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Characterization of Gunshot Residues by X-Ray Diffraction

REFERENCE: Tassa, M., Leist, Y., and Steinberg, M., **"Characterization of Gunshot Residues by X-Ray Diffraction,"** *Journal of Forensic Sciences,* JFSCA, Vol. 27, No. 3, July 1982, pp. 677–683.

ABSTRACT: The application of X-ray diffraction complemented by scanning electron microscopy and energy dispersive X-ray analysis to the characterization of gunshot residues is reported. Lead in the metallic form is found to be the main constituent of all gunshot residues tested. Several mechanisms are proposed to explain the appearance of lead in the metallic state as well as the formation of gunshot residues.

KEY WORDS: criminalistics, gunshot residues, X-ray diffraction, scanning electron microscopy, metallic lead, energy dispersive X-ray analysis, chemical analysis

The commonly used methods for detecting gunshot residue (GSR) in specimens obtained from the skin are scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDA) [*1*], neutron activation analysis [*2*], and atomic absorption spectrophotometry [*3,4*]. These methods, although very useful, cannot identify the compounds in such specimens. For example, while confirming the presence of lead, these methods cannot show whether it occurs in the metallic form, as lead oxide, or as lead sulfide. However, as the identification of such compounds may provide important clues to the origin of the residue and the physical and chemical processes by which it was formed, it is important to use a method that enables identification of compounds and not merely elements or ions.

Perusal of the relevant literature indicates that no comprehensive attempt to identify the compounds present in GSR has been reported. Wolten et al [*1*] and Wolten and Nesbitt [*5*] reported detecting the following compounds by limited X-ray diffraction (XRD) and high energy electron diffraction (HEED): barium *m*-antimonate, lead oxysulfate, graphite, metallic lead, lead sulfide, and antimony oxide. In the present study GSR derived from a large variety of weapons and ammunition fired under controlled laboratory conditions was examined by the powder X-ray diffraction method. All specimens were also analyzed by SEM-EDA.

Received for publication 13 Nov. 1981; accepted for publication 29 Dec. 1981.
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Experimental Methods

Instrumentation

Analyses were carried out with a microprocessor-controlled Diano 8000 instrument. A standard copper target tube (wavelength $\lambda = 0.15415$ nm) with a nickel filter was used. Several specimens were examined with a graphite monochromator. All analyses were carried out by the powder method, the diffractograms being registered on a recorder. The instrumental conditions are listed below:

Voltage	40 kV
Current	25 mA
Range	1000 counts/s
Time constant	2.5 s
Scan rate	1°/min
Chart speed	1 cm/min

For several specimens demanding better resolution, the scan rate was reduced to 0.2°/min.

Specimens were embedded in a thin film of petroleum jelly on a glass slide. Clean glass slides did not produce significant peaks but slides with pure petroleum jelly produced two minor peaks at $d = 4.13$ and 3.72, where d is grating space. The compounds were identified using the file of the Joint Committee on Powder Diffraction Standards [*6,7*] and confirmed by comparison with pure standard compounds run under identical conditions.

Elemental analysis of GSR was carried out with a CamScan 3-30 ADP SEM equipped with an Elscint Proxan 3 energy dispersive X-ray analyzer system with a Seforad Si(Li) solid state detector. The SEM is equipped with a backscattered electron detector [*8*], providing a contrast between particles composed of elements of different atomic numbers.

Specimen Collection

Residues were collected on two surfaces. For XRD analysis, a 45- by 30- by 1-mm glass slide covered with a thin film of petroleum jelly was used; the collecting surface analyzed by SEM-EDA was an adhesive tape attached to an aluminum disk (stub).

Primer Shots—The bullet and gunpowder were removed from the cartridge case and test shots performed as follows. The barrel of the weapon was positioned at a distance of 10 to 20 cm from the glass slide. Four to twelve test shots were made onto each slide subjected to XRD analysis. Eleven types of primers were examined by this method. For most of the SEM-EDA specimens, one primer shot was made on each stub.

GSR Emitted from Barrel—A 15- by 25-cm Perspex® board with a 6-cm-diameter hole at its center was mounted in a special holder. Shots were fired with the barrel positioned 20 to 40 cm from the hole (Fig. 1). After the firing, the GSR emitted from the barrel adhered to the area surrounding the hole, which had been covered in advance with a film of petroleum jelly. The GSR was transferred from the margins of the hole to a glass slide. Between 8 and 25 test shots were made for each specimen.

GSR Emitted from Breech—The bottom of a plastic bag was removed to produce a sleeve. The sleeve, internally covered with a thin film of petroleum jelly, was attached to the weapon in such a way that the barrel protruded from it. Residue emitted from the rear sections of the weapon during firing accumulated on the internal parts of the plastic sleeve. For each specimen 15 to 20 shots were fired. All residues were transferred to glass slides for examination by XRD. To evaluate the reproducibility of the results, duplicate test shot series were made for several types of ammunition (Tables 1 and 2). The residues were collected from the inside of the sleeves and mounted on stubs for SEM-EDA.

GSR Deposited on Shooter's Hands—Test shots with various types of weapons and am-

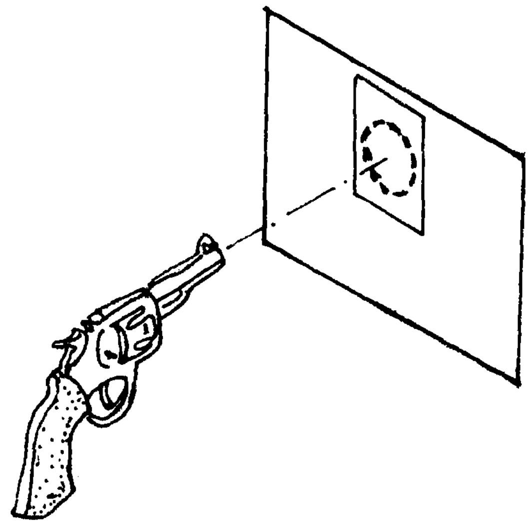

FIG. 1—*Collection of GSR emitted from the barrel on Perspex board (schematic).*

munition were carried out by laboratory personnel. The GSR from the shooter's hands was collected with adhesive stubs [*9*] several minutes after firing. The GSR specimens thus collected were coated with a conducting layer of graphite. Microanalysis was performed on dozens of particles on each stub.

Results

XRD and SEM-EDA data for eleven types of primer are listed in Table 1. Since manufacturers' data on primer compositions are not readily available, the probable constituents of the primers (not including such minor components as sensitizers and stabilizers) were deduced from the results. The XRD data indicate that metallic lead is present in the primer shots when lead compounds are a major primer constituent. In one case where such compounds were absent (7.62 mm E. Germany), lead was absent in the residues. In several cases lead also appeared in the divalent state as sulfide and oxide.

Several interesting compounds derived from the oxidizing agents and fuels appeared in primer shot residues. Antimony sulfide was reduced to metallic antimony, the sulfur sometimes combining with lead to form lead sulfide. Calcium silicide and barium nitrate formed the nonstoichiometric compound $Ba_{1.55}Ca_{0.45}SiO_4$. In two types of ammunition containing aluminum powder and barium nitrate, $BaAl_2O_4$ (barium aluminate) was identified in the residues (Fig. 2). Barium nitrate remained unchanged in the GSR of several types of ammunition, whereas potassium chlorate was converted to potassium chloride.

SEM-EDA revealed the presence of small particles ranging from 0.5 to 100 μm in diameter. The majority exhibited the spheroidal morphology typical of GSR particles.

The XRD data obtained for GSR emitted from the barrel are given in Table 2. These results indicate that the GSR contained large quantities of metallic lead (Fig. 3). When the bullet incorporated a copper-rich jacket or plate, metallic copper was also found in the residue. In one case potassium chloride, derived from potassium chlorate, was identified. SEM-EDA substantiated the XRD data and showed that the majority of particles contained a heterogeneous mixture of lead, copper, nickel, and brass originating from the bullet and the primer.

The composition of the residues emitted from the breech was similar to that obtained from

TABLE 1—*Data from XRD and SEM-EDA on GSR obtained from primer shots.*

Type of Ammunition and Weapon	Major Primer Compounds	Number of Shots	Elemental Composition (SEM-EDA)	Composition (XRD)
.22 long-rifle Eley semiautomatic pistol	lead styphnate, $Ba(NO_3)_2$	7	Pb, Ba	Pb, $Ba(No_3)_2$, PbO
.22 long-rifle Winchester Super X revolver	lead styphnate, $Ba(NO_3)_2$	10	Pb, Ba	Pb, $Ba(NO_3)_2$, Cu, PbO
5.56 mm, Winchester (USA) M-16 rifle	lead styphnate, $Ba(NO_3)_2$, Sb_2S_3, aluminum powder	7	Pb, Ba, Al, Sb	Pb, $BaAl_2O_4$, Sb, PbS[a]
6.35 mm, Hirtenberg semiautomatic pistol	lead styphnate, $Ba(NO_3)_2$, $CaSi_2$	9	Pb, Ba, Ca, Si	Pb, $Ba(NO_3)_2$, PbO[a]
7.62 mm NATO, FN[b] Mauser rifle	lead styphnate, $Ba(NO_3)_2$, Sb_2S_3, $CaSi_2$	8	Pb, Ba, Ca, Si, Sb	Pb, PbS, Sb, $Ba_{1.55}Ca_{0.45}SiO_4$
7.62 × 39 mm, AK-47 (E. Germany) ammunition	$KClO_3$, Sb_2S_3	6	S, Cl, K, Sb	KCl, Sb
7.62 mm NATO, FNM[c] (Portuguese) Mauser rifle	lead styphnate, $Ba(NO_3)_2$, Sb_2S_3, CaSi	4	Pb, Ba, Ca, Si, Sb	Pb, PbS, Sb $Ba_{1.55}Ca_{0.45}SiO_4$
7.65 mm, SBP[d] semiautomatic pistol	lead styphnate, $Ba(NO_3)_2$, $CaSi_2$, tin	7	Pb, Ba, Ca, Si, Sn	$Ba(NO_3)_2$, Sn, Pb, $Ba_{1.55}Ca_{0.45}SiO_4$
.38 Kynoch revolver	lead styphnate, $Ba(No_3)_2$, $CaSi_2$	5	Pb, Ba, Ca, Si	Pb, $Ba(NO_3)_2$, $Ba_{1.55}Ca_{0.45}SiO_4$
.38 Remington Peters revolver	lead styphnate, $Ba(NO_3)_2$, Sb_2S_3, aluminum powder	6	Pb, Ba, Al, Sb	Pb, $Ba(NO_3)_2$, $BaAl_2O_4$, PbS
9 mm, parabellum Israeli SMG[e]	lead compound, $KClO_3$, Sb_2S_3	12	Pb, Cl, K, Sb	Pb, KCl, PbS, Sb

[a]Two samples were analyzed.
[b]Fabrique Nationale.
[c]Fabrica Nationale Munitiones.
[d]Silleir Bellot Prague.
[e]Submachine gun.

the barrel. The residues deposited on shooters' hands, which were subjected only to SEM-EDA, were found to be similar to those identified in the GSR emitted from the barrel and the breech of the weapon.

Discussion and Conclusions

The results of this study can lead to the elucidation of GSR formation processes and may promote development of more effective methods of identification. X-ray diffraction revealed that lead in GSR appears mostly in the metallic form. Metallic copper appears only in ammunition incorporating copper-rich jackets or plating on the bullet. Because copper does not generally occur in primer residues, it can be concluded that the main source of copper in GSR is the bullet itself and not the cartridge case. The fact that lead occurs in the metallic

TABLE 2—*Analysis by XRD of GSR emitted at the barrel.*

Type of Ammunition and Weapon	Bullet Type	Number of Shots	Composition (XRD)
.22 long-rifle Eley semiautomatic pistol	lead	25	Pb
.22 long-rifle Winchester Super X revolver	lead with copper plate	15	Pb, Cu[a]
5.56 mm, Winchester (USA) M-16 rifle	lead with brass jacket	8	Pb, Cu
6.35 mm, Hirtenberg semiautomatic pistol	lead with copper and nickel jacket	20	Pb
7.65 mm, SBP[b] semiautomatic pistol	lead with copper and nickel jacket	15	Pb, Cu
.38 Kynoch (England) revolver	lead with brass jacket	10	Pb, Cu
9 mm, parabellum Israeli SMG[c]	lead with brass jacket	20	Pb, Cu, KCl[a]

[a]Two samples were analyzed.
[b]Silleir Bellot Prague.
[c]Submachine gun.

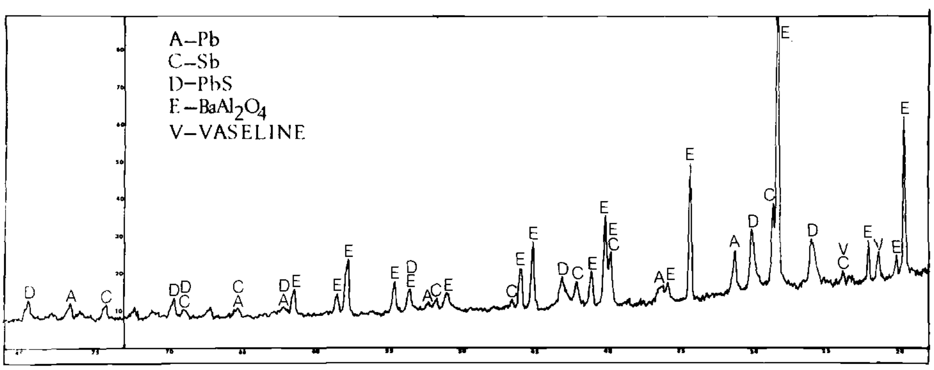

FIG. 2—*X-ray diffraction pattern of GSR obtained from primer shots of 5.56-mm Winchester ammunition.*

state probably accounts for the inefficiency of several methods in detecting lead on shooters' hands and around bullet holes. The occurrence of metallic lead and copper in GSR suggests that any dissolution methods used for these metals prior to an attempt at identification, for example, by spot tests, be altered. The presence of metallic lead in GSR can be explained by

(1) an oxygen-poor environment, which is substantiated by the presence of unburned powder articles [*10*] and of metallic antimony and metallic tin in primer residues;
(2) formation of a protective layer preventing oxidation [*11*]; and
(3) the relative stability of the lead-antimony alloys used in bullets [*12*].

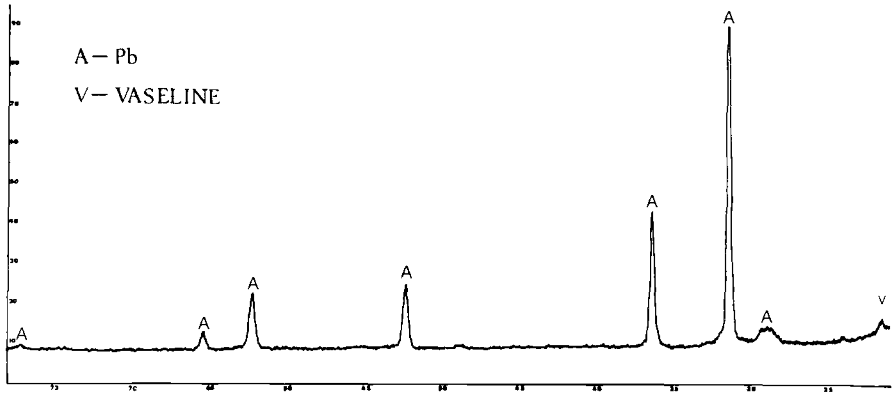

FIG. 3—*X-ray diffraction pattern of GSR emitted from the barrel of 0.22 long-range Eley.*

Barium nitrate appeared only in primer shot residues where barium nitrate was present as an oxidizing agent in the primer. This can be attributed to the low efficiency of the reactions in primer shots or to a slow rate of oxidation.

The presence of most of the compounds observed by X-ray diffraction in this study has not been reported previously [*1*, *5*]. Furthermore, some compounds mentioned in those reports were not detected in this study. However, it should be stressed that the limit of detection of the XRD method is about 2 to 4%. SEM-EDA shows that GSR emitted from the barrel and the breech of the weapon consist of small spheroidal particles derived mainly from the bullet but also from the primer. Thus, it can be concluded that, when a gun is fired and the bullet ejected, the residues are formed from a mixture of partially molten and vaporized materials, which are derived mainly from the bullet and the primer. These are the residues deposited on the shooters' hands and clothing.

The significant difference between the GSR formed by ordinary shots and by primer shots can be explained by the far higher temperature and pressure of the former, resulting in almost total combustion of the primer components. Another interesting phenomenon of GSR formation is the absence of crystalline organic compounds, which can also be attributed to the high temperature and pressure in the firing process.

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