

Evaluation of persistence of gunshot residue (GSR) using graphite furnace atomic absorption spectrometry (GFAAS) method

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In this study, the contents of Sb, Pb, and Ba in GSR collected simultaneously from the hands and clothes of the shooter and the barrel of the firearm, were determined by GFAAS in order to determine the time-dependent persistence of GSR. The most intensive GSR was found in the samples collected from the hands of the shooter, and it was observed that the persistence of GSR is longer on the barrel of firearms since this area is less prone to the effects of environmental conditions. Therefore, we were able to analyze the gunshot residues deposited on the barrel of the firearm in a longer time interval. The average half-time of the GSR particles obtained from the hands and clothes of the shooter was found to be one hour. The importance of the time factor in collecting the samples is evident from the findings. The density of the GSR detected varies depending on the type of ammunition used. Although the density of the GSR collected from the hands and clothes of the shooter depends on the type of firearm, it is evident that the surface and environmental factors are very important for the persistence of residues collected.

Keywords: Forensic Sciences, Firearm Investigation, Gunshot Residues.

INTRODUCTION

In forensic science, chemical analysis has gained importance in recent decades [1]. Identifying trace elements in gunshot residues (GSR) provides useful information helping to find the suspect and the victim. The primers of cartridges used in firearms contain lead styphnate, barium nitrate, and antimony trisulfate [2]. When a weapon is fired, the heat and pressure lead to the deposition of residual organic and inorganic substances in the gunpowder and shot shell. In addition, to reveal the shooter, firearm, and ammunition and to obtain other useful information about the shot fired, gunshot residue (GSR) analysis should be performed. There are detailed studies on the detection, identification, and analysis of the firearms that left inorganic GSR [2]. Atomic absorption spectrometry (AAS) is a common method for the analysis of trace elements [3-6]. The morphological and elemental characteristics of the GSR of the fired firearms can be analyzed using scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDS) imaging techniques [7]. Analysis of the residue of the products attributable to the explosion of the shots is of great importance [6-12] to determine whether the person in question has fired a shot with that firearm [12, 13].

All of these particles can also contain abundant or trace amounts of elements such as aluminum, calcium, sulfur, and silicon; trace amounts of

chlorine, copper, iron, potassium, and zinc, as well as traces of magnesium, sodium, and phosphorus [13]. In the last three decades, the lead-free, heavy-metal-free, pollutant-reduced, or even low-emission primers are trending. The conventional pyro-system is now being replaced by “environmentally compatible” components, due to concerns about the health of shooters that contact the vapors of GSR in daily work [14]. When a firearm is fired, a cloud of various substances, which are called GSRs, leaves the muzzle along with the bullet. These particles are deposited mostly on the hands, clothes, and hair of the shooter, and on the barrel of the firearm [15]. These findings can be used to reveal the suspect and the details of the incident. If performed and interpreted correctly, such analyses distinguish between homicide and suicide [16]. In studies carried out to date, the focus was on the collection of GSR from the hand of the shooter immediately after shooting [14]. As a result of many years of experience, it was observed that GSR can be detected on the clothes and hair of the shooter after some time following the incident, despite the negative GSR-detection results in the samples collected from hands [17]. In their study conducted in 2008, Rosenberg and Dockery showed that GSR could be detected on the hands of shooters up to nine days later, according to measurements made at one-day intervals [18]. However, in practice, the swab samples are collected from the suspect a few hours after the incident.

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The purpose of this study is to investigate the time-dependent permanence of GSR traces obtained from three different forms of ammunition used with two different brands of pistols. This information can contribute to the routine GSR examination.

EXPERIMENTAL

Gunshot experiments

A Smith-Wesson (S&W) brand revolver and a semi-automatic Glock 17 brand pistol were used with proper Machine Chemistry Institute (MKE), Czech Republic Sellier and Bellot (S&B), and Germany (Geco) brand full-metal-jacket ammunition. GSR samples were collected from the right hand of the shooter, from a 10×10 cm area on the right sleeve of the shooter and from the interior of the barrel of the firearm used, in order to determine the time-dependent change of the persistence of GSR. All ammunition used had conventional lead-, antimony-, and barium-based primers.

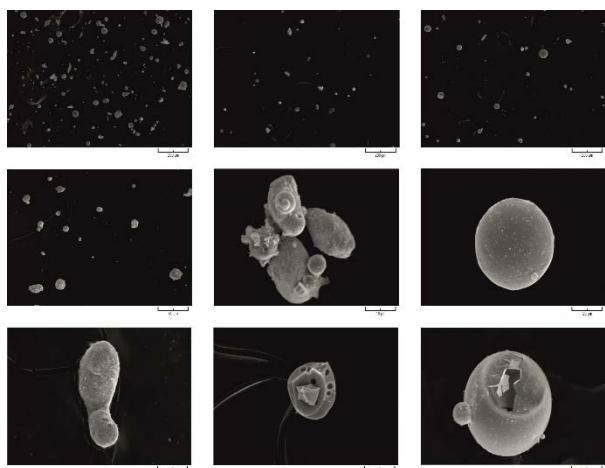


Fig.1. Backscattered electron images of chosen examples of GSR.

Each test shot took place in an indoor firing range after turning off the flow-through ventilation. Air circulation was minimal. The firearms and ammunition are listed in Table 1.

A standard solution of 5% nitric acid was prepared by diluting a 1000 mg/l stock standard solution of 50 ml, and the barrel was rinsed with this solution to obtain a solution of GSR [19]. The samples were collected immediately after each shot from the shooter's right hand and right sleeve on aluminum stubs using double-sided adhesive tape. GSR was collected by pressing the stub for 100 times to the hand skin including thumb and index finger of the right hand and the right sleeve of the shooter. To prevent any accidental contamination, the shooters did not collect any samples. For the same reason, the residues were collected by only one person, and analyzed under the same strict conditions.

Samples were collected by using different carbon tapes for each measurement, and after putting them into sterile sampling containers, 5 ml of 5% nitric acid solution was added to the containers and allowed to stay for 24 h after centrifuging for 2 h. The related samples were transferred to 5 ml vessels made for the GFAAS device. The control samples were collected from clean barrels, empty carbon tapes, empty tubes, and target areas after applying cleaning procedures.

Apparatus

A Varian (Australia) electrothermal atomic absorption spectrometer model SpectrAA 240Z equipped with a Zeeman background correction system, a thermal graphite atomizer (TGA-120), and an autosampler (PSD-120), was utilized for the determination of analytes. Integrated mode was used for the absorbance measurements throughout the studies. An antimony hollow cathode lamp (Varian), a multi-element (Co-Mo-Pb-Zn) hollow cathode lamp (Varian), and an electrothermal atomizer were used for the determination of Sb and Pb under the conditions suggested by the manufacturer. The wavelength, lamp current, and slit width were 217.6 nm, 10 mA, and 0.2 nm for Sb and 217.0 nm, 10 mA, and 1.0 nm for Pb. A Varian AA240FS was used for Ba in atomic emission (AES) mode under the conditions suggested by the manufacturer. The wavelength, slit width, and acetylene flow rate were 553.6 nm, 0.2 nm, and 2.15 L/min.

Table 1. Pistol and cartridge mark list.

Pistol Mark	Smith&Wesson			Glock 17		
Cartridge	MKE	Geco	S&B	MKE	Geco	S&B
Caliber	38 special	38 special	38 special	9 mm	9 mm	9 mm

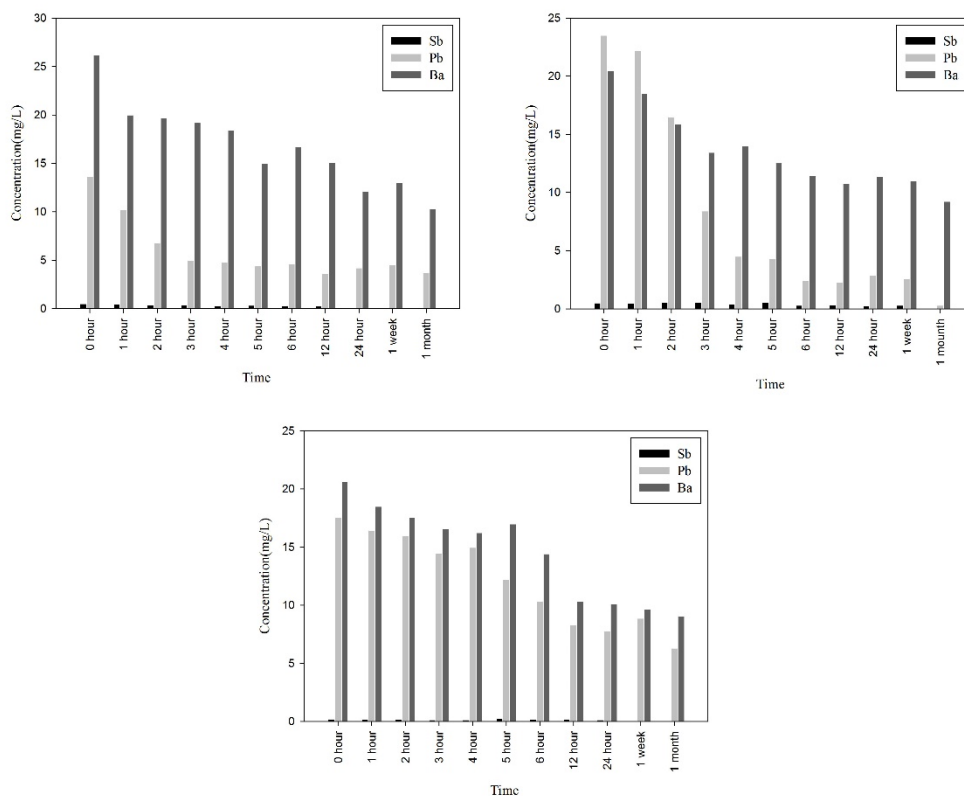


Fig. 2. Time-dependent change of the persistence of GSR particles deposited on the barrel of the S&W brand revolver for a) MKE b) Geco c) S&B brand 38 special caliber cartridges.

RESULTS AND DISCUSSION

Time-dependent amount of particles

The formation of GSR particles is a very dynamic and complex process. This process can involve numerous metal particles [20]. All of these particles can also contain abundant or trace amounts of elements such as aluminum, calcium, sulfur and silicon; trace amounts of chlorine, copper, iron, potassium, and zinc; as well as traces of magnesium, sodium, and phosphorus [15]. Quantitative analysis of antimony (Sb), barium (Ba), and lead (Pb), which are the major elemental components of most of the cartridge primers, performed on the GSR collected from the hands of a suspect, provides valuable data to be used for associating the suspect with recently discharged or contaminated firearms, or with an ammunition component. Therefore, Sb, Pb, and Ba present in the ammunition analyzed were preferred in detecting the traces of GSR. The most important factor in determining the persistence of GSR is the collection of GSR particles in a quality and steady manner. Therefore, swabs should be simultaneously taken from the same areas of the only shooter to minimize the variables, and the GSR collection method should be completely consistent.

The time-dependent persistence of the amount of

Sb, Pb, and Ba obtained from the GSR collected from the hands and clothes of the shooter, and the barrel of the firearm used is shown in figures 2-7. Naturally, GSR deposition is denser in the barrel of firearms, and it was observed that the amount deposited on the right hand of the shooter was higher than the amount collected from the clothes of the shooter.

Although the GSR density occurring after firing shots depends on the type of ammunition used, the dispersion of the particles into the environment after the explosion varied according to the type of firearm used. It is shown in figures 2-7 that the amount of particles formed significantly decreases as the distance from the barrel increases.

In Figure 2, time-dependent changes of the persistence of Sb, Pb, and Ba obtained from the particles deposited on the barrel of the S&W brand revolver were examined up to one month later. It was observed that GSR particles can be detected even after one month, since the interior of the firearm's barrel is the least affected part by environmental conditions. Of the three elements examined, the amount of Sb was found to be lower than the amounts of Pb and Ba, and its persistence was minimal. The amount of Ba was found to be significantly higher in GSR obtained from the MKE brand cartridges. In addition, they have the minimum

amount of Pb compared to other types of ammunition. Additionally, the amount of GSR particles deposited in the S&W brand revolver is expected to be lower since it has a shorter barrel than the Glock 17 brand pistol because of the design of the revolver.

In Figure 3, the time-dependent change of the persistence of Sb, Pb, and Ba obtained from the particles deposited on the barrel of the Glock 17 brand pistol were examined up to 1 month at various intervals. Although the amount of GSR deposited is approximately two times higher in a Glock 17 brand pistol due to its longer barrel in comparison with the S&W brand revolver, these two firearms had similar time-dependent persistence of GSR change.

In Figure 4, the time-dependent change of the persistence of Sb, Pb, and Ba obtained from the GSR particles collected from the right hand of the shooter after firing shots with the S&W brand revolver, examined in the range of 0-5 h, is shown. The amount of GSR dispersed was higher after the explosion in the S&W brand revolver due to the effective ballistic power of revolver ammunition and the design of the revolver [21]. Thus, the amount deposited on the hands of the shooter was higher

using a S&W brand revolver. The amount of Pb was found to be lower in GSR obtained from the MKE brand ammunition compared to other types of ammunition. GSR was detected on the hands of the shooter up to the fifth hour.

In Figure 5, the persistence of the amount of Sb, Pb, and Ba obtained from the GSR particles collected from the right hand of the shooter, using Glock 17 brand pistol, examined in the range of 0-5 h, is shown. It was observed that the amount of GSR deposited on the hands of the shooter was significantly lower compared to a revolver. This may be caused by the design of the revolver and the effective ballistic power of the ammunition used [21]. The amount of GSR collected from the shooter was maximum when the MKE brand ammunition was used.

In Figure 6, the persistence of the GSR deposited on the clothes of the shooter, using a S&W brand revolver, examined in the range of 0-5 h, is shown. Taking swabs from the shooter's clothing is a less preferred method than taking swabs from the hands of the shooter. However, GSR particles were found to stay longer on the shooter's clothes. This result is critical in evaluating cases.

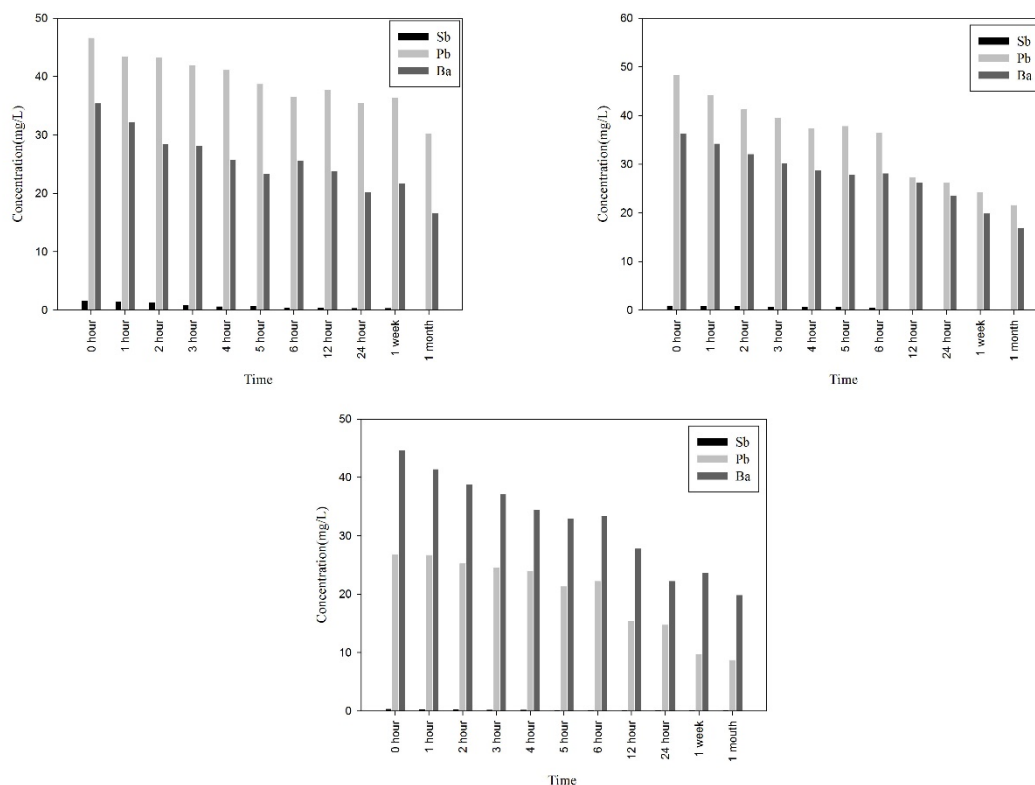


Fig. 3. Time-dependent change of the persistence of GSR particles deposited on the barrel of the Glock 17 brand pistol for a) MKE b) Geco c) S&B brand 9 mm cartridges.

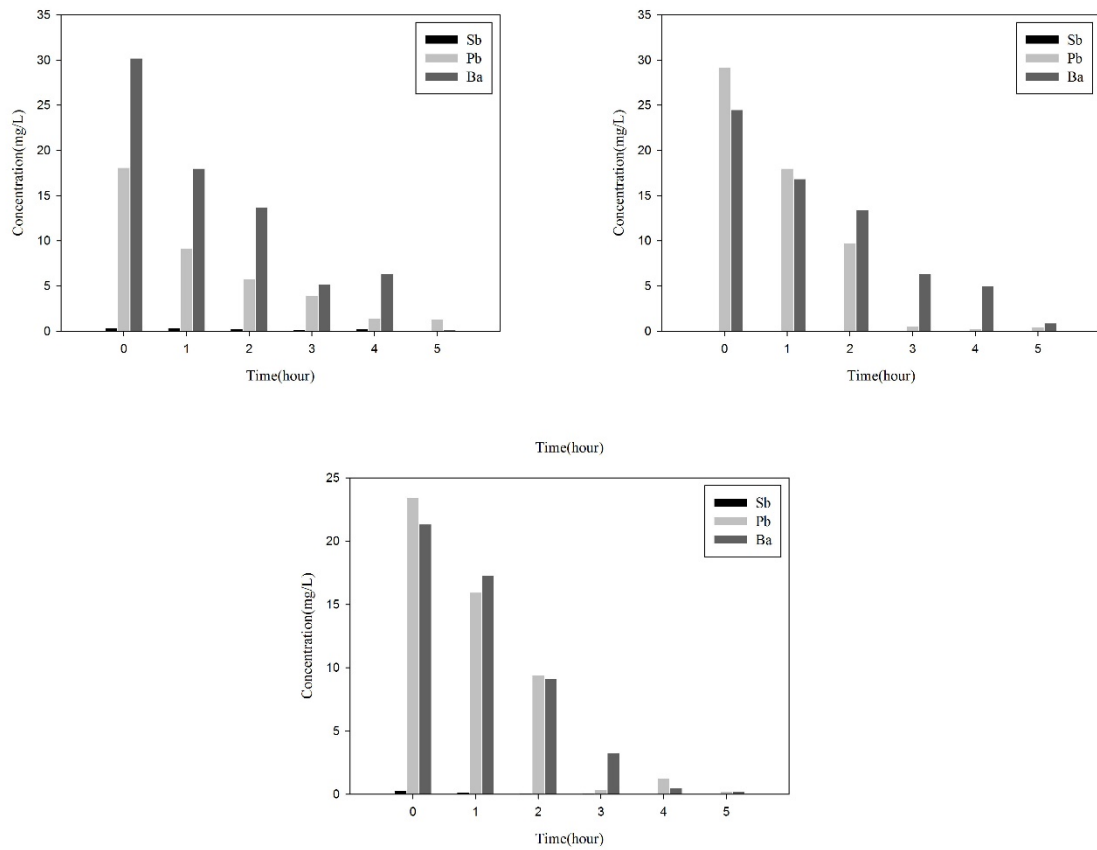


Fig. 4. Time-dependent change of persistence of GSR particles deposited on the hands of the shooter using S&W brand revolver for a) MKE b) Geco c) S&B brand 38 special caliber cartridges.

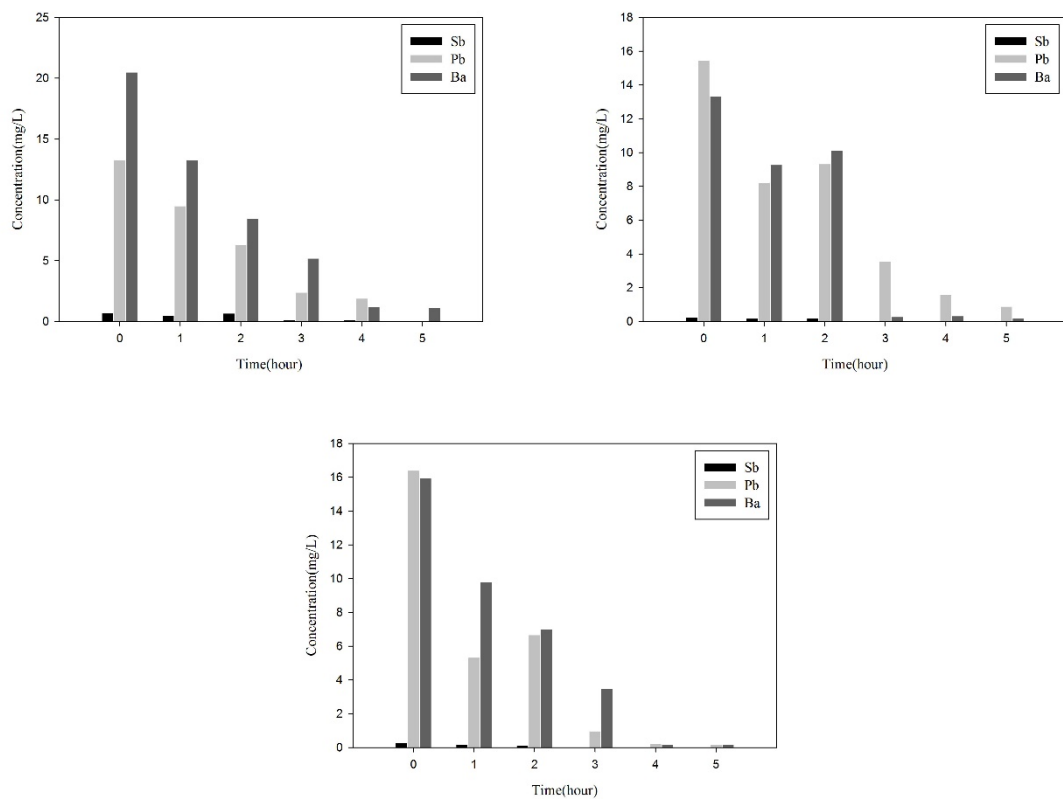


Fig. 5. Time-dependent change of persistence of GSR particles deposited on the hands of the shooter using Glock 17 brand pistol for a) MKE b) Geco c) S&B brand 9 mm cartridges.

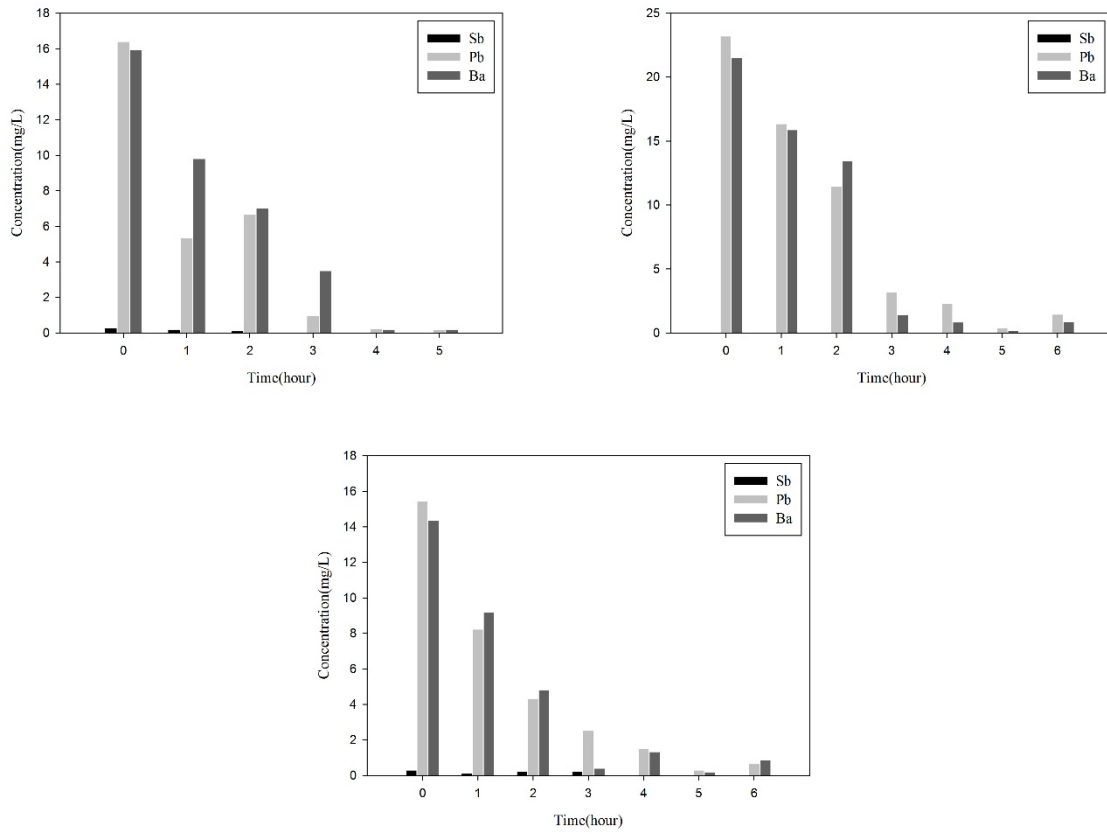


Fig. 6. Time-dependent change of persistence of GSR particles deposited on the right sleeve of the shooter using S&W brand revolver for a) MKE b) Geco c) S&B brand 38 special caliber cartridges.

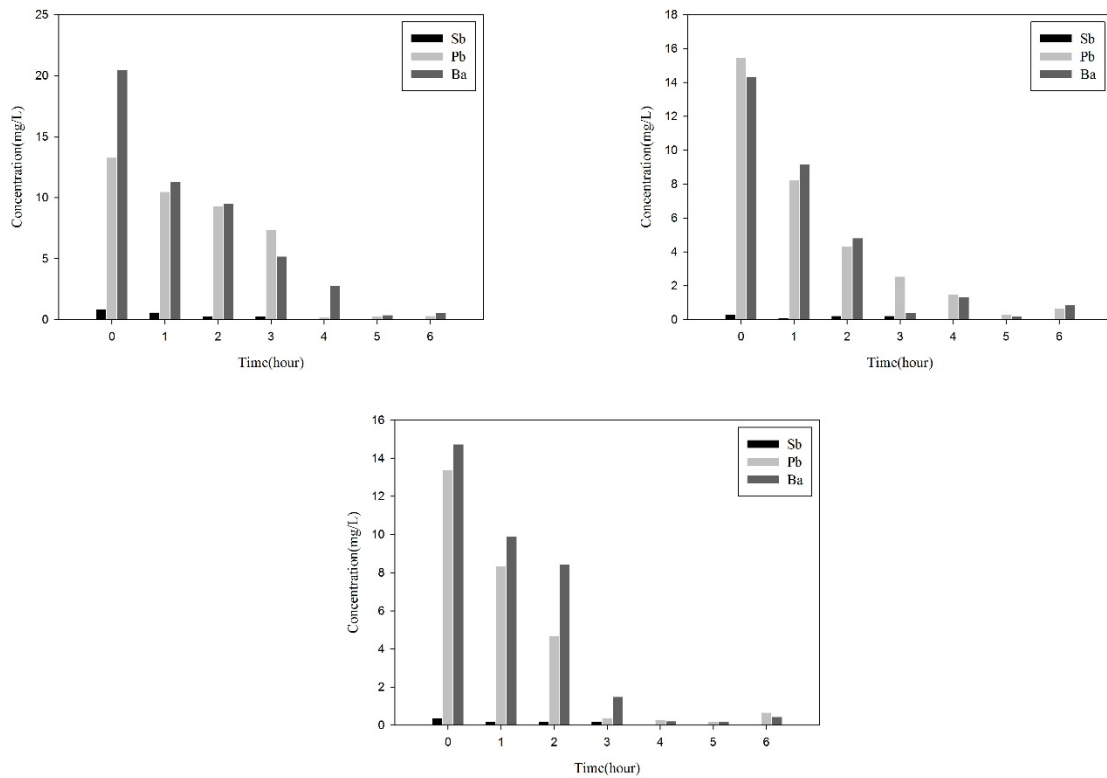


Fig. 7. Time-dependent change of persistence of GSR particles deposited on a 10x10 cm area on the right sleeve of the shooter using Glock 17 brand pistol for a) MKE b) Geco c) S&B brand 9 mm cartridges.

In Figure 7, the time-dependent persistence of GSR particles deposited on the clothes of the shooter using a Glock 17 brand pistol, examined in the range of 0-6 h, is shown. Although the GSR density was lower than that obtained with a S&W revolver, it was observed that the GSR particles could be detected up to the sixth hour later.

The persistence of GSR was found to decrease quickly after firing shots, and it was also observed that it can be detected on the hands of the shooter up to five hours later; whereas from the clothes of the shooter it can be detected up to six hours later. Hence, taking swabs from the clothes and the hands of the shooter will be beneficial for justice providers in evaluating the incident.

CONCLUSIONS

While the persistence of GSR particles is higher in the firearms' barrel, they disappear first from the hands and clothes of the shooter with time. This can be caused by the GSR particles loosely bound to the surface of the hand compared to the surface of cloth, or by the daily activities of the shooter affecting the particles on the surface of the hand. The intensity of GSR particles that occurred as a result of the explosion is highly dependent on the type of ammunition used. The intensity of GSR particles dispersed in the environment varies depending on the type of firearm. Since the barrels of firearms are less affected by the environmental conditions, the GSR particles on the barrel can be detected for a longer time. This result showed that the environmental conditions are very effective on the GSR.

This study can be considered as a recommendation for justice providers. In the detection of GSR, the type of firearm used in the incident and ammunition types were also found to be of significance. Taking swabs from the clothes and the hands of the shooter was found to be potentially advantageous. These analytical data will be beneficial in practice.

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ОЦЕНЯВАНЕ НА ТРАЙНОСТТА НА ОСТАТЪЦИ ОТ ИЗСТРЕЛИ (GSR) С АТОМНО-АБСОРБЦИОННА СПЕКТРОФОТОМЕТРИЯ В ГРАФИТНА ПЕЩ (GFAAS)

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(Резюме)

В тази работа се изследва съдържанието на някои елементи (Sb, Pb и Ba) в остатъците от изстрели (GSR), събрани едновременно от ръцете и дрехите на стрелеца и от цевта на оръжието по метода GFAAS и трайността на замърсяването от остатъка (GSR). Най-интензивно замърсяване (GSR) се забелязва в пробите, взети от ръцете на стрелеца и се установява, че трайността на замърсяването е по-голяма по цевта на оръжието, тъй като тя е по-малко изложена на околна въздействие. Средното полу-време на трайност на остатъците по ръцете и дрехите на стрелеца е един час. От това се установява значението на момента на пробовзимането, Плътността на откритите GSR варира според използваните амуниции и типа на оръжието. Въпреки това се установява, че повърхността и околната среда са важни за трайността на взиманите проби.