TITLE: Detecting gunshot residue from Sellier & Bellot Nontox heavy metal free primer by in-situ cathodoluminescence.

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ABSTRACT:

Inorganic gunshot residue (GSR), the residue from the discharge of ammunition primer, can give crucial information in reconstructing criminal cases. Traditional primers create GSR of heavy metals such as lead, barium and antimony. In forensic labs, automatic particle detection is performed by scanning electron microscopy (SEM), using the backscattered electron signal to search for bright heavy particles among the many darker particles of environmental origin. Some innovative mixtures, indicated as heavy metal free (HMF) primers, produce a residue of elements with atomic numbers below 21, urgently demanding new detecting solutions. In this research, inorganic residues from a HMF primer, Sellier & Bellot Nontox, are demonstrated to emit visible light under beam stimulation in a SEM. Cathodoluminescence emission can be used to both detect and characterize residues in forensic cases involving HMF primers, with minor changes to traditional analytical apparatus.

KEYWORDS: forensic science, gunshot residue, cathodoluminescence, heavy metal free primer, Nontox.

Since its introduction in forensic labs in the late seventies (1, 2), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) has been considered the best analytical approach to detection and analysis of inorganic gunshot residue particles (GSR). At that time, the majority of primer mixtures in western countries contained lead styphnate, barium nitrate

and antimony sulfide, creating inorganic particles essentially composed of heavy metals such as lead, barium and antimony (3). In a SEM, automatic particle detection is performed using the microscope backscattered electron (BSE) signal, searching for bright particles (i.e. heavier than a set threshold) against a dark background. Starting from the eighties (4), new primer formulations appeared on the market, developed to avoid harmful exposure to lead, especially for indoor range use (5). Lead styphnate was removed from primer mixtures, usually in favour of organic explosives such as diazodinitrophenol and tetrazene (4, 6). Without lead, although still containing other heavy elements as titanium, zinc (7) or strontium (8), those mixtures are termed lead-free/non-toxic primers (9). GSR from these kind of lead-free primers are still detected by SEM-EDS, eventually with a slight increase in sensitivity threshold. In more recent years, the on-going research for pollution reduction has lead to what is considered, from a forensic perspective, to be a second generation (10, 11) of non-toxic primers. The innovative solution is the wide use of organic compounds such as specific-sized nitrocellulose (12) or nitroesters and nitramines (13), avoiding the need for heavy elements in primer mixtures. Such formulations should correctly be termed heavy metal free (HMF) primers (14) because their gunshot residues contain only lighter elements, with atomic numbers below 21, such as boron, sodium, aluminium, silicon, potassium and calcium (10, 15, 16).

In forensic cases involving HMF primers, new analytical solutions are required for GSR analysis, because SEM-EDS systems cannot automatically detect the resulting inorganic residues among the many particles of environmental origin with a corresponding average atomic number. Kmjek and Fojtasek (10) reported that the Sellier & Bellot Nontox primer is to be considered a "*nightmare of all GSR experts*", as its GSR is "*one of the worst residues for analysis*" by SEM-EDS. Likewise, Martiny et al. (11) studied another HMF primer, CBC/Magtech CleanRange, and concluded that "*identification of GSR derived from CBC second generation lead-free ammunition on suspects' hands may be impossible without the addition of a distinct metallic taggant in the primer*".

Moreover, extensive characterization of GSR from HMF primers, beyond mere morphology description and elemental composition analysis (15, 16), is required. A deeper knowledge could help in identifying if there exists some characteristic physical property potentially useful to distinguish HMF-GSR, whose thermodynamics of formation are expected to be a very specific one (17, 18, 19), from environmental particles of similar composition.

In the past, some analytical approaches to the problem, such as Particle Induced X-ray Emission (PIXE), Rutherford Backscattering Spectrometry (RBS) and Particle Induced Gamma Ray Emission (PIGE), have been suggested (20). Unfortunately, this suite of new techniques requires a proton beam of a few MeV that cannot be incorporated into a common SEM. Other authors (21) proposed the introduction, in HMF-GSR analysis, of a high sensitivity technique known as Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Raman micro-spectroscopy could be coupled to ICP-MS to analyze, beyond inorganic particles, organic gunshot residues (22) also.

But the ideal solution would be an in-situ analysis, integrated into the SEM-EDS system, which would allow automatic analysis of GSR particles from both traditional and HMF primers, without removing the stubs from the microscope chamber.

Cathodoluminescence (CL) analysis is a technique specifically developed for electron microscopes, usually coupled to SE/BSE imaging and to EDS analysis for deeper sample characterization. Light emission is due to the relaxing of excited modes in optically active centres under electron beam stimulation, in the region of the electromagnetic spectrum between near infrared and near ultra-violet (23). CL emission could be used for particle imaging, detecting all frequencies of the light signal in panchromatic mode. Moreover, adding a dispersive device along the optical path to the detector, it is possible to collect the frequency spectrum of the polychromatic CL signal, useful for characterizing the emitting centres.

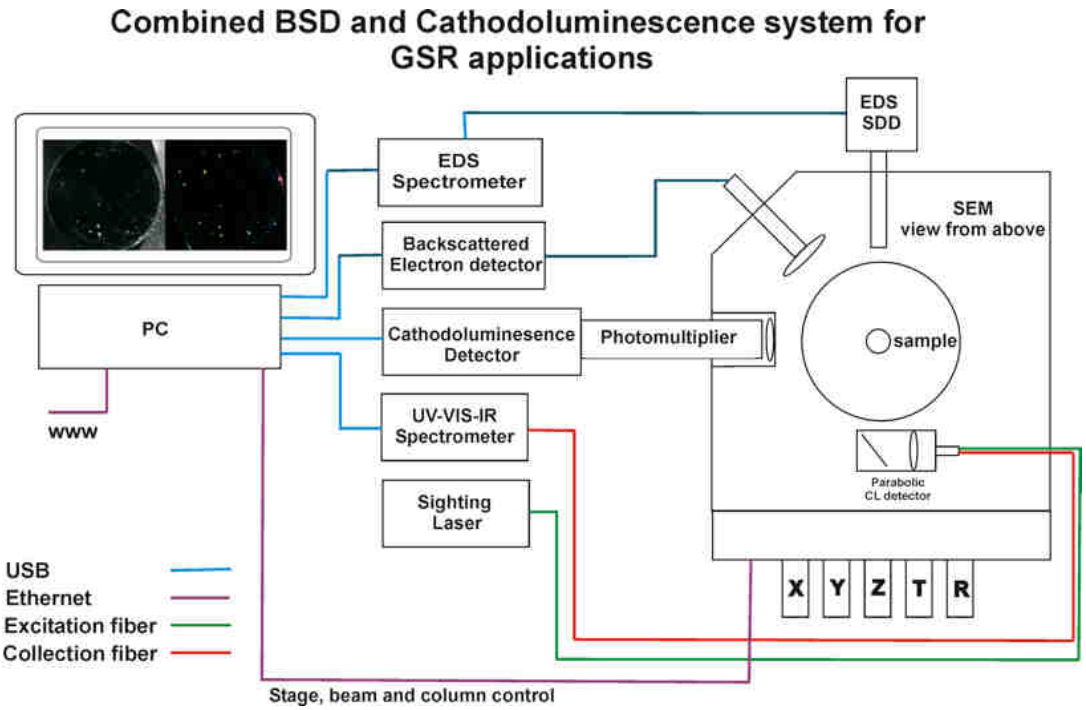
As far as we know, CL has never been previously tested to search and analyze GSR particles. Aim of the present research was to experimentally test and document CL capabilities to detect and characterize residues from Sellier & Bellot Nontox primed cartridges.

Materials and Methods

Shooting tests

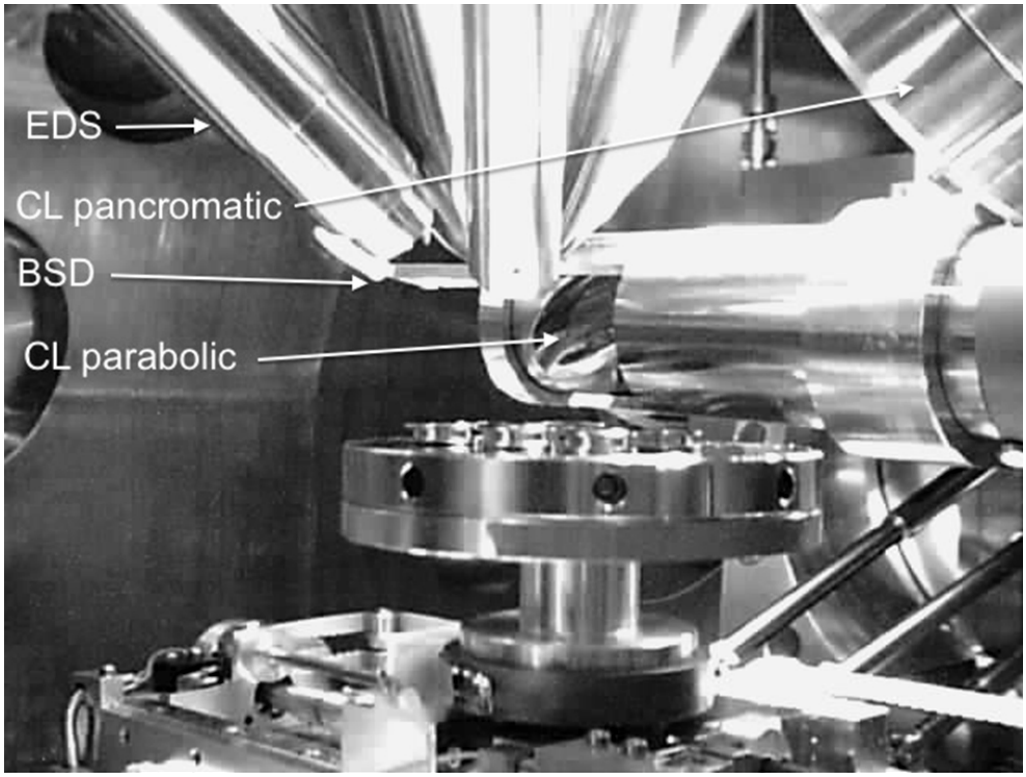
Shooting test were performed at the indoor shooting range Privatir Sarl in Le Mont-sur-Lausanne, Switzerland, using a Glock model 19 (Glock Ges.m.b.H., Deutsch Wagram - Austria) 9mm Luger semi-auto pistol. Shooters thoroughly washed their hands before handling the pistol. In the shooting tests, two 9 mm Luger Nontox-primed rounds (Sellier & Bellot, Vlasim – Czech Republic) were discharged. Gunshot residues were collected both from the cartridge cases and from the shooters' hands immediately after shooting. GSR particles from the two spent cartridge case were collected using a single cotton swab type 5100/SG/CS (Nuova Aptaca, Canelli – Italy). Cotton swab was soaked in ethanol before collection, to limit cotton fibre release when touching, for GSR transfer, an adhesive carbon disc type C249/N (TAAB Laboratories Equipment Ltd, Aldermaston – UK) positioned on top of a half inch aluminium stub. Two stubs of the same type, indicated as *Shooter 1* and *Shooter 2*, were also used for direct collection of GSR from both shooters' hands.

A Quanta 600 SEM (FEI Europe B.V., Eindhoven – Netherlands), fitted with a XFlash 30 mm^2 silicon drift detector (Bruker, Billerica – MA, USA), was the basis of the analytical platform. The SEM was equipped with GSR Magnum software (Eastern Analytical, Stavelot Belgium) for automatic detection and classification of GSR particles.



[FIG.1 – Scheme of the SEM and the detectors used]

An especially designed CL detector was fitted to the column, in the place where the secondary electron detector was previously located by the SEM producer. The CL detector was made using a 29 mm diameter 9924QB blue-sensitive photomultiplier tube (ET Enterprises Ltd., Uxbridge – UK) feeding into a transimpedance amplifier (ET Enterprises Ltd., Uxbridge – UK) and then into the SEM video input. The CL detector was placed as close as possible to the sample so as to achieve optimum sensitivity to CL emission. A parabolic mirror/collimator device was placed over one side of the sample area to enable measurement of the wavelengths of the CL emissions using a fibre coupled thermoelectrically cooled CCD spectrometer model QE-Pro (Ocean Optics Inc., Dunedin – FL, USA). With this system we were able to detect panchromatic CL and BSE signals, X-ray emission and CL spectroscopy signals simultaneously.



[FIG.2 – Inner view of the SEM chamber with indications of the detectors]

In addition, the GSR program for automatic detection and measurement of traditional GSR was modified to allow CL to be the primary detection mechanism as will as BSE. As usual, the sample was scanned with the electron beam and, where bright CL-emitting particles was found, the beam was placed on them and X-ray analysis performed.

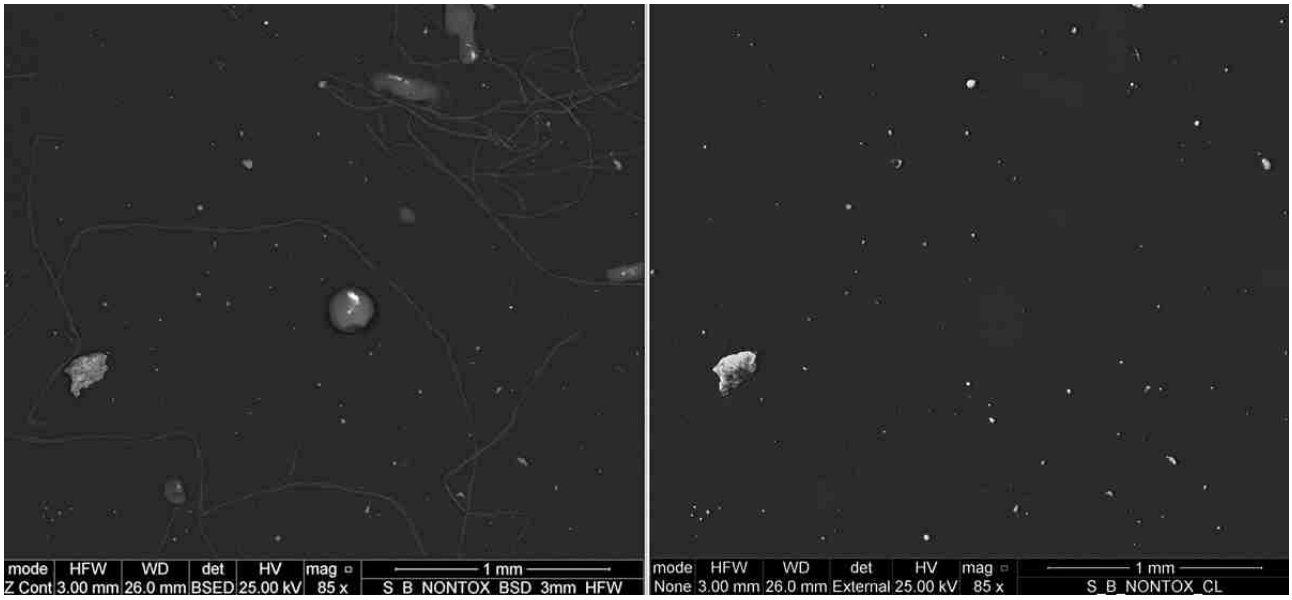
Experimental conditions were the following: beam voltage 25 kV, beam current 0.6 nA, working distance 25 mm, 10 mm^2 solid-state backscattered detector (BSD), both high vacuum (HV) mode and low vacuum (LV) mode with chamber pressure of 11 Pa (0.08 torr). Stubs were analyzed without any further carbon coating deposition.

Results

Sellier & Bellot NONTOX spent cartridge cases

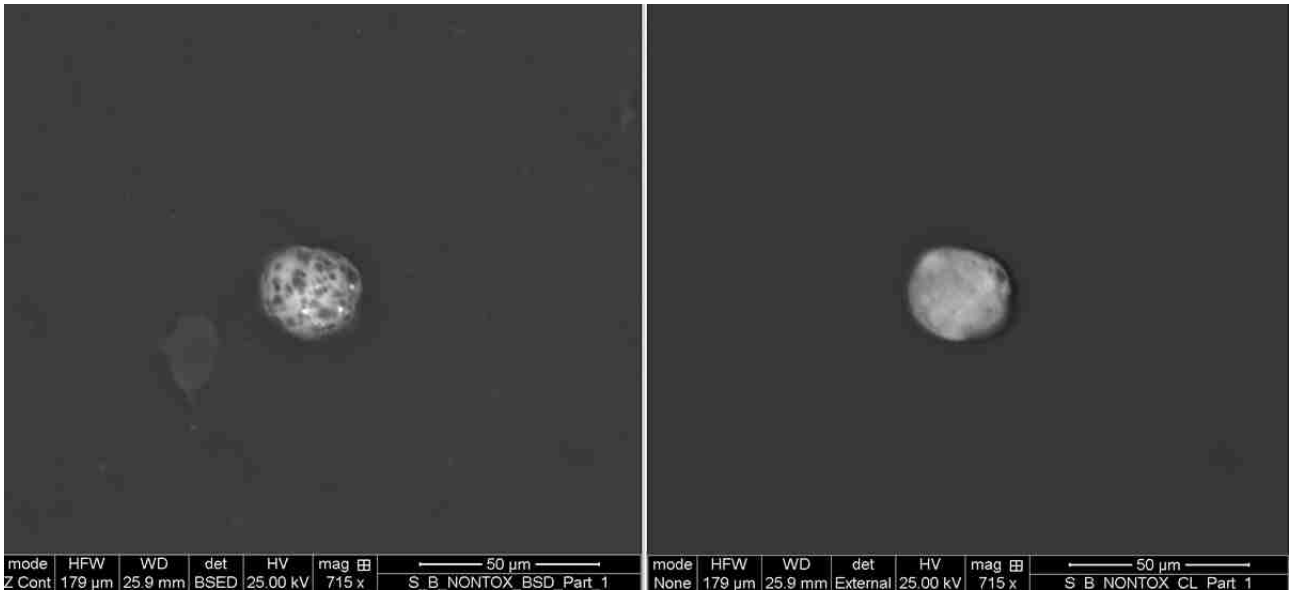
The stub where residues from Sellier & Bellot Nontox spent cartridge cases were transferred was firstly manually observed using both the backscattered electron signal and the panchromatic CL signal.

In the panchromatic CL image, with a scan field size of 3 mm HFW (corresponding to a field digital matrix of 4096x3536 pixels), many bright features were revealed (see FIG.3), mostly corresponding to those visible with a lower contrast in the BSE image,).



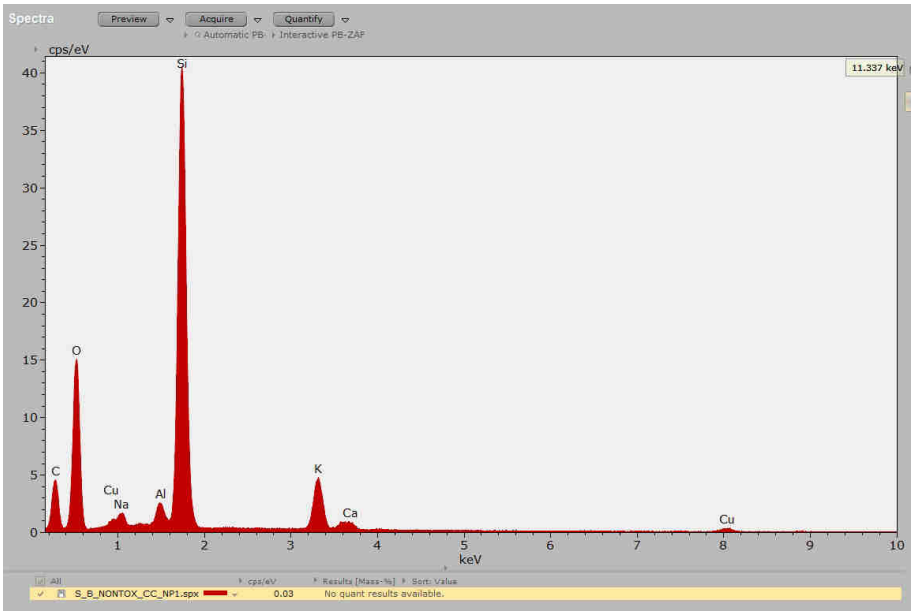
[FIG.3 – Sellier & Bellot Nontox cartridge case sample. Images of a 3 mm field: BSE (on the left) and panchromatic CL signal (on the right)]

In panchromatic CL images, light emitting particles appear as bright spots on a darker background: panchromatic CL signal could then be used by ordinary GSR automatic detection routines to seek for HMF GSR particle candidates, the same way BSE signal is commonly used to detect GSR residues from lead-based primers. An automatic scan of a 10 mm^2 area of the same stub was then performed, without any prior pre-defined chemical classes, with the following parameters: pixel dimension 0.5 µm, dwell time 16 µs, lower gray level threshold 70 in a range 0-255. More than 400 particles were detected by their CL panchromatic video signal. Most candidates were spheroids in the size range from 10 µm to 30 µm. Few larger aggregates (100+ µm) were found also. The BSE and panchromatic CL images from a typical light emitting particle (named *Particle 1*) is shown in FIG.4.



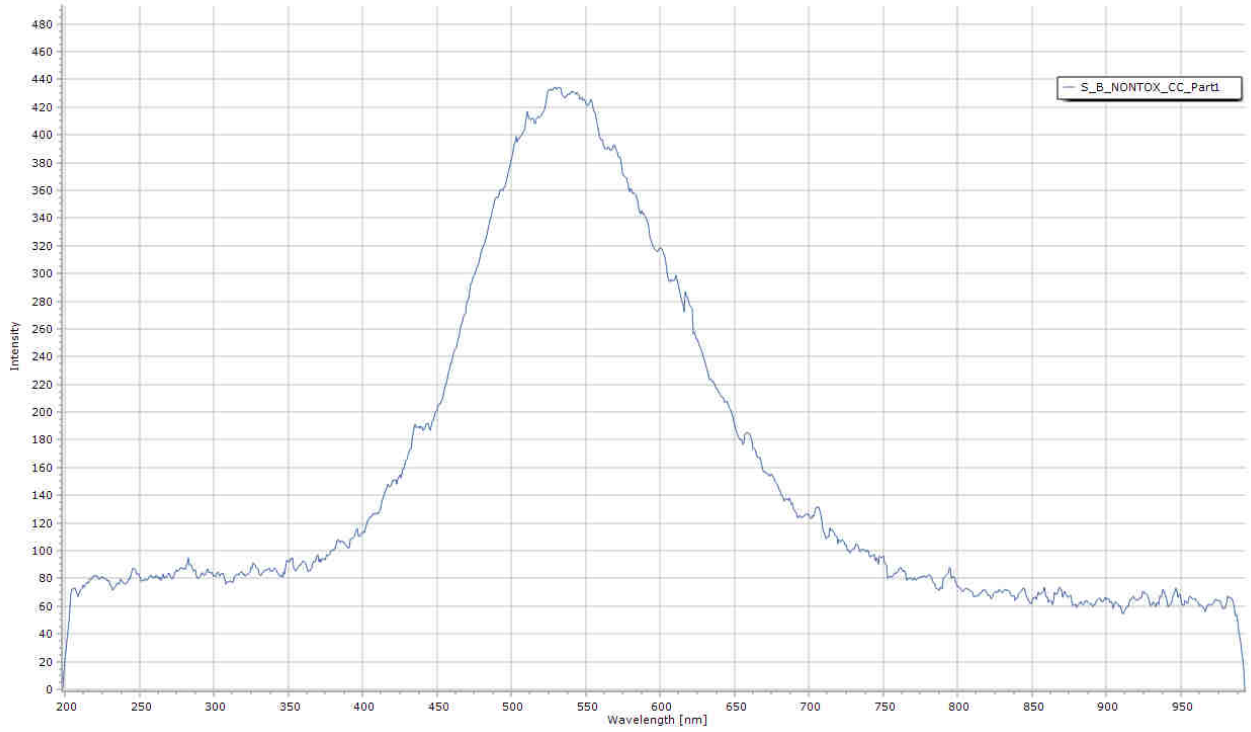
[FIG.4 – Sellier & Bellot Nontox cartridge case sample. Images of a 20 µm light emitting particle, named *Particle 1*: BSE (on the left) and panchromatic CL signal (on the right)]

Light emitting particles were found to be contain O, Si, K, Al and Na - the composition expected for residues from Sellier & Bellot Nontox primer [10, 16, 20] - always with high levels of Si and low levels of K and Al. In addition to these elements Cu, often found as metallic droplets at GSR particles surfaces, and low levels of Ca and S, were also present in some residues. The EDX spectrum from *Particle 1*, a typical light emitting particle, is shown in FIG.5.



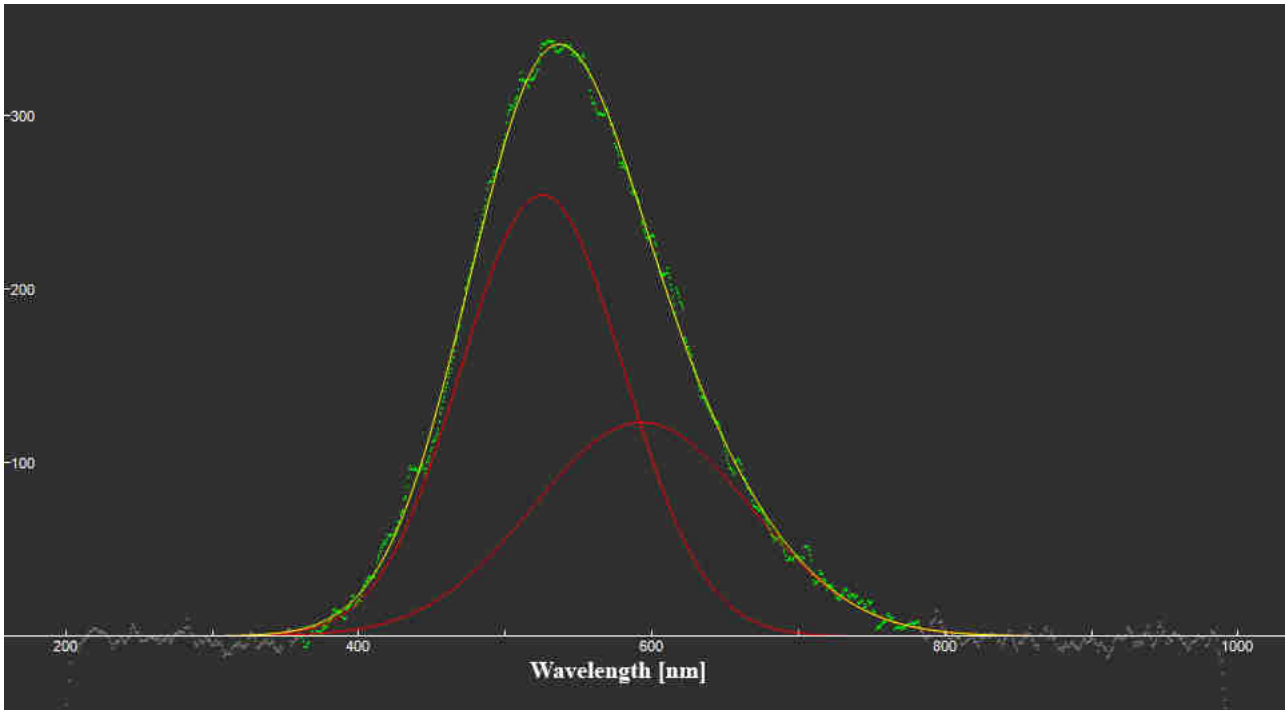
[FIG.5 – EDX spectrum of *Particle 1*, an OSiKAlNa residue from S&B Nontox cartridge case]

Residues containing O, Si, K, Al and Na typically show a CL spectrum with a large wide peak centred at around 535 nm. The CL spectrum, collected from *Particle 1* using the parabolic mirror and the thermoelectrically cooled CCD spectrometer, is reported in FIG.6.



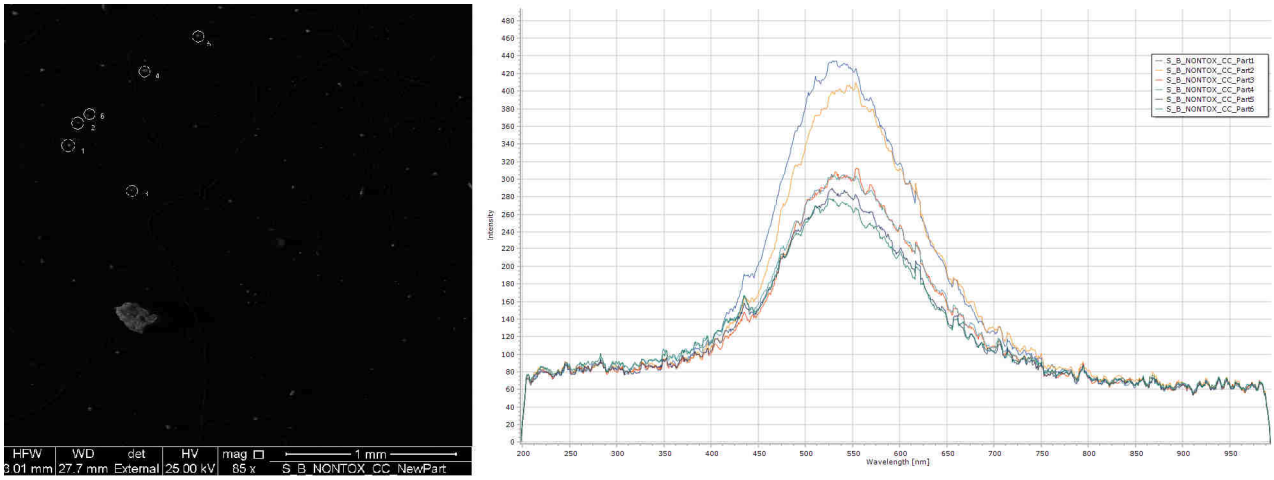
[FIG.6 – CL spectrum of *Particle 1*, a GSR residue from a S&B Nontox cartridge case]

Data deconvolution using Gaussian functions (see FIG.7) shows contributions of two main peaks: a first one centred at 531 nm (Height = 326; FWHM = 139) and a second one centred at 628 nm (Height = 71; FWHM = 133).



[FIG.7 – Deconvolution, using Gaussian functions, of the CL spectrum of *Particle 1*, a GSR residue from a S&B Nontox cartridge case]

Six different glowing residues from the same stub showed CL spectra having similar shapes (see FIG.8).

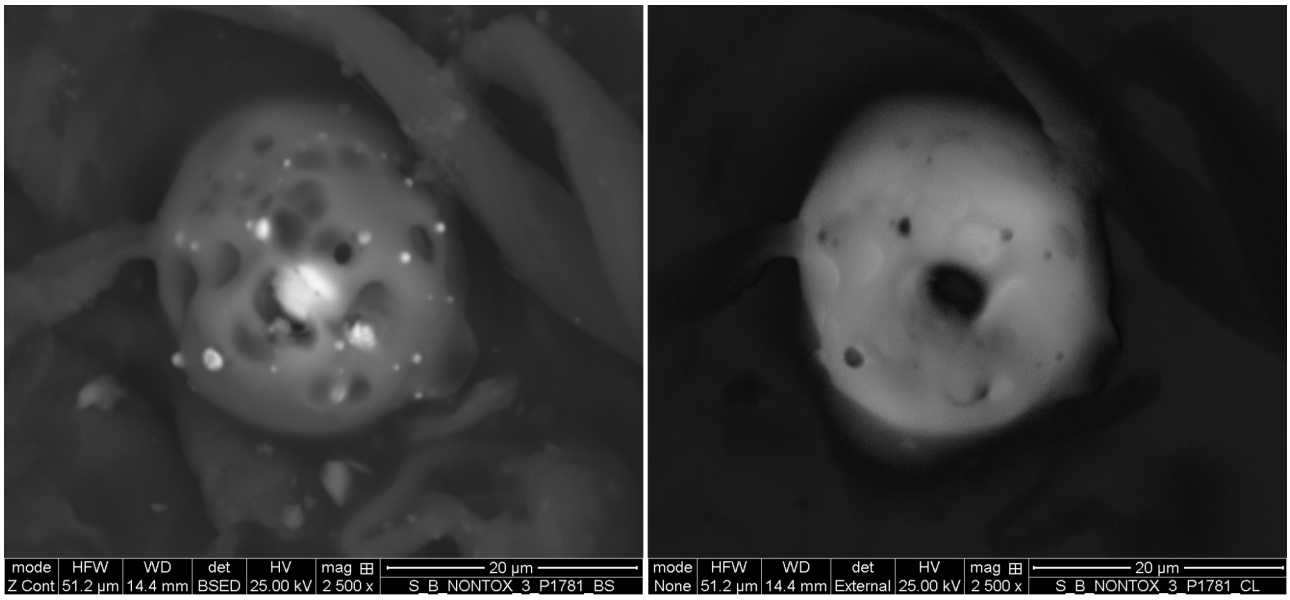


[FIG.8 – Relative positions on the stub and CL spectra of six different OSiKAlNa GSR residues from a S&B Nontox cartridge case]

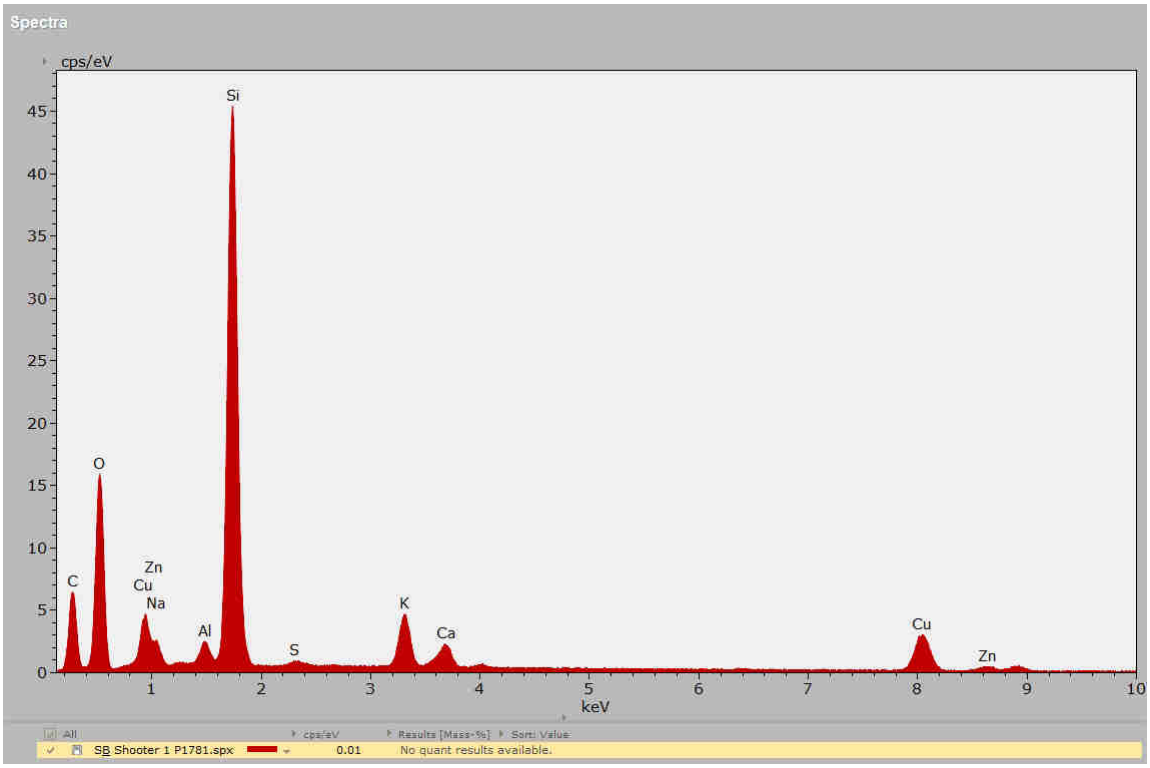
Sellier & Bellot NONTOX shooters

The number of S&B Nontox GSR particles on stubs taken from S&B Nontox shooters was expected to be low [16 - Importante da controllare]. For this reason stubs taken from the two S&B Nontox

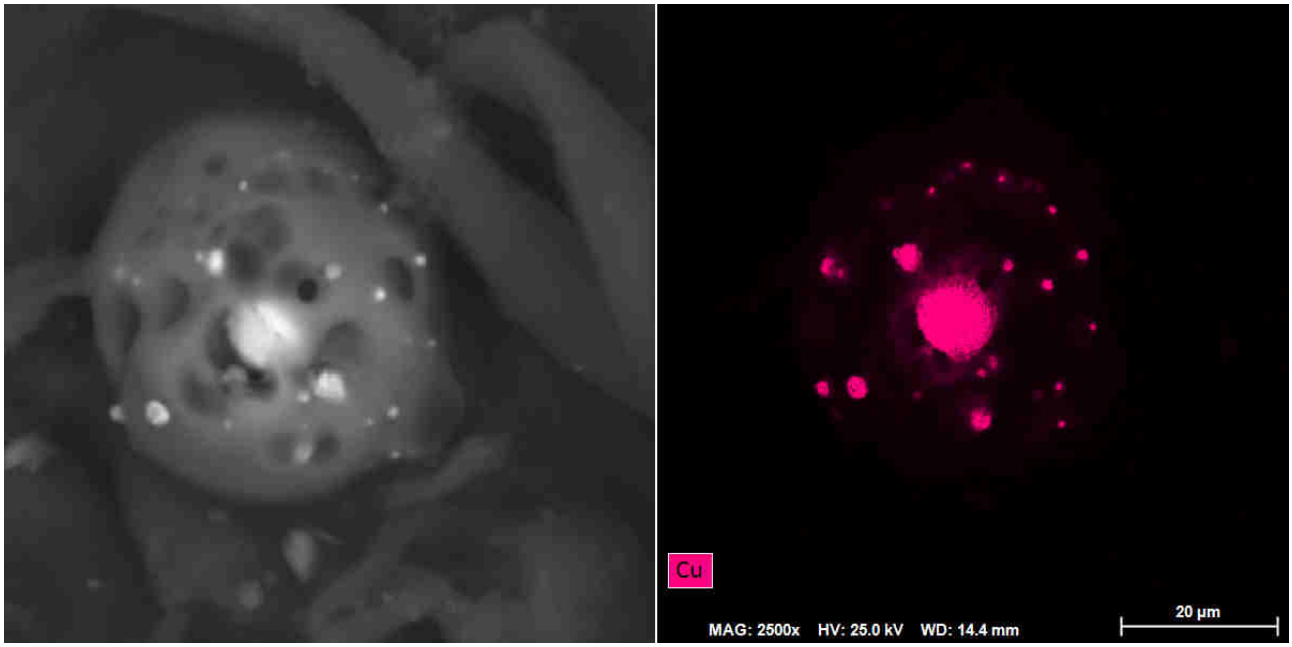
shooters were manually analysed, seeking for OSiKAlNa (eventually OCuSiKAlNa) candidates with characteristic morphology. In this context, as previously verified with residues collected directly from S&B Nontox spent cartridge cases, a sponge-like appearance with copper spots at surface is considered highly indicative of S&B Nontox residues for residues bigger than 10 µm. By manual research, a limited number (units) of GSR residues were found on each stub. All of them were CL-active particles, emitting visible light.



[FIG.9 – Sellier & Bellot Nontox *Shooter 1* stub. Images of a 20 µm light emitting particle, named *Particle 1781*: BSE (on the left) and panchromatic CL signal (on the right)]

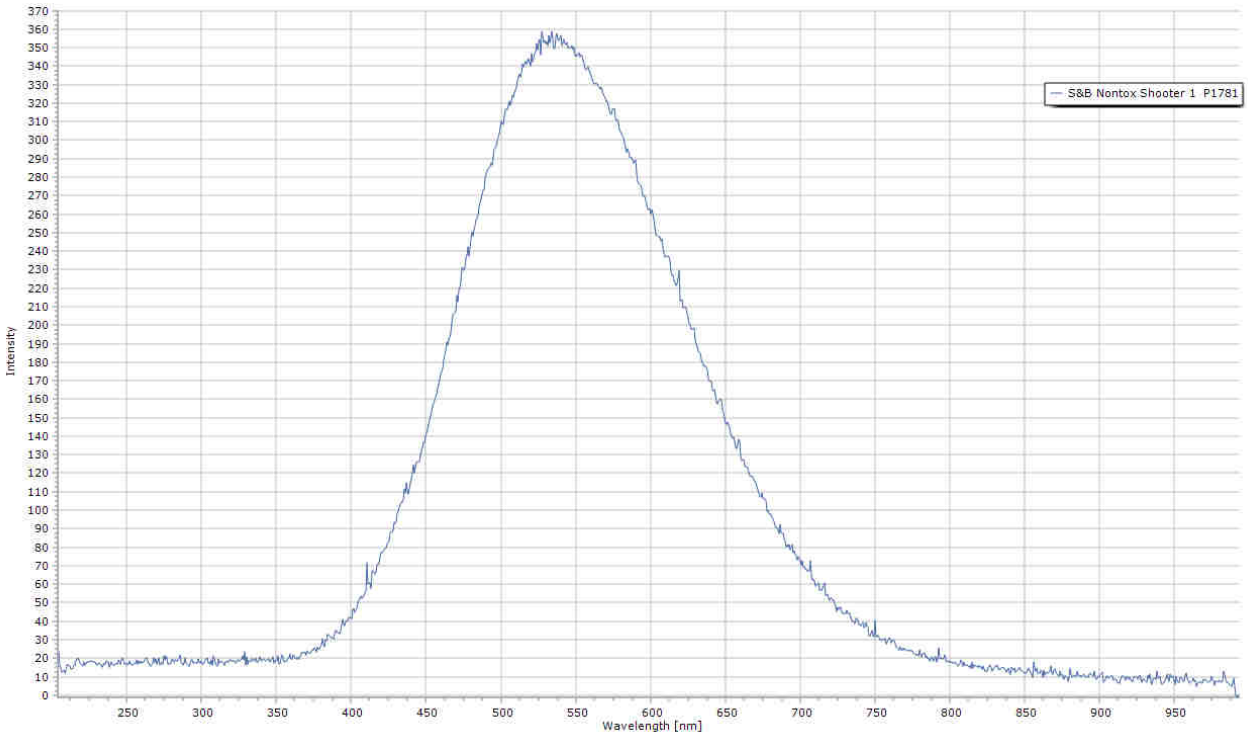


[FIG.10 – EDX spectrum of *Particle 1781*, a residue from S&B Nontox *Shooter 1* stub]



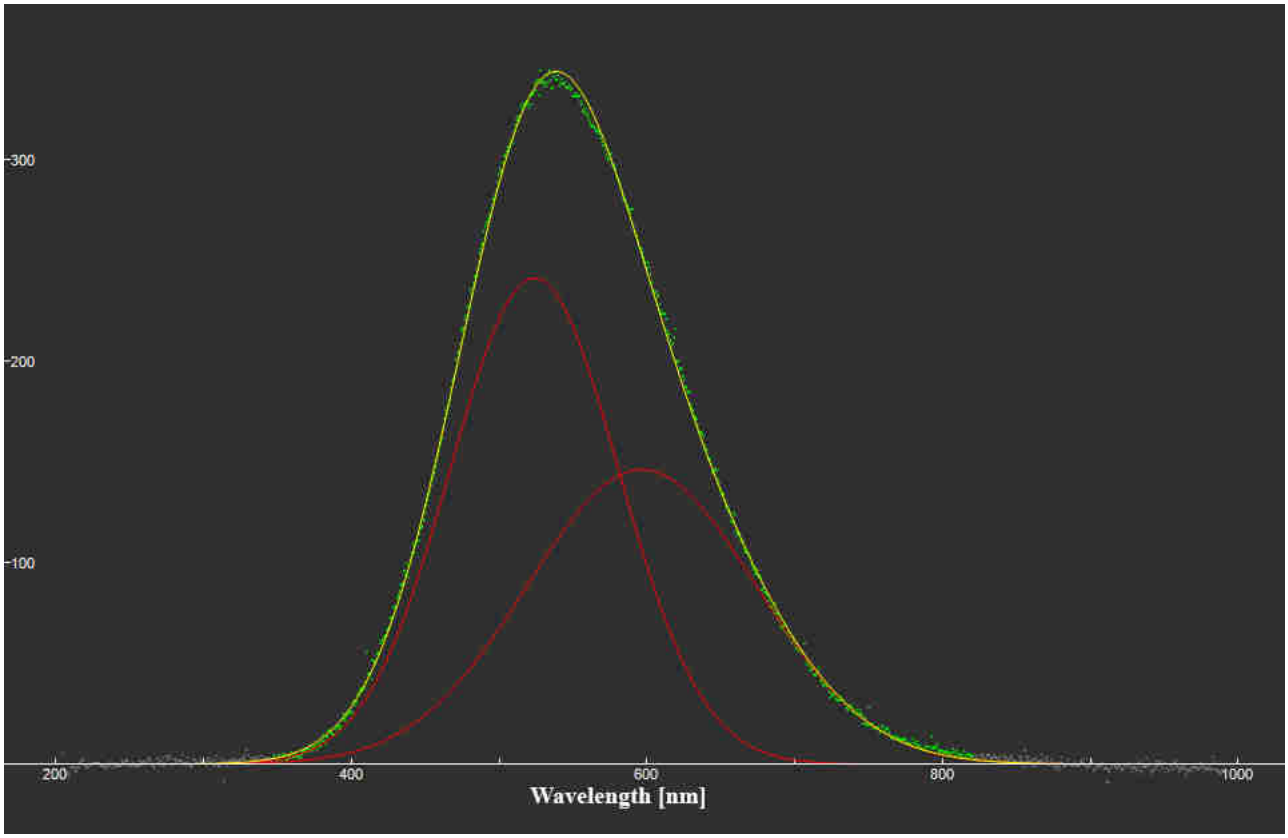
[FIG.11 – EDX copper map of *Particle 1781*, a residue from S&B Nontox *Shooter 1* stub]

GSR candidates typically show a CL spectrum with a large wide peak centred at around 535 nm. The CL spectrum, collected from *Particle 1781* using the parabolic mirror and the thermoelectrically cooled CCD spectrometer, is reported in FIG.12.



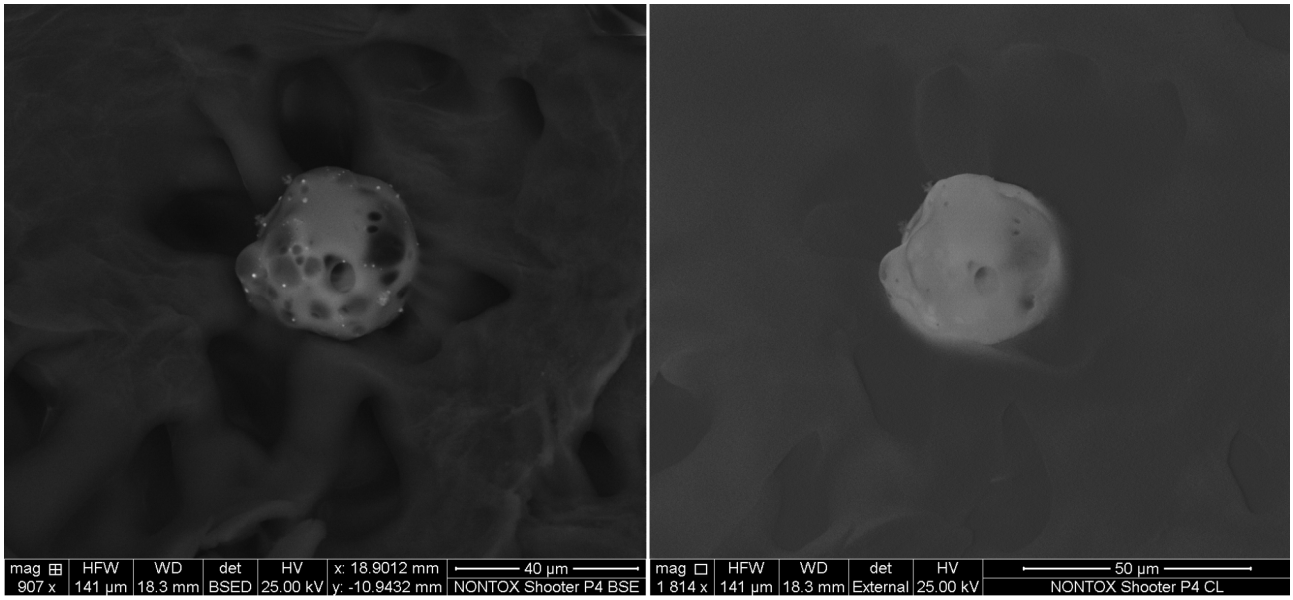
[FIG.12 – CL spectrum of *Particle 1781*, a GSR residue from a S&B Nontox *Shooter 1* stub]

Data deconvolution using Gaussian functions (see FIG.13) shows contributions of two main peaks: a first one centred at 524 nm (Height = 241; FWHM = 134) and a second one centred at 596 nm (Height = 146; FWHM = 182).

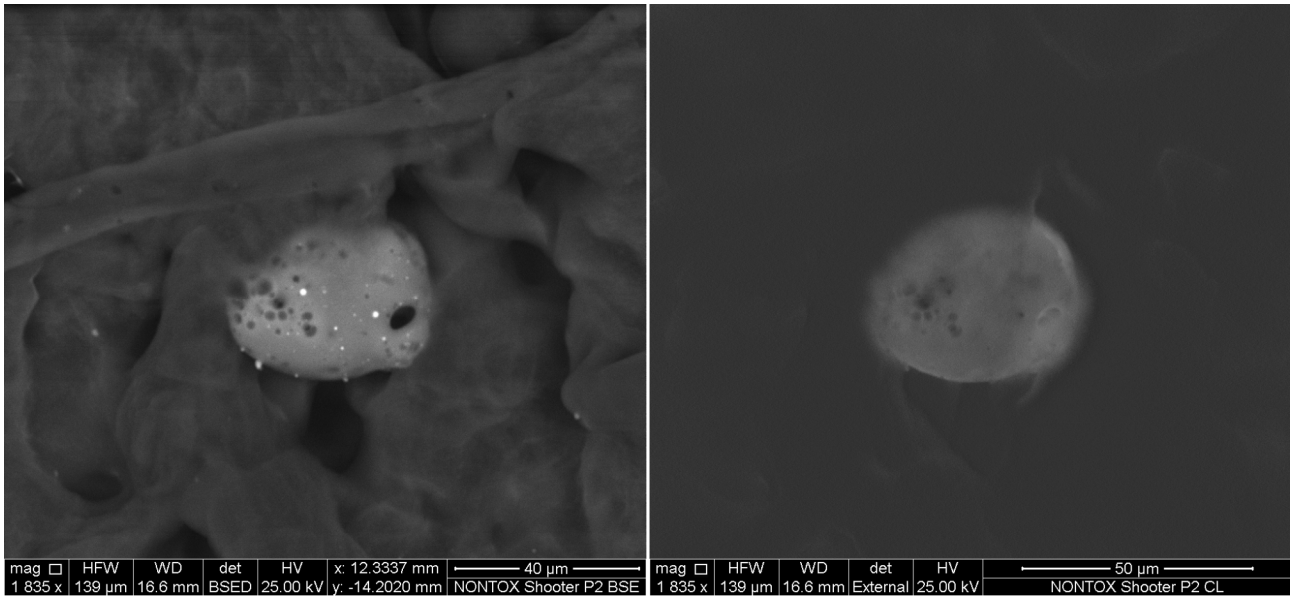


[FIG.13 – Deconvolution, using Gaussian functions, of the CL spectrum of *Particle 1781*, a GSR residue from a S&B Nontox *Shooter 1* stub]

Other examples of CL-active GSR particles, found on the S&B Nontox *Shooter 2* stub, are reported in the following figures.



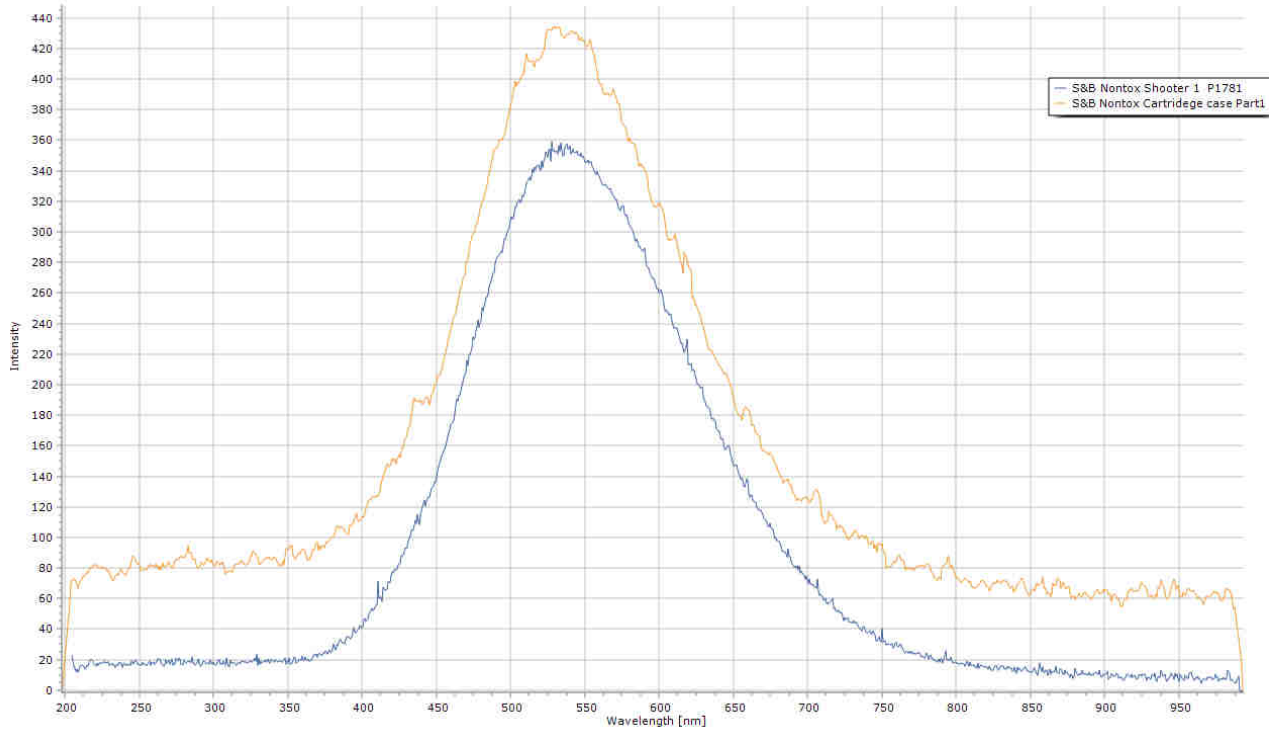
[FIG.14 – Sellier & Bellot Nontox *Shooter 2* stub. Images of a 40 µm light emitting particle, named *Particle 4*: BSE (on the left) and panchromatic CL signal (on the right)]



[FIG.15 – Sellier & Bellot Nontox *Shooter 2* stub. Images of a 50 µm light emitting particle, named *Particle 2*: BSE (on the left) and panchromatic CL signal (on the right)]

Discussion

For the first time, GSR residues from Sellier & Bellot Nontox primer mixture were demonstrated to be CL-active under electron beam stimulation. The panchromatic CL signal could then be used to seek for GSR candidates by both manual research and automatic detection routines. Particles having chemical composition and morphology matching those expected for Sellier & Bellot Nontox GSR particles were found to emit light over a broad range of the visible region of the electromagnetic spectrum. The shape of the CL emission in the visible range has been found to be similar between residues taken from the spent cartridge cases and collected on shooters' hands, as reported in FIG.16, suggesting the possibility to use the CL spectrum as a new characteristic useful to describe Sellier & Bellot Nontox GSR particles.



[FIG.16 – CL spectra of *Particle 1*, a GSR residue from a S&B Nontox cartridge case, and of *Particle 1781*, a GSR residue from a S&B Nontox *Shooter 1* stub]

Conlusions

In forensic cases involving Sellier & Bellot Nontox or similar HMF primers, GSR automatic detection routines based on BSE signal cannot automatically detect the resulting inorganic residues among the many particles of environmental origin having a corresponding average atomic number. New analytical solutions are required for HMF GSR analysis. In-situ CL analysis has been shown to be useful in both HMF residue detection and description. It is possible to scan samples with ordinary GSR program using CL as the primary detection mechanism as well as the BSE signal. However the CL signal is relatively weak compared with the BSE one so a longer pixel dwell time, and eventually a smaller area, is suggested to be used. However, one interesting point is that it is in principle possible, with minor software modifications, to combine both these mechanisms of detection into a single application. The CL detection needs further optimization in order for it to

compete alone with the BSE detection method. In future, CL properties of different HMF primer mixture residues are to be investigated also.

References

1. Andrasko J, Maehly AC. Detection of gunshot residue on hands by scanning electron microscopy. J Forensic Sci 1977 Apr;22(2):279–87.

2. Wolten GM, Nesbitt RS, Calloway AR, Loper GL, Jones PF. Particle analysis for the detection of gunshot residue. I. Scanning electron microscopy energy dispersive X-ray characterization of hand deposits from firing. J Forensic Sci 1979Apr;24(2):409–22.

3. Dalby O, Butler D, Birkett JW. Analysis of gunshot residue and associated materials - a review. J Forensic Sci 2010 Jul;55(4):924-943.

4. Hagel R, Redecker K, inventors. Dynamit Nobel Aktiengesellschaft, assignee. Primer charges free of Lead and Barium. US patent 4,581,082. 1986 Apr 2.

5. Crouch KG, Peng T, Murdock DJ. Ventilation control of lead in indoor firing ranges: inlet configuration and booth and fluctuating flow contributions. Am Ind Hyg Assoc J 1991;52(2):81-91.

6. Mei GC, Pickett JW, inventors. Olin Corporation, assignee. Nontoxic priming mix. US Patent 5,167,736. 1992 Dec 1.

7. Gunaratnam L, Himberg K. The identification of gunshot residue particles from lead-free Sintox ammunition. J Forensic Sci 1994 Mar;39(2):532–6.

8. Harris A. Analysis of primer residue from CCL Blazer® lead-free ammunition by scanning electron-microscopy energy dispersive X-ray. J Forensic Sci 1995 Jan;40(1):27–30.

9. American Society for Testing and Materials, E1588–16a, Standard guide for gunshot residue analysis by scanning electron microscopy/energy dispersive X-ray spectroscopy. Annual Book of ASTM Standards. Vol. 14.02. West Conshohocken, PA: American Society for Testing and Materials, 2016.

10. Kmjek T, Fojtasek L. NONTOX® - call appeal for GSR analysis. doi:10.13140/2.1.1420.5762. https://www.researchgate.net/publication/270804790_NONTOX_R_-call_appeal_for_GSR_analysis

11. Martiny A, Campos APC, Sader MS, Pinto MAL. SEM/EDS analysis and characterization of gunshot residues from Brazilian lead-free ammunition. Forensic Sci Int 2008;177(1):e9–e17.

12. Filho LM, inventor. Companhia Brasileira de Cartuchos, assignee. Non-toxic composition for priming mixture for small caliber arms ammunition. US patent 6,786,986 B2. 2004 Sep 7.

13. Nesveda J, Brandejs S, Jirasek K, inventors. Sellier & Bellot A.S., assignee. Non-Toxic and non-corrosive ignition mixture. US patent 6,964,287 B1. 2005 Nov 15.

14. Erickson JA, Melberg JM, Sandstrom JL, inventors. Federal Cartridge Company, assignee. Lead-free, heavy metal-free rim-fire primer composition dedicated for Ralph B. Lynn. US patent 5,993,577. 1999 Nov 30.

15. Oommen Z, Pierce SM. Lead-free primer residues: a qualitative characterization of Winchester Winclean™, Remington/UMC Leadless™, Federal Ballisticlean™, and Speer Lawman Cleanfire™ handgun ammunition. J Forensic Sci 2006 May;51(3):1–11.

16. Hogg SR, Hunter BC, Smith RW. Elemental characterization and discrimination of nontoxic ammunition using scanning electron microscopy with energy dispersive X-Ray analysis and principal components analysis. J Forensic Sci 2016 Jan;61(1):35-42.

17. Basu S. Formation of gunshot residues. J Forensic Sci 1982 Jan;27(1):72–91.

18. Nuziata F, Morin M. On the Formation and On the Surface of Inorganic Lead, Barium and Antimony Based Gunshot Residues: A Thermodynamic Approach. J Forensic Sci Criminol 2017;5(3):303-324

19. Bauer F, Hiscock M, Lang C. Advances in the Analysis of Gunshot Residue and Other Trace Evidence using EDS and EBSD in the SEM. Microsc. Microanal. 2016;22(3 Suppl):2046-7.

20. Romolo FS, Christopher ME, Donghi M, Ripani L, Jeynes C, Webb RP, Ward NI, Kirkby KJ, Bailey MJ. Integrated ion beam analysis (IBA) in gunshot residue (GSR) characterisation. Forensic Sci Int 2013 May;231(1-3):219-28.

21. Costa RA, Motta LC, Destefani CA, Rodrigues RRT, do Espírito Santo KS, Aquije GMFV, Boldrini R, Athayde GPB, Carneiro MTWD, Romão W. Gunshot residues (GSR) analysis of clean range ammunition using SEM/EDX, colorimetric test and ICP-MS: a comparative approach between the analytical techniques.Microchem J 2016 Nov;129:339-47.

22. Abrego Z, Grijalba N, Unceta N, Maguregui M, Sanchez A, Fernández-Isla A, Aranzazu Goicolea M, Barrio RJ. A novel method for the identification of inorganic and organic gunshot residue particles of lead-free ammunitions from the hands of shooters using scanning laser ablation-ICPMS and Raman micro-spectroscopy. Analyst 2014;139:6232-41.

23. Garcia de Abajo FJ. Optical excitations in electron microscopy. Rev Mod Phys 2010 Jan-Mar;82:209-75.

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