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Characterization of Brazilian ammunitions and their respective gunshot residues with ion beam techniques

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ABSTRACT

In this work we explore the potentialities of analytical techniques based on swift ion beams for the analysis of ammunitions and the respective gunshot residues (GSR). To that end, PIXE (Particle-Induced X-ray Emission), RBS (Rutherford Backscattering Spectrometry) and micro-PIXE were employed in order to provide elemental characterization of three different ammunitions, namely CHOG, EXPO +P+ and Clean Range (CR). Pristine cartridges were taken apart for the characterization of bullets, cases, primer and propellant. Subsequently, shooting sessions were carried out and relatively large GSRs (of the order of 50–150 μm across) ejected in the forward direction were collected and analyzed. The PIXE experiments were carried out employing 2.0 MeV protons with a beam spot size of 1 mm^2. For the micro-PIXE experiments, the samples were irradiated with 2.2 MeV proton beams of 2×2 μm^2. Finally, 1.2 MeV alpha particles were used for the RBS experiments. Quantitative analyzes were obtained for all constituents of the cartridges. The results show that elements like Pb, Ba and Sb are present in the primer of CHOG and EXPO +P + ammunitions. Traces of Ba and Pb were found in the CR primers as well, while Sb is absent from these primers. The morphology of the GSRs reveals a spherical-like shape for GSRs from EXPO +P+ and Clean Range ammunitions. On the other hand, particles with an uneven shape were detected for the CHOG ammunition.

1. Introduction

According to a compilation carried out by the Brazilian government, Brazil ranks 11th among 90 countries concerning deaths caused by firearms with 21.9 deaths per hundred thousand people during 2012 [1]. This fact places firearms as the main weapon used by criminals in order to perpetrate their crimes. In this context, all data regarding firearms and ammunition becomes a valuable tool for forensic scientists to elucidate crimes.

Once a firearm is discharged, particles known as gunshot residues (GSR) are formed during the burnout process that is triggered by the primer during its compression caused by the firearm's hammer. GSRs are scattered around the firearm and eventually are deposited in objects, clothes and exposed body parts of the shooter and the victim. Despite such particles may vary in size and shape, GSRs of the order of a few micrometers across with a spherical shape are the most common ones and are usually used by forensic scientists during the analysis of material collected in connection with any event involving a firearm. Such particles are characterized by the presence of Pb, Sb and Ba [2] which are commonly found in the primer in the form of barium nitrate, antimony sulphide and lead styphnate [3].

Several techniques have been used for the element characterization of residues stemming from the discharge of a firearm [4]. Among them, Neutron Activation Analysis (NAA) was considered as an innovative analytical technique in early seventies by the law community [5] and it is used until today in forensic analysis [6] due to its high sensitivity and its non-destructive feature. Other high sensitivity techniques like those based on the principles of the Inductively Coupled Plasma (ICP) are frequently employed in forensic analysis as well [7,8]. However, ICP-based techniques require the destruction of the samples under analysis, which limits their use in court laws.

The analysis of GSRs gained a new impetus when scanning electron microscopes coupled with energy dispersive spectrometers (SEM-EDS) came to the attention of forensic scientists [9]. The SEM-EDS technique employs electrons of the order of 10–20 keV in order to induce the production of characteristic X-rays in the

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target atoms. The X-rays produced in the sample are usually energy-analyzed by silicon-based detectors [10,11]. Nowadays, SEM-EDS systems constitute one of the most important tool for the analysis of GSRs [4,12] due to its cost-effective relation.

Another category of analytical techniques makes use of energetic ions for the analysis of a wide variety of materials. In particular, the Particle-Induced X-ray Emission (PIXE) technique [13] is based on the excitation of the target atoms by MeV protons. This technique began to be explored as a potential technique for use in forensic sciences long ago [14,15]. However, the use of broad beam to analyze GSR proved to be a drawback when compared to SEM results.

The advent of the scanning microprobe capability delivering ion beams in the range of micrometer scale together with better X-ray spectrometers brought new impetus to ion-based techniques applied to forensic sciences. In this case, micro-PIXE shares the basic principles with the SEM-EDS technique. However, important differences emerge due to the nature of the charged particle employed by these techniques. Table 1 summarizes such differences for 15 keV electrons (typical for SEM-EDS applications) and 2 MeV protons (typical for PIXE and micro-PIXE applications) interacting with Al, Ti and Ge. Concerning the K shell ionization cross sections, the results differ less than one order of magnitude considering protons and electrons. Indeed, 2 MeV protons [16] are more efficient than 15 keV electrons [17] for Al only. Electrons have better yields for heavier elements like Ti and Ge. The range of 15 keV electrons [18] and 2 MeV protons [19] in these materials show that electrons probe essentially the surface while protons are suitable for bulk analysis. The most striking difference between protons and electrons is the differential cross section for bremsstrahlung evaluated for 5 keV photons [20]. The bremsstrahlung yield generated by electrons is several orders of magnitude higher than that generated by protons. Indeed, the bremsstrahlung yield is proportional to the square of the particle acceleration. Since the Coulomb force acting on both electrons and protons is the same, the ratio between the bremsstrahlung yields for protons and electrons is about 3×10^{-7}, in close agreement with the results shown in Table 1. Although techniques like SEM-EDS and micro-PIXE can be used as complementary techniques [21], the results shown in Table 1 suggest that protons have better sensitivity for bulk analysis than electrons. As a matter of fact, not only PIXE but other ion-based techniques have already been used in the analysis of GSR [2,12,22].

The aim of the present work is to employ ion-based techniques like PIXE, micro-PIXE and Rutherford Backscattering Spectrometry (RBS) in order to characterize the elemental composition of three Brazilian ammunitions and their respective GSR's of relatively large size (between 50 μm and 150 μm across). This work is a follow-up of some results already published on this subject [23].

2. Experimental procedure

Three different ammunitions manufactured by CBC (*Companhia Brasileira de Cartuchos*) were chosen for the present study: i) lead rounded nose (CHOG); ii) hollow point (EXPO +P+); and iii) and lead-free Clean Range (CR). For each type of ammunition, 30 cartridges were carefully taken apart for the analysis of the primer, bullet, propellant, jacket and case.

Pieces of the bullet, jacket and case were cut and shaped with a flat surface for analysis. The propellant was homogenized with a mortar and pestle and pressed into pellets of 1 cm diameter and about 3 mm thick. For the analysis of the primer, two different protocols were devised. For the first one (referred to as primer-capsule), its capsule was cut open to allow the proton beam through. For the second one (referred to as primer-pellet), two samples of primers were obtained by scratching several primer capsules. The material was then pressed into pellets of 1 cm diameter and about 300 μm thick.

For the PIXE experiments, the targets were placed in the target holder inside the reaction chamber. During the experiments, the pressure inside the chamber was kept at about 10^{-5} mbar. The targets were positioned in the proton beam through an electric-mechanical system assisted with a webcam installed inside the chamber. The targets were irradiated with 2.0 MeV proton delivered by a 3 MV Tandetron accelerator from High Voltage Engineering Europa. The beam spot size was about 1 mm^2 for the analysis of the primer-capsule, jacket and bullet, while 2 mm^2 beam spot sizes were used for the analysis of the case, propellant and primer-pellet.

Relatively small currents were employed during PIXE experiments. The reason for that is twofold: i) keep the system dead time at reasonable levels; ii) avoid ignition of the primers during the experiments. Typical currents and irradiation times were 0.3 nA and 200 s respectively for all targets but the propellant. For the latter one, currents of 3 nA and irradiation times of 400 s were employed in the experiments. Finally, the X-rays induced by the proton beam in the targets were detected by a Si(Li) detector placed at 135° with respect to the beam direction. The energy resolution of the detector is about 150 eV at 5.9 keV.

RBS experiments were intended to be carried out for the analysis of primers and propellants. However, the relative high currents (of the order of tens of nA) required by this technique proved to be inadequate for the analysis of primers. Therefore, RBS experiments were carried out for the analysis of the propellants only. To that end, 1.2 MeV He^+ particles were directed to the RBS chamber kept a pressure of 10^{-5} mbar. Typical currents and irradiation times were 20 nA and 30 min respectively. Two surface barrier detectors

Table 2
Major elements present in the propellants of the CHOG, EXPO +P+ and CR ammunitions. The atomic concentrations were obtained from the fitting of the RBS spectra using the SIMNRA software [25].

Propellant	Atomic Concentration		
	C	N	O
CHOG	70%	16%	13%
EXPO +P+	69%	10%	20%
CR	78%	11%	10%

Table 1
K-shell ionization cross sections (σ_{ION} in barns) [16,17], range (in micrometers) [18,19] and differential cross sections for bremsstrahlung ($d\sigma_B/dE_R$ in barns per keV) [20] evaluated for 15 keV electrons and 2 MeV protons. The range of electrons in matter shown in the table represents the Continuous Slowing Down Approximation (CSDA) value and therefore must be considered as an upper limit for the range in these elements [18]. The cross sections for bremsstrahlung radiation were evaluated at E_R = 5 keV.

Element	15 keV Electrons			2 MeV Protons		
	σ_{ION} (b)	Range (μm)	$d\sigma_B/dE_R$ (b/keV)	σ_{ION}(b)	Range (μm)	$d\sigma_B/dE_R$ (b/keV)
Al	9818	2.6	3.6	27851	42	1.2×10^{-5}
Ti	1355	1.8	10.3	945	30	3.5×10^{-5}
Ge	144	1.8	21.8	41	32	7.5×10^{-5}

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