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Nano characterization of gunshot residues from Brazilian ammunition

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ABSTRACT

Gunshot residues (GSR) from a total of nine different caliber ammunitions produced in Brazil were analyzed and characterized by transmission (TEM) and scanning electron microscopy (SEM). GSR particles are composed of spherical particles of several micrometers of diameter containing distinct amounts of lead, barium and antimony, along with other organic and inorganic elements arising from the primer, gunpowder, the gun and the bullet itself. This study was carried out to obtain additional information on the properties of GSR nanoparticles originated from different types of regular ammunition produced in Brazil by CBC. Besides the SEM, we have used a TEM, exploring its high magnification capability and ability to explore internal structure and chemical composition of submicron particles. We observed that CBC ammunition generated smaller particles than usually reported for other ammunitions and that the three component particles are not a majority. TEM analysis revealed that GSR are partially composed of sub-micron particles as well. The electron diffraction pattern from these particles confirmed them to be mainly composed of lead oxides crystalline nanoparticles that may be agglomerated into larger particles. Energy dispersive X-ray spectroscopy revealed that most of them were composed of two elements, especially PbSb. Ba was not a common element found in the nanoparticles.

1. Introduction

Gunshot residues (GSR) from traditional ammunition are mostly composed of heavy metals as well as trace elements from the cartridge casing, bullet jacket, bullet core and gun barrel. It can also consist of organic elements from the propellant (smokeless gunpowder) such as nitrates and stabilizers usually detected by colorimetric and chromatographic methods. These particles are deposited on the hands, clothing, surrounding areas and objects as well as on other people in the immediate vicinity of the shooter. GSR originates from the rapid condensation of elements from the primer mixture vaporized during firearm discharge, sometimes called pGSR. Consequently, common metallic elements used nowadays for GSR detection are lead, barium and antimony originated from the primer mixture [1–3]. Different ammunition producers may use primers that generate residues comprised of distinct metallic elements. Metallic elements may also be partially or completely absent such as in environmental or heavy metal free ammunition [4,5]. The classical morphology of GSR particles is spheroidal with diameters ranging from .5 to 10.0 μm. This morphology is described as arising from the rapid cooling occurring after the extreme high temperature and pressure conditions from the discharge [6,7]. Some evidence has shown that primer particles are formed even before the ignition of the propellant [7]. Wolten and Nesbitt [6] suggested that pGSR contain oxides, sulfides and oxysalts, since it cannot be expected that compounds from the primer mixture would be reduced to metallic elements during primer ignition. Morphology can be altered by impact, especially particles coming from the muzzle, depending on the conditions of the shooting (e.g. short distances from the target). However, these particles are described as being mostly formed by lead from the bullet and not from the primer. Either way, the formation of GSR particles described elsewhere [6,7] was considered consistent with an amorphous structure based on the external morphology.

Attempts at fully characterizing GSR date back to the 1970s [3,8–11]. The use of scanning electron microscope (SEM) coupled with energy dispersive X-ray spectrometer (EDX) is indeed the

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most valuable method for the identification of GSR due to the possibility of simultaneously combining morphology and chemical information of individual particles and not only the composition of bulk samples. However, this spectroscopic method yields no information about the bonding environment of the elements, preventing the determination of phases and compounds present.

Despite all the information available, only a few comprehensive successful attempts to identify the compounds present in GSR have been reported. Wolten et al. [3] and Wolten and Nesbitt [6] reported the presence of metallic lead, lead sulfide, lead oxysulfate, barium *m*-antimonate and antimony oxide by employing diffraction techniques. Tassa et al. [12] analyzed different ammunition types by powder X-ray diffraction as compared with SEM–EDX and found different compounds such as metallic lead sulfide, lead oxide, metallic antimony, depending on the ammunition type. Raman spectroscopy has also been used to make this characterization [13] and Raman Microscopy may lead to a powerful combination of capabilities particularly if phases are previously identified and uniquely attributed to GSR residues.

Transmission electron microscope (TEM) is not a standard forensic technique, mostly because of its complexity and of the need for sample preparation. However, it may be a powerful tool for further investigation on trace evidence [14] such as GSR [15], especially the submicron particles which are considered to be more persistent in the environment [16]. It is also possible to explore the structure of matter with respect to its crystallinity and elemental composition, which may allow for phase identification. Also, electron diffraction poses some benefits over X-ray diffraction, especially when studying sub-micron crystals ($<.1\ \mu m$). Electron diffraction patterns can be directly observed on the viewing screen of the electron microscope, what makes crystal orientation easy while simultaneously observing changes of the diffraction pattern. Diffraction patterns can be obtained from individual small crystals selected with an aperture (selected area electron diffraction or SAED) or with convergent beam for nanometric crystals. Yang et al. [15] and Hill [16] studied the GSR by TEM in regard to its size and morphology but electron diffraction was not conducted in either study.

The current study was undertaken to obtain information on the properties of GSR nanoparticles originated from different types of regular ammunition produced in Brazil by Companhia Brasileira de Cartuchos (CBC), in regard to composition, phases, size and crystallinity. It is not our goal to propose TEM as a substitute or complementary technique for SEM–EDX, but to characterize the elemental composition, morphology and diffraction pattern of nanometric residues to gain a better understanding of both the structure and the formation process of GSR.

2. Materials and methods

2.1. Firearms and ammunition

The present study employed ammunition produced by Companhia Brasileira de Cartuchos (CBC, sold in the United States and in European countries by its counterpart Magtech Inc.). The calibers and ammunition types used were as follows: .32 S&WL lead round nose, 7.65 × 51 mm full metal jacket boat tail, .38 SPL lead round nose and hollow point, .380 AUTO + P full metal jacket hollow point, .40 S&W full metal jacket hollow point, .45 M4 full metal jack, 5.56 × 45 mm boat tail and 12 ga High Impact. All firearms employed in this study were produced in Brazil and are property of the Bahia State Crime Laboratory (Salvador, BA, Brazil): Imbel 7.62 M964 FAL, Imbel 5.56 MD97, Taurus .40 PT940 semi-automatic, Taurus .45 ACP PT145, Taurus PT380, Taurus .38 SPL M82, Rossi .32 and caliber 12 Rossi shotgun.

2.2. GSR collection

All samples were collected in a Bahia State Police open firing range in good weather conditions. All firearms were carefully cleaned with petroleum spirits before the firing rounds. Two rounds were fired for each caliber. For the TEM analysis, particles from the plume were collected placing the 400 mesh holey carbon copper grids (EMS, Hartsfield, PA) at approximately 20 cm facing the cylinder gap or ejection port and just below the muzzle opening, employing a high precision non-magnetic stainless steel reverse action (self-closing) tweezer (Ted Pella Inc., Redding, CA). The grids were left in place during the first round and then moved to a region near the muzzle opening until approximately 1 min after second firing was made. They were then stored in grid boxes under desiccation conditions until analysis. Samples for SEM analysis were collected as described elsewhere using Spectro grade conductive carbon adhesive tape (Ted Pella Inc., Redding, CA) in 12.7 mm standard aluminum pin stubs mounted on single Storages Tubes. Spectro grade tape was chosen because it has only minor impurities of Al and Si which is important since CBC primer mixture has aluminum powder in its formulation. Stubs were placed as described above for grid collection.

2.3. SEM analysis

Samples were analyzed as described elsewhere [17,18] in a FEI Quanta 450 FEG ESEM equipped with an EDAX probe with a working distance of 10 mm and accelerating voltage of 25 keV. Automated search was conducted employing the GSR Magnum software v. 6.0. Brightness threshold for GSR was set using a XCS-7 standard containing Ge, Nb, Au, C and Si and a 200 μm Cu aperture grid (Ted Pella Inc.; Redding, CA) for the backscattered electron (BSE) detector (BSD) response curve calibration. Image magnification was calibrated as described in ISO 16700 [19]. Each stub was entirely scanned yielding 5000 to 25,000 particles per sample, depending on the ammunition type.

2.4. TEM analysis

Samples were analyzed under a JEOL 2100F TEM, equipped with a Noran Voyager EDX detector with an accelerating voltage of 200 kV. Diffraction patterns, conventional and dark field images were obtained with a 11 MPixel Orius SC1000B CCD camera. Images were analyzed using the software Digital Micrograph™ (Gatan, Inc.). DiffTools package was used to analyze the diffraction patterns [20]. Results were interpreted using the JCPDS–ICDD database of powder diffraction patterns, which includes *d*-spacings and relative intensities of observable diffraction peaks [21].

In all samples, several particles were analyzed throughout the grid. Usually, grids were examined in low magnification mode for GSR particles. The nanoparticles were usually found in the vicinity of micrometric ones which are too thick to be observed at the TEM. EDX spectra and mappings were collected with a low time constant for increased energy resolution.

3. Results and discussion

3.1. SEM analysis

The results from regular SEM/EDX automated search (Table 1) yielded the expected spherical morphologies and compositions for GSR. All samples analyzed presented characteristic PbBaSb particles. However, some of the ammunition analyzed presented a very low population of these three-element particles. For example, in CBC 12 ga 3T ammunition less than five in a population of thousands were found. Therefore, it should not be uncommon to