



## Investigation of the use of luminescent markers as gunshot residue indicators



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### ABSTRACT

The addition of luminescent markers into ammunition cartridges is an appealing proposal to achieve a greater individual identification of the ammunition. The lanthanide elements present in these luminescent materials act as characteristic chemical markers that, also, offer the great benefit of making gunshot residues (GSR) collection easier. Although the use of luminescent markers offers numerous advantages, and can be a reliable future option in the cartridge ammunition market, little or nothing is known about the interaction of the marker with the ammunition compounds after the shot. For the forensic laboratories, it is of utmost importance to anticipate the commercialization of tagged luminescent ammunition by knowing the type of particles produced after the discharge. That is, to investigate if markers merge with GSR to form single particles or, on the contrary, they form individual particles that travel separately from the GSR particles. In this work, conventional ammunition cartridges tagged with two types of luminescent markers were shot. Then, the particles produced were visualized under UV light on the floor, clothing targets and the shooter. The luminescent particles spread over the floor determined the shooter position and the bullet trajectory. The illumination of the shot targets allows the visualization of the GSR patterns only using a portable UV lamp, avoiding the use of colorimetric test. The GSR particles were collected and subjected to SEM-EDX and Raman spectroscopy analysis to get information about their inorganic and organic composition. The results indicated that part of the marker and the GSR merge and travel together. With this, particles composed by the marker and propellant organic compounds can be identified by Raman spectroscopy, and the unequivocal identification of the GSR and the marker can be achieved by SEM-EDX. Consequently, the luminescent particles detected under UV light improve the evidence collection and offer information about the GSR and the marker. Additionally, this study support the use of luminescent ammunition to study, for example, the transfer or persistence of GSR.

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## 1. Introduction

The products of the primer detonation and gunpowder combustion, as well as partially unburned gunpowder and metallic particles taken from the gun barrel, projectile and cartridge, comprise the so-called gunshot residues (GSR) [1–4]. These

residues spread out after leaving the gun and deposited on any surface in the shooting surroundings. Therefore, GSR are commonly used to reconstruct a firearm-related offense, helping to confirm (or deny) the implication of a suspect, a suicide hypothesis, to estimate firing distance, to identify bullet holes, among others. For these reasons, GSR are physical evidence with great forensic value [1–5].

Nowadays, the recommended technique for GSR characterization is Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM-EDX) [6]. The GSR particles from conventional ammunition are identified by SEM-EDX by their spheroidal shape

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and the simultaneous presence of Sb, Ba and Pb at the same particle [4]. However, the introduction in the market of lead-free ammunition has resulted in the development of new analytical methods focused on the additional identification of the organic compounds of GSR. For this, Raman spectroscopy, a non-destructive spectroscopic technique that offers information about both organic and inorganic samples, was proposed to identify the organic components present in GSR particles. In turn, López-López et al. [7] showed that the Raman spectra of the macroscopic GSR particles have high similarity to the unburned gunpowder and, therefore, may help to trace ammunition. Furthermore, an GSR-discrimination based on the stabilizers used in the propellant (diphenylamine or ethylcentralite) proved to be efficient. In other work, the same research group [8] showed that the weapon memory effect is insignificant when analyzing the organic part of the GSR particles by Raman, reducing the risk of contamination by previous shots. Meanwhile, Abrego et al. [9] used an adhesive polytetrafluoroethylene tape lift for collecting GSR particles from shooters' hands to analyze the particles by a confocal Raman microscope. In this study, the gunpowder stabilizers were also detected in the GSR particles collected. Bueno et al. [10] used a near-infrared confocal Raman microscope and chemometrics to discriminate GSR particles from two different ammunition calibers (9 mm and 0.38). More recently, Raman imaging was used to characterize the organic components of the GSR particles [11,12]. In short, Raman spectroscopy, stand out since it has numerous advantages over other techniques. As example, it does not require sample preparation (the measurements can be performed directly on SEM stubs commonly used to collect the GSR particles as well as on a blood-stained victim's clothes) [12], performs nondestructive analysis (important to characterize forensic evidence) and provides spectra that can be compared with the profile of known samples in a fast way. Additionally, the mapping of the particle can be performed with some imaging equipment, allowing to visualize the spectra of the particle at different points of the sample [12].

When it comes to GSR analysis, a source of false negatives that should be considered is the possibility of non-collecting the GSR. Due the micron size of these particles, many times the forensic expert collect the sample without visualizing the residues. In this context, Weber et al. [13–19] proposed the addition of luminescent markers into ammunition cartridges to assist the visual detection of their residues, their collection and the crime scene investigation. Luminescent markers, when added into ammunition, allow the visual detection of luminescent residues directly in loco, using only a portable UV lamp. Furthermore, once the lanthanide elements present in these materials are uncommon in the environment, they act as chemical markers and can assist in the identification of GSR particles, especially those coming from lead-free ammunition [16–19]. Besides, different emission colors can be used to differentiate ammunition by usage type (e.g. civilian, police or military) [18].

Although the characterization of isolated luminescent markers (after shots with conventional [14,15] and NTA [14,16–19]) is well established by using techniques such as SEM-EDX and emission spectroscopy, the interaction of these markers with the ammunition compounds after the shot was not studied to date. Then, it is of utmost importance to know if the dispersion of the luminescent markers is similar to the GSR particles by knowing if they give rise to two different types of particles (marker and GSR particles), or, on the contrary, they lead to particles consisting of a mixture of GSR and lanthanides. In other words, it is important to assess whether the markers improve the collection of organic and inorganic GSR particles or not.

This work aimed to study the GSR particles produced after the discharge of conventional ammunition cartridges tagged with two types of luminescent markers. Firstly, the visualization of the

luminescent particles under UV light on the floor, clothing targets and shooters was pursued. Then, the particles were collected using SEM stubs and characterized by the reference technique, SEM-EDX, and also, by Raman spectroscopy, which is one of the most promising techniques for the analysis of the organic components of the GSR.

## 2. Material and methods

### 2.1. Sample preparation

The bullets of 9 × 19 mm semi-jacketed hollow point conventional ammunition manufactured by Sellier&Bellot (Czech Republic) were removed from the cartridges using a bullet puller. Then, a green ( $[Y_{0.85}Yb_{0.10}Tb_{0.05}(BTC)]$ ) or red ( $[Y_{0.95}Eu_{0.05}(BTC)]$ ) luminescent marker (wherein BTC = trimesic acid), prepared as previously reported in Ref. [19], was added to the gunpowder (5 wt%). The handloading process of the tagged ammunition was performed in a press.

The floor of a shooting range was covered with a 10-m black paper strip in order to keep the floor surface where the GSR particles are going to be collected as clean as possible. Then, a shot was performed using a Glock G17 pistol and an ammunition cartridge tagged with the red marker. After the shot, the shooter and the floor were observed under UV radiation ( $\lambda = 254$  nm) with a portable lamp (UVGL-58 Handheld UV Lamp, UVP). Particles were collected from the shooter's hands, firearm and the floor (around 0.1, 0.3, 1.2, 2 and 8 m from the shooting point) with 13 mm diameter aluminum SEM stubs with adhesive carbon tape (one stub for the hands, one stub for the firearm, and one stub for each distance). Then, the black paper strip was replaced by a new one and the same procedure was repeated for the ammunition tagged with the green marker (different shooter and G17 pistol). In both cases, the pistols were not previously cleaned to provide a more realistic scenario. The stubs ( $n = 14$ ) used to collect the particles at the different distances, the shooter's hands and the firearms were then analyzed by SEM-EDX.

In a second step, 35 × 35 cm cardboard targets covered with black fabric were shot at five different distances (0.1, 0.3, 1.2, 2 and 8 m) with the two types of tagged ammunition cartridges. Photos (Fuji Finepix S100 fs) of the targets were taken under UV radiation ( $\lambda = 254$  nm) to visualize the GSR patterns. The GSR particles on the targets were collected with SEM stubs (one stub for each target), and then, analyzed using Raman spectroscopy. The particles that emit luminescence were focused under the Raman microscope, and analyzed.

### 2.2. Instrumentation

The scanning electron microscope Quanta 200 from FEI (Brno, Czech Republic) with an energy dispersive X-ray spectrometer EDAX, (Si(Li) detector, SUTW—Super Ultra Thin Window, resolution 135 eV for Mn  $K\alpha$ ) was used at low-vacuum. The automatic identification of GSR was performed with a Gunshot program (GSR-XT V3.1 for FEI). A 160× magnification and an accelerating voltage of 25 kV were employed. The entire area of each stub was analyzed. The agreement of the chemical composition of a particle (resulting from its X-ray spectrum) with the class assigned to it by the program was checked and corrected manually.

A DXR Raman Microscope from Thermo Scientific (Waltham, MA) controlled by the Thermo Scientific Omnic for dispersive Raman 8.1 software was employed. A laser of 532 nm with potency ranging from 1 to 10 mW and a confocal pinhole size of 50  $\mu$ m was used. The microscope objective was set to 50× magnification, and at least 10 spectra were acquired for each particle. Spectra were acquired with fluorescence correction.

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