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Measurements of gunshot residues by sector field inductively coupled plasma mass spectrometry—Further studies with pistols

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Abstract

The most popular handgun in Brazil is the single round-barrel caliber 0.38 revolver. In recent years, however, owing to the modernization of police arms and their availability on the legal and illicit markets, pistols have become increasingly popular and currently represent about 20% of police seizures. In a previous paper we presented a novel collection method for gunshot residues (GSR) using a sampling procedure based on ethylenediamine–tetraacetic acid (EDTA) solution as a complexing agent on moistened swabs with subsequent detection using sector field-high resolution-inductively coupled plasma-mass spectrometry (SF-HR-ICP-MS). In the present paper, we discuss the capability of this methodology to identify antimony (Sb), barium (Ba) and lead (Pb) on the hands of volunteers after shot tests with 9 mm and 0.40 in. caliber pistols. Two types of munitions were tested: 9 mm Taurus and clean range. The use of a technique with high sensitivity, such as SF-HR-ICP-MS, permits the identification of low concentrations (less than 1 μg/L) of metals in firearm residue and constitutes a powerful tool in forensic science. We also discuss the importance of the sampling procedure, including collection from a different body part than the gun hand of the suspect. Comparison of the analytical data obtained allows clear discrimination between samples from the hands of shooters and non-shooters.

Keywords: Pistols; Gunshot residues; Collection; Barium; Lead; Antimony; Inductively coupled plasma-mass spectrometry

1. Introduction

The investigation of gunshot residue (GSR) is essential to the forensic examination of suspected cases of firearm use. In São Paulo State, Brazil, about 1500 firearms are seized each month with the following distribution: 70% single round-barrel revolvers, 20% pistols and 10% other types, i.e. sub-machine guns, shotguns, rifles, etc. Although the total number of weapons seized appears to be extremely large, it represents only a small fraction of the number of firearms possessed by criminals, citizens and employees of private security firms. Recent studies show that in 2000 about eighty people were killed daily by firearms in Brazil [1]. Consequently, firearms are a major concern in public safety. Antimony, lead and barium are the major elements present in GSR. The amount of these elements on the hands of shooters depends on several factors, such as the type of weapon and munitions used, the age and condition of the weapon, the suspect's personal hygiene and occupational habits, biometrics, and the time elapsed since the firing. The quantification of the elements removed from the hands of shooters depends on both the quality of the sampling protocol and the analytical instrumentation employed.

Several analytical techniques have been used for GSR analysis, each exhibiting advantages and drawbacks [1–3]. One often critical deficiency in conventional analyses using techniques such as flame atomic absorption spectrometry is insufficient sensitivity. More recently, a sector field inductively coupled plasma mass spectrometer (SF-ICP-MS) was used to successfully identify GSR from 0.38 caliber handguns (single round-barrel revolvers) supplied with 0.38 SPL LRN (lead round-nose cartridges) [4,5]. The sampling regions were the back of the thumb and forefinger or palm areas of volunteers

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chosen at random who did not usually handle firearms. Samples were obtained by scrubbing one of these regions with swabs moistened with 2% ethylenediamine–tetraacetic acid (EDTA) solution. This type of weapon is associated with a relatively large emission of particles and the concentrations of the elements of interest recovered ranged from one to several hundred micrograms per liter. In the present work, the same methodology was used to identify GSR from 9 mm and 0.40 in. caliber pistols on the hands of 40 volunteers. Two types of munitions were tested: 9 mm Taurus and clean range.

2. Materials and methods

To evaluate the proposed method for GSR detection, a sequence of 40 test shots was undertaken at the Ballistics Laboratory of the São Paulo Criminalistics Institute (I.C.-S.P.), São Paulo, SP, Brazil. Forty volunteers who do not generally use firearms were selected and a single shot at a time taken. Although under supervision by specialists from the Ballistics Laboratory, each volunteer fired in his own way. For the shots with pistols, Taurus (Forjas Taurus) of caliber 9 mm (Luger) and caliber 0.40 in. (S&W) and cartridges with jacketed projectiles of the FMJ type were used.

All of the munitions used were produced by the Cia Brasileira de Cartuchos (CBC). For the 9 mm pistols, two types of munitions were used: 9 mm Luger FMJ Round Nose with projectiles of 124 grains and a muzzle energy of 339 ft/lbs and a Magtech Clean Range munition, with a fully encapsulated bullet of 124 grains and a muzzle energy of 338 ft/lbs.

For the 0.40 in. S&W pistols, munitions of 0.40 in. S&W full metal jacket (FMJ) and projectiles of 180 grains and a muzzle energy of 390 ft/lbs were used.

The choice of 9 mm and 0.40 in. caliber Taurus pistols as well as the munitions from CBC (Cia Brasileira de Cartuchos) was based on their widespread use in São Paulo city as revealed by São Paulo Police firearm seizure statistics.

To eliminate any possibility of contamination from previous discharges, all the weapons were cleaned prior to each test shot. The collection and recovery procedures used here were slightly modified from those reported in an earlier study [4]. Up to an hour after the discharges, swabs moistened with 2% EDTA solution were employed for scrubbing around the back of the thumb and forefinger of the volunteers for about 30 s. The procedure was also applied to a different body part of the suspect (the non-gun hand, for example) to provide a blank test. The cotton swab was then sectioned using scissors (which were washed between each sample) and placed inside a polypropylene tube, which was closed, identified, and taken to the laboratory. Elements of interest were recovered from the swabs with 2 mL of a 10% nitric acid (65% Suprapur MERCK, Germany) solution, followed by 5 min agitation at 25 KHz in an ultrasonic bath (UNIQUE, Model TA1800, Brazil) and 30 min in an 80 °C water bath. Afterwards, extract sample solutions were diluted to 10 mL with deionized water (of resistivity 18 MΩ cm) and aspirated directly into a sector field inductively coupled plasma mass spectrometer (ELEMENT 1, Finnigan MAT, Bremen, Germany) for the determination of Sb, Ba and Pb. To determine total analyte concentrations responses of the following isotopes were measured: ^{121}Sb, ^{138}Ba and ^{208}Pb. Table 1 shows the main operating conditions. Working standard solutions of 1, 5, 10, 50, 100, 200 and 300 μg L^{-1} in 1% nitric acid were prepared by dilution of original 1000 μg L^{-1} Sb, Ba and Pb SPEX standards (NJ, USA). A Meinhard concentric nebulizer was used for sample introduction to a quartz torch, with peristaltic pumping, and 10 μg L^{-1} of ^{115}In solution was used as an internal standard.

Table 1
SF-HR-ICP-MS main operation conditions

Cool gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.10 L min^{-1}
Sample gas	0.97 L min^{-1}
RF power	1300 W
Runs/passes	10/6
Wash time	40 s
Take up time	30 s
Sampling cone	Nickel, 1.0 mm orifice
Skimmer cone	Nickel, 0.8 mm orifice
Flow rate	1.0 mL min^{-1}
Samples per peak	20
Integration window	80
Sample time	0.0100 s
Segment duration	0.240 s
Mass window	120
Search window	150
Scan type	Escan
Detection mode	Both
Spray chamber	Scott type (PE-Sciex)

3. Results and discussion

Table 2 presents the concentration data obtained from both hands of each volunteer. First, it is clearly seen that there is a significant difference between the concentrations of the elements of interest on both hands of the shooters, indicating that despite the differences to be expected amongst the volunteers, the quantities of residues on the gun hand are certainly greater than those found on the other hand. The amount of residue left on the volunteers' hands with 0.40 in. and 9 mm caliber pistols is of the same order of magnitude, and greater than that obtained with clean range. The clean range munitions leave a small quantity of metallic residue, difficult to determine by conventional analytical techniques, but easily detected by SF-ICP-MS.

Careful observation of the data presented in Table 2, reveals a random distribution of elemental concentrations about their mean values, which makes a general interpretation of the results difficult. The same distribution has been observed in previous studies with 0.38 caliber revolvers [4,5]. In fact there is no sense in using the mean value and its standard deviation to establish a

Table 2
Statistics of Sb, Ba and Pb concentrations (ng L^{-1}) in samples obtained from the hands of shooters

	Sb	Ba	Pb
Non-shot hand, $n = 80$			
Max.	3.03	31.59	168
Min.	[a]	0.66	0.028
Median	–	7.22	9.43
Mean	–	9.54	24.52
S.D.	–	7.59	38.89

	$n = 53$ (9 mm)			$n = 21$ (0.40 in.)			$n = 6$ (9 mm clean range)		
	Sb	Ba	Pb	Sb	Ba	Pb	Sb	Ba	Pb
Shot hand									
Max.	60.70	140.74	199.66	14.84	136.04	338.41	3.19	15.97	48.66
Min.	0.33	3.89	11.72	0.74	3.64	10.36	1.70	8.39	29.73
Median	6.64	35.56	55.74	3.47	8.42	48.87	2.47	11.77	38.12
Mean	12.54	43.74	63.15	5.09	23.02	91.42	0.65	3.22	8.28
S.D.	13.3	33.6	55.70	3.47	8.42	48.90	2.30	10.76	34.83

The sampling areas were the palm, back, thumb and forefinger palm (TF-Palm) and back of the thumb and forefinger (TF-Back).
[a] <Detection limit.

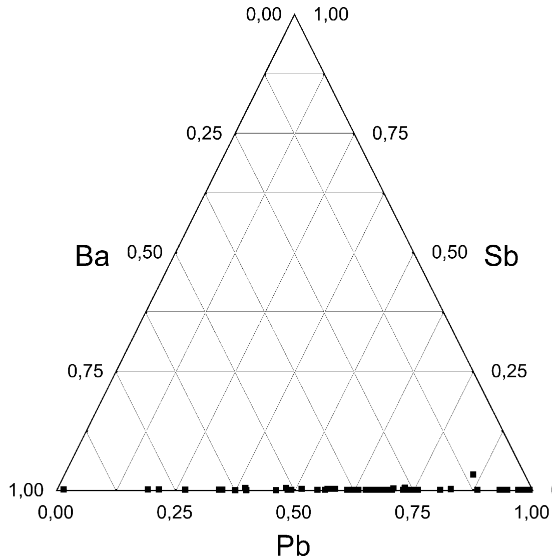

Fig. 1. Ternary plot of the distribution of metals from blank samples taken from the non-gun hand.

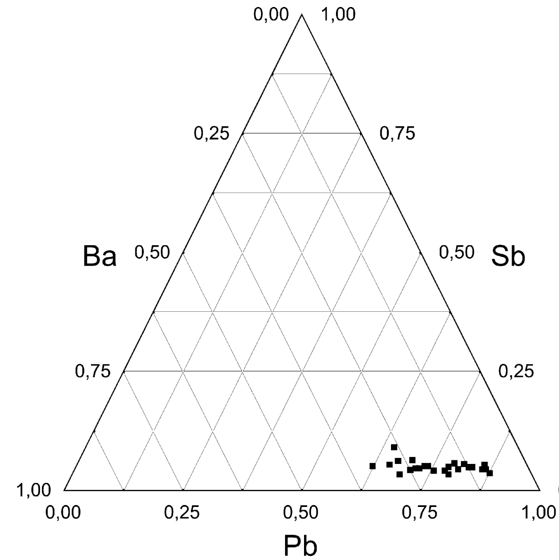

Fig. 3. Ternary plot of the distribution of metals after a shot with a 0.4 in. caliber pistol.

recovery criterion for the residues. In practice the presence of these metals on a suspect's hands depends on many factors such that there is the risk of erroneous interpretations of their significance. Caution is needed therefore, to avoid false positive or negative interpretations based on the confirmed detection of metals on the hands of firearm users.

As shown in Figs. 1–4, to better visualize the results obtained, ternary graphs were obtained using ORIGIN [6]. Such ternary diagrams represent the relative percentage of three studied components, providing a direct comparison among the three components studied, Pb–Sb–Ba, for each shooter in each situation studied. A given point, at one of the vertices of the triangle, indicates that the relative concentration of the corresponding component at that point is 100%. In contrast, a given point exactly in the center of the triangle shows that the relative percentage of the three components is equal. The data are automatically normalized when the diagrams are created.

Fig. 1 shows the results obtained from the non-shooting hand of each volunteer. It is clearly seen that a random distribution of Ba and Pb and the virtual absence of Sb are obtained. This distribution profile for non-shooters is the same observed in previous studies [4,5], and is readily explained by the natural abundance of these two elements in the environment.

Figs. 2 and 3 show ternary plots of the normalized distribution of the three elements on the hands of shooters following firing of pistols with 9 mm and 0.40 in. munitions. Observation of these figures reveals some overlapping of the points, making the clear distinction of the use of the 9 mm from the 0.4 in. caliber pistols difficult. As can be observed, the data obtained with 9 mm pistols present a greater dispersion than

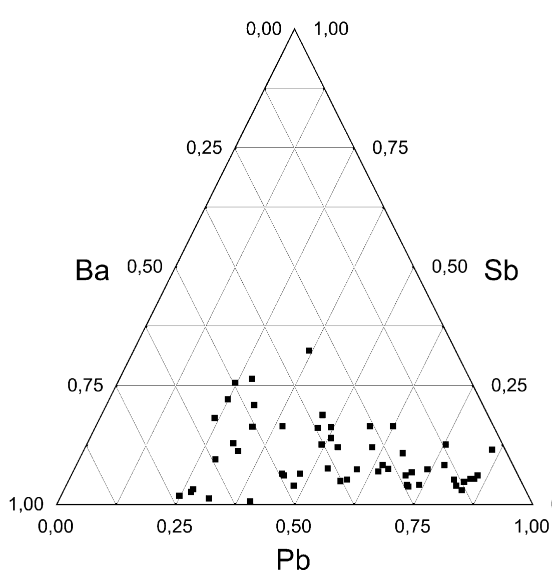

Fig. 2. Ternary plot of the distribution of metals after a shot with a 9 mm caliber pistol.

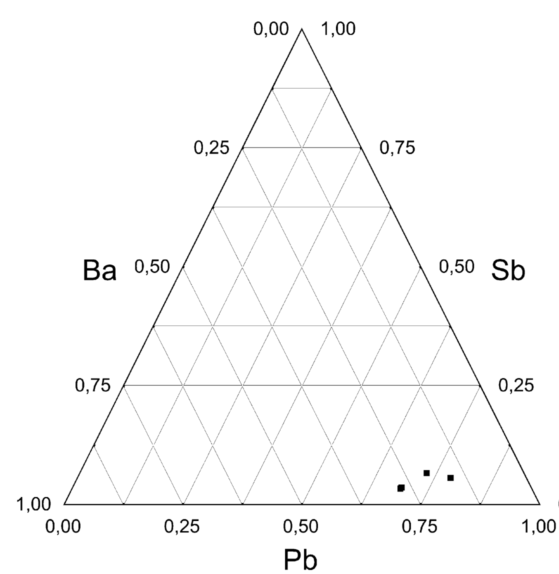

Fig. 4. Ternary plot of the distribution of metals after a shot with a 9 mm caliber pistol (clean range munitions).

those obtained with the 0.40 in. pistols. A possible explanation is a lower quantity of gunpowder in the 9 mm Luger carridges compared to that found in the 0.4 in. S&W cartridges, such that the residues of shots from the 9 mm Luger are ejected with less energy and disperse over a shorter distance. Thus biometric factors and the state of preservation of the firearms may represent the greater influence in the distribution of the residues on the hand of shooters.

The distribution obtained with the clean range munitions is very closely grouped and distinctive. Most importantly, the groupings of the data on the ternary plots in cases where a gun was discharged (Figs. 2–4) are totally distinct from that of Fig. 1. Thus gun firing is readily established with a very high degree of certainty.

4. Conclusions

Confirmation of firearm discharge is one of the commonest routine police activities, requiring fast, precise and trustworthy analytical procedures. The method used here meets these requirements. The use of a very sensitive technique such as SF-ICP-MS allows the identification of quantities of metals at trace levels, which permits the identification of distributions even with clean range munitions. The use of a region not directly exposed to the residues as a reference is very useful for the interpretation of the data, allowing the clear identification of the origin of the metallic elements present on the hands of volunteers. Differences found in GSR recoveries for the same firearm may be related to personal hygiene, biometrics and occupational factors of the volunteers and especially the state of preservation of the firearm, which can provide more or less GSR.

Quantitative determination of the metals is not critical since the elements measured are also present on the non-gun hand. Recoveries of the metals also do not need to be determined since, as was observed above, the concentrations found on the hands of shooters depend on many factors. Ternary plots, however, are an important tool for data analysis.

Antimony is an uncommon element and may be a strong indicator of gunshot firing. Concentrations of Sb on the hands of non-shooters are extremely low, however, necessitating the use of a very sensitive technique, such as high resolution ICPMS, for its detection.

Based on the data presented here, and those obtained earlier for 0.38 revolvers [5], it is possible, using distribution models of the measurements (ternary graphs), to produce strong evidence concerning the origin of the metals on the hand of suspects, which represents a great advance in police procedures. Complementary studies, however, are still necessary, dealing with other metals released during firing, perhaps enabling the confident identification of the type of firearm and munitions used. Apart from the operation of the mass spectrometer, which requires specialized technicians, all the other procedures described here are simple to perform and may be undertaken by police officers at any time or place and do not require extensive knowledge of chemistry.

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