
Research article

Chemical analysis of gunshot residues (GSR): historical evolution, forensic relevance, technological advances, and contemporary challenges

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Abstract: This paper addresses the main methods of chemical analysis of gunshot residues (GSRs), highlighting both their social and forensic relevance. Forensic authorities have determined that crimes involving firearms, including homicides and suicides, constitute a significant portion of the cases examined. In these cases, GSR plays a central role in the reconstruction of crimes. Classical instrumental techniques such as atomic absorption spectroscopy (AAS) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) remain widely used; however, recent advances have introduced innovative approaches including electrochemical sensors, portable

devices, and luminescent metal–organic frameworks (MOFs). The objective of these novel methodologies is to enhance sensitivity, selectivity, and accessibility in forensic analysis. The objective of this article is to provide a critical overview of the historical development, current practices, and recent technological innovations in GSR detection. The text places particular emphasis on the challenges posed by heavy-metal-free “green” ammunition and highlights perspectives where electrochemistry, chemical markers, and artificial intelligence (AI) can enhance the robustness of forensic investigations. The primary findings indicate that the amalgamation of nanomaterials, portable platforms, and chemometric instruments possesses the capacity to transform the domain of GSR analysis, thereby enhancing the reliability of forensic evidence and fortifying its application within the justice system.

Keywords: analytical techniques; ballistics; electrochemical sensors; forensic chemistry; gunshot residues

1. Introduction

Firearm-related crimes represent one of the most critical social and forensic challenges in modern times, particularly in Brazil, where incidents involving weapons account for a significant proportion of criminal cases reported to law enforcement agencies [1]. The accurate identification of the shooter and the reconstruction of the firing event are fundamental to the administration of justice [2]. However, the absence of precise analytical procedures may hinder the differentiation between guilty and innocent individuals, compromising judicial reliability [3]. Hence, forensic science plays a pivotal role by applying rigorous chemical and physical analyses to identify and characterize gunshot residues (GSRs) generated during firearm discharges [4].

The study of GSR has historically been rooted in the integration of physics, chemistry, and legal sciences. Analytical chemistry, in particular, provides the quantitative and qualitative tools necessary for determining the composition of residues and associating them with specific firearms or ammunition types [5]. The incorporation of alternative analytical strategies, such as chemometric and multivariate statistical methods, has strengthened the interpretative robustness of forensic data, allowing the generation of probabilistic conclusions rather than binary “presence or absence” assessments [6].

Forensic sciences are classically defined as the systematic application of the scientific method to the investigation of crimes, seeking to establish both materiality and authorship [7]. Evidence analysis must never be isolated from the investigative context, as its credibility depends on the interconnection between technical, procedural, and legal elements [8]. The accurate collection and interpretation of scientific information reduce the likelihood of misjudgments, thus reinforcing the reliability of judicial deliberations [9]. Within this multidisciplinary framework, analytical chemistry contributes to the enforcement of justice by transforming microscopic traces into scientifically verifiable information [10].

Among the various types of microtraces examined in forensic laboratories, GSR is one of the most significant [11]. These residues, typically composed of a heterogeneous mixture of metallic, inorganic, and organic constituents, can adhere to the shooter’s hands, clothing, or nearby surfaces [12]. Their identification provides valuable information about the occurrence of gunshots, the relative position of the shooter and the victim, and potential links between suspects and crime scenes [13]. The interpretation of such traces is governed by Locard’s exchange principle, which posits that every contact leaves a trace,

thereby enabling the establishment of connections between individuals, objects, and the environment [14].

The Brazilian Federal Constitution of 1988 reinforces the importance of properly collected and interpreted material evidence by prohibiting the use of illegally obtained proofs in criminal proceedings [15]. Therefore, the technical rigor of GSR analysis is not only a scientific necessity but also a legal imperative [16]. As emphasized, “whenever a forensic examination is performed, regardless of its simplicity, someone’s life is at stake” [17]. Ensuring the reliability of results depends on both analytical precision and adherence to validated protocols [18].

The chemical analysis of GSR encompasses a broad spectrum of methodologies aimed at identifying the characteristic elements lead (Pb), barium (Ba), and antimony (Sb), commonly present in conventional ammunition primers [19]. Traditional instrumental techniques such as atomic absorption spectroscopy (AAS), graphite furnace atomic absorption spectroscopy (GFAAS) [20], and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) [21] remain central to forensic workflows due to their precision and reproducibility [22]. Complementary methods, including laser-induced breakdown spectroscopy (LIBS) and inductively coupled plasma mass spectrometry (ICP-MS) [23], have enhanced multi-element detection capabilities, improving trace-level quantification and reducing false positives [24].

Nevertheless, the detection of GSR is challenged by environmental and physiological factors that affect residue persistence. Variables such as humidity, temperature, and individual activity can influence the retention of residues on skin and clothing, thereby impacting the interpretation of analytical findings [25]. These challenges have motivated the continuous evolution of forensic methodologies toward more robust, sensitive, and portable approaches.

Recent developments have introduced electrochemical sensors, luminescent markers, and portable analytical platforms that enable on-site GSR detection with reduced analysis time and cost [26]. Such innovations align with global trends emphasizing field-deployable technologies and environmentally safer alternatives to heavy-metal-based ammunition. Moreover, the integration of interdisciplinary knowledge—ranging from nanotechnology to data science—has opened new avenues for the development of intelligent forensic systems capable of real-time detection and interpretation of evidence [27].

In this context, the present study aims to provide a comprehensive and critical overview of the chemical analysis of gunshot residues. It delineates the evolution of classical techniques and highlights the emergence of novel methodologies that enhance analytical sensitivity and forensic reliability. Particular attention is given to recent advances in electrochemical sensing, luminescent chemical markers, and the growing application of artificial intelligence (AI) and chemometric tools. By bridging traditional and contemporary approaches, this study underscores the transformative potential of integrating analytical innovation with forensic practice to meet the challenges of modern crime investigation.

1.1. Methods currently in use for GSR analysis

The detection of gunshot residues has evolved considerably over the past century, transitioning from rudimentary colorimetric assays to advanced instrumental and electrochemical methodologies. Early tests, such as the Griess and sodium rhodizonate assays, represented the first significant progress in the field, providing rapid and inexpensive means for identifying nitrites and lead residues on the

shooter's hands or surrounding surfaces [28]. Despite their simplicity and continued applicability for distance estimation, these tests are limited by their qualitative nature and susceptibility to false positives.

Subsequent technological advances revolutionized GSR analysis, particularly with the introduction of atomic absorption spectroscopy (AAS) in the 1950s and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) in the 1970s [20]. AAS enabled the quantitative detection of characteristic metallic elements such as lead (Pb), barium (Ba), and antimony (Sb), whereas SEM-EDX provided morphological and compositional identification at the microstructural level, establishing itself as the gold standard in forensic laboratories worldwide [29].

Further developments in multi-element techniques, including inductively coupled plasma mass spectrometry (ICP-MS) [30] and gas chromatography-mass spectrometry (GC-MS) [31], expanded analytical capabilities by allowing the simultaneous detection of inorganic and organic components of residues. High-performance liquid chromatography (HPLC) also contributed to the identification of stabilizers and explosive compounds such as nitroglycerin, diphenylamine, and ethylcentralite [32]. These instrumental methods provided unparalleled sensitivity and specificity, yet they require sophisticated infrastructure, complex sample preparation, and highly trained personnel.

In parallel, electrochemical methods have emerged as promising alternatives for rapid and portable GSR detection. Techniques such as anodic stripping voltammetry (ASV) enable the quantification of trace metals, including Pb, Sb, and Ba, using inexpensive and miniaturized setups [33]. Their low operational cost and ability to perform on-site analysis make them attractive for preliminary screening in field investigations.

Recent years have witnessed the integration of nanomaterials, metal–organic frameworks (MOFs) [34], and AI to enhance analytical performance, selectivity, and data interpretation [35]. This convergence marks a new phase in forensic science, where hybrid approaches combine traditional and modern tools to address the growing complexity of ammunition compositions and environmental interferences [36].

Figure 1 summarizes key milestones in the historical evolution of GSR detection, illustrating how different techniques—rather than replacing each other—have evolved in parallel, complementing one another to improve accuracy, speed, and reliability in forensic practice.

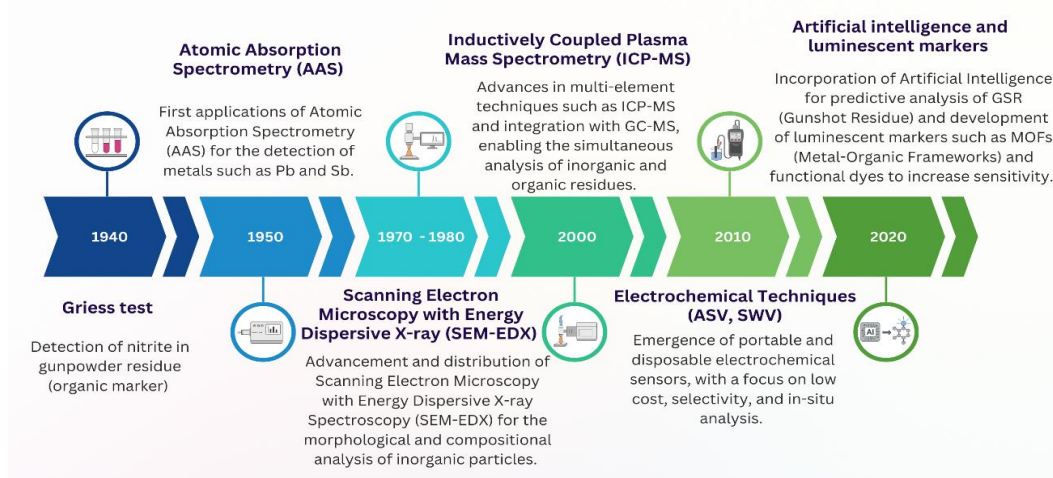


Figure 1. Evolution of analytical methods for the detection of GSR.

2. Analysis methods

2.1. Conventional methods of detecting GSRs

The conventional methods for detecting GSR, which are widely applied in forensic analyses, include approaches based on chemical tests, spectrometric techniques, and microscopic methods [37].

These procedures are instrumental in the identification of the inorganic and organic components of the residues generated by the discharge of a firearm, thereby playing a pivotal role in criminal investigations [38]. Despite their established and reliable nature, many of these methods are encumbered by limitations, including the necessity for sophisticated equipment, considerable operational expenditures, and the potential for environmental interferences [38].

As Harshey et al. (2021) have demonstrated, colorimetric tests are among the pioneering methods employed in GSR detection, a method that maintains its relevance due to the speed and simplicity inherent in the procedure [27]. The Walker test and the Griess test are frequently employed to identify nitrites, which are compounds formed by the combustion of gunpowder. Conversely, the sodium rhodizonate test is employed for the specific detection of lead [39].

These tests offer several advantages, including the ability to perform rapid and cost-effective screening, which makes them a popular choice for use at crime scenes. However, the authors emphasize that the interpretation of the results can be subjective, as it depends on the analyst's visual perception. In addition, the presence of substances in the environment can react with the reagents used, generating false positives.

AAS has been extensively utilized to detect characteristic GSR metals, including lead (Pb), barium (Ba), and antimony (Sb). As Madeira et al. (2020) explain, this technique is highly precise and allows for the quantification of these metals in samples collected from the shooter's hands or surfaces near the shooting location [40].

However, a salient limitation of AAS is the necessity to dissolve the sample prior to analysis, which renders the process more time-consuming and labor-intensive. Furthermore, the technique fails to provide information regarding the morphology of the particles, thereby hindering the ability to distinguish between residues from a shot and environmental particles with analogous compositions.

Another conventional approach for GSR analysis is X-ray fluorescence spectroscopy (XRF), which allows for the rapid detection of the characteristic metals in gunshot residues. Madeira et al. (2020) highlight that this nondestructive technique eliminates the necessity for sample preparation, rendering it appealing for forensic investigations [40].

However, a salient challenge associated with XRF is its relatively high detection limit, which can impede the identification of elements present in low concentrations. Moreover, although XRF is effective for the elemental analysis of residues, it does not provide detailed information about the morphology of the particles, which can represent a limitation in differentiating between GSR and environmental particles [40].

Miranda et al. (2019) have demonstrated through experimental investigation that, despite their destructive nature, techniques such as neutron activation analysis (NAA), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) have been shown to exhibit greater sensitivity in the detection of GSR. These techniques enable the precise quantification of antimony, barium, and other elements present in the gunshot residue, thereby providing high specificity to the analysis [41].

However, its application is constrained by the necessity for specialized infrastructure, including a nuclear reactor for the excitation of the elements. In addition to the elevated operational cost, the stringent regulatory framework governing radioactive materials imposes significant constraints on its utilization, limiting its application to a select group of forensic laboratories on a global scale. Consequently, despite its precision, NAA is not widely used in the routine of criminal investigations [42].

Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) is considered the gold standard in GSR analysis. The technique allows for the characterization of GSR particles, identifying not only their chemical composition but also their morphology [43]. Figure 2 presents the energy-dispersive X-ray spectrum for the elements present in conventional energetic munitions, as well as the micrograph that characterizes the elements present in a firearm discharge residue.

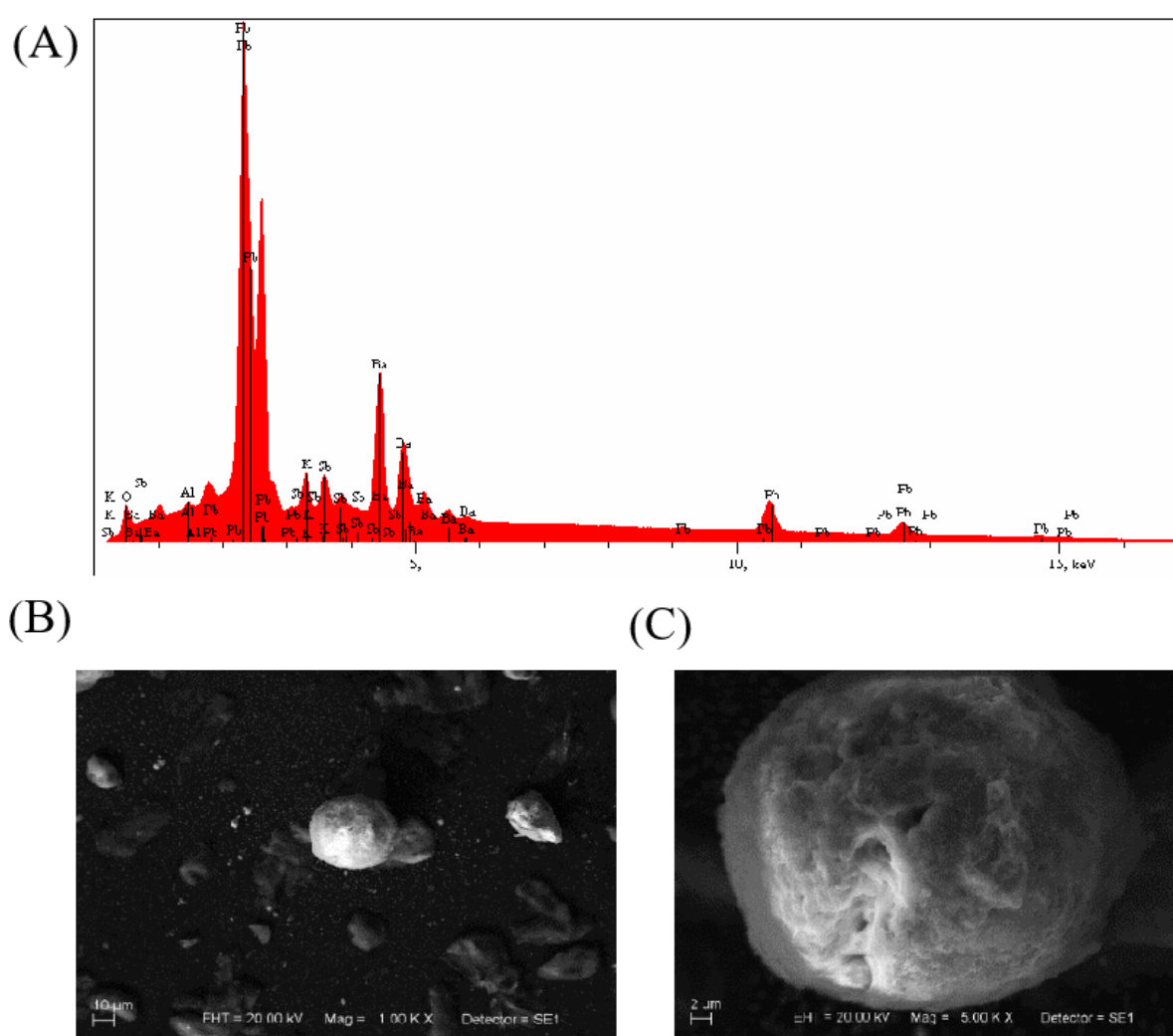


Figure 2. (A) Energy dispersive X-ray spectrum for the elements presented in conventional ammunition of energy. (B) and (C) Micrographs of the element lead at 10 μm and at 2 μm . [1]

Figure 2 illustrates that GSR particles generally manifest a spherical morphology, a consequence of the condensation of evaporated material during the combustion process. These particles

concurrently comprise the elements lead (Pb), barium (Ba), and antimony (Sb). Consequently, it can be deduced that SEM-EDX is among the most dependable methods for verifying the existence of gunshot residues. However, the authors indicate that the technique necessitates advanced technology, labor-intensive analysis, and highly skilled workers, which may restrict its utilization in smaller forensic laboratories.

In addition to techniques aimed at metal detection, gas chromatography coupled with mass spectrometry and high-performance liquid chromatography have been employed for the analysis of organic compounds in GSR [44]. The high sensitivity of these techniques allows for the identification of powder stabilizers and propellants, fundamental compounds for differentiating between ammunition from different manufacturers [45].

However, such approaches present challenges, such as the need for meticulous sample preparation and the high cost of analytical equipment. Moreover, the deterioration of organic compounds over time can compromise the detection of residues in investigations conducted in periods following the discharge [46].

Despite the efficiency of conventional methods, the necessity for faster, portable, and accessible techniques has driven the development of new approaches for GSR detection. It is imperative to underscore the practical forensic applicability of these methods. The detection of Pb, Sb, and Ba does not inherently signify the identification of GSR; rather, it necessitates a contextual evaluation of particle morphology, composition, and its association with shooting events. Consequently, emerging techniques must undergo critical evaluation not only for their analytical performance but also for their reliability as admissible forensic evidence [47].

Table 1 presents a synthesis of these methodologies, facilitating enhanced sensitivity in analytical processes, reduced false positive results, and expedited detection of traces in fieldwork, thereby accelerating criminal investigations.

Table 1. Comparative overview of analytical techniques employed in the detection of GSR.

Analytical technique	Target analytes	Main advantages	Main limitations
Colorimetric tests	Nitrites, Pb	Simple methodology; low operational cost	Subjective interpretation; susceptible to false positives
Atomic absorption spectroscopy (AAS)	Pb, Sb, Ba	High analytical sensitivity	Requires sample pre-treatment
Scanning electron microscopy with energy Dispersive X-ray (SEM-EDX)	Particle morphology; metals	High specificity; morphological and elemental analysis	High equipment cost; time-consuming analysis
Inductively coupled plasma mass spectrometry (ICP-MS)	Multi-elemental metals	Capable of detecting trace levels of multiple elements	Expensive instrumentation; complex operation
Electrochemical techniques (ASV, SWV)	Pb, Sb, NO_3^- , NO_2^-	Portable instrumentation; rapid analysis; low cost	Susceptible to interferences; requires accurate calibration

The continuous evolution of analytical techniques has enabled forensic science to enhance its capacity to identify gunshot residues. Conventional methods remain in widespread use; however, the development of new technologies has resulted in significant advances in the detection and characterization of GSR. The prevailing future trend is the incorporation of hybrid approaches, combining traditional and innovative techniques to increase the reliability and efficiency of forensic analyses [48].

In recent years, research in the field of GSR detection has undergone a significant transition, shifting from a reliance on classical instrumental techniques to a more integrated approach that incorporates portable electrochemical sensors, luminescent chemical markers, and machine learning tools [49]. This trend is indicative of an increasing demand for forensic methodologies that are characterized by their expeditious implementation and field deploy ability, along with their exceptional selectivity. As Weyermann et al. (2025) have recently emphasized, there is an urgent need to reposition forensic research and development in GSR analysis. Innovation in this field must remain aligned with practical applicability and the real challenges faced by forensic laboratories [50].

3. Perspectives

3.1. Application of electrochemistry in the forensic analysis of GSR

The application of electrochemical methods in the forensic analysis of gunshot residues has been the subject of extensive investigation due to their ability to provide rapid, sensitive, and cost-effective detection [51]. These methods have proven to be particularly useful for the simultaneous identification of metallic and organic GSR compounds, enabling on-site analyses without the need for bulky equipment and sophisticated laboratory infrastructure [52].

Among the methodologies employed for the detection of characteristic GSR metals, anodic stripping voltammetry (ASV) stands out for its effectiveness [53]. As Shrivastava et al. (2021) have noted, the technique is employed in the detection of metals, such as lead (Pb), antimony (Sb), and barium (Ba). The underlying principle of the technique involves the pre-concentration of metal ions on the electrode surface, followed by a redissolution step that facilitates the identification of elements at extremely low concentrations [54].

However, the authors emphasize particular challenges in the detection of barium, stemming from its high electrochemical potential, which hinders its deposition on conventional electrodes, as documented in the extant literature of the field.

In this context, the modification of the electrode surface with conductive nanomaterials has been investigated as a promising strategy to overcome this limitation [55]. The sensitivity of electrochemical sensors for GSR detection is significantly enhanced by modifying screen-printed carbon electrodes (SPCEs) with metallic nanostructures, as demonstrated by Wongpakdee et al. (2024) [56]. The study demonstrated that the electrodeposition of gold on SPCEs led to a substantial enhancement in the concurrent detection of lead (Pb), antimony (Sb), and zinc (Zn), thereby facilitating the acquisition of distinct electrochemical signatures for various types of ammunition [56]. The efficacy of modifying the electrodes with copper in detecting organic residues, such as nitrates and nitrites, frequently present in unburned gunpowder, was also demonstrated. The methodology employed constitutes an innovation, as it allows for the combined analysis of metallic and organic residues, providing valuable information about the origin and composition of the ammunition used [57].

The combination of cyclic voltammetry (CV) and square wave voltammetry (SWV) to enhance the detection of gunshot residues was explored by O'Mahony and Wang (2013). Conversely, CV facilitates the characterization of the redox processes involved in the oxidation and reduction of GSR compounds, while SWV enhances detection sensitivity by mitigating capacitive interferences [37].

Figure 3 demonstrates the voltage profile obtained through SWV for GSR samples extracted from the shooter's hands. The investigations utilized carbon paste electrodes (CPE) in an acidic buffer solution (pH 4.5), facilitating the identification of the metallic ions Pb^{2+} and Sb^{3+} , indicative of inorganic residues from ammunition. Two discrete current peaks were identified: the primary peak at approximately -0.45 V, associated with lead, and the secondary peak at around 0.05 V, linked to antimony. The electrochemical reactions vary according to the bullet caliber. For instance, .32 S&W ammunition (blue curve) exhibited the greatest signal for Pb^{2+} , while .357 Magnum ammo (black and red curves) displayed elevated currents linked to Sb^{3+} . The results demonstrate variations in the composition of residues produced by different calibers and underscore the selective capability of the voltammetric technique in characterizing GSR based on the electroanalytical signatures of the constituent metals.

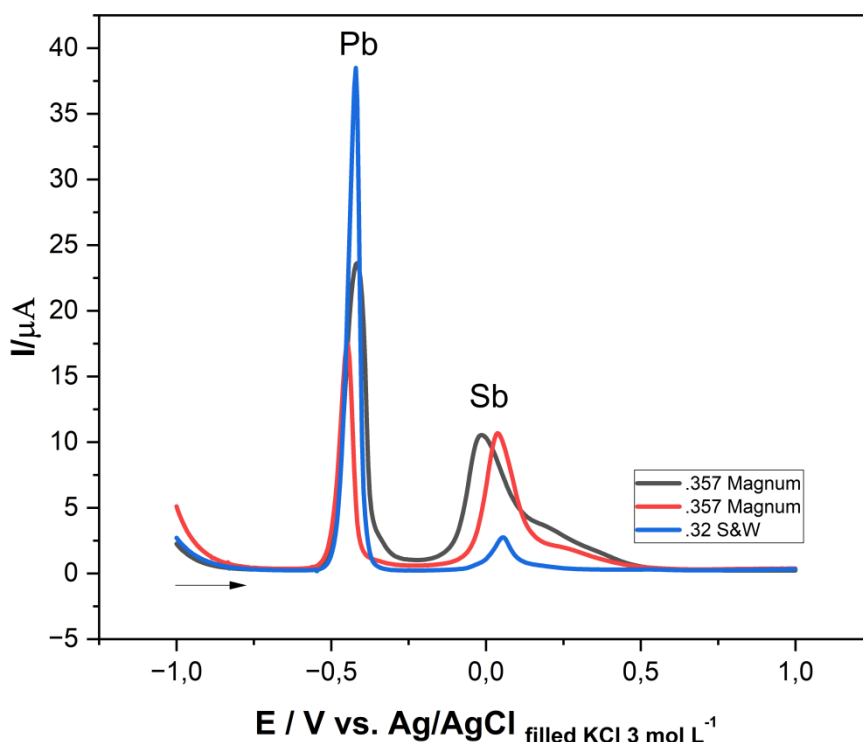


Figure 3. SWV of GSR samples collected from the shooter's hands, analyzed with CPE in buffered medium (acetic acid/acetate) at pH 4.5.

Advances in the miniaturization of potentiostats have enabled the creation of portable devices that can be utilized directly at the crime scene. This development has led to a significant acceleration in the process of obtaining results, as well as a reduction in the necessity of transporting samples to central laboratories.

A comparative analysis of the performance of portable electrochemical instruments and conventional bench systems in the detection of GSR in real samples was conducted by Dalzell et al. (2022). The findings suggested that portable devices demonstrate performance that is comparable to that of laboratory equipment, thereby establishing themselves as a viable alternative for preliminary analyses in criminal investigations [58].

Additionally, the authors investigated the application of electrodes modified with bismuth film (BiFE), which exhibited enhanced selectivity and diminished detection limits for metals present in GSR. Furthermore, this modification signifies a safer and more environmentally sustainable alternative to mercury-based electrodes, which have historically been utilized for the detection of heavy metals [55].

The research conducted by Silva et al. (2024) lends further credence to the importance of optimizing experimental parameters in the electrochemical detection of GSR. To this end, the authors employed multivariate optimization techniques to evaluate the electrochemical response of various metals present in gunshot residues, including Pb, Cu, Zn, and Cd. The findings indicated that precise calibrations in electrolyte composition and electrode modification can substantially enhance the selectivity of the analysis, thereby minimize environmental interferences and augment the robustness of the electrochemical sensors [55].

This approach enhances the precision of the analyses and expands the scope of GSR detection, enabling the differentiation between conventional ammunition and lead-free “green” ammunition. Electrochemistry has also been applied in the differentiation of gunshot residues from different types of firearms [59].

Recent studies have demonstrated that the electrochemical signature of GSR can vary according to the caliber of the weapon used, thereby enabling more precise identification of the source of the gunshot [59]. Furthermore, the utilization of machine learning-based methodologies has been investigated for the purpose of processing substantial quantities of electrochemical data, thereby enhancing the accuracy of sample classification and reducing the influence of subjective interpretation on the results [60].

These advances substantiate the potential of electrochemistry as a versatile and accessible tool for forensic science, thereby enhancing the efficiency and reliability of criminal investigations. Given these advances, the application of electrochemical methods in GSR analysis continues to evolve, with the development of increasingly selective, reproducible, and user-friendly sensors.

The amalgamation of nanomaterials, experimental optimization techniques, and machine learning holds the potential to transform electrochemistry into a routine investigative tool in forensic science, facilitating rapid, reliable, and cost-effective analyses. The continuous improvement of these approaches should consolidate electrochemistry as a complementary or even substitute method for the conventional techniques used in GSR analysis [61].

3.2. Development of modified electrodes for metal detection

The advancement of modified electrodes is imperative in enhancing the electrochemical detection of metals, particularly in forensic applications. Figure 4 illustrates the surfaces of CPE, with (A) representing the unmodified electrode and (B) depicting the electrode post-chemical modification, which results in the creation of a layer of iron (II) hexacyanoferrate, commonly referred to as “Prussian blue”. The objective of surface functionalization is to enhance analytical parameters, including selectivity and sensitivity, while reducing interferences associated with complex matrices. This method

facilitates the concurrent identification of various metallic ions at trace concentrations, thereby enhancing the efficacy and performance of electrochemical sensors utilized in forensic analysis [27].

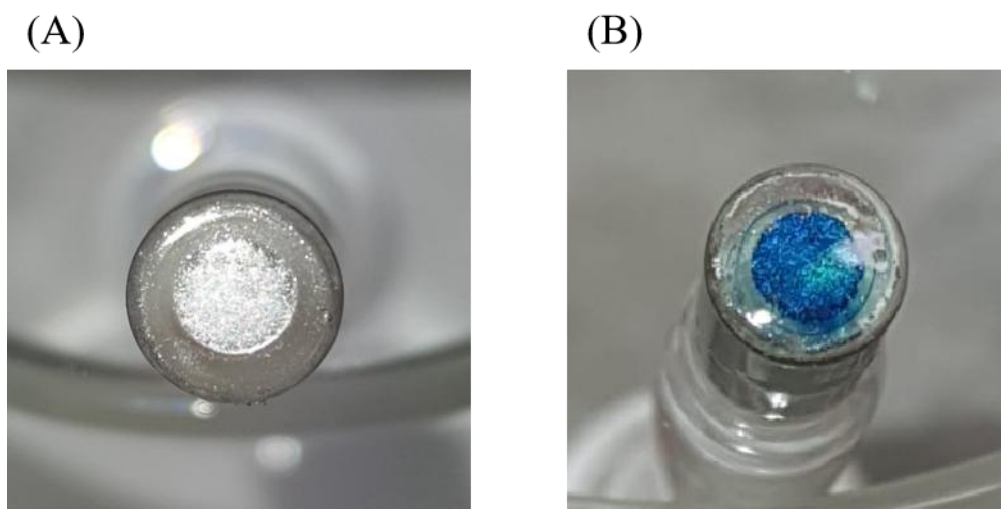


Figure 4. CPE surface. (A) Electrode without modification. (B) Chemically modified surface.

Wongpakdee et al. (2024) demonstrated that the electrodeposition of gold nanostructures on SPCEs significantly enhances the detection of metals such as lead (Pb), antimony (Sb), and zinc (Zn). The incorporation of gold has been demonstrated to expand the active surface area of the electrode, thereby facilitating the adsorption of metal ions and enhancing the electrochemical response [56].

The efficacy of copper (Cu) deposition in detecting organic compounds associated with GSR, such as nitrates and nitrites, has been demonstrated, underscoring the potential of the approach for forensic investigations. Dalzell et al. (2022) investigated the sequential electrodeposition of gold and copper, observing improvements in measurement stability and metal quantification accuracy [58].

The incorporation of copper into the modification process led to an enhancement in the detection of nitrates and nitrites. This, in turn, enabled the multicomponent analysis of GSR, thereby facilitating more robust forensic investigations. Bismuth (Bi) has emerged as a promising alternative in the field of electrode modification. Silva et al. (2024) utilized printed electrodes modified with bismuth film (BiFE) for the concurrent detection of Pb, Cu, and Zn [55]. The material exhibited excellent analytical performance, with low detection limits and high reproducibility. The lower toxicity of bismuth, when compared to mercury, suggests that it is an environmentally safe option for the analysis of heavy metals in shooting residues and environmental samples.

The employment of carbon-based materials has also been instrumental in the advancement of electrochemical sensors. Shrivastava et al. (2021) demonstrated that the incorporation of carbon nanotubes in supercapacitors (SPCEs) increases electrical conductivity, thereby favoring electron transfer and the adsorption of metal ions. This modification has been shown to result in lower detection limits, greater selectivity, and improved sensor stability [24]. The advent of printed three-dimensional electrodes (3D-SPCEs) comprising graphene and conductive polymers signifies a noteworthy innovation [62]. Dalzell et al. (2022) observed that these electrodes exhibit excellent electrochemical response for the simultaneous detection of heavy metals and organic compounds [58]. The 3D-printed

structure has been demonstrated to enhance reproducibility and stability of the sensors, while concomitantly reducing production costs [63].

The modification of electrodes with specific ligands, such as porphyrin and phthalocyanine complexes, has been explored with the aim of improving selectivity in metal detection. As demonstrated by Shrivastava et al. (2021), such ligands exhibit high selectivity for transition metals, including iron (Fe) and copper (Cu), thereby minimizing interferences and improving the accuracy of forensic analysis [24].

The advent of nanotechnology has rendered the combination of different materials, including nanomaterials, noble metals, conductive polymers, and new electrode structures, a tangible reality. This combination facilitates the development of analytical devices that exhibit a high degree of sophistication, as well as accessibility and adaptability for use in both laboratory and field environments [48].

The prevailing future trend indicates an imminent integration of machine learning techniques in the analysis of electrochemical data. This integration is expected to yield two primary benefits: first, it will improve sample classification, and second, it will reduce subjectivity in result interpretation. It is anticipated that electrochemistry will evolve into a pivotal instrument in the identification of metallic residues in forensic investigations and environmental analysis [24].

3.3. Chemical markers in gunshot residues

The utilization of chemical markers in firearm discharge residues represents a novel approach to enhance detection and forensic analysis. The strategy in question enables the precise identification of residues, distinguishing them from environmental particles and providing additional information about the origin of the ammunition used [64].

The visualization of residues under ultraviolet (UV) light demonstrated high efficacy when luminescent markers based on rare earth elements, such as europium and terbium, were incorporated into the ammunition [64,65]. The application of UV light facilitated the immediate identification of residues on the hands and surfaces of shooters in close proximity to the discharge, thereby eliminating the necessity for additional chemical reagents. This approach was investigated by Weber et al. (2014) and Arouca et al. (2017) [66,67].

The fluorescence exhibited by the markers exhibited variation according to the type of ammunition, thereby enabling the differentiation between disparate batches of cartridges. Arouca et al. (2017) investigated the use of luminescent metal-organic frameworks in cartridge formulation [67]. These materials, engineered to emit distinct colors based on the chemical composition of the ammunition, enabled the traceability of the collected residues. The findings from the experimental trials demonstrated the stability of the fluorescence of the MOFs, even after extended periods, thereby ensuring the detection of residues for a duration of hours following the firing process [64]. Furthermore, the markers exhibited efficacy in the identification of residues from lead-free ammunition, a feat that conventional methods based on heavy metal detection struggle to accomplish [64].

The integration of spectroscopic and chemometric techniques has enhanced the efficacy of chemical markers. Carneiro et al. (2019) employed a combination of fluorescence and Raman spectroscopy to identify luminescent markers in gunshot residues. The integration of spectroscopic data and the implementation of advanced statistical methodologies facilitated the reliable identification of residues, thereby attaining a 100% accuracy rate [68]. The methodology employed resulted in an

enhancement of the selectivity of the analyses and a reduction of false positives, a common problem in traditional GSR detection methods. Furthermore, Polovková et al. (2015) investigated the introduction of specific chemical substances, such as gadolinium (Gd), into gunpowder to provide a unique chemical signature to gunshot residues [65].

Notwithstanding the findings of the residue analysis by SEM-EDX, which did not demonstrate significant advantages of gadolinium over luminescent markers based on MOFs, it is proposed, based on the authors, that gadolinium may be useful in differentiating residues from different ammunition manufacturers [34]. Arouca et al. (2017) conducted a study that examined the persistence and transfer of the labeled residues on various surfaces. Their findings demonstrated that the luminescent markers remained detectable even after multiple washes [67]. The distribution of residues across the crime scene facilitated the tracking of the bullet's trajectory and the determination of the shooter's position with greater precision [69].

3.4. AI and chemometrics in GSR analysis

The merging of AI techniques and chemometrics represents a highly promising frontier in the forensic examination of gunshot residues (GSR) [70]. As the volume and complexity of analytical data escalate—particularly from multi-instrumental platforms, such as SEM-EDX, LIBS, ICP-MS, and electrochemical sensors—conventional interpretation methods prove inadequate for managing the multidimensionality of the information produced in research. Artificial intelligence and chemometrics facilitate the identification of concealed links, patterns, and correlations within these datasets, hence enhancing objectivity and reproducibility in forensic determinations [71].

Chemometrics, through multivariate statistical techniques, facilitates the reduction of extensive data matrices into comprehensible components [72,73]. Methods such as principal component analysis (PCA) and linear discriminant analysis (LDA) have been utilized to classify GSR samples based on ammunition type, firing distance, and ambient contamination levels.

The emergence of machine learning (ML) techniques further transforms this domain, offering adaptive algorithms that can learn from data without requiring explicit rule programming [74]. Supervised methods, including random forest, support vector machines (SVM), and artificial neural networks (ANN), have been effectively utilized to identify GSR particles according to their chemical composition and morphological attributes [75].

A significant benefit of AI-based methodologies is data fusion, which involves the amalgamation of information from several analytical sources (e.g., inorganic signatures such as Pb, Sb, Ba; organic stabilizers; morphological descriptors) into cohesive predictive models. This integration significantly enhances the differentiation between genuine GSR particles and ambient or occupational particles, which frequently display overlapping elemental signatures. Moreover, AI can facilitate the detection of anomalies or outliers, recognizing abnormal samples that may signify lead-free ammunition or secondary contamination incidents [35].

The utilization of AI facilitates real-time forensic analysis through portable devices [74]. Electrochemical sensors integrated with embedded machine learning algorithms can categorize voltammetric signals obtained in the field, diminishing dependence on laboratory facilities and facilitating prompt decision-making at crime scenes [76]. The integration of nanomaterials, refined voltammetric methods, and data-driven analysis enhances the sensitivity and interpretability of gunshot residue detection in the field [77].

Nevertheless, these advancements, numerous difficulties persist. A significant drawback is the absence of standardized and publicly accessible resources for training and verifying models, which constrains algorithmic generalization across laboratories. The transparency of AI-assisted choices, known as “explainable AI”, is essential for ensuring legal admissibility and the ethical integrity of automated forensic interpretations. Forensic laboratories must create explicit processes for algorithm validation, data security, and model interpretability to adhere to judicial norms [36].

In summary of AI and chemometrics in GSR analysis is revolutionizing forensic science from a descriptive domain to a data-centric analytical discipline. These advancements provide enhanced analytical precision, less subjectivity, and improved reproducibility in forensic analyses. Future research must emphasize the establishment of standardized procedures, open-access datasets, and transparent algorithms to fully harness AI’s potential as a supplementary tool to conventional analytical approaches, thereby reinforcing the scientific basis of criminal investigations.

4. Conclusions

Advancements in nanotechnology have facilitated the functionalization of metallic nanoparticles with fluorescent ligands, generating more robust and specific markers. These nanoparticles can be engineered to selectively interact with gunpowder and primer compounds, ensuring their detection even in contaminated or highly diluted samples. The integration of these nanoparticles with portable sensors has the potential to transform GSR detection, rendering analyses faster, more accessible, and more reliable. The prevailing trend in the field is the incorporation of chemical markers into emerging analytical platforms, including sensors based on fluorescence spectroscopy, chemiluminescence, and mass spectrometry.

By integrating artificial intelligence (AI), chemometric modeling, and data fusion, contemporary analytical strategies allow the correlation of morphological, inorganic, and organic information within a single predictive framework. Such integration enhances the interpretation of complex datasets, minimizes analyst-dependent subjectivity, and improves the reproducibility of forensic assessments. The convergence of analytical chemistry, materials science, and computational intelligence establishes a new paradigm for GSR analysis, shifting it from a merely descriptive approach to a predictive, data-driven, and intelligent forensic methodology.

In conclusion, while SEM-EDX and AAS remain indispensable cornerstones of GSR analysis, this study highlights that the field is undergoing a decisive transition. Electrochemical sensors, luminescent markers, and chemometric models represent promising additions that complement rather than replace established methodologies. By distinctly delineating between the realm of elemental detection and the broader domain of forensic identification of GSR, it becomes imperative to underscore the importance of maintaining a close synergy between analytical innovation and its practical forensic applicability. A synthesis of classical and emerging techniques—supported by AI-assisted interpretation and multimodal data integration—holds the potential to enhance the reliability of forensic evidence, address the challenges posed by lead-free “green” ammunition, and provide examiners with more robust and versatile tools for firearm-related investigations. The convergence of electrochemical, luminescent, and data-driven approaches not only redefines GSR detection but also exemplifies the growing synergy between forensic chemistry and bioengineering technologies.

Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

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Conflict of interest

The authors declare no conflict of interest.

Author contributions

Larissa Silva de Azevedo, Marcelo Firmino de Oliveira, and João Paulo Mardegan Issa were accountable for the conceptualization and design of the study. Larissa Silva de Azevedo and Alex Soares Castro formulated the approach, whilst Larissa Silva de Azevedo, Alex Soares Castro, Daniela Vieira Buchain, and Regerio Leone Buchain executed the research. Data curation and formal analysis were performed by Larissa Silva de Azevedo and Alex Soares Castro. The manuscript's original version was authored by Larissa Silva de Azevedo, with critical opinion and editing conducted by Larissa Silva de Azevedo, Marcelo Firmino de Oliveira, and João Paulo Mardegan Issa. Funding acquisition was spearheaded by Marcelo Firmino de Oliveira and João Paulo Mardegan Issa, who also oversaw the project comprehensively. All authors reviewed and endorsed the final version of the text.

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