A174 Transmission Electron Microscopy Characterization of Gunshot Residues From Brazilian Ammunition

Lis G.A. Melo, MS, Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud 150, Urca, Rio de Janeiro 22290-180, BRAZIL; André L. Pinto, PhD, Centro Brasileiro de Pesquisas, Físicas/CBPF, Rua Dr. Xavier Sigaud 150, Urca, Rio de Janeiro 22290-180, BRAZIL; and Andrea Martiny, PhD, Nat Inst Metrology, Quality & Technology, AvNossa Senhora das Graças 50 Bldg 27, Xerem, Duque de Caxias, Rio de Janeiro 25250-020, BRAZIL*

After attending this presentation, attendees will gain a better understanding of both the structure and the formation process of Gunshot Residue (GSR) and also be provided with new perspectives for GSR analysis.

This presentation will impact the forensic community by questioning previous knowledge about GSR and discussing some of the implications of the new findings.

GSR originates from the rapid condensation of elements from the primer mixture vaporized during firearm discharge, and are usually described as spheroidal with diameters ranging from 0.5 to 10.0µm. Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-Ray Spectrometry (EDS) has been recognized as the most useful method for its identification. Transmission Electron Microscope (TEM) is not a usual forensic tool because it requires sample preparation and interpretation is not straightforward. Nevertheless, it combines high magnification capability and the ability to explore the internal structure together with the chemical composition, a combination which is essential for nanometric analysis. The goal was to analyze GSR from different types and calibers of ammunition produced in Brazil and sold worldwide employing TEM to characterize elemental composition and morphology of nanometric residues. Characteristic GSR, combining spherical morphology and three-component content, were found in all nine samples analyzed by SEM but only in two when analyzed by TEM. By SEM, characteristic and consistent particles were found to be in average ≥4µm. TEM showed particles much smaller, approximately 100 to 200nm, probably due to the collection technique and the fact that larger particles may be lost from the grids by gravity. A typical characteristic GSR nanoparticle observed by TEM is spherical and heterogeneous in contrast. The nanoparticles appear to be composed of even smaller agglomerates. There is an accepted notion that these particles are amorphous. Results show that this reasoning is due to a limitation of SEM's resolution. Selected Area (Electron) Diffraction (SAED) pattern shows that GSR are essentially crystalline, opposed to the ASTM E-1588 standard description. The presence of diffuse rings was seen in almost all particles observed, indicating that crystalline nanoparticles are present in most GSR. Although only slightly apparent in conventional TEM images, the presence of smaller nanoparticles agglomerates forming larger GSR is clearly visible in Dark Field (DF) images. Employing High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF STEM) mode, characteristic three-element GSR composed of 5-10nm nanoparticles was observed and also seen in the DF image taken from diffraction spots. Inconsistent particles composed of PbSb, the DF image from a diffraction spot with interplanar distance of 0.29nm showed that they are also composed of agglomerates sized approximately 2-10nm. This characteristic was observed in nearly all particles observed regardless of the ammunition caliber used, suggesting that this may comprise a specificity derived from the formation process of GSR. Most GSR automatic search systems are limited by the minimum particle size of 0.5-0.7µm detected. The results show that particles of 100-200nm are present in a concentration equivalent to microscopic GSR, and are essentially agglomerates of much smaller nanoparticles of approximately 2-10nm. The interplanar distances in the Diffraction Patterns (DP) taken from several particles in all samples were calculated. Some of the values found were a good match to phases that could form the GSR, considering that the reflections with the highest intensities were found in the DPs of the GSRs. The phases considered were lead oxides, lead and antimony oxides, barium oxides, metallic lead, and metallic antimony. The results demonstrate that there is a large population of GSR nanoparticles overlooked. These nanoparticles are prone to stay airborne and can have the potential to coalescence in larger particles and contaminate the scene and non-related bystanders. Most of the crime labs filter the <1µm particles in order to avoid airborne contamination and also to reduce errors due to the resolution limitations of the SEM. Nevertheless, these nanoparticles, mostly composed of Pb, may also constitute another problem unrelated to forensic investigation. The threshold limit value of exposure for lead in a workplace is 50mg/m^3. The method for collecting particles consists of a 220nm passing filter. Although TEM analysis is much more complex than SEM, it could also be used as a tool to investigate evidence collected from gun-related suspects and crime scenes as it can provide unique information from different ammunition.

This research was supported by FINEP grant # 1539/10 and CNPq/Prometro grant# 563093/2010-

 ** Presenting Author*

2.

TEM, Gunshot Residue, Nanoparticle

 ** Presenting Author*