Primer Gunshot Residue Detection from the Firing of a Black Powder Revolver[a]

L. T. Briscoe, K. L. Kosanke, and R. C. Dujay
Mesa State College, Center for Microscopy, PO Box 2647, Grand Junction, CO 81501

Abstract: *A study was conducted to determine the potential for being able to identify primer gunshot residue (PGSR) within the substantial quantities of particulate residues produced during the firing of a revolver using Black Powder propellant and a percussion cap primer. Samples of gunshot residue (GSR) were collected from the shooter's hands, from surfaces to the side of the shooter, from surfaces near the muzzle of the weapon, and from various locations on the weapon itself (both inside and outside). It was found to be relatively easy to identify PGSR from the hand of the shooter, from surfaces to the side of the weapon, and from most locations on the weapon. However, using the methods of this study, no PGSR was identified within the large amount of Black Powder residue projected out the muzzle of the weapon and on the inside of its barrel.*

Keywords: *gunshot residue, GSR, Black Powder, percussion cap primer, scanning electron microscopy, SEM, energy dispersive spectroscopy, EDS*

Introduction

When a weapon is fired, gunshot residue (GSR) can originate from the primer, the propellant, the metals contained in the bullet, the bullet jacket, the cartridge case, and the gun barrel. For the purposes of determining whether a suspect is likely to have fired a weapon (or has otherwise been exposed to a weapon firing), most generally only those residues originating from the primer are sought in the analysis. For most ammunition these primer gunshot residues (PGSR) contain lead, barium and antimony and are detected using a combination of scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS).[1] Unlike weapons using modern propellants, when a Black Powder weapon is fired, a substantial quantity of solid propellant residue is produced in addition to the relatively small amount of PGSR. This gave rise to concern that PGSR might be difficult or impossible to identify in samples taken from many surfaces typically sampled by investigators. The purpose of this brief study was to determine whether the firing of a Black Powder revolver is likely to produce readily detectable amounts of PGSR.

Background

To better quantify the basis for concern regarding the relatively small amount of PGSR produced, consider the following. A common type of primer available for Black Powder weapons is Remington's No. 10 percussion cap, the construction of which is illustrated in Figure 1. These percussion caps measure approximately 4.5 mm in length and diameter, and they were found to contain approximately 22 milligrams (mg) of primer composition. While the exact chemical formulation of the percussion cap composition is unknown to the authors, the presence of barium, antimony/sulfur, lead, aluminum, copper/zinc, and iron were identified using EDS, see Figure 2 in which the elements associated with particles of primer composition are identified. (A small metallic appearing filament composed of copper and zinc is thought to have been produced from the brass cup of the percussion primer when the primer composition was being cautiously scraped from it.) Based on the elements found in the primer composition and information from the material safety data sheet for the percussion caps, it seems most likely that the formulation is similar to one identified in the literature[2] as being among those commonly used. The formulation is presented in Table 1. Using this formulation as input, thermodynamic free energy modeling predicts that

a. Originally printed in the Spring 2005 MAFS Newsletter

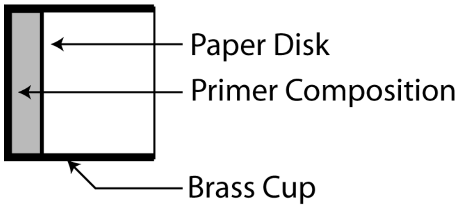

Figure 1. *An illustration of the construction of a percussion cap primer. (Not to scale.)*

approximately 60% of the reaction products from such a primer will be solids. Thus such a primer can be expected to generate approximately 14 mg of PGSR. On the other hand, a typical load for a Black Powder weapon is 2.6 grams (40 grains) of Black Powder. Upon firing, this is expected to produce approximately 65% solid residues,[4] for a total of approximately 1.7 grams. Thus the relative amount of PGSR produced upon firing under these conditions amounts a little less than 1% of the amount of Black Powder residue.

If such a small amount of PGSR is reasonably well mixed within the substantially greater quantity of Black Powder residue, it is unlikely that the normal protocol for PSGR detection will be successful in finding it. However, if the PGSR is not well mixed chemically with the Black Powder residues, there is still the possibility for locating PGSR from the firing of a Black Powder weapon. There are two mechanisms through which this might occur.

The simplest and most obvious mechanism is if some portion of the PGSR escapes the weapon prior to mixing with the high temperature reaction products from the burning Black Powder. Because of the high pressures produced inside a weapon when it is fired, and the necessary clearances (small gaps) between various component parts of the weapon, gunshot residue has the opportunity to exit the weapon at several points. If the weapon is of the type that uses a percussion cap, the area of the nipple (over which the percussion cap is slipped) offers the best chance for undiluted PGSR to escape. (Figure 3 is a conceptualized illustration of one chamber of a Black Powder revolver, in which the basic configuration of the parts of the revolver is shown.)

The second means by which detectable PGSR might be produced from a Black Powder weapon arises if there is some mechanism by which the once diluted PGSR might subsequently become concentrated. A process such as this has been observed to occur when there are substantial differences in the melting and boiling points of the mixture of reaction products.[3] In that event, as some chemical reaction products are condensing and solidifying, others can be temporarily left behind as vaporized products to condense and solidify later in the process. In so doing, there can be a segregation of some of the various reaction products.

Table 2 is a list of the principal reaction products of the primer composition given in Table 1, as well as those from Black Powder.[4] Also given in Table 2 are the melting and boiling points for most of those reaction products.[5] While there are individual differences in the melting and boiling

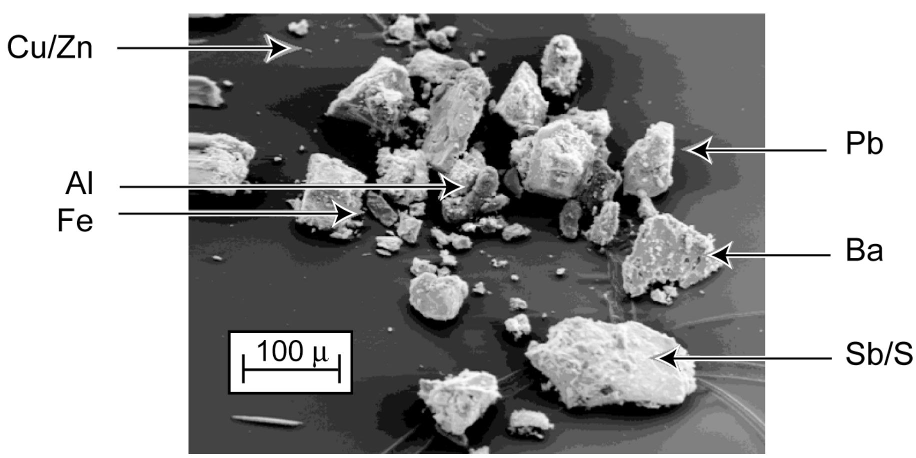

Figure 2. *Electron micrograph of the elements found in a Remington No. 10 percussion cap.*

Table 1. A Common Percussion Cap (Primer) Composition.[2]

Ingredient	%
Lead styphnate	46
Tetracene	4
Barium nitrate	25
Antimony sulphide	20
Aluminum	5

points, it would seem that those differences are neither sufficient nor systematic enough (between the Black Powder residues and PSGR) to produce the type of segregation of reaction products that would allow the relatively easy detection of PGSR. (Note that thermodynamic modeling predicts the reaction temperature to be approximately 1800 °C when burning at a pressure of 100 atmospheres.)

Materials and Methods

Weapon and Ammunition

The weapon used in this study was a 44 caliber "New Army Colt Reproduction in Stainless Steel" revolver made by Fillipietta. The propellant used was 40 grains (2.6 grams) of 3Fg Goex Black Powder. A 185-grain (12-gram) lead ball was then loaded on top of the powder, and a mixture of paraffin and Vaseline was packed over each loaded cylinder to seal it and prevent cross firing of the weapon. (Figure 3 is a conceptualized illustration of one chamber of a Black Powder revolver, in which the basic configuration of the parts of the revolver is shown.) Prior to loading, the weapon

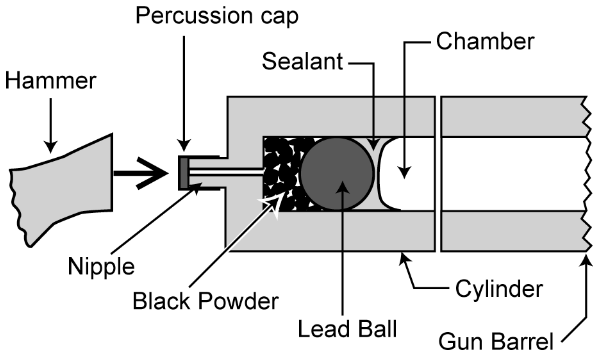

Figure 3. *A conceptual illustration of the configuration of a Black Powder revolver. (Not to scale.)*

was very thoroughly cleaned. Remington No. 10 primers were the only primers used in this study.

Setup of Collecting Surfaces

Three collecting surfaces were prepared prior to the test firings. Each collecting surface had four standard Amray 0.5-inch diameter SEM stubs, with conductive adhesive carbon dots attached. Previous analysis of the blank stubs confirmed that they were free of contamination. The stubs were placed in a four corner arrangement on the cleaned collecting surface. Two such collecting surfaces were positioned to the sides (one right and one left) of the shooter at a distance of approximately 12 inches from the weapon and at a point directly in line with the weapon's cylinder. A third such collecting surface was positioned approximately 12 inches in front of the end of the barrel of the weapon; however, this collecting surface had

Table 2. *The Primary Solid Reaction Products Expected To Result when Firing a Black Powder Weapon.*

Source	Solid Reaction Products	Weight %	Temperature (°C)[a] Melting	Boiling
Percussion Cap	Barium sulfide	26	1200	(ns)
	Lead sulfide	26	1114	(ns)
	Antimony metal	23	630	1750
	Aluminum oxide	15	2015	2980
	Lead metal	10	327	1740
Black Powder[b]	Potassium carbonate	43	891	(d)
	Potassium thiosulfate	25	>200	(d)
	Potassium sulfate	20	1069	1689

(a) CRC 1995 (b) von Maltitz 2001 (d) = decomposes (ns) = not specified

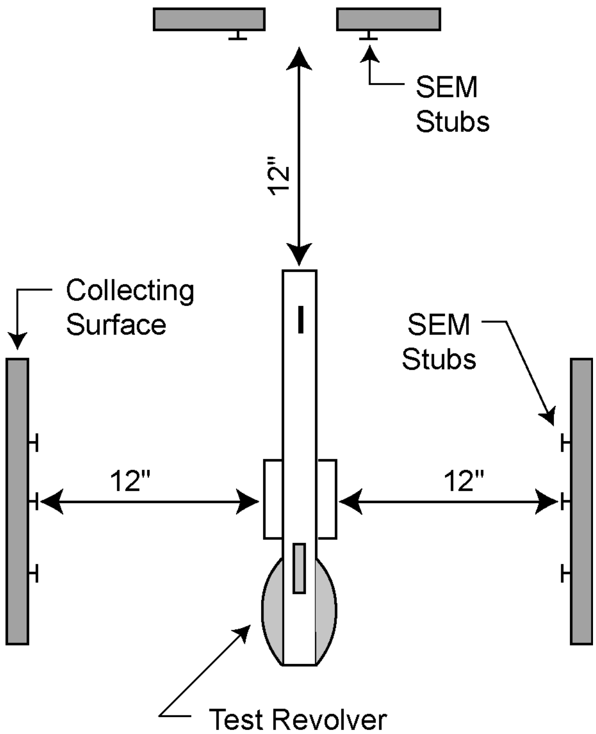

Figure 4. *A sketch illustrating the setup for the test.*

a hole in the middle to allow the passage of the bullets. Figure 4 is a sketch illustrating the setup for the test.

Firing of the Weapon

The test firings occurred outdoors in an area free from residues from any previous weapon firings. The weather was sunny and clear with only a very slight breeze. Prior to firing the first shot, the adhesive covering was removed from each stub on all collecting surfaces. The weapon was held in the right hand of the shooter, while the left hand supported the grip of the revolver. Once the weapon was properly positioned in the middle of the three collecting surfaces, a shot was fired through the pre-cut hole in the front collecting surface. One SEM stub on each side collecting surface was removed after the first shot. Because of the large amount of Black Powder residue observed to have been deposited on the front collecting surface, two stubs were removed from the front collecting surface. To avoid contamination, this was done by a researcher other than the shooter. (The shooter was solely responsible for handling and firing the weapon.). The stubs that were removed were immediately placed in a storage case and the lid was shut tightly before the second shot.

The shooter proceeded to fire the weapon a second time. Another stub was removed from each of the side collecting surfaces. Because of the very large amount of residue that had been deposited on the front collecting surface, both remaining stubs were removed after the second shot. For the two collecting surfaces located to the side of the shooter, the third stub was removed after three shots, and the final stub was removed after a total of six consecutive firings of the weapon.

GSR Sampling of the Weapon and Shooter's Hands

Immediately after completion of the test firings, the outside and inside of the shooting hand as well as the opposing hand were sampled. First the web area on the outside of each hand was dabbed with a conductive adhesive carbon dot a total of thirty times. Then, using a new stub and carbon dot, the entire surface of the inside of each hand was sampled in a similar manner. This sampling was performed by a researcher, not the shooter, to ensure that there was no contamination of the samples. Each sample was immediately placed in a storage case after sampling.

Exterior and interior surfaces of the weapon were also sampled using conductive adhesive carbon dots. Depending on the nature of the surfaces being sampled, various methods were used. For irregular surfaces the carbon dot was attached to a small piece of Velostat film (conductive plastic film). After sampling, the carbon dot and Velostat were attached to a standard 0.5-inch SEM stub using a second conductive adhesive carbon dot. For sampling some confined surfaces on the interior of the weapon, double-sided conductive adhesive strips were temporarily attached to the end of thin rod and pressed against the surfaces. After sampling, the adhesive dot was carefully peeled off the rod and placed on a stub.

PGSR Analysis

The search for PGSR was accomplished using a manually operated AMRAY 1000 (recently remanufactured by E. Fjeld Co.) and equipped with digital imaging software. The instrument was operated with an accelerating potential of 20 kV. Prior to analysis, the GSR samples were

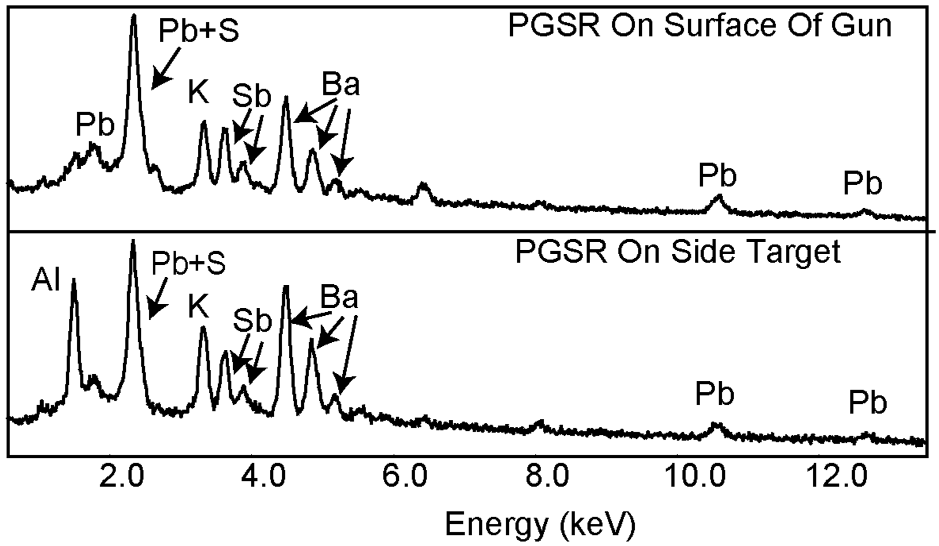

Figure 5. *X-ray spectra of typical unique PGSR particles.*

carbon coated to improve the quality of the images produced. The X-ray spectrometer used was energy dispersive, using a Kevex Si(Li) detector (with a beryllium window) in conjunction with an American Nuclear System model MCA 4000 multichannel analyzer using Quantum-X software (version 03.80.20). The EDS system was calibrated prior to analysis using a copper and aluminum sample.

To facilitate the identification of particles of interest on the SEM image screen, backscatter imaging and a careful adjustment of contrast and brightness were required. In the backscatter imaging mode, objects composed of chemical elements with relatively high atomic number appear brighter than those with lower average atomic number. After a brief period of experimentation, imaging settings were found that aided in the identification of PGSR particles among very large numbers of non-PGSR particles. For the purposes of the work, a particle of interest was defined as those for which the particle itself appeared noticeably brighter than the bulk of other material. Once a particle of interest was located, an X-ray spectrum was acquired, with the resulting peaks used to identify the chemical elements that were present. Figure 5 is an example of an X-ray spectrum of two PGSR particles. Because of the beryllium window on the detector, X-rays less than approximately 1 keV do not reach the detector. In contrast to the elements found in PGSR, Black Powder residues produce only those X-ray peaks from potassium and sulfur. (A prior examination of unreacted and reacted primer composition had confirmed that it contained substantial quantities of three key indicators of PGSR, i.e., lead, barium and antimony). Consistent with commonly used definitions,[1] in this work: unique PGSR particles were those producing X-ray peaks for lead, barium and antimony, whereas characteristic PGSR particles were those producing peaks for only two of the three unique PGSR elements.

The propose of this brief study was only to determine whether it was likely that one could detect PGSR particles from the firing of this type of Black Powder weapon. It was not intended to statistically quantify the PGSR distribution or its abundance relative to Black Powder residue particles. In addition, the instrument was manually operated, making the effort labor intensive. Accordingly, in this study the analysis only proceeded until a relatively few particles of interest were located and characterized, this ranged from 5 to 26 particles. See Figure 6 for an electron micrograph of two typical PGSR particles.

Results

The results of this study are summarized in Table 3 and in the text below. Although not specifically included in Table 3, the GSR on each of the samples consisted primarily of those residues produced by the burning of the Black Powder propellant.

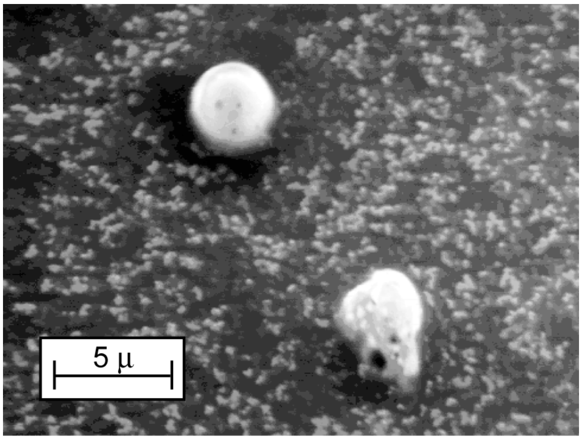

Figure 6. *Electron micrograph (secondary electron imaging mode) showing typical PGSR particles.*

Shooting Hand

From the sample taken from the shooting hand (the hand that pulled the trigger) 22 particles of interest were examined. Of these, two particles were found to be unique and three particles were found to be characteristic. The non-shooting hand was not examined for PGSR; it was assumed that the results would be consistent with common experience with regard to finding PGSR on non-shooting hands.

Left-Side Collecting Surface

From the stub from the collecting surface placed to the left side of the weapon after one shot was fired, 23 particles of interest were examined. Of these, two particles were found to be unique and three particles were characteristic. Because a reasonable number of PGSR was found on the collecting surface to the left side of the shooter after only one shot, only that one sample was examined. It was assumed that similar results would have been found after two, three, or even six shots of the weapon. Given the geometry of the weapon it can be assumed that similar results would be found on the collecting surface located to the right of the shooter.

Front Collecting Surface

After an extended search of the large amount of particulate matter expelled from the muzzle of the revolver, after just one shot was fired, 26 particles of interest were found and analyzed. Of these, no unique or characteristic particles were found. Twenty two of the particles were found to contain lead (presumably bullet lead), of which most had a generally spheroidal appearance. No other elements other than those from the Black Powder (potassium and sulfur) were found. This is not to say that absolutely no PGSR was emitted from the muzzle of the weapon. Because of time constraints and lack of an automated scanning system, the search for PGSR was abandoned after a few hours, and the entire surface of the collecting stub was not searched. However, it does seem clear that, at the very least, it is much more difficult to find PGSR that has been expelled from the muzzle of the revolver than it is to find PGSR that have escaped elsewhere.

Outside Surface of the Revolver

A total of 15 particles of interest particles were examined from the outer sample collected from the surface of the gun. Of the 15, four of the particles were unique, and none of the particles were

Table 3. *A Summary of the Results of the Search for PGSR from the Firing of a Black Powder Revolver.*

	Number of Particles of Interest				
Sample Source	Analyzed[(a)]	Unique[(b)]	Pb/Ba	Pb/Sb	Ba/Sb
Shooting Hand	22	2	1	1	1
Left Collecting Surface	23	2	3	0	0
Front Collecting Surface	26	0	0	0	0
Revolver Outside – Surface	15	4	0	0	0
Revolver Outside – Nipple	5	3	0	0	0
Revolver Inside – Nipple Screw	6	2	1	0	0
Revolver Inside – Barrel	12	0	0	0	0

(a) This is the number of "particles of interest" that were analyzed by EDS. These particles were selected because their image in the backscatter mode was noticeably brighter than the bulk of the rest of the particles. (b) Unique particles had all three elements (Pb, Ba, and Sb) visibly present in the EDS spectra.

characteristic. From the outside of a nipple (over which the percussion cap had been installed), only five particles of interest were examined. Of these, three were found to be unique, and none were characteristic.

Inside Surfaces of the Revolver

From the end of the nipple screw (the end at the entrance to the rear of the weapon's chamber), of the six particles of interest examined, two were found to be unique and one characteristic. From the inside of the barrel, 12 particles of interest were located. Consistent with what was found for material expelled from the muzzle of the weapon, none of the particles were unique or characteristic. Six of the particles contained lead (presumably bullet lead) and somewhat unexpectedly, one of the particles contained a small amount of barium, presumably from the primer composition.

Conclusions

As expected, PGSR can be located with relative ease amid the copious Black Powder residue from certain areas surrounding at least some types of Black Powder weapons after their having been fired. These areas are those from which PGSR can escape prior to its intimate high temperature mixing with the Black Powder combustion products. Specifically, for a revolver using percussion caps, such as used in this study, that includes the shooting hand (and presumably the face) of the shooter, objects to the side of the weapon (presumably including clothing), the outside surfaces of the weapon especially the interior and exterior surfaces near the nipple (over which the percussion cap is positioned). However, it appears that once the PGSR has thoroughly mixed with the high temperature Black Powder combustion products, it becomes so diluted that it is either quite difficult or impossible to locate. Specifically, this includes the material expelled from the muzzle of the weapon and the inside of the barrel (and presumably the inside of the chamber and cylinder ahead of the nipple).

Although not specifically studied in this investigation, these results suggest that significant quantities of PGSR may not be found from the firing of some types of Black Powder weapons. This includes any Black Powder weapon that does not provide a ready path that allows the escape of PGSR without it first having mixed with copious quantities of Black Powder residue. One such example would likely be a weapon using sealed metal cartridges with an integral primer. For such a weapon it would be expected that there will be almost no chance for PGSR to escape without its intimate high temperature mixing with, and dilution by, the much greater quantities of Black Powder combustion products

Obviously much additional research should be performed in this area. It would be preferred to have run an automated scan over the entire stub of material collected from near the muzzle of the weapon. This would more definitely establish the statistical probability of finding occasional PGSR intermixed with the Black Powder residues. Although it would be expected to yield substantially similar results, it would also be appropriate to test different types of primers and various Black Powder substitutes for their production of PGSR. Finally it would be appropriate to investigate the production of PGSR from Black Powder weapons using sealed metal cartridges.

References

1. ASTM E 1588-95: Standard Guide for Gunshot Residue Analysis by Scanning Electron Microscopy / Energy Dispersive Spectroscopy. ASTM ,1995.
2. J. S. Wallace, Chemical Aspects of Firearms Ammunition. *AFTE*, vol. 22(4), 1990, p. 374.
3. K. L. Kosanke, R. C. Dujay and B. J. Kosanke, Characterization of Pyrotechnic Reaction Residue Particles by SEM/EDS, *Journal of Forensic Science*, vol. 48(3), 2003, pp. 157–168.
4. I. von Maltitz, Our Present Knowledge of the Chemistry of Black Powder, *Journal of Pyrotechnics*, *vol.* 14, 2001, pp. 25–39.
5. CRC Handbook of Chemistry and Physics, 75th ed., CRC Press, 1995.