

Chemical analysis of components in burned and unburned propellant powders

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After firing a shot, gunshot residue (GSR) compounds containing burned and partially unburned particles are dispersed in the environment. The partially unburned GSR compounds contain elements that are ready to explode in appropriate circumstances. This can lead to serious safety problems, especially in indoor shooting ranges. In this study, the GSR compounds collected from Machine Chemistry Institute brand 9×19 mm parabellum shells were analyzed using gas chromatography/mass spectrometry (GC-MS) method. As a result of the analysis, nitroglycerin, dimethyl phthalate, 2,4-dinitrotoluene, diphenylamine, n-diphenylamine, trimethyl, 2,4-methypropyl and dibutyl phthalate compounds were detected in the GSR compounds. The changes in the amounts of these compounds depending on the number of shots were discussed.

Keywords: Chemical analysis, Gas chromatography-mass spectrometry (GC-MS), Propellant powder, GSR (Gunshot residue).

INTRODUCTION

When a firearm is used, gunshot residues (GSR) are formed following the combustion that takes place inside the chamber, and these residues spread into the gun, especially in the vicinity of the firing bed. Some of them exit the barrel and disperse in burned and partially unburned form [1,2]. GSR analysis is one of the most important tests in forensic sciences [3,4]. This analysis is of great importance in identifying the shooter, as well as for clarification of the origin (i.e., suicide, murder, accident) of the incidence [5].

The shooting range is widely used in comparison with suspect firearms in forensic investigations, in sports, military or police training [6,7]. As a result of the intense shooting, GSR compounds spread in the environment. The scattered GSR compounds contain elements that are ready to explode in appropriate circumstances [8-10]. Unless necessary measures are taken, there may be accidents that can cause death, especially in indoor shooting ranges.

The GC-MS method is a technique used in GSR analysis since it yields robust results with high sensitivity and authenticity for the appropriate analyte classes (Fig. 1). Inorganic and organic gunshot residues (Table 1) were analyzed in the studies carried out with the methods of liquid or gas chromatography [11,12].

The objective of this study was to use GC-MS method to investigate the change in amounts of GSR compounds identified after firing MKE brand

9×19 mm parabellum, depending on the number of shots.

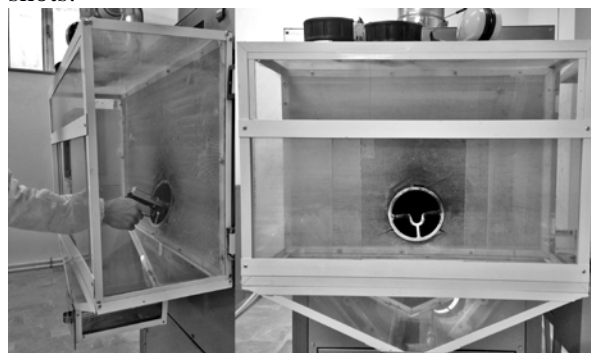


Fig. 1. The shooting tank and its front chamber.

EXPERIMENTAL

Samples

This experimental study was carried out at the directorate department of the Ankara Criminal Police Laboratory (in Turkish: KPL). All of the tests were carried out in the KPL shooting room. In test shooting, we used a Sarsilmaz brand Mega 2000 Kilinc model semi-automatic 9×19 mm parabellum pistol {Machine Chemistry Institute (MKE)} with a 2010 gun cartridge. Propellant powders from one ammunition type [9×19 mm parabellum type MKE brand cartridge were of 38% lead styphnate (TNR Pb), 6% tetracene (TRZN), 34% barium nitrate Ba(NO₃), 15% antimony sulfide Sb₂S₃, 4% pentrite (PETN), and 3% aluminum powder [4], full metal jacket (Turkey)} were supplied by the Turkish National Police.

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Table 1. Characteristic organic and inorganic gunshot residue components.

Compound	Abbreviation	Usage
Resorcinol	Rs	Stabilizer
2,4-Dinitrotoluene	24-DNT Flash	inhibitor
2,6-Dinitrotoluene	26-DNT Flash	inhibitor
2,3-Dinitrotoluene	23-DNT Flash	inhibitor
Dimethyl phthalate	MF	Plasticizer
Diethyl phthalate	EF	Plasticizer
Dibutyl phthalate	BF	Plasticizer
Diphenylamine	DPA	Stabilizer
Methyl centralite	MC	Stabilizer
Ethyl centralite	EC	Stabilizer
Antimony	Sb	Fuel
Calcium	Ca	Fuel
Magnesium	Mg	Fuel
Aluminum	Al	Fuel
Nickel	Ni	Bullet material
Zinc	Zn	Bullet material
Copper	Cu	Bullet material
Iron	Fe	Bullet material
Barium	Ba	Oxidizing agent
Lead	Pb	Explosive (lead styphnate)

The chemical compounds of gunshot residues in this list do not represent a comprehensive study [5].

Sample preparation

In the experiment, the barrel of the firearm was cleaned before firing each shot.

The cleaning process began with mechanical cleaning. Then, the barrel was washed in deionized water in an ultrasonic bath. Finally, the barrel was dried with dry nitrogen gas. Before applying the method to real samples, it was necessary to find the best sampling conditions. GSR compounds scattered around after firing were collected by a paper screening (by coating the inside) placed in the front chamber of the shooting tank (Fig. 1). The samples were collected under the same conditions since the physical conditions and method of collection may have an effect on the sampling procedure.

RESULTS

Sample analysis and chromatographic conditions

The samples were dissolved in 25 ml of acetone and were mixed with a vortex mixer for 30 min. Each was filtered with a syringe and 0.45 µm nylon

filter. The results were analyzed using an AOC-20i auto-sampler and chromatograph interfaced to a mass spectrometer (Model: QP2010 PLUS Shimadzu, Japan).

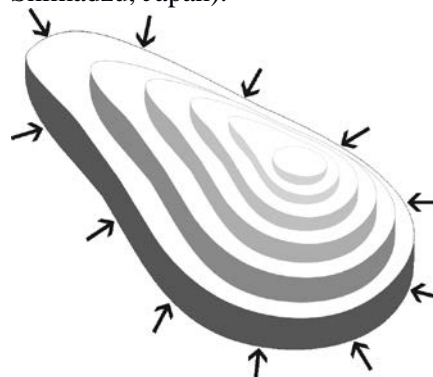


Fig. 2. Gunpowder particle, emerged layers, and combustion process.

The instrument was equipped with a VF 5 ms fused silica capillary column of 30 m length, 0.25 mm diameter and 0.25 µm film thickness. The temperatures employed were: column oven temperature 70°C, injection temperature 170°C, pressure of 108.0 kPa, with total flow and column flow of 6.20 ml/min and 1.15 ml/min, respectively.

The linear velocity was 46.3 cm/sec and the purge flow was 3.0 ml/min. The GC ion source and interface temperature were 150°C and 290°C, respectively with solvent cut time of 3.50 min. The MS program starting time was 3.00 min, which ended at 30.0 min with event time of 0.50 sec, scan speed of 1666 μ l/sec, scan range 40-8 00 u (split ratio 10:1). The total running time of GC-MS was 30 min. The relative percentage of the extract was expressed as a percentage with peak area normalization.

DISCUSSION

Each explosive can be burned by using processed gunpowder and a sufficient amount of oxygen molecules. The energy required for combustion is initially provided externally (spark or flame), and combustion is maintained as it reaches to layers of gunpowder. Gunpowder particles burn starting from the outer surface inward in parallel layers (Fig. 2) [4].

The powder gases formed during the combustion process increase continuously with rising temperature, pressure, and combustion speed [4,13]. The pressure wave, which occurs as a result of the energy released during this event, causes disintegration of explosives at a constant rate [6]. This pressure wave can be obtained by impact or friction; hence, cartridges include a primer capsule to achieve this. If the primer capsule or firing pin's hit is weak, then the pressure wave will not be sufficient to achieve complete combustion (causing unburned particles).

To achieve complete combustion, the average kinetic energy resulted from the pressure wave caused by the collision of molecules should be greater than the critical energy required for the breakdown of the molecules. Accordingly, mechanical effects, in addition to thermal effects of the gases, also play a major role in combustion. Here, these two factors prepare the necessary environment for detonation and provide the required activation energy.

As the manufacture of gunpowder progressed, it was observed that the main part of the gunpowder, which consists of cellulose, glycerin, and nitrates, lost its characteristics as a result of successive solving, evaporation, drying, hot pressing, and final forming processes, and it was concluded that it would be possible to eliminate these problems with various agents. In addition, the lowest priced gunpowder is preferred, which complies with the production specifications. These products burn quickly and pollute internal parts of the gun as well as the environment [1].

The combustion rates of gunpowder vary by ammunition brand. However, no gunpowder burns completely [14]. Partially unburned GSR compounds can be detected correctly by using GS-MS method with high precision (Fig. 3).

In Figure 3, the mean peak areas of the GSR compounds obtained from MKE brand 9 \times 19 mm parabellum indicate nitroglycerin, dimethyl phthalate, 2,4-dinitrotoluene, diphenylamine, n-diphenylamine, trimethyl, 2,4 methypropyl, and dibutyl phthalate compounds. Although these compounds are unique to the selected type of ammunition, they are consistent with Table 1. The change in the amount of the detected compounds depending on the number of shots was investigated. Therefore, the GSR samples were collected after firing 10, 50, and 100 shots. The results found were combined in a single graphic to compare, as shown in Figure 3. As can be seen, peaks of all compounds increase with increasing number of shots.

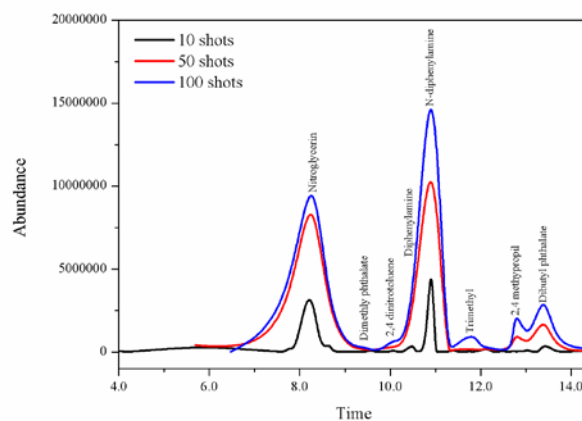


Fig. 3. Changes in the amounts of GSR compounds obtained from MKE brand 9 \times 19 mm parabellum for 10, 50, and 100 shots, according to GC-MS analysis.

CONCLUSIONS

The gas chromatographic (GC-MS) technique selected for interpreting the GSR compounds formed after firing shots is very suitable to analyze different properties, compared to other methods. The selected MKE brand cartridges have contaminated the shooter's firearm and surroundings extremely. In the examination of these GSR compounds, it was observed that they contain elements that are ready to explode in appropriate conditions. The amount of these compounds increased depending on the number of the shots fired.

This result leads to serious problems in the areas of intense shooting. Therefore, the area in front of the shooting range should be cleaned regularly, and unburned GSR compounds must be collected and

disposed to prevent possible accidents. As a rare contribution to the literature, this study shows the danger of compounds of gunshot residues formed after firing a shot according to type of cartridge selected; however, repeated studies are necessary utilizing more samples (employing a variety of cartridge brands).

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Химичен анализ на компонентите в изгорели и недоизгорели горивни прахове

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(Резюме)

След произвеждане на изстрел, остатъци от стрелбата (ОС), съдържащи изгорели и недоизгорели частици се разпръскват в околната среда. Частично недоизгорелите ОС съединения съдържат елементи, които са готови да експлодират при подходящи условия. Това може да доведе до сериозни проблеми с безопасността, особено при стрелба в затворени помещения. В настоящата статия, ОС съединения, събрани от гилзи от парабел тип 9×19 mm са анализирани чрез газова хроматография/маспектрометрия (GC-MS). От получените резултати следва, че ОС съединения съдържат нитроглицерин, диметилфталат, 2,4-динитротолуен, дифениламин, п-дифениламин, триметил-, 2,4-метилпропил- и дибутилфосфат. Дискутирани са промените в количествата на тези съединения в зависимост от броя изстрели.