Forensic Science International 273 (2017) 124–131

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

An exploratory study of the potential of LIBS for visualizing gunshot residue patterns

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ARTICLE INFO

Article history:
Received 4 October 2016
Received in revised form 8 February 2017
Accepted 14 February 2017
Available online 21 February 2017

Keywords:
LIBS
Gunshot residues
Distance estimation
Forensic analysis
Imaging

ABSTRACT

The study of gunshot residue (GSR) patterns can assist in the reconstruction of shooting incidences. Currently, there is a real need of methods capable of furnishing simultaneous elemental analysis with higher specificity for the GSR pattern visualization. Laser-Induced Breakdown Spectroscopy (LIBS) provides a multi-elemental analysis of the sample, requiring very small amounts of material and no sample preparation. Due to these advantages, this study aims at exploring the potential of LIBS imaging for the visualization of GSR patterns. After the spectral characterization of individual GSR particles, the distribution of Pb, Sb and Ba over clothing targets, shot from different distances, were measured in laser raster mode. In particular, an array of spots evenly spaced at 800 μm, using a stage displacement velocity of 4 mm/s and a laser frequency of 5 Hz was employed (e.g. an area of 130×165 mm^2 was measured in less than 3 h). A LIBS set-up based on the simultaneous use of two spectrographs with iCCD cameras and a motorized stage was used. This set-up allows obtaining information from two different wavelength regions (258–289 and 446–463 nm) from the same laser induced plasma, enabling the simultaneous detection of the three characteristic elements (Pb, Sb, and Ba) of GSR particles from conventional ammunitions. The ability to visualize the 2D distribution GSR pattern by LIBS may have an important application in the forensic field, especially for the ballistics area.

1. Introduction

Gunshot residues (GSR), also known as cartridge discharge residues or firearms discharge residues, are particles produced during the discharge of a firearm [1]. These particles, typically of micron dimensions, are a mixture of organic compounds, coming mainly from the propellant, and inorganic compounds from the primer, propellant, cartridge case, bullet or the firearm itself. GSR particles are launched with the projectile and are transferred to the victim (target), the shooter or to different objects at the scene. In addition, after leaving the firearm bore, the GSR particles result in a conical plume of particles that creates a pattern on the target depending on different factors. The factors that affect the appearance of these GSR patterns include the type of ammunition and firearm, barrel length, firing angle, atmospheric conditions, target material, muzzle-to-target angle and, especially the firing distance [2]. Thus, a question commonly asked to the forensic firearm analysts, besides the identification of the GSR particles, is the estimation of the shooting distance (muzzle to target distance). This range, which has an extensive forensic significance for the reconstruction of a firearm-related offense, is estimated by the examination of the bullet entry hole and its surroundings [3].

Tests based on color chemical reactions that reveal the presence of nitro groups or heavy metals (e.g., Walker test, Marshal and Tewari test, sodium rhodizonate test, etc.) are used by the forensic analysts to visualize the GSR particles in the patterns [1]. Color tests show important drawbacks like non-specificity to GSR, application using long and tedious proceedings, requirement of proper storage and disposal of the hazardous chemicals. Therefore, some other interesting approaches for shooting distance estimation not based on color chemical tests were reported in the literature. A recent review covers the latest methods proposed in this new field [3]. Visual methods based on video spectral comparators [4], digital infrared imaging [5], or light microscopy and image analysis [6,7], as well as instrumental approaches for

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http://dx.doi.org/10.1016/j.forsciint.2017.02.012
0379-0738/

elemental analysis, like X-ray Fluorescence [8], Atomic Absorption Spectroscopy [9], or Inductively Coupled Plasma Mass Spectrometry [10] were proposed to visualize GSR patterns. The main advantage of elemental techniques is the capability to perform simultaneous multielemental analysis, which provides valuable information.

Laser Induced Breakdown Spectroscopy (LIBS) is an analytical technique that allows performing simultaneous multielemental analysis. LIBS is based on the use of a short duration laser pulse (on the order of ns or below) focused on a small area of the sample. The high fluence (energy per area) over the sample surface produces the ablation of a tiny quantity of sample and the formation of a laser-induced plasma. The species present in the plasma suffer processes of atomization, ionization and excitation; and the radiation coming from the excited species can be detected by an spectroscopic device [11]. LIBS provides some advantages over other methods of elemental analysis, such as simple and rapid analysis, or the requirement of very small amounts of material ($\sim$0.1 μg). Moreover, it has the possibility for stand-off and in-lab capabilities of analysis, and little or no sample preparation is required [12,13]. In view of these benefits, some works reported the use of LIBS for the identification of GSR particles.

Dockery and Goode [14] used LIBS to determine whether the hands of a suspected gun user contained traces of GSR. The GSR particles were collected by dabbing with adhesive tape the hands of shooters as well as volunteers that have not fired a gun within 24 h before sampling (only one type of firearm and ammunition was employed). Positive results were obtained in case of samples collected from the hands of a shooter, who fired multiple shots, or in the case that the gun was not cleaned before the shot. However, this positive identification is actually not so simple in case of a single shot using a clean gun. In a second work [15], the same research group investigated the period of time that a shooter will test positive for GSR after firing six shots with a revolver and afterwards continuing normal daily activities. Samples were collected at multiple hour intervals using the same collection approach above mentioned. The Ba II emission line at 455.403 nm was used as evidence of GSR presence. The authors claimed that, statistically, the results were positive for GSR 5.27 days after a firearm discharge.

A similar, but broad investigation, was performed some years later by Silva et al. [16]. Different types of ammunition cartridges were fired using two different firearms. The hands of the shooters were sampled just after firing, and also after washing their hands with soap and water. The hands of non-shooters as well as automobile brake repair workers were also sampled to test if false-positives could also arise.

Additionally, two sampling approaches were tested, pressing a small piece of adhesive tape against the dorsal region of the hands of shooters and using a polymeric resin. Both sampling methods showed the same efficiency for removing the GSR from the hands; however, due to the time required for resin polymerization, and the irregular morphology of the resin that complicates the analysis, the authors recommended the use of the adhesive tape. Averaged spectra of 20 laser shots of each adhesive tape were treated using Soft Independent Modeling of Class Analogy (SIMCA) pattern recognition method. The shooters and non-shooters were corrected classified, even after washing their hands with soap. Although no false-negative results were found, a false positive result was obtained from one of the samples taken from an automobile brake repair worker.

The occurrence of environmental and/or occupational false-positive tests for GSR using the emission line of Ba was studied by Dockery et al. [17]. LIBS spectra obtained from samples collected using the tape-lift technique from welding, pyrotechnics, key cutting, mechanics, and paper product occupations or simulations, were compared with the one collected from the hands of a shooter producing significant false positive results. These findings highlight the importance of performing multi-elemental analysis.

Hondrogiannis et al. [18] explored the ability to identify GSR from the inside of cartridge casings using a commercial field-portable LIBS system and to link the elements measured with the ammunition manufacturer. The GSR particles were collected from the fired cartridges by swabbing with cotton swabs. Then, the swab was placed in the LIBS sample chamber and ablated with multiple shots at different swab locations. Although they detected several elements (including Ba and Sn) the mathematical model generated was not able to unequivocally identify the ammunition manufacturer (classified with 67% accuracy). This result may be due to the similar composition of the primers present in the different ammunition cartridges.

The combined use of Gas Chromatography coupled to Mass Spectrometry (GC–MS) and LIBS was recently proposed for the characterization of both organic and inorganic GSR compounds [19]. The hands of shooters and non-shooters were sampled using cotton swabs. First, a headspace extraction of volatile organic compounds using capillary microextraction of volatiles was performed, followed by the liquid extraction of the inorganics. Due to the possibility of obtaining false-negatives (e.g. due to the lower detectability of Sb), the authors proposed the sequential analysis of the same swab by both techniques.

These investigations support the use of LIBS as a fast and relatively inexpensive screening technique for GSR detection; for example, to differentiate shooters and non-shooters or to investigate the period of time that a shooter will test positive for GSR. Despite these findings, no attempts have been made to visualize the GSR patterns by LIBS imaging. Therefore, and due to the mentioned need for alternative methods capable of furnishing simultaneous elemental analysis of higher specificity for GSR, we investigate the use of LIBS to reveal the Pb, Sb, and Ba firing patterns on clothing targets. First, the simultaneous multielemental analysis of individual macroscopic GSR particles were performed in order to investigate the LIBS conditions under which the GSR patterns can be visualized. Then, cotton cloths targets that were shot with conventional ammunitions at different distances were measured. Since in the forensic field the preservation of the forensic evidences is required, the LIBS imaging analyses were carried out on a specific support, where the GSR patterns were previously transferred. Therefore, the integrity of the clothing targets is assured being possible further forensic tests.

2. Experimental

2.1. Ammunition and firearms

Three different 9 × 19 mm conventional ammunition cartridges were fired at 0.5 m from the target. Two full metal jacket (FMJ) ammunitions manufactured by Santa Barbara (Spain), called SB-T 93+ and SB 96+, and one semi-jacketed hollow point (SJHP) ammunition manufactured by Sellier & Bellot (Czech Republic), called S&B. Then, S&B cartridges were also fired at 30, 50, and 150 cm distances from the target. White cotton cloths of 20 cm × 20 cm size fixed in cardboards were used as targets. Shots were performed in a shooting gallery with a semi-automatic Glock 17 pistol (Glock Ges.m.b.H., Austria).

2.2. Sample collection

To study the capability of LIBS technique to analyze GSR macroscopic particles, 5–10 GSR macroscopic particles from each different ammunition were measured. The particles were collected from the clothing targets using metal tweezers, and then placed on