

G. M. Wolten,¹ Ph.D. and R. S. Nesbitt,¹ B.A.

On the Mechanism of Gunshot Residue Particle Formation

REFERENCE: Wolten, G. M. and Nesbitt, R. M., "On the Mechanism of Gunshot Residue Particle Formation," *Journal of Forensic Sciences*, Vol. 25, No. 3, July 1980, pp. 533-545.

ABSTRACT: The results of the present study are consistent with the hypothesis that gunshot residue is formed by the condensation of vaporized bullet and primer materials that segregate into metallic and compound particles. Some of the metallic vapors are oxidized and "scavenged" by oxygen and sulfur-rich primer compounds, among which the sulfur compounds appear to be more effective. The "bullet" particles of the residue thus originate in the bullet material, and the "primer" particles are a mixture of primer-derived and bullet-derived materials.

KEY WORDS: criminalistics, gunshot residues, chemical analysis, particle analysis

The development of the particle analysis method of gunshot residue detection was described in detail in a report [1] and in condensed form in a series of three papers in this journal [2-4].

Gunshot residue is mostly particulate, and extensive statistics were collected in our previous work on the distributions by size, shape, and elemental composition of the particles deposited on the firing hand by many types of handgun cartridges. The results suggested hypotheses, some obvious, some speculative, about the nature of the processes that could produce the particles and the distributions observed. To provide a better experimental basis for the more speculative aspects of these hypotheses, we have undertaken a limited series of further experiments that were different from those previously reported [1-4]. Since the results both supported and clarified the hypotheses, we will first explain what those hypotheses were, then what experiments were done, and how they relate to the theory.

Implications of Past Work

As shown in our previous work, lead bullets result in residue in which from 70 to 100% of all the particles are lead. For slow bullets, the number of particles (found in prompt collections) is extremely high.

If the bullet is coated with copper or brass, the result is the same, except that a substantial portion of all the particles, not just the lead particles, contains some copper.

If, on the other hand, jacketed or semijacketed bullets are used, the fraction of lead particles in the total collection is greatly reduced, the reduction being somewhat correlated with the fraction of the bullet's surface that is covered by the jacket. Only a small

Received for publication 11 Oct. 1979; accepted for publication 23 Nov. 1979.

¹Members of the technical staff, The Ivan A. Getting Laboratories, The Aerospace Corporation, El Segundo, Calif.

percentage of the particles contains copper. The total number of particles is smaller as well.

One conclusion that these observations led to was that most of the lead in residue comes from the bullet rather than the primer. Although there are contrary claims in the literature [5], this conclusion has recently been confirmed by a definitive experiment using radioactive tracers [6].

Through the ability of an electron beam to melt low-melting but not high-melting particles in an electron microscope, evidence was obtained that at least the smallest of the lead particles consisted of metallic lead rather than lead oxides. Considering the bullet origin of the lead, it was considered probable that most of the lead particles consisted of metallic lead. Unless a windowless detector is used, the X-ray analyzer of the scanning electron microscope cannot detect oxygen and hence cannot distinguish between an element and its oxide, so that indirect evidence, such as the above, must be used if available.

On the other hand, those particles classified as "primer particles" because of their elemental content were shown to contain oxides, sulfides, and salts in which the anion contained oxygen (oxysalts), for example, barium meta-antimonate and basic lead sulfate (lanarkite). Except for the occasional presence of (easily oxidized) powdered metal, the primer ingredients are compounds initially and cannot be expected to be reduced to elements in the oxidizing environment of the primer explosion.

Using the observations and the reasoning described, one can picture the process of particle formation to proceed in the following manner. The expanding gases from the burning powder initially compress the bullet axially, so that it expands radially. The enlarged bullet is then "swaged," as it were, through the barrel by the rapidly increasing gas pressure. This results in strong frictional heating. Also, the rifling rips small fragments from the bullet, and these particles are in part melted and in part vaporized. The metal vapors from the bullet mix with the vapors of inorganic compounds from the primer and are driven out of the flash gap or ejection port at high velocities. In flight, the vapors condense into particles that then impinge on the firing hand where many of them stick.

While all vapors are miscible, most inorganic compounds in the liquid and even more in the solid state cannot dissolve metals and vice versa. One would therefore expect that, upon solidification, the metals will separate from the compounds and form separate particles. This is the basis for the classification of residue into "bullet particles" and "primer particles."

To explain why copper from coated bullets is found both in the bullet and the primer particles, one needs to assume that some portion of the metallic vapors becomes oxidized, first by oxygen or sulfur from the vaporized primer material and then, after escape from the gun, perhaps by atmospheric oxygen as well. Thus, the primer particles contain a contribution from oxidized bullet material and might better be termed "compound" particles.

Occasionally, some soot is found on the hand, and, quite infrequently, one finds flakes of partially burned smokeless powder. In another previous investigation [7,8], no organic compounds were found on the hand, other than these occasional flakes. It seems that most of the time the powder burns completely enough to leave no characteristic residues.

In our speculations, we also attempted to explain the drastic reduction in the particle count on the hand as the bullet velocity increases [1,2]. The experiments reported here did not address this question, and it is taken up only to complete the record.

It is suggested that the observed reduction does not result from the production of fewer particles but from the greatly increased suction in the wake of the faster bullet. This draws the particles forward more strongly and causes more of them to exit through the muzzle, leaving fewer to be forced out at the breech.

This explanation is consistent with the fact that, in the hand residue, the number of bullet particles is reduced slightly more as a function of velocity than the number of

primer particles. Primer particles, on the average, are larger and are produced farther back of the bullet than the bullet particles. It is also consistent with the rather tentative observation [1] that the residue issuing from the muzzle may be richer in bullet and poorer in primer particles than the hand residue.

Present Investigation

The experiments performed in the present work consisted of adding materials not normally found in residue to cartridges, firing the cartridges, and determining whether any of the residue particles and which kinds contained these "tracers" and how much.

Adding various oxides and salts to the powder tested the hypothesis that they should be found, if at all, dissolved in the oxides and salts that were thought to be the ingredients of the primer particles, but should not be found in the bullet particles. Adding several metals that differed in their refractoriness and oxidation resistance both to the bullet and to the powder tested the hypotheses that the dissolving action of low-melting lead promotes the transfer of a copper coating into the residue and that partial oxidation of the copper is responsible for it being found both in metallic (bullet) and compound particles.

The need for independent bulk elemental analysis in this work arises from the following circumstances. The X-ray analyzer of a scanning electron microscope can perform a fair quantitative analysis for specimens that are large and have flat surfaces, but it cannot do so for micrometre-sized particles that do not have flat surfaces. While most metals are miscible, lead behaves somewhat abnormally in that it is almost immiscible with several other metals, including copper and cobalt. This raises the possibility that a relatively small amount of copper in lead could be expelled upon solidification and coat the surface of a lead particle. In that case, the X-ray analyzer would detect copper "in" lead particles much more frequently than the actual amount of copper would warrant and give an exaggerated impression of its concentration. The results of this work suggest that this did indeed happen with both copper and cobalt. Therefore, a quantitative bulk analysis is necessary.

Instrumentation

Scanning Electron Microscopy

The same AMR-1200 scanning electron microscope (SEM) with a Kevex 5100-D X-ray system was used in this work as was used in all the previous work described in Refs 1 to 4.

Flame Emission

An Instrumentation Laboratory AA/AE spectrophotometer, Model 251, was used for flame emission studies. The flame was produced by an acetylene/air mixture when rubidium was analyzed and by an acetylene/nitrous oxide mixture in the case of strontium and indium.

Atomic Absorption

The same spectrophotometer was used, with an acetylene/air flame, for atomic absorption analysis of cobalt.

In both flame emission and atomic absorption procedures, the instrument integrates the signal for a set time, which was chosen to be 4 s. A concentration in $\mu\text{g/mL}$ is then displayed. Sample is introduced continuously until about ten readings have been obtained, which are averaged. In this report results are stated in micrograms per ten (rather than

one) millilitres, because that is the volume of solution containing the entire amount recovered from the hand.

Photoluminescence Spectroscopy

The instrumentation used for photoluminescence measurements was an Aminco-Bowman Model 4-8202 spectrofluorometer equipped with a photomultiplier tube with S-20 spectral response and a modified sample compartment to accommodate a liquid nitrogen-cooled sample holder. Reference 9 describes the modifications in detail, as well as the experimental procedures.

Sample Handling

Hands were always sampled by the adhesive lift technique in this work [1]. It consists of depositing adhesive on top of a 25-mm (1-in.) diameter cylindrical aluminum disk by means of Scotch #465 transfer tape. The disk, adhesive side down, is then pressed against the hand for sampling.

If the examination is by SEM, the disk is searched for particles. Because of the time-consuming nature of this work, only a fraction of the total area of the disk surface is systematically scanned. Reference 1 presents evidence that the variations in particle density from area to area are smaller than the variations in total number of particles from shot to shot. Therefore it is valid, within the standard deviations discussed in Ref 1, to extrapolate the results obtained from a fraction of the area to the total area.

If the examination is by any form of bulk elemental analysis, the residue collected in the adhesive is dissolved off the surface of the disk in its entirety.

For particle analysis, the adhesive lift technique is by far the most convenient technique. It has also been adopted as the standard technique for photoluminescence analysis in conjunction with a 7M hydrochloric acid leach, which produces the chloride ion complexes required for the observation of luminescence from the elements of interest [9]. To conduct elemental analyses for the present project, the adhesive lift technique was modified slightly in two respects. The composition of the leach solution was chosen to meet the requirements both of the tracer in question and of the particular analysis method. A sheet of polyethylene was used between the aluminum disk and the adhesive layer. After the hand was sampled, the polyethylene, with the residue-containing adhesive, was lifted off the disk and placed into 10 mL of the leach solution. In this way, longer soaking times could be used without excessive dissolution of aluminum or impurities contained in the aluminum.

A rather mildly acidic solution was used for the recovery of rubidium sulfate and strontium sulfate tracers. A more strongly acidic solution was also tried to test whether the sulfates had been converted to less soluble forms. This did not seem to be the case. To recover indium and cobalt tracers, enough nitric acid was used in the leach solutions to insure ready dissolution of both the metals and their oxides. The volume of leach solution per sample disk was standardized at 10 mL.

Cross-Contamination

In doing the analyses, one must be aware that conventional cleaning of a handgun with commercial solvent, patches, and wire brushes, even if done thoroughly, does not remove all residue. Residue resulting from a particular firing is usually slightly contaminated with residue from many previous firings of the same weapon. Small percentages of particles that contain copper or antimony are observed fairly often in residue from cartridges that contain neither element. In the present work, the same phenomenon was observed for all the tracers used. Quite often, one or several particles would be found that

contained the tracer employed in a previous rather than the current test, although the gun had been cleaned. To make sure that this contamination came in fact from the gun and not the range or any other source, a test was conducted with two guns. One was the same gun used for the entire series; the other had never been used to fire any cartridges that contained tracers. Contamination was observed in the former but not the latter.

Specifications and Protocols

Hand-Loaded Cartridges

Smokeless powder was Hercules double-base, cut round flakes (disks). Bullseye was used for mild loads and Unique for medium power loads.

All primers were the standard "small pistol" primer, Winchester 1½-108. A Remington 1½ was used only for comparison and was richer in calcium and silicon than the Winchester product.

Cartridge cases were brass, not plated, and only new cases were used. Federal 38 UP was used for all .38 Special cartridges, and Winchester UW9LP for the few 9-mm cartridges included in the tests.

Three types of bullets were used, two for the .38 Special and one for the 9-mm Luger:

Code A: .38-caliber, 158-grain round-nose lead, Speer #4647, lubricated, flat base. This was combined with 3.0-grain (194-mg) Bullseye for a mild load.

Code B: .38-caliber, 125-grain jacketed hollow-point, Sierra #8320, diameter 0.357 in. (9.07 mm), called "hollow cavity." The base is flat and the nose is a straight-sided, hollowed-out cone. The jacket covers the base and most of the nose. This bullet was combined with 5.3-grain (343-mg) Unique for a medium powered load.

Code C: 9-mm, 100-grain jacketed hollow-point. Speer #3983, diameter 0.355 in. (9.02 mm). These bullets have a hollow base, a rounded, hollowed-out nose, and a jacket that covers the base and most of the nose. They were combined with 5.7-grain (369-mg) Unique for what is a medium load for this type.

These combinations were chosen to be representative of common commercial cartridges. However, the loading apparatus secured the bullets in the case only by friction and did not produce a cannelure around the case. This probably resulted in easier release of the bullets with somewhat lower power and velocity. Velocities were not measured.

Addition of Tracers to Powder

Initial attempts to mix some of the tracer compounds into bulk powder resulted in poor mixing and separation. The procedure adopted was to drop a weighed amount of the tracer compound directly into the case during the loading of each individual cartridge. It made no detectable difference whether the tracer was introduced above or below the powder.

Addition of Tracers to Bullets

Tracers were added to bullets by electroplating or solution-plating the bullet with the following procedures, which were optimized only until a usable but not necessarily perfect plating was obtained.

1. **Surface Preparation:** Lead bullets were cleaned ultrasonically in trichloroethylene for at least 20 min. This was followed by hot, cathodic, alkaline cleaning, for 1 min, at 60

to 70°C, in a 10% (w/v) solution of sodium hydroxide, at 4 V and 50 mA. The bullet was the cathode, and a carbon rod was used as the anode.

2. Plating Conditions: The plating conditions are given in Table 1. For indium, the amounts deposited were a linear function of time, 0.03 g/h, under the stated conditions.

Cobalt plated well on copper but was difficult to plate over lead. Three different sets of conditions, giving three different rates of deposition, were used. The most satisfactory one is listed in Table 1.

For bismuth, the rate of deposition could not be determined, because substantial quantities of lead were dissolving while bismuth was being deposited.

Attempts to electroplate bismuth resulted in ample deposits of bismuth, which, however, were of very poor quality. Acceptable results were obtained by first electrodepositing a "strike" of copper on the bullet and then dipping the latter in the following solution without passage of current: 15 mL of 70% perchloric acid was diluted to 100 mL and about 0.04 g mucilage added. A piece of bismuth metal was partially immersed into the magnetically stirred solution, into which the bullets were then dipped for approximately 1 h. This procedure was also used to coat the jackets of jacketed bullets with bismuth. These did not need the preliminary strike of copper, but some lead dissolved from the exposed lead tip.

Results and Discussion

Additions to Smokeless Powder

In separate experiments, rubidium sulfate and strontium sulfate were added in amounts ranging from 0.05 to 0.17% (rubidium) or to 0.37% (strontium) of the weight of the smokeless powder. These two materials exhibited substantially different behavior. In SEM analysis, only the high levels of addition occasionally led to the observation of a small number of rubidium-containing particles. With strontium, from one quarter to one third of the compound particles contained strontium at the lower levels of tracer addition. At high levels, the fraction occasionally rose to above 80% of the primer particles but no strontium was ever detected in a bullet particle. Tables 2 and 3 list these data. In the

TABLE 1—*Plating conditions.*

Condition	Indium	Cobalt	Gold	Copper (Strike)
Cathode	bullet	bullet	bullet	bullet
Anode	indium	carbon	gold	copper
Current	50 mA	100 mA first 20 min, then 225 mA	low, not measurable	100 mA
Voltage	4 V	3 V first 20 min, then 4 V	approximately 1 V	1 V
Temperature	ambient	ambient	warm	60–65°C
Composition of plating solution	KCN, 28.0 g; NaOH, 6.0 g; dextrose, 6.0 g; InCl ₃ , 3.0 g; H ₂ O, to make 200 mL	CoSO ₄ · 7H ₂ O, 55.0 g; NaCl, 1.7 g; boric acid, 5.0 g; H ₂ O to make 100 mL	commercial plating solution containing gold and KCN	CuCN, 50 g; NaCN, 66 g; Na ₂ CO ₃ , 106 g; KNa tartrate · 4H ₂ O, 85 g; copper (metal), 35 g; H ₂ O to make 1.9 L (0.5 gal)
Plating time	45 min to 2 h	60 to 75 min	30 min (to deposit 0.08 grain = 52 mg)	9–15 min (to deposit about 0.02 g)

analysis of promptly collected firing samples by flame emission, rubidium was never detected above background. Strontium could always be seen to be present. Usually, it could not be quantitated because the signals were barely above background. Only at the highest levels of addition did the signals rise sometimes but not consistently to as much as six times background, as shown in Table 4.

Experiments with the oxides of samarium, gallium, and zirconium, listed in Table 5, gave SEM results similar to those for strontium sulfate. Thus, rubidium sulfate appears to act anomalously.

Table 5 also lists experiments with germanium, cobalt, and gold in elemental form. The compounds previously discussed were found exclusively in primer (compound) particles, as expected, and so was the elemental germanium, which, apparently, became completely oxidized. Cobalt and gold, added in elemental form, were found both in metallic and nonmetallic particles, but cobalt was oxidized to a significant and gold only to a slight extent. It was quite rare to find the additive forming a particle by itself. Of the additives in Table 5, only the cobalt experiment was subjected to bulk elemental analysis, for comparison with bullet coating experiments.

Bullet Coatings

Copper, Lualoy, or brass-coated bullets give residues in which high percentages of both the metallic and the primer particles contain copper [1,2]. The example of copper led us to coat bullets with indium, cobalt, bismuth, and gold. In all cases, substantial fractions of both metallic and compound particles contained the tracer, as shown in Table 6. Flame emission results for indium and photoluminescence results for bismuth are given in Tables 7 and 8, respectively.

TABLE 2—SEM examination of residue when rubidium was added to powder.^a

Rubidium Sulfate Added to Powder, μg	% of Powder	Particles Found		Primer Particles, n	Particles Containing Tracer Material, n	Types of Tracer-Bearing Particles	Notes
		n	% of Area				
234	0.068	50	50	34	0	...	1, 6
538	0.157	100	2	95	0	...	2, 3, 6
172	0.050	36	50	31	0	...	2, 6
130	0.067	111	6	19	0	...	5
	(see Note 5)						
187	0.054	39	15	6	0
252	0.073	24	30	13	0
496	0.144	53	50	39	2	primer	4
515	0.150	64	70	44	6	primer	...
538	0.157	36	50	31	0	...	2
562	0.164	36	50	32	0	...	2

^aNotes:

1. Rubidium sulfate crushed in mortar.
2. Not crushed (to leave closer to smokeless powder size).
3. Muzzle blast collected in bag; all others are adhesive lifts from firing hand.
4. Added on top of powder; all others below powder directly above primer.
5. Round-nose lead bullet with 3.0 grain Bullseye; bullet weight, 158 gr; 4-in. (102-mm) .38 Special revolver.
6. Jacketed hollow-point bullet with 5.3 grain Unique; bullet weight, 125 grain; 4-in. (102-mm) .38 Special revolver.
7. Jacketed hollow-point bullet with 5.7 grain Unique; bullet weight, 100 grain; 9-mm semiautomatic.

TABLE 3—SEM examination of residue when strontium was added to powder.^a

Strontium Sulfate, μg	% of Powder	Particles Found		Primer Particles, n	Particles Containing Tracer Material, n	Types of Tracer-Bearing Particles	Notes
		n	% of Area				
100	0.051	200	10	41	6	all primer	5
120	0.062	318	10	56	6	all primer	5
312	0.160	133	3	16	7	4 primer, 3 strontium-sulfur only	4, 5
317	0.163	128	6	26	3	2 primer, 1 strontium-sulfur only	4, 5
307	0.158	127	10	42	15	all primer	5
174	0.051	15	50	8	0	...	6
186	0.054	73	50	63	30	27 primer, 3 strontium-sulfur	6
188	0.055	53	50	47	14	13 primer, 1 strontium-sulfur	6
188	0.055	29	50	26	17	all primer	6
192	0.056	22	50	13	4	all primer	6
556	0.162	71	50	64	34	32 primer, 2 strontium-sulfur only	6
570	0.166	11	50	9	3	all primer	6
188	0.055	29	50	26	17	all primer	6
554	0.161	74	50	70	59	58 primer, 1 powder flake	6
532	0.155	83	50	77	33	all primer	4, 6
189	0.051	7	50	6	0	...	7
205	0.055	11	50	10	1	primer	7

^aNotes: see Table 2.

Because photoluminescence in the past has been less commonly employed for gunshot residue than atomic absorption or neutron activation, and its use to determine bismuth in gunshot residue is new, experimental spectra for bismuth are shown in Figs. 1 and 2.

In the case of indium, handblank² levels of twice that of a tape blank appear to be due to some interfering substance that has not yet been identified rather than to a background of indium. The firing handsamples gave indium levels twice those of the handblanks and four times that of the tape blank.

In the case of bismuth, determined by photoluminescence, there was no signal at all from tape blanks and handblanks. Firing handsamples gave levels of bismuth ranging from 10 to 100 times the detection limit.

Atomic absorption analysis was applied to residue from eight cartridges plated with amounts of cobalt ranging from 18 to 87 mg, and two cartridges that contained 563 and 635 μg (0.29 and 0.33%) cobalt powder in the smokeless powder. All results were uniformly at background levels, that is, no cobalt was detected. Although the detection limit (in atomic absorption) for cobalt is not as good as for most of the other analyses done, the number of cobalt-containing particles detected was also modest, and it may be that little

²Handblanks are samples taken from a hand without prior firing of a gun.

TABLE 4—*Flame emission results for strontium.*

Sample and Concentration	Strontium per Handsample or Equivalent (10 mL Solution), μg
Blank solutions	0–0.02
Tape blank	0.00
Standard solution	
0.03 $\mu\text{g}/10\text{ mL}$	0.03
0.06	0.07
0.06	0.07
0.09	0.09
Handblank	0.04
Handblank	0.04
Handsamples	
0.14% strontium sulfate in powder	0.04
0.14	0.06
0.15	0.06
0.16	0.06
0.20	0.12
0.20	0.06
0.21	0.03
0.22	0.06
0.24	0.07
0.26	0.06
0.28	0.13
0.37	0.12

TABLE 5—*SEM results for various tracers added to the powder.*

Tracer	% of Powder ^a	% of Sample Area Examined	Tracer- Containing over Total Bullet Particles	Tracer- Containing over Total Primer Particles
675 μg Sm_2O_3	0.020	25	0/7	15/33
940 μg samarium acetate	0.27	33	0/28	12/32
	(0.1% samarium)			
532 μg Ga_2O_3	0.16	25	0/6	11/20
683 μg Ga_2O_3	0.20	25	0/3	10/24
716 μg ZrO_2	0.21	25	0/26	15/48 ^b
732 μg germanium	0.21	25	0/72	21/41
451 μg cobalt	0.23	2	3/99	18/26
2.4 mg gold	1.2	6.9	9/95	1/20

^aAll cartridges Code B except gold, which was Code A.

^bOne particle containing zirconium only.

cobalt is present and is seen in the SEM only because it forms a surface coating, as explained earlier.

A dramatic difference was observed with gold. Gold plating the bullet resulted in the detection of gold in 97% of the metallic particles and 59% of the (much fewer) primer particles. However, gold in the powder resulted in a rather small number of gold-containing particles.

TABLE 6—SEM analyses of residues from coated bullets.

Coating	Remarks	% of Sample Area Searched	Tracer-Containing Particles over Total Particles		
			Bullet	Primer	Other
Cobalt	...	10	11/158	14/41	11 cobalt only
Cobalt	...	10	8/178	16/41	...
Cobalt	...	3	26/95	23/25	...
Cobalt	...	4.6	8/84	8/21	...
Cobalt	base only plated	20	9/98	10/23	...
Bismuth	round nose lead	1.8	33/96	14/26	2 bismuth only
Bismuth	jacketed hollow point	10	61/64	13/14	2 bismuth only
Indium	... ^a	2	58/101	7/19	...
Gold	...	2	157/162	13/22	...

^aTraces of indium were masked by potassium X-ray lines, and hence ratios are lower limits.

TABLE 7—Flame emission results for indium-plated bullets (Code A).

Sample	Indium per Handsample or Equivalent, μg
2% hydrochloric acid solution	0.015 ± 0.013
0.15 μg standard	0.15 ± 0.01
0.25 μg standard	0.24 ± 0.01
0.50 μg standard	0.52 ± 0.01
0.75 μg standard	0.71 ± 0.03
1.08 μg standard	1.10 ± 0.02
Tape blank	0.21 ± 0.02
Handblank	0.59 ± 0.05
Handblank	0.58 ± 0.02
Handsample	0.57 ± 0.03
Handsample	1.04 ± 0.02
Handsample	1.33 ± 0.03
Handsample	1.23 ± 0.03

TABLE 8—Photoluminescence results for bismuth, lead, and antimony from bismuth-coated bullets, in μg per handsample or equivalent (10 mL solution).

Sample	Bismuth	Lead	Antimony
Tape blank	...	0.05	...
Handblank	...	0.32	...
Handblank	...	0.26	...
Handsample, Code B cartridge	> 1.00	1.24	0.095
Handsample, Code A cartridge	0.28	1.44	0.072
Handsample, Code A cartridge	0.34	2.00	0.082
Handsample, Code A cartridge	0.12	1.36	0.052
Handsample, Code A cartridge	0.24	1.44	0.052
Approximate detection limits ^a	< 0.01	< 0.01	0.02

^aThese are practical limits for handsamples. The inherent sensitivity of the method can be considerably better if ideal (background-free) samples are used.

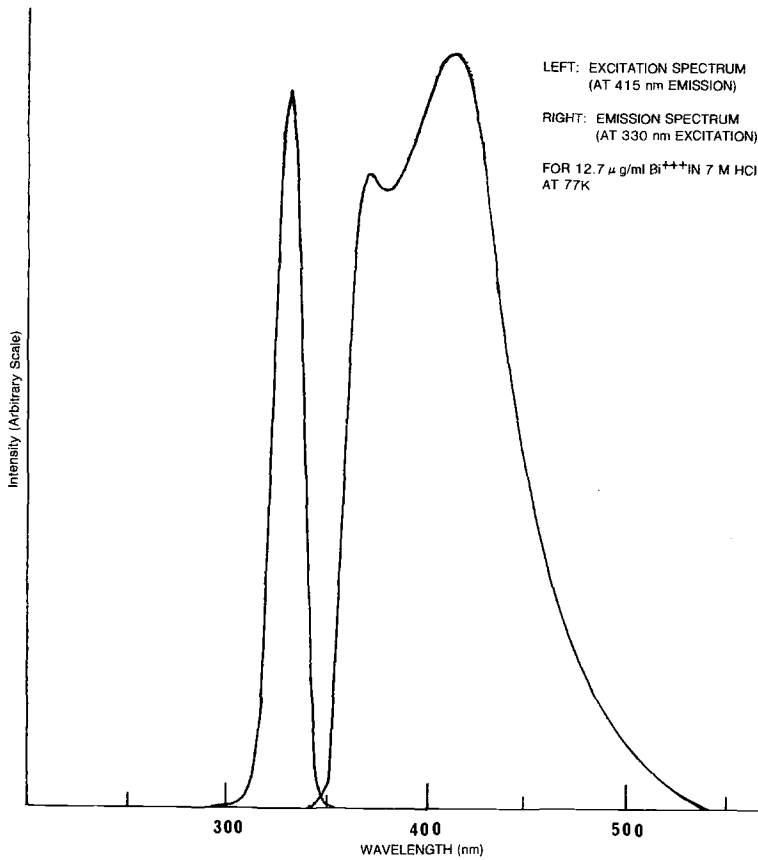


FIG. 1—*Bismuth excitation and emission spectra.*

The difference can be understood if one considers the following: Molten droplets of primer material that spray into the powder when the primer detonates will dissolve material that is soluble in primer material. Since gold is very oxidation resistant, very little gold will be taken up in this fashion. Gold also has high melting and boiling points, and therefore not much of it will melt and none of it is likely to vaporize. To vaporize gold, it must first be dissolved by melting lead. This occurs very effectively when the gold is placed on the bullet, but when it is in the powder its contact with melting and vaporizing lead is minimal, and most of it will probably stay behind in solid form, in the gun or in the casing.

The high amounts of gold, and of indium and bismuth as well, in residue when the metals are in contact with melting lead on the bullet can be attributed to mixtures of lead with either bismuth or indium having lower melting points than pure lead at all concentrations. In the lead-gold system, melting points stay below that of lead until the composition reaches 32% by weight of gold [10-12]. In all three cases, one should expect substantial amounts of the tracer metal to be carried along with the lead that leaves the bullet by melting or evaporation. Although most of the gold in residue is found in the metallic particles, more of it is seen in the nonmetallic particles than one would expect on the basis of its high resistance to oxidation. This could be explained by the known solubility of gold in the molten sulfides present in the primer.

One would predict slightly less copper in the residue than bismuth, indium, or gold,

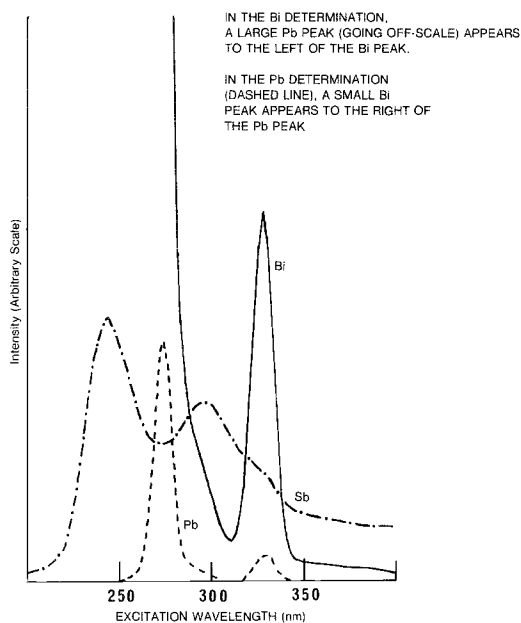


FIG. 2—Photoluminescence analysis of a sample from a hand that fired a bismuth-plated bullet (lead intensity reduced by a factor of 10) (slit widths: antimony, 3 mm and lead, 1 mm).

because at copper concentrations above about only 0.1%, the melting points become higher than that of lead. They do stay below 1000°C until quite large concentrations of copper are reached. One must note, as explained earlier, that there is virtually no solid solubility in the copper-lead system. Consequently, when a copper-lead mixture solidifies, the copper may segregate to the surfaces of the particles, where it would be detected much more frequently than would be the case if it were uniformly distributed in the bulk of each particle. Thus, in this case, the number of particles that appear to contain copper by SEM examination would give an exaggerated impression of the copper content of the sample. To gain a better measure of the copper content, atomic absorption analyses were performed on handsamples of residue from two firings of Lubaloy-coated .22-caliber bullets. Both samples indicated 0.4 μg copper. This is in the same range as the bismuth results and less than the indium results and is consistent with the prediction based on a phase diagram.

The cobalt-lead system shows the same lack of solid solubility as the copper-lead system [13,14]; even above 1500°C, only 0.25% cobalt will dissolve in lead. Even with this small cobalt content, the melting points rise much faster than they do with equivalent amounts of copper; at a concentration of 0.2% by weight cobalt, the melting point is 1300°C.

The prediction that results from this is that much less cobalt would be dissolved but that this smaller amount would again segregate to the surfaces of the particles. This is consistent with seeing some cobalt-containing particles in the SEM but failing to find it by bulk analysis.

References

- [1] Wolten, G. M., Nesbitt, R. S., Calloway, A. R., Loper, G. L., and Jones, P. F., "Final Report on Particle Analysis for Gunshot Residue Detection," Report ATR-77 (7915)-3, The Aerospace Corporation, El Segundo, Calif., Sept. 1977.

- [2] 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.
- [3] Wolten, G. M., Nesbitt, R. S., Calloway, A. R., and Loper, G. L., "Particle Analysis for the Detection of Gunshot Residue. II: Occupational and Environmental Particles," *Journal of Forensic Sciences*, Vol. 24, No. 2, April 1979, pp. 423-430.
- [4] Wolten, G. M., Nesbitt, R. S., and Calloway, A. R., "Particle Analysis for the Detection of Gunshot Residue. III: The Case Record," *Journal of Forensic Sciences*, Vol. 24, No. 4, Oct. 1979, pp. 864-869.
- [5] Keisch, B. and Callahan, R. C., "Potential Uses of Lead Isotope Ratios in Gunshot Cases," *Journal of the Association of Official Analytical Chemists*, Vol. 61, No. 3, 1978, pp. 520-525.
- [6] Purcell, M. A., "Radiotracer Studies of Test-Fired Bullets," Master's thesis, University of California, Irvine, 1976 (contact Prof. V. P. Guinn, Dept. of Chemistry).
- [7] Mach, M. H., Pallos, A., and Jones, P. F., "Feasibility of Gunshot Residue Detection Via Its Organic Constituents. Part I: Analysis of Smokeless Powders by Combined Gas Chromatography-Chemical Ionization Mass Spectrometry," *Journal of Forensic Sciences*, Vol. 23, No. 3, July 1978, pp. 433-445.
- [8] Mach, M. H., Pallos, A., and Jones, P. F., "Feasibility of Gunshot Residue Detection Via Its Organic Constituents. Part II: A Gas Chromatography-Mass Spectrometry Method," *Journal of Forensic Sciences*, Vol. 23, No. 3, July 1978, pp. 446-455.
- [9] Loper, G. L., Calloway, A. R., O'Neill, M. A., Peak, S. A., Wolten, G. M., and Jones, P. F., "A Field Test of Photoluminescence for Investigating Suicides by Firearms," Report ATR-77 (7915)-2, The Aerospace Corporation, El Segundo, Calif., Feb. 1978.
- [10] Lyman, T., Ed., *Metals Handbook*, 1948 ed., American Society for Metals, Cleveland, Ohio, 1948.
- [11] *Landolt-Börnstein Zahlenwerte und Funktionen*, 6th ed., Part III, *Melt-Equilibria and Surface Phenomena*, Springer-Verlag, Berlin, 1960.
- [12] Levin, E. M., Robbins, C. R., and McMurdie, H. F., *Phase Diagrams for Ceramists*, American Ceramic Society, Columbus, Ohio, 1964 and Supplements, 1969 and 1975.
- [13] Elliot, R. B., *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York, 1965, p. 328.
- [14] Shunk, F. A., *Constitution of Binary Alloys, Second Supplement*, McGraw-Hill, New York, 1969, p. 262.

Address requests for reprints or additional information to
 G. M. Wolten, Ph.D.
 Ivan A. Getting Laboratories
 The Aerospace Corporation
 P.O. Box 92957
 Los Angeles, Calif. 90009