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Detection of Gunshot Residues on Hands by Scanning Electron Microscopy

Several methods have been developed by law enforcement agencies for determining whether or not an individual has recently handled or discharged a weapon. When a suspect has been apprehended following a shooting, detection of gunshot residues on his hands may provide significant evidence. The value of such a test is substantial in the investigation of alleged suicides, armed assaults, poaching, and other violations involving the use of firearms.

The development of various methods for detecting gunshot residues has recently been reviewed by Midkiff [*1*]. Previous methods such as the color test for nitrates [*2*] and the color tests for antimony, barium, and lead [*3*] have been replaced in recent years by more reliable instrumental methods such as neutron activation analysis (NAA) [*4*], flameless atomic absorption spectroscopy (FAAS) [*5*], X-ray fluorescence [*6*], and photoluminescence techniques [*7*]. These methods are capable of analyzing small amounts of metallic elements (lead, antimony, barium, copper, mercury, and so forth) deposited on the firing hand. The FAAS and NAA methods are now used by several laboratories for the measurement of barium and antimony, FAAS also being used for the determination of lead. These three elements are most commonly found in primer residues.

The shortcoming of these quantitative tests is their lack of specificity for detection of gunshot residues since they measure the average barium and antimony concentrations of various particles including dirt and grime. The large spread in the amount of barium and lead found as "background" on the hands in addition to the large spread in the amounts of firing discharges deposited on the hands indicate that care must be taken for discriminating between gunshot residues and high occupational blanks. The credibility of the quantitative analysis of gunshot residues was tested by Cornelis and Timperman [*8*] as well as other authors [*9,10*]. In many firing tests the median ratios of firing values to blank values on swabs from a firing hand were found to be close to unity even when the analysis was carried out immediately after the firing.

The previously reported methods make use of only one criterion for the presence of gunshot residues: the chemical composition of the entire sample taken from the firing hand. In the present study, scanning electron microscopy (SEM) makes it possible to establish a further criterion: the shape and the appearance of the individual particle. Only those objects which look like potential gunshot residues are analyzed.

The combination of these two criteria would be expected to increase the confidence level of such determinations considerably. Several reports presented recently at national and international meetings have also dealt with the use of scanning electron microscopy in detecting gunshot residues [*11–14*].

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Experimental Methods

Instrumentation and Sample Collection

A Jeol JSM-35 scanning electron microscope equipped with an energy dispersive X-ray analyzer (PGT-1000) was used in these investigations. An accelerating voltage of 25 kV and an ordinary tungsten filament gun were employed.

The gunshot residues were collected from hands by the use of Sellotape transparent adhesive tape (12 mm wide). The tape (approximately 5 cm long) was pressed three or four times onto the skin on the thumb, web, and forefinger area of the suspected firing hand and rubbed to insure good surface contact. This technique is very simple, convenient for use in the field, and suitable for microscopic investigations. Furthermore, adhesive tapes have good lifting efficiency for recovery of particles from hands [*15*]. For examination in the SEM a short section of the collected tape (about 1 cm long) was attached to a brass specimen mount with silver colloidal dispersion, and the tape was coated by carbon to prevent charging effects.

Choice of Suitable Tape

Different types of adhesive tapes have been tested to select the tape most suitable for examination by SEM. In addition to good stickiness, the tape should have a smooth surface so that small particles embedded in the adhesive material can easily be observed in the microscope. More than ten types of tapes including Scotch® Brand tapes (transparent and opaque), Sellotape, Tesa-film, aluminum tape, Norton Bear® tape, and Garco transparent tape[2] were tested. The tapes were pressed three times onto the skin, coated with carbon, and examined in the SEM. Sellotape transparent adhesive tape was found to be the most favorable for the examination. This tape has a weakly interfering background and is also a reasonable thermal and electrical conductor for use as a mounting substrate in scanning electron microscopy.

Identification of Gunshot Residues

The aim of the first set of experiments was to identify particles deposited on firing hands by examining their morphology and elemental composition. Two five-shot tests were carried out using a Smith & Wesson revolver (Model 14, caliber .38 Special) and a Walter automatic pistol (Model PP, 7.65 mm) with Norma ammunition. After being transferred to tape, the embedded particles were examined in the SEM. By moving the specimen in the microscope in various directions, a large number of particles were selected and analyzed. Starting with lower magnification (× 50 to 100) the larger particles (0.01 to 0.1 mm) were first selected for analysis. The magnification was then successively increased and the smaller particles (1 to 10 μm) were observed and analyzed. During this examination several particles consisting of lead, barium, and antimony in various proportions were discovered. These particles were identified as gunshot residues (GSR) since their elemental composition corresponded to that of the cartridge primer. The detection of all three elements typical for GSR in one and the same particle is the decisive improvement for the identification of GSR by SEM. In addition to distinct elemental composition the GSR particles appear to have a characteristic morphology (suggestive of melted and rapidly cooled-down material) as illustrated in Figs. 1*a*, *c*, and *e*. Figures 1*b*, *d*, and *f* show the corresponding X-ray spectra.

[2] Manufacturers of the tapes mentioned in the text were Minnesota Mining & Manufacturing Co., St. Paul, Minnesota, U.S.A. (Scotch Brand and aluminum tapes); Bayersdorf AB, W. Germany (Tesa tape); SC Tapes Ltd., England (Sellotape); Nashua, U.S.A. (Norton Bear tapes).

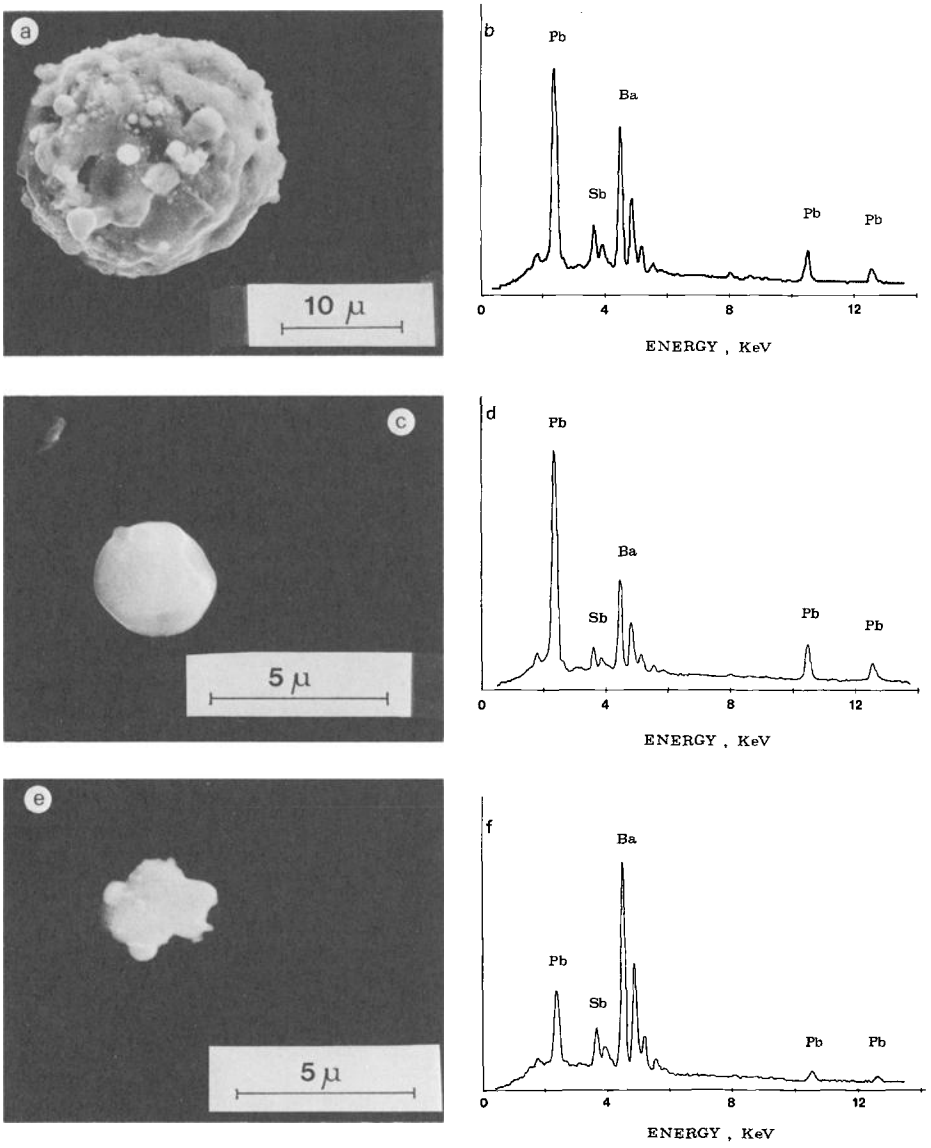

FIG. 1—*Morphology and X-ray analysis of several GSR particles deposited on hands. Norma ammunition was used throughout.* (a) *Large GSR particle embedded in adhesive tape. Note the characteristic morphology of the particle. Different regions of this particle were found to vary in their elemental composition; nevertheless, all the regions analyzed contained lead, barium, and antimony.* (b) *X-ray spectrum resulting from a 200-s analysis of the particle in* (a). (c) *Another GSR particle exhibiting high brightness.* (d) *X-ray spectrum resulting from a 200-s analysis of the particle in* (c). (e) *GSR particle found on tape. This sample was collected 3 h after the weapon was fired.* (f) *X-ray spectrum resulting from a 200-s analysis of the particle in* (e).

The size and total shape of the GSR particles varies; however, most of the observed GSR have a diameter of 1 to 5 μm and are almost spherical. A few larger particles with diameters of up to 30 μm were occasionally found, particularly in test firings with the pistol.

The sensitivity of X-ray analysis in the SEM is not sufficient for detecting microgram amounts of lead, barium, or antimony at lower magnifications on a large section of tape and locating GSR in this way. Dividing up the tape into small areas and analyzing these at higher magnifications would demand a very long time for a total analysis. It seems to us that the most efficient technique for such an examination would be searching systematically throughout the whole tape at a certain magnification, selecting particles believed to be GSR, analyzing them for a relatively short time interval, and in the case of a negative result continuing the search.

It has been noted that the GSR particles embedded in the tape show very high brightness when observed by SEM (secondary electron image), in contrast to other kinds of particles. This fact is helpful in the examination. Figure 2 shows a typical GSR particle

FIG. 2—*Typical GSR particle embedded in adhesive tape as seen in the SEM at lower magnification used for searching for GSR on the tape.*

as it appears on tape at lower magnification. In the actual investigation the X-ray analyzing system was programmed for continuously displaying the X-ray fluorescence counting rate in an energy range that included the M-lines for lead. Bright and preferably spherical particles were then selected. The selected particle was analyzed only if the counting rate for lead increased with higher magnification. Afterwards the magnification was decreased again and the search continued. The basic magnification employed in the examination was × 600, so that the most frequent GSR particles (size 1 to 3 μm) appeared as bright points on the cathode ray tube.

Results

The following experiments were carried out to determine the adequacy of the SEM technique in detecting GSR on hands in different situations. Ammunition of Norma manufacture was used in all the experiments. The particles were collected and the tapes were examined in the manner described above. Each of the tapes was examined in the SEM for a maximum of 2 h. Only the shooting hand was sampled. Except for the test of firing single shots with different types of guns, all experiments were conducted with a 7.65-mm Walter automatic pistol, Model PP.

Firing Single Shots with Different Types of Guns

Ten single-shot tests with various guns (pistol, revolver, and rifle) and calibers (7.65 mm, 0.38 in., 9 mm, 7.62 × 63 mm, and 30-06) were carried out indoors by three persons. After each firing the persons washed their hands and continued their daily activity for at least 5 h before the next experiment was performed. The samples were collected immediately after the shooting and examined by SEM. In each of the tests GSR particles were detected on the tape within the first 30 min of searching. One shot with a manual rifle (Huskvarna, caliber 30-06, bolt-action rifle) deposited less GSR particles, and a longer time (about 1 h) was needed to detect GSR with certainty.

Influence of Rinsing and Wiping the Hands

After discharging the test weapon, the shooting hand was rinsed with low-pressure running water for a few seconds and wiped with a cloth laboratory towel. The tape used for collection immediately after this procedure was found to contain GSR. The number of GSR particles was, however, much less than in previous experiments, and particles larger than about 3 μm were absent. Within 2 h of searching only two particles consisting of lead, barium, and antimony were identified. In addition, several round particles consisting of lead plus a small amount of antimony or *lead* plus *copper* plus antimony plus nickel[3] were observed. Such particles, although often found in our experiments and presumably GSR, have not been considered as sufficient evidence of shooting.

Influence of Washing the Hands

In this experiment one person discharged a weapon, washed his hands carefully with water and soap, and then wiped them with paper towels. This procedure appears to remove GSR from firing hands completely. Only two round particles (1 to 2 μm in size) consisting of lead but lacking antimony and barium were found in the course of 2 h, the limit for our examination.

The Time Factor

In actual cases, when a person is suspected of discharging a gun it is of considerable importance to detect gunshot residues on hands some time after the shooting. It is known that the amount of GSR on hands accompanied by normal unrestricted activity decreases rapidly with time. This problem obviously does not occur in a suicide.

For determining the effect of the time factor on the detection of GSR by SEM, five single-shot tests were conducted. After the shooting the subjects continued their normal daily activity (such as typing, writing, reading, engineering work, or laboratory work). The only restriction was that they were not supposed to wash their hands. The time between the shooting and the sample collection was 1, 2, 2½, 3, and 5 h. Upon examination, GSR were detected in all tests with the exception of the last one (5 h). In one of the tests (3 h) the subject (a chemist) handled powdered Sb_2O_3 after the shooting. A number of cubic, bright particles containing antimony were discovered in this sample; nevertheless, GSR could also be detected.

Our observations confirm that the number of GSR particles on the firing hand decreases rapidly with time. It was also noted that particles larger than approximately 10 μm dis-

[3] When describing the elemental composition of various particles, the elements found in trace amounts appear in parentheses. The major constituents are italicized.

appeared from the hands during the first hour after the firing. Only small GSR particles (< 3 μm) were observed after 2 h or more.

Unknown Firer Tests

To evaluate the credibility of the detection of GSR on hands by SEM, a series of tests was conducted where it was not known whether or not the person examined had fired a gun. In each of the tests two persons were involved. One or both of them fired a single shot. After collection, the tapes were examined without knowledge of which of the two persons had discharged a weapon. In two of the experiments the samples were collected immediately after the shooting. In the other three experiments the samples were taken 3 h after the shooting.

The subjects continued their daily activity during that time but were not supposed to wash their hands. The results of these tests are shown in Table 1, which indicates that in one case (Subject E) GSR were not detected on a firing hand. By contrast, the conclusion of nonfiring was always correct.

TABLE 1—*Results of blind tests.*

Test	Subjects	Subjects Who Fired a Gun	GSR Found
1[a]	A + B	A	A
2[a]	A + B	B	B
3	B + C	B + C	B + C
4	B + C	C	C
5	D + E	D + E	D

[a] Sample collection immediately after the shooting.

An interesting circumstance should be mentioned about Test 4. Subject C, as it happened, washed his hands twice during the time between the shooting and collecting the samples. Nevertheless, one particle with lead, barium, and antimony was found on the collection tape; this is sufficient evidence of GSR when using the SEM method.

Composition of Different Priming Mixtures

In the test firings described in this study ammunition of Norma manufacture was employed. This type of ammunition is the most common one in Sweden. The priming mixture of Norma ammunition contains the elements lead, barium, and antimony; furthermore, calcium and silicon are present. Primers of other manufacture may have a different composition.

We have carried out qualitative analyses of priming mixture residues from several types of ammunition. The mixture was scraped off the inside of discharged cartridge cases and analyzed by SEM. Unfortunately, the year of manufacture was known in only a few cases. The elements determined by this analysis are listed in Table 2. When trace amounts were found, the values appear in parentheses.

Scraping of residue from the inside of discharged cartridge cases does not fully indicate the true composition of the priming mixtures. Some elements may be totally lost and various ingredients of the shell casing, propellant, or other areas may be added to the residue. However, these facts must also be considered when relating the composition of GSR to that of the corresponding priming mixture.

TABLE 2—*Qualitative analysis of residue removed from discharged cartridge cases of various brands of ammunition.*

Ammunition	Caliber	Elements Found (Traces)
Norma (Sweden)	7.65 mm	Pb, Ba, Sb (Cu, Ca, Si)
Sako (Finland)	7.65 mm	Pb, Ba, Sb, Ca, Si, Hg (Fe, Cu)
SM[a] (Sweden)	7.65 mm	Pb, Ba, Sn, Ca, Si (Fe, Cu)
Lapua (Finland)	7.65 mm	Pb, Ba, Sb
S-40 (Finland, 1940)	9 mm	Pb, Ba, Sb, Sn, Ca, Si, Mn (Cu)
51 K (Sweden, 1951)	9 mm	Pb, Ba, Sn, Ca, Si (Fe)
Geco (W. Germany)	7.65 mm	Pb, Ba, Sb (Cu, Sn)
FN[a] (Belgium)	9 mm	Sb, Hg
RWS[a] (W. Germany)	9 mm	Pb, Sb, Sn, K, Cl, Hg (Cu)
H (USA) (Winchester)	0.22 in.	Pb, Ba, Si
ICI (England)	0.22 in.	Pb, Ba (Ca, Si)
X-Super (USA) (Winchester)	0.22 in.	Pb, Ba, Si
HP (Austria) (Hinterberger)	0.22 in.	Pb, Ba, Sb (K, Cl)
RWS (W. Germany)	0.22 in.	Pb, Ba, Sb, Si (Ca, Cu)
U (USA) (Remington)	0.22 in.	Pb, Si, Ca (Fe)
E (England)	0.22 in.	Pb, Ba, Si, Ca, P (Na, K, Cl, Fe, Cu)
Peters HV (USA) (Remington)	0.22 in.	Pb, Si, Ca (Fe, Cu)
Z (Czechoslovakia)	6.35 mm	Pb, Ba, Si, Ca (Cu, Fe)
FN[a] (Belgium)	6.35 mm	Sb, Hg, Sn, K, Cl
61 K (Sweden, 1961)	9 mm	Pb, Ba, Sn, Ca, Si

[a] The ammunition analyzed was presumably of older date (1940-1950).

Table 2 indicates that lead, barium, and antimony were found in many types of modern ammunition. Primers of rim-fire shells (0.22 in. in Table 2) often lack antimony, and ammunition of Remington manufacture lacks both barium and antimony. In older ammunition tin and mercury were frequently found to be present.

Discussion

In this work particles consisting of lead, barium, and antimony present on tapes lifted from hands were identifed as GSR. In addition to these elements many GSR particles were found to contain copper. Control experiments with samples collected from nonfiring subjects in a variety of occupations have never shown particles with that particular composition. However, particles with lead, *lead* plus chlorine (plus potassium), *lead* plus bromine, *barium* plus *sulfur* (plus zinc plus calcium), *lead* plus calcium, *antimony* plus *chlorine* (plus tin), *lead* plus *barium* (plus chromium plus calcium), and other combinations were found.

In some of the test firings, particles with lead, barium, calcium, and silicon were discovered. Although these elements represent an integral part of some of the priming mixtures (Table 2), they could be of different origin (for example, ink). For the same reason, particles consisting of *lead* plus antimony or *lead* plus copper (plus antimony) were not considered as evidence for the presence of GSR.

In the test experiments conducted in this study, the SEM method has always been successful in detecting GSR on hands immediately after shooting, and GSR were also found after rinsing the hands with low pressure water and wiping them with a towel. Washing hands carefully with water and soap is apt to remove GSR particles from the hands completely. Nevertheless, in one case (Subject C, Table 1), GSR were identified. Investigation of the effect of time on the examination revealed that GSR may still be detected 3 h after a single pistol shot has been discharged. This time limit will of course

depend on the activity after shooting, and the SEM technique may be successful in detecting GSR after a longer time period.

When the hitherto known quantitative methods such as NAA and FAAS for the detection of GSR are compared with the SEM technique, it appears that the latter method is much less dependent on the presence of environmental amounts of lead, barium, and antimony on the hands of the subjects examined. The SEM technique also appears to be superior to other techniques in cases when samples are collected after a longer period of time after the actual shooting [*8–10*]. It has been noted in our experiments that the larger GSR particles disappear from the hands very rapidly with time. Only small (1 to 3-μm diameter) particles were observed 1 to 2 h after the shooting. Since the weight of a 2-μm GSR particle is on the order of 10^{-11} g, the presence of such particles can hardly be detected by the previously published quantitative methods.

The method of searching for GSR described in the text is based on the presence of lead in the observed particle. Since the X-ray energy of the M-lines for mercury and the K-lines for sulfur are very close to that of the M-lines for lead, this examination is also sensitive for particles containing sulfur or mercury, and furthermore for particles with thallium, molybdenum, and bismuth. For this reason, many particles consisting of *barium* plus *sulfur* were detected during the examination. These particles (presumably $BaSO_4$, perhaps from paper) are probably the dominant source of environmental barium on hands. The sensitivity of the analysis for mercury should be important for the identification of GSR when certain ammunition of older manufacture is used (Table 2).

It can be seen in Table 2 that the priming mixture for many types of ammunition contains the elements lead, barium, and antimony. When such a type of ammunition is used GSR can be identified by SEM with great confidence. In addition to the results presented in this work for ammunition of Norma manufacture, some test shootings with a High Standard revolver and Hinterberger ammunition (0.22 in., rim-fire shells) were carried out. Gunshot residues consisting of lead, barium, and antimony of morphology and brightness similar to those of Norma ammunition were found. Since the relative amounts of lead, barium, and antimony in different particles vary, the type of ammunition employed cannot be determined by this technique. It should also be pointed out that GSR deposited on hands by ammunition of types like those of Remington manufacture (0.22 caliber) cannot be detected with certainty using the technique described in this study. Whenever possible the suspected gun should be used for firing ammunition of the suspected type, and tests should be performed on the experimental firer's hands. In this way, the particular GSR produced in the actual case can be reproduced.

Acknowledgment

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Addendum

After the completion of the manuscript for this paper, the following publications on the use of SEM for gunshot residue analysis have appeared:

Nesbitt, R. S., Wessel, J. E., and Jones, P. F., *Journal of Forensic Sciences,* Vol. 21, No. 3, 1976, pp. 595–610.
Keeley, R. H., *Proceedings of the Analytical Division of the Chemical Society,* Vol. 13, No. 6, 1976, pp. 178–181.

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