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ASSESSMENT OF GUNSHOT RESIDUE DETECTION ON ANY TYPE OF SURFACE BY PORTABLE LIBS SYSTEM FOR CRIME SCENE APPLICATION

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ABSTRACT

The application of Laser-Induced Breakdown Spectroscopy (LIBS) in forensic science has garnered increasing attention. The ability to perform real-time, on-site analysis of Gunshot Residue (GSR) particles and potential elements originating from bullets or projectile cores on various surfaces holds the potential to assist in resolving firearms-related cases. This includes facilitating trajectory determination by locating distinct impact points and identifying the types of ammunition used. This study evaluates the utilization of a portable LIBS device for ballistic forensic purposes. Additionally, it focuses on the assessment of potential false positives and false negatives arising from the different materials where the shots have been fired. Since the system performs laser ablation of both surface particles and the substrate, it emphasizes the importance of conducting preliminary screening in an area with the same composition as the impact zone to minimize potential false positives during direct surface analysis. Furthermore, the results demonstrate the capability to detect the constituent elements of characteristic gunshot residue particles (GSR particles): lead (Pb), antimony (Sb), and barium (Ba) adhering to bullets, as well as the principal elements composing the jacket or core of the projectile: lead (Pb), copper (Cu), and zinc (Zn) through direct analysis, without the need for a sampling kit, on different surfaces such as walls, furniture, or fabrics. Analyses conducted a month after the shots were fired indicate the potential for finding residues in the vicinity of the bullet hole. Analyses conducted a month after the shots were fired indicate the possibility of finding residues in the area around the bullet hole.

Keywords: LIBS, gunshot residues, portable system, iForenLIBS, field analysis, crime scene

Highlights:

- Conducting a prior screening to verify the composition of the surface is essential for minimizing the risk of false positives when detecting gunshot residues using LIBS.

- Portable LIBS devices can detect gunshot residue elements: lead (Pb), antimony (Sb), barium (Ba), zinc (Zn) and copper (Cu) on evaluated surfaces in real-time, without the need for sampling kits.

- The element of gunshot residues can be detected even after more than a month from the firing through LIBS screening in the field.

1. INTRODUCTION

In any crime scene, obtaining the maximum amount of information possible regarding the events that occurred and the elements involved is crucial for achieving the accurate resolution of the case. The investigator must have access to all available tools that aid in visualizing the scene with utmost clarity and precision [1] [2]. Currently, field analysis equipment is being evaluated [3] [4] [5]. In cases involving firearms, the ability to differentiate between various types of ammunition and determine the potential impact areas (intermediate and/or final shots) at the crime scene can facilitate the identification of possible trajectories and ultimately lead to the successful resolution of the case [6] [7] [8]. The primary evaluated gunshot residues are the GSR particles (gunshot residues) [9]. GSR particles are subdivided into two specific classes based on chemical composition; these subclasses are known as inorganic gunshot residue (IGSR) and organic gunshot residue (OGSR) [10]. IGSRs are primarily derived from the primer and have also been found to contain contributions from the projectile, cartridge case, and discharged firearm [11]. The main technique used for studying and classifying these particles is SEM-EDX [12]. On the other hand, OGSR mainly originates from gunpowder, explosives, and additives [13] [14]. The standardized techniques for the analysis of OGSR currently are Liquid Chromatography-Mass Spectrometry (LC-MS) [15] [16] or Gas Chromatography-Mass Spectrometry (GC-MS) [17]. Trejos et al. propose the integration of LIBS and electrochemical methods as fast and reliable detection tests for GSR (iGSR and OGSR), which enable subsequent confirmatory analysis using SEM-EDX [18]. Nowadays, with the introduction of lead-free ammunition, the number of particle types considered characteristic and compatible has grown exponentially [19] [20] [21]. However, when a projectile impacts a surface, there is also a transfer of material between them. The composition and quantity of residues may vary depending on the nature and density of the material, the distance from which the shot was fired, environmental conditions, the type of ammunition used, and the firearm employed [22] [23] [24] [25].

The analytical techniques that can be used in situ at a firearms scene are limited; primarily, the most commonly used ones are colorimetric techniques [26]. Methods like the Sodium Rhodizonate method need to be optimized, considering parameters such as buffer composition, pH, type of textile used as a substrate, etc., as they can affect the obtained results, as demonstrated by N. Geusens et al. [27]. Other methods, such as the Modified Dithizone Test, allow determining the presence of titanium and zinc [28]. As indicated in SWGGUN Guidelines for Gunshot Residue Distance Determinations [29], the DTO and 2-NN tests are specific for the detection of copper residues from the passage of a copper-jacketed bullet or Chlorindazon DS as improved reagent for the detection of trace amounts of copper [30]. The modified Greiss test is used for the detection of nitrite ions and smokeless powder residues and can be performed by transfer of the target to an adhesive lifter, as described by B. Glattstein et al. [31] On the other hand, the Total Nitrite Pattern Visualization (TNV) is evaluated for its application to casework samples [32]. The main concern lies in the fact that, depending on the substrate where the analysis is required, obtaining a clear and significant colouring could be quite challenging. This creates difficulties in determining whether the observed colouring is a result of the presence of gunshot residue or the presence of potential interfering elements on the surface.

The use of Laser-Induced Breakdown Spectroscopy (LIBS) technology in forensic applications [33], [34] particularly for the study of gunshot residues in forensic ballistics [35] [36] and the assessment of LIBS-based portable systems [37] [38] [39] [40], has experienced a significant growth in recent decades. As early as 2002, S. Goode et al. conducted a study on the characterization and identification of ammunition using this technique [41] [42]. Detecting gunshot residues on the hands of shooters [43] and determining the lifetime of detectable amount are critical factors, with statistically significant results obtained even up to 5.27 days after the shooting [44]. Other authors, such as A. Tarifa and J. Almirall [45], have proposed a combined method involving headspace extraction of volatile organic compounds using a capillary microextraction of volatiles device, previously reported as a high-efficiency sampler, followed by detection using GC-MS and rapid LIBS analysis. This approach enables the detection of both organic and inorganic gunshot residues, resulting in a comprehensive screening method. The combined analysis of LIBS with other techniques, such as Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), can offer an additional level of confidence in the analysis results when studying GSR on the hands of shooters, thus complementing the chemical profiles obtained by LIBS [46]. Furthermore, due to its capability for simultaneous detection of multiple chemical elements, LIBS enables the characterization of lead-free ammunition by identifying barium, aluminum, silicon, potassium, and even trace amounts of titanium, iron, and sulfur [47]. By analysing copper, boron, and zinc, it becomes possible to distinguish between lead-free ammunition from Fiocchi, SeCA, and Sellier & Bellot, and even estimate the shooting distance using GSR particle density maps containing copper, which are generated around the bullet hole [48]. The ability to estimate shot distance using this spectroscopic technique is being widely appreciated. LIBS produces permanent chemical images that allow an objective statistical treatment of the data [49] [50]. Principal Component Analysis and Discriminant Analysis of LIBS data resulted in 100% correct classification of the shooting distance ranges, while color tests resulted in 78.6% correct classification [51].

This study evaluates the field-deployable simultaneous analysis capability, not only of the elements comprising adhered gunshot residue particles (GSR particles) but also of potential metallic elements from the projectile jacket or core that may be present on a specific surface, such as lead (Pb), copper (Cu), and zinc (Zn). To achieve this, a portable device based on LIBS technology was utilized. Prior investigations validating the equipment's sensitivity and specificity demonstrated its ability to detect GSR particles based on the simultaneous analysis of antimony (Sb), lead (Pb), and barium (Ba), even when only a single particle with a diameter greater than 1 µm is present [52]. The analysis is carried out directly on the surface without prior collection using any sampling kit. The system performs laser ablation of both surface particles and the substrate where it is located, providing a result of the elemental composition of the entirety. Therefore, a preliminary assessment of the substrates is necessary to identify potential false positives in gunshot residue detection, particularly when common elements are present in their composition, and to determine the most appropriate analysis protocol.

2. MATERIAL AND METHODS

The samples and their analyses with LIBS equipment have been conducted in the laboratory, except for the samples indicated in the first column of Table 2, which were analysed on-site, as shown in Fig.1.

2.1. Material

The materials used in this study included a shooting bench, a semi-automatic pistol (H&K USP Compact, Heckler and Koch GMBH), conventional ammunition (Semi-Jacketed, soft point, 124 g, Calibre: 9x19 mm Parabellum Sellier&Bellot, Vlasim, Czech Republic), and disposable tips (iForenLIBS consumables).

2.2. Portable LIBS device

The measurements were carried out using a portable LIBS system (iForenLIBS), designed to serve both laboratory and field purposes. The system's compact design (Fig.1) and technical specifications allow for safe sample screening.

Table 1. Physical dimensions

PHYSICAL DIMENSIONS	SIZE (L x W x H)	WEIGHT
Head	390 x 121 x 110 mm	3,7 kg
Backpack	500 x 370 x 185 mm	12 kg

The portable equipment (Fig.1) employs an Nd:YAG 1064 nm laser with an energy density of >6 GW/cm2. This laser can be configured according to the specific sample to be analyzed. Its internal optics system focuses the laser onto the sample surface with a 500 µm spot diameter. The system is equipped with a set of Czerny-Turner spectrometers covering a spectral range from 225 to 960 nm, featuring an average resolution of 0.1 nm, enabling the simultaneous identification of all elements present. The system encompasses various operational modules: the Ballistic Module, the Toxic Module, and the Laboratory Module. Each module comes with pre-configured analysis conditions, including laser energy, spectrometer delay, and integration time. These conditions are designed to optimize the signal-to-noise ratio and streamline on-site work at crime scenes. Within the Laboratory Module, users have the flexibility to adjust analytical parameters, such as laser energy and spectrometer delay, to meet specific analysis requirements and adapt them to the type of analysis or sample under examination.

For our study, the Automatic Surface Gunshot Residue Detection Module was selected. Within this module, users have the option to analyze either "gunshot residue kits" or "other surfaces." The equipment automatically configures the analysis conditions, which are not user-adjustable. However, this module does offer the capability to adjust the frequency and number of shots per series to enhance ease of use. The analysis takes place in ambient air, eliminating the need for any inert gases. Disposable tips designed for field-work were used to provide easy access to the impact zone and prevent cross-contamination between samples. The operator directly analyses the samples, and a camera (Fig. 1) allows for prior visualization of the impact area, aiding in identifying the exact point to be analysed. The equipment can operate with batteries (> 4 h of autonomy) or can be connected to the electric current (Voltage: 110-240 V).

Fig.1. Images of iForenLIBS System and working procedure

Upon completion of the analysis, the results are displayed on the device's user-friendly interface (Fig.2). The system indicates a positive result when all characteristic gunshot residue elements (lead, barium, antimony, copper, and zinc) are detected, and it flags suspicious results when some of these elements are found, specifying which one have been detected. A negative result is given when no elements are detected.

Fig.2. Image of the SW interface where the results of the analysis are displayed

The system is capable of performing qualitative and semi-quantitative analyses, automatically and simultaneously detecting 45 chemical elements. This feature enables the evaluation of the detected element's quantity and its reference to other samples, whether from previous control analyses or samples within the same group. Real-time ".txt files" are generated by the system, displaying the relative concentration of all detected elements in each analysis. The report provides comprehensive data for each measurement. The concentration values are expressed in arbitrary units (a.u), an internal unit of the system, corresponding to the net peak intensity. It would be possible to perform quantification by generating the appropriate calibration curves for each element. The automatically provided values allow for verifying an increase or decrease in the quantity of each element on the surface, always referencing the element to itself and to analyses conducted under the same analytical conditions. Comparing values between different elements would not be appropriate. Moreover, specialists can view the spectra in situ at the system's interface to verify any other element. The system has a database ensuring compliance with necessary requirements for chain of custody and established procedures for results obtained during field analysis.

2.3. **Sample Collection**

A total of fifty-seven samples of surfaces/materials commonly encountered in real scenarios were carefully selected. All sample analyses were conducted in the laboratory, except for those samples that, due to their nature, could not be transported. These on-site samples were analysed in situ. All analyses were conducted using the same portable equipment.

These samples were classified into three sets:

- Set 1: Building materials and common surfaces (Table 2)
- Set 2: Fabrics, including various compositions and colours, encompassing both clothing and decorative elements (Table 3).
- Set 3: Other surfaces, comprising objects susceptible to bullet impact, such as different parts of a car, helmet, and bulletproof vest (Table 4)

Before analysis, all samples underwent a thorough cleaning process with acetone to eliminate any potential contamination.

Table 2. Building materials and common surfaces selected

BUILDING MATERIALS AND COMMON SURFACES	
IN SITU ANALYSIS	**LABORATORY ANALYSIS**
Catch basin cover (plastic)	Concrete block
Grey Silestone (90% quartz)	Concrete brick
Reinforced door	Clay brick
Fire door	Mix: clay brick with concrete
Garage door (Aluminium)	Mortar
Wood Furniture (varnish)	White ceramic tile
Wrought iron table	Red ceramic tile
Wallpaper	Marble tile
Outdoor paint (beige)	Painted (black) and unpainted woods
Indoor Paint (beige)	Wrought iron table
Metal drain grate (outdoor)	Plaster Wall
Garage Wall (concrete + paint)	Plywood
Metal drain grate (indoor)	Medium-density fibreboard
White lacquered wood door	Decorative laminate furniture
Asphalt	Porcelain tiles

Table 3. Fabric selected

FABRIC
Upholstery: 50% viscose 26% Rayon 24 % polyester
100 % Polyester (different colours)
Alcantara fabric: 68% polyester 32% Polyurethane
Leatherette: 90% Polyurethane
Leatherette: 90% PVC (Polyvinyl chloride) (different colors)
Leather
100 % Silk (different colours)
100 % Wool (different colours)
100% Cotton
100 % Nylon

Lyocell
Synthetic silk: 60% silk 40% viscose
Woollen coats: 50% wool 50% polyester

Table 4. Other surfaces selected

SURFACES	SURFACES VEHICLE
Stainless Steel piece	Car door
High-density polyethylene (PE-HD)	Fender
Metal shelf	Tyres
Safety clothing: riot helmet	Alloys Wheels
bulletproof vest	
Polypropylene (PP)	Headlights (red)
Paper	
Cotton swab	
Paperboard	

2.3.1. Firing on a surface

From the total set of samples, a representative group of materials (24 samples-**¡Error! No se encuentra el origen de la referencia.**) commonly found at a crime scene was selected. These samples were subjected to firing using the following procedure.

The gunshots for each sample were discharged in a shooting gallery by specialists under controlled environmental conditions. To prevent cross-contamination, a vacuum cleaner was employed before each shot. For the shooting, a semi-automatic pistol H&K USP Compact was utilized. The ammunition used was conventional 9 mm Parabellum with semi-jacketed soft point and weighing 124 grains (Sellier&Bellot).

Conditions of shooting were the same for all samples:

- Distance from the firearm to the sample: 50 centimetres
- Only one shot was fired to every surface.
- Incidence angle: 90º

To ensure uniform conditions, a shooting bench was utilized to position the gun for each shot (Fig. 3). The samples were individually stored in paper bags and evidence cardboard boxes in the evidence custody room to prevent cross-contamination between them.

Table 5. Surfaces selected for gunshot residue assessment

SURFACES (1)	SURFACES (2)
Concrete block	Stainless Steel piece
Concrete brick	Polypropylene (PP)
Clay brick	High-density polyethylene (PE-HD)
Mix: clay brick with concrete	Paperboard
White ceramic tile	Paper
Red ceramic tile	Cotton Swab
Decorative laminate furniture	Silk
Plaster Wall	Wool
Wallpaper	Cotton
Painted Wood (black)	Leather
Unpainted wood	Riot helmet
Metal shelf	Bulletproof vest

Fig. 3. Image of the assembly performed

In the Fig. 4 shows a detail of the samples before and after taking a shot.

Fig. 4. Images of two surfaces before and after shooting in the gallery.

2.3.2. Firing on multiple surfaces

To replicate potential real-life scenarios, the analytical capability was tested when a projectile pierces multiple surfaces along its trajectory during a shooting incident. In these type scenarios, the main hypothesis proposed is that gunshot residues originating from the primer will progressively decrease as successive cleaning rings are formed with each passage over a surface. It is anticipated that on the ultimate surfaces, the residues predominantly encountered will arise from the transfer of material from the projectile's jacket onto the surface. To achieve this, a specific ammunition retriever from the shooting gallery was employed (model: multiple suspended rubber sheets to stop the projectile), along with a shooting bench (Fig. 5).

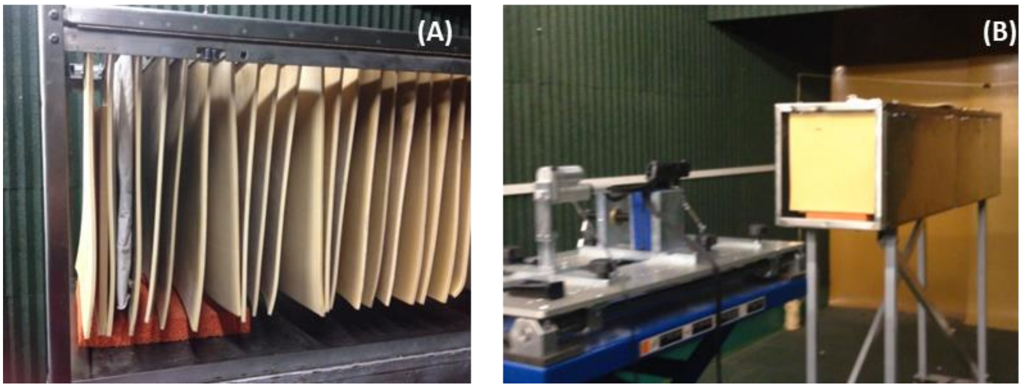

Fig. 5. Image of the arrangement of the samples within the retriever (A). Image of the set up of the assembly to make the shot (B).

To conduct the test, a 1 cm thick sheet of MDF (medium density fibreboard) is positioned immediately after the first rubber sheet. A grey cotton T-shirt is placed between the second and third rubber sheets, which is further secured to a cardboard sheet to provide additional stiffness. The materials, conditions, and procedures are consistent with those described in the section 2.

2.4. **Analysis protocol**

Although the LIBS equipment is capable of automatic screening using a platform, the study was conducted manually following the established crime scene procedure and utilizing fieldwork-specific disposable tips. All analyses were conducted using the same portable equipment. The operator directly performed the analysis on the surface, without the need for a sample collection kit. The impact zone could be controlled and visualized using the camera on the control device. All laser pulses were randomly fired on the surface of the samples. The influence of the firing frequency is not significant in the case of surface analysis, preventing any sample heating due to the laser's repetitive targeting of the same spot. Nevertheless, to mitigate potential variations related to this parameter, the frequency is set at 1 Hz. This setting also enhances the comfort and precision of the operator during the analysis procedure, facilitating accurate positioning of the head within the analysis area. A total of 50 analyses were carried out for each sample (two series).

The system's response time, including data processing, was 40 seconds per series. Although the ballistic module automatically detected the elements for analysis, all spectra were examined to confirm the results.

3. RESULTS AND DISCUSSION

3.1. **Evaluation of false positive in different materials**

As LIBS is an elementary technique, in the initial phase, different materials are evaluated which could potentially yield false positives due to their composition containing elements that are also constituents of gunshot residues. This approach aids in formulating a crime scene protocol for the application of this technique. Prior to conducting the shooting tests, forty-six reference samples were subjected to analysis.

In our study, we exclusively focused on evaluating the main elements considered to be constituents of gunshot residues: lead (Pb), barium (Ba), antimony (Sb) as components of GSR particles, and copper (Cu) and zinc (Zn). These elements are fundamental components of prevalent types of jacketed bullet ammunition, such as brass (72-28 or 90-10), cupronickel, bimetal, or Lubaloy. It is noteworthy that lead is a recurrent element found in both GSR particles and the projectile itself.

Even though the equipment incorporates automatic detection, all spectra were thoroughly examined to verify true positives and negatives, as well as false positives and negatives. The selected wavelengths for verification are as follows: antimony (Sb (I): 259.8 nm), lead (Pb (I): 405.6 nm), barium (Ba (II): 455.4 nm), copper (Cu (I): 324.7 nm), and zinc (Zn (I): 472.2 nm). The emission lines of the studied elements have been cross-referenced with the NIST database and validated against certified standards, confirming the automatic detection for these elements. Furthermore, others emission lines were observed, such as Ba (493.2 nm), Zn (480.9 nm), Cu (327.3 nm), Sb (252.8 nm), and Pb (368.3 nm).

<u>Detection criteria:</u>

The sensitivity, specificity, and accuracy of the system in detecting the elements comprising GSR particles have previously been evaluated in the studies presented by A. Doña-Fernandez et al [52], and these findings were considered as reference values. For copper and zinc, the reference values adopted were the limit of detection (LOD) from the technical specifications provided by the supplier: Zn (49.5 ng/mm^2) and Cu: (2.1 ng/mm^2). Additionally, preliminary detection tests for these elements were conducted using certified standards with varying compositions (metal and soil): Standard Reference Material C2416 (Bullet Lead) (Table 7) and Microanalytical Reference Material SdAR-H1*-NP Nano-particulate pressed powder pellet (Table 6). For the test, the same detection module that has been used throughout the study is employed, ensuring that the analysis conditions remain consistent.

Table 6. Concentration data for Cu, Zn, Ba and Pb extracted from the product information sheet of Reference Material SdAR-H1*-NP

ELEMENTS	VALUE	UNCERTAINTY (95% CL)	UNIT
Copper	1170	12	μg/g
Zinc	3725	60	μg/g
Barium	866	15	μg/g
Lead	3895	75	μg/g

Table 7. Concentration data for Cu and Sb extracted from the standard's certificate of analysis

ELEMENTS	CERTIFICATE VALUE (PERCENT BY WEIGHT)
Copper	0,065
Antimony	0,79

Series of 50 depth shots were conducted on each of the standards, resulting in positive detections of copper, zinc, lead, barium, and antimony in all analyses.

Below, the criteria for positive and negative detection are defined:

1. **Positive detection:** A positive result is considered when the chemical element is detected in any of the 50 shots. This is indicated in the table with "+". If the percentage of positive results in the series is less than 25%, its concentration is considered non-homogeneous in the sample. This is indicated in the table with "*".

2. **Negative detection:** A negative result is considered when the chemical element is not detected in any of the 50 shots. This is indicated in the table with "-".

Chemical elements can be evaluated according to their relative concentration (arbitrary units: a.u.):

a) The symbol "↓" is indicative a low relative concentration of the element in the sample.

b) The symbol "↑" is indicative an elevated concentration of the element in the sample. Elements with a high signal before firing cannot be evaluated for the detection of gunshot residues.

The results obtained from analysing different sample groups (fabric, construction material, and the exterior surface of a vehicle) prior to firing are presented in the following sections.

3.1.1. Fabric analysis

In Fig. 6 spectra obtained before and after firing on a cotton fabric are presented. The B1 graphs depict the spectral range where the emission lines of antimony (Sb) and copper (Cu) are observed. The B2 graph illustrates the spectral range where the emission lines of lead (Pb), barium (Ba), and zinc (Zn) can be seen. In the A1 and A2 graphs, none of the characteristic emission lines of gunshot residues are observed.

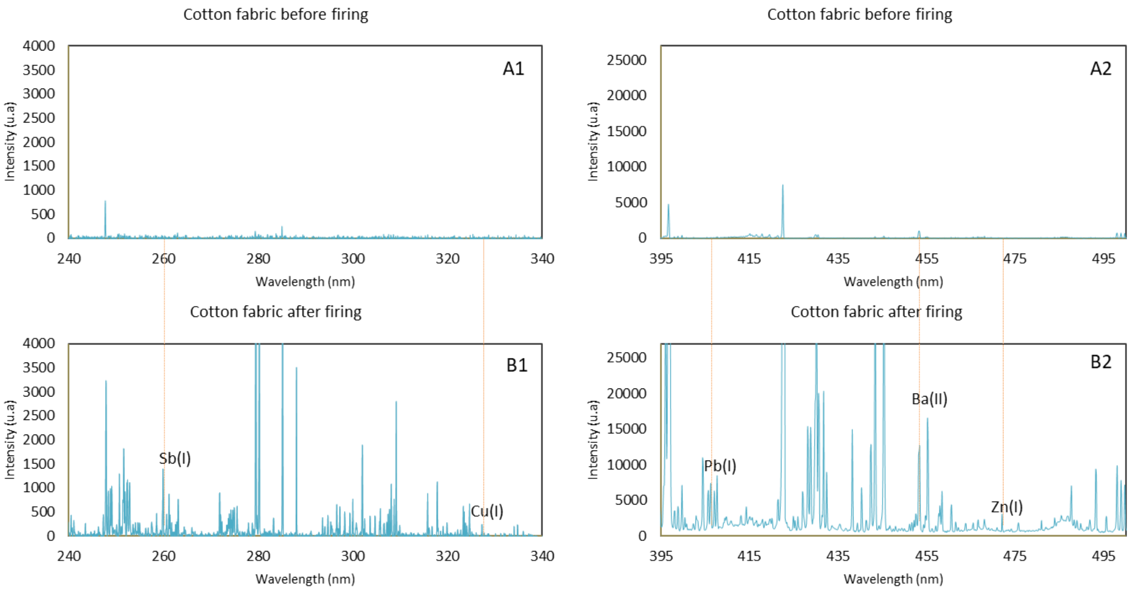

Fig. 6. Spectral ranges corresponding to spectra obtained from the analysis of cotton fabric before (A1 and A2) and after firing (B1 and B2).

The results obtained in the study of the different selected fabrics are shown in Table 8. No lead, antimony, or copper residues were found in any of the evaluated fabrics. However, barium was detected in all fabrics, being considered a common element. This element is often used as a filler or as a base for pigments. The values of this element vary depending on the fabrics, but it is detected homogeneously in each one of them. According to the results obtained, barium is considered a highly common element in materials. It will be regarded as a constituent element of gunshot residues if its relative concentration value is twice the initial value obtained in the control sample analysis before being fired, as defined in the detection criteria outlined in section 3.2.

Zinc was detected in some fabrics (silk and nylon) at very low concentrations and not homogeneously, indicating that it may not belong to the general composition of the substrate, but there are traces.

Table 8. Results of detection of Sb, Pb, Ba Cu and Zn in unfired fabrics

FABRIC	DETECTION RESULTS				
	Sb	Pb	Ba	Cu	Zn
100 %Silk (different colours)	-	-	+	-	+↓*
100 % Wool (different colours)	-	-	+↓*	-	-
100 % Polyester (different colours)	-	-	+	-	-
100% Cotton	-	-	+↓	-	-
100 % Nylon	-	-	+	-	+↓*
Lyocell	-	-	+↓	-	-
Leather	-	-	+↓	-	-
Leatherette: 90% PVC (Polyvinyl chloride)	-	-	+↓	-	-

Leatherette: 90% Polyurethane	-	-	-	-	-
Alcantara fabric: 68% polyester -32% Polyurethane	-	-	+	-	-
Upholstery: 50% viscose 26% Rayon 24 % polyester	-	-	+	-	-
Synthetic silk: 60% silk 40% viscose	-	-	+	-	-
Woollen coats: 50% wool 50% polyester	-	-	+	-	-

3.1.2. Construction materials and furniture analysis

In the analysis of construction materials and furniture, barium has been detected in all samples (Table 9). In the marble samples and asphalt analysis, lead was detected at low concentrations and in a non-homogeneous distribution. In the case of marble, it is considered to be part of the sample composition, although not evenly distributed. The lead found in asphalt can be attributed to contamination from vehicle fuels. The results confirmed that the concentration values (u.a.) in the measurements where this element is detected are very low. Zinc was predominantly detected in metal materials and wood, regardless of whether they have been treated. However, in these cases, a homogeneous distribution of Zinc was not observed on the different surfaces. In the analysis of various porcelain tiles, a high and constant concentration of Zinc was observed, making it difficult to evaluate this element in this material.

Table 9. Results of detection of Sb, Pb, Ba Cu and Zn in unfired construction materials and furniture

SURFACES	DETECTION RESULT				
	Sb	Pb	Ba	Cu	Zn
Porcelain tiles	-	-	+	-	+↑
Marble tile	-	+↓*	+↓*	-	+↓*
Outdoor paint (beige)	-	-	-	-	-
Indoor Paint (beige)	-	-	+	-	-
Plaster Wall	-	-	+	-	-
Garage Wall (concrete+ paint)	-	-	+	-	-
Wallpaper	-	+↓*	+↓*	-	-
Metal drain grate (outdoor)	-	-	+	-	+↓*
Metal drain grate (indoor)	-	-	+	-	+↓
Catch basin cover (plastic)	-	-	+	-	+↓*
Asphalt		+↓*	+	+↓*	+↓*
Mortar	-	-	+	-	-
Grey Silestone (90% quartz)	-	-	+	-	-

Reinforced door	-	-	+↑	-	-
Fire door	-	-	+	-	-
Garage door (Aluminium)	-	-	+↓	-	-
Wooden furniture (varnished)	-	-	+	-	+↓*
Wrought iron table	-	-	+	-	-
Natural wood	-	-	+	-	+↓*
Decorative laminate furniture	-	-	+	-	+↓*
Plywood	-	+↓*	+↓	-	+↓*
Medium-density fibreboard	-	-	+	-	-
White lacquered wood door	-	-	+	-	-

3.1.3. Analysis of exterior surfaces of a vehicle

In line with the previous groups, the presence of barium is consistently observed in all the analysed areas (Table 10). Regarding zinc, small and uniform quantities were detected on all surfaces.

Table 10. Results of detection of Sb, Pb, Ba Cu and Zn in exterior surfaces of an unfired vehicle

SURFACES VEHICLE	DETECTION RESULTS				
	Sb	Pb	Ba	Cu	Zn
Car door (green, white and red colours)	-	-	+	-	+↓*
Fender	-	-	+	-	+↓*
Tyres	-	-	+	-	+↓*
Alloys Wheels	-	-	+	-	+↓*
Headlights (red colour)	-	-	+	-	+↓*

3.2. Analysis of bullet holes in different materials. Verification of the permanence of residue over time

From the total number of materials examined to validate the detection of the characteristic elements of gunshot residues, a set of twenty-four surfaces was selected (Table 5). The results are presented in Table 11 and Table 12 showing the detection of gunshot residues before, one day after, and a month after the shooting. The study assesses the persistence of residue over time. The detection criteria for the elements in the samples before being fired are as indicated in section 3.1.

Detection criteria for elements after shooting:

1. **Positive element detection:** A positive result is considered when the chemical element is detected in at least 25 % of the total analyses performed. This is indicated in the table with "+".
   In samples where a common element with gunshot residues is found in their composition, the presence of these elements can be determined based on the signal value and by comparing the relative concentration (arbitrary units: a.u.). A positive detection is considered when the relative concentration value is greater than two times the initial value in the sample (control analysis).

2. **Negative element detection:** A negative result is considered when the chemical element is not detected in any of the 50 shots. This is indicated in the table with "-".

3. **Inconclusive element detection**: A result is considered inconclusive when the element is detected, but its relative concentration is not greater than 2 times the initial value in more than 25% of the results obtained or is not detected in at least 25 % of the total analyses performed. It is indicated with "/".

Detecting a possible gunshot hole on a metallic or stainless steel object is a rather common scenario. This type of material could pose challenges in detecting the characteristic elements of gunshot residues. Due to their high density and resistance, the transfer of projectile material onto the surface is greater compared to other materials such as plastics or fabrics. The graphs (Fig. 7) provide a detailed depiction of the results of surface analysis before and after a gunshot on a metal shelf and a stainless steel piece. In the pre-shooting control analysis, a consistent concentration of lead, copper, and zinc was observed in both materials. Furthermore, in the case of the metal shelf, the zinc concentration is very high before being fired, preventing evaluation. In stainless steel piece, no significant variation in the concentration of this element is observed after shooting compared to the initial sample concentration. The positive detection of lead and copper residues, elements of the projectile, is evident on both surfaces, with the concentration of these elements exceeding the established threshold, being twice the initial concentration detected in the sample. Moreover, antimony, along with a substantial increase in the level of barium -both characteristic elements of GSR particles from the primer- are detected on both surfaces even after one month (Table 11).

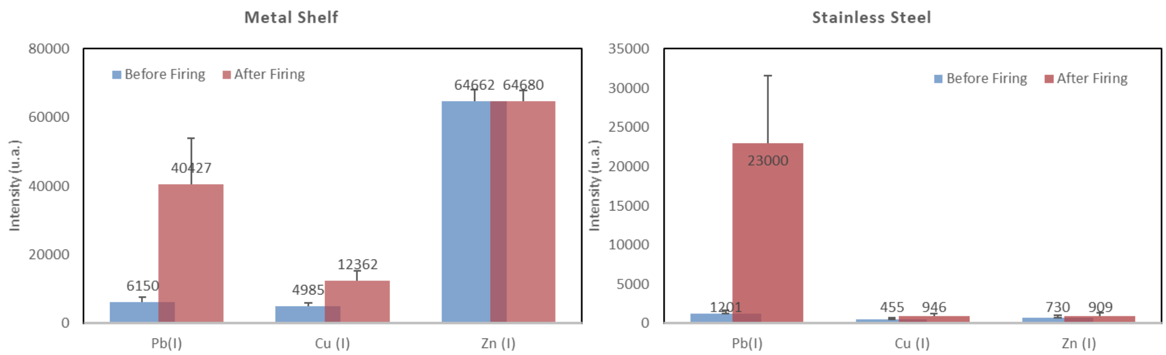

Fig. 7. Lead, copper and zinc relative concentration values of metal shelf and the stainless steel piece

The analysis reveals the presence of specific materials which, along with traces of barium, also contain zinc (54% of the samples). Moreover, lead is detected in wallpaper, decorative laminate furniture, and red ceramic tile before firing (Table 11). In these instances, detection relies on the comparison of element concentrations. Positive detection of gunshot residues (lead, barium, copper, and zinc) was confirmed in these materials, except for red ceramic. Due to its composition, the results have been inconclusive for all elements via direct surface analysis.

Table 11. Results of detection of Sb, Pb, Ba Cu and Zn in surfaces (1) before, after 1 day, and 1 month firing

SURFACES (1)	BEFORE					AFTER (1DAY)					AFTER (1MONTH)					COMPATIBILITY WITH GUNSHOT RESIDUES
	Sb	Pb	Ba	Cu	Zn	Sb	Pb	Ba	Cu	Zn	Sb	Pb	Ba	Cu	Zn	
Concrete block	-	-	+	-	+↓*	/	+	+	-	+	+	+	+	-	+	**Suspicious**
Concrete brick	-	-	+	-	-	-	+	+	+	+	-	+	+	+	+	**Compatible**
Clay brick	-	-	+↑	-	+↓*	-	+	+↑	+	/	-	+	+↑	+	/	**Suspicious**
Mix: clay brick with concrete	-	-	+	-	+↓*	/	+	+	+	/	+	+	+	+	/	**Suspicious**
White ceramic tile	-	-	+	-	+↑*	-	+	+	-	/	-	+	+	-	/	**Inconclusive**
Red ceramic tile	-	+↑	+↑	+	+↑	-	/	/	/	/	-	/	/	/	/	**Inconclusive**
Decorative laminate furniture	-	+↓*	+↓	-	+↓*	+	+↑	+↑	/	/	+	+↑	+↑	+	/	**Suspicious**
Plaster Wall	-	-	+↓*	-	+↓*	+	+	+	+	+	+	+	+	+	+	**Compatible**
Wallpaper	-	+↓*	+↓*	-	-	+	+↑	+↑	+↑	+	+	+↑	+↑	+↑	+	**Compatible**
Painted Wood (black)	-	-	+↓*	-	-	+	+	+	+	+	+	+	+	+	+	**Compatible**
Unpainted wood	-	-	+	-	+↓*	+	+	+	+	+	+	+	+	+	+	**Compatible**
Metal shelf	-	+↓	+↓	-	+↑	+	+↑	+↑	+↑	/	+	+↑	+↑	+↑	/	**Compatible**
Stainless Steel piece	-	+↓	+↓	+↓	+	+	+↑	+↑	+↑	/	+	+↑	+↑	+↑	/	**Compatible**

The white ceramic sample fragmented into numerous pieces, making it challenging to identify the precise area of impact by the projectile. Nevertheless, a previously undetected concentration of lead was successfully determined. Copper, however, was absent in all the assessed fragment areas. The presence of lead would be indicative of a potential impact but not confirmatory. In the case of ceramic material, the composition varies depending on the pigments used in its manufacture. This circumstance complicates the direct surface analysis for gunshot residue detection. In this scenario, it would be necessary to collect a sample using a kit and confirm the findings through SEM-EDX analysis.

Table 12. Results of detection of Sb, Pb, Ba Cu and Zn in surfaces (2) before, after 1 day and 1 month firing

SURFACES (2)	BEFORE					AFTER (1DAY)					AFTER (1MONTH)					COMPATIBILITY WITH GUNSHOT RESIDUES
	Sb	Pb	Ba	Cu	Zn	Sb	Pb	Ba	Cu	Zn	Sb	Pb	Ba	Cu	Zn	
Polypropylene (PP)	-	-	-	-	-	+	+	+	+	+	+	+	+	+	+	**Compatible**
High-density polyethylene (PE-HD)	-	-	-	-	-	+	+	+	+	+	+	+	+	+	+	**Compatible**
Paperboard	-	-	+	-	-	+	+	+	+	+	+	+	+	+	+	**Compatible**
Paper		-	+↓	-	-	+	+	+	-	+	+	+	+	-	+	**Suspicious**
Cotton Swab	-	-	-	-	-	+	+	+	+	+	+	+	+	+	+	**Compatible**
Silk	-	-	+	-	+↓*	+	+	+	+	+	+	+	+	+	+	**Compatible**
Wool	-	-	+↓*	-	-	+	+	+	+	+	+	+	+	+	+	**Compatible**
Cotton	-	-	+↓	-	-	+	+	+	+	+	+	+	+	+	+	**Compatible**
Leather	-	-	+↓	-	-	+	+	+	+	+	+	+	+	+	+	**Compatible**
Riot helmet	-	-	+↓	-	+↓*	+	+	+	+	+	+	+	+	+	+	**Compatible**
Bulletproof vest	-	-	+↓	-	+↓	+	+	+	+	+	+	+	+	+	+	**Compatible**

The fabrics (silk, wool, cotton and leather) (Table 12) are soft materials, resulting in a decreased contribution of bullet jacket residues upon impact. The residues come mainly from the cleaning of the bullet, from adhering primer particles, or from gases reaching the surface (GSR particles). Positive detection is confirmed for all elements constituting gunshot residues.

There were no significant variations in the results of lead, barium, copper, and zinc observed for each analysed surface between one day after and one month after. The disparity in the detection of Sb (concrete block and clay brick with concrete-Table 11) in the analyses conducted one day later and one month later could be attributed to the random screening process carried out over the edge and the area near the hole (radius: approx. 2 mm), leaving certain areas unanalysed. The estimated total ablated area in each sample with 50 shots is 9.8 mm². Increasing the number of shots taken could enhance the results. While our testing has covered a wide range of surfaces, it is essential to recognize that the results cannot be extrapolated to the countless potential surfaces that may be encountered at a crime scene. This limitation should be acknowledged as inherent to the study. Consequently, we recommend the consistent practice of conducting a preliminary test on the surface slated for analysis, selecting a residue-free area in a random and expansive manner, always away from the direct impact zone. While a minimum of 50 shots has been established as the threshold for obtaining optimal results, this number may need adjustment depending on the nature of the material or the preliminary findings from both the initial test and the gunshot residue elements assessment series. Based on our experience, this approach helps mitigate potential sources of confusion arising from the variety of surfaces under examination. However, it's important to note that these are preliminary findings and should be further refined through additional comparative tests conducted in real-world scenarios.

As an assessment of the results for the detection of the ensemble of elements, the following criteria for compatibility with gunshot residues are defined:

1. A result is deemed "**compatible with**" gunshot residues concerning the control analysis when positive detections, according to the criteria described earlier, have been considered for all the elements studied.
2. It is considered "**compatible with**" gunshot residues regarding the control analysis when positive detection has been considered for the constituent elements of the bullet jacket (copper, zinc, and lead).
3. A result is classified as "**suspicious**" for gunshot residues when there is positive detection of at least two elements compared to the control analysis.
4. An outcome is regarded as "**inconclusive**" when it does not meet any of the criteria mentioned above.

The results of applying these criteria for gunshot residue compatibility are shown in the last column Table 11,Table 12 andTable 13.

The obtained results demonstrate a balance of "compatible" detection with gunshot residues in 17 out of the 24 samples evaluated, with 5 results being categorized as "suspicious," and 2 results being "inconclusive." Although in the case of samples with "suspicious" results, the presence of elements such as copper, lead, or antimony suggests gunshot residues, these should be assessed using other techniques to verify the outcome and confirm the presence of residues on the surface. For the "inconclusive" samples, the procedure will be the same as for the "suspicious" samples.

4.3. **Analysis of intermediate bullet holes on multiple surfaces. Preliminary study.**

The first rubber sheet, the wooden plate, the T-shirt and the rubber sheet number 8 are extracted and analysed. The projectile pierced all the surfaces until it impacted in the eighth rubber sheet without sufficient energy for it to perforate.

The results of the analysis of the various surfaces are shown in Table 13.

Table 13. Results of detection of Sb, Pb, Ba Cu and Zn in multiple surfaces

SURFACES	BEFORE					AFTER (1 DAY)					AFTER (1 MONTH)					COMPATIBILITY WITH GUNSHOT RESIDUES
	Sb	Pb	Ba	Cu	Zn	Sb	Pb	Ba	Cu	Zn	Sb	Pb	Ba	Cu	Zn	
Initial impact rubber	-	-	+	-	-	+	+	+	+	+	+	+	+	+	+	**Compatible**
MDF (medium density fiberboard)	-	-	+	-	-	+	+	+	+	+	+	+	+	+	+	**Compatible**
Cotton T-shirt	-	-	+	-	-	/	+	+	+	+	/	+	+	+	+	**Compatible**
Final impact rubber	-	-	+	-	-	-	+	+	+	+	+	+	+	+	+	**Compatible**

The results of gunshot residue detection across multiple surfaces are presented in Table 13. It is evident that the detection has been positive across all levels, indicating a transfer of gunshot residues retained by the projectile even after passing through multiple surfaces. The variation in antimony detection could be attributed to the random screening carried out during sampling. Furthermore, the contribution of antimony on the surface is attributed to GSR particles originating from the primer, while for elements like lead and copper, the concentration is due to the combination of residues from both the projectile jacket and the primer adhered to the bullet.

4. CONCLUSIONS

The analysis of the surfaces using the LIBS technique, it determines evident that several of them share common elements with components of gunshot residues. To reduce false positives in scenarios involving firearms, conducting a preliminary surface screening, known as control analysis, is required.

The positive results obtained by analysing bullet holes in various materials underscore the ability of LIBS to directly detect the characteristic chemicals elements of gunshot residue on the tested surfaces: antimony, lead, barium, copper, and zinc.

In instances where lead, antimony, copper, and/or zinc are detected on the control surface, a semi-quantitative assessment of the analysis values is essential for confirming the presence of residues through LIBS. To this end, a threshold for positive detection is established, signifying a relative concentration value twice that of the control sample.

No significant disparities surfaced in the temporal stability assessment study, comparing analyses carried out one day and one month later.

In the preliminary multi-surface residue assessment study employing a single shot, positive detection transpired on both intermediate and final surfaces.

These results confirm the portable system as an optimal tool for both detecting and confirming the presence of the gunshot residue elements. The selected number of analyses (50 shots) is considered optimal for obtaining fast and reliable screening field results. These results confirm the portable system as an optimal tool for detecting and confirming the presence of the gunshot residue elements assessed. The chosen number of analyses (50 shots) is considered optimal for obtaining quick and reliable screening results in the field.

The qualitative and semi-quantitative analytical capacity of the device would enable the real-time confirmation of residues at the crime scene, eliminating the need to send samples to a laboratory. This approach would expedite response time in cases involving potential gunshot-induced holes. Furthermore, as a portable device, it facilitates access to challenging areas like ceilings.

While these findings are promising, it is necessary to increase the number of replicates, expand the array of elements to be assessed, including those from different types of ammunition (lead-free ammunition), study diverse forms of projectile jackets, and continue exploring a wider range of potential surfaces.

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