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G. M. Wolten,[1] Ph.D.; R. S. Nesbitt,[1] B.A.; A. R. Calloway,[1] B.A.; and G. L. Loper,[1] Ph.D.

Particle Analysis for the Detection of Gunshot Residue. II: Occupational and Environmental Particles

The first paper in this series [*1*] described the application of particle analysis to the identification of gunshot residue. In the course of developing this application, gunshot residue was identified in each of several hundred samples collected. In many instances, the nonfiring hand was sampled as a control, or "handblank" samples were taken from persons who had not fired a gun [*2*]. Some of these many tests were performed "blind," that is, without prior knowledge by the analyst of the nature of the sample. No false positives were obtained from nonfiring samples. Nevertheless, it was thought that better proof of the uniqueness of gunshot residue particles was required and that an investigation should be made of the possibility that particles in the natural environment or particles produced by man could closely resemble gunshot residue.

Small spheroidal particles of biological origin, such as pollen or cells, are easily recognized in the scanning electron microscope (SEM) as being composed of organic materials and do not constitute a problem. Small spheroidal particles of an inorganic or metallic nature can be produced by milling, wear in bearings, rapid condensation from a melt, and especially a vapor. Spheroidal particles containing elements heavier than sodium are not abundant in the natural environment. Irregular particles are the rule. Particles that give visible evidence of crystallinity can be immediately eliminated from further consideration.

Industrial and commercial operations that involve the metals or compounds of lead, barium, and antimony were surveyed with special emphasis on activities that may involve melting and vaporization, the so-called critical occupations. Samples were obtained from persons engaged in several of the critical occupations and some others. Approximately 80 samples were submitted for particle analysis. Many of the samples, which included those considered most critical (from people working with lead smelting and explosive rivets), were submitted for analysis in blind tests (without identification) and were randomly mixed with genuine gunshot residue samples representing both prompt and delayed collections. None of the occupational samples was falsely identified as gunshot residue by the experienced analysts; however, less experienced personnel may sometimes have encountered difficulties.

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[1] Members of the technical staff, Analytical Sciences Department, The Ivan A. Getting Laboratories, The Aerospace Corp., El Segundo, Calif.

Results of the Study

Stud Guns

A stud gun is a firearm used in construction for driving nails, rivets, and staples, usually into hard materials such as concrete and steel, but also into wood. The cartridges used in stud guns are composed of two parts, a projectile and a "powercap" (Omark) or "powerload" (Remington). The projectile, which takes the place of the bullet, is a nail, rivet, or staple that is placed ahead of the powercap or powerload. The powercaps or powerloads can be made with wad-type construction. In that case, they have the appearance of blank cartridges, including the head stamps. They can also be made with crimp-type construction, in which the front end is crimped to a fluted cone. The powercaps or powerloads are available in .22-, .25-, and .32-caliber sizes, with .22 caliber being the most common. Each caliber is available in several power or load levels.

Duplicate test firings were made of one .22-caliber Remington wad-type standard velocity (22W3) cartridge and one .22-caliber Omark crimp-type low velocity cartridge. The studs fired were made of zinc-coated steel, as is generally the case. The samples were analyzed in blind tests in which the operators had no information about the nature of the samples and performed a standard examination for the presence of gunshot residue. This consists of searching the specimen for particles which, by their visual appearance, might be gunshot residue particles and obtaining an X-ray spectrum of each to determine its elemental composition. This composition is then checked against a list of compositional criteria. This list was explained in the first paper of this series [*1*] and is reproduced here in Table 1. The list evolved during the course of the work, and its present form reflects the information acquired as a result of the work described here.

When examining the first sample of the Remington cartridge, the operator performed an X-ray analysis for 40 particles and immediately eliminated 36 that contained no lead, barium, or antimony. Only 13 of the 40 were spheroidal. The characteristics of the four remaining particles are given in Table 2. The first three were rejected because they contained zinc in the absence of detectable copper. The last one was rejected as nontypical because the ratio of the zinc to copper peak heights was 5:1, the opposite of what would normally result from a brass particle. The operator concluded that there were no particles consistent with gunshot residue.

TABLE 1—*Compositions of gunshot residue particles.*

1. Unique
   (a) Lead, antimony, and barium
   (b) Barium, calcium, silicon, with a trace of sulfur
   (c) Barium, calcium, silicon, with a trace of lead if copper and zinc are absent (stud gun residue contains copper and zinc)
   (d) Antimony and barium
2. Characteristic, especially if spheroidal, but not unique
   (a) Lead and antimony
   (b) Lead and barium
   (c) Lead if iron and phosphorus are absent
   (d) Barium if sulfur is absent or present only in trace amounts (larger amounts of sulfur with barium suggest origin other than gunshot)
   (e) Antimony (rare)
3. Any of the above (unique and characteristic) may also contain only these elements (unless specifically excluded above)
   (a) Silicon, calcium, aluminum, copper, iron, sulfur, phosphorus (rare), zinc (only with copper), nickel (rare, and only with copper and zinc), potassium, and chlorine
   (b) Tin is possible in obsolete ammunition
   (c) The presence of any other element usually indicates origin other than gunshot

TABLE 2—*Characteristics of four samples from stud guns.*

Shape	Size, μm	Major Elements	Minor Elements	Trace Elements
Irregular	2.5	barium, lead, zinc	silicon, iron	...
Irregular	3.8	barium, zinc, silicon, lead	...	iron
Spheroidal	5.8	barium, silicon, calcium	sulfur, aluminum, iron, chlorine, zinc, lead	...
Spheroidal	2.9	calcium, lead	barium, zinc, silicon, iron, chlorine, copper	...

The second test sample of the same cartridge (again analyzed blind) revealed 28 particles that contained barium and lead. All but one also contained iron, and all but three contained zinc, including the one without iron. Six of the barium, lead, and zinc particles were spheroidal, and the remainder were irregular. Many contained traces of copper, but in only two of these were the copper peaks larger than the zinc peaks. Taken alone, these last two are consistent with gunshot residue. A few of the barium, lead, and zinc particles also contained manganese and chromium, elements that, like zinc without copper, are inconsistent with gunshot residue.

The two particles that were consistent with gunshot residue were questioned on the ground that they were associated with a larger number of very similar particles that were not considered to be gunshot residue. However, if these two particles had been the only ones found, they would have been accepted as being consistent with gunshot residue.[2]

One of the Omark cartridge samples in the blind tests was dismissed by the operator (who was looking for gunshot residue) as containing nothing of interest. Thirty-nine particles of possible interest were recorded for the second Omark sample, twelve of them spheroidal. They generally contained barium and lead and often copper and zinc either as minor constituents or as traces. Thirty-five contained iron. There were 13 particles in which the copper peak was higher than the zinc peak. A typical composition, with a 3:1 ratio for copper/zinc, consistent with yellow brass, was lead, iron, and barium (major) with silicon, potassium, copper, calcium, and zinc (minor). Such particles are consistent with gunshot residue. There were, however, many particles clearly inconsistent with gunshot residue, such as the following two: (1) chlorine, sulfur, and zinc (major) with copper, silicon, iron, calcium, potassium, barium, and lead (minor), and (2) titanium, barium, and lead (major) with copper and zinc (minor). In addition, there were two irregular lead-only particles, but no spheroidal particles. This is significant, because all but one of the pistol cartridges examined yielded at least some spheroidal lead-only or lead-plus-copper particles, usually in excess.

The crimp-type powercap has a high incidence of copper and zinc in proportions consistent with brass. The crimp construction greatly increases the exposure of the front end of the brass case to the burning powder and could cause evaporation of copper and zinc.

The operators were impressed with the low percentage of spheroidal particles, the great sparsity of any lead-only particles, and the absence of spheroidal lead-only particles. They also noticed the presence of many particles similar to, but inconsistent with, gunshot residue either because the particles contained elements not found in gunshot residue or because the copper/zinc intensity ratio was nontypical. Finally, it seemed that the per-

[2]The record of this examination also shows a few particles of gold, silver, and copper, a composition that suggests jewelry. A ring worn by the carpenter who fired the stud gun may have received some rough treatment. This is an indication of the high probability of detecting whatever is present, and that what is present may be unexpected and possibly irrelevant. The less common heavier calibers of stud guns, .25 and .32, may be expected to have some antimony as well. Antimony was not found in the .22s.

centage of particles similar to gunshot residue particles, but containing iron, was too high for any except steel-jacketed bullets.

Considering the basic similarity of stud guns and conventional firearms, it is understandable that the operators, who had not previously seen residue from stud guns and had not known the nature of the samples, were cautious in their verdict. Noting the differences enumerated, they refused to call the samples gunshot residue despite the presence of some particles consistent with gunshot residue.

The rule (given in Ref *1*) that excludes stud gun residues is that the presence of substantial numbers of inconsistent particles overrules the evidentiary significance of particles consistent with gunshot residue, if the not-consistent particles are similar to those that are consistent and cannot be identified with an obviously separate origin. If the sample had been a mixture of genuine gunshot residue and stud gun residue, the rule would result in a false negative, but it would prevent the possibility of a false positive.

Children's Cap Guns and Blank Pistol Cartridges

Residue from children's cap guns contained antimony but no lead or barium. Distinctly crystalline fragments of an antimony compound were much in evidence, as were others that contained antimony, sulfur, and potassium as major and chlorine and phosphorus as minor constituents. There were particles, some spheroidal, that contained potassium, chlorine, calcium, and phosphorus and others that had calcium, phosphorus, zinc, and potassium as major and antimony, chlorine, and sulfur as minor ingredients. One spheroidal particle was found that gave only a phosphorus spectrum.

Two blank pistol cartridges were examined. One was a Winchester .22 Short with black powder and the other a Winchester-Western .38 Special with smokeless powder. Neither of them, when fired from a clean gun, gave any detectable gunshot residue or particles resembling gunshot residue.

Lead Smelting

Hand samples were examined from 13 different persons performing various jobs in a lead smelting operation.[3] While there were some minor individual differences, the samples were similar enough to permit the following summary: Despite wearing work gloves, all workers sampled had numerous particles containing heavy metals on their hands. Twenty-five to 75% of the particles were spheroidal, with an average of 50%. The sizes fell mostly into categories A (0.5 to 2 μm) and B (2.0 to 8.0 μm) [*1*], with 1 to 2 μm very common. In order of typical frequency of occurrence, the compositions were as follows:

(1) lead and zinc, which constituted 12 to 90% of the total and were usually the most numerous;

(2) only lead, which was present in about equal numbers of spheroidal and irregular particles;

(3) lead, zinc, and antimony;

(4) lead and antimony;

(5) only zinc; and

(6) some of the above with one or several of the following: cadmium, arsenic, titanium, manganese, tellurium, silver, chromium, and copper.

Although Compositions 2 and 4 are consistent with gunshot residue, the average 50% irregular morphology is not consistent, and neither are the remaining compositions in the list.

[3]Obtained from a lead smelting plant in Idaho by Mr. John F. Anderson, director of the Eastern Washington State Crime Laboratory.

The following is a list of the occupations of the subjects along with special features of the residues:

(1) lead refinery operator—lead-only particles most common;

(2) blast furnace topper—no copper-containing particles;

(3) blast furnace operator foreman—all spheroidal particles; most were lead, antimony, and zinc, and most of the remainder were lead and zinc;

(4) fuming plant operator—many zinc-only, no lead-only particles;

(5) cupola operator—typical, as described;

(6) kettle operator—typical, as described;

(7) laborer in ore mixing area—typical, as described;

(8) sulfur operator—typical, as described;

(9) security manager—typical, as described;

(10) maintenance man—typical, as described;

(11) pellet plant operator—typical, as described, except very few spheroidal particles;

(12) straight line machine operator—typical, as described, except very few spheroidal particles; and

(13) electrician—typical, as described, except for one particle.

The one nontypical particle found on the electrician's hand was a spheroidal particle, 5 μm in diameter, composed of barium, lead, zinc, copper, silicon, potassium, calcium, and iron. It was the only barium-containing particle in the entire lot and resembled particles found occasionally on other electricians not associated with lead smelting.

As in the case of the stud guns, all samples in this series were analyzed in blind tests. The operators' verdicts for all of these tests were "not gunshot residue." Possible difficulties can arise if very few particles are found, and the same comments made for stud gun residues apply here.

Automobile Brake Mechanic

The samples described below were taken from the palms and backs of both hands of a subject who is employed in an automobile supply store and who turns brake drums.[4]

Many irregular particles containing lead were found. Most of them contained one or several of these additional elements: iron, zinc, phosphorus, bromine, chlorine, and chromium. The combination of lead with bromine is highly characteristic of the exhaust of automobiles running on leaded gasoline. Presumably, the turning of the drums produced steel particles containing iron and chromium. The origin of the zinc is uncertain, but zinc is found in many parts of an automobile. Phosphorus is present in some gasoline and oil additives. There were nine barium-containing particles:

(1) spheroidal; iron, copper, sulfur, silicon, barium, and lead (major);

(2) spheroidal; lead, phosphorus, and calcium (major) with barium, zinc, and iron (minor);

(3) spheroidal; lead and zinc (major) with calcium, barium, and iron (minor);

(4) irregular; barium, lead, and magnesium (major);

(5) irregular; barium, lead, magnesium, and chromium (major);

(6) irregular; lead, barium, zinc, and iron (major);

(7) irregular; barium, calcium, phosphorus, lead, and zinc (major) with iron (minor);

(8) irregular; lead and iron (major) with phosphorus, barium, zinc, and calcium (minor); and

(9) irregular; lead, iron, copper, silicon, and barium (major) with chlorine (minor).

[4]These samples and those from the battery assembler tests were provided by Mr. Gary Gonzales of the Orange County, California, Sheriff's Crime Laboratory.

Only the first of the spheroidal and the last of the irregular particles pass the compositional criteria for particles consistent with gunshot residue, but only marginally. There is a combination of lead and barium, accompanied by elements that can occur in gunshot residue. However, these additional elements are present in rather larger proportions than is typical for gunshot residue of this composition, so that these particles would be considered somewhat questionable even if found in isolation. Their association with other quite similar particles that do not meet the criteria would tend to rule them out, as in the similar circumstances of the residue from stud guns.

Compounds of barium have wide industrial uses, including lubricating oil additives, greases, thickeners for pastes of various kinds, pigment fillers, and extenders for paints and rubber. Automotive brakes collect a miscellany of ground-up metal and brake lining particles, oil, grease, dirt, and debris of various kinds. Turning brake drums is a good way of producing particles compounded of many such ingredients, which could explain the presence of barium.

Lead-Acid Battery Assemblers

Samples were obtained from one person each in two different battery manufacturing establishments. The subjects were involved in assembling the battery plates. The traditional composition of such plates is an alloy of 94% lead and 6% antimony, but the proportions can vary. Barium sulfate is used as a plate filler.

The samples from the first person engaged in this work contained many irregular particles and one spheroidal lead-only particle. In addition, the following three were of special interest:

(1) spheroidal; lead (major) with antimony (minor);
(2) spheroidal; lead (major) with antimony, iron, silicon, and zinc (minor); and
(3) spheroidal; lead (major) with calcium, barium, iron, and zinc (minor).

The palm sample from the second person contained many irregular lead-only particles, but it also contained 40 spheroidal lead particles, many of which contained traces or more from among the following: iron, antimony, copper, zinc, and barium. The following three were typical:

(1) spheroidal; lead (major) with iron and barium (trace);
(2) spheroidal; lead, copper, and silicon (major) with zinc (minor); and
(3) irregular; lead, calcium, antimony, zinc, and silicon (major) with copper (minor).

Of all the spheroidal particles, one had a diameter of 2 μm and one, 3 μm. The others were all 5 μm or more in diameter, a size distribution not typical of most gunshot residues. With this many particles found, even those cartridges that give relatively large particles would have a few below 2 μm. Some of these particles pass the compositional criteria for gunshot residue, and their probable true nature can only be inferred from the other particles with which they are associated.

Auto Mechanics, Automobile Exhaust, Environmental Lead

The largest source of environmental lead contamination is leaded gasoline. Additional localized sources are lead smelting and secondary lead refining operations. Nonairborne lead contamination comes from peeling paint in old buildings. Lead issues from the exhaust of motor vehicles in the form of lead chlorides, bromides, oxychlorides, and oxybromides. In moist air, these are hydrolyzed to lead oxides, and some lead oxides issue directly from exhausts. However, most fresh exhaust that has been tested contains particles in which both lead and bromine are present. Also, most lead particles that are found on the hands of people and are not due to gunshot residue or specific occupations contain bromine and often chlorine. Chlorine is too commonplace to be an accurate indicator, but the presence of bromine in a lead particle can be taken to identify the particle as being from automobile exhaust. A minority of exhaust particles gives only a lead spectrum. The vast majority of automobile exhaust particles, with or without bromine, are irregular. A solitary spheroid is seen only occasionally. Spheroidal exhaust particles without bromine have not been observed in any of these tests.

Automobile exhaust particles are abundant on the hands of many of the automobile mechanics who were sampled. They are found on the hands of servicemen who drive trucks from job to job, and they can be found occasionally on almost anybody's hand. The auto mechanics also had various kinds of metal-containing particles, but none were of interest in this study, except for the particles already discussed from the brake installer's hand.

Other Occupations

None of the remaining handblanks from a large variety of occupations indicated potential conflicts with gunshot residue determinations; therefore, they are discussed only briefly.

The plumbers, machinists, laboratory technicians, and, to a lesser extent, electricians, tended to have collections of mostly irregular particles with complex compositions on their hands. The compositions include a wide variety of common and sometimes uncommon metals but no combinations other than lead particles that would meet the criteria for gunshot residue. Lead particles, in addition to the same variety of particles already described, were also quite numerous on the hands of a glassblower.

The particles found on painters' hands are also of the complex, many-element variety, except that the quantity of lead particles is low. In recent years, lead has been almost eliminated from ordinary paints. It is present, however, in the oil paints of artists, in ceramic glazes, and in printing inks, especially colored inks. Similar particles, in this instance rich in lead, titanium, and chlorine, were found on a person assembling stained glass windows.

Lead-tin combinations, which are indicative of solder, are found on the hands of television repairmen and electronic technicians. Spheroidal particles, which have the appearance of typical gunshot residue particles but which consist of iron or combinations of iron and various alloying elements used in steel, are numerous on the hands of welders and flame-cutters. These particles are tiny weld beads and are picked up occasionally by nearly everyone who handles objects made of iron or steel.

Another surprisingly common particle that looks like gunshot residue comes from the sparking flints used in cigarette lighters or the lighters used for gas burners, acetylene torches, and the like. They are spheres, sometimes porous like a sponge, and consist of cerium and iron, often with lanthanum. Occasionally, one is found on the hand of a nonsmoker. Sparking flints are made of a pyrophoric alloy of 70% "mischmetal" and 30% iron. Mischmetal is a mixture of rare earth elements from which the less abundant and more valuable elements have been removed. What is left may be mostly cerium, or a mixture of cerium and lanthanum, sometimes with traces of other elements. No particles that are relevant to the purposes of this study were found in the examinations of hand samples from one or several of the following: carpenters, floor sanders, bicycle tire assemblers, secretaries, pharmacists, liquor store clerks, janitors, furniture refinishers, gardeners, and printers.

Chemical Notes of Interest on Sources Not Tested

Pyrotechnic materials (rockets, firecrackers, and so forth) use black powder and powdered metals. Barium compounds are used to produce a green light, but antimony is not used. Lead (together with selenium) occurs only in delays for blasting caps. Similar delays in blasting caps for explosives contain lead, selenium, and tellurium as well; barium is used in gasless fuse powders.

Lead-base babbitts and Cerro alloys are low-melting-point alloys of lead and antimony, most with detectable amounts of tin, that are used in fusible links for sprinkler systems, as fillers in bearings for machinery, and less commonly as fillers in automobile body repair work. It would be appropriate to examine hand samples from users of these materials. Time constraints have prevented this information from being obtained for this report.

The second edition of *The Particle Atlas* [3] listed only one particle that would be considered consistent with gunshot residue. It was a very smooth sphere, about 46 μm in diameter, giving an X-ray spectrum in which the dominant element is barium and minor elements are iron, calcium, silicon, and aluminum. This particle is a glass bead of a type used in reflecting signs.

Conclusions

A subject's occupation is relevant to the evaluation of evidence furnished by particle analysis. The exploration of occupational particles described in this paper has been used to carefully frame such criteria for the identification of gunshot residue that occupational residues will be excluded. These criteria were given in the previous paper in this series [1], and the list of characteristic compositions has been reproduced in Table 1.

Summary

Particulate matter was removed from the hands of a variety of industrial and commercial workers and examined for resemblance to gunshot residue particles. In most cases, there was no resemblance. In some cases, the particles were similar. The results were used to formulate criteria for distinguishing gunshot residue particles from particles not of gunshot origin.

References

[1] Wolten, G. M., Nesbitt, R. S., Calloway, A. R., Loper, G. L., and Jones, P. F., "Particle Analysis for the Detection of Gunshot Residue. I: Scanning Electron Microscopy/Energy Dispersive X-Ray Characterization of Hand Deposits from Firing," *Journal of Forensic Sciences*, Vol. 24, No. 2, April 1979, pp. 409–422.

[2] Nesbitt, R. S., Wessel, J. E., and Jones, P. F., "Detection of Gunshot Residue by Use of the Scanning Electron Microscope," *Journal of Forensic Sciences*, Vol. 21, No. 3, July 1976, pp. 595–610.

[3] McCrone, W. C. and Delly, J. G., *The Particle Atlas*, Vol. 3, 2nd ed., Ann Arbor Science Publishers, Ann Arbor, Mich., 1973, particle No. 512, p. 758.

Address requests for reprints or additional information to
G. M. Wolten, Ph.D.
Analytical Sciences Department
The Ivan A. Getting Laboratories
The Aerospace Corporation
Box 92597
Los Angeles, Calif. 90009