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"Evaluation of the Sub-Surface Morphology and Composition of Gunshot Residue using Focussed Ion Beam Analysis"

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Highlights

- FIB was used to section GSR particles generated by different ammunitions.
- Sub-surface morphology appears to differ between ammunition.
- Distinct compositional features are observable in cross-section.
- Additional information may be obtained from GSR, at the sub-particle level.

Abstract

Recent work in the forensic analysis of Gunshot Residues (GSR) has suggested that the sub-surface or internal composition and morphology of these residues be explored. A particular area of interest is in heavy metal free, or non-toxic ammunition, which are becoming more frequently encountered in the marketplace. As the formulation of the primer compound changes the conditions of the firearm discharge, there is the possibility that different primer formulations may result in the formation of different GSR particles with distinct internal morphologies and compositions. To that end, the internal morphology and composition of GSR particles may provide additional information that could be useful in the investigation of firearms crime.

This research investigated the internal morphology of GSR originating from a variety of different ammunition products. Both traditional three-component primed ammunition, and a selection of heavy metal free and non-toxic alternatives were considered. Particles were identified using SEM-EDS, before being cross-sectioned using a focussed ion beam (FIB) instrument. The FIB-sectioned particles were then re-acquired and mapped using SEM-EDS, to assess both internal morphology and composition.

Particles observed in this study presented distinct morphological and compositional features at the sub-particle level that may provide an indication of the primer formulation from which they originated. That said, further investigation of a variety of samples should be undertaken to verify the consistency of these features, or any deviations that may be observed based on primer type. However, these results indicate that there may be promise in obtaining additional detail from sub-particle morphology and composition.

Keywords

Forensic science; gunshot residue; Focused Ion Beam; scanning electron microscopy;

Introduction

Gunshot residue (GSR) particles are formed through a series of complex, high temperature and pressure interactions in the immediate aftermath of a firearm discharge. Under firing conditions, temperatures may reach levels in excess of 2000°C, with pressures reaching levels of 9500 kPa [1]. GSR particles have been observed to be composed of elements originating from the ammunition's primer, as well as inclusions from the cartridge case, projectile, firearm, or previous firings [2-4]. Identifying the provenance of suspected GSR particles, including differentiating GSR from non-GSR, provides valuable information able to contribute to criminal investigations. Prior research conducted on particles similar to GSR, generated from explosive residues, has demonstrated that different explosive compositions are capable of generating particles that can be differentiated based on their internal morphology [5]. Therefore, the composition of the primer in ammunition may also influence both the composition and morphology of GSR particles.

While firearm primers tend to have similar major components, an example of which can be seen in Table 1, individual ammunition manufacturers modify the composition of their primers and powders based on their individual needs and requirements.

Table 1 - Typical composition of a Sinoxid type primer compound, relative abundance and purpose in primer mix [6]

Compound	Concentration	Purpose
Lead Styphnate	25 % - 55%	Explosive
Barium Nitrate	24% - 25%	Oxidising Agent
Antimony Sulphide	0% - 10%	Fuel
Lead Dioxide	5% - 10%	Oxidiser/Corrosion Inhibitor
Tetracene	0.5% - 5%	Sensitiser
Calcium Silicide	3% - 15%	Fuel / Frictionator
Powdered Glass	0% - 5%	Frictionator

An example such a change of requirements is the transition to lead or heavy metal free primers. Repeated firing of ammunition containing Sinoxid type primers can result in significant exposure to airborne lead and other heavy metals that may pose a risk to the health of those exposed [7-10]. To address these concerns, steps have been made to remove lead compounds from a variety of ammunition [11]. An example of one such primer is 'Sintox' type primers, containing titanium and zinc compounds. A typical composition can be seen in Table 2.

Table 2 – Typical Composition of a Sintox type primer compound, relative composition and purpose in the primer mix [6]

Compound	Concentration	Purpose
Diazodinitrophenol (DDNP)	~15%	Explosive
Tetracene	~3%	Explosive
Zinc Peroxide	50%	Oxidiser
Powdered Titanium	5%	Fuel
Nitrocellulose	27%	Fuel

Alternative heavy metal free primer compositions have used strontium salts of dinitrodihydroxydiazobenzene as explosive compounds, coupled with strontium sulfate or oxalate as passivating compounds, alongside components such as tetracene and zinc peroxide [12].Changing primer formulations impacts the types, compositions, and morphologies of particles that may be observed in casework. To ensure that GSR evidence is analysed and placed in the appropriate context, ongoing investigation of primer composition and the particle types generated, using a variety of techniques, is essential.

In practice, the most well-established technique for the analysis of GSR particles is scanning electron microscopy with energy dispersive x-ray microanalysis (SEM-EDS). While this technique allows the assessment of both morphology and composition of GSR particles, it is limited in that only the surface features of the particle are observable. Focussed ion beam (FIB) systems have the capability to cross-section small particles, permitting their internal morphology to be observed. The technique has been well established in the semiconductor industry, but has also seen use in materials science and micro- and nanoscale fabrication applications [13-16]. This technique has also been explored for forensic applications, and shown promise as a means of obtaining additional information from GSR particles [17-19].
Work conducted by Niewöhner and Wenz [20] on the application of the focussed ion beam to gunshot residues showed that each of the four different ammunition products in their study produced particles with different internal morphologies. Further work has indicated that the use of FIB for GSR analysis has utility in providing additional information to the assessment of this type of evidence [17]. Additional recent research has suggested that assessing the internal structure of GSR particles, particularly those originating from non-toxic primers, may be of benefit in providing additional information to GSR investigations [21].

Another potential contribution to the composition of GSR particles is the phenomenon known as the 'weapon memory effect'. The 'weapon memory effect' describes the circumstances in which particles retained within the firearm from previous firings are ejected alongside, or incorporated into, particles generated from subsequent firings. This effect has been demonstrated to result in the formation of mixed primer composition particles – particles that contain elements that are known to be absent in the primer mix of the ammunition used [21-23]. Recent work has further explored the origin of mixed primer composition particles, suggesting that particles retained from previous firings are incorporated into the structure of new particles generated in subsequent firings [24]. This results in particles with distinct compositional domains becoming visible using EDS mapping.

This study seeks to build upon the existing knowledge of the different types of particles and their internal morphologies that has previously been explored. An expanded mix of ammunition, including heavy metal-containing and lead-free variants has been included to investigate the impact of different primer formulation on the particle types formed. This research set out to assess the internal morphology and composition of GSR particles originating from a variety of different ammunition products, in an attempt to determine if differentiation of ammunition based on internal structure was possible.

Materials and methods

Sample Collection

All samples collected for the purposes of this research were collected using 12.5mm diameter Aluminium SEM pin stubs coated in double sided carbon-tape adhesive (Tri-Tech Forensics Inc. North Carolina, USA).

Representative GSR samples were collected from a selection of different ammunition, chosen to include exemplars of non-toxic primed and traditional three-component primed ammunition in a variety of calibres. A complete list of the ammunition used, the typical GSR particle types and components of their primers, cartridge and projectile can be seen in Table 3 and Table 4.

Table 3 - Ammunition Tested and Major Components present [11]

Ammunition Type	Batch	Calibre	Primer
PMC Zapper	*22-D-794*	*0.22 Long Rifle*	*Ba, Pb,*
Winchester Winclean (HMF)	*SL10*	*0.40 S&W*	*Ba, Al,*
American Eagle (Toxic Metal Free Primer)	*V42Z457*	*0.40 S&W*	*Sr, Al*
Federal Premium HST	*C19V26*	*0.40 S&W*	*Pb, Sb, Ba*
Norinco	-	*7.62 x 39mm*	*Pb, Sb, Ba*

Table 4 - Components Present in Cartridge Casing and Projectiles

Ammunition	Cartridge Casing	Projectile Type
PMC Zapper	*Brass (Cu, Zn)*	*Pb (Sb, Cu traces)*
Winchester Winclean (HMF)	*Brass (Cu, Zn)*	*Pb, Brass Enclosed Base (Cu, Zn)*
American Eagle (MFP)	*Brass (Cu, Zn)*	*Cu TMJ, Pb core.*
Federal Premium HST	*Ni coated Brass (Cu, Zn)*	*Hydra-Shok (Cu jacketed HP with Pb core)*
Norinco	*Steel Case (Fe)*	*Cu FMJ, Pb core.*

n.b.: HMF = Heavy Metal Free, MFP = Metal Free Primer, TMJ = Total Metal Jacket, HP = Hollow Point, FMJ = Full metal Jacket. HST is a brand indication, and does not represent an initialism that can be defined.

PMC Zapper ammunition (22 Long Rifle rimfire) was included in the survey in order to investigate the generation of three-component particles from a two-component primed ammunition. PMC Zapper was included as analysis of unfired primer has demonstrated that it only contains Pb and Ba compounds, but has small quantities of Sb in the projectile, which is included to harden the lead of the projectile [25].

Three-component particles generated from two-component primers have been observed, and their possible origins have been previously investigated [26, 27]. It has been hypothesised that the Sb incorporated into three component particles originates from the surface of the projectile. FIB milling and mapping of the interior of one such particle was used as a technique to investigate if internal composition could provide additional information that would allow the source of the Sb to be determined.

To address this possibility, a Ruger 77/22 bolt action, 0.22 calibre rifle was thoroughly cleaned. Ten rounds of PMC Zapper 0.22LR ammunition was discharged through the firearm to condition the barrel. A wooden probe was used to collect a sample from the inside of the barrel, which was then rolled onto an SEM stub. The breech was then also sampled with a wooden probe, and recovered to an SEM stub. A plastic (PET) catcher, fashioned from a clean, dry water bottle of approximate volume 1.25L was then affixed to the barrel using cloth adhesive tape. A further three rounds were discharged through the catcher. The holes in the catcher were sealed with cloth tape, and the catcher was removed from the barrel and sealed. The catcher was then transported back to the laboratory, where it was cut open, and the inside surfaces directly sampled with an SEM stub.

Ultimately, the particles used for the FIB analysis were present on the sample from the inside of the catcher.

Samples from additional ammunition with different primer compositions were then collected as a means of investigating how primer composition may impact sub-particle morphological features. Particular focus was given to ammunition that have particular significance in the local jurisdiction.

Winchester WinClean was included as a primer composition that lacked both Pb and Sb, but did contain Ba, to serve as a basis of comparison to other primer formulations.

American Eagle MFP 0.40 S&W is the standard issue ammunition used in firearms training for SA Police (SAPOL). Similarly, Federal Premium HST 0.40 S&W was included as it is the standard issue operational ammunition carried by SAPOL. All 0.40 calibre ammunition was fired using a 0.40 Smith and Wesson Military and Police (M&P) Semi-Automatic Handgun.

Norinco 7.62x39mm is a Chinese made, steel-cased ammunition with a Copper FMJ projectile. Although in most markets it is no longer available or sold, it is of particular interest in the Australian context, as stockpiles of this ammunition are still routinely encountered in firearms casework, particularly in situations involving outlaw motorcycle gangs [28]. A similar situation may also be relevant beyond Australia. The Norinco ammunition was fired through a Norinco SKS Self-loading rifle.

In each case, the firearm was conditioned by discharging six rounds of the nominated ammunition through the firearm into a bullet recovery (water) tank. Following this, samples were taken from the hands of the shooter using an adhesive SEM pin stub. The shooter's hands were washed thoroughly before commencing each sample run, and a blank sample of their hands was collected prior to handling and discharging the firearm.

Cartridge casings were collected to verify the components that were detected in the hand residues. Residues from the casings were recovered to an SEM Stub prior to analysis using a wooden probe.

Equipment

All collected samples were analysed by SEM-EDS using an Inspect F50 Scanning Electron Microscope (FEI Inc., Oregon, USA) equipped with an EDS detector (EDAX Inc., New Jersey, USA.) Instrument operating parameters were established as per the American Society of Testing and Materials (ASTM) E1588-10-17 Standard guide for gunshot residue analysis by SEM/EDS [29] .

Automated particle search was conducted using the GSR Magnum Particle analysis system (FEI Inc., Oregon USA), and TEAM elemental analysis software (EDAX Inc., New Jersey, USA).

The GSR Magnum system brightness and contrast settings were calibrated through use of a Gold/Niobium/Germanium/Silicon/Carbon (Au/Nb/Ge/Si/C) standard (Ardennes Analytique, sprl. Belgium).

A positive control for the FEI system, a synthetic particle standard (PLANO W. Plannet GmbH, Wetzlar, Germany) consisting of accurately deposited particles of known size was analysed at the start and end of every sample run. The 'particles' deposited on the glassy carbon surface of this standard are thin Pb/Sb/Ba films of sizes 0.5-10 µm.

The Focussed Ion Beam used in this study was an FEI DualBeam Helios Nanolab 600 SEM/FIB system hosted at the Australian Microscopy and Microanalysis Research Facility (AMMRF) Facility at Adelaide Microscopy, University of Adelaide, South Australia.

Particle Analysis

ASTM E1588-10-17 was used to classify detected particles as either 'characteristic of' or 'consistent with' a firearms origin.

Particles of interest were first found and visualised using the FEI F50 SEM operating in back-scattered electron mode (BSE), and images captured in both SE and BSE mode. Representative spectra of the whole particles were collected using the TEAM elemental analysis software. The locations of these particles were mapped so that they could be examined in greater detail later using EDS.

Several particles were identified *via* SEM for sectioning by FIB. Particles were selected based on composition and morphology, and were chosen to be representative of the population of particles originating from the ammunition. To make this assessment, information about the primer composition, cartridge and projectile were obtained. All samples were processed through GSR particle analysis software to ascertain the number of particles in each classification, and then a selection was made based on particle composition, size, shape, and the region of the stub in which it was located.

Composition of particles was determined by re-acquisition of the particles and a 30 second EDS scan of the bulk of the particle. Compositional elements were compared against known components of the ammunition based on literature and cartridge recovery samples.

Particle size was a selection criterion for particles that were to be sectioned using the FIB process. Particles that are large are easy to find in the FIB instrument, but take a long time to section and polish for mapping. Smaller particles are harder to locate, but are faster to section. For the purposes of this analysis, features within the particles were the primary interest, so the particles that were selected ranged in size between 5µm and 50µm in diameter.

The shape of the particle was considered as a means of ensuring the FIB process could proceed unhindered. Non-spheroidal particles, or those with protrusions or odd shapes were excluded, as this made it difficult to accurately cross-section across the bulk of the particle. Selected particles were spheroidal in nature, with every attempt made to section across the bulk of the particle.

The region of the stub was a concern as the area around the particles of interest impacted the ability of the FIB to access the particle. For example, particles resting in a depression on the stub, or partially obscured by other features of the stub were excluded due to the technical difficulty in accessing them with the FIB instrument.

Particles were relocated on the stub using the FEI Dualbeam Instrument, and images collected in secondary electron mode. The stage was then tilted to an angle of 52° to expose the side of the particle, and confirm that the particle was accessible for cross-sectioning.

The particles of interest were cross-sectioned by milling using a Ga liquid metal ion source (LMIS). Prior to sectioning, a 2µm thick layer of Pt was deposited over the location to be cut. The Pt is deposited using a Pt gas injection system, and serves a number of purposes in FIB analysis. First, it provides a conductive layer in proximity to the freshly milled surface, which serves to minimise or prevent the appearance of artefacts of the FIB process. One such artefact is the 'curtaining' or 'waterfall' effect, which is characterised by pronounced lines visible on the milled surface [13, 30].

The Pt layer also confers a level of protection and stability to the surface of the sample to allow it to withstand the milling process. It should be noted that the Pt cap is visible in the figures of the cross-sectioned particles. It appears as a region around the top surface of the particle that appears bright in the BSE image, but shows low x-ray counts in the resultant maps.

FIB operational parameters used were determined based on the advice of an experienced operator. A beam current of up to 21nA was used to mill the bulk of the particle mass away and expose the interior of the particle. Once the surface was milled, it was polished using a reduced beam current of approximately 2.8nA. Using the SEM within the Dualbeam instrument, images were collected before, during and after the milling process.

After the particles had been cross-sectioned using the FIB, their EDS spectra were re-acquired using the FEI F50 SEM instrument. A stage tilt of 45° was used to permit clear imaging of the exposed surface. Images were collected in both SE and BSD mode. To assess the internal composition of the particle, an elemental x-ray map was collected using TEAM software.

Results and Discussion

0.22 Long Rifle PMC Zapper Rimfire -

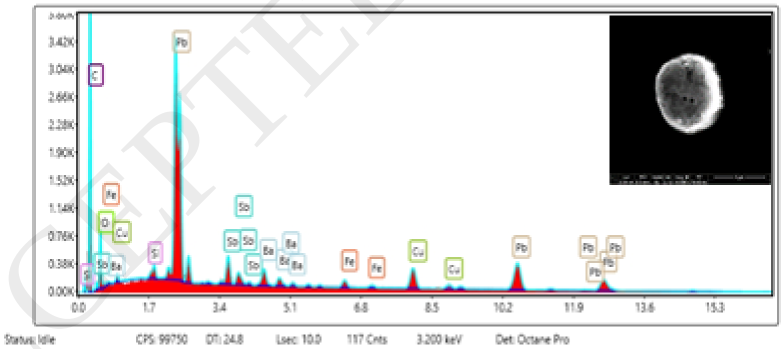

Figure 1 - Exemplar EDS spectrum of GSR from 0.22LR calibre PMC Zapper ammunition (Inset - SE Image)

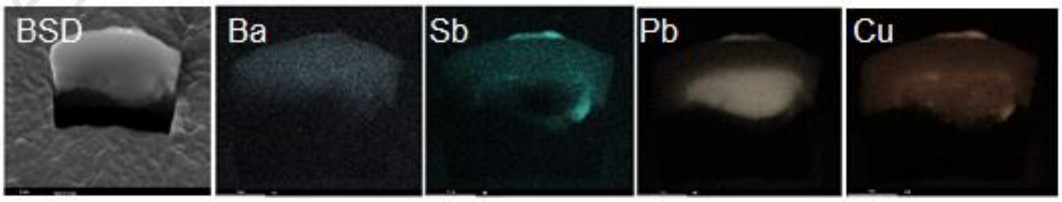

Figure 2 - EDS maps of FIB sectioned particle from 0.22 LR calibre PMC Zapper ammunition. (L to R - Backscattered electron image, Ba map, Sb map, Pb map, Cu map)

Figure 1 shows the EDS spectrum and whole particle secondary electron image from a three component particle, approximately 5µm in diameter, generated from 0.22 calibre rimfire PMC Zapper Ammunition. This particle was collected on an SEM stub from the interior of the plastic catcher. Figure 2 shows the same particle after cross-sectioning, and the collected EDS maps. In Figure 1, the particle is seen perpendicularly from the stub surface. The particle was then cut perpendicularly, but in Figure 2 the view is at a 45° angle to the surface of the stub and the surface of the cut to allow the cross-section to be seen.

PMC Zapper only contains Sb in the projectile, where it is used to harden the Pb. In this case, like many 0.22 rimfire ammunition, PMC Zapper does not use antimony sulphide as a component of the primer, but does have Pb- and Ba- containing compounds. This composition has been documented previously by Seyfang et al. [25]. Analysis of primers taken from unfired PMC Zapper cartridges using SEM-EDS, showed only Cu compounds present in addition to Ba and Pb. This ammunition does however have antimony present as a component of the projectile, where antimony is used to harden the lead. The particle pictured in Figure 1 was recovered from barrel residues, and therefore may be expected to include components of the projectile that have been retained in the barrel. It is also therefore possible that the composition of particles from the barrel discharge is different to that of particles distributed from the ejection port of a firearm. Previous work conducted by Zeichner et al. [27] has indicated that Sb enrichment on a projectile's surface results in only a small probability of finding this element in GSR from ejection port residues.

From the SE image in Figure 1, it can be seen that morphologically the particle exhibited a pockmarked and irregular surface appearance. In cross-section, observable in Figure 2, the internal structure of the particle appears to be regular and uninterrupted, free of voids or cavities. Compositionally, the Pb is present toward the centre, and appears to make up the bulk of the particle. Although it is present, Ba is at minor to trace levels across the particle. Based on the BSE signal, Ba appears to be richest in regions where Pb is absent and Sb is diffuse. Where it is present, Sb is seen in higher concentrations in discrete regions of the particle. This can be observed at the top of the particle in a small 'cap' and towards the bottom right of the particle; it appears that the bulk of the central Pb deposit does not contain Sb. It is also notable that Sb and Ba are co-located as trace deposits in regions where

Pb is absent. Regions of the particle that have Sb present also show the presence of Cu and Pb. There are numerous sources of Cu within this ammunition, including as a component of the primer, within the cartridge brass, and as a Cu wash applied to the surface of the projectile. The absence of Zn in the spectrum of the full particle, or the EDS maps, suggests that the source of Cu is not the cartridge brass. Similarly, Cu compounds in the primer would be predicted to co-locate with other elements in the primer, such as the Ba and Pb. Taken together, the fact that the Cu appears to be most concentrated into areas in which Sb and Pb are also located suggests that the Sb present in these particles has originated from the surface of the projectile. Increases in the number of particles of Pb when using non-jacketed ammunitions (compared to jacketed ammunition) has previously been reported by Wolten [2], Wallace [6], and Udey et al [31].

However, it has also been documented that particles from previous firings can be retained in the barrel or on surfaces of the weapon, only to then be deposited in subsequent firings. This phenomena is known as the weapon memory effect, and has been described in detail elsewhere [22-24, 32, 33]. In this instance, steps were taken to minimise the impact of the weapon memory effect. The firearm was thoroughly cleaned before use, and was then conditioned with several rounds of the PMC Zapper ammunition before samples were taken. The stub on which this particle was located reported in excess of 200 three-component particles in approximately 25% of the stub area. A complete breakdown of the particles detected can be seen in Table 5.

Table 5 – Particle count from PMC Zapper ammunition barrel discharge sample (25% of available stub area).

Particle Types	Particles Present (n)	% of Classified	% total particles
Characteristic of GSR			
PbSbBa	200	1.4	1.0
Consistent with GSR			
BaSb	106	0.7	0.5
PbSb	1161	8.0	5.6
PbBa	335	2.3	1.6
BaCaSi	4	0.03	0.02
Total Consistent	*1606*	*11.0*	*7.7*
Commonly Associated with GSR (Single Element Particles)			
Pb	5244	36.0	25.2
Sb	509	3.5	2.5

Ba	353	2.4	1.7
Total Commonly Associated	*6106*	*41.9*	*29.4*
*Total Other Classified Particles**	*6650*	*45.7*	*32.0*
Total Classified	*14562*		
Total Unclassified	*6211*		
Total Particles	*20773*		

*The 'Other Classified particles' category includes any particles identified that are not pertinent to GSR analysis. This includes, but is not limited to, particles such as Fe, Au, Ag, BaS, Bi, Zr.

As a means of ascertaining the extent of the contribution of the weapon memory effect to these data, first, it is important to note that the firearm was thoroughly cleaned prior to collection of GSR. Second, as it is known that even thorough cleaning cannot completely remove GSR from previous firings from within the barrel [34], the firearm was further conditioned with the discharge of 10 rounds of PMC Zapper through the firearm. The rationale behind this was to displace particles in areas that cleaning might not reach and to 'load' the barrel with particles originating from the ammunition of interest, such that any particles retained from previous discharges would represent a smaller percentage of the total residues. A sample was collected directly from the barrel using a wooden probe and compared against the discharge residues. Following this, three rounds were discharged through a plastic catcher, with the inside of the catcher being sampled directly using an SEM stub. Finally, a scraping from the breech was collected using a wooden probe. A comparison between the results from the three samples can be seen in Table 6.

Table 6 - Comparison of particle types collected from barrel scraping, barrel discharge, and breech scraping.

Particle Types	**Particles Present (Barrel Scrape)** (100% Stub Analysed)	**Particles Present (Barrel Discharge)** (25% Stub Analysed)	**Particles Present (Breech Scrape)** (100% Stub Analysed)
Characteristic of GSR			
PbSbBa	3	200	0
Consistent with GSR			
BaSb	2	106	0
PbSb	19	1161	53
PbBa	110	335	16
BaCaSi	8	4	0
Total Consistent	*139*	*1606*	*69*
Commonly Associated with GSR (Single Element Particles)			
Pb	1095	5244	1087
Sb	2	509	20
Ba	68	353	5

Total Commonly Associated	*1165*	*6106*	*1112*
*Total Other Classified Particles**	*32*	*6650*	*332*
Total Classified	*1339*	*14562*	*1513*
Total Unclassified	*933*	*6211*	*355*
Total Particles	*2272*	*20773*	*1868*

*The 'Other Classified particles' category includes any particles identified that are not pertinent to GSR analysis. This includes, but is not limited to, particles such as Fe, Au, Ag, BaS, Bi, Zr.

While the possibility that some of the particles present on the discharge stub originate from previous firings cannot be excluded, the conditioning step, coupled with the number of particles detected on the post-discharge stub suggests that the proportion of particles originating from PMC Zapper ammunition would outnumber those retained from previous firings. This indicates that a significant number of three component GSR particles are generated from this ammunition. It should be noted based on the samples collected from the barrel and breech, that very few characteristic particles were observed on these samples, compared to those observed in the barrel residues. This suggests a lower contribution of the projectile composition to GSR particles from the breech and barrel. The selection of the particle to cross-section was targeted to ensure that it was typical of the population of three component particles present and was therefore most likely to have originated from the PMC Zapper ammunition used in test firings rather than from previous firings. However, even with these controls in place, we acknowledge the possibility that the particle that was sectioned is a three-component particle retained from a previous firing and collected coincidentally.

0.40 Smith and Wesson American Eagle MFP –

When considering the 0.40 calibre American Eagle MFP ammunition, two main types of particles were observed. The first were uniform, regular spheroids that contained both Sr and Al. A trace amount of Cu was also present in many of the particles. Figures 3 and 4 show a representative particle of this classification approximately 40µm diameter. In cross-section, it can be seen from figure 4 that the interior of the particle is smooth and uninterrupted, with neither voids, nor regions of high concentrations of specific elements present. It should be noted that the region visible in figure 4 that appears as a bright crescent shape in the BSE image is the Pt deposit, which was deposited as a part of the FIB process.

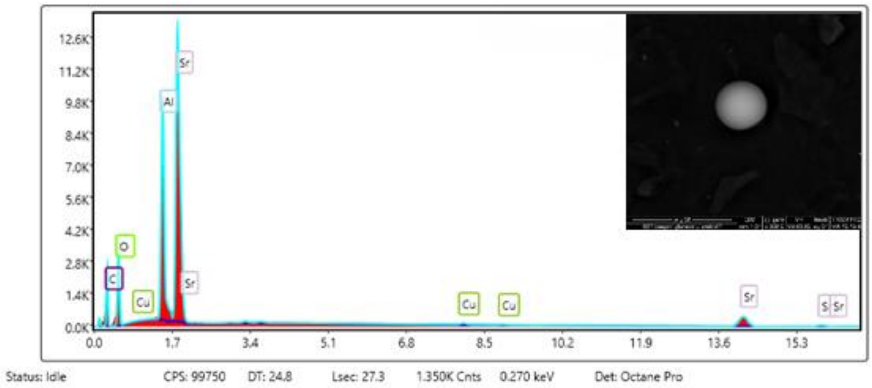

Figure 3 - Exemplar EDS spectrum of GSR from 0.40 American Eagle MFP ammunition (Inset - SE Image)

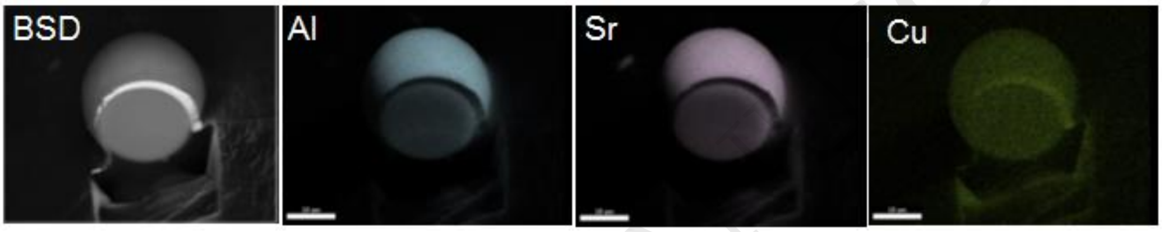

Figure 4 - EDS maps of FIB section particle from 0.40 American Eagle MFP ammunition (L to R - Backscattered electron image, Al map, Sr map, Cu map)

The second particle type were rough, irregular spheroids, with some exhibiting cracking or fissures on their surface. Compositionally, these were primarily composed of Sr, with no observable traces of other elements from the primer, firearm or cartridge. A comparison of particles of similar sizes can be seen in figure 5.

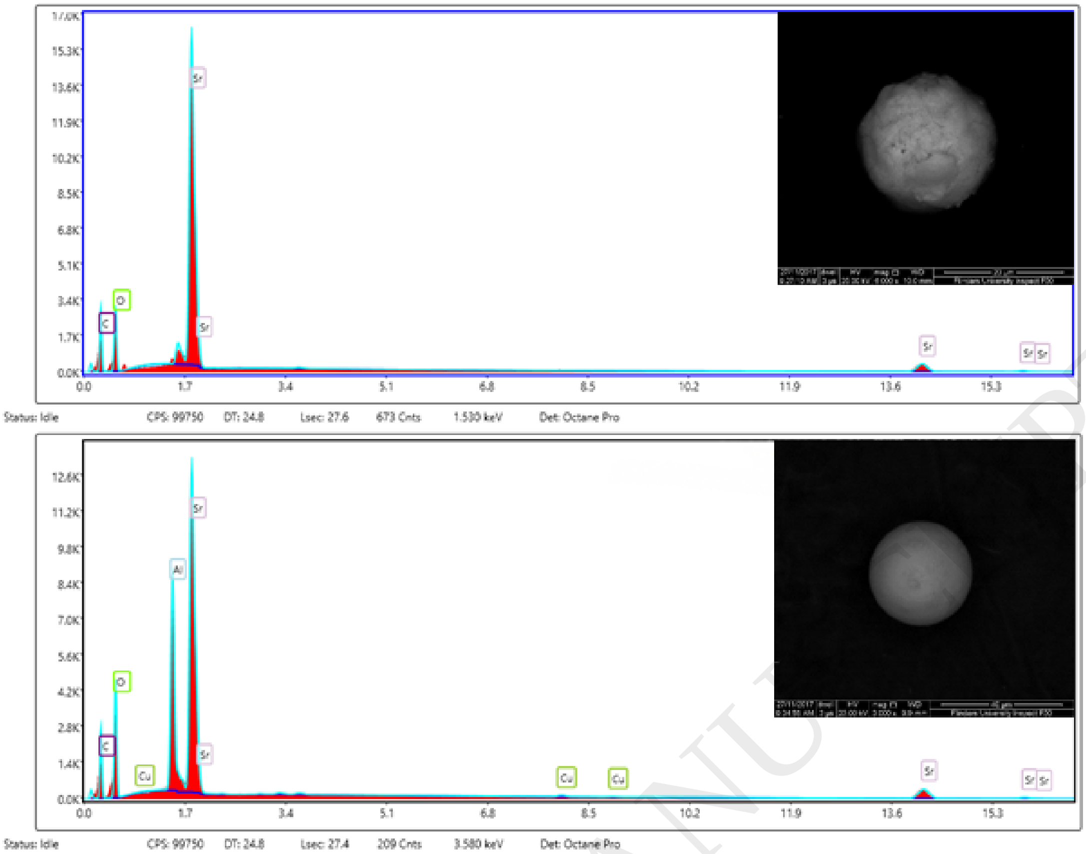

Figure 5 - Comparison of morphological differences between Sr only (top) and SrAl (bottom) containing GSR particles originating from HMF ammunition (American Eagle 0.40 MFP)

A similar observation of cracked, fissured particles was observed by Oommen et al. in their study of Speer Lawman Cleanfire ammunition [11], but in that work the particles contained Sr and Al. In the current study, however, it appears that the presence of these two elements within a single particle tends to result in a more rounded, smooth, and uniform appearance. When Al is absent, the particles generated tend to display a more irregular and cracked appearance at their surface.

0.40 Smith and Wesson WinClean -

Particles originating from the 0.40 Winchester Winclean ammuntion exhibited an amorphous, and 'bubbly' morphology which can be observed in figure 6 and 7. The internal morphology of these particles exhibited high porosity.

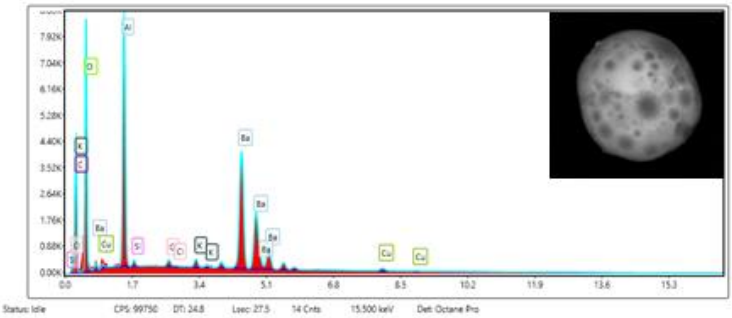

Figure 6 - Exemplar EDS spectrum of GSR from 0.40 Winchester Winclean ammunition (Inset - SE Image)

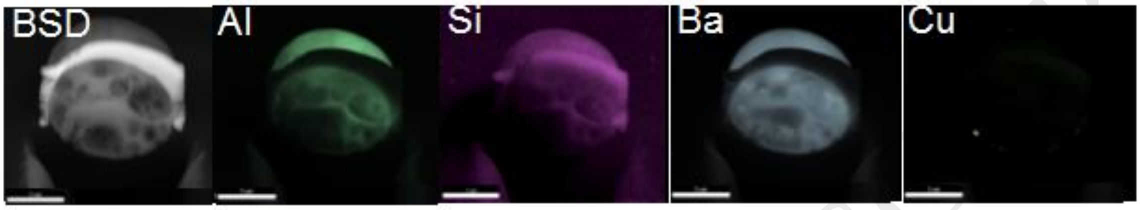

Figure 7 - EDS maps of FIB sectioned particle from 0.40 Winchester Winclean ammunition. (L to R - Backscattered electron image, Al map, Si map, Ba map, Cu map)

The particle that was cross-sectioned was approximately 10µm in diameter. The regular spheroidal shape of the bulk of the particle suggests that the particle is solidified foam, or the solid particle matrix condenses from the vapour or liquid phase. In this case, Ba and Al are co-located throughout the bulk of the particle, with small amounts of Si also present throughout. Additionally, a small amount of Cu is visible in both the spectrum in Figure 6 and the maps in Figure 7. The fact that the Cu appears localised to small nodules on the surface of the particles, and is not co-located with any other elements (especially Zn) suggests that these small inclusions originate from the Cu jacket of the projectile rather than the brass cartridge case. This further speaks to the possibility of incorporation of elements present only in the projectile into the GSR particles that are generated.

0.40 Federal Premium HST -

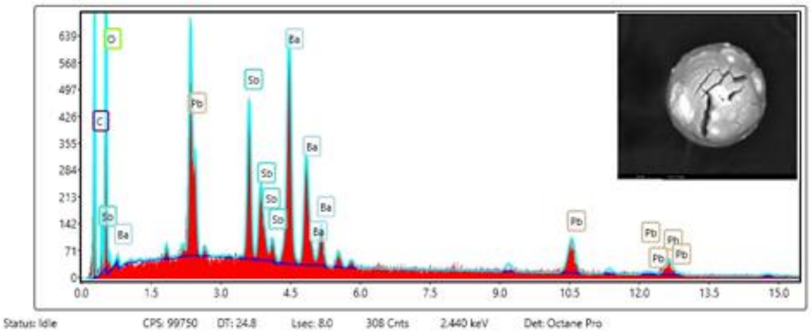

Figure 8 - Exemplar EDS spectrum of GSR from 0.40 Federal Premium HST ammunition (Inset - SE Image)

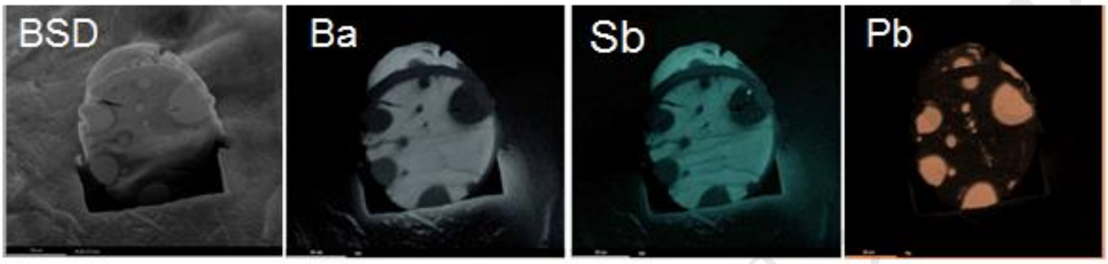

Figure 9 - EDS maps of FIB sectioned particle from 0.40 Federal Premium HST ammunition (L to R - Backscattered electron image, Ba map, Sb map, Pb map)

In Figure 8, the collected spectrum and SE image of a GSR particle originating from 0.40 S&W calibre Federal Premium ammunition are shown. The particle is approximately 50µm in diameter. The inset SE image shows that although the particle has some surface cracking, it is spheroidal, with small nodules evident. The particle was identified as having 'characteristic' GSR particle composition (Pb, Ba, and Sb). In Figure 9, the heterogeneous distribution of elements within the cross-section of the particle can be observed. When considering the EDS maps collected from the cross section, it can be seen that Ba and Sb are co-located, and appear to make up the bulk of the particle. The Pb, however, is located in discrete regions throughout the particle, and does not appear to be uniformly incorporated into the particle. The presence of this Pb as spheres embedded in a Ba and Sb matrix suggests that the nodules of Pb condense first, followed by the Ba and Sb condensing around them to form the final particle.

In this ammunition there are two potential sources of Pb – the Pb compounds used in the primer, and alloyed Pb in the core of the projectile. In this case, the core of the projectile, including the base, is encapsulated in a Cu jacket, making it unlikely that the Pb core of the projectile would be exposed to either friction in the barrel, or the burning powder. Therefore, it is comparatively unlikely that the Pb observed in this particle is derived from the core of the projectile. This indicates that the small nodules of Pb visible in this particle are derived from the Pb compounds in the primer, suggesting that either the primer formulation, or the conditions of the firearm discharge have allowed the Pb to separate and condense independently of Sb and Ba. An alternative possibility is that the small Pb particles are already present in the firearm due to the weapon memory effect, and are incorporated into the final particle during the firing process.

7.62 x 39mm Norinco Steel Case -

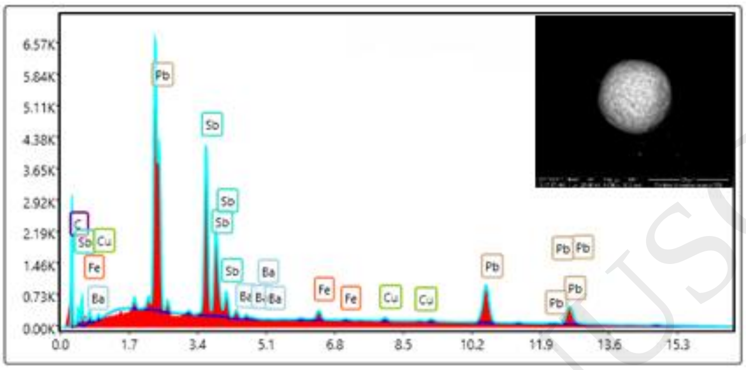

Figure 10 - Exemplar EDS spectrum of GSR from 7.62x39 calibre Norinco ammunition (Inset – SE Image)

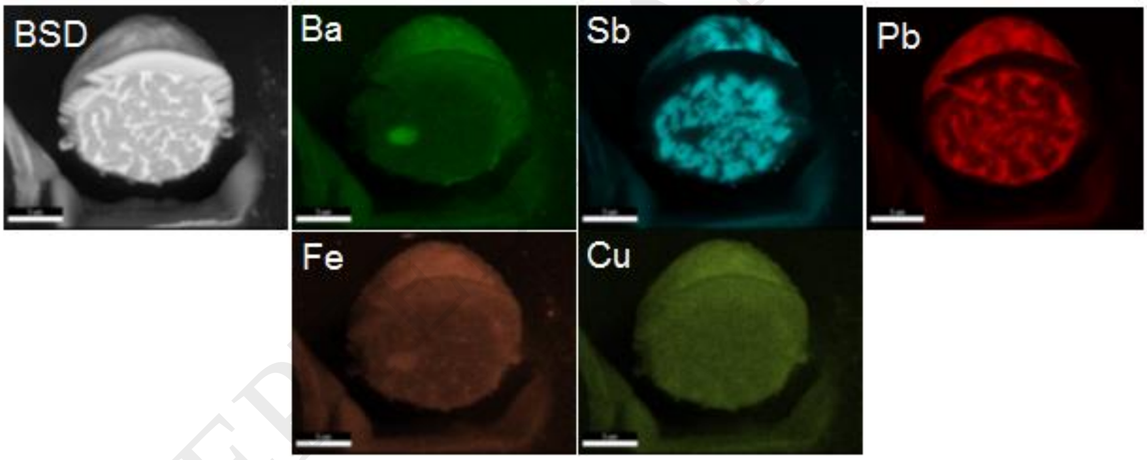

Figure 11 - EDS map of FIB sectioned particle from 7.62x39 Norinco (Steel Case) (L to R - Backscattered electron image, Ba map, Sb map, Pb map, Fe map, Cu map)

Particles originating from Norinco ammunition exhibited interesting morphological and compositional features that have not been widely observed or reported in GSR from other sources. As can be observed in Figure 10, this ammunition generated particles that meet the requirements for 'characteristic' morphology and composition under the ASTM standard. The exemplar particle was approximately 15µm in diameter, and contained Pb and Sb at a major level, with trace amounts of Ba, along with trace quantities of Fe and Cu. In Figure 11, the internal morphology of the particle can be observed. From this cross-section it is evident that the Pb-rich and the Sb-rich regions do not appear to co-locate. Interestingly, it appears as though small nodules of Sb are captured in a Pb-containing matrix. While not as pronounced, this separation of components was visible on the surface of the particles, with a number of particles exhibiting a mottled or speckled appearance. Although the spectrum in figure 10 indicates that Ba is present at trace levels in the whole particle, upon sectioning, a region of high Ba concentration was observed inside the particle with small nodules of Ba present on the underside of the particle.

Trace concentrations of Fe were present in a number of the particles observed, showing some co-location with Ba. Trace levels of Cu were observed homogeneously across the entire particle.

While the particle type observed in Figure 10 was commonly observed in this sample, other types were observed. Figure 12 shows a particle that exhibits some of the features observed in the previous particle type, notably the mottled-type particle containing discrete regions of Pb and Sb, however this was observed to be embedded in a larger primarily Ba-containing matrix.

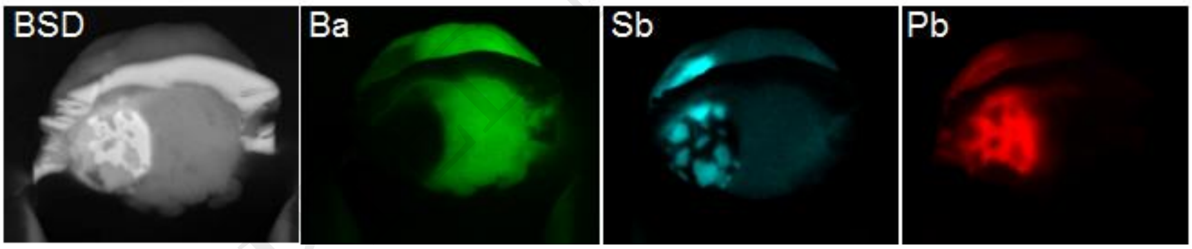

Figure 12 - EDS Maps of FIB sections second particle from 7.62x39 Norinco (Steel Case) (L to R - Backscattered electron image, Ba map, Sb map, Pb map)

The presence of both types of these particles suggests complex interactions at play in the formation of these GSR particles. The appearance of the PbSb particle embedded in the Ba matrix as observed in figure 12 suggests that Pb and Sb coalesce first, occupying discrete regions within the same spheroidal particle, then allowing the two component particle to be absorbed into a still molten Ba matrix. However, the particle pictured in figure 11 indicates that Ba may be similarly captured within a PbSb droplet. In either case, particles of this particular composition and morphology were only observed in the Norinco ammunition, suggesting that the specific components of the primer itself and/or the idiosyncrasies of the discharge pressure and temperature result in the formation of particles of this type.

Conclusions

Several samples from different ammunition, including heavy metal free variants, were observed to generate particle populations with distinct compositions and morphologies. The use of FIB-sectioning coupled with EDS-mapping was useful in identifying distinct compositional domains in a cross-sectioned GSR particle that provide further information to the particle formation. In some cases, different components of the ammunition were seen to co-locate with each other. In three-component primed 0.40 calibre Federal ammunition, Ba and Sb were seen to co-locate, while these same elements occupied discrete regions in the particles from three-component primed 7.62x39 calibre Norinco ammunition. When considering heavy metal-free or non-toxic variants of different compositions, particle types ranged from solid spheroidal, SrAl-containing particles to porous, but regularly shaped, BaAl-containing particles. These observed differences between ammunition suggest, at least tentatively, that sub-particle morphology and composition may be used to provide additional information to forensic GSR analysis.

This study also provided additional support for the mechanism behind three component particles being observed in situations that involve only two-component primed ammunition. Previous work has indicated that even with thorough cleaning, the weapon memory effect can have an impact on the particles generated [35, 36]. In the work described here, controls were implemented to minimise the impact of the weapon memory effect, and yet FIB sectioning and EDS mapping still indicated mixed composition particles were present. These particles exhibited compositional elements that were not present in the primer mix, but had possible origins elsewhere in the ammunition. The origin of these elements, based on their location and composition was determined to be most likely originating from the surface of the projectile in a number of cases. Given the controls used to address the memory effect, the significant number of these three-component particles observed when using two-component primed ammunition are more than would be expected if they were retained from previous firings.

However, this finding is interpreted cautiously, and does not discount the contribution of the weapon memory effect to the detection of mixed composition particles, especially in casework where the prior usage of the firearm is not known. While the precise mechanism behind the formation of these particles has been difficult to ascertain, recent research has suggested that their formation may be due to incorporation of existing particles into the pre-solidified particle matrix. If this is the case, then the same mechanism that allows the incorporation of existing particles from previous firings to be incorporated into new particles would theoretically also allow for incorporation of particles generated from other parts of the firing process. To that end, a cautious, case-by-case approach to the assessment of GSR is still encouraged.

It should be noted that there are difficulties inherent in evaluating evidence at the single particle level. This research has highlighted the highly variable and heterogeneous nature of GSR particles, and therefore any assessment or conclusions based on single particle composition or morphology must be treated with utmost caution and preferably involve the evaluation of the wider population of particles collected from the crime scene or person of interest. Although in this case care was taken in selecting the particles to ensure that they were representative of the wider population, this study still only considered individual particles. While surface features present in the cross-sectioned particles were observed in a number of others in the sample, it was impractical to cross-section large numbers of them in this study. Despite this, as a proof-of concept for the ammunition selected, the use of FIB on GSR particles did allow the internal morphology of GSR to be assessed, thereby gaining additional information about the samples and perhaps, more fundamentally, indicating that some ammunition-specific characteristics are present in GSR. It is evident that different primer compositions and different ammunition can produce particles that exhibit characteristics that have distinct sub-particle features, compositions and morphologies, information which can potentially assist discriminating ammunition products and enhancing the overall quality of GSR evidence.

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We wish to dedicate this work to James Wallace, who tragically passed away while this work and the associated manuscript was being completed. The authors acknowledge the support and guidance provided by him in regards to the field of GSR examination in general, and the collection of barrel discharge residues in particular. He literally 'wrote the book' on the analysis of firearms, ammunition and GSR, and the field is much richer for his dedicated contributions. He will be missed.

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