

Review Article

Analysis of Polymers and Organic GSR from 3D Printed Firearm using Direct Analysis in Real-time Mass Spectrometry (DART-MS)

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Abstract

Several methods were developed in lab work, including forensic analysis of polymers & organic GSR from 3D printed firearms using Direct Analysis in Real Time Mass Spectrometry (DART-MS) for a wide variety of applications. Since its introduction, DART-MS has been studied for forensic use in areas including drug detection, gunshot residue, printer inks, and even insect identification. We used DART-MS to characterize the polymer evidence left behind by a 3D-printed firearm on cartridge cases, bullets, and the receiving surface. According to James Cizdziel, "There is concern with these 3D printed guns because they have no serial numbers. The fire gun barrels made with Acrylonitrile Butadiene Styrene (ABS), Polylactic Acid, PETG, Chlorinated Polyethylene (CPE) & Nylon were examined by DART-MS. The resulting cartridge cases, bullets & GSR are examined by Direct Analysis of Real Time-Mass Spectrometry". It successfully detects and identifies the traces of polymer and organic GSR compounds on the bullets, cartridge cases, and in GSR collected from clothing. While detecting polymer in the trace evidence was challenging, DART-MS obtained clear spectra that matched the plastic from the gun from clothing used as a backdrop for test fire. According to the study, DART-MS readily detected three chemicals commonly found in firearm propellants (ethyl centralite, methyl centralite, and diphenylamine) on the bullet and cartridge case, as well as in the solvent wash of the GSR stub. 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. This study states that analysis of firearm trace evidence using DART-MS needs more attention & that the technique may be particularly useful for investigating crimes involving 3D-printed guns. I'm writing my review paper on this topic because it's important for addressing challenges related to 3D-printed firearms. These weapons often don't have traditional serial numbers, making them difficult to trace. However, by analyzing polymer residues left on bullets, cartridge cases, or nearby surfaces, investigators can potentially identify the firearm used. The unique chemical makeup of polymers used in 3D printing can help ink the residue back to a specific gun or even a particular 3D printer model. This study states that analysis of firearm trace evidence using DART-MS needs more attention & that the technique may be particularly useful for investigating crimes involving 3D-printed guns.

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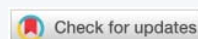
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Introduction

The earliest officially recorded criminal case involving a firearm manufactured via 3D printing took place in the United Kingdom in 2013. Since that time, the occurrence of these types of weapons has grown substantially. These 3D-printed firearms, which fall under the broader classification of Privately Made Firearms (PMFs), have gained traction largely due to technological advancements and the rising frequency of their detection by law enforcement. Commonly referred to as “ghost guns,” these weapons signify a transformative shift in firearm production and distribution. The advent of 3D printing has effectively democratized access to firearm manufacturing, enabling individuals to construct functional weapons using digital schematics and desktop 3D printers [1].

In the forensic investigation of firearm-related crimes, the analysis of polymer-based and organic gunshot residue (OGSR) plays a vital role in crime scene reconstruction [2]. Gunshot residue (GSR) analysis is instrumental in associating a suspect with the act of firing, determining the sequence of shots, assessing the distance between the shooter and the target, and identifying the specific type of ammunition used [3]. While conventional GSR analysis focuses on inorganic components, organic residues provide additional, complementary insights. OGSR primarily accumulates on surfaces that have been exposed to gunfire and originates from smokeless powders. These powders are composed of various chemicals, including primary explosives, stabilizers, plasticizers, gelatinizers, sensitizers, and flash inhibitors [4]. A key objective of GSR analysis is to ascertain whether the trace materials present originated from the discharge of a firearm.

Direct Analysis in Real Time–Mass Spectrometry (DART-MS) has emerged as a rapid and efficient analytical technique for the examination of diverse samples [5]. This method allows for the acquisition of mass spectra under varying in-source collision-induced dissociation (CID) voltages, yielding unique spectral signatures through distinct fragmentation patterns, which also facilitates the differentiation of isomeric compounds. The core mechanism of DART-MS involves the use of heated metastable gas atoms to desorb and ionize target substances. The technique has proven effective in the detection and characterization of compounds commonly found in propellants and ammunition, including smokeless powders, traditional black powder, and alternative black powder substitutes [6].

Given the growing trend toward self-manufacturing firearms using 3D printing technology, it is anticipated that such weapons will increasingly feature in criminal activities. Consequently, forensic investigations must consider the unique material composition of these firearms [7]. Currently, 3D-printed gun barrels are most often manufactured using polymer-based materials like acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), polyethylene terephthalate glycol (PETG), chlorinated polyethylene (CPE), and nylon.

Understanding the properties and forensic implications of these materials is essential for identifying and interpreting physical evidence in cases involving the discharge of 3D-printed firearms [8].

Instrumentation and methodologies of DART-MS

Direct Analysis in Real Time Mass Spectrometry (DART-MS) has emerged as a pivotal analytical technique in forensic science, particularly in the examination of polymers and organic gunshot residue (OGSR) associated with 3D-printed firearms [9]. The fundamental components of the DART-MS system include the DART ion source, which comprises a discharge chamber, heating mechanisms, and a gas inlet system; a sample introduction interface, a detection system, and a data analysis module.

Central to this setup is the ion source, which serves as the core element responsible for initiating the ionization process. Commonly employed carrier gases such as helium and argon are preferred due to their capacity to generate metastable species efficiently. These excited-state species interact with reagent molecules and, through subsequent collisions, facilitate the ionization of sample analytes. The ion species generated within the DART source are primarily classified into metastable species, positive ions, and negative ions. Sample introduction can be performed either by immersing a glass rod into the sample or placing the sample on a holder in proximity to the ion stream [10]. The discharge source typically operates at a current of approximately 2 mA, with a gas flow rate of 1–2 litres per minute. A direct current (DC) potential ranging from 1000 to 5000 volts is applied, while the grid voltage is generally set to +250 V for positive ion detection and –250 V for negative ion detection. Inside the DART ion source, the plasma gas typically attains a temperature ranging from approximately 50 to 60 °C.

This heated plasma, comprising ions and electrons, ionizes sample molecules in an open-air environment, thus eliminating the necessity for chromatographic separation prior to analysis.

In DART-MS, the mass analyzer serves to differentiate ions based on their mass-to-charge (m/z) ratios. This system is often integrated with a time-of-flight (TOF) analyzer, offering high mass resolution and accuracy essential for the rapid identification of target compounds. Additionally, DART-MS systems may be configured with a quadrupole or ion-trap analyzer in conjunction with TOF mass spectrometers. The TOF analyzer measures the duration ions require to reach the detector from the ion source, enabling accurate determination of their m/z values. The detector subsequently transforms the ion signal into digital data, producing a mass spectrum that plots ion intensity against m/z ratios [11].

DART-MS is renowned for its versatility, capable of detecting a broad spectrum of chemical substances on various surfaces, including pesticides, pharmaceuticals, and



trace forensic residues. The technique’s efficiency is further underscored by its streamlined workflow, which requires minimal to no sample preparation. Individual samples can be analyzed within seconds, and high-throughput screening of 384-well plates can be completed in under 25 minutes [12].

Based on a review of existing literature, the DART ion source was initially developed by JEOL USA Inc. in late 2002. It underwent initial testing on a mass spectrometer in 2003 and was subsequently patented in 2005 [13]. Its first public demonstration occurred at the American Society for Mass Spectrometry (ASMS) conference. DART sources function by generating excited-state species in a thermally energized gas stream, which trigger a series of gas-phase (Figure 1).

Reactions upon interacting with atmospheric molecules. The primary mechanism within the ion source involves helium plasma, which is generated through an electrical discharge inside a ceramic flow cell [14]. This process involves applying a potential difference between a needle electrode and a grounded counter-electrode. Additional components, such as a heating coil, elevate the temperature of the carrier gas as it approaches the source’s exit orifice, while an insulating cap ensures electrical safety by containing high voltage within the plasma chamber [15]. Furthermore, thermal desorption capabilities enhance the speed and accuracy of sample analysis.

Comparative analysis of analytical techniques for 3D-printed firearm evidence

The selection of an appropriate analytical technique for examining polymer and organic GSR from 3D-printed firearms

requires careful consideration of each method's capabilities and limitations. Table 1 presents a comprehensive comparison of DART-MS with established forensic techniques.

Comparative analysis of analytical techniques

Analysis of polymers from 3D printed firearm

Identifying polymeric materials as trace evidence from 3D-printed firearms presents significant challenges, particularly due to the use of low-powered cartridges in such weapons. These firearms are typically manufactured using thermoplastic polymers through Fused Deposition Modelling (FDM) technology. The most frequently employed polymers include Polylactic Acid (PLA), Acrylonitrile Butadiene Styrene (ABS), Nylon, Polycarbonate (PC), and Polyethylene Terephthalate Glycol (PETG) [16]. Key factors influencing the detectability of these polymers include the manner in which the material is transferred to the ammunition and the degree of fit between the cartridge and the firearm barrel.

Upon discharge, 3D-printed firearms release numerous fine particles or fragments of polymer into the surrounding environment, with some residues transferring directly onto the ammunition components. These polymeric traces can provide vital forensic evidence during chemical analysis by linking the firearm to the scene of a crime [17]. The examination of these residues offers insight into the manufacturing and operational characteristics of the weapon. Polymer identification in forensic contexts is frequently conducted using analytical techniques such as Fourier Transform Infrared (FTIR) Spectroscopy, Raman Spectroscopy, and Direct Analysis in Real Time Mass Spectrometry (DART-MS). These methods enable precise characterization of polymer composition and associated additives, including plasticizers, stabilizers, and fillers, as well as degradation products, all of which may offer valuable information regarding the firearm’s history and usage [18].

DART-MS, in particular, has proven effective in examining particles that visually resemble plastic under a microscope, generating clear spectral profiles that can be matched with materials from the 3D-printed weapon. Additionally, the integration of commercially available thermal desorption-pyrolysis attachments with DART-MS enhances the capability

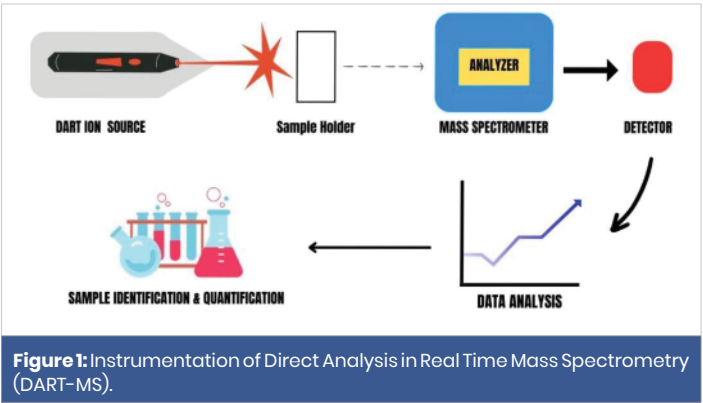


Figure 1: Instrumentation of Direct Analysis in Real Time Mass Spectrometry (DART-MS).

Table 1: Comparative evaluation of analytical techniques for forensic analysis of 3D-printed firearm evidence. Performance ratings are based on published literature and manufacturer specifications. Cost estimates reflect 2024 pricing for basic instrument configurations.

Parameter	DART-MS	GC-MS	LC-MS	SEM-EDS	FTIR
Sample Preparation	Minimal/None	Extensive extraction & derivatization	Moderate extraction	Minimal coating	Minimal
Analysis Time	Seconds-minutes	20-60 minutes	10-30 minutes	Minutes	Minutes
Sensitivity	Ng-µg range	Pg-ng range	Pg-ng range	0.1% to 1%	µg range
Polymer Detection	Excellent for thermoplastics	Limited (requires pyrolysis)	Limited	Poor	Excellent
OGSR Detection	Excellent	Excellent	Excellent	Not applicable	Limited
Destructive Nature	Non-destructive	Destructive	Partially destructive	Non-destructive	Non-destructive
Cost	Moderate (\$140K)	High (\$200K+)	High (\$250K+)	Very High (\$500K+)	Moderate (\$100K)
Operator Expertise	Moderate	High	High	High	Moderate

Detection ranges: pg = picogram (10⁻¹² g), ng = nanogram (10⁻⁹ g), µg = microgram (10⁻⁶ g), % level = >0.1% by weight



to generate both desorption profiles and mass spectra from a single sample [19]. This approach minimizes background interference and facilitates the separation of polymeric evidence specific to the firearm from other materials, such as the GSR stub base polymer [20]. The presence and analysis of polymer fragments expelled during the discharge of a 3D-printed firearm also allow forensic examiners to distinguish between different 3D printing methods and materials used in firearm fabrication [21].

Analysis of organic GSR from 3D printed firearms

Efforts to enhance the forensic value of gunshot residue (GSR) have led to the characterization and examination of Organic Gunshot Residue (OGSR), which originates primarily from the propellant and other components involved in firearm discharge. Recent advancements in analytical techniques have enabled rapid, sensitive, and comprehensive screening of OGSR, particularly beneficial when working with limited sample quantities [22].

OGSR primarily consists of organic compounds originating from smokeless powder, firearm lubricants, transformation by-products, and hydrocarbons [23]. Studies have identified over 130 chemical species associated with OGSR, including nitrocellulose—the primary component of most modern propellants—as well as other significant compounds such as phthalates, nitrobenzenes, nitrates, and polycyclic aromatic hydrocarbons (PAHs) like naphthalene derivatives, benzo[a]pyrene, and chrysene. Additionally, primer residues may also contribute to the OGSR chemical profile [24].

The detection and identification of OGSR are well-established within forensic science, with DART-MS emerging as a particularly powerful tool in this domain. DART-MS enables rapid detection of key compounds such as ethyl centralite, methyl centralite, and diphenylamine—substances commonly found in propellants, bullet coatings, or cartridge casings [25]. Due to its high sensitivity to compounds with elevated proton affinities, DART-MS can efficiently identify OGSR signatures on even minimal evidence samples. This capability significantly enhances the ability to associate firearms with criminal activity, particularly in cases involving non-metallic, 3D-printed weapons [1].

Applications of Direct Analysis in Real Time Mass Spectrometry (DART-MS) in polymer and Organic Gun Shot Residue (OGSR) from 3D printed firearms

- Forensic analysis of smokeless powders and gunshot residue (GSR).
- Thermal desorption techniques applied to the study of smokeless powder compositions.
- Identification and characterization of polymer materials, including their structural and chemical properties.

- Distinguishing between traditional black powder and modern black powder substitutes through comparative analysis [26].
- Comparative evaluation of various smokeless powder formulations for forensic profiling.
- Identification of gunpowder components and forensic analysis of polymer materials utilized in 3D-printed firearms [27].

Advantages of Using Direct Analysis in Real Time Mass Spectrometry (DART-MS) for Polymer and Organic Gun Shot Residue (OGSR) from 3D Printed Firearms

- The DART-MS technique enables the analysis of a wide range of sample types.
- It facilitates sample examination with minimal or no preparation, depending on the ionization source configuration.
- Only a small quantity of the sample is required, allowing the remainder to be retained for additional testing.
- The system functions under ambient conditions, eliminating the need for vacuum environments or supplementary heating devices [28].
- It offers rapid, real-time analysis, delivering immediate results.

Challenges or limitations and future directions

The analysis of polymers and organic gunshot residue (OGSR) from 3D-printed firearms using Direct Analysis in Real Time Mass Spectrometry (DART-MS) involves various analytical challenges and inherent limitations. These firearms often incorporate a wide variety of polymers, frequently blended with additives, which can result in complex and inconsistent spectral outputs. Additionally, the use of helium as the carrier gas in DART may induce thermal degradation of some polymeric materials, complicating accurate identification. A commercial DART ionization system with common peripherals may be purchased for \$40,000, although various low-temperature plasma and flowing afterglow ionization systems can be built by an experienced instrumentalist. Various new and used mass spectrometers with respective resolution capabilities may be purchased from vendors for \$100,000.

Standardizing DART-MS methodologies and adhering to consistent analytical protocols is critical for reliable forensic application. Furthermore, the development of robust, comprehensive spectral libraries for both polymeric materials and organic GSR compounds is necessary to support confident identification [29]. Some non-polar or thermally stable compounds may demonstrate low ionization efficiency under DART conditions, which could result in incomplete or



inaccurate chemical profiles [1]. Additionally, environmental contamination poses a threat to the reliability of GSR analysis. Optimizing instrumental parameters and employing a high-resolution mass analyzer are essential for achieving accurate and reproducible results. Broader acceptance of DART-MS within legal and forensic frameworks will require continued method validation, technological advancements, and inter-laboratory collaborative studies. The integration of conformationally resolved sampling techniques can aid in the spatial localization of residues on surfaces such as hands or clothing [30]. Additionally, the use of standard reference materials is indispensable for method development and validation.

The application of DART-MS in the forensic examination of polymers and organic GSR associated with 3D-printed firearms is rapidly expanding. However, ensuring the technique's credibility in real casework hinges upon rigorous evaluation of its reliability and forensic admissibility. These issues continue to be key factors in its wider adoption. With continued collaboration between researchers and forensic professionals, the limitations of DART-MS can be effectively addressed. By refining current techniques and establishing validated procedures, DART-MS holds immense potential to become a vital tool in the forensic analysis of 3D-printed firearm evidence. Its advantages, once fully realized, can significantly enhance the scope and precision of modern forensic investigations [31].

Conclusion

DART-MS is a recently developed mass spectrometry ionization technique. It is known that DART-MS methods can be utilized to detect and identify compounds linked to organic gunshot residue (GSR) and polymers from 3D-printed firearms in trace evidence. The application of Direct Analysis in Real Time Mass Spectrometry (DART-MS) for the analysis of polymers and organic gunshot residue (GSR) from 3D-printed firearms represents an early stage of development that is capable of success in the field of forensic science. The DART interface is specific to the different types of mass spectrometers. We normally use it in such cases where the chromatography is less important. Also, it is easy to change the interface, and it only takes five minutes to change back and forth between DART and the regular interface [32].

The ability of DART-MS to perform rapid, non-destructive analysis with minimal sample preparation makes it highly effective for the detection of complex chemical signatures that are associated with modern polymer-based weapons. Although currently there are some challenges or limitations, such as the variability in materials, limited spectral libraries, and environmental contamination, and others. But being all the limitations and challenges, we can develop the DART-MS method in forensic analysis by conducting more effective research in lab work to increase its validation in court evidence [33].

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