

The Collection and Identification of Gunshot Residues to Distinguishing 4 Types of Bullets by ICP-MS

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Abstract. The identification of gunshot residue (GSR) dispersed in a shooting is important for forensic evidence to solve the firearm shooting crimes. In this experimental study, the residue of specific elements, namely: Lead (Pb), Antimony (Sb) and Barium (Ba) were compared using Inductively Coupled Plasma Mass Spectro photometer (ICP-MS) from 4 types of 9 mm ammunition labeled as A is Lead Round Nose (LRN) 135 gr., B is Jacketed Hollow Point (JHP) 115 gr., C is Full Metal Jacketed (FMJ) 124 gr. all of Bullet Master and D is Full Metal Jacketed (FMJ) of Thai Arms. The Bullet holes from wooden and metal targets at 7 firing ranges; 0.00, 0.15, 1.00, 1.50, 2.00 and 2.50 meters were investigated by cotton swab dripped with 5% nitric acid. The analytical results showed that at the firing range of 0.00 meters, very high concentrations of Pb was found more than Sb and Ba, while the outer side of the hole found more amount of the elements than the inner side. Moreover, the results shown the amount of Pb, Sb and Ba of ammunition A (LRN), B (JHP) and C (FMJ) of Bullet Master are significant difference, and classify the ammunition C (FMJ) of Bullet Master from the ammunition D (FMJ) of Thai Arms using Pb and Sb concentration. From the results of this study can be useful scientific evidence for forensic science investigation in order to estimate the ammunition and firing distances.

1. Introduction

Gunshot Residue (GSR) is a forensic tool that is collected as evidence; of which is very important to solve crimes related to guns cases. This evidence is gathered from homicide and suicide cases, by the detection of gunshot residue. There is a case study using fresh pork and rotten pork; to study about gunshot residue, by shooting the gun to study the relationship between the gun, bullet type, and firing distance by ICP-MS and ICP-AES [1-2]. A study collection the samples of gunshot residue from the hands, wrists, arms, and clothing from the suspect, and shooting targets for distribution analysis by SEM-EDX technique was reported [3]. Also, gunshot residue is collected from the suspect's clothing, by using ICP-MS technique to indicate the quantifiers of the gunshot residue from the clothing, and distance of time after shooting the trajectory [4]. Furthermore, studies are done by keeping gunshot

residue from the hands of the shooter by using nitric acid solution, when they shot the gun, different types of gun rifling, and various types of bullets [5-7]. Studies about gunshots simulations in a car by AAS technique; in order to see the area where the gunshot residue would be located in, to find where the bullet was shot [8]. ICP-MS is an advanced diagnostic tool for high level analysis to check and confirm gunshot residue to show elements and analysis of parts-per-billion level (ppb). This includes studies about the analysis of gunshot residue, but there isn't any information to find gunshot residue on the surface of the bullet hole that has marks from shooting; of which are caused by various types of bullets.

This research studied about the quantifiers of the gunshot residue on the wood and metal target by using the ICP-MS technique of the 4 different types of 9 mm ammunition at the different shooting range. This studied the change of the trace elements (Pb, Sb, Ba), about the distance of the shooting and type of ammunition. The results of this research can be adapted for forensic science. Altogether, this evidence can be used to make forensic science much more accurate in criminal cases.

2. Materials and method

2.1. Experimental protocol

This research used an automatic firearm, 9 mm Glock Model 34 handgun; having 5.43 inch barrel length. There are about 4 types of bullets listed as follows: A is Lead Round Nose 135gr., B is Jacketed Hollow Point (JHP) 115 gr., C is Full Metal Jacketed (FMJ) 124 gr. all of Bullet Master and D is a Full Metal Jacketed (FMJ) of Thai Arms. Shooting targets are made of wood, about 30cm × 40cm × 1cm with a metal plaque 30cm × 30cm × 1 mm. There was a table about 10cm × 10cm and was closed with plastic to protect impurity. The study about the shooting distance had 7 measurements: 0.0, 0.15, 0.5, 1.0, 1.5, 2.0 and 2.5 meters.

2.2. Sample collection

The sample of the shooting was repeated three times (n = 3) by using a circular plastic sheet (2.5 cm. radius). A cotton swab with 5% nitric acid was applied, wiped the inside bullet hole 1 cotton bud, around the bullet hole in a 2.5 cm. radius 1 cotton bud. It was placed in a baking oven at 80 °C, for 1 night. After that, the cotton swab was cut and put into a conical centrifuge tube (15 ml) and extracted with 2 ml 10% nitric acid, baked at 80 °C, for 2 hours. Then the solution was shaken for 30 seconds again. The solution was collected in a microcentrifuge tube (2 ml) and stored in a refrigerator at 2–8 °C.

2.3. Inductively Coupled Plasma Mass Spectrophotometer analysis

To prepare the sample solution for the analysis of trace elements (Pb, Sb, Ba), they were derived by the solution; dilute with Deionized water, 18 MΩ, 1:9 ratio, and then it was analyzed by ICP-MS Agilent 7500ce; of which used the tool. (Table 1)

Table 1. The parameter and value of ICP-MS Agilent Model 7500ce.

Plasma condition		Reaction parameter	
RF Power	1500 W	Cell entrance	-50 V.
Carrier gas	0.9 L/min.	Cell exit	-80 V.
Makeup gas	0.31 L/min.	Makeup gas	0.31 L/min.
Nebulizer Pump	0.1 rps	OctP RF	175 V.
		OctP bias	-8 V.

3. Results and discussion

3.1. Study of the efficacy of the tool and method of extraction.

Standard Calibration Curve by using Standard Lead nitrate (SCP), standard antimony oxide (SCP) and Standard Barium carbonate (SCP) were shown. The results are given in Table 2.

Table 2. The efficacy of extraction methods and the tool in the research.

Parameters		Pb	Sb	Ba
Working range (ppm)		0.002 – 1.200	0.002 – 1.200	0.002 – 1.200
LOD (ppm, n=10)		0.0015	0.0005	0.0011
LOQ (ppm, n=10)		0.0021	0.0011	0.0016
% Recovery ± SD	0.025 ppm	100.62±4.03	102.66±3.91	100.99±4.38
	0.100 ppm	100.26±3.19	100.23±3.74	100.52±2.72
	0.500 ppm	100.87±3.47	104.14±2.19	104.30±1.91

3.2. Comparative study of gunshot residue at different firing distances

When comparing the amount of trace element by using the ICP-MS analysis was used at 7 firing distances from 0.0, 0.15, 0.5, 1.0, 1.5, 2.0 and 2.5 meters. This found that when the firing distance was increased, the measurement of the amount of trace elements on wood and metal from both the inside and outside of the bullet holes had trended to decrease ($P < 0.05$), at a 95% confidence interval. Due to the increased firing distance, windage from the environment was measured to see the impact on the target. At a distance of 2.5 meters, it can be analyzed efficiently. As shown in Table 3, it was found that at the firing distance of 0.0 m, the most amount of trace elements were lead, rather than barium and antimony, respectively. Overall, lead is the main component of the bullet and the gunpowder (primer).

Table 3. The amount of trace element (ppm) by using ICP-MS analysis.

Bullet holes	Tar get	Ele ment	The amount of trace element (ppm) at different shooting distance (n=3)±SD						
			0.0 m.	0.15 m.	0.5 m.	1.0 m.	1.5 m.	2.0 m.	2.5 m.
A (LRN)	wood	Pb	8.021±1.560	2.606±0.352	1.627±0.132	1.143±0.168	0.889±0.074	0.763±0.036	0.343±0.005
		Sb	0.638±0.029	0.498±0.003	0.392±0.035	0.191±0.052	0.143±0.002	0.097±0.026	0.063±0.004
		Ba	2.186±0.117	1.631±0.167	0.270±0.008	0.253±0.010	0.222±0.019	0.157±0.012	0.075±0.006
	inside	Pb	3.279±2.257	1.404±0.072	1.256±0.115	0.933±0.049	0.810±0.026	0.440±0.024	0.286±0.029
		Sb	0.387±0.016	0.244±0.009	0.221±0.011	0.132±0.006	0.091±0.003	0.056±0.007	0.024±0.004
		Ba	1.711±0.149	0.488±0.056	0.268±0.020	0.212±0.014	0.156±0.009	0.070±0.004	0.027±0.006
A (LRN)	wood	Pb	47.617±4.160	4.705±0.436	2.156±0.108	0.939±0.052	0.579±0.081	0.244±0.033	0.132±0.012
		Sb	7.014±0.165	0.416±0.013	0.174±0.009	0.089±0.012	0.029±0.004	0.024±0.002	0.015±0.001
		Ba	26.057±0.941	1.562±0.142	0.465±0.045	0.173±0.025	0.101±0.013	0.052±0.001	0.022±0.002
	outside	Pb	16.693±1.233	5.529±0.352	1.761±0.057	0.858±0.027	0.645±0.020	0.440±0.029	0.331±0.022
		Sb	5.076±0.129	1.278±0.032	0.431±0.033	0.147±0.011	0.079±0.002	0.035±0.003	0.022±0.002
		Ba	5.755±0.225	2.806±0.019	0.645±0.033	0.349±0.008	0.234±0.017	0.120±0.008	0.089±0.007
B (JHP)	wood	Pb	46.470±3.685	12.53±0.845	7.580±0.881	5.661±0.151	4.266±0.300	3.515±0.145	0.138±0.014
		Sb	2.785±0.046	0.925±0.067	0.663±0.029	0.415±0.046	0.254±0.026	0.192±0.012	0.025±0.003
		Ba	3.400±0.221	0.372±0.047	0.171±0.012	0.123±0.014	0.114±0.014	0.092±0.002	0.081±0.003
	inside	Pb	71.070±3.288	57.63±1.001	42.61±0.694	37.47±2.584	27.99±0.910	24.07±0.325	16.23±1.302
		Sb	3.172±0.013	3.013±0.079	2.693±0.051	2.115±0.058	1.786±0.055	1.449±0.099	0.941±0.037
		Ba	15.777±0.845	0.494±0.034	0.362±0.009	0.241±0.016	0.153±0.001	0.137±0.006	0.086±0.003
B (JHP)	wood	Pb	506.00±24.723	70.83±3.791	5.946±0.203	1.558±0.045	1.211±0.090	0.867±0.032	0.052±0.007
		Sb	23.730±0.236	5.280±0.453	0.367±0.003	0.137±0.006	0.070±0.006	0.035±0.003	0.014±0.001
		Ba	24.773±1.613	2.658±0.216	0.253±0.021	0.078±0.005	0.056±0.003	0.045±0.004	0.034±0.001
	outside	Pb	6700.±336.414	249.5±17.69	149.2±9.846	132.9±3.350	125.0±3.035	105.9±8.979	85.17±7.353
		Sb	13.493±0.817	7.518±0.244	6.478±0.417	5.671±0.269	5.004±0.252	3.308±0.240	1.597±0.056
		Ba	35.423±2.179	14.06±0.644	2.619±0.205	0.281±0.017	0.099±0.006	0.081±0.005	0.050±0.004

Bullet holes	Tar get	Ele ment	The amount of trace element (ppm) at different shooting distance (n=3)±SD						
			0.0 m.	0.15 m.	0.5 m.	1.0 m.	1.5 m.	2.0 m.	2.5 m.
C (FMJ) inside	wood	Pb	3.933 ± 0.050	2.847±0.259	1.429±0.016	0.950±0.016	0.847±0.034	0.191±0.021	0.070±0.003
		Sb	1.380 ± 0.069	0.217±0.029	0.164±0.003	0.129±0.003	0.095±0.013	0.038±0.006	0.024±0.002
		Ba	2.444 ± 0.138	0.194±0.004	0.172±0.002	0.133±0.001	0.115±0.008	0.097±0.008	0.053±0.008
	metal	Pb	3.672 ± 0.856	2.398±0.072	1.640±0.051	1.228±0.119	0.834±0.021	0.556±0.039	0.141±0.011
		Sb	0.758 ± 0.038	0.370±0.007	0.232±0.028	0.173±0.003	0.131±0.012	0.095±0.003	0.075±0.005
		Ba	0.808±0.008	0.469±0.015	0.238±0.022	0.165±0.009	0.134±0.005	0.075 ± 0.002	0.025±0.002
C (FMJ) outside	wood	Pb	14.400 ± 1.345	2.816±0.258	1.445±0.062	0.204±0.010	0.163±0.008	0.131 ± 0.005	0.097±0.010
		Sb	2.671 ± 0.226	0.831±0.012	0.120±0.012	0.022±0.003	0.012±0.001	0.011 ± 0.001	0.007±0.003
		Ba	5.169 ± 0.257	1.792±0.111	0.227±0.013	0.134±0.007	0.085±0.002	0.073 ± 0.004	0.057±0.002
	metal	Pb	18.491 ± 0.978	9.264±0.600	1.917±0.177	0.424±0.005	0.143±0.013	0.112 ± 0.008	0.061±0.008
		Sb	7.409 ± 0.406	2.035±0.164	0.258±0.016	0.067±0.004	0.032±0.003	0.024 ± 0.004	0.018±0.001
		Ba	15.810 ± 0.746	2.821±0.155	0.336±0.021	0.054±0.003	0.038±0.006	0.030 ± 0.003	0.017±0.002
D (FMJ) inside	wood	Pb	2.301 ± 0.169	1.214±0.150	0.913±0.071	0.592±0.052	0.419±0.017	0.154 ± 0.018	0.074±0.013
		Sb	1.256 ± 0.112	0.122±0.013	0.094±0.008	0.071±0.008	0.054±0.008	0.013 ± 0.001	0.007±0.003
		Ba	0.859 ± 0.046	0.739±0.024	0.515±0.015	0.476±0.021	0.313±0.012	0.233 ± 0.015	0.125±0.010
	metal	Pb	41.940 ± 1.990	17.57±0.747	11.02±0.589	9.509±0.341	6.600±0.160	4.114 ± 0.362	1.433±0.110
		Sb	1.169 ± 0.060	0.823±0.038	0.739±0.023	0.492±0.024	0.288±0.018	0.186 ± 0.018	0.115±0.007
		Ba	3.607 ± 0.173	0.403±0.018	0.247±0.006	0.135±0.007	0.085±0.008	0.060 ± 0.002	0.046±0.001
D (FMJ) outside	wood	Pb	17.608 ± 0.665	2.276±0.093	1.053±0.025	0.356±0.021	0.221±0.019	0.175 ± 0.011	0.071±0.005
		Sb	13.256 ± 0.449	0.555±0.047	0.143±0.019	0.019±0.001	0.008±0.001	0.003 ± 0.001	N/A ^a
		Ba	26.460 ± 1.731	1.436±0.112	0.449±0.022	0.084±0.005	0.047±0.004	0.038 ± 0.004	0.023±0.004
	metal	Pb	36.750± 1.232	26.96±1.210	15.58±0.929	12.29±0.217	10.69±0.332	6.936 ± 0.359	2.241±0.014
		Sb	4.695 ± 0.212	1.880±0.114	1.315±0.073	0.584±0.031	0.538±0.034	0.286 ± 0.011	0.208±0.002
		Ba	5.169 ± 0.257	1.792±0.111	0.227±0.013	0.134±0.007	0.085±0.002	0.073 ± 0.004	0.057±0.002

^a Not detection

When comparing trace elements of gunshot residue (Pb, Sb, Ba) between metal shooting targets and wood shooting targets, tendency found that metal shooting targets had more gunshot residue than wood shooting targets ($p < 0.05$), at a 95% confidence interval. Because the skin of the wood has grooves a lot, it makes gunshot powder get stuck instead relatively easier than metal; however gunshot residue can easily be found from the damage marks on the wood. The collection of gunshot residue was found from the inside and outside area of the target. The outside bullet holes were significantly higher than the inside bullet holes ($p < 0.05$), at the 95% confidence level. The outside area of the target is better for the bullet to move and can cause a large amount of gunpowder to found in that region. In the bullet hole, can found to show of details.

3.3. Comparative study of the amount of gunshot residue to identify each type of bullets.

From the results, it was found that the bullet of B can find the trace elements (Pb, Sb, Ba), with three types higher than other types of bullets. Considering the Pb in both side of the bullet holes, it was found that in the range of 0-2.5m, bullet B had a higher Pb content than D, A, and C, respectively, making it possible to separate bullets B and D from bullets A and C. Then consider the Sb and Ba to support classification of the bullet. It was found that at the firing distance of 0.00 - 0.15 m it can be separated in types of bullets A and C out of each other, with the Sb content of C higher than A ($P < 0.05$) at the 95%

confidence level and Ba with the amount of A tend to be higher than C. At 0.5-2.5 m showed a quantity of similar metal trace elements. That results can be seen in figure 1.

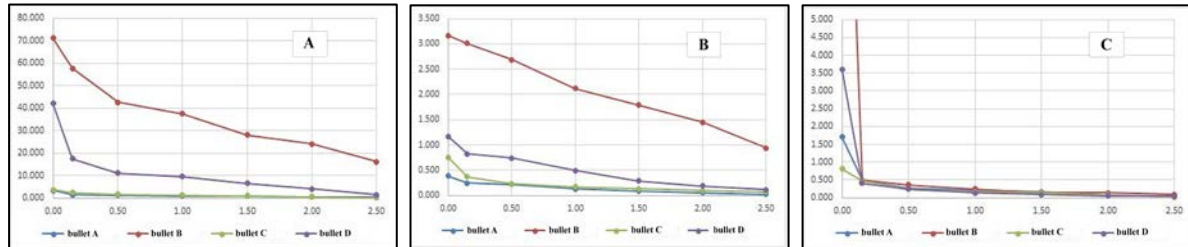


Figure 1. The comparison of gunshot residue (Pb, Sb, Ba) of inside on metal shooting targets of 4 types of bullets (A) Lead (B) antimony (C) Barium

4. Conclusions

Gunshot residue (GSR) is important forensic evidence in the investigation process. The collection and identification of GSR in each organization had been used the differences. In this study, the residue of specific elements (Pb, Sb, Ba) were compared using ICP-MS from 4 types of 9 mm ammunition. The results showed that the amount of Pb was found more than Sb and Ba, while the outer side of the hole found more amount of the elements than the inner side ($p < 0.05$) at the 95% confidence level. Moreover, the amount of Pb, Sb and Ba of ammunition A (LRN), B (JHP) and C (FMJ) of bullet master are a significant difference and classify the ammunition C (FMJ) of bullet master from the ammunition D (FMJ) of Thai Arms using Pb and Sb concentration. This research can be used to predict ammunition for forensic evidence.

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