Annalivia Harris,[1] *M.S.*

Analysis of Primer Residue from CCI Blazer® Lead Free Ammunition by Scanning Electron Microscopy/Energy Dispersive X-Ray

REFERENCE: Harris, A., "**Analysis of Primer Residue from CCI Blazer® Lead Free Ammunition by Scanning Electron Microscopy/Energy Dispersive X-ray,**" *Journal of Forensic Sciences,* JFSCA, Vol. 40, No. 1, January 1995, pp. 27–30.

ABSTRACT: Traditional gunshot residue analysis is based on the detection of lead (Pb), barium (Ba) and antimony (Sb). CCI's recent development of a lead free centerfire primer for their Blazer® Lead Free ammunition presents a new challenge for forensic scientists since it does not contain lead, barium or antimony. Research presented here is the result of the analysis of this new primer by scanning electron microscopy/energy dispersive X-ray which involved analyzing CCI's lead free primer directly as well as the gunshot residue obtained by test firing a series of firearms using CCI's Blazer® Lead Free ammunition. Analysis of the residue from a fired primer determined that the only metal present was strontium; however, when the lead free ammunition is discharged in firearms previously fired using traditional primer ammunition, particles containing lead, barium and antimony were detected. These findings hold true for older firearms cleaned prior to testing as well as a "new" firearm that had only been test fired by the manufacturer.

KEYWORDS: forensic science, gunshot residue, primer analysis

Cascade Cartridge Industries (CCI) has recently developed a lead free primer [*1*]. CCI's lead free primer is a patented formula that does not contain the traditional primer elements of lead (Pb), barium (Ba) or antimony (Sb). CCI combines this primer with a fully jacketed bullet that is marketed under the registered trade name of Blazer® Lead Free TMJ (total metal jacket). This combination of a lead free primer and fully jacketed bullet is intended to eliminate hazardous airborne lead particulates and is being marketed for use in indoor firing ranges. Because of this health concern, the introduction of more lead free primers can be expected in the future. Therefore, it may be worthwhile for gunshot residue analysts to familiarize themselves with the composition of these new primers as they become commercially available.

Listed in Table 1 are the components typically found in traditional primers [*2,3*] and the corresponding components found in CCI's lead free primer.[2]

According to CCI, the only metal in their lead free primer is strontium. Strontium is detectable by both Scanning Electron Microscopy/Energy Dispersive X-Ray (SEM/EDX) or Atomic Absorption Spectroscopy (AAS), the two most common methods currently used by forensic laboratories to analyze gunshot residue [*4*]. While strontium may not be a commonly encountered element and its use as an oxidizer in primer ammunition is patented by CCI, it does have commercial uses that will limit its uniqueness to gunshot residue. Various strontium salts are used in pyrotechnic materials, not only as an oxidizer, but also to produce a red flame [*5*]. Three common pyrotechnic materials that use strontium are flares, fireworks [*6*] and red tracer ammunition. The *Merck Index* [*7*] also lists matches as a use for strontium nitrate, however, the *Encyclopedia of Chemical Technology* [*5*] does not mention the use of strontium in matches in either the section on strontium or the section on matches. Neither Andrasko [*8*] nor Glattstein, Landau, and Zeichner [*9*] mention the detection of strontium in their respective papers on the analysis of matches by SEM/EDX.

Three SEM/EDX studies relating to CCI's lead free primer were undertaken: 1) the direct analysis of CCI's lead free primer; 2) analysis of gunshot residue generated by test firing CCI's lead free ammunition in a series of firearms of different calibers; and 3) analysis of the metal shavings from inside the chamber of a used firearm.

Materials and Methods

Firing of Weapons and Collection of Gunshot Residue

The shooter washed and dried his hands prior to firing the weapon. The researcher, wearing latex gloves, sampled the front and back of the shooter's thumb, web and index finger of his firing hand by repeatedly touching those areas with a carbon sticky tab on an aluminum SEM stub.

Electron Microscopy

Gunshot residue analyses were performed at the Image and Chemical Analysis Laboratory (Montana State University) on a JEOL 6100 Scanning Electron Microscope with a NORAN Energy Dispersive X-Ray Detector. The SEM was operated under the following conditions:

LaB_6 filament
25 kV accelerating voltage
39 mm working distance
×1500 magnification

Received for publication 18 April 1994; revised manuscript received 13 June 1994; accepted for publication 15 June 1994.

[1] Montana Department of Justice, Forensic Science Division, Missoula, MT.

[2] Personal communication with Jim Ward, Chemist, CCI INC., Lewiston, ID.

Presented at the Northwest Association of Forensic Scientists Fall Meeting in Boise, ID, 1993.

TABLE 1—*Components typically found in traditional and CCI lead free primers.*

	Traditional Primers	CCI Lead Free Primer
Sensitizers	Tetracene	Tetracene
Initiators	Lead styphnate	Diazodinitrophenol
Fuels	Antimony sulfide	Smokeless powder
Oxidizers	Barium nitrate	Strontium nitrate

TABLE 2—*The firearms and ammunition used in this research.*

Firearm	Ammunition
(A) Beretta 9mm Semiauto	CCI Blazer® lead free 9mm LUGER 124 GR. TMJ
(B) Glock .45 APC Semiauto	CCI Blazer® lead free .45 Auto 230 GR. TMJ
(C) Smith and Wesson .38 SPL Revolver	CCI Blazer® lead free .38 SPL +P 158 GR. TMJ
(D) Ruger .357 MAG Revolver	CCI Blazer® lead free .38 SPL +P 158 GR. TMJ
(E) Ruger .357 MAG Revolver (new)	CCI Blazer® lead free .38 SPL +P 158 GR. TMJ
(F) Ruger .357 MAG Revolver (metal shavings)	

The carbon coated SEM stubs were searched manually by a single operator in the backscattered electron (BSE) imaging mode. The morphology of particles of interest was also examined in the secondary electron imaging (SEI) mode.

Firearms and Ammunition

The primer residue from a CCI Blazer® .38 SPL +P lead free cartridge was obtained by discharging a cartridge from which the bullet and powder had been removed. The cartridge was placed in a clamp with the mouth of the cartridge facing an SEM stub. The primer was discharged by striking the primer cup and the residue analyzed by SEM/EDX.

Cleaning Procedures

Firearms A, B, C, and E were cleaned using Breakfree® copper borebrushes, and cloth patches. The shooter fired three consecutive rounds then had gunshot residue collected from his firing hand.

Firearm D was disassembled and sonicated in Breakfree® prior to reassembly and cleaning as described above. Sonication was performed to test if this procedure would ensure complete removal of previous firing residue. In addition, two rounds of Blazer® Lead Free ammunition were fired from each chamber (twelve rounds total). The shooter washed his hands, fired three consecutive rounds and then had gunshot residue collected from his firing hand. The entire cleaning and firing procedure for firearm D was then repeated.

Results

Analysis of a CCI lead free primer discharged directly over an SEM stub determined that the only significant element present was strontium. Some particles were as large as 35 μm in diameter (Fig. 1), but most were in the 10.0 μm to 0.5 μm range. In addition to the size, the spherical morphology of these particles was typical of gunshot residue particles seen with traditional primers. It was noted that some of the strontium particles also contained trace amounts of barium, the presence of which is interesting in view of the manufacturer's claim that it is not a component of CCI's lead free primer. Natural deposits of strontium are often associated with barium [5] and it could be present in the primer as a carry over product from the commercial processing of strontium nitrate. It should also be mentioned that titanium, an element detected in the work by Lawrence [1] on CCI's lead free primer, was not detected during this research.

The results of the analysis of gunshot residue from firearms using CCI's lead free ammunition are presented in Table 3. Tri-component particles containing lead, barium, and antimony were found in all cases (Fig. 2), even after the extensive and repeated cleaning of firearm D. Discrete strontium particles were detected in the two semi-automatics (firearms A and B), while four-component particles of strontium/lead/barium/antimony were detected in the older revolvers (firearms C and D). Except in the case of the new

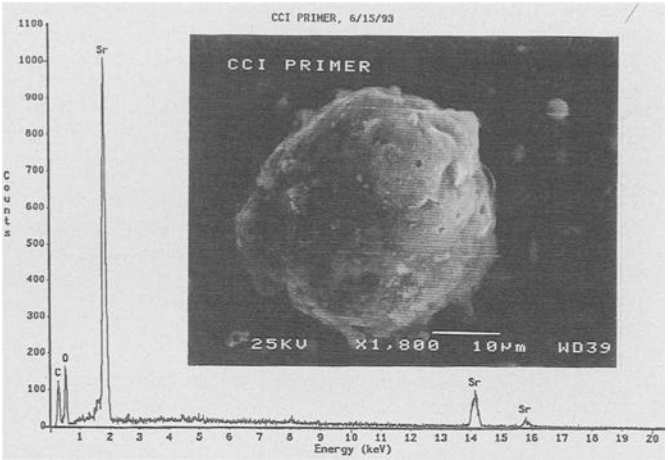

FIG. 1—*Secondary electron image and corresponding energy dispersive X-ray spectrum of a strontiun particle obtained by exploding the primer directly onto an SEM stub.*

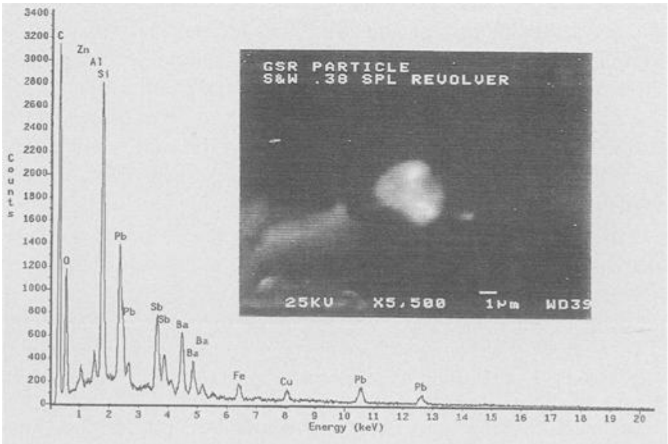

FIG. 2—*Secondary electron image and corresponding energy dispersive X-ray spectrum of a Pb, Ba and Sb particle obtained by firing CCI Blazer® Lead Free ammunition from a Smith and Wesson .38 SPL revolver.*

TABLE 3—*Summary of gunshot residue analyses.*

Firearms	Pb/Ba/Sb	Pb/Ba	Pb/Sb	Pb	Sr	Sr/Pb/Ba/Sb	#Pb/Ba/Sb > Sr
(A) *Beretta* 9mm Semiauto	X	X			X		YES
(B) *Glock* .45 ACP Semiauto	X		X		X		YES
(C) *Smith & Wesson* .38 SPL Revolver	X			X		X	YES
(D) *Ruger* .357 MAG Revolver	X		X			X	YES
(D) *Ruger* .357 MAG Revolver	X		X	X		X	YES
(E) *Ruger* .357 MAG Revolver "New"	X			X	X		NO

Ruger (firearm E), all of the firearms deposited a greater number of tri-component particles than strontium particles or four-component particles.

Metal shavings removed from the inside of the chamber of firearm F with a file were analyzed by SEM/EDX and lead, barium and antimony were found to have been deposited inside the chamber (Fig. 3). This build-up on the inside of the chamber is presumably the source of lead, barium and antimony detected in the gunshot residue collected after test firing firearms A–E.

Conclusions

Direct analysis of CCI's lead free primer by SEM/EDX detected significant amounts of strontium and traces of barium. Analysis of the gunshot residue collected after shooting CCI's lead free ammunition in a series of firearms found that significant numbers of tri-component lead, barium, and antimony particles were also present in addition to strontium or strontium/lead/barium/antimony particles.[3] The analysis of the metal shavings from inside the chamber of an older revolver revealed that lead, barium and antimony had been deposited inside the chamber. Routine cleaning with copper borebrushes does not remove these deposits, nor does sonicating the firearm in Breakfree®.

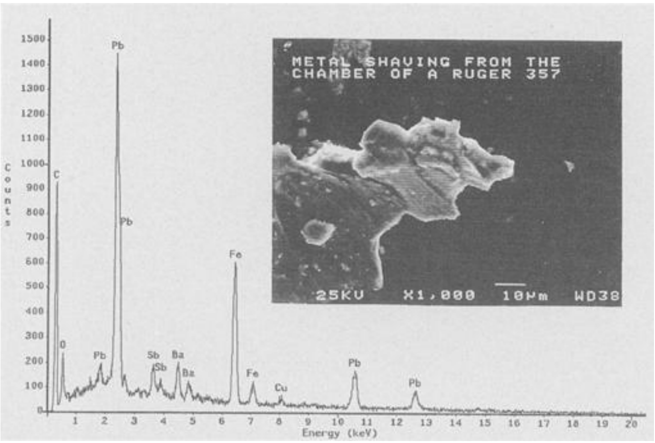

FIG. 3—*Secondary electron image and corresponding energy dispersive X-ray spectrum of a metal shaving from the chamber of an older Ruger .357 magnum revolver.*

[3]Gunshot residue particles composed of elements from different types of ammunition fired from the same firearm have also been reported by Zeichner, Levin and Springer [*10*] and by Gunaratnam and Himberg [*11*].

These results indicate that the use of CCI's lead free ammunition does not necessarily eliminate the presence of lead, barium and antimony from gunshot residue. The amount of these metals deposited from a firearm will be dependent on a number of factors including the age and previous use of the firearm, the history of ammunition types used, and the frequency and methods of cleaning.

There is a potential for carry-over from metals previously deposited in the firearm's chambers by traditional ammunition. The detection of strontium along with the traditional primer metals (lead, barium, and antimony) should be expected from older firearms using CCI's lead free ammunition. The mechanism by which lead, barium and antimony from inside the chamber is redeposited outside the firearm is not known; however, it is likely to be a function of the high temperatures and pressures created inside the chamber by exploding primer and burning powder. It seems likely that strontium may also build up inside a firearm's chamber over time, and then be redeposited on a shooter's hands during future use regardless of the type of ammunition being used.

Caution must be used when interpreting the presence of strontium found on SEM stubs collected in shooting incidences. Particles of strontium with spherical morphology could result from exposure to ignited flares and fireworks, limiting the uniqueness of strontium particles found in residue collected from shooting incidences. Gunshot residue containing strontium particles and lead, barium and antimony particles may also be deposited from tracer ammunition, as red tracer ammunition can also contain strontium. The metals detected in gunshot residue resulting from the use of red tracer ammunition have not been investigated by this laboratory, but cannot be ruled out as a potential source of strontium particles.

Acknowledgments

I would like to thank the Montana Department of Justice for the time and support needed to perform this research. I would also like to thank my co-workers A. Boehm, B. Bouley, and G. Dale, for their guidance and participation in this project.

References

[*1*] Lawrence, G. M., " 'Lead-Free' or 'Clean-Fire'?," presented at the Southwestern Association of Forensic Scientists Spring Meeting, South Padre Island, TX, Spring 1993.
[*2*] Bydal, B. A., "Percussion Primer Mixes," *AFTE Journal,* Vol. 22, No. 1, Jan. 1990, pp. 1–25.
[*3*] Wallace, J. S., "Chemical Aspects of Firearms Ammunition," *AFTE Journal,* Vol. 22, No. 4, Oct., 1990, pp. 364–389.
[*4*] DeGaetano, D. and Siegel, J. A., "Survey of Gunshot Residue Analysis in Forensic Science Laboratories," *Journal of Forensic Sciences,* Vol. 35, No. 5, Sept. 1990, pp. 1087–1095.

[5] *Encyclopedia of Chemical Technology,* Vol. 13, R. E. Kirk and D. F. Othmer, Eds., New York, The Interscience Encyclopedia, Inc., 1954.
[6] Davis, T. L., *The Chemistry of Powder and Explosives,* Angriff Press, California, 1943.
[7] *The Merck Index,* 11th Edition, Ed., Budavari, S., Merck & Co., Inc., 1989.
[8] Andrasko, J., "Identification of Burnt Matches by Scanning Electron Microscopy," *Journal of Forensic Sciences,* Vol. 23, No. 4, Oct. 1978, pp. 637–642.
[9] Glattstein, B., Landau, E., and Zeichner, A., "Identification of Match Head Residues in Post-Explosion Debris," *Journal of Forensic Sciences,* Vol. 36, No. 5, Sept. 1991, pp. 1360–1367.
[10] Zeichner, A., Levin, N., and Springer, E., "Gunshot Residue Particles Formed by Using Different Types of Ammunition in the Same Firearm," *Journal of Forensic Sciences,* Vol. 36, No. 4, July 1991, pp. 1020–1026.
[11] Gunaratnam, L. and Himberg, K., "The Identification of Gunshot Residue Particles from Lead-Free Sintox Ammunition," *Journal of Forensic Sciences,* Vol. 39, No. 2, March 1994, pp. 532–536.

Address requests for reprints or additional information to:
Annalivia Harris
554 W. Broadway, Room 600
Missoula, MT 59802