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Identification of Gunshot Residues by Using a High Resolution Inductively Coupled Plasma Mass Spectrometry Technique

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ABSTRACT

During the last years, it has being observed a continuous increase of crimes involving the use of fire arms. After gunshot, a portion of solid waste remains in the shooter's hand and the target. These residues, known as gunshot residues-GSR, are formed by the detonation of the primer and deflagration of the propellant, the addition of metal casings and projectiles are characterized by the simultaneous presence of barium, lead and antimony. Its precise identification is an important evidence in investigations within the field of forensic science. Several methodologies have been used to identify GSR. In this paper it will be discussed the use of a high resolution inductively coupled plasma mass spectrometry technique (HR-ICPMS) for this purpose. GSRs, from pistols and round barrel revolvers, were collected in the hands of shooters and from different fabrics (simulating real targets). A chemical fingerprint was established allowing identifying the type of the used firearm.

1. INTRODUCTION

The identification of particles derived from waste by shooting firearms (gunshot residue - GSR) is an important tool in investigations within the field of forensic science.

Deaths from firearms represent the majority of homicides in the brazilian population[1]. In 2006 the city of Rio de Janeiro, achieved the first place, with 2,235 deaths. Second, São Paulo, with 2,151 and third, Recife 1,198. Concerning the total deaths by firearms, homicide account for most: 92.5%, suicides account for 3.1% of the deaths and accidents account for 1.1%. In 3.3% of cases, the intention of the death is unknown. Between 1979 and 2003[2], over 550 000 people died in Brazil victims of some kind of shooting a firearm at an increasing pace and constant over time. In these 24 years, victims of firearms increased by 461.8%, while the country's population grew only 51.8%. The growth was fueled by the murders with firearms, which recorded a growth of 542.7% in that period. Suicides with firearms rose 75% and deaths from accidental shootings fell 16.1%. Since 2003 there was a decrease in the number of deaths by firearms as a result of the policy of disarmament.

In 2010 18.755 weapons were seized in São Paulo and only in the first quarter, 4,590 weapons[3]. On average 900weapons/month are sent for examination at the Institute of Criminology of São Paulo, 65% gun, 30% semi-automatic pistols and 15% of other models.

The control of firearms is the major concern for public safety and industries, it is necessary the use of comprehensive and efficient methods to identify suspects in crimes involving firearms, associating the gun used with the shooter. In these cases it is very important to relate the instrument (weapon) to the shooter (suspect) and the victim (target). Based on this assumption, we have sought to relate analytical methods suspect (shooter) and instrument (weapon) to the victim (target) at the crime scene more efficiently, thinking that this relation is essential in the solution, keeping in mind that it can determine the freedom of an innocent or criminals[4].

After firing a firearm, a portion of solid waste remains in the shooter's hand and in the target. These residues, known as gunshot residues, are formed by the detonation of the fuze and deflagration of the propellant, the addition of metal casings and projectiles and are characterized by the simultaneous presence of barium, lead and antimony[5]. Its precise identification is an important evidence in investigations within the field of forensic science. Several methodologies have been used to identify GSR.

Spectrometry with inductively coupled plasma source (ICP)[6] has become an important methodology for rapid analysis, and simultaneous multi-element, with a series of attributes, such as low detection limits, wide range of reading, effect of relatively small arrays, high precision and application for analysis of gases, liquids or solids. Since the ICP can efficiently generate charged ions of chemical species present in the sample, then becomes an ion source is ideal for use in conjunction with mass spectrometers. The combination of an ICP with a mass spectrometer is known for ICP-MS.

The High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS)[6] has been used as a powerful analytical technique for the detection of a wide range of elements in concentration levels ranging from high levels to trace and ultra-trace (0.1 to 0.01 parts per billion). Despite of its high sensitivity, is recognized for its ability multi-elemental and

isotopic measurements by isotope dilution analysis for samples that require high precision and accuracy.

In this paper it will be discussed the use of a (HR-ICPMS) for identification of gunshot residues from pistols and round barrel revolvers, the shooters hands and from different textiles (simulating real targets). A chemical fingerprint was established allowing identifying the type of the used firearm.

2. MATERIALS AND METHODS

A sequence of test shots was undertaken at the Ballistics Laboratory of São Paulo Criminalities Institute (I.C.-SP). The shot tests were executed with Taurus 0.38 caliber revolver, supplied with 0.38 SPL LRN, and Taurus pistols 0.40, supplied with S&W full metal jacket cartridges ammunition, and 9mm caliber pistols, supplied with Luger FMJ Round Nose ammunition. All the ammunitions used in this experiment were produced by the Companhia Brasileira de Cartuchos (CBC). The selection of these firearms was based on São Paulo Police's firearm seizure statistics. The most seizure firearms and ammunitions were found in the cases registered by the Police Department.

Each experiment was performed with 10 volunteers. Its daily routine was not changed to the proper tests for a result closer to reality. There was the positioning of snipers to target 50 cm, and with the gun at right angles to the fabrics. This distance was chosen because it represents the distance similar to great actual number of cases notified by the forensic science of São Paulo.

Five different fabrics were used as targets: microfiber, flannel, jeans, tergal (polyester) and tricoline (variety of cotton).

The basal levels of each element in the fabrics were determined before the experiments with firearms and the values used as blank test to avoid contamination, gathering after the shots were made immediately and the hand samples of each person were controlled by the laboratory moreover.

These tests were based on the technique of smear, which uses swabs soaked in EDTA solution (Ethylenediamine tetraacetic acid) diluted to 2%. The solution was implemented in the palms region (Tweezers-palmar), dorsal (tweezers-dorsal), stretching to the back of the hands for about 1 min, separately for each hand. These swabs were kept isolated in sachet for future analysis in the laboratory.

Regarding the fabrics, each one was cut about 2,25cm² for the analysis of the residue. In this procedure the fabrics samples were placed at radial distances of 0, 5, 10 and 15 cm from the target for each fabric and weapon.

This technique consists in the dilution of testimonies collected, which were severed and placed inside a centrifuge tube, 15 mL with polypropylene cover (Sarstedt, Germany), using 2 mL of nitric acid solution 10% (65% Suprapur MERCK, Germany), followed by agitation for 20 min at 25 KHz in an ultrasonic bath (UNIQUE, model TA1800, Brazil) in 80^{o}C water bath. In the next step solution containing the GSR extracted was diluted to 10 mL and 7 mL

Milli-Q water (18.2 MΩ. cm at 25°C), and 1 ml of In-115 100 ppb. These samples were read in a mass spectrometer with induced coupled plasma source (element 1, Finnigan MAT, Bremen, Germany) for the determination of ^{121}Sb, ^{138}Ba and ^{208}Pb, having the In-115 as internal standard and an analytical curve with concentrations recorded.

3. RESULTS AND DISCUSSION

With the values of concentrations obtained after discounting the whites made in advance, it was possible to make a ternary graph for hands and another graphic for the fabrics.

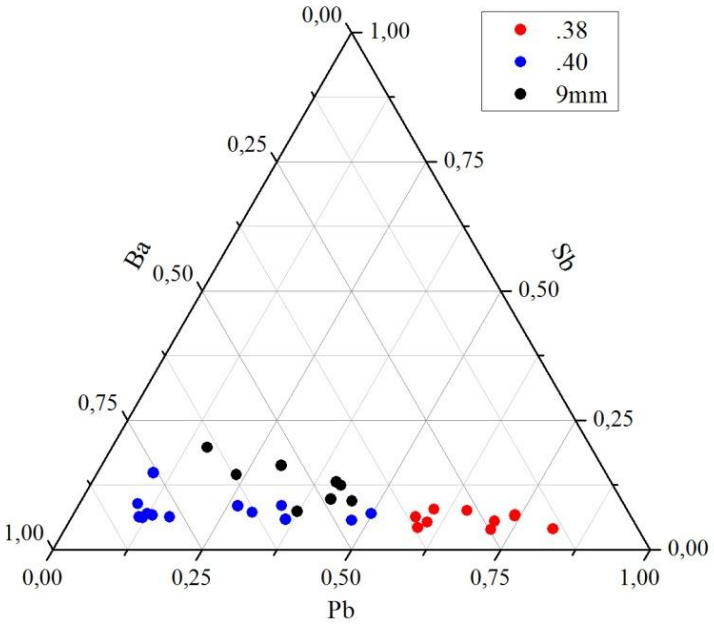

Figure 1. Junction of the three weapons after the shooting, referring to the hands.

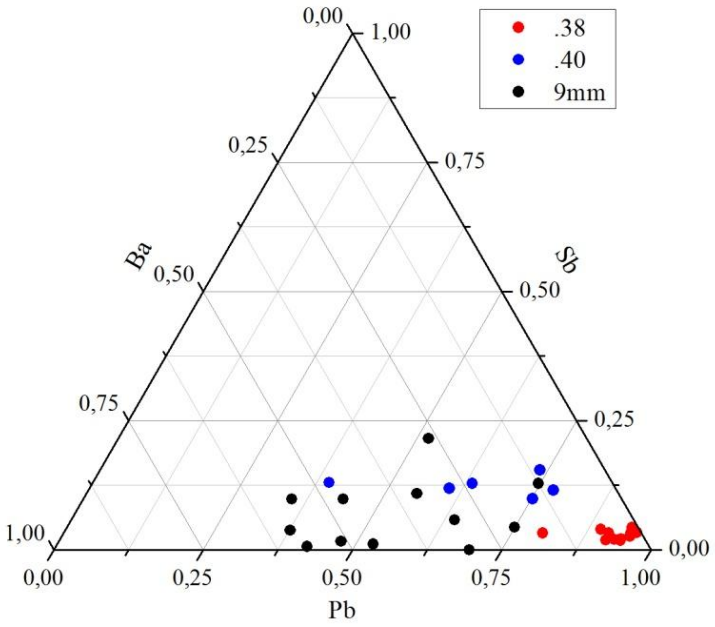

Figure 2. Junction of the three weapons after the shooting, referring to the fabrics.

It is observed distinct fingerprints for each type of weapon in the hands and the fabric.

4. CONCLUSIONS

This study demonstrated the high sensitivity of HR-ICPMS technique to determine ultra trace level of the GSR in different types of target tissues and in the hands of the gunmen after shooting a firearm enabling the measurement of items of interest (Pb, Ba and Sb).

The use of graphics ternary identified specific patterns of distribution for both revolvers and pistols in the hands of shooters and tissues. Thus, the comparison of these patterns in the hands of suspects and tissues used by victims of the shooting of firearms, may provide important clues for the elucidation of cases.

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