

TECHNICAL NOTE

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Investigation of Gunshot Residues by Means of Auger Electron Spectroscopy

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ABSTRACT: In the past years, scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX) has displayed many advantages over established methods such as optical emission spectroscopy (OES), atomic absorption spectroscopy (AAS), and neutron activation analysis (NAA) for the investigation of gunshot residues (GSR). In a research project, Auger electron spectroscopy was used instead of EDX. This method makes possible analyses of the chemical elements with superior lateral resolution. Furthermore, elements with low mass numbers and elements whose peaks overlap at EDX can be measured. In addition, sputtering equipment depth profiles can be established. Our experiments demonstrate the potential of Auger electron spectroscopy for the investigation of GSR. Also, they produced many details on GSR from various ammunition.

KEYWORDS: criminalistics, gunshot residues, spectroscopic analysis

The investigation of gunshot residues (GSR) from a suspected shooter's hands has long been performed with different analytical methods, essentially with optical emission spectroscopy (OES), atomic absorption spectroscopy (AAS), and neutron activation analysis (NAA). Lead, barium, and antimony were considered as the main elements. Depending on the circumstances of the respective case, the presence of certain amounts of these elements is taken as proof of, or a hint to, the presence of GSR.

Over the past few years, investigations with the scanning electron microscope (SEM) combined with energy dispersive X-ray analysis (EDX) have gained considerable importance. With this instrumental combination, not only the presence of certain chemical elements can be proved, but also their location, their combination in individual particles, and the morphology of these particles. Despite many efforts in the past, however, the method is still

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time-consuming. On the other hand, the significance of the method is superior by far to the purely elemental analytical methods [1].

Auger electron spectroscopy (AES) has been used in various nonforensic science fields for some years, normally in the scanning mode (SAM) like the SEM [2]. It could be expected that the SAM would supply valuable information on GSR, even in comparison with SEM/EDX.

Auger electron spectroscopy is a surface sensitive technique, but unlike EDX where the characteristic X-rays used for the analysis come from an area that has a width and a depth in the order of 1 μm , the excited Auger electrons originate from the uppermost atomic layers only (typical escape depth ranges from 0.3 to 3 nm depending on their kinetic energy). Therefore, the indicated compositions refer to this surface region. The lateral resolution in SAM is also significantly better. Another point is, perhaps, even more important: as most instruments have an ion gun the atomic layers can be removed successively and a depth profile can be established. Additionally, some elements whose peaks overlap with EDX can be investigated. Furthermore, Auger electron spectroscopy offers the possibility of determining elements with low atomic numbers. The special advantages of AES/SAM are summarized in Table 1.

Experimental Procedure

For our investigations we used a PHI 600 SAM system with a lateral resolution of about 30 nm. This Auger system also permitted us to take secondary electron images from the surface area to be analyzed so that lateral variations in the surface composition, as they become evident from the "Auger maps," can be correlated with corresponding features in the surface topography. Since the formation of these secondary electron images occurs through the same mechanism as in the scanning electron microscope, the information from both techniques can be directly compared with each other.

Techniques and factors involved in the quantitative interpretation of the Auger data are very similar to those involved with the electron microprobe. The peak-to-peak amplitude in

Table 1

Features of AES/SAM for the investigation of GSR

- elements with low atomic mass numbers can be investigated (carbon, nitrogen, oxygen)
- lateral resolution better than with EDX
- in combination with a sputtering equipment depth profiles of the elements can be measured
- some elements of which the peaks overlap with EDX can be differentiated;
- in special cases, it is possible to determine the compound in which an element is present

the Auger spectrum, a differentiated energy spectrum, is proportional to the amount of the respective element present on the GSR surface. The concentrations measured were obtained from the AES data by use of the following expression:

$$x_i = \frac{I_i/S_i}{\sum_j I_j/S_j} \times 100$$

Here x_i is the concentration of the element i in atom percent, I_i is the peak-to-peak height for a given Auger transition of the element i , and S_i the relative elemental sensitivity factor [3]. The sum over j has to be taken over all elements present. When highly accurate quantitative analysis is desired, standards of known concentration similar to that of the actual chemical compound should be used.

As has been mentioned, by using simultaneous Auger electron spectroscopy and ion sputter etching, a profile of the in-depth composition variations of the GSR can be obtained. The basic procedure used in the profile mode consists of measuring the peak-to-peak amplitudes of Auger signals from selected elements as a function of etching time. Etching rates are easily controlled, so depth profiles ranging to a thickness of several microns can be analyzed conveniently.

The sputter rates of depth profiles are normally related to tantalum oxide (Ta_2O_5). Using this reference material, in most of our measurements a sputter time of 20 min corresponds to a depth of 40 nm. Sputter rates of many other elements and chemical compounds are in the same order of magnitude. For a more accurate thickness calculation, however, it would be necessary to take into account the different sputtering yields on different materials.

Weapons and Ammunition, Sample Preparation

After some preliminary investigations in 1983–1984 with different weapons and ammunition, we started a research project in 1985. Up to now, we have restricted the investigations to only one weapon, namely a Smith & Wesson pistol, cal. 9-mm Para, but with varying ammunition and, to some degree, various jackets of the bullet (see Table 2). A common procedure of collecting GSR from a suspected shooter's hands is the use of adhesives. These adhesives are evaporated for investigations by SEM/EDX to obtain a conductive surface. This method, however, causes problems in Auger electron spectroscopy, since Auger electrons originate from the uppermost atomic layers only. For this feasibility study we therefore chose indium foils as a target to avoid electrical charging effects during the analysis and because GSR particles adhere quite well to the smooth indium surface. The shooting distance (distance between muzzle and In target) was 20 cm.

Results

In the following, examples of these first investigations are given.

Geco Ammunition

Figure 1 in the upper part shows the Auger spectra of a GSR particle before and after sputtering, this particle originating from a cartridge with a fully jacketed bullet of the Geco brand. In the lower part the depth profile can be seen. It shows that the nucleus consists of barium, oxygen, and sulfur. A layer of lead, antimony, and tin surrounds the nucleus, the tin having a thickness of only a few atomic layers. Other particles reveal the same principal features, but may differ in details.

Table 2

No.	Brand name	Special features of the cartridge and the bullet
1. 2. 3. 4. 5. 6. 7.	Geco 9 mm Para Hirtenberger 9 mm Para Remington 9 mm Para Fiocchi 9 mm Para Norma 9 mm Para Sako 9 mm Para Winchester Western 9 mm Para	bullet fully jacketed (bottom of the bullet not closed)
8.	CCI (Blazer) 9 mm Para	cartridge case made of aluminium; bullet completely jacketed (bottom of the bullet closed)
9.	Speer 9 mm Para	bullet completely jacketed (bottom of the bullet closed)
10.	Norma Hollow Point 9 mm Para	bullet fully jacketed (bottom of the bullet closed)
11.	Sintox 9 mm Para	newly developed primer (no lead etc.); the characteristic elements are zinc and titanium; bullet completely jacketed (bottom of the bullet closed)

CCI Ammunition

With CCI 9-mm Para Blazer ammunition, practically all investigated particles were nearly spherical with a smooth surface, diameters of 8 to 15 μm , and very similar compositions (Fig. 2). Using this ammunition with a completely jacketed bullet, no lead has been found in the particles (Fig. 3). On the other hand, besides barium and oxygen, aluminum is found as main component perhaps coming from the primer, as our parallel systematic investigations of primers by X-ray fluorescence (XRF) and X-ray diffraction (XRD) could suggest. The spectra further show the presence of potassium, sulfur, antimony, and very often of carbon as may be seen in the spectrum of another particle (Fig. 4). The measurement of the depth profile gave the following result (Fig. 5): nearly the whole particle is made up homogeneously of barium, aluminum, and oxygen. Only a thin film of a few atomic layers containing sulfur, antimony, potassium, and carbon is present at the surface.

This becomes evident also in the mappings of some of these elements. Figure 6 shows a particle before sputtering. Barium is spread out over the whole particle, while antimony, potassium, and sulfur are located on the surface only. From these figures, it seems that these elements have been peeled off by the impinging particle.

An interesting feature should be mentioned: in one corner of the figure apparent traces of incompletely burnt propellant are found, since besides sulfur, the main elements are carbon and nitrogen.

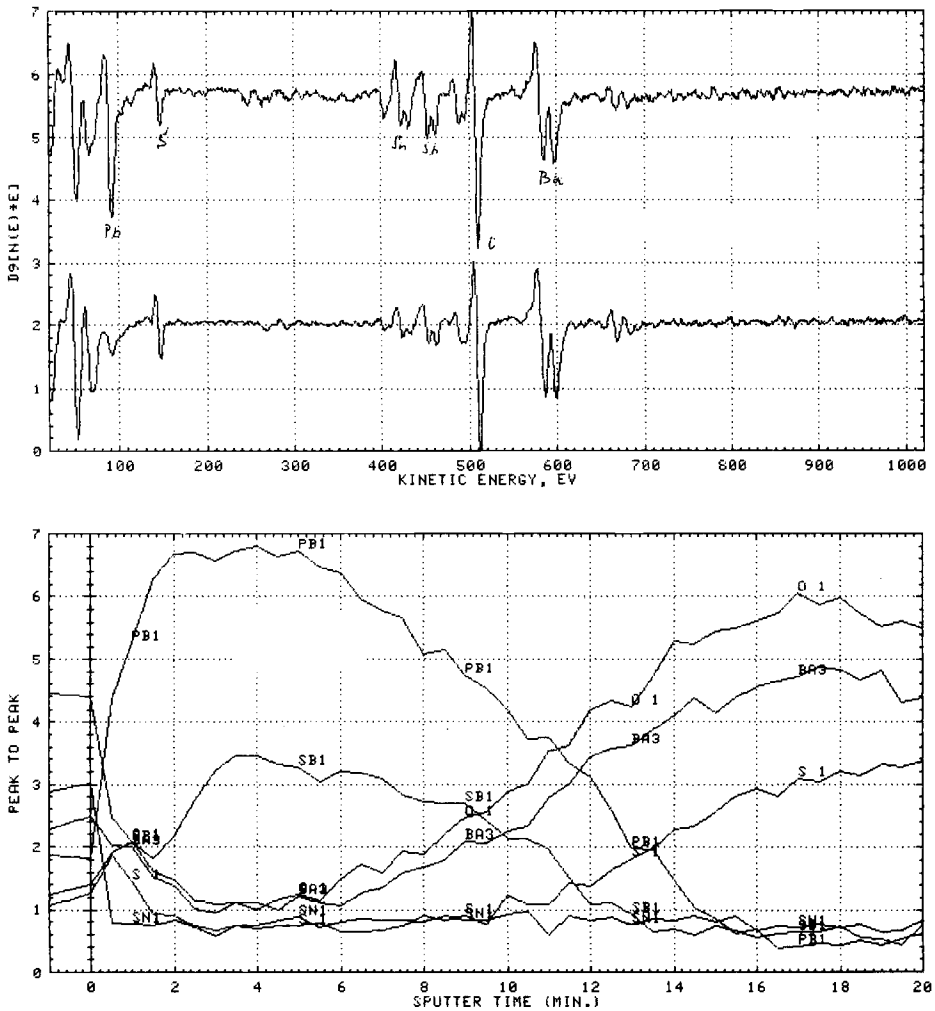


FIG. 1—Auger spectra of a GSR particle of Geco 9-mm Para ammunition before and after sputtering (upper part); depth profile of a GSR particle (lower part).

Norma Ammunition

In another case, that is, using Norma 9-mm Para ammunition, and even more so with Norma 9-mm Hollowpoint, the results were essentially more complicated. There were at least four or five different categories of particles, and it was difficult to classify at all particles with regard to morphology as well as chemical composition.

Sintox Ammunition

A very clear picture, on the other hand, is obtained with Sintox 9-mm Para. This no lead primer ammunition developed by Dynamit Nobel in the Federal Republic of Germany for environmental reasons does not contain lead in the primer, but titanium and zinc com-

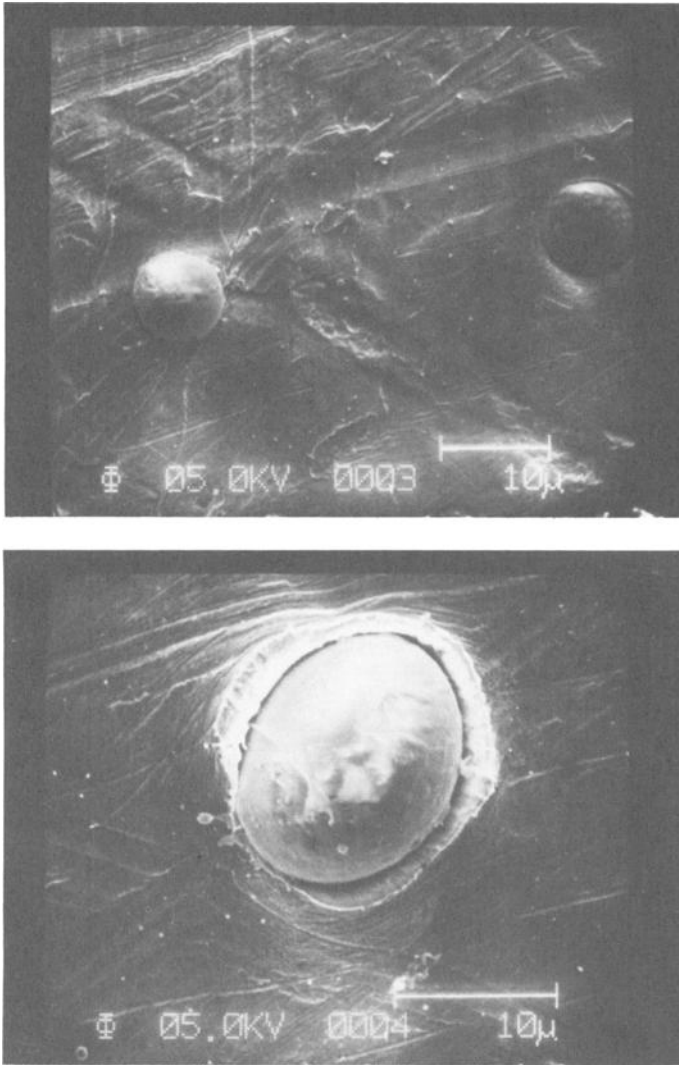


FIG. 2—GSR particle of the CCI 9-mm Para Blazer ammunition.

pounds. Two essentially different kinds of particles have been found: one kind of particle consists of titanium dioxide with only a thin layer of nearly 5 nm on top of it containing different elements like zinc, sulfur, potassium, calcium, carbon, oxygen, and silicon (Fig. 7). The surface contains many holes and appears to have a fairly irregular form (Fig. 8). Sometimes smaller particles of calcium oxide stick to the surfaces which on the other hand also appear as separate particles (Fig. 9).

The second kind of particle, mostly with a size of 7 to 12 nm, like the first one has a porous surface and contains considerable amounts of copper, obviously from the jacket of the bullet (Fig. 10).

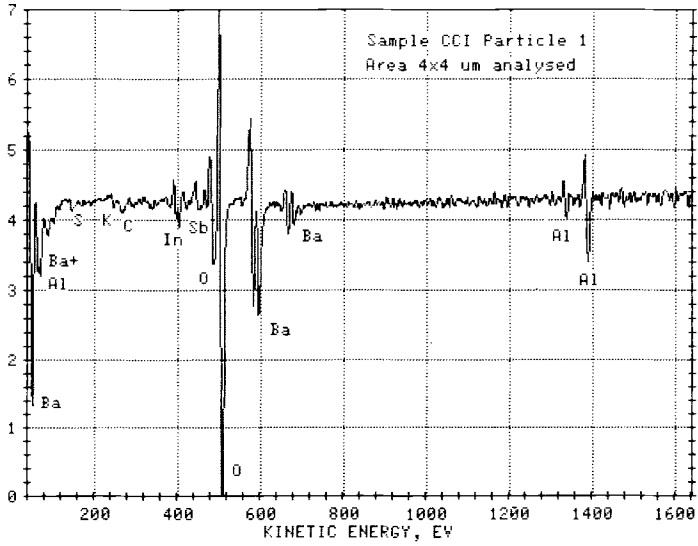


FIG. 3—Spectrum of a GSR particle of CCI 9-mm Para ammunition.

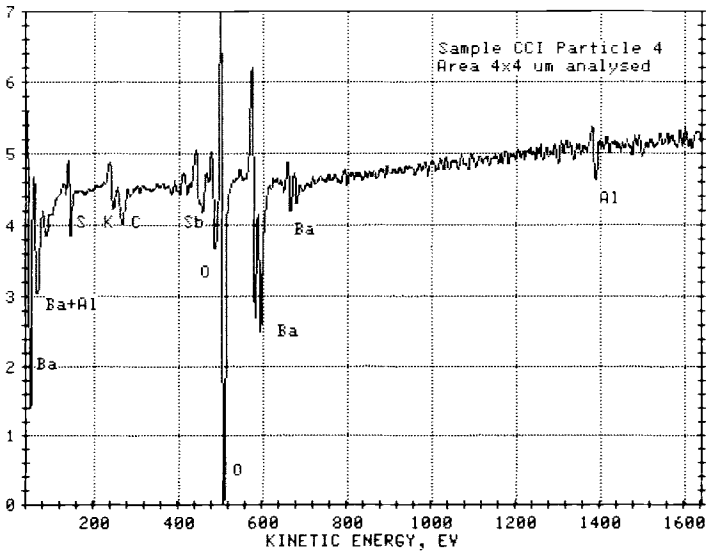


FIG. 4—Spectrum of another GSR particle of the CCI ammunition with higher amounts of surface elements S, Sb, K, and C.

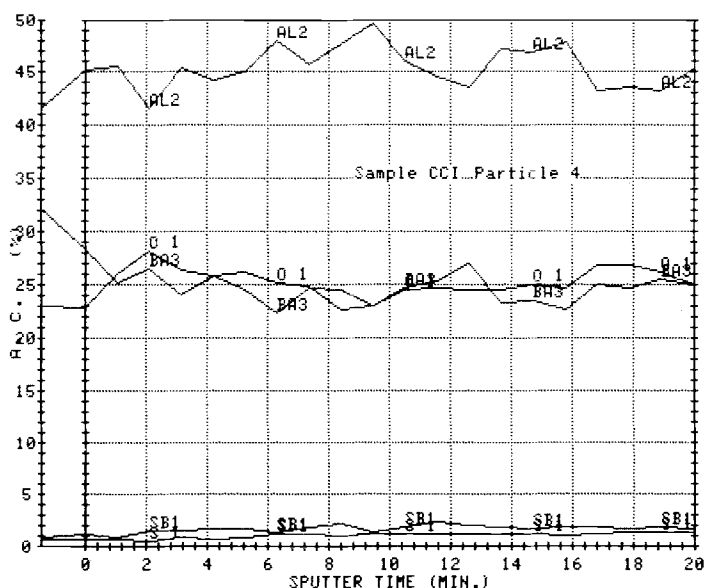


FIG. 5—Depth profile of the particle as in Fig. 4.

Remington Ammunition

As a very impressive example, Figs. 11 and 12 show the depth profiles of various GSR elements from Remington 9-mm Para ammunition. As can be seen, the nucleus is made up of aluminum, barium, and oxygen, as with the CCI ammunition, and again potassium and carbon form only a very thin surface layer. The lead, antimony, and sulfur contents on the other hand increase first, and, after passing a maximum, decrease.

Winchester Western Ammunition

Only very few chemical elements are found, namely, barium, antimony, lead, carbon, sulfur, and oxygen, and the particles are relatively small, the largest being of the order of 3 to 4 nm. The peaks of antimony and sulfur are very pronounced, indicating an ammunition with a high content of antimony sulfide. The particles, furthermore, have a considerable amount of carbon in the upper parts and frequently a cloud of carbon and (sometimes) antimony surrounds it. This can be seen, for instance, in Fig. 13, though this particle itself is not a very typical one.

Conclusions and Further Investigations

Even the results of these first investigations with only one weapon, but with primers of different manufacturers (and only to some degree different jacket, and cartridge case, materials), allow some general conclusions. The nucleus of most particles consists of barium or a barium-aluminum-oxide, the nucleus of the no lead primer ammunition of titanium dioxide. Particles with a nucleus of lead, iron, or copper compounds seem to be rare.

Nevertheless, a great deal of information is lost if we look at barium and the other so-called main GSR elements of lead and antimony only. Other chemical elements play an

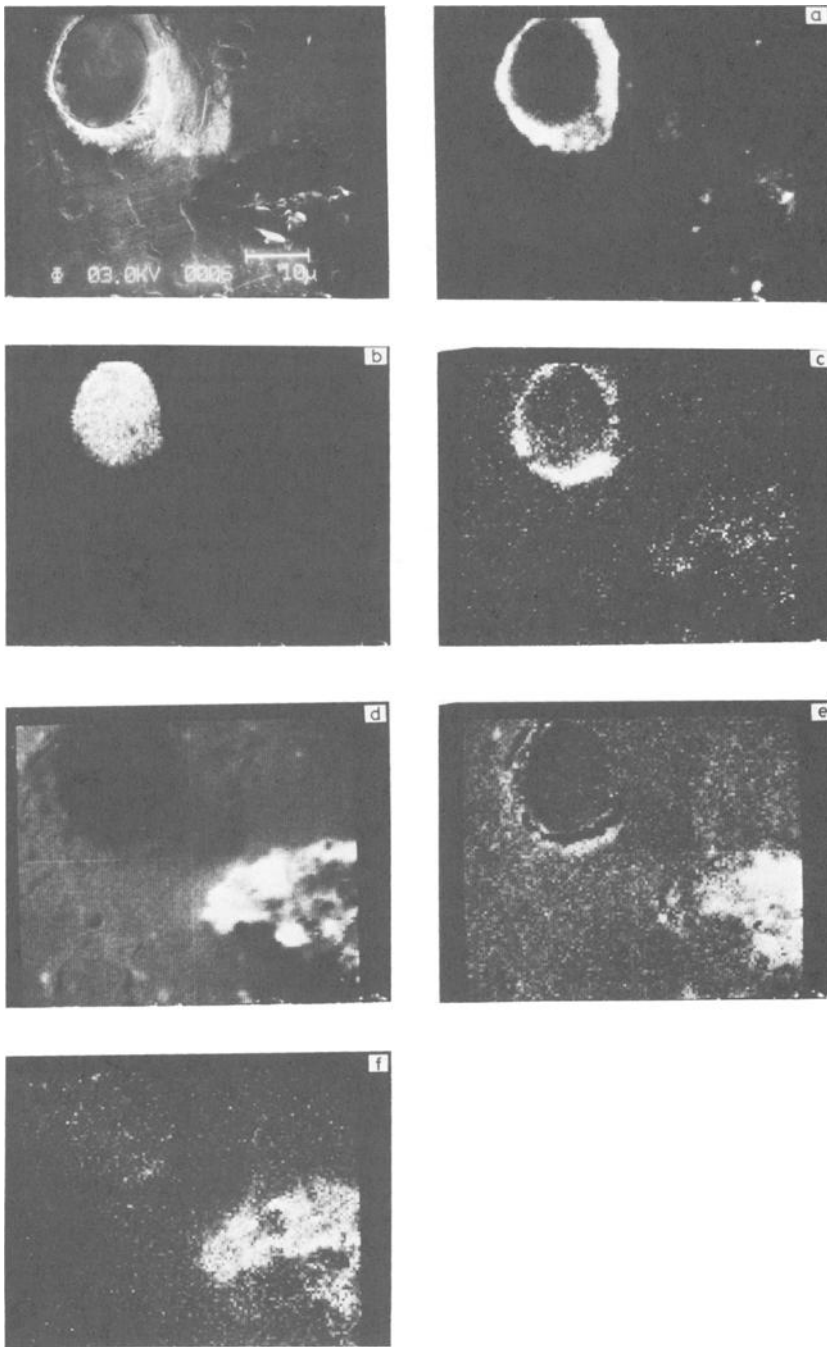


FIG. 6—Mappings of the elements *K* (a), *Ba* (b), *Sb* (c), *C* (d), *S* (e), and *N* (f), respectively, of the particle as in Fig. 4.

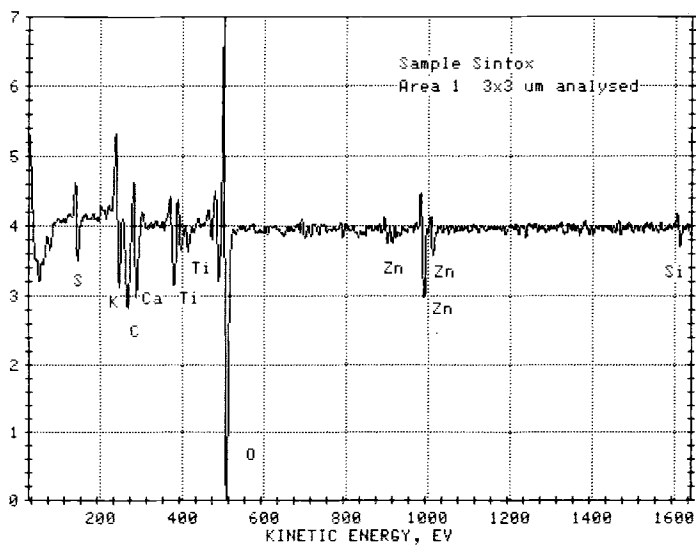


FIG. 7—Spectrum of the Sintox 9-mm Para ammunition.

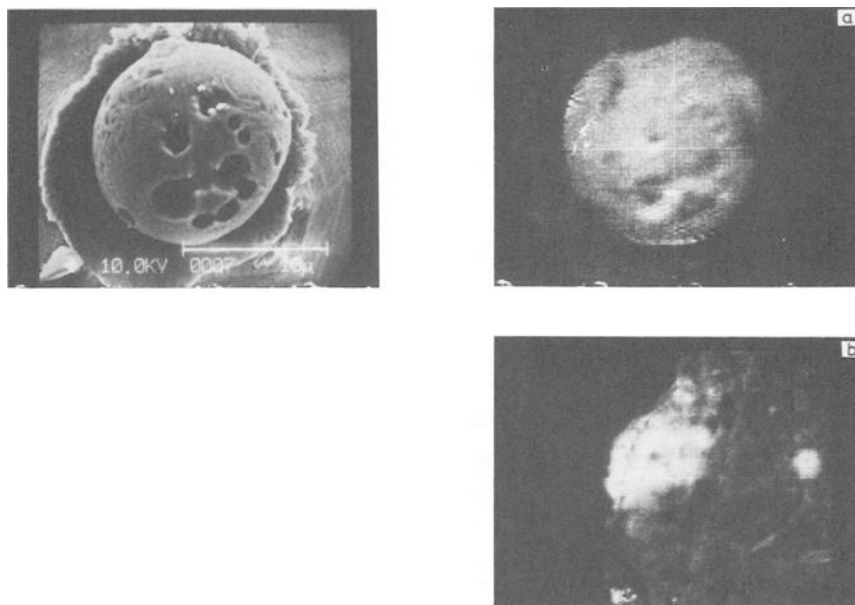


FIG. 8—GSR particle of the Sintox 9-mm Para ammunition together with the mappings of the elements Ti (a) and K (b).

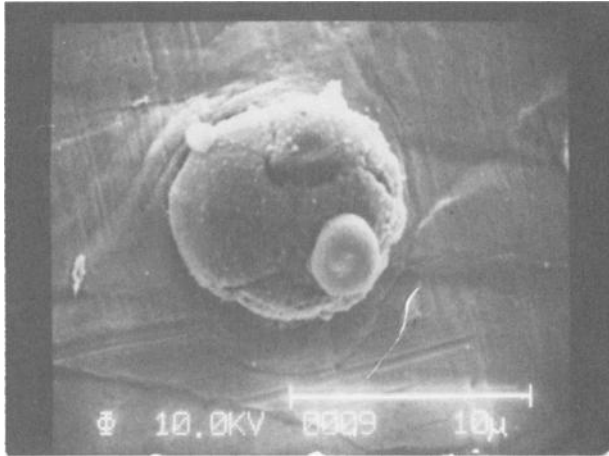


FIG. 9—GSR particle of the Sintox 9-mm Para ammunition with a smaller particle (CaO) affixed to the surface.

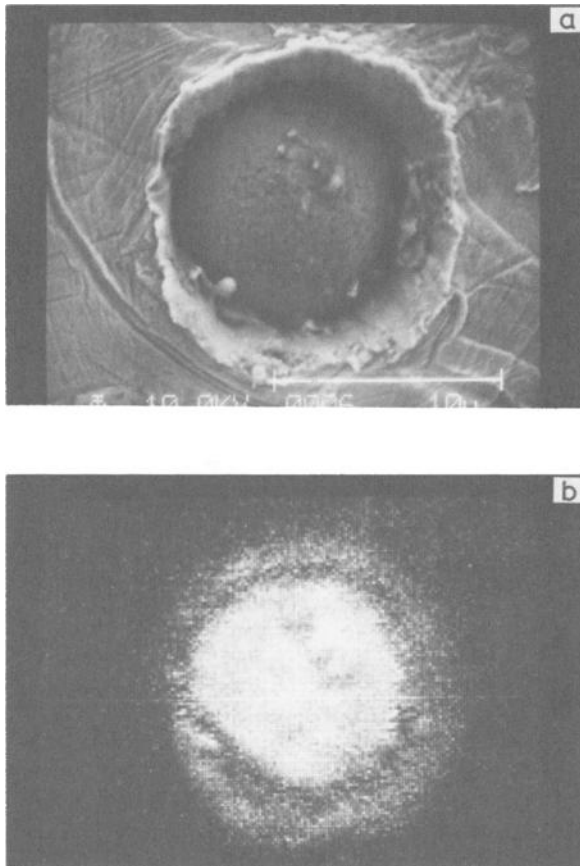


FIG. 10—High-grade copper GSR particle of the Sintox ammunition together with the mapping of the element Cu.

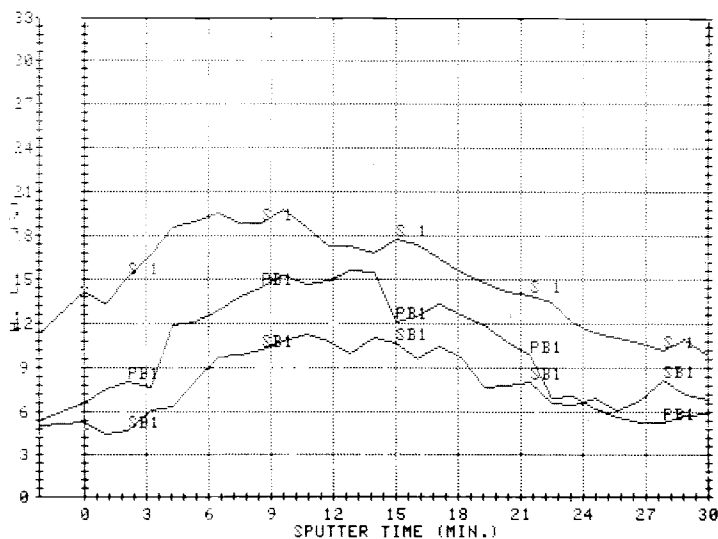


FIG. 11—Depth profiles of the elements Pb, Sb, and S of a GSR particle originating from the Remington 9-mm Para ammunition.

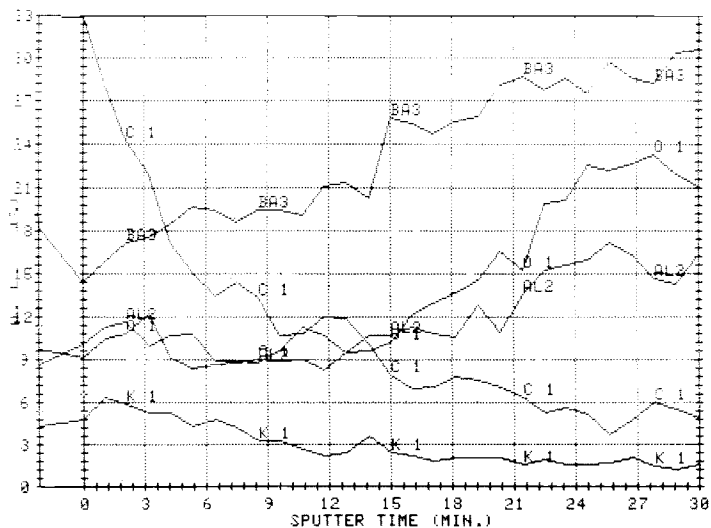


FIG. 12—Depth profiles of the elements Ba, O, Al, C, and K of a GSR particle originating from the Remington 9-mm Para ammunition.

important role in the formation of GSR particles: calcium, silicon, sulfur, aluminum, and iron from the conventional primers; titanium and zinc from certain no lead primers; potassium, calcium, aluminum, silicon, and carbon from various additives of the propellants; lead, tin, and titanium from the separating material between primer and propellant; and of course, also the elements from the jacket material (especially copper and zinc).

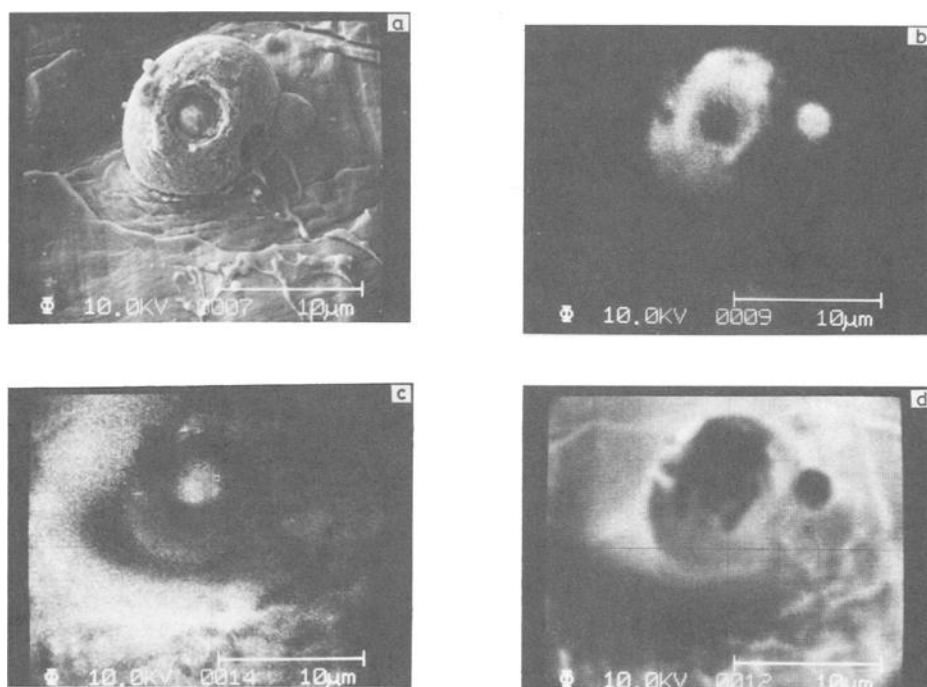


FIG. 13—GSR particle (a) of the Winchester Western 9-mm Para ammunition together with the mappings of the elements Ba (b), Sb (c), and C (d).

Apart from barium, aluminum, oxygen, and titanium, respectively, most of these various elements seem to be concentrated in a more or less extended surface layer. Our SAM investigations revealed pronounced depth profiles of the individual elements; individual particles, however, may vary considerably with regard to composition.

There seem to be distinctive differences between characteristic particles from ammunition with different primers, propellants, and other features. Concerning primers, these results are in agreement with parallel systematic investigations by X-ray diffraction and fluorescence which show that presence and amount of the individual elements may vary considerably [4].

Auger electron spectroscopy also offers some problems, especially if one thinks of an application for practical casework. Equipment costs are much higher than for SEM/EDX since ultrahigh vacuum and special analyzer techniques are required. Like with the SEM/EDX, the procedure is still more or less time-consuming and laborious.

Furthermore, as has been mentioned before, the normally used adhesives are nonconductive.

First investigations with evaporated and subsequently sputtered adhesives proved the applicability of the method even with such a substrate, though there seems to be a loss of information in comparison with GSR on In foils.

References

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