TECHNICAL NOTE

Brigitte Charpentier,[1] B.Sc. and Collin Desrochers,[1] B.Sc.

Analysis of Primer Residue from Lead Free Ammunition by X-Ray Microfluorescence

REFERENCE: Charpentier B, Desrochers C. Analysis of primer residue from lead free ammunition by X-ray microfluorescence. J Forensic Sci 2000;45(2):447–452.

ABSTRACT: In forensic science, the analysis of gunshot residues was traditionally done by the detection of lead (Pb), antimony (Sb) and barium (Ba) usually found in a primer. However, the recent development of lead-free ammunition represents a new challenge for ballistic specialists. This analysis study gunshot residues from primers and ammunitions in the area surrounding bullet holes, a very important tool to determine the shooting distance. The ammunitions used were 9 mm Luger and .38 spl + p calibers, where lead in the primer was replaced with strontium (Sr) and where the lead bullet was plated with copper (Total Metal Jacket). Gunshot analysis results were obtained using an energy dispersive X-ray microfluorescence spectrometer. The method allows the detection and quantification of strontium residues on the target up to a distance of 45 cm.

KEYWORDS: forensic science, ballistics, gunshot residue, shooting distance, X-ray microfluorescence

In the last few years, environmental science has become very popular. The words pollution, contamination and the associated health hazards are often making news. Lead contamination is known to be harmful if someone is in contact. When high-risk individuals such as firearm instructors or competitive shooters inhale lead, particles enter the lungs and then the blood stream. For the shooter, lead particles have two origins: 80% of airborne lead on a firing range originates from the projectile while the remaining 20% comes from the combustion of the primer mixture (1). However, the latter is more hazardous because lead from primers is burned into a finer particule size than lead scrubbed from the bullets, resulting in greater absorption through the respiratory tract (2).

For this reason, many manufacturers have decided to change their ammunitions. Some ammunition is designed to virtually eliminate airborne lead at the firing point. The lead, barium and antimony found in conventional primer are replaced to some extent with a strontium-based formulation. Moreover, the lead bullet core is totally encapsulated in a copper jacket. The result is a clean-burning training round which greatly reduces airborne lead. Because health is a concern, the introduction of more lead-free ammunitions can be expected.

In forensic science, the firing distance yields a lot of information for the reconstruction of a crime where a gun has been used. These data can orientate the police investigation towards suicide, manslaughter or an homicide in cases of suspicious death.

When a shot is fired, the discharge is due to detonation of the primer, followed by the controlled burning of gunpowder. Traditionally, in our laboratory, the determination of whether a shot was fired at close range ($<$2 ft) or not has been based on the detection of lead, barium and antimony around the bullet wound. With the advent of lead-free primers, chemists in forensic science must now consider the possible presence of strontium in gunshot residues. All published analyses carried out so far on lead-free primers have examined gunshot residues on the shooters (Basu et al. (3), Harris (4), Hsien-hui et al. (5), Wolten (6)). This study focuses on the residues left on the target. The aims of our experiments were first, to detect the presence of inorganic elements in non toxic primers and second, to generate preliminary results to eventually create an accuracy table of firing distances using X-ray microfluorescence.

Method

Reproduction of Bullet Wound

The firearms used in this study were a Berretta pistol 9 mm Luger with a 5″ barrel and a Smith and Wesson revolver .38 special with a 2″ barrel. Both firearms used were thoroughly cleaned before test firing to avoid contamination. CCI® CF (clean fire) and LF (lead-free) primers manufactured by Blount, (Lewinston, ID) were analyzed. Sintox primers manufactured from Geco (Germany) and Fiocchi (Italy) were also analyzed.

Ammunitions used for firing tests were first, CCI .38 special + p cartridges (158 gr. TMJ Blazer®) from Blount, (Lewinston, ID) and second, CCI 9 mm Luger cartridges (124 gr. TMJ Blazer®) also from Blount Inc. We chose to study 9 mm Luger and .38 spl + p calibers ammunitions as these are the most readily available.

The shooting target was 3 MM Chromatographic paper from Whatman. Ten shots for each calibers were fired at the following distances: 2, 15, 30, 45, and 60 cm.

Instrumentation

An X-ray diffractometer (XRD) D5000 Siemens (Germany) was first used to determine primer composition before shooting. The

[1] Laboratoire de Sciences judiciaires et de Médecine légale, Montreal, (Quebec) H2K 3S7, Canada.

Received 8 Feb. 1999; and in revised form 29 June 1999; accepted 29 June 1999.

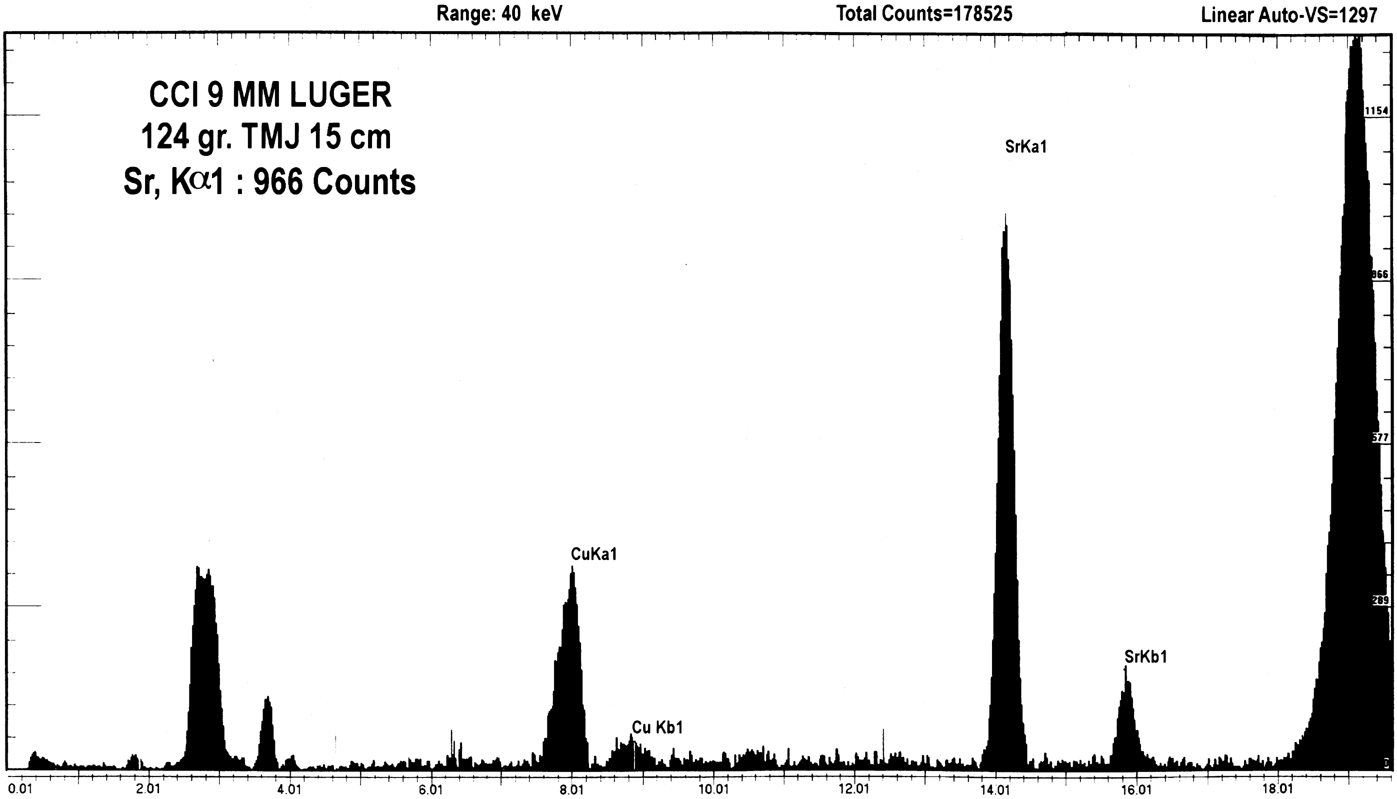


FIG. 1—*XRMF spectrum obtained for strontium. Shown here a representative pinpoint analysis for a shot fired at 15 cm from the target. Experimental conditions were as described in materials and methods.*

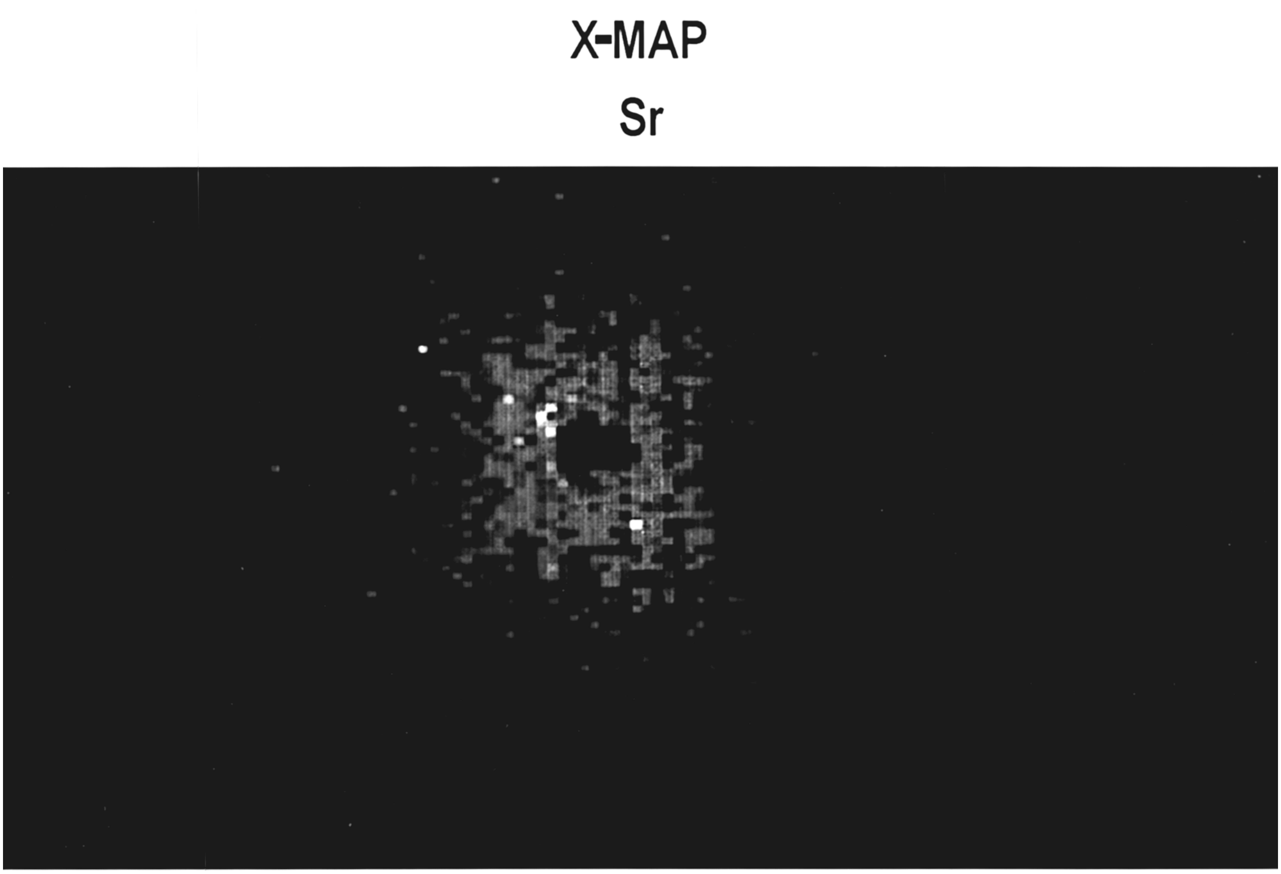


FIG. 2—*Representative XRMF mapping data obtained for strontium. Shown here is a result for a shot fired at 15 cm from the target. Experimental conditions were as described in materials and methods.*

analytical conditions were 30 mA and 40 kV. The scans were performed at 5° to 55° with steps of 0.02°/s for a total time of 41 min and 40 s.

The gunshot residue analysis results were obtained using a Kevex (Valencia, California), Omicron energy dispersive X-ray microfluorescence spectrometer (XRMF) equipped with a Rhodium anode microfocus X-ray tube. Two kinds of analytical results were obtained using maximum operating tube voltage (50 kV) and maximum amperage (1,0 mA). Elemental composition of a zone (300 or 500 micron) was first determined with an analysis time of 250 s to optimize data throughput. In addition, the XRMF has a mapping system which provides data on element distribution in a given area. Representative outputs are shown in Figs. 1 and 2. The mapping system was used at 200 steps per second and seven scans were done. For each test, three distinct areas outside a 1 cm circle surrounding the hole were selected. A 300 micron final beam collimator for distances 2, 15, and 30 cm was used, while a 500 micron collimator for 45 and 60 cm shooting distances was preferred.

Since X-rays emissions are extremely swift (10^{-8} s), sufficient time must be allowed for the detector to register correctly each emission, thus making it necessary to adjust the dead time on the equipment. Theoretically, for a zone analysis, the dead time should be adjusted at approximately 50% to permit an optimal recording of the transitions of interest. In this study, better reproducibility and repeatability was obtained by keeping voltage and amperage constant to the detriment of dead time. The range for the deadtime was between 30 to 70% in relation with the amount of residues.

Results and Discussion

An initial analysis was performed on the primers prior to the shooting experiments. By XRD analysis, it was possible to determine grossly the inorganic components that we were likely to detect in subsequent experiments. Strontium nitrate was detected in CCI CF primers while barium nitrate is the main inorganic component of CCI LF primers. Fiocchi primers contain a combination of barium nitrate and antimony sulfide. As for Syntox primers, the presence of zinc and titanium was determined using XRMF and XRD because these primers contain zinc peroxide and titanium dioxide, but it was difficult to see them by XRD (7).

For all shooting experiments, we used CCI CF ammunition and primers exclusively. Firstly, ten shots were fired with both guns at 2, 15, and 30 cm from the target. By comparing the patterns on the chromatographic paper (Fig. 3), four criteria were considered:

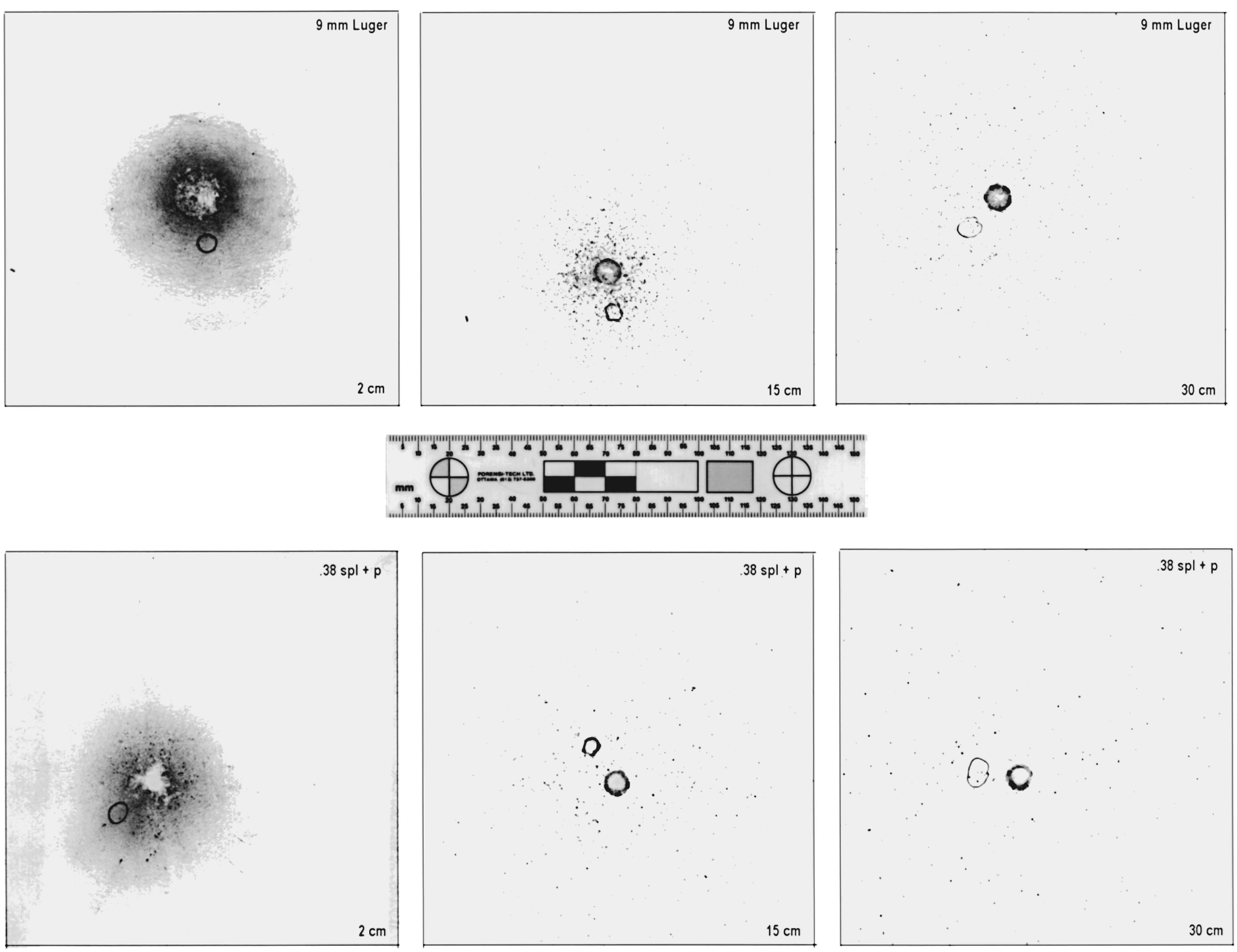


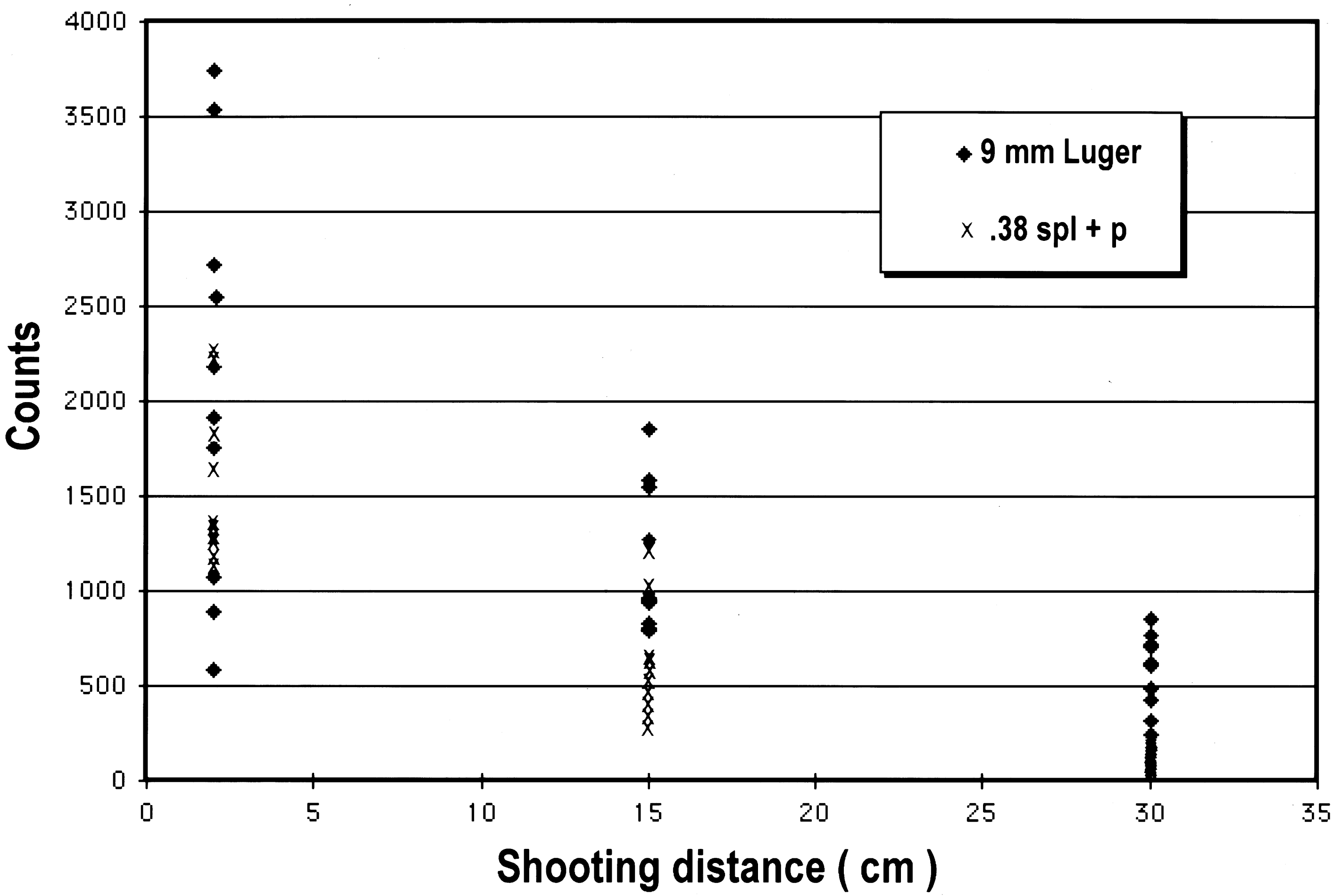
FIG. 3—*Comparative residue patterns observed for shot fired at 2, 15, and 30 cm with CCI CF ammunitions. Representative results for shots fired with the 9 mm Luger pistol (upper three panels) and the .38 spl Smith and Wesson revolver (lower three panels).*

shape, diameter, intensity, and homogeneity. When a shot is fired, gunpowder residues are dispersed in a cone shape. This radial dispersion can be noted even at 2 cm shooting distance. In addition, the cone shape was more wide-mouthed in each shot fired with the short barrel (Smith and Wesson revolver) compared to the long one (Luger pistol) at the same distance (Fig. 3, upper versus lower panels). The intensity and homogeneity of gunshot residue deposition were studied by XRMF and the results are shown in Figs. 4 and 5.

Residues count numbers were significantly lower for the .38 special revolver compared to the 9 mm Luger pistol at all shooting distances (tables in Figs. 4 and 5). Two factors can explain this result: the energy of cartridges used for the .38 special revolver was lower than the 9 mm pistol cartridges (241 versus 345 ft-lb) (9) and the revolver barrel length was shorter than the pistol (2 versus 5 in.).

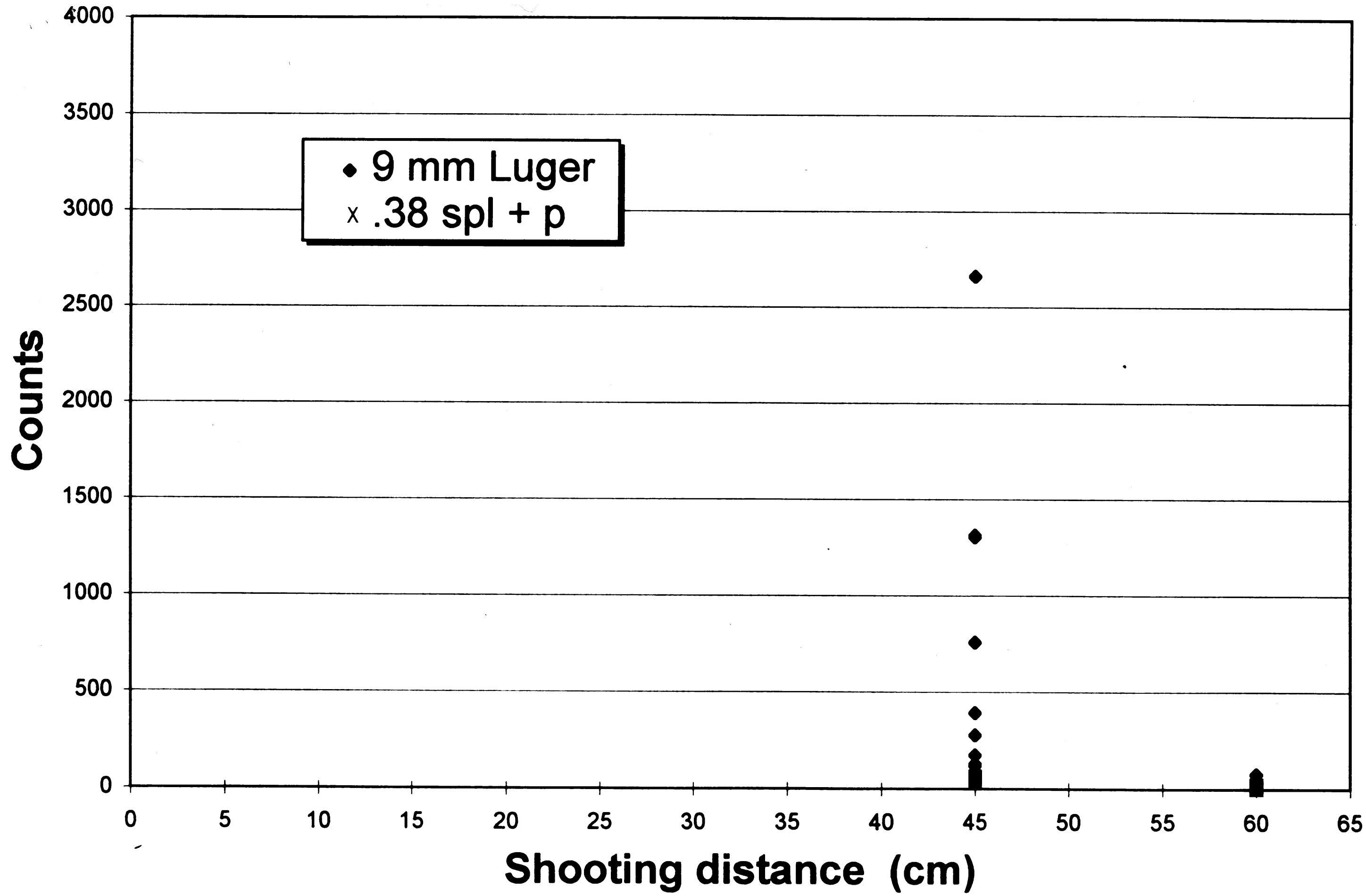
A large standard deviation is apparent in the count number for the Kα1 strontium transition. The effect is particularly marked for shots fired at very close range (2 cm) with the 9 mm Luger pistol, but decreases in proportion at 15 and 30 cm (Fig. 4) where data dispersion is clearly decreased. A probable explanation is the higher concentration per surface unit of larger particles at shorter shooting distances, thereby resulting in aberrant data points. Further experiments using scanning electron microscopy analysis with energy dispersive X-rays (SEM/EDX) (Gunaratnam et al. (8)), could be carried out to confirm this hypothesis.

Results for the 45 and 60 cm shooting distances are presented in Fig. 5. A 500 micron collimator was used in each case. The objective of the collimator change was to increase the detection limits. This was helpful only at 45 cm for the 9 mm Luger where counts were still fairly low; as for .38 spl revolver, the count numbers,



Calibre	9 mm Luger			.38 spl + P		
Distance	2 cm	15 cm	30 cm	2 cm	15 cm	30 cm
Mean counts	2094	1154	575	1554	594	69
Std dev.	1070	383	200	426	305	64

FIG. 4—*Relationship of Kα1 Sr transition count number with shooting distance (2, 15, and 30 cm). Each data point represents the average of a minimum of two measurements (data not shown). Mean counts and standard deviation (SD) for each shooting distance are indicated in the table below the figure.*



Calibre	9 mm Luger		.38 spl + p	
Distance	45 cm	60 cm	45 cm	60 cm
Mean counts	720	< 80	< 70	< 20
Std dev.	830	ND	ND	ND

FIG. 5—*Relationship of Kα1 Sr transition count number with shooting distance (45 and 60 cm). Each data point represents the average of a minimum of two measurements (data not shown). Mean counts and standard deviation (SD) for each shooting distance are indicated in the table below the figure.*

while similar to the level observed at 30 cm, were not significant considering the higher background levels of the 500 micron collimator. Total counts below 100 are considered to represent background levels with this collimator. It is clear that at distances greater than 45 cm, the amount of strontium residues is too low to be quantified accurately under current experimental conditions. No significant signals were obtained at 60 cm with either gun. Analysis with SEM/EDX could be more appropriate for the latter distances because in a very diluate case, his sensibility should be higher.

In summary, with the current analysis, it is possible to evaluate the shooting distance for the guns used, the data being valid exclusively with CCI® CF ammunitions. For the 9 mm pistol with a 5 in. barrel, the maximum shooting distance detectable is 45 cm. In the case of the .38 special with a 2 in. barrel, the maximum detectable is 30 cm.

Conclusion

We have shown that it is possible to establish a maximum shooting distance at close range for non-toxic primers. Of course, the exact shooting distance cannot be determined under these conditions. This was a preliminary study for a large new serial analysis where at least one hundred shots will be fired at each distance and a database of different primers available will be established and kept up-to-date. The purpose is to eventually assist ballistic specialists to testify in court cases where non-toxic primers have been used. This situation is likely to arise more often in the coming years.

Several further studies should be undertaken. For instance, various target types like nylon, polyester, leather, and bone could be tested. Since we have shown that a relationship between count number and shooting distance can be determined, it will be very useful to repeat these experiments with traditional primers. For example, barium detection by XRMF should be feasible. Finally, of course, all the characteristics of a weapon and other parameters such as the manufacturer, batch of ammunitions, and the wind factor level will have to be considered when carrying out this type of analysis.

Acknowledgments

The authors thank people who graciously gave us specific ammunitions and primers: Normand Héroux from SNC (Montreal, Canada), Régis Gisèque from the Montreal area police force (SPCUM) (Montreal, Canada) and Pierre Paquet from Centaure Ltd (Laval, Canada). We also thank the staff of the Quebec forensic laboratory (LSJML) and particularly Dr. France Mailly for her support in writing this article.

References

1. Sanow E. Stay healthy with CCI's clean-fire ammo. Handguns 1994;(8)8.
2. Yuhasz AA. The reduction of airborne lead in indoor firing ranges by using modified ammunition. U.S. departement of commerce, N.B.S. special publication: 480–26.
3. Basu S, Boone CE, Denio DJ, Miazga RA. Fundamental studies of gunshot residue deposition by glue-lift. J Forensic Sci 1997;42(4):571–81.
4. Harris A. Analysis of primer residue from CCI Blazer® lead free ammunition by scanning electron microscopy/energy dispersive X-ray. J Can Soc Forensic Sci 1995;40(1):27–30.
5. Meng HH, Caddy B. Gunshot residue analysis—A review. J Forensic Sci 1997;42(4):553–70.
6. Wolten GM, Nesbitt RM. On the mechanism of gunshot residue particle formation. J Forensic Sci 1980;25(3):533–45.
7. Beijer R. Experience with Zincon, a useful reagent for the determination of firing range with respect to leadfree ammunition. J Forensic Sci 1994;39(4):981–7.
8. Gunaratnam L, Himberg K. The identification of gunshot residue particles from lead-free Sintox ammunition. J Can Soc Forensic Sci 1994;39(2): 532–6.
9. Federal Cartridge, company catalog, 1996.

Additional information and reprint requests:
Brigitte Charpentier
Laboratoire de Sciences judiciaires et de Médecine légale
Ministère de la Sécurité publique
Edifice Wilfrid—Derome
1701 Parthenais—12 'étage
Montréal, (Québec) H2K 3S7
Canada
e-mail:chimie.physique@secpub.gouv.qc.ca