamine and ethyl centralite in the mass spectra is characteristic of compounds that have low ionization energy as well as high proton affinity. The relatively high abundance of ethyl centralite may be associated with the ammunition in these experiments. Because smokeless powder formulations vary with manufacturer and brand, the pattern or organic GSR components is expected to vary for different ammunition [9].

A database search of the mass spectrum of the methanol wash of the GSR stub against an in-house DART polymer database returned nitrocellulose as the best match. The peaks observed in the DART database spectrum for nitrocellulose (Fig. 6A) are pyrolytic fragments containing only carbon, hydrogen, and oxygen from cellulosic saccharides. Saccharide fragments can be observed for other polysaccharides, such as the cotton from the shirts used as receiving surfaces in these experiments. However, the positive-ion DART mass spectra for nitrocellulose (Fig. 6A) shows a clearly different pattern from the positive-ion DART mass spectrum for cotton (Fig. 6B). Fig. 6C shows a head-to-tail comparison of the measured mass spectrum (top) against the database mass spectrum for nitrocellulose.

Negative-ion DART can provide complementary information about organic GSR by detecting explosives from double-base and triple-base powder. Fig. 6A shows the negative-ion DART mass spectrum of the methanol extract from the GSR stub. Nitroglycerine (NG) is typically detected in DART as an anion adduct, and NG is detected as the nitrate adduct $[M + NO_3]^-$ where the nitrate anion arises from the nitroglycerine itself [5]. The other peaks in Fig. 6B are background peaks that were detected in a methanol wash of a blank SEM stub that had not been used to sample GSR.

Additional studies are needed to optimize DART-MS parameters using experimental design and to explore automated approaches for introducing various firearm evidence samples to create a rapid screening method. Removal or nano-extraction of the selected particles from the GSR stub should minimize organic background and improve selectivity and limits of detection. Adding spectroscopy (e.g. micro-Raman) can give confirmatory information on the same sample.

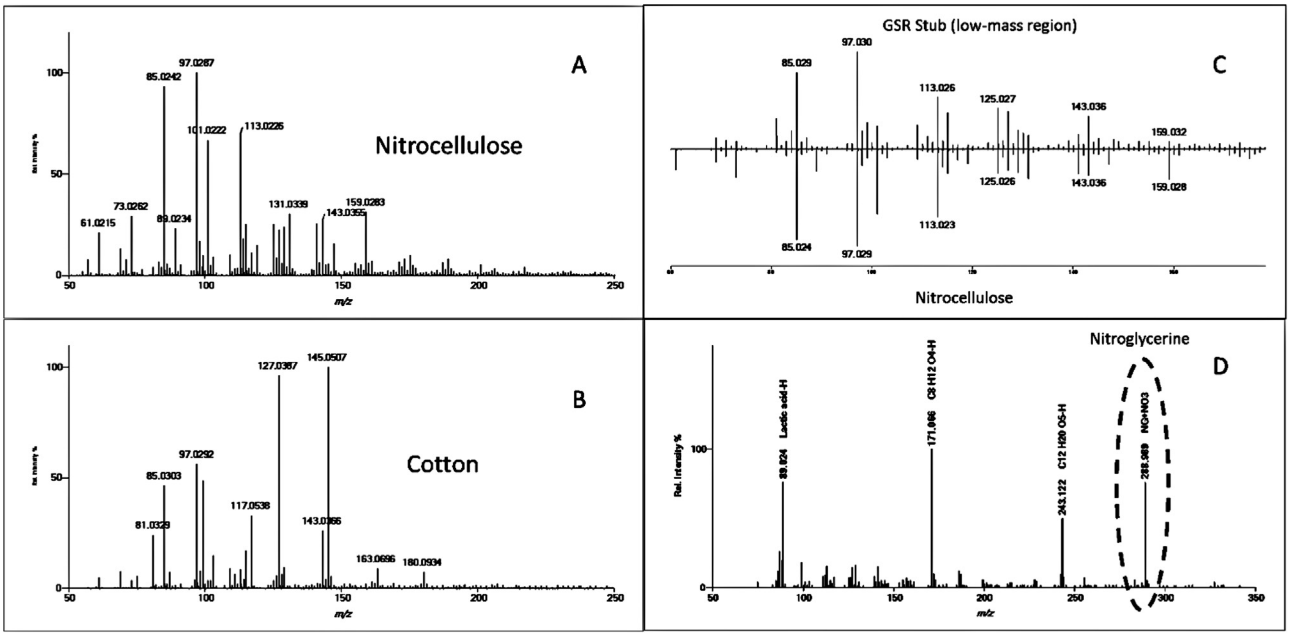

Fig. 6. (A) Positive-ion DART mass spectra of nitrocellulose. (B) Positive-ion DART mass spectrum of cotton. (C) Head-to-tail display showing an expanded view of the low-mass region in the positive-ion DART mass spectrum of the methanol wash from the GSR stub from Fig. 5A (top) compared to the positive-ion DART mass spectrum of a nitrocellulose standard. (D) Negative-ion DART mass spectrum showing nitroglycerine (circled) detected as $[M + NO_3]^-$ at m/z 288.989. The other peaks are background peaks present in the methanol wash of a blank SEM stub (not shown).

4. Conclusions

We have shown that DART-MS methods can be used to detect and identify compounds associated with organic GSR as well as polymers from 3D-printed guns in trace evidence. Thus, a spectral library of polymers commonly used in 3D-printing can be used for characterizing samples from crime scenes where a 3D-printed gun is suspected of being involved. Moreover, because DART-MS can rapidly detect OGSR signature compounds on small evidentiary samples, the technique deserves to be further scrutinized as an alternative approach for OGSR analysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.forc.2017.05.003.

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