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Antimony Enrichment on the Bullets' Surfaces and the Possibility of Finding It in Gunshot Residue (GSR) of the Ammunition Having Antimony-Free Primers*

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ABSTRACT: Projectiles of twenty brands of ammunition were examined by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX). In all of them antimony enrichment was found on the surface (about 10 μm depth or less) of the lead alloy as compared to the bulk. In some of the bullets the enrichment was high—as much as tens of times the bulk concentration. Concentration depth profiles in several of the projectiles were also studied by Auger electron spectroscopy (AES), and much higher concentrations of antimony on the surface than in the bulk were observed even where this effect could hardly be detected by SEM/EDX. Shooting tests were carried out using ammunition having antimony-free primers and in which the highest content of antimony on the surface of projectiles was observed. A very small percentage of gunshot residue particles containing antimony was found in these tests.

KEYWORDS: forensic science, gunshot residue, antimony enrichment, antimony-free primer

It has been stated that. ''To characterize a residue from a particular cartridge it is essential to start with a clean gun, or else residue from previous firings may be mixed with residue from the current firing. On several occasions, antimony-containing particles were found in test firings of .22 caliber ammunition whose primer did not contain antimony. The antimony was never in evidence if the gun was given a thorough cleaning prior to firing the antimony-free ammunition'' (1). In a later study by the same group it was claimed that conventional thorough cleaning of a handgun does not remove all residue and ''small percentages of particles that contain copper or antimony are observed fairly often in residue from cartridges that contain neither element'' (2). The presence of antimony-containing particles in similar circumstances was also reported by Wallace and McQuillan (3), without, however, specifying their abundance. Gunaratnam and Himberg (4) reported on finding ''mixed composition'' particles (5) containing lead and barium in addition to titanium and zinc after firing Sintox lead-free ammunition even though the revolver used in the study was thoroughly cleaned before test firing. Titanium and zinc are characteristic elements of the Sintox lead-free ammunition primer. Similar results were reported by Harris (6) in her study on primer residues from CCI Blazer lead-free ammunition. In this study not only ''mixed composition'' but three-element (lead, barium, and antimony) particles were found as well, and often in a greater number than strontium particles, strontium being the characteristic element of the CCI Blazer lead-free ammunition primer.

We have not found in the literature a study reporting on a phenomenon of a higher antimony concentration on the surface of bullets than in the bulk. On the contrary, as far as we know, in the only study concerning this matter which used neutron activation analysis (NAA), it was found that the concentration of antimony is uniform in various types of bullets (7).

The purpose of this work is twofold:

(*a*) To report on the observation of a higher concentration of antimony on the surface of bullets than in the bulk. The phenomenon was studied by scanning electron microscopy/energy-dispersive X-ray (SEM/EDX) and by Auger electron spectroscopy (AES).

(*b*) To study the possibility, of finding antimony and assessing its concentration in gunshot residue (GSR) particles originating particularly in the firing of ammunition having primers with lead and barium but antimony-free, and, having projectiles which have a considerably higher concentration of antimony on the surface than in the bulk.

The study started due to an investigation of a homicide. The particular importance of the answer to question (*b*) above pertains to the evidential point of view. Although particles containing lead, barium, and antimony are regarded as characteristic or unique to GSR, particles containing only lead and barium are considered to be merely consistent with GSR (1,3).

Case Examination—Experimental Procedure

At the scene of a homicide two cartridge cases of South Korean .22 caliber PMC Zapper high velocity hollow point ammunition were found. It was determined that the ammunition was fired by a Ruger 10/22 rifle, which had not been found. Samples of particles were collected from the bullet entrance holes in the victim by 12.5 mm (half-inch) aluminum stubs coated with a double-sided

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adhesive. The samples were examined using an automated search system attached to a CamScan IV SEM with a motorized stage drive combined with a Tracor Northern TN 5500 EDX system. An accelerating voltage of 25 kV was used in all the SEM/EDX examinations.

GSR particles from the cartridge cases found at the scene were sampled using wood sticks and then transferred to aluminum stubs which were analyzed by SEM/EDX manually using a CamScan III SEM combined with a Tracor Northern TN 5400 EDX system (5).

It was found that characteristic elements of the PMC Zapper primer are lead and barium without antimony. In a sample from one of the entrance holes in the victim most of the particles contained lead only. Some particles, however, contained lead and barium, among which about 20% also contained quite high concentrations of antimony (Fig. 1).

A reasonable explanation for such a percentage of three-element (lead, barium, and antimony) GSR particles in the homicide entrance hole would be the firing of three-element PMC Zapper primer ammunition without first a thorough cleaning of the weapon (1,2).

In this case, however, an alternative explanation should be considered: a contribution of antimony to GSR particles from the projectiles, since the SEM/EDX analysis of PMC Zapper projectiles showed that the surface concentration of antimony (under the copper plating) is much higher than its bulk concentration (Fig. 2). Note that although these projectiles have a copper plating, it is very thin and not uniform so that EDX spectra (accelerating voltage 25 kV) through the coating contain lead and antimony peaks. Furthermore, it was found that most of the copper plating on the bottom and in the area in contact with a cartridge case was removed during firing, thus exposing the lead core. Actually, even in unfired PMC Zapper bullets we found a considerable area of the projectiles' bottoms with exposed lead.

The analysis was carried out on unscraped and scraped (by scalpel) areas of projectiles, using standardless semiquantitative ZAF analysis (SSQ). The measured surface concentration of antimony was variable, in the range of 3% to 6% (weight percent) as compared to about 0.5% in the bulk.

These results prompted an examination of additional brands of bullets to study the possible effect of a high surface concentration of antimony in the projectiles on the composition of GSR particles.

SEM/EDX Analysis of Various Bullets and Shooting Experiments

In addition to .22 caliber PMC Zapper ammunition we examined by SEM/EDX other brands of ammunition, mainly of .22 caliber. The examined ammunition is listed in Table 1.

The chosen brands of 9 mm and .38 caliber ammunition had antimony-free primer. The method of analysis was the same as for the PMC bullets.

The highest surface concentrations of antimony were found in the .22 caliber PMC Zapper. Peters High Velocity (HV) and RWS, as well as in .38 caliber S&W Hirtenberg projectiles. Therefore, shooting experiments for the examination of antimony content in the GSR particles were carried out only with the projectiles of these ammunitions.

However, to obtain a combination of lead and barium as characteristic elements in a primer, and a projectile having high surface concentration of antimony (like in the PMC Zapper ammunition), it was necessary to change the primers for Peters and RWS. This was done because the characteristic element of the Peters primer is lead only and the characteristic elements of RWS primer are lead, barium, and antimony. Projectiles were therefore removed from bullets of these two brands of ammunition and installed into the Winchester Super X cartridge cases (including gunpowder) having lead and barium as characteristic elements in the primer.

In every shooting experiment three rounds were fired into a water trap from a thoroughly cleaned weapon. The weapons used in the tests were a Ruger 10/22 rifle, a .22 caliber Beretta semiautomatic pistol, and a .38 caliber S&W revolver. The fired projectiles were recovered from the water trap for SEM/EDX examination of GSR particles on their bottoms (8). A sample of particles was

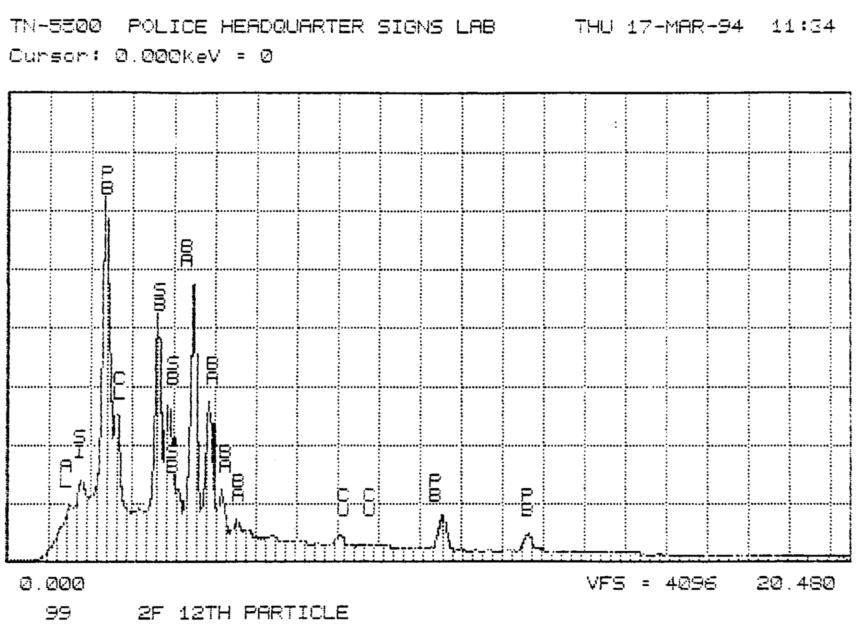


FIG. 1—*EDX spectrum of a GSR particle having a high content of antimony in a sample from the victim.*

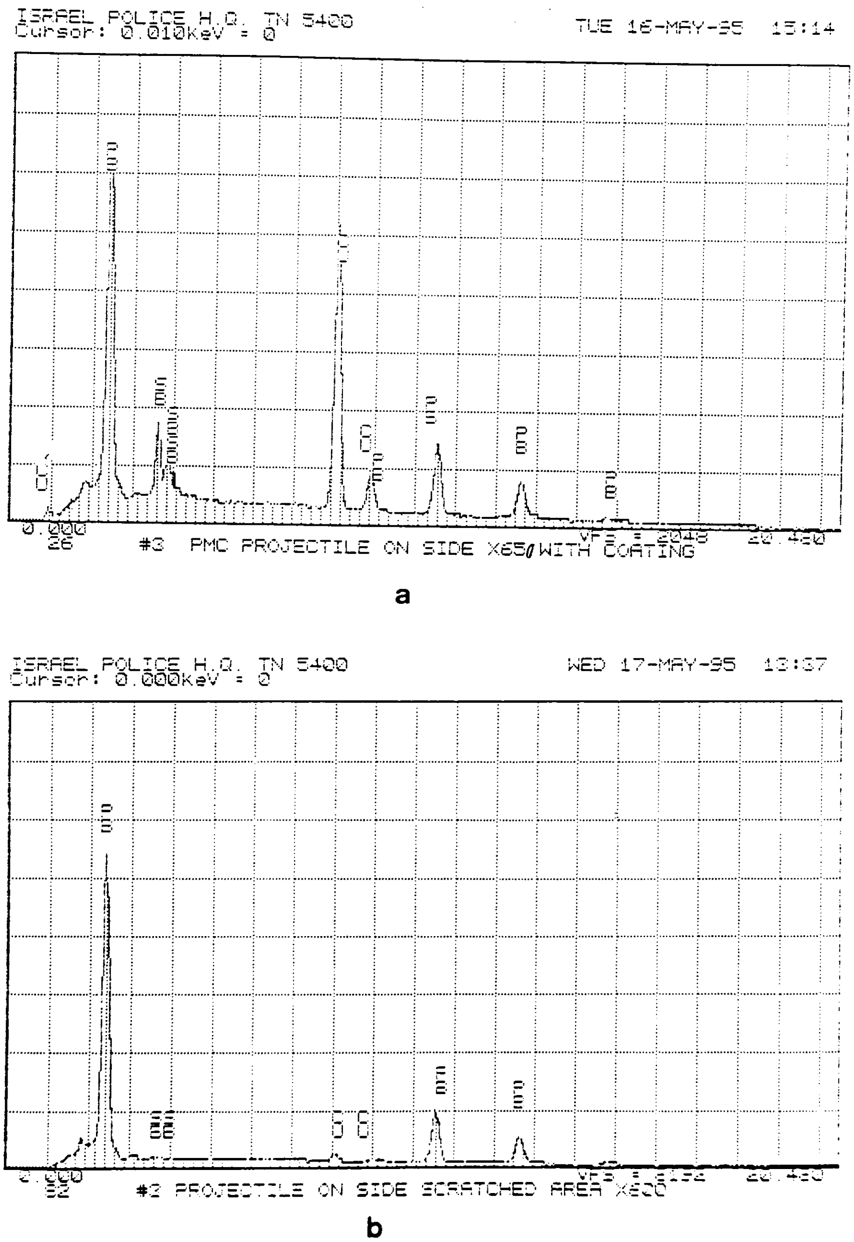


FIG. 2—*EDX spectra of a PMC Zapper bullet: (a) unscraped area; Pb = 53.0%, Sb = 5.5%, Cu = 41.5%; (b) scraped area; Pb = 97.9%, Sb = 0.3%, Cu = 1.8%.*

collected from the chamber as well from the muzzle of the weapon, using a wood stick, and then transferred to an aluminum stub coated with a double-sided adhesive (''Scotch Tape'' No. 465, 3M Company).

Particles were examined manually by SEM/EDX. In every experiment we continued to examine particles in both samples (from the muzzle and chamber) until about 50 particles containing both lead and barium were analyzed. The tests are listed in Table 2.

Surface Analysis of Bullets by Auger Electron Spectroscopy

Since SEM/EDX is not a ''true'' surface analysis method it was interesting to study the antimony enrichment on the surface of bullets by Auger electron spectroscopy (AES). The analysis was carried out in a Perkin-Elmer. PHI Model 590 scanning Auger microscope. Spectra were acquired in the first derivative mode (with 6 eV peak-to-peak modulation) using a rastered primary beam of 5.0 keV, 1.5 μA electrons. Depth profiles were obtained by 3.0 keV Ar+ ion sputter etching with simultaneous monitoring of the peak-to-peak intensities (the intensity of the first derivative mode) of the corresponding Auger transitions of C(KLL), S(KLL), Cl(KLL), O(KLL), Pb(MNN), Sb(MNN), and Cu(LMM). The sputter rate was estimated using a 100-nm-thick Ta205 standard and published data on sputter rates of relevant materials. Prior to analysis, cleaning of all the samples was carried out in an ultrasonic bath using acetone, ethanol, and deionized water.

Analysis was made of PMC Zapper and Peters HV bullets which were found by SEM/EDX to have a much higher surface concentration of antimony than in the bulk, and also Eley bullets in which hardly any difference in antimony concentration between the surface and the bulk was found.

To demonstrate the fact that a uniform composition of antimony in a lead alloy is not a stable composition, an accelerated aging test was performed as follows: disks were cut out from an Eley bullet, ground on silicon carbide emery paper, and polished with a 1 μm diamond finishing compound. They were examined by AES, then kept in a Memmert GmbH clean oven opened to air at 200°C for 35 h, following which they were again examined by AES.

Results and Discussion

In all the 20 examined (by SEM/EDX) brands of ammunition (Table 1) a higher antimony concentration was observed on the surface of a projectile lead alloy than in the bulk. The bulk content of antimony in all the bullets was not higher than about 0.5% (weight percent). It should be noted that the concentration results reported here are approximate values only, since the analyzed specimens were neither flat nor polished and the standardless semiquantitative ZAF (SSQ) method was used. However, for the purpose of this study, exact concentrations of antimony are of minor importance; what does matter is the difference in concentration of surface-to-bulk of the bullets. EDX spectra of the projectiles having the highest content of antimony on the surface are shown in Figs. 2–4.

TABLE 1—*Brands of bullets examined by SEM/EDX.*

Brand No.	Brand	Caliber[a]	Plating/Jacket
1	PMC Zapper	.22	yes
2	Peters H.V.	.22	no
3	Eley	.22	no
4	Federal	.22	yes
5	Eley H.V.	.22	yes
6	Western	.22	yes
7	Winchester Super X	.22	yes
8	CCI	.22	yes
9	RWS	.22	yes
10	Winchester T-22	.22	no
11	Swartklip	.22	no
12	Winchester X-pert	.22	no
13	Musgrave	.22	no
14	Fiochi	.22	yes
15	S&B	.22	no
16	Unknown	.22	no
17	Lapua	.22	no
18	Hirtenberg	.38 S&W	no
19	Hirtenberg	.38 Special	no
20	SBP	9 mm	yes

[a]Caliber in inch unless stated otherwise.

Note that in the case of the PMC and RWS bullets, which are copper plated, the content of antimony in the lead-antimony alloy (without the contribution of copper) would be considerably higher than reported. Thus, in the case of the RWS projectile, for instance, the content of antimony would be about 15%. In all other bullets the surface content of antimony was smaller and sometimes the difference between the surface concentration and the bulk concentration was hardly detectable, such as in the case of Eley H.V. (Fig. 5).

As already mentioned, these results differ from the results of uniform composition in bullets' lead alloys, reported in the only other study found on the subject (7). It is quite possible, however, that in the other study the surface segregation of antimony could not be detected, because quite large samples were taken from the exterior to the interior of the bullets (the minimum sample was 8 mg) and analyzed by NAA.

Auger depth profiles show much higher surface than bulk concentration of antimony in all the three examined bullets, including Eley (Fig. 6) in which hardly a difference was detected by SEM/EDX. It can be seen that thickness of the enrichment layer was about 0.5 μm in this bullet. Figure 7 shows the Auger depth profile of a PMC Zapper projectile. It can be seen in this profile that the enrichment layer of antimony was about 10 μm thick. Such thicknesses explain the possible detection of antimony surface enrichment by SEM/EDX (depth resolution of about 1 μm (9)). Figure 7 shows apparent increase in the antimony intensity before appreciable decrease in the copper intensity occurs. This may be explained either by nonuniform thickness of the copper plating of the PMC Zapper bullets (as was already mentioned) and/or by formation of the copper-antimony (Cu-Sb) phase or by both.

It should be noted that in unplated projectiles (Fig. 6) a higher antimony concentration on the surface was accompanied by a higher concentration of oxygen. A similar phenomenon was reported for lead-tin alloys (10). This was not the case for a plated bullet (PMC) where the antimony enrichment was without oxygen (Fig. 7). Figures 8 and 9 show that a uniform content of antimony in a lead alloy is apparently not stable. Over time the antimony will migrate toward the surface of the projectile.

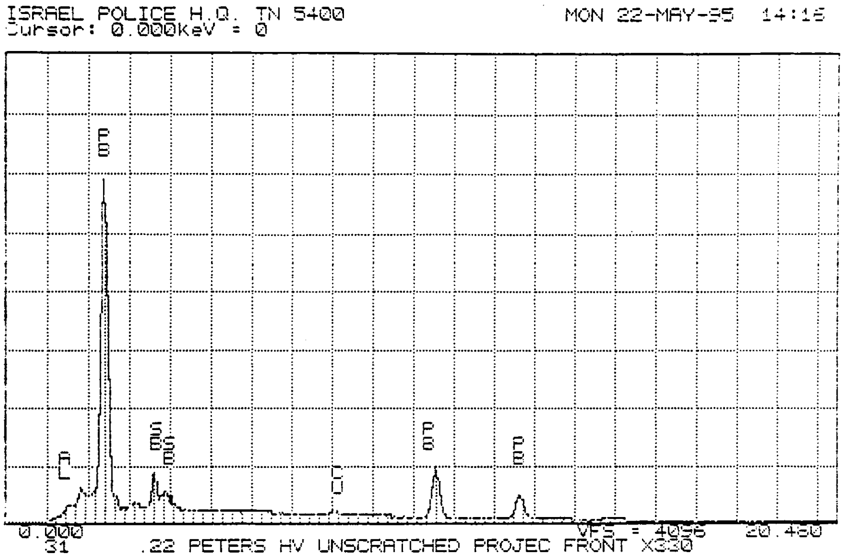
With regard to lead bullets it was reported that, ''In a large commercial operation bullets are not cast; they are produced in a press. All such bullets start from extruded lead wire. Wire is either

TABLE 2—*Shooting experiments for examination of GSR.**

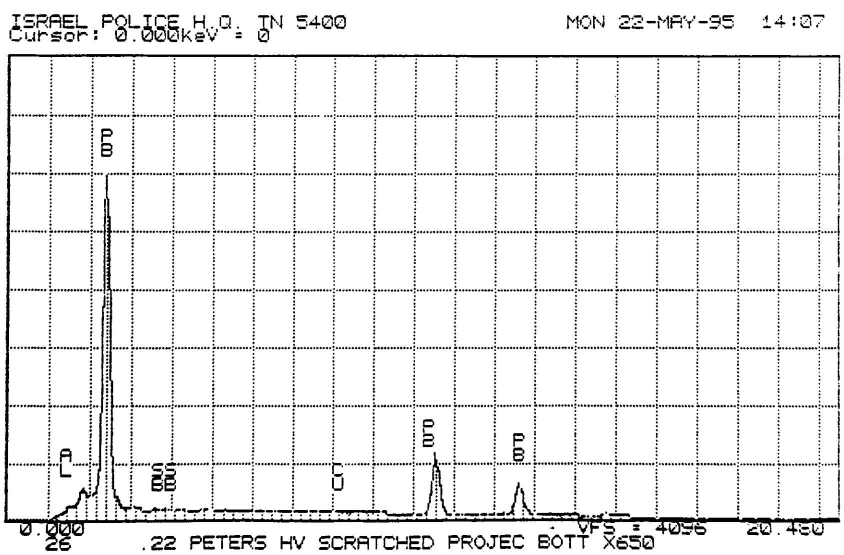
Exp. No.	Caliber, in.	Projectile	Cartridge	Weapon	Number of Particles Containing Antimony†
1	.22	PMC Zapper	PMC Zapper	rifle	1
2	.22	Peters H.V.	Super X	rifle	0
3	.22	Peters H.V.	Super X	pistol	0
4	.22	RWS	Super X	rifle	2
5	.22	RWS	Super X	pistol	0
6	.38 S&W	Hirtenberg	Hirtenberg	revolver	2

*See text.

†Number of particles having in addition a considerable content of antimony (higher than the content in the bulk of the projectiles), found among about 50 particles containing both lead and barium.



a



b

FIG. 3—*EDX spectra of a Peters HV bullet: (a) unscraped area; Pb = 92.0%, Sb = 6.6%, Cu = 1.4%; (b) scraped area; Pb = 99.2%, Sb = 0.4%, Cu = 0.4%.*

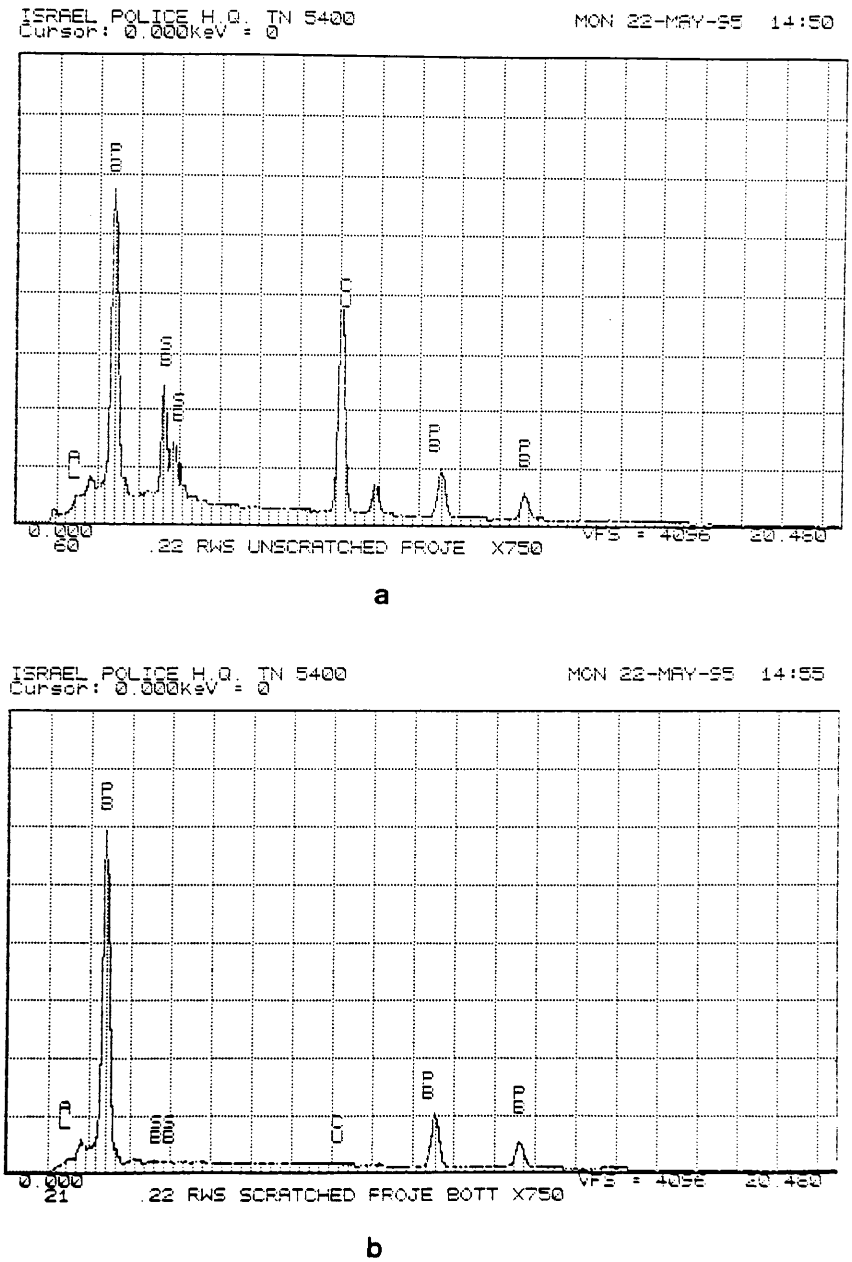


FIG. 4—*EDX spectra of an RWS bullet: (a) unscraped area; Pb = 54.6%, Sb = 9.9%, Cu = 35.5%; (b) scraped area; Pb = 99.8%, Sb = 0.1%, Cu = 0.1%.*

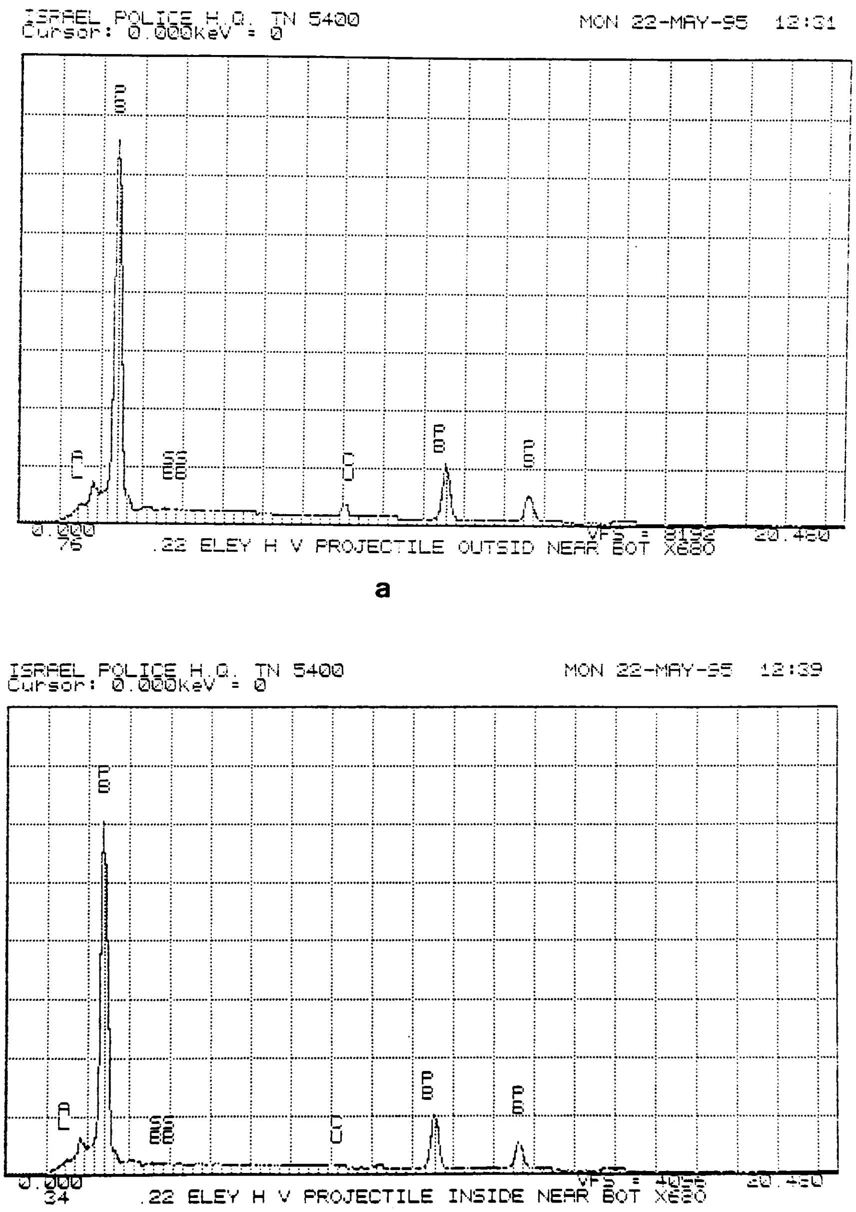


FIG. 5—*EDX spectra of an Eley HV bullet: (a) unscraped area; Pb = 96.2%, Sb = 0.6%, Cu = 3.2%; (b) scraped area; Pb = 99.3%, Sb = 0.3%, Cu = 0.4%.*

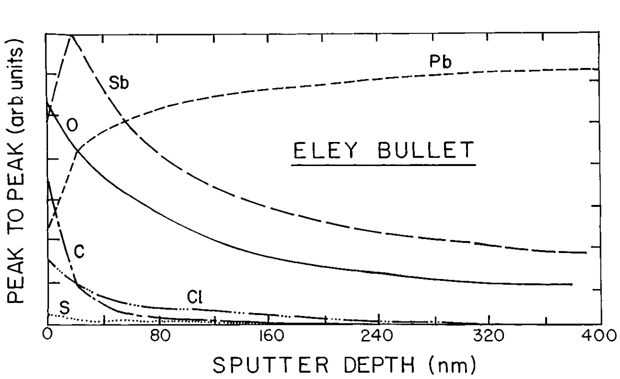


FIG. 6—*AES depth profile of an Eley bullet.*

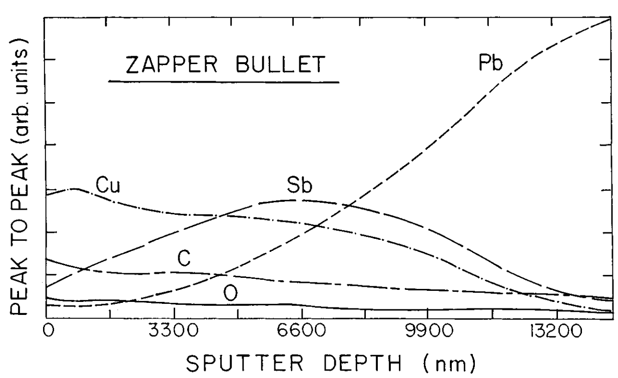


FIG. 7—*AES depth profile of a PMC Zapper bullet.*

extruded cold or hot. Bullets to be plated should be undersize by about the thickness of the plating'' (11). Possible reasons for a variation in antimony enrichment levels for different projectiles that we have found may stem from different extrusion temperatures in a manufacturing process, from a difference in a storage time after manufacture, or from a contribution of both effects.

The GSR particles found in the samples from the shooting tests contained either lead or lead and barium; the content of barium was usually much less than lead. As can be seen from Table 2, only a very small percentage (on average in all the tests, not more than about 2%) of particles containing lead and barium was found to have also a considerable content of antimony (higher than the content in the bulk of the projectiles). However, in all these particles having a higher content of antimony, it was still relatively low compared with the usual content of antimony in GSR particles originating from primers containing antimony. Figure 10 shows the EDX spectrum of a GSR particle found to have the highest concentration of antimony in addition to lead and barium (compare Fig. 1).

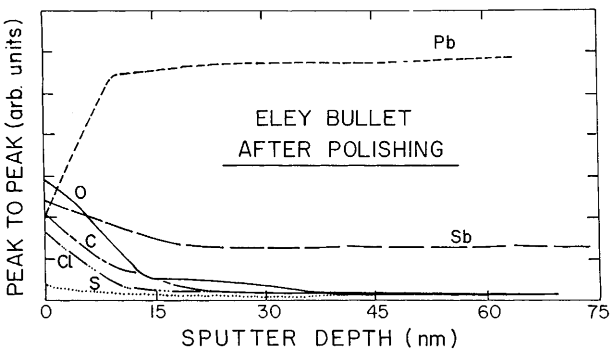


FIG. 8—*AES depth profile of a polished Eley bullet.*

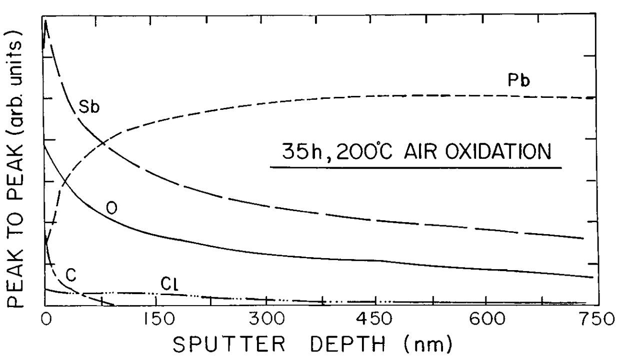


FIG. 9—*AES depth profile of a polished Eley bullet that has undergone accelerated aging by heating.*

Similar results were obtained for the particles examined on the bottoms of projectiles. The EDX spectrum of a particle found to have the highest content of antimony is shown in Fig. 11. Also, a very small percentage of particles having a considerable concentration of antimony, in addition to lead only, was found.

The results of this study show that even in the cases when the surface of a bullet is highly enriched by antimony, there is a small probability of finding GSR particles containing a considerable concentration of this element if it is absent in the primer of the fired ammunition.

With regard to the homicide case, this study proves that a high surface concentration of antimony in the PMC Zapper projectiles could not be the source for the high percentage of the three-element GSR particles found in the sample from the bullet entrance hole in the victim. A plausible explanation for the evidence might be the firing of the three-element primer ammunition prior to firing the PMC Zapper bullets in the Ruger rifle.

Conclusions

It was found that the concentration of antimony on the surface of the lead alloy bullets is higher than in the bulk. The extent of antimony enrichment on the surface was different for various bullets. It was found that there is a small probability of finding GSR containing a considerable concentration of antimony if the primer of the fired ammunition is antimony-free, even when the surface of the bullet is highly enriched by this element.

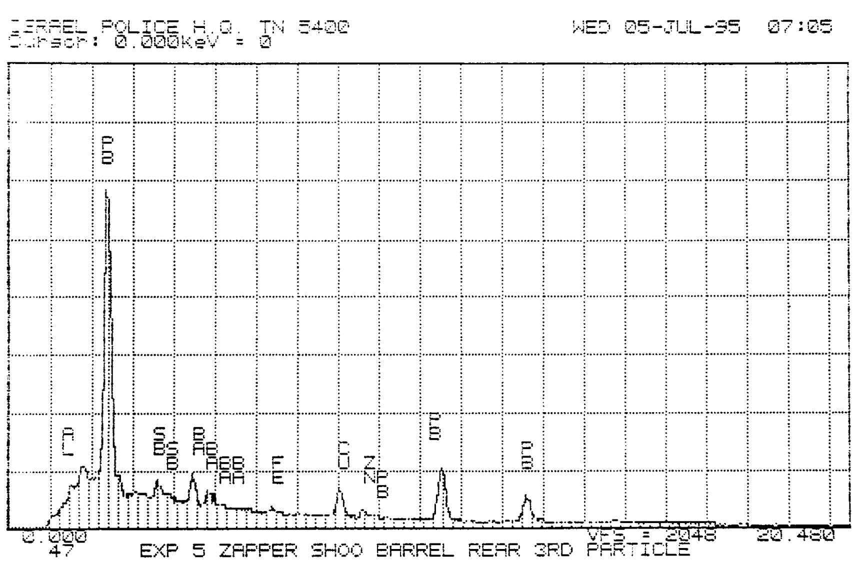


FIG. 10—*EDX spectrum of a GSR particle having the highest antimony content in addition to lead and barium found in the samples from a weapon (Table 2, Experiment 1).*

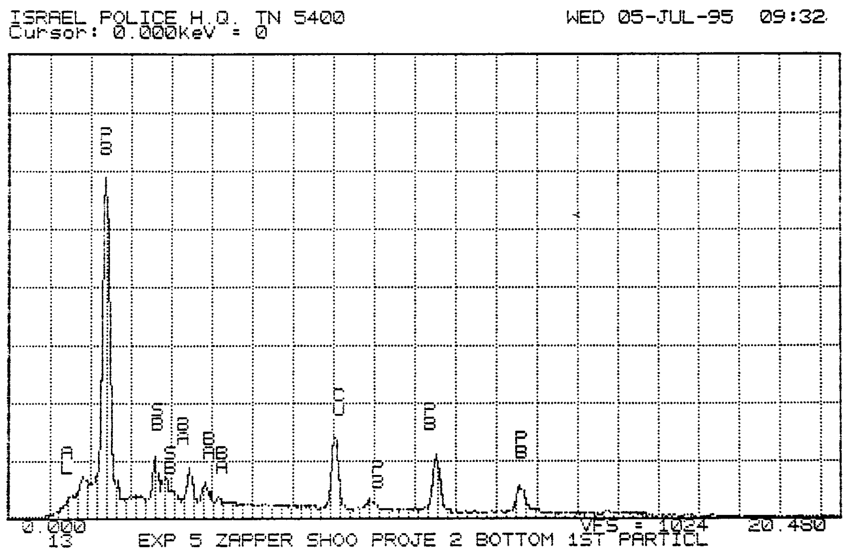


FIG. 11—*EDX spectrum of a GSR particle having the highest antimony content in addition to lead and barium found on the bottom of a projectile (Table 2, Experiment 1).*

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References

1. Wolten GM, Nesbitt RS, Calloway AR, Loper GL, Jones PF. Particle analysis for the detection of gunshot residue. I: Scanning electron microscopy/energy dispersive X-ray characterization of hand deposits from firing. J Forensic Sci 1979 Apr;24(2):409–22.
2. Wolten GM, Nesbitt RS. On the mechanism of gunshot residue particle formation. J Forensic Sci 1980 Jul;25(3):533–45.
3. Wallace JS, McQuillan J. Discharge residues from cartridge-operated industrial tools. J Forensic Sci 1984;24:495–508.
4. Gunaratnam L, Himberg K. The identification of gunshot residue particles from lead-free Sintox ammunition. J Forensic Sci 1994 Mar;39(2):532–6.
5. Zeichner A, Levin N, Springer E. Gunshot residue particles formed by using different types of ammunition in the same firearm. J Forensic Sci 1991 Jul;36(4):1020–6.
6. Harris A. Analysis of primer residue from CCI Blazer lead free ammunition by scanning electron microscopy/energy dispersive X-ray. J Forensic Sci 1995 Jan;40(1):27–30.
7. Lukens HR, Schlesinger HL, Guinn VP, Hackelman RP. Forensic neutron activation analysis of bullet-lead specimens. USAEC Repot GA-10141, Gulf General Atomic Incorporated 1970.
8. Bergman P, Enzel P, Springer E. The detection of gunshot residue (GSR) particles on the bottom of discharged bullets. J Forensic Sci 1988 Jul;33(4):960–8.
9. Goldstein JI, Newbury DE, Echlin P, Joy DC, Fiori C, Lifshin E. Scanning Electron Microscopy and X-Ray Microanalysis. Plenum Press, New York, 1984:109.
10. Konetzki RA, Chang YA. Oxidation of Pb-2.9 at.% Sn alloys. J Mater Res 1988 May/Jun;3(3):466–70.
11. Frost G. Ammunition making. The National Rifle Association of America, Washington, DC, 1990:28–30.

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