

Recent Advances in LIBS for Forensic Gunshot Residue Analysis: Applications, Limitations, and Future Prospects

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ABSTRACT

Gunshot residue (GSR) analysis is a fundamental component of forensic investigations, providing crucial evidence for reconstructing shooting incidents, identifying suspects, estimating firing distance, and linking firearms to crime scenes. Conventional analytical techniques, particularly scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDS), have long served as the benchmark for inorganic GSR detection due to their high sensitivity and ability to characterize particle morphology and elemental composition. However, these methods often require extensive sample preparation, sophisticated instrumentation, prolonged analysis times, and laboratory-based operation, limiting their applicability for rapid forensic screening. Laser-Induced Breakdown Spectroscopy (LIBS) can effectively be used for GSR analysis owing to its rapid, minimally destructive, and multi-element detection capabilities. LIBS enables direct elemental analysis with little or no sample preparation and can be applied to diverse substrates, including skin, clothing, firearms, spent cartridge cases, and environmental surfaces. Recent advances in laser technology, spectrometer design, gated detectors, and portable instrumentation have significantly enhanced the analytical performance of LIBS. Furthermore, the integration of LIBS with chemometric and machine learning algorithms has substantially improved the discrimination of GSR from environmental contaminants and facilitated ammunition source classification.

This review provides a comprehensive overview of the principles of LIBS, the formation and composition of gunshot residue, sampling strategies, instrumentation, experimental methodologies, spectral interpretation, and recent forensic applications. Comparative discussions with established analytical techniques highlight the strengths and limitations of LIBS in terms of sensitivity, specificity, portability, analytical speed, and operational cost.

Keywords: Laser-Induced Breakdown Spectroscopy; Gunshot Residue; Forensic Science; Elemental Analysis, portable LIBS, hybrid LIBS

INTRODUCTION

Gunshot residue (GSR) is a complex mixture of particulate and gaseous materials released during the discharge of a firearm, where the ignition of the primer initiates a rapid combustion process, producing high-temperature and high-pressure gases that propel the projectile through the barrel (Chang et al, 2013). Simultaneously, microscopic particles originating from the primer, propellant, bullet, cartridge case, and firearm components are expelled into the surrounding environment. These particles, collectively referred to as gunshot residue, are deposited on the hands and clothing of shooters, nearby surfaces, victims, firearms, and other objects in close proximity to the discharge (Charles et al, 2022). The elemental and chemical composition of GSR serves as an important forensic indicator that can provide investigative leads when interpreted in conjunction with other evidence.

GSR analysis plays a pivotal role in forensic science by providing valuable physical and chemical evidence that assists in reconstructing shooting incidents, identifying suspects, estimating firing distance, and establishing links between firearms, ammunition, and crime scenes (Miniziere et al, 2023). Thus, GSR analysis is commonly used to

establish a potential link between a suspect and a shooting event, although such findings must be interpreted cautiously within the context of the case (Wolten et al, 1979, Romolo & Margot, 2001).

Traditionally, GSR has been classified into Inorganic Gunshot Residue (IGSR) and Organic Gunshot Residue (OGSR) based on composition (Krishna & Ahuja, 2026). Inorganic GSR primarily consists of metallic particles originating from primer compositions and typically contains lead (Pb), barium (Ba), and antimony (Sb), along with elements such as copper (Cu), zinc (Zn), aluminium (Al), titanium (Ti), calcium (Ca), potassium (K), iron (Fe), and silicon (Si), depending on the ammunition type. These particles are generally spheroidal due to rapid cooling after discharge and are considered characteristic indicators of firearm use. Organic GSR comprises partially combusted or unburned propellant constituents, stabilizers, plasticizers, and combustion by-products, including nitrocellulose, nitroglycerin, diphenylamine, ethyl centralite, and dinitrotoluene. Unlike IGSR, OGSR is molecular in nature and is analyzed using spectroscopic and chromatographic techniques such as Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography – Mass Spectrometry (GC-MS). It has gained importance in modern forensic analysis, particularly where IGSR signatures are absent or inconclusive (Brozek-Mucha 2017, Goudsmits et al, 2019).

The continuous development of lead-free and heavy-metal-free ammunition, driven by environmental and health concerns, has altered the elemental composition of GSR, making conventional identification methods increasingly challenging and necessitating the development of advanced analytical techniques capable of detecting a broader range of elemental signatures (Carneiro et al, 2023).

Over the past two decades, Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM–EDS) has become the internationally accepted reference technique for inorganic GSR analysis because of its capability to simultaneously examine particle morphology and elemental composition (Sacco et al, 2025; Askar et al, 2025). Although SEM–EDS provides high specificity and excellent evidential value, it requires sophisticated instrumentation, skilled operators, lengthy analytical procedures, and laboratory-based analysis. Other analytical methods, including Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP–MS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP–OES), X-ray Fluorescence (XRF), Raman spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR), have also been employed for GSR detection (Brunjes et al, 2022; Vanini et al, 2015; Bueno et al, 2012; Bueno et al, 2013; Sarapura et al, 2019). ICP–MS and ICP–OES deliver excellent quantitative elemental analysis but require destructive sample preparation and lack morphological information. AAS, while historically significant, is limited by its single-element capability and has largely been superseded by multi-element methods. XRF enables rapid, non-destructive screening but generally lacks sufficient sensitivity for microscopic GSR particles. Raman spectroscopy and FTIR are indispensable for identifying organic GSR but provide limited elemental information (Pharmpornsagul et al, 2020; Wilschefski et al, 2019; Senila, 2024). These limitations have stimulated considerable interest in alternative analytical methods that combine speed, sensitivity, portability, and multi-element detection.

Laser-Induced Breakdown Spectroscopy (LIBS) has emerged as one of the most promising spectroscopic techniques for elemental analysis in forensic science (Naozuka et al, 2019). LIBS is based on the interaction of a high-energy pulsed laser with the sample surface, resulting in material ablation and the formation of a transient microplasma. As the plasma cools, excited atoms and ions emit characteristic optical radiation that is collected and spectrally resolved to identify the elemental composition of the sample (Shah et al, 2020). Because every element exhibits a unique emission spectrum, LIBS enables rapid qualitative and quantitative elemental analysis without requiring complex sample preparation. The entire analytical process is completed within a few microseconds, making LIBS one of the fastest elemental analysis techniques currently available (Gardette et al, 2023).

Table 1: Comparative analytical characteristics of major spectroscopic and elemental techniques used in GSR analysis

Technique	Analytical sensitivity	Sample preparation	Typical analysis time	Portability	Approximate detection capability*
SEM-EDS	High for elemental microanalysis; excellent for particle-level characterization	Minimal; mounting on conductive stub, sometimes carbon coating	~15–60 min/sample, depending on imaging and particle search	low; laboratory-based	~0.1–1 wt% for many elements; particle-level detection possible
ICP-MS	Very high elemental/isotopic sensitivity	Usually digestion/extraction; often acid digestion	~10–30 min/sample after preparation	low; laboratory-based	ng/L–μg/L in solution; sub-μg/g possible in solids after digestion
ICP-OES	High elemental sensitivity, generally lower than ICP-MS	Digestion/extraction usually required	~5–20 min/sample after preparation	low; laboratory-based	μg/L–mg/L in solution
XRF	Moderate to high, depending on configuration and element	Little or none; solid evidence can often be analyzed directly	Seconds–several minutes/sample	Moderate; handheld systems available	ppm–% levels, highly matrix dependent
Raman spectroscopy	Moderate; highly dependent on analyte and substrate	Usually none; direct measurement possible	Seconds–minutes/sample	Moderate, portable Raman systems available	Often μg–mg/g, but highly compound-dependent; trace detection possible with SERS
FTIR	Moderate for molecular identification; generally lower trace sensitivity than elemental techniques	Minimal; ATR often allows direct analysis	Seconds–few minutes/sample	Moderate; portable FTIR available	μg–mg range, depending on sampling mode and compound
LIBS	Moderate to high for elemental screening; highly matrix dependent	Minimal or none; direct analysis of solids often possible	Seconds–minutes; rapid multi-point mapping possible	Moderate; readily adapted to portable systems	ppm–% levels; optimized systems can reach lower levels for selected elements

For GSR analysis, the techniques occupy complementary analytical positions. SEM-EDS remains particularly valuable when the forensic question requires particle morphology together with elemental composition, making it an important benchmark for inorganic GSR characterization. ICP-MS and ICP-OES provide highly reliable bulk elemental measurements, with ICP-MS offering superior trace and isotopic sensitivity, but both generally require destructive sample preparation.

XRF provides a useful non-destructive alternative for rapid elemental screening, particularly when relatively high elemental concentrations are present. Raman and FTIR are primarily molecular techniques and therefore provide information that is complementary to elemental methods, especially for organic components, propellants, binders and associated materials.

In comparison, LIBS occupies an attractive intermediate position: it provides rapid multi-elemental analysis with little or no sample preparation while retaining the ability to analyze heterogeneous surfaces and perform spatially resolved measurements. Its compatibility with portable instrumentation, automated scanning, imaging and chemometric classification makes it particularly promising for crime-scene and field-based GSR analysis. However, LIBS generally does not yet match ICP–MS in trace sensitivity or SEM–EDS in particle-level morphological characterization.

The application of LIBS to GSR analysis offers several distinct advantages over conventional analytical techniques. It enables simultaneous detection of multiple elements with minimal or no sample preparation, requires only microscopic amounts of material, and causes minimal damage to forensic evidence (Zhang et al, 2024). LIBS can analyze a wide variety of substrates, including adhesive tape lifts, skin, clothing, firearms, cartridge cases, bullets, spent primers, glass, and environmental surfaces. Furthermore, the availability of compact lasers, miniature spectrometers, fiber-optic probes, and portable LIBS systems has significantly expanded the potential for field-deployable forensic investigations. These characteristics make LIBS particularly attractive for rapid crime scene screening, preliminary forensic examinations, and situations where immediate analytical information is required (Lazik et al, 2024; Balaram, 2026).

Recent technological developments have substantially enhanced the analytical capabilities of LIBS for forensic applications. Advances in laser technology, including femtosecond and double-pulse excitation, have improved signal intensity, reduced matrix effects, and enhanced detection limits. Improvements in detector sensitivity, high-resolution spectrometers, and time-gated data acquisition have increased spectral quality and reproducibility (Shahbaz et al, 2026; Villas Boas, 2026). Equally significant has been the integration of chemometric and machine learning techniques with LIBS spectral data. Multivariate statistical methods such as Principal Component Analysis (PCA), Linear Discriminant Analysis (LDA), Partial Least Squares–Discriminant Analysis (PLS-DA), Support Vector Machines (SVM), Random Forests (RF), Artificial Neural Networks (ANN), and deep learning algorithms have demonstrated remarkable success in classifying GSR, distinguishing ammunition types, discriminating shooter from non-shooter samples, and separating GSR from environmentally similar particles. These computational approaches have transformed LIBS from a purely elemental characterization tool into an intelligent forensic analytical platform capable of automated decision-making (Ledergerber et al, 2025; Cioccia et al, 2024; Gallidabino et al, 2019).

The objective of this review is to provide a comprehensive and critical assessment of the application of Laser-Induced Breakdown Spectroscopy in gunshot residue analysis. The review discusses the principles of LIBS, the physicochemical characteristics of gunshot residue, sampling methodologies, instrumental configurations, analytical performance, and recent advancements in chemometric and artificial intelligence-assisted data analysis. Comparisons with established forensic techniques are presented to highlight the strengths and current limitations of LIBS. Finally, emerging trends, including portable LIBS instrumentation, imaging LIBS, hybrid spectroscopic approaches, automated spectral databases, and AI-driven forensic analytics, are examined to provide insight into the future direction of LIBS as a powerful tool for modern forensic investigations. This review aims to serve as a comprehensive resource for researchers, forensic scientists, analytical chemists, and law enforcement professionals interested in advancing the application of LIBS in forensic gunshot residue analysis.

REVIEW METHODOLOGY

This review was conducted as a structured literature search to identify studies addressing the application of Laser-Induced Breakdown Spectroscopy (LIBS) to forensic gunshot residue (GSR) analysis. Literature was searched using

Scopus, Web of Science, ScienceDirect, and Google Scholar, with additional relevant publications identified from the reference lists of key articles. The principal search terms and their combinations included “Laser-Induced Breakdown Spectroscopy” OR “LIBS”, “gunshot residue” OR “GSR”, “inorganic gunshot residue”, “organic gunshot residue”, “forensic analysis”, “portable LIBS”, “imaging LIBS”, “chemometrics”, “machine learning”, “lead-free ammunition”, and “GSR detection”.

The search primarily covered publications from 2000 to 2026, while earlier seminal studies were retained where they provided important methodological or historical foundations for LIBS-based GSR analysis. Studies were included when they (i) investigated LIBS or a LIBS-based hybrid approach for GSR or firearm-related forensic evidence, (ii) reported experimental, analytical, instrumental, or chemometric findings relevant to forensic applications, and (iii) provided sufficient methodological information to support interpretation of their findings. Studies were excluded when they were unrelated to GSR or forensic applications, focused exclusively on non-LIBS analytical applications without relevance to LIBS, were duplicate publications, or lacked sufficient scientific information for meaningful evaluation.

Study selection was performed in three stages: title and keyword screening, abstract screening, and full-text assessment. The final set of studies was selected based on their relevance to the principal themes of this review, namely LIBS fundamentals and instrumentation, GSR sampling and characterization, conventional versus LIBS-based analysis, portable and imaging LIBS, lead-free ammunition, chemometric and machine-learning approaches, and emerging hybrid techniques. Reference-list screening of particularly relevant publications was additionally used to identify important studies that might not have been retrieved through the primary keyword search. The selected literature was then organized chronologically and thematically to critically discuss the development, analytical performance, limitations, and future prospects of LIBS for forensic GSR analysis.

PRINCIPLE OF LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

The analytical principle of LIBS is based on the generation of a high-temperature plasma through laser ablation of a sample surface. The optical emission produced during plasma cooling contains characteristic atomic and ionic emission lines that serve as unique fingerprints of the constituent elements. Because almost every element in the periodic table exhibits distinct emission wavelengths, LIBS enables simultaneous qualitative and quantitative elemental analysis within a few microseconds (Brunnbauer et al, 2023).

Laser-Induced Breakdown Spectroscopy operates by focusing a high-energy pulsed laser onto a small region of the sample surface. When the irradiance exceeds the breakdown threshold of the material, typically ranging from 10^8 to 10^{11} W cm⁻² depending on the laser pulse duration and sample properties, rapid heating results in melting, vaporization, and ionization of the target material. This process creates a luminous microplasma containing atoms, ions, electrons, and small molecular fragments (Shah et al, 2020; Diaz et al, 2012)

Stages of LIBS

The analytical process of LIBS can be divided into several sequential stages:

1. **Laser irradiation:** A nanosecond, picosecond, or femtosecond pulsed laser is focused onto the sample using an optical lens.
2. **Material ablation:** The intense laser energy vaporizes a minute quantity of material (typically nanograms to micrograms).
3. **Plasma generation:** The vaporized material absorbs additional laser energy, producing a transient plasma with temperatures ranging from 10,000 to 30,000 K. The plasma generated during LIBS is the primary source of

analytical information. Understanding plasma formation and evolution is essential for optimizing analytical performance and improving spectral reproducibility (Kwapis et al, 2024)

4. **Atomic excitation:** Atoms and ions within the plasma are excited to higher electronic energy levels through collisions with energetic electrons.
5. **Optical emission:** As the plasma expands and cools, excited species return to lower energy states, emitting photons at discrete wavelengths characteristic of each element.
6. **Spectral detection:** The emitted light is collected using optical fibers or lenses and dispersed by a spectrometer before being recorded by a gated detector, typically an intensified charge-coupled device (ICCD) or complementary metal-oxide semiconductor (CMOS) detector.
7. **Spectral analysis:** Emission spectra are processed to identify elemental composition and estimate elemental concentrations using calibration methods or chemometric algorithms.

Laser–Matter Interaction

When the focused laser pulse reaches the sample surface, photons transfer their energy to the material through absorption mechanisms such as Photoionization, Multiphoton ionization, Avalanche ionization and Thermal absorption. The absorbed energy rapidly increases the surface temperature beyond the melting and boiling points of the material, causing explosive vaporization known as laser ablation. The vaporized material continues absorbing laser energy, leading to ionization and plasma formation (Saxena et al, 2019)

Plasma Evolution

The plasma undergoes several distinct stages (Harmon & Senesi, 2021)

Stage I: Plasma Initiation (0–100 ns): In this stage, the Laser pulse interacts with the sample. The material is ablated, free electrons are generated and plasma temperature reaches approximately 20,000–30,000 K.

Stage II: Plasma Expansion (100 ns–5 μ s): In this stage, the plasma expands rapidly into the surrounding atmosphere producing shock waves. The electron density may exceed 10^{17} cm^{-3} and intense continuum radiation dominates the spectrum.

Stage III: Atomic Emission (5–50 μ s): In this stage, the Plasma cools, as a result of which the continuum emission decreases and sharp atomic and ionic emission lines appear. This is considered as the optimum analytical window for LIBS measurements.

Stage IV: Plasma Decay (>50 μ s): In this stage, the plasma temperature decreases and recombination occurs, due to which molecular emissions (CN, C₂, OH) may appear. The analytical signal gradually diminishes.

Factors Influencing Plasma Characteristics

Several parameters affect plasma properties and analytical performance. The laser parameters that affect the plasma characteristics include pulse energy, pulse duration, repetition rate, laser wavelength and spot size. The properties of the sample like surface roughness, thermal conductivity, reflectivity, hardness and chemical composition also affect the plasma characteristics. Other environmental conditions like ambient gas, pressure, humidity and temperature may also affect the characteristics of the Plasma. Optimization of these parameters significantly improves sensitivity, precision, and detection limits (Fikry et al, 2026).

LIBS: Principle and Forensic Applications

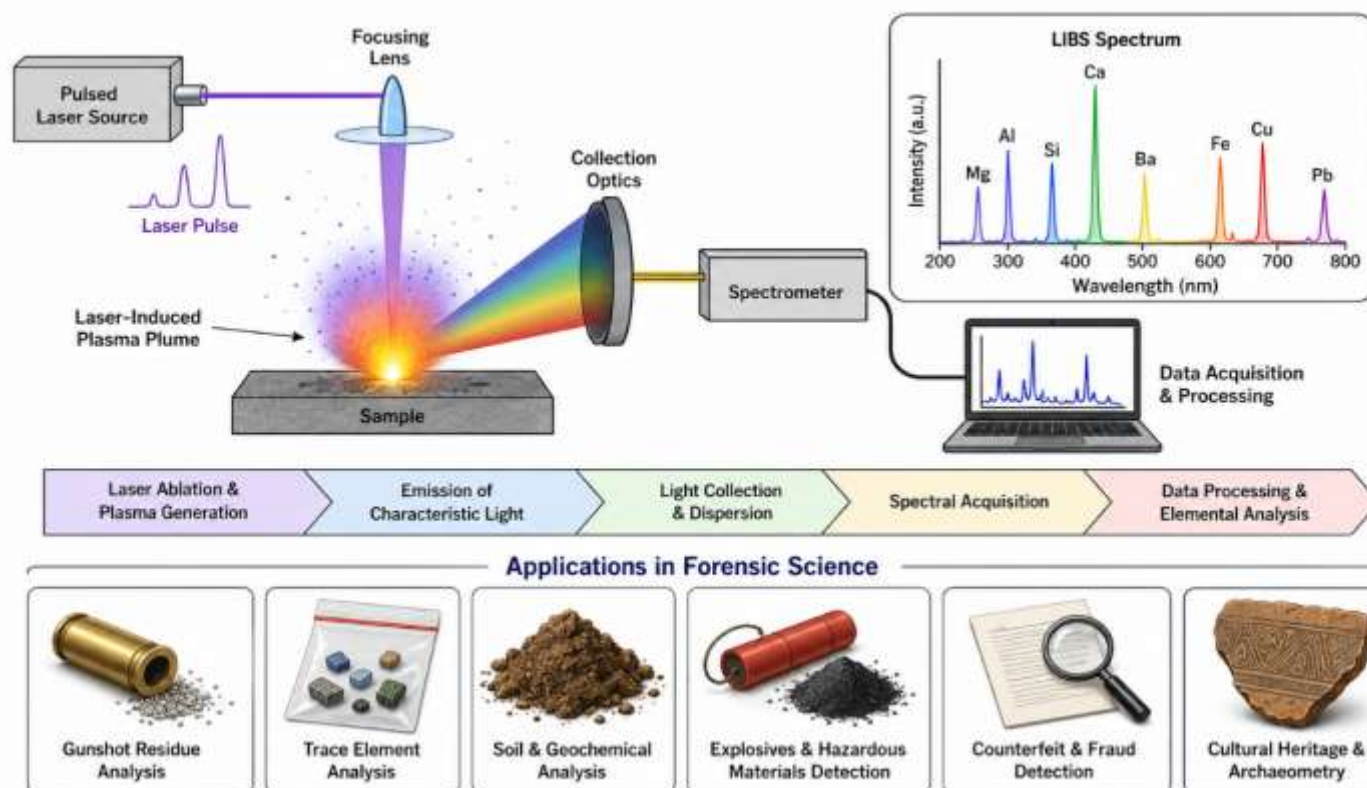


Fig 1: Schematic representation of the LIBS setup.

Fig 1 illustrates the fundamental components of a LIBS setup, including a pulsed laser source, focusing optics, sample surface, plasma plume generation, optical emission collection system, spectrometer, time-gated detector, and data acquisition and processing unit. The laser pulse is focused onto the sample surface, generating a micro-plasma whose characteristic atomic and ionic emission is collected and spectrally resolved for elemental analysis.

FORMATION OF GUNSHOT RESIDUE (GSR)

Gunshot residue (GSR) is a complex mixture of microscopic particulate and gaseous materials produced during the discharge of a firearm. It is one of the most significant forms of trace evidence encountered in forensic investigations, as it provides valuable information for reconstructing shooting incidents, identifying potential shooters, estimating firing distance, determining the discharge direction, and linking firearms to crime scenes (Shrivastava et al, 2021). GSR originates from the combustion of primer compounds, propellant powders, projectile materials, cartridge cases, and the internal components of the firearm. The composition, morphology, and distribution of GSR particles are influenced by firearm type, ammunition composition, shooting conditions, environmental factors, and post-discharge activities (Fojtasek et al, 2003)

Following the discharge of a firearm, a cloud of high-temperature gases carrying particulate matter is expelled from the muzzle, breech, cylinder gap (in revolvers), and cartridge ejection port. These particles are deposited on the shooter's hands, clothing, face, nearby surfaces, victims, and surrounding environment. Because GSR particles are generally microscopic (typically ranging from 0.5 to 20 μm in diameter), they can be easily transferred, dispersed, or removed, making prompt evidence collection essential for forensic analysis (Burnett and Nunziata, 2023)

Formation Mechanism of Gunshot Residue

The formation of gunshot residue begins immediately after the trigger is pulled and is governed by a sequence of rapid physicochemical events occurring within a few milliseconds. The firing process involves the ignition of the primer, combustion of the propellant, projectile acceleration, and the expulsion of combustion products and particulate matter from the firearm. These events occur under extreme conditions, with temperatures often exceeding 2,500–3,500 K and pressures reaching 200–400 MPa, depending on the firearm and ammunition (Pitts and Lewis, 2019; Camci and Findik, 2025)

Ignition of the Primer

The firing sequence begins when the firing pin strikes the primer cup located at the base of the cartridge. The mechanical impact compresses the primer composition against the anvil, generating sufficient friction and heat to initiate an explosive chemical reaction (SWGSR Guide).

Traditional primer mixtures commonly contain lead styphnate (primary explosive), Barium nitrate (oxidizer), Antimony sulfide (fuel), Aluminum powder, Calcium silicide, Tetrazene (sensitizer). The detonation of the primer produces extremely hot gases, molten metallic droplets, and partially reacted primer particles that become the primary source of inorganic gunshot residue (SWGSR Guide).

Propellant Combustion

The intense heat generated by primer ignition ignites the smokeless powder propellant, which primarily consists of Nitrocellulose, Nitroglycerin, Nitroguanidine (in triple-base propellants), Stabilizers, Plasticizers, Flash suppressants, Burn-rate modifiers.

The combustion of the propellant produces Carbon dioxide (CO₂), Carbon monoxide (CO), Nitrogen (N₂), Water vapor, Nitrogen oxides, Carbonaceous soot and Partially burned propellant particles. Incomplete combustion contributes significantly to the formation of organic gunshot residue (OGSR) (SWGSR Guide).

Projectile Acceleration

The rapidly expanding combustion gases propel the bullet through the barrel. During its movement, friction between the projectile and barrel causes abrasion of the bullet jacket, cartridge case, barrel steel and primer cup. These processes introduce additional metallic particles containing Copper, Zinc, Iron, Nickel, Tin and Aluminum. The exact elemental composition depends on ammunition design and firearm construction (Kneubeuhl, 2022)

Particle Formation and Dispersion

As the projectile exits the muzzle, high-pressure gases carrying molten metal droplets expand rapidly into the atmosphere. Rapid cooling transforms these droplets into solid particles exhibiting characteristic spherical morphology due to surface tension. Gunshot residue particles may be spherical, irregular, agglomerated, hollow or fragmented. Typical particle diameters range from 0.5 to 20 µm, although larger particles are occasionally observed. The particles may get expelled through the muzzle, cylinder gap (revolvers), breech opening or cartridge ejection port. The resulting particle cloud disperses according to firearm geometry, ammunition characteristics, and environmental conditions. (Kara, 2020; DeSouza et al, 2025)

Deposition on Surrounding Surfaces

Following discharge, GSR particles may settle on the shooter's hands, face, clothing, firearm surfaces, the victim, nearby furniture, vehicles, floors or walls. Some particles remain airborne before deposition, while others may undergo secondary transfer through physical contact. (Tahirukaj et al, 2022)

Factors Affecting Gunshot Residue Deposition

The deposition, persistence, and distribution of GSR are influenced by numerous variables related to the firearm, ammunition, shooting conditions, environmental factors, and post-discharge activities. Understanding these factors is essential for accurate interpretation of GSR as evidence (Lucas et al, 2016; Ledergerber et al (2), 2025)

Firearm Characteristics

Firearm design significantly influences GSR production and dispersion. The factors affecting GSR production and dispersion include barrel length, barrel wear, muzzle brake, cylinder gap, semi-automatic or automatic operation. Revolvers typically produce greater sideward GSR deposition due to the cylinder gap, whereas semi-automatic pistols eject residue through the ejection port (Ditrich, 2012; De Souza et al, 2025)

Ammunition Composition

Different ammunition formulations produce distinct GSR signatures. The influencing factors include primer composition, lead-free versus conventional primers, propellant type, bullet jacket material and cartridge case alloy (Askar et al, 2025; Brozek-Mucha, 2007)

Firing Distance

The amount and spatial distribution of GSR decrease with increasing muzzle-to-target distance. The contact shots lead to dense GSR deposition, the close-range shots (<30 cm) lead to abundant residue, the intermediate range gives reduced particle density and the long-range shots provide sparse or absent GSR. This relationship forms the basis for firing distance estimation in forensic investigations. (Krishna & Ahuja, 2024; Brozek-Mucha, 2017)

Environmental Conditions

Environmental factors strongly influence GSR persistence and transfer. These factors include wind speed, rainfall, humidity, temperature, airflow and surface contamination. Outdoor environments generally promote faster dispersion and loss of GSR than controlled indoor settings. (Blakey et al, 2018)

Surface Characteristics

Deposition efficiency varies with substrate properties like surface roughness, porosity, electrostatic properties, moisture content, fabric texture, porous materials such as cotton fabrics tend to retain GSR more effectively than smooth, non-porous surfaces. (Charles et al, 2013)

Time After Shooting

Gunshot residue is inherently transient. Following deposition, particles may be lost through normal activities such as hand washing, rubbing, changing clothes, or contact with other surfaces. Numerous studies have demonstrated that the quantity of recoverable GSR decreases rapidly with time, particularly from the hands, emphasizing the importance of collecting samples as soon as possible after a shooting event (Jalanti et al, 1999; Blakey et al, 2018)

Secondary Transfer and Contamination

GSR particles can be transferred indirectly through contact between individuals or objects, creating the possibility of secondary deposition. Additionally, certain occupational and environmental sources—including brake pad dust, fireworks, welding fumes, and industrial emissions—may contain elements similar to those found in GSR, potentially leading to false-positive interpretations. Modern analytical approaches therefore combine elemental

composition, particle morphology, and multivariate statistical analysis to distinguish true GSR from environmentally derived particles (Seyfang et al, 2019).

In summary, the formation, composition, and deposition of gunshot residue are governed by a complex interplay of firearm mechanics, ammunition chemistry, environmental conditions, and post-discharge activities. A comprehensive understanding of these factors is essential for the accurate interpretation of GSR evidence. Advanced analytical techniques such as LIBS, particularly when integrated with chemometric and machine learning methods, provide a robust framework for characterizing both traditional and lead-free GSR, thereby enhancing the reliability and evidential value of forensic investigations.

LIBS For Gunshot Residue Analysis

Experimental Methodology

The experimental methodology employed in LIBS-based GSR analysis is designed to obtain reproducible emission spectra while minimizing sample damage and maximizing analytical sensitivity. Although instrumental configurations vary among laboratories, the general workflow remains largely consistent. (Lopez-Lopez, 2017)

Experimental Workflow

The LIBS analysis of GSR typically involves the following steps:

1. **Collection of GSR samples** from the shooter, firearm, clothing, or target.
2. **Mounting of samples** on a suitable substrate or direct analysis of the surface.
3. **Laser focusing** onto the sample to generate a microplasma.
4. **Collection of plasma emission** using optical fibers or collection optics.
5. **Spectral dispersion** through a spectrometer.
6. **Detection** using an ICCD or CMOS detector.
7. **Spectral preprocessing**, including background subtraction, normalization, and wavelength calibration.
8. **Elemental identification** using reference spectral databases.
9. **Quantitative or chemometric analysis** for classification and discrimination.

The entire analytical process generally requires only a few seconds per sample, making LIBS highly suitable for high-throughput forensic screening.

Instrument Configuration

A typical LIBS system used for GSR analysis consists of a Pulsed laser (Nanosecond/picosecond/femtosecond), Beam delivery optics, Focusing lens, XYZ translation stage, sample holder, plasma collection optics, optical fiber, high-resolution spectrometer, ICCD or gated CMOS detector and Computer with spectral acquisition software (Limbeck et al, 2021). Portable LIBS instruments integrate these components into compact systems capable of field deployment.

Sample Collection

Proper sample collection is critical for obtaining representative GSR evidence. Since GSR particles are microscopic and easily lost through normal activities, samples should be collected as soon as possible after a shooting event.

Sampling Sites

Common forensic sampling locations include hands of accused or victim (palms and dorsal surfaces), Clothing, Face, Firearms, Cartridge cases, Bullets, Shooting targets, Vehicle interiors and nearby surfaces. For shooter identification, the back of the hands and thumb-index finger web is generally considered the most informative sampling areas (Reis et al, 2023)

Collection Techniques

Several collection methods have been reported for GSR analysis. (OSAC Guidelines, 2021)

Adhesive Tape Lifting: This is the most common method involves collecting GSR particles using double-sided carbon adhesive tape. This method is simple, non-invasive, compatible with SEM-EDS and LIBS and preserves particle morphology

Cotton Swabs: Moistened or dried cotton swabs may be used for collecting residue from skin, firearms as well as cartridge cases

Direct Surface Analysis: LIBS permits direct analysis without sample transfer. Suitable surfaces include clothing, metallic surfaces, glass, polymer materials, firearms and cartridge cases. Direct analysis minimizes contamination and sample handling.

Vacuum Collection: Vacuum devices equipped with filters are useful for collecting GSR from large surfaces and crime scenes.

Sample Preservation

For sample preservation, the collected samples should be stored in clean containers, protected from contamination, analyzed promptly and excessive handling needs to be avoided. Environmental contamination may significantly influence elemental composition.

Laser Parameters

The analytical performance of LIBS strongly depends on laser operating conditions. Optimization of laser parameters is essential for obtaining reproducible plasma generation and high-quality emission spectra.

Laser Wavelength

For forensic GSR studies, lasers with nano second pulses are the commonly used one. 1064 nm Nd:YAG lasers (along with their first and second harmonics) remain the most frequently employed due to their robust plasma generation and compatibility with a wide range of substrates. However other picosecond or femtosecond laser pulses can also be used for GSR analysis (Khan et al, 2022).

Pulse Energy

Typical pulse energies range from 20–150 mJ. Increasing pulse energy generally enhances plasma emission intensity but excessive energy may increase continuum emission, produce larger craters, cause self-absorption, reduce

analytical precision. (Rankovik et al, 2025)

Spot Size

Typical laser spot diameters are 30–200 μm . Smaller spot sizes provide higher spatial resolution, lower sample consumption and improved mapping capability. Larger spot sizes generate stronger analytical signals but increase material removal.

Repetition Rate

Typical repetition frequencies are 1 Hz, 5 Hz, 10 Hz and 20 Hz. Lower repetition rates reduce cumulative heating and improve spectral stability.

Spectral Characteristics

LIBS spectra consist of discrete atomic and ionic emission lines superimposed on a continuum background generated during the initial stages of plasma evolution. Following plasma cooling, characteristic emission lines become dominant and serve as elemental fingerprints (Gajarska et al, 2024). Rather than relying solely on individual elemental peaks, LIBS generates a comprehensive elemental fingerprint comprising the relative intensities of multiple emission lines. This multidimensional signature enables differentiation of ammunition manufacturers, identification of primer formulations, classification of lead-free and conventional ammunition, discrimination between GSR and environmental particles. When combined with chemometric methods, elemental fingerprinting substantially enhances forensic interpretation.

Recent Advances in LIBS For GSR Analysis

Recent technological advancements have significantly enhanced the analytical performance of LIBS, making it an increasingly reliable technique for GSR analysis. Improvements in laser technology, detector sensitivity, spectrometer design, and data processing have addressed many of the limitations associated with conventional LIBS, including matrix effects, limited sensitivity, and spectral variability. Some notable developments are described below.

Portable LIBS

The miniaturization of lasers, spectrometers, and detectors has enabled the development of portable and handheld LIBS systems suitable for on-site forensic investigations. Portable LIBS allows rapid elemental analysis of GSR directly at crime scenes with minimal sample preparation. These systems can analyze residue on hands, clothing, firearms, cartridge cases, and other surfaces, providing immediate investigative information while reducing sample transportation and contamination risks. Although portable instruments generally offer lower spectral resolution than laboratory-based systems, ongoing improvements in detector technology and data processing have substantially enhanced their analytical performance (Senesi et al, 2021)

Double-Pulse LIBS

Double-pulse LIBS (DP-LIBS) employs two sequential laser pulses separated by a short time interval. The first pulse ablates the sample, while the second pulse reheats and re-excites the expanding plasma, resulting in greater plasma temperature and volume. This approach significantly enhances emission intensity, improves the signal-to-background ratio, lowers detection limits, and increases analytical precision (Rizwan et al, 2025)

Femtosecond LIBS

fractionation, and improved crater morphology compared with conventional nanosecond LIBS. These

characteristics result in better analytical reproducibility, higher spatial resolution, and reduced matrix effects, making femtosecond LIBS particularly suitable for analyzing microscopic GSR particles. Despite its superior analytical performance, widespread forensic application is currently limited by the high cost and complexity of femtosecond laser systems (Giannakaris et al, 2022).

LIBS–Raman Hybrid Systems

The combination of LIBS with Raman spectroscopy is a powerful hybrid analytical platform capable of providing complementary elemental and molecular information from the same sample. While LIBS identifies inorganic elemental constituents such as Pb, Ba, Sb, Cu, Zn, and Ti, Raman spectroscopy characterizes organic compounds including nitrocellulose, nitroglycerin, diphenylamine, and other propellant residues. This integrated approach enables simultaneous analysis of inorganic and organic GSR, improving source attribution, ammunition characterization, and discrimination of GSR from environmentally similar particles. Hybrid LIBS–Raman systems therefore offer a more comprehensive forensic assessment than either technique alone (Shin et al, 2023).

Imaging LIBS

Imaging LIBS extends conventional point analysis by acquiring spectra across a predefined grid to generate two-dimensional elemental distribution maps. This technique provides spatial information on the distribution of GSR particles over surfaces such as hands, clothing, firearms, and shooting targets. Elemental imaging assists in understanding residue dispersion patterns, estimating firing distance, and identifying localized elemental hotspots associated with primer and projectile materials. When combined with chemometric analysis, imaging LIBS further enhances the visualization and classification of GSR evidence, offering valuable insights into shooting-event reconstruction (Richiero et al, 2025).

Overall, these recent advancements have considerably expanded the capabilities of LIBS for forensic GSR analysis. Continued integration of advanced laser technologies, portable instrumentation, multimodal spectroscopic systems, and artificial intelligence-driven data analysis is expected to further improve the sensitivity, reliability, and field applicability of LIBS, supporting its evolution into a routine analytical tool for modern forensic investigations.

CHALLENGES AND LIMITATIONS

Despite the significant advancements in LIBS for GSR analysis, several scientific and technical challenges continue to limit its widespread adoption as a routine forensic technique. Although LIBS offers rapid, multi-elemental, and minimally destructive analysis with little or no sample preparation, issues related to analytical reproducibility, quantitative accuracy, matrix effects, and the absence of standardized forensic protocols remain important concerns. Addressing these limitations is essential for ensuring the reliability, reproducibility, and legal admissibility of LIBS-based evidence.

One of the major challenges in LIBS analysis is the matrix effect, where variations in the physical and chemical properties of the sample influence laser absorption, plasma formation, and emission intensity. Differences in surface roughness, thermal conductivity, hardness and moisture content can produce significant variations in spectral intensity, even for samples containing similar elemental concentrations. Since GSR is deposited on diverse substrates such as skin, clothing, firearms, cartridge cases, glass, and painted surfaces, matrix-dependent plasma behaviour complicates direct comparison between samples and limits quantitative accuracy (Villas-Boas, 2026).

Another important limitation is shot-to-shot variability. Plasma formation is inherently dynamic, and fluctuations in laser pulse energy, focusing conditions, atmospheric composition, and sample heterogeneity can result in inconsistent emission intensities between successive laser shots. These variations reduce analytical precision and often require multiple measurements and signal averaging to obtain reproducible spectra. Careful optimization of laser parameters and instrumental conditions is necessary to minimize experimental variability (Dorscht et al, 2026).

The complexity of LIBS spectra presents another analytical challenge. Emission spectra often contain hundreds of closely spaced atomic and ionic lines together with continuum radiation, molecular emissions, and self-absorption effects. Spectral overlap between elements can hinder accurate peak assignment, particularly for complex GSR mixtures. Consequently, advanced spectral preprocessing, wavelength calibration, and chemometric algorithms are frequently required to achieve reliable elemental identification and sample classification (Yan et al, 2026)

Another significant challenge is the lack of standardized operating procedures for forensic LIBS applications. Instrumental parameters—including laser wavelength, pulse energy, gate delay, gate width, spectral range, and data preprocessing methods—vary considerably among laboratories, resulting in differences in analytical performance and limiting inter-laboratory reproducibility. The establishment of standardized protocols for sample collection, instrumental optimization, spectral processing, quality assurance, and reporting is essential before LIBS can be widely accepted in forensic practice (Yang et al, 2020).

Finally, legal admissibility and forensic validation remain important considerations. For LIBS-generated evidence to be accepted in judicial proceedings, the technique must demonstrate validated analytical performance, reproducibility, known error rates, and compliance with forensic quality standards. Large-scale inter-laboratory validation studies, certified reference materials, and standardized spectral databases are still limited, highlighting the need for collaborative efforts among forensic laboratories, instrument manufacturers, and regulatory organizations (Scurich et al, 2023)

Case Studies

For the detection of GSR on the hands of a suspected shooter Goode et al. (2002) used LIBS for the detection and elemental characterization of GSR, with particular emphasis on characteristic elements such as barium (Ba) and lead (Pb). GSR samples were collected from the hands of individuals following firearm discharge using double-sided adhesive tape, which was subsequently subjected to LIBS analysis. The study demonstrated that LIBS was capable of detecting characteristic GSR elements even after hand washing, although a reduction in emission intensity was observed. These findings demonstrate the potential of LIBS as a sensitive and rapid analytical technique for GSR examination, offering minimal sample preparation and the possibility of near-real-time forensic screening following a shooting incident.

Dockery and Goode (2003) also investigated the detection of GSR on the hands of firearm using LIBS. They successfully identified characteristic GSR constituents, including barium (Ba), lead (Pb), and antimony (Sb), directly from residues collected on adhesive tape. To improve the reliability of GSR classification, the study incorporated a statistical framework involving Monte Carlo simulations, which enabled assessment of the probability of detection and helped minimize false-positive results arising from environmental or background elemental contamination. Importantly, LIBS demonstrated the capability to detect low levels of GSR following a single firearm discharge. This finding highlights the potential of LIBS for forensic investigations in which the number of shots fired is limited and conventional analytical approaches may face challenges associated with low residue deposition.

Rosenberg and Dockery (2008) addressed the persistence of GSR on a shooter's hands when there is a time gap between the incident and the investigation. Using a 0.357 calibre revolver, they demonstrated that LIBS could detect GSR up to 5.27 days after firing. This challenges previous assumptions about how long GSR remains detectable and illustrates the importance of high-precision analysis, as GSR distribution can be uneven across a shooter's hand. These findings expand the temporal window during which forensic investigators can reliably use LIBS for detecting GSR.

Fambro et al. (2017) investigated the challenges associated with the forensic analysis of GSR generated by lead-free ammunition using LIBS and SEM-EDX. Their findings indicated that lead-free GSR predominantly comprises Ba, Al, Si and K, with smaller contributions from Ti and Fe. LIBS enabled the detection of characteristic Ba emission

lines, which provided sufficient discriminatory information to differentiate samples obtained from shooters and non-shooters. Complementary SEM-EDX analysis confirmed the predominantly spherical morphology of the lead-free GSR particles, demonstrating similarities in particle geometry to residues produced by conventional lead-containing ammunition. Importantly, the study indicated that LIBS analysis could be performed without compromising the integrity of the examined evidence, supporting its use as a rapid preliminary screening technique prior to more detailed SEM-EDX characterization. These findings highlight the potential of LIBS as a minimally destructive approach for the forensic examination of GSR associated with emerging lead-free ammunition formulations.

Doña-Fernández et al. (2018) conducted a comparative evaluation of SEM-EDX and the portable LIBS system for the detection of GSR particles. The portable LIBS system achieved a 100% detection rate when at least three characteristic GSR elements—Ba, Pb, and Sb, were simultaneously present. However, false-negative results were observed in samples containing fewer GSR particles, particularly those characterized by smaller particle sizes. Subsequent re-analysis using SEM-EDX confirmed the presence of GSR in these samples, indicating that particle abundance and size can influence the detection capability of portable LIBS. Overall, the findings demonstrate that portable LIBS provides reliable and rapid GSR screening, particularly for samples containing relatively abundant or larger particles, while SEM-EDX remains valuable for confirming low-abundance and fine particulate residues.

Martinez-López et al. (2018 and 2019) demonstrated an early systematic application of LIBS as a chemical imaging tool for visualizing GSR patterns on target materials. In their study, clothing samples obtained from different muzzle-to-target distances were examined using a raster-scanning LIBS approach coupled with a dual-spectrograph detection system, enabling the simultaneous acquisition of characteristic emission lines of Pb, Sb, and Ba, which are commonly associated with conventional primer residues. By scanning predefined grids across the fabric surface, the authors generated two-dimensional elemental distribution maps that revealed the spatial characteristics of the GSR plume surrounding bullet entry holes. These chemically resolved maps provided a more objective and chemically specific means of visualizing GSR patterns than conventional colorimetric methods, which may be affected by cross-reactivity and subjective interpretation. Although the mapping procedure involved relatively long acquisition times and the spatial resolution was influenced by factors such as laser spot size and stage-movement parameters, the study established the feasibility of LIBS for spatially resolved GSR imaging and demonstrated its potential for reconstructing residue deposition patterns on target materials.

Vander Pyl et al. (2020) investigated the applicability of LIBS for characterizing GSR deposited on blood-stained fabric surrounding bullet holes and demonstrated its potential for distinguishing different shooting distances based on the elemental residue profiles. The data from LIBS were evaluated using discriminant analysis, which achieved 100% correct classification of the investigated shooting distances under the experimental conditions. This level of discrimination indicates the potential of LIBS-based elemental analysis to provide objective and chemically specific information for shooting-distance estimation. Compared with conventional approaches based primarily on physical examination and colour-based testing, LIBS offers the additional advantage of multielement detection and reduced susceptibility to subjective visual interpretation, thereby highlighting its potential utility in forensic crime scene reconstruction.

Menking-Hoggatt et al. (2021) developed a micro-spot LIBS approach for the precise detection and classification of IGSR. The method employed a two-pulse laser configuration focused on a 100- μ m diameter spot, enabling enhanced spatial resolution and localized interrogation of individual or small clusters of residue particles. When compared with a conventional bulk-line analysis, the micro-spot approach demonstrated superior classification performance, achieving an accuracy exceeding 99.5% for characteristic GSR marker elements, including Ba, Pb, and Sb. In addition, machine-learning algorithms, including logistic regression and neural networks, were employed to classify samples obtained from shooters and non-shooters using LIBS spectral data. The combination of high-resolution micro-spot interrogation and machine-learning-based classification highlights the potential of LIBS for sensitive, spatially resolved, and automated IGSR analysis in forensic investigations.

Vander Pyl et al (2021) studied the integration of LIBS and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for microanalytical characterization of individual residue particles. Using matrix-matched standards and authentic hand-collected samples, the study employed micro-spot ablation patterns to chemically map individual primer GSR particles and compare their elemental signatures across the two analytical platforms. LIBS exhibited strong performance for conventional Pb–Ba–Sb-containing residues, providing rapid multi-element detection while preserving spatial information about particle distribution. In comparison, LA-ICP-MS offered enhanced analytical sensitivity and greater elemental specificity, thereby providing valuable confirmatory information. However, for lead-free residues, LIBS exhibited reduced sensitivity, primarily owing to weaker characteristic emission signals and greater spectral interference from environmental background constituents. These findings highlight the complementary nature of LIBS and LA-ICP-MS and suggest that their combined application can provide a more comprehensive strategy for the rapid screening and high-sensitivity confirmation of primer GSR, particularly when dealing with diverse ammunition compositions.

In a separate investigation, Vander Pyl et al. (2023) evaluated a custom-designed mobile LIBS instrument against a validated laboratory-based LIBS system for the detection of inorganic gunshot residue in hand-swab samples. The study analysed 100 samples obtained from shooters and 200 samples from non-shooters. Both LIBS systems targeted characteristic emission lines of Pb, Ba, and Sb. The mobile instrument incorporated high-resolution imaging, an argon-purged multisample chamber, and a CMOS detector to enhance analytical performance under field conditions. It correctly classified all shooter samples and achieved a true-negative rate of 97.5%, closely comparable to the 98.5% obtained with the laboratory system. Notably, the mobile system demonstrated enhanced sensitivity for Ba detection and facilitated single-particle targeting, thereby providing additional morphological information alongside elemental characterization. These findings demonstrate the feasibility of mobile LIBS for rapid, field-deployable IGSR screening while highlighting its potential to provide both chemical and morphological information from individual residue particles.

Doña-Fernández et al (2023) investigated the application of LIBS for shooting-distance estimation using lead-free ammunition, addressing the challenges associated with the altered elemental composition of GSR generated by lead-free primers and projectiles. Their study demonstrated that LIBS could successfully detect and characterize Cu-containing particles deposited on fabric targets at different shooting distances. The results highlighted the suitability of LIBS for distinguishing residue deposition patterns associated with variations in muzzle-to-target distance, thereby extending the applicability of the technique to modern ammunition systems that do not produce conventional Pb-containing GSR signatures. Furthermore, the integration of automated analysis and a portable instrumental configuration enhanced the potential for rapid, on-site forensic examination. Such developments demonstrate how LIBS can bridge the gap between the analytical sensitivity and precision of laboratory-based measurements and the operational requirements of field-level forensic investigations.

Rodríguez-Pascual et al (2023) further investigated the application of a portable LIBS system for rapid GSR analysis on diverse surfaces encountered at crime scenes, including walls, furniture, and fabrics. The system offered flexibility in optimizing instrumental parameters according to the characteristics of the analysed substrate and enabled the detection of characteristic GSR elements, including Pb, Ba, and Sb. This adaptability highlights the potential of portable LIBS for on-site crime scene examination and reconstruction. Notably, the study demonstrated that GSR particles, including residues associated with projectile deposition, could still be detected on various surfaces up to one month after the firearm discharge. These findings highlight the potential of portable LIBS for the analysis of aged GSR deposits and demonstrate its value as a rapid, minimally destructive technique for field-based forensic investigations.

Lazic et al. (2024) developed a compact dual-mode LIBS sensor capable of operating both as a handheld probe for direct surface interrogation and as a tabletop system for controlled analysis of collected fragments. The platform integrates a colour camera, LED illumination, and a precision focusing and pointing mechanism to facilitate accurate micro-targeting of forensic specimens. Optimized for single and few-pulse measurements, the system achieved absolute detection limits below approximately 10 pg for several elements on test substrates while maintaining a low

degree of micro-destructiveness. These findings demonstrate the potential of portable LIBS platforms to provide high elemental sensitivity and spatially resolved analysis under field conditions, while minimizing sample handling and preserving valuable forensic evidence for subsequent examination using complementary techniques.

Cioccia et al (2024) proposed a probabilistic framework for the identification of GSR using LIBS coupled with principal component analysis (PCA) and a support vector machine (SVM) classifier. GSR samples were collected from the hands of shooters and non-shooters using double-sided adhesive tape, followed by LIBS spectral acquisition in the ultraviolet region (190–300 nm). The resulting spectra were subjected to appropriate preprocessing and dimensionality reduction before classification using the SVM algorithm. The model was trained and independently validated to discriminate among shooter, non-shooter, and “undetermined” classes using a predefined probability threshold. The proposed approach achieved 100% classification accuracy in both the training and external validation datasets and demonstrated the ability to reject contaminated or ambiguous samples during stress testing. By incorporating probabilistic classification rather than relying solely on binary decision rules, the methodology reduced the potential for false-positive assignments and provided an explicit mechanism for handling uncertain samples. These findings highlight the potential of LIBS combined with multivariate statistical and machine-learning methods as a reliable complementary approach for GSR screening and classification, with possible advantages in rapidity and field applicability compared with conventional SEM-EDX based analysis.

Rodríguez-Pascual et al. (2025) have demonstrated the potential of LIBS for Gun shot trajectory reconstruction through systematic characterization of GSR distributions around bullet entry holes produced at controlled angles of incidence (30°, 60°, and 90°). In their study, residues deposited during projectile passage were collected using adhesive lifts and subsequently analysed using an automated 1064 nm LIBS system with an approximate laser spot size of 500 µm. The approach enabled the rapid generation of two- and three-dimensional elemental density maps of Cu and Pb on stainless steel, particleboard, and PVC foam board substrates, with mapping completed in approximately 5 min. The resulting elemental distribution maps exhibited distinct angle-dependent asymmetry, with higher residue densities consistently observed on the side corresponding to greater projectile–surface interaction, thereby providing an indication of the direction of fire. At normal incidence (90°), GSR deposition produced approximately circular perimetric patterns, whereas oblique impacts at 60° and 30° resulted in progressively elongated and crescent-shaped distributions, reflecting increasing projectile obliquity. Residue signatures were also influenced by ammunition type and substrate characteristics. Jacketed ammunition generated stronger Cu signals, whereas semi-jacketed ammunition produced comparatively higher Pb concentrations, particularly on stainless steel, where differentiation between ammunition types was achievable. Although substrate composition affected background elemental signals and residue morphology, the spatial concentration gradients of Cu and Pb provided chemically specific indicators of projectile direction. Thus, LIBS-based elemental mapping can complement conventional geometric examination of bullet holes by providing chemically resolved information on residue deposition patterns, supporting the estimation of angle of incidence and contributing to ballistic trajectory reconstruction.

Thomas et al (2025) have reported controlled firing experiments involving multiple ammunition types and eight commonly encountered construction and automotive substrates. A field-deployable LIBS system incorporating high-magnification imaging and single-particle targeting was employed to characterize residues collected from shooters’ hands, bullet entry holes, impacted surfaces, and recovered projectiles. Approximately 2,000 spectral comparisons with known reference materials demonstrated the system’s ability to reliably identify characteristic GSR signatures while simultaneously differentiating substrate-derived materials. The results revealed complex patterns of both primary and secondary transfer among the shooter, projectile, and surrounding environment. High detection rates of GSR were observed on shooters’ hands and around bullet entry holes, while additional analyses demonstrated the transfer of materials such as drywall, concrete, and automotive-derived components to projectiles and subsequently back to the shooter. Metal particulates generated from bullets and cartridge cases were also identified as transferable trace evidence. These findings demonstrate that mobile LIBS can extend beyond conventional primer-residue detection to provide valuable information on material-transfer pathways and

interactions occurring during a shooting event. The integration of high-resolution imaging, targeted single-particle analysis, and field-deployable instrumentation further enhances the operational potential of LIBS for rapid and on-site examination of firearm-related forensic evidence.

To overcome the analytical challenges associated with nontoxic ammunition, Wenceslau et al (2026) have combined LIBS with multivariate chemometric and machine-learning techniques. Broad-range LIBS spectra were evaluated using supervised classification algorithms to discriminate between shooter and non-shooter samples based on subtle variations in trace-elemental signatures, rather than relying exclusively on conventional Pb–Sb–Ba markers. Elements including Zn, Ti, Cu, and Fe contributed significantly to sample discrimination, with classification accuracies approaching 100% under controlled experimental conditions. This approach represents a transition from conventional deterministic elemental identification toward data-driven spectral pattern recognition, thereby extending the applicability of LIBS to the analysis of contemporary ammunition formulations. However, the reported performance was obtained under controlled conditions, and further validation is required to establish the robustness and generalizability of these models in the presence of environmental variability, substrate effects, ammunition diversity, and mixed background signatures encountered in real-world forensic investigations.

Table 2. Summary of representative case studies demonstrating the application of LIBS for forensic gunshot residue analysis

Study	Forensic objective	Sample/ substrate	LIBS approach	Principal elements/ features	Key findings	Forensic significance
Goode et al. (2002)	Detection of GSR from shooter hands and assessment of persistence after washing	Shooter hands collected using double-sided adhesive tape	Conventional LIBS	Ba, Pb	Characteristic GSR elements were detected; signals decreased after hand washing but residues remained detectable	Demonstrated early feasibility of LIBS for rapid hand-GSR screening and its potential following post-shooting hand washing
Dockery & Goode (2003)	Reliable identification of low-level GSR and reduction of false positives	Adhesive tape lifts from hands	LIBS with statistical/Monte Carlo analysis	Ba, Pb, Sb	GSR was detected following a single firearm discharge; statistical treatment helped assess detection probability and background contamination	Demonstrated that statistical analysis can improve interpretation of LIBS-based GSR results
Rosenberg & Dockery (2008)	Investigation of GSR persistence over time	Shooter hands following discharge	LIBS	Characteristic GSR elemental signatures	GSR was detected up to 5.27 days after firing, although distribution across the hand was uneven	Extended understanding of the temporal persistence and spatial variability of hand GSR
Fambro et al. (2017)	Characterization of GSR from lead-free ammunition	GSR particles from shooters/non-shooters	LIBS and SEM–EDX	Ba, Al, Si, K, with Ti and Fe	LIBS detected characteristic Ba emissions and differentiated shooter/non-shooter samples; SEM–EDX	Important for forensic examination of lead-free ammunition, where conventional

					showed predominantly spherical particles	Pb-based criteria may be inadequate
Doña-Fernández et al. (2018)	Comparison of portable LIBS with SEM-EDX for GSR detection	GSR particles collected from hands	Portable LIBS and SEM-EDX	Ba, Pb, Sb	Portable LIBS achieved 100% detection when ≥ 3 characteristic elements were present; false negatives occurred with fewer/smaller particles	Demonstrated rapid field screening capability while highlighting SEM-EDX's advantage for low-abundance/fine particles
Martínez-López et al. (2018/2019)	Visualization and reconstruction of GSR deposition patterns	Clothing around bullet-entry holes	Raster-scanning LIBS and dual spectrograph	Pb, Sb, Ba	Generated 2-D elemental maps showing spatial distribution of GSR around bullet holes	Established LIBS chemical imaging as a tool for shooting-distance estimation and reconstruction
Vander Pyl et al. (2020)	Estimation of shooting distance	Blood-stained fabric surrounding bullet holes	LIBS and discriminant analysis	Elemental GSR profiles	Achieved 100% classification of investigated shooting distances under experimental conditions	Demonstrated potential for objective, chemically specific crime-scene reconstruction
Menking-Hoggatt et al. (2021)	Micro-spatial detection and classification of inorganic GSR	Individual/small clusters of GSR particles	Two-pulse micro-spot LIBS, $\sim 100 \mu\text{m}$ spot	GSR elemental signatures	Improved spatially localized interrogation of individual or small clusters of residue particles	Demonstrated the value of micro-spatial LIBS for particle-level GSR analysis
Vander Pyl et al. (2021)	Elemental characterization and confirmatory analysis of primer GSR	Primer GSR particles	LIBS and LA-ICP-MS	Conventional and trace elemental signatures	Demonstrated complementary capabilities of LIBS and LA-ICP-MS; particularly relevant for detailed elemental characterization	Shows how LIBS can function as a rapid screening technique with a highly sensitive confirmatory method
Vander Pyl et al. (2023)	Translation of LIBS from laboratory to crime-scene investigation	Hands, surfaces, projectiles and firearm-related evidence	Mobile LIBS, high-resolution imaging and single-particle targeting	Pb, Ba, Sb and other elemental signatures	Mobile LIBS correctly classified shooter samples and provided enhanced Ba sensitivity and single-particle targeting; metal particulates from bullets/cartridge	Demonstrated the feasibility of field-deployable, real-time firearm investigation

					cases could also be investigated	
Doña-Fernández et al. (2023)	Estimation of shooting distance using lead-free ammunition	Fabric targets	Portable/automated LIBS	Particularly Cu-containing particles	LIBS characterized Cu-containing residue at different muzzle-to-target distances	Extended shooting-distance estimation to modern lead-free ammunition
Rodríguez-Pascual et al. (2023)	Crime-scene GSR detection on diverse substrates	Walls, furniture, fabrics and other surfaces	Portable LIBS	Pb, Ba, Sb	GSR was detected on diverse surfaces, including residues persisting for up to one month	Demonstrated flexibility of portable LIBS for aged GSR and real-world crime-scene examination
Lazic et al. (2024)	Development of a compact field-capable LIBS sensor	Forensic fragments/test substrates	Dual-mode handheld + tabletop LIBS; micro-targeting	Multiple elemental signatures	Detection limits below approximately 10 pg were reported for several elements on test substrates with low micro-destructiveness	Demonstrated substantial progress toward sensitive, spatially resolved portable forensic LIBS
Cioccia et al. (2024)	Probabilistic discrimination of GSR from non-GSR samples	Shooter/non-shooter hand samples collected on adhesive media	LIBS with PCA and SVM analysis	UV-range elemental spectral signatures	Machine-learning classification provided a probabilistic framework for distinguishing GSR from background samples	Represents transition from simple elemental identification toward statistical and AI-assisted forensic interpretation
Wenceslau et al. (2026)	Classification of GSR associated with non-toxic/modern ammunition	Shooter and non-shooter samples	LIBS + multivariate chemometrics/machine learning	Zn, Ti, Cu, Fe and broader elemental fingerprints	Classification accuracy approached 100% under controlled conditions	Demonstrates the potential of data-driven LIBS when conventional Pb–Ba–Sb markers are absent or insufficient; further real-world validation is required

FUTURE PROSPECTS

The continued development of LIBS is expected to substantially enhance its role in forensic GSR analysis. Although LIBS has demonstrated considerable potential for rapid elemental screening, portable analysis, spatial mapping, and chemometric classification, its transition from a promising research technique to a routinely accepted forensic method requires improvements in analytical sensitivity, reproducibility, standardization, data interpretation, and evidential validation.

Development of High-Sensitivity and Low-Destructive LIBS

Future research needs to be focussed on improving the detection of trace quantities of GSR while reducing material ablation. Advances in laser sources, time-gated detection, high-resolution spectrometers, intensified detectors, and optimized plasma-generation conditions can improve signal-to-background ratios and detection limits. Double-pulse and femtosecond LIBS are particularly promising because they can enhance plasma emission while reducing some matrix-related effects and improving spatial resolution. Such developments are important for the examination of extremely small or sparsely distributed GSR particles, where preservation of evidence is a major forensic consideration.

Portable, Handheld and Remote LIBS Systems

Miniaturization of lasers, spectrometers, detectors and optical components is likely to further expand the use of LIBS at crime scenes. Future portable systems could incorporate automated focusing, surface recognition, single-particle targeting, wireless data transfer and integrated imaging. These systems may enable investigators to examine hands, clothing, firearms, cartridge cases, bullet holes and surrounding surfaces without transporting samples to a laboratory. The development of robust remote and stand-off LIBS configurations could further extend the technique to difficult-to-access surfaces and large crime-scene areas.

Automated GSR Imaging and Spatial Mapping

Imaging LIBS represents an important future direction because GSR is inherently heterogeneous and spatially distributed. Automated scanning combined with high-resolution imaging could generate two- and three-dimensional elemental maps of residue deposition. Such maps may provide information on the spatial distribution of primer and projectile-derived materials and contribute to shooting-distance estimation and reconstruction of firearm-related events. Automated identification of elemental hotspots and individual particles could substantially reduce operator dependence and analysis time.

Integration with Chemometrics and Artificial Intelligence

Future LIBS-based GSR analysis is expected to increasingly depend on chemometric and machine-learning approaches. Rather than relying exclusively on individual elemental markers such as Pb, Ba and Sb, multivariate models can exploit the complete spectral fingerprint of a residue. Algorithms such as principal component analysis, linear discriminant analysis, support vector machines, random forests, artificial neural networks and deep-learning approaches may improve discrimination between GSR, environmental particles and occupational or background contaminants.

The development of large, representative spectral databases will be essential for this purpose. Future databases would incorporate different ammunition manufacturers, primer formulations, firearm types, environmental conditions, substrates, collection methods and lead-free ammunition. Importantly, machine-learning models should be externally validated using independent samples rather than relying solely on controlled laboratory datasets. This becomes necessary to establish their robustness and generalizability in real forensic investigations.

Analysis of Lead-Free and Next-Generation Ammunition

The increasing use of lead-free and environmentally safer ammunition represents both a challenge and an opportunity for LIBS. Conventional GSR identification strategies based primarily on Pb–Ba–Sb signatures may have reduced applicability when these elements are absent or present at substantially different concentrations. Future LIBS investigations need to emphasize comprehensive elemental fingerprints involving elements such as Cu, Zn, Ti, Al, Si, K and Fe, together with chemometric classification.

This approach could allow LIBS to remain relevant as ammunition formulations evolve. Nevertheless, studies using realistic ammunition diversity and samples obtained under operational forensic conditions will be required before such classification strategies can be considered sufficiently reliable for casework.

Hybrid LIBS-Based Forensic Platforms

Combining LIBS with complementary spectroscopic and analytical methods is another promising direction. LIBS provides rapid elemental information, whereas Raman and FTIR spectroscopy provide molecular information. A LIBS–Raman platform could therefore simultaneously characterize inorganic elements and organic constituents of GSR and propellant residues. Similarly, integration of LIBS with SEM–EDS, LA–ICP–MS or other confirmatory techniques could provide complementary information at different spatial and analytical scales.

A practical future workflow may therefore involve LIBS as a rapid screening method followed by targeted confirmatory analysis using high-sensitivity or high-resolution laboratory techniques. Such an approach would maximize the advantages of LIBS while reducing the consequences of its current limitations in trace sensitivity and morphological characterization.

Development of Standardized Protocols and Reference Materials

One of the most important requirements for the forensic implementation of LIBS is the development of standardized analytical protocols. Differences in laser wavelength, pulse energy, spot size, repetition rate, detector configuration, acquisition timing, sample substrate and spectral preprocessing can produce substantial variations in LIBS spectra. Standardized operating procedures should therefore define sampling, instrumental conditions, calibration, quality control, spectral processing and reporting requirements.

The development of certified or well-characterized GSR reference materials would also improve interlaboratory comparability. Collaborative studies involving multiple forensic laboratories could establish reproducibility, uncertainty estimates, detection criteria and performance standards for LIBS-based GSR analysis.

Establishment of Forensic Spectral Databases

Comprehensive spectral databases could become an important component of future LIBS-based forensic interpretation. Such databases should include spectra from conventional and lead-free ammunition, different firearm and primer types, environmental background materials, clothing and other common substrates. Metadata describing ammunition composition, firearm characteristics, firing conditions, substrate and environmental conditions should accompany each spectrum.

A sufficiently diverse database could support automated comparison, source classification and probabilistic interpretation. Integration of standardized spectral libraries with machine-learning algorithms may eventually enable near-real-time identification and classification of GSR at crime scenes.

Validation, Uncertainty and Legal Defensibility

Technological development alone will not establish LIBS as a routine forensic method. Future studies must address analytical uncertainty, false-positive and false-negative rates, reproducibility, environmental variability and the influence of substrates. Large-scale blind and interlaboratory validation studies will be particularly important.

Forensic interpretation should also move beyond reporting the mere presence or absence of individual elements. Probabilistic frameworks that incorporate background populations, ammunition variability and measurement uncertainty may provide more scientifically defensible conclusions. Establishing validated performance characteristics and transparent decision criteria will be essential for the eventual acceptance of LIBS-derived evidence in judicial proceedings.

Towards Intelligent and Autonomous Forensic LIBS

The long-term prospect is the development of intelligent LIBS systems capable of automated sample positioning, spectral acquisition, data preprocessing, particle targeting, classification and reporting. Integration of miniature LIBS instruments with artificial intelligence, robotics, hyperspectral imaging and wireless communication could facilitate semi-autonomous examination of large or complex crime scenes.

Such systems could first locate elemental hotspots, target individual particles, acquire multiple spectra, compare the results with validated spectral databases and provide a probabilistic classification for subsequent expert review. Human oversight would remain essential, particularly for evidential interpretation and court reporting, but automation could substantially improve consistency and reduce analysis time.

CONCLUSION

This review has discussed the fundamental principles of LIBS, plasma formation, instrumentation, and the mechanisms underlying GSR generation and deposition. It has also summarized conventional analytical techniques used in forensic GSR investigations and highlighted the growing role of LIBS in elemental identification and quantitative analysis. Recent technological developments, including portable LIBS systems, double-pulse and femtosecond LIBS, imaging LIBS, and hybrid LIBS–Raman platforms, have substantially enhanced analytical sensitivity, spatial resolution, and forensic applicability. Despite these advances, challenges related to matrix effects, spectral variability, quantitative calibration, and the lack of standardized operating procedures continue to limit the routine implementation of LIBS in forensic laboratories. Various recent case studies incorporating LIBS for GSR analysis under different conditions and with different objectives are also mentioned.

Future progress regarding using LIBS for GSR analysis as forensic evidence depends on the development of validated analytical protocols, certified reference materials, comprehensive spectral databases, and robust chemometric and artificial intelligence-based models capable of providing accurate, reproducible, and legally defensible results. Collaborative efforts among forensic scientists, instrument developers, and regulatory organizations are essential to establish standardized methodologies and quality assurance practices.

Overall, LIBS represents a powerful and rapidly evolving analytical technology with considerable potential to complement and, in certain applications, augment conventional GSR analytical methods. Continued advances in instrumentation, hybrid spectroscopic approaches, data analytics, and portable systems are expected to strengthen its role in forensic science, ultimately enabling faster, more reliable, and field-deployable gunshot residue analysis for modern criminal investigations.

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Competing Interests

The author has declared that no competing interests exist.

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