## B158 Low-Cost Lanthanide-Organic Framework Markers for Gunshot Residue (GSR) Identification

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After attending this presentation, attendees will better understand the new types of low-cost markers for non-toxic ammunition using luminescent materials, which simplify the investigative routines but also allow the use of the characterization method already used for conventional munitions.

This presentation will impact the forensic science community by adding to research by providing the synthesis of a new type of luminescent markers for GSR based on the Metal-Organic Framework (MOF) [Zn(BDC)(H2O)2]n doped with the lanthanide ions terbium and europium, by a simple, fast, and reliable methodology with low-cost production.

GSRs are an important source of information in forensic analysis; however, with the advent of Non-Toxic Ammunition (NTA), also known as lead-free ammunition, the characterization of GSR became a very difficult task since GSR produced by NTA does not contain any characteristic elements (for example, Pb, Sb, and Ba) that allow unequivocal characterization. Thus, the standard methodology for GSR characterization adopted by the American Society for Testing and Materials (ASTM) International based on Scanning Electron Microscopy coupled to Energy Dispersive Spectroscopy (SEM/EDS) becomes inadequate. In this context, luminescent ammunition markers were developed. These markers allowed the visual identification of the Luminescent GSR (LGSR) on the shooters' hands, the firearm, and at a simulated crime scene using only an Ultraviolet (UV) lamp. It provides a simple, fast, and reliable methodology that improves the crime scene investigation.[1-3]

Among many materials tested as possible markers, the MOFs containing lanthanide ions were shown to have a large potential to be used as GSR markers due to their high luminescence and high chemical and thermal stability. Excellent results were obtained with lanthanide-based MOFs; however, in general lanthanide-based materials are relatively expensive.[2,3] On the other hand, the cost of the markers can be reduced by using d-metal-based MOFs doped with lanthanides. Thus, in this work, the coordination network [Zn(BDC)(H2O)2]n doped with different proportions (0.01% to 100%) of $Tb^{3+}$ or $Eu^{3+}$ evaluated as GSR luminescent markers. The materials were synthetized at room temperature by direct precipitation reaction and incorporated into the gunpowder of 9mm CleanRange® NTA cartridges in a ratio weight of 4%. Then, for each marker, three shots were performed using Glock® G17 pistols at the indoor shooting range in the ballistics service of the National Institute of Criminalistics of the Brazilian Federal Police (NIC/BFP). Next, LGSR particles were visualized on the firearm, the shooter's hands, and the target when MOFs containing more than 1% of lanthanide were used. The best results were obtained when 10% of $Tb^{3+}$ or $Eu^{3+}$ were incorporated into the MOF. Finally, the LGSR were collected with stubs covered with double-sided adhesive conductive carbon tape and analyzed by SEM/EDS and by video spectral comparator (where emission spectra were acquired).

The emission spectra of LGSR showed the characteristic transitions $^5D_4 \rightarrow {}^7F_J$ ($J$=3-6) of $Tb^{+3}$ and $^5D_0 \rightarrow {}^7F_J$ ($J$=0-4) of $Eu^{+3}$, with the most intense the transitions at 543nm and 614nm (responsible for the green and red emission colors of these markers, respectively). Additionally, the EDS spectra confirmed the concomitant presence of the zinc and Tb or Eu ions in the LGSR, showing that in addition to the optical signature, the markers confer a chemical signature to ammunition. $[Zn(BDC)(H_2O)_2]n$: Tb or Eu presents an interesting effective cost, being up to eight times less expensive than the fully lanthanide-based marker.





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**Reference(s):**

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**Luminescent Marker, Metal-Organic Framework (MOF), Gunshot Residue**