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Is it possible to determine firearm calibre and shooting range from the examination of gunshot residue in close range gunshot wounds? An experimental study.

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ABSTRACT

Introduction: The aim of the study was determining the type of weapon and shooting distance depending on chemical analysis of inorganic gunshot residue from the skin gunshot wounds in experimental animals (pigs).

Methods: Experimental study was conducted in order to determine components and their percentage in gunshot residue (GSR). In 60 samples, pig skin was shot by firing projectiles from four different weapons and from three different distances (contact wound and near contact wound from 5 cm and 10 cm). The methodology included determining the presence of inorganic material: antimony, barium, lead, nickel, zinc and copper in the skin and subcutaneous tissue using atomic absorption spectrophotometry (AAS).

Results: Formula for determining weapon type was provided cutt-off points for different weapons, with 78.6% of original grouped cases being correctly classified. Formula for determining weapon type was provided cutt-off points for different distances, with 58.9% of original grouped cases being correctly classified, which was slightly less reliable compared to weapon type discrimination analysis.

Conclusion: The presented study showed that chemical analysis of GSR in entrance wound with AAS could be useful in determining the type of weapon, as well as the shooting distance, i.e. in our study, determining whether the wound is contact or near contact. This could be particularly useful in postmortally putrefied or charred bodies with gunshot wounds.

Keywords: near contact wound, experimental study, gunshot residue, AAS (atomic absorption spectrometry).

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INTRODUCTION

Gunshot residue (GSR) consists of particles composed of antimony, barium and lead that arise from the condensation of primer vapors (1) and also soot debris consisting of carbon and metallic fragments

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from the bullet and cartridge case (2). In the matter of reconstruction of gunshot fatalities, the macroscopic examination of gunshot wounds as well as the investigation of GSR particles gains extensive forensic significance (1,2). Physical and chemical investigations of firearm discharge residues are nowadays performed routinely in order to solve a number of forensic problems such as identification of gunshot wounds together with establishing of the entrance and exit (3), estimation of the time since discharge of a firearm (4, 5), distribution of GSR at the crime scene, estimation of shooting distance (6, 7), as well as establishing whether a person has fired a gun (8). Sensitive analytical methods are required for the identification of inorganic gunshot residues that are usually presented in very small quantities on a substratum, and commonly used methods include atomic absorption spectroscopy (AAS), neutron activating analysis (NAA) (1) , X-ray fluorescence spectrometry (XRF), inductively coupled plasma mass spectrometry (ICP-MS) (9).

The aim of the study was determining the type of weapon and shooting distance depending on chemical analysis of inorganic gunshot residue from the skin gunshot wounds in experimental animals (pigs).

METHODS

Experimental study was conducted in order to determine components and their percentage in gunshot residue (GSR). In 60 samples, pig skin was shot by firing projectiles from four different weapons and from three different distances, five times from each distances (contact wound, and near contact wound 5 cm and 10 cm). Characteristics of weapons and projectiles are presented in (Table 1). The research is performed in accordance with the ethical principles in compliance with the law on the protection of animals in our country.

Part of the pig body size is approximately 120 x 45x 20 m composed of skin, subcutaneous and muscle tissue, areas of the chest and abdomen, which is attached to a solid surface. Shooting was conducted using a system for safe firing from the firearm (Verifire-The Secure Firing Device, Twin Tooling, Canada). The weapons used in the experiment were most commonly used in the Balkan region in last 10 years according to Federal and local police. The methodology included determining the presence of inorganic material: antimony, barium, lead, nickel, zinc and copper in the skin and subcutaneous tissue using Atomic Absorption Spectrometry (AAS) Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). Samples for chemical analysis were clips of skin and subcutaneous tissue size about 3x3x3 cm, each sample was labeled and packed in a plastic container filled with buffered 10% of formalaldehyde.

In order to perform an AAS and ICP-OES analysis and determine content of these elements using an appropriate method, it was necessary to put each sample in the acid-water solution. To achieve this, it was necessary to perform so-called *mineralization*, i.e. destruction of all organic material. Given the amount of organic matter from several grams (even tens of grams), "mineralization" samples corresponding mineral acids (nitric, sulphuric and hydrochloric) would be completely impractical, because it would require the use of large amounts of these acids. This would be a great possibility of contamination of the sample metals (which are, as a rule contained in these acids, regardless of the degree of purity) whose content is determined, and would be increased and the detection limit. Because it is dedicated to the mineralization patterns make burning in platinum dishes.

After the process of burning the sample is placed in a bowl incandescent furnace where, at a temperature of 900°C for 30 minutes, elemental carbon burn completely.

Temperature at which the thermal process unfolded mineralization samples were below 1000°C, which is more than 400°C temperature below the sublimation of lead oxide, which has a lowest temperature of vaporization or sublimation (1470°C). Here, based on the realistic assumption that metals whose content determination completely oxidized, as are the non-precious metals, and the samples are accumulated in the form of very fine particles (large specific surface area), where the whole process of mineralization took place in contact with air.

After incineration of elementary carbon, content in the container was moistened with about 1 ml of redistilled water, after which exactly 3 ml of nitric acid (1.65%) very high purity (“Aristar”) were added and

TABLE 1. Weapons used in the experiment

Weapons	Caliber	Ammunition	Mark missiles	Manufacturer	Number of shoots	Notation of GSR sample
Pistol Crvena zastava 'M70'	7.65 mm	7.65x17 mm (.32AUTO)	PPU .32AUTO	' Prvi Partizan' Užice, Serbia	15	A
Pistol Crvena zastava 'M57'	7.62 mm	7.62x25 mm	ППУ 2001	'Prvi Partizan' Užice, Serbia	15	B
Pistol Češka Zbrojovka Model „CZ 85 B“	9 mm LUGER	9x19 mm	PPU 9mm LUGER	'Prvi Partizan' Užice, Serbia	15	C
Automatic rifle „Zavod Crvena zastava“ M70AB2	7.62 mm	7.62x39 mm	IK 91	Igman Konjic, Bosnia and Herzegovina	15	D

TABLE 2. Distribution of percentage different elements in weapon with regard to shooting distance

	%Pb	%Cu	%Zn	%Ni	%Sb	%Ba
A 10 cm	54.89	13.55	14.25	1.89	4.44	10.99
A 5 cm	37.57	14.64	37.14	1.78	3.78	5.08
A contact	29.66	21.31	32.58	1.84	6.42	9.47
Total average A	40.93	16.63	27.34	1.84	4.85	8.76
B 10 cm	47.55	25.51	18.21	1.01	6.71	1.02
B 5 cm	28.4	39.08	21.96	0.56	8.74	1.26
B contact	14.62	52.45	14.72	0.33	17.16	0.73
Total average B	27.52	41.09	18.31	0.57	11.51	1
C 10 cm	46.46	27.39	15.75	0.31	3.27	6.83
C 5 cm	37.86	21.78	21.98	0.63	11.72	6.03
C contact	35.08	34.21	5.75	0.83	14.24	9.9
Total average C	39.8	27.79	14.49	0.59	9.74	7.59
D 10 cm	17.7	42	33.75	0.18	5.28	1.1
D 5 cm	11.89	67.09	7.07	0.1	12.75	1.11
D contact	12.28	60.33	5.73	0.28	20.59	0.79
Total average D	13.96	56.47	15.52	0.18	12.87	1

Legend: A (caliber 7,65x17mm), B (caliber 7,62x25mm), C (caliber 9x19mm), D (caliber 7,62x39mm), Pb (lead), Cu (copper), Zn (zinc), Ni (nickel), Sb (antimony), Ba (barium)

slightly heated in order to completely dissolve salts. Preliminary measurements were used for calibration, after which final measurements were performed with types of AAS. Contents of lead, copper, zinc and nickel in all solutions samples were determined on flame AAS. Due to interference of antimony and barium on flame AAS, probably caused by chemical interactions due to its high content of sodium (occurring during atomization in flames), we also used ICP-OES which was due to significantly higher temperatures atomisation, resistant to chemical interference.

Statistical analysis

All data were analyzed using the following: descriptive statistics, Kruskal-Wallis one way test, discriminatory equations. $P < 0.05$ was considered significant and $p < 0.01$ was considered highly significant.

RESULTS

Distribution of different percentage of different elements in different types of weapon with regard to shooting distance is presented in Table 2.

Since the samples were rather small, due to significant cost of the study, in statistical analysis we used

TABLE 3. Kruskal-Wallis one way test to determine differences in elements distribution depending on type of weapon within the same shooting distance

Shooting distance		%Pb	%Cu	%Zn	%Ni	%Sb	%Ba
10 cm	Chi-Square	10.825	9.889	5.604	11.487	5.014	13.477
	P	0.013	0.020	0.133	0.009	0.171	0.004
5 cm	Chi-Square	10.094	15.632	11.938	12.442	8.970	13.983
	P	0.018	0.001	0.008	0.006	0.030	0.003
contact	Chi-Square	11.549	12.680	15.549	8.775	8.305	14.311
	P	0.009	0.005	0.001	0.032	0.040	0.003

Pb (lead), Cu (copper), Zn (zinc), Ni (nickel), Sb (antimony), Ba (barium)

TABLE 4. Cutt-off points for different weapons

Weapon	Result for discriminant function (cutt-off discriminant score)
A	≤ (-1.984)
C	(-1.985) – 0.125
B	0.126 – 1.984
D	≥ 1.985

Legend: A (pistol, caliber 7,65x17mm), B (pistol, caliber 7,62x25mm), C (pistol, caliber 9x19mm), D (automatic rifle, caliber 7,62x39mm)

nonparametric Kruskal-Wallis one way test in order to analyze differences in elements distribution depending on the type of weapon (Table 3), regardless of the shooting distance. Since this analysis has shown that differences in elements distribution depending on type of weapon within the same shooting distance were mainly statistically significant (for 88.89% of cases), we analyzed it further using statistical discrimination function. The analysis showed statistical significance for all elements except barium which didn't meet tolerance criteria (canonical correlation 0,911, Eigen value = 4,874, Wilks' Lambda = 0,101, p<0,001), with 78,6% of original grouped cases being correctly classified. The following formula for determining weapon type is provided (cutt-off points for different weapons are presented in Table 4):

weapon type = – 3.691+0.313·%Pb+0.344·% Cu+ 0.315·%Zn-0.66·%Ni+0.354·%Sb

In order to determine differences in elements distribution depending on shooting distance within the same type of weapon, we used the Kruskal-Wallis one way test once more (Table 5). Since this analysis has shown that differences in elements distribution depending on the shooting distances within the same type of weapon were mainly statistically significant (for 54.17% of cases), we again analyzed it further using statistical discrimination function. The analysis showed statistical significance for the all elements again except barium which didn't meet tolerance criteria (canonical correlation 0,669, Eigen value = 0,811, Wilks' Lambda = 0,51, p<0,001), with 58,9% of original grouped cases being correctly classified, which was slightly less reliable compared to weapon type discrimination analysis. The following formula for determining weapon type is provided (cutt-off points for different distances are presented in Table 6):

shooting distance = –8.917+0.13·%Pb+0.099·%Cu+ 0.111·%Zn-0.145·%Ni-0.053·%Sb

We used atomic absorption spectrophotometry (AAS) as a method of gunshot residue particles analysis from gunshot entrance wounds for determining which type of weapon was used in contact or near contact wound. Due to the fact that we have used small number of samples it was necessary to perform discrimination analysis in a way to show the formulas for determining weapon type and shooting distances. Mentioned analysis showed that formulas for determining types of weapon were precise in nearly 80% of cases.

DISCUSSION

Gunshot residue particles form during the discharge of a firearm. As the firing pin strikes the primer cap, the primer mixture is ignited, creating an environment of rapid temperature and pressure increases within the cartridge. This increase in temperature melts the primer mixture and within a few milliseconds the vaporization points of lead (Pb), barium (Ba), and antimony (Sb) are exceeded (Pb 1620/C, Ba 1140/C, Sb 1380/C). The effects of supersaturation cause vaporized particles to condense back onto the liquefied primer surface as droplets. There has been evidence to suggest that inorganic GSR particles of materials originating solely from the primer

TABLE 5. Kruskal-Wallis one way test in order to analyze differences in elements distribution depending on the shooting distances within the same type of weapon

Weapon		%Pb	%Cu	%Zn	%Ni	%Sb	%Ba
A	Chi-Square	7.586	3.103	7.491	0.463	1.876	8.691
	P	0.023	0.212	0.024	0.793	0.391	0.013
B	Chi-Square	6.251	8.316	1.829	1.325	8.264	1.280
	P	0.044	0.016	0.401	0.516	0.016	0.527
C	Chi-Square	1.220	2.060	9.780	4.371	9.420	4.348
	P	0.543	0.357	0.008	0.112	0.009	0.114
D	Chi-Square	3.892	8.240	9.980	9.512	9.740	8.325
	P	0.143	0.016	0.007	0.009	0.008	0.016

Legend: A (pistol, caliber 7,65x17mm), B (pistol, caliber 7,62x25mm), C (pistol, caliber 9x19mm), D (automatic rifle, caliber 7,62x39mm), Pb (lead), Cu (copper), Zn (zinc), Ni (nickel), Sb (antimony), Ba (barium)

TABLE 6. Cutt-off points for different shooting distances

Distance	Result for discriminant function (cutt-off discriminant score)
Contact	≤ (-0.484)
5 cm	(-0.485) – 0.575
10 cm	≥ 0.576

(primer GSR) are formed even before the propellant is ignited. As the primer mix ignites the propellant powder, a second rapid increase in pressure and temperature occurs and the bullet is expelled from the firearm barrel. During this process, the particles involved are subjected to extreme temperature and pressure is followed by rapid cooling. Particles form as liquid droplets, which subsequently solidify (11).

The areas from which GSR may be collected are wide ranging. Skin, vehicles (seats and seat backs, doors, windows, dashboards, headliners, interiors, and exteriors), the surroundings of an incident, doors, windows, body parts, clothing, and any surfaces in the immediate vicinity of a firearm discharge may all be sample targets (11). We analyzed these components in gunshot entrance wound.

When the reconstruction of gunshot fatalities is in question, the macroscopic examination of gunshot wounds as well as the investigation of GSR particles gains extensive forensic significance (1). Gunshot analysis has been widely studied in the forensic literature for the estimation of the firing range and in the last decades a lot of techniques have been used for the detection and identification of GSR particles in the gunshot wound (11). These experiments have clarified that the amount is strictly correlated to the shooting distance (2, 12, 13). There are many histochemistry (12-15) studies and electron microscopy methods who are accurate and precise for estimating firing distance (16,17). However, most of these studies, if not all of them, are not applicable in every day forensic work, mostly due to their cost, as well as a necessity for sophisticated and expensive equipment.

A lot of different methods in GSR analyzing have been used (3,11), but only a few of them dealt with analyzing gunshot wounds. In one of them, gunshot wounds from previously amputated human parts, both normal and charred, were used in analysis with micro CT, and the conclusion was that this analysis could provide the differential diagnosis between gunshot and sharp force wounds, entry and exit holes (1, 2) artefacts and gunshot lesions. In another study by the same authors, micro CT analysis was conducted on fresh and decomposed gunshot wounds, suggesting it could be useful screening tool for differentiating entrance from exit wounds (18). Other authors analyzed GSR in gunshot wounds using confocal laser scanning microscopy (13), or radiochemical neutron activation analysis (19). Regardless of the good results of these studies in analyzing gunshot wounds, these types of methods and devices (such as micro CT, confocal laser scanning microscopy, neutron activation analysis etc.) are often neither accessible, nor affordable in everyday forensic practice.

In practical work different difficulties and controversies may arise in forensic evaluation of gunshot wounds, which may include estimation of calibre, shooting distance, and sometimes even estimation of whether the wound is entrance or exit may be difficult. Our presented method in GSR analysis – atomic absorber spectrophotometry (AAS) in the close range entrance gunshot wounds could bridge these difficulties. This method is easily available, relatively cheap and practicable. In the case where

we have small samples and differences in elements distributions which were depending of type of weapon within the same shooting distances, we can use discriminant functions. It could provide help in determining the type of weapon (of four different weapons in our study) with relatively good precision (nearly 80%, or in 4 out of 5 cases). This gives rise to the possible weakness of our study, since we have examined for the most commonly used weapons in the Balkans' region. In other regions and parts of the world, the other types of weapons are possibly used, which could be the possible subject for some future studies. Although all the examined cases were in close range shots (contact, 5 cm, 10 cm). This method could be helpful in determining whether the gunshot wound is contact or near contact, even though with slightly lesser precision (nearly 60%, or in 3 out of 5 cases).

This analysis could be especially useful in cases where for some reason it is not easy to determine whether the gunshot wound is entrance or exit. One of such situations could be in cases of postmortally putrefied bodies. Putrefaction changes will eventually dissolve all of the body's soft tissues and organs, to an extent that even makes them unrecognizable (19). However, inorganic materials such as examined metals (lead, copper, zinc, nickel, antimony and barium) remain unchanged and therefore they could be further analyzed, regardless of the putrefaction changes. This could be particularly useful in cases where missile trajectory only involves only soft tissue. Another possible application of this method could be in charred bodies with gunshot injuries, or even in some cases in fresh bodies when it's not easy to macroscopically differentiate entrance from exit wound.

CONCLUSION

The presented study showed that chemical analysis of GSR in entrance wound with atomic absorber spectrophotometry could be useful in determining the type of weapon, as well as the shooting distance, i.e. in our study, suggesting whether the wound is contact or near contact. This could be particularly useful in postmortally putrefied or charred bodies with gunshot wounds. The limitation of this survey is that it is based on most commonly used weapons in the Balkans' region, and therefore its applicability to other regions must be taken cautiously, also another limitation of the study, is small sample, but we think this could be a subject for the future studies.

COMPETING INTERESTS

The authors declare no conflict of interest.

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