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Methods for Analysis of Glass in Glass-Containing Gunshot Residue (gGSR) Particles

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Highlights

- Methods are evaluated for the analysis of glass-containing GSR (gGSR) particles
- Glass is stable during firearm discharge, although it melts and incorporates Pb/Ba
- Pre- and post-fired samples from similar sources can be linked through composition

Abstract

When lead, barium and antimony, or lead, barium, calcium, silicon and tin are found together in particles associated with a shooting investigation they are considered characteristic of gunshot residue (GSR). Antimony and tin are often absent from the primer of many low calibre rimfire ammunitions, which are the type most commonly used in Australia. Therefore, the likelihood of characteristic particles forming during the firing process of such rimfire ammunition is significantly less than the likelihood of these particles arising from higher calibre ammunition. The majority of rimfire ammunition examined in this research contains ground glass in the primer, which functions as a frictionator. These ammunitions produce a small number of gunshot residue particles containing glass coated with other primer components, which we refer to as glass-containing GSR (gGSR). If these particles are observed in an investigation, they have the potential to add a new dimension to gunshot residue analysis because they are not common in the environment. Furthermore, the composition of glass frictionator is stable during firing, which raises the possibility that chemical testing of the glass in gGSR may be used to identify the ammunition from which the residue was derived or to link deposits of GSR.

This paper examines the application of scanning electron microscopy – energy dispersive X-ray spectrometry (SEM-EDS), focussed ion beam (FIB) techniques and time of flight–secondary ion mass spectrometry (ToF-SIMS) to the semi-quantitative analysis of gGSR and frictionator extracted from unfired cartridges. SEM-EDS is effective for comparing gGSR with unfired frictionator, but the use of FIB to expose clean glass from the centre of gGSR followed by ToF-SIMS, or ToF-SIMS using ion sputtering to expose clean glass, offers more power for glass discrimination.

Introduction

There are approximately three million legally owned firearms in Australia, and a further 260 thousand suspected to be owned illegally [1]. Of these, small calibre long rifles and shotguns are subject to the least regulation, and make up a large majority of the firearms in the country, even on the illicit market [1]. Small calibre long rifles and shotguns are also the most commonly associated with crime and death in Australia [2]. This represents a significant difference to other jurisdictions, especially the USA, where handguns and other types of weapons are much more commonly associated with crime [3]. This regional divergence is noteworthy, because while many centrefire ammunition primers contain lead styphnate, barium nitrate, and antimony trisulfide as the major ingredients (Table 1) [4, 5], the majority of rimfire ammunitions available in Australia do not contain any antimony compounds in their primer formulation [6]. Therefore in typical Australian shooting investigations the majority of particles present in gunshot residues (GSR), and on occasions the only type of particles present, have a composition that only allows them to be classified as 'consistent' with firearm origin under the ASTM guidelines [7]. This terminology is intended to indicate that the residue is of comparatively low probative value compared to residues containing lead (Pb), barium (Ba), and antimony (Sb), which are classified as 'characteristic' of firearm origin. As all rimfire ammunition available in Australia is either fully imported or assembled using imported, ready-primed cartridge cases, the comments above are relevant overseas as well. This situation led us to seek new attributes of rimfire residues that may be used enhance the relatively low significance currently attached to them.

In the majority of rimfire ammunition, ground glass is used as a frictionator, instead of the more traditional antimony sulfide or calcium silicide [6] present in high calibre ammunition. In early work [6] a combination of SEM-EDS and time of flight-secondary ion mass spectrometry (ToF-SIMS) demonstrated the presence of glass particles with Pb and Ba fused to the surface in GSR residues from 0.22-calibre rimfire ammunition. Further research has indicated that other primers, including those for larger calibre and heavy metal free ammunitions can also contain glass as a frictionator [8-14].

It was proposed that this glass-containing gunshot residue (gGSR) may have a higher probative value than the usual rimfire GSR evidence if it can be established that particles of this nature do not originate from industrial or non-firearm sources. Additionally, if it could be shown that glass frictionators are elementally stable during firearm discharge, and that glass frictionators are elementally variable between manufactures or samples, glass analysis could be used to associate GSR with a putative source ammunition or spent cartridge case, allow discrimination between GSR deposits, or to show associations between GSR deposits. Our previous work has shown that frictionator composition varies across different ammunition sources [16] and current investigations [17] have shown that particles resembling gGSR are rare in the community. However, in order to advance the field, robust methodology for analysing glass in gGSR particles and comparing it to unfired frictionator or glass in other gGSR is required; the present article deals with the development of such methodology.

As gGSR is usually encrusted with residues arising from the other primer components, the biggest operational hurdle to exploiting the value of these particles is finding or exposing a clean surface of glass to analyse. A dual beam SEM-EDS with a focused ion beam (FIB) system allows particles of gGSR to be dissected, revealing their interior morphology and composition.

A focussed ion beam (FIB) system is similar to an SEM system, except that instead of, or in addition to an electron source, it has a liquid metal ion source (LMIS), often using a Ga^+ beam. The benefits and mechanics of this system have been described elsewhere [18-21] as this technique is routinely used by the semi-conductor industry, for TEM sample preparation, and for nano-etching. However, this technique has undergone rapid improvement and expansion of applications in the last two decades. The LMIS makes highly site-specific ion sputtering possible, which allows sectioning of 'casework-size' GSR particles [18]. The instrument used for this investigation was a dual beam instrument, equipped with a platinum gas injection system (GIS) and a nano-manipulation system, which allowed *in situ* lift out (INLO) of slices of glass.

FIB has only occasionally been utilised for forensic applications. In 1999, Niewöhner and Wenz [22] used a FIB instrument to ablate the edges of GSR particles from ammunitions of different composition, focussing on heavy metal free (HMF) brands, and assessing their internal morphologies. They examined one type of 3-component primer, and three different HMF brands with differing formulations. Their investigation focussed on particle morphology, and in attempts to look at composition, they noted a limitation in that the instrument they used for SEM-EDS mapping could not 'resolve' or perceive elemental differences in the separate phases visible in the backscatter images. Sarvas *et al.* and *W*uhrer *et al.* [23, 24] also used FIB to investigate internal particle morphologies and composition, and to examine possible distinguishing features of GSR compared to environmental particles.

A similar assessment of sub-surface morphology was attempted by Basu [25] by using a microtome to section particles prior to analysis. However, the morphologies observed by Basu were quite different to what was observed by Niewöhner and Wenz [22], and many of the particles had a scratched interior morphology, which were potentially artefacts of the microtome process used to section the particles. An advantage of using FIB for this application is that the ion milling process is "essentially stress free"[20] and does not usually affect the morphology of the exposed surface, meaning that it potentially gives a much clearer picture of the true internal morphology of the particle [20, 21].

Another approach is to use an ion beam in a ToF-SIMS to sputter away the encrustation on gGSR prior to analysis of the exposed glass. This approach was used in the initial exploration of the utility of gGSR [26]and was re-examined in the work described here and compared to methods involving FIB sectioning of particles.

Materials and Methods

Sample Collection

Sample Collection of gGSR Particles using Manual Discharge of Cartridge Cases

Exemplar ammunition cartridges were collected from commercially obtained 0.22 Winchester Powerpoint (batch 1DMH6) and PMC Zapper (batch 22-D-446) rimfire ammunition. Projectiles were removed from cartridge case with pliers. The propellant was decanted. The cartridges containing only primer were then placed into a machined aluminium holder. When placed in the holder, the cartridge extended through a hole leading down onto the bench, but 'legs' on the holder ensured that the mouth the cartridge was held just above the bench, which was covered with a piece of clean waterproof parchment paper. The primer was then manually discharged using a punch and mallet. Residues were collected off the paper with a GSR stub. A diagram of the holder is shown in Figure 1, together with a photomicrograph showing typical particles collected using this approach. Glass-containing gunshot residue particles (gGSR) were located using BSE SEM imaging to find Pb- or Ba-containing particles and then EDS analysis was used to determine whether any of these particles displayed co-located Si, Na, Al and O signals, which indicates the presence of glass.

PMC Zapper gGSR Particles using Muzzle-Discharge Collection

A 10/22 Ruger firearm was cleaned, conditioned with 20 rounds, and then fired once through a PET catcher, following the method described in Seyfang *et al.* [17]. The inside of the catcher was stubbed with a GSR stub. The samples were analysed, and gGSR particles were located using BSE-SEM and SEM-EDS as described above; images of typical particles collected using this method are provided in Figure 2.

Collection and Preparation of Unfired (Rimfire) Frictionator Samples for Comparison

For the comparison between Winchester gGSR and unfired frictionator, a cartridge taken from a Winchester Powerpoint rimfire ammunition (batch 1DMH6, not the same box as above) was disassembled and emptied as described above. The cartridge was filled with a mixture of 3:1 acetone: water and left overnight. A fine, curved metal probe was used to dislodge primer particles from within the rim of the cartridge, and the acetone: water solution was emptied into the cup of a spin filter using a disposable plastic pipette. The spin filter was centrifuged at 13 krpm for one minute to remove any solvent. The filtrate was discarded, and the cartridge was then rinsed a further two times with acetone: water, with each rinse transferred into the spin filter and centrifuged. The spin filter was then rinsed with acetone three times - each time the tube was half-filled, agitated with a vortex mixer for ten seconds, and centrifuged for one minute. The residues were then rinsed three times with nitric acid (5%) and then three final times with methanol.

For the PMC Zapper samples, each cartridge was dismantled and manually discharged onto parchment paper as described above. The residues were transferred from the paper into a spin filter, any residues left inside the cartridge were rinsed with acetone and added to the spin filter. After centrifugation the contents of the spin filter were washed with nitric acid and methanol, as described above. A cartridge from one of the PMC Zapper samples was also prepared by the first method (sample Korean batch 22-D-446 (1) in Figure 15) and analysed against the samples prepared by the second method, to discern whether the two methods appeared to clean the glass for analysis equally. Both methods removed traces of Pb and Ba to below the detection limit of SEM-EDS, and the frictionator from the other cartridge appeared to have an elemental profile that was indistinguishable by SEM-EDS.

Collection of Federal (centrefire) Premium Particles using Hand-Stubbing

A volunteer SAPOL officer's hands were washed and blank hand stubs were collected from the backs of hands, trigger finger and webbing between thumb and forefinger using GSR stubs, stubbing approximately 50 times or until stubs were no longer sticky. The officer fired 20 shots of .40 Smith and Wesson (centrefire) Federal Premium Law Enforcement HST Ammunition from a Smith and Wesson Military and Police (M&P) .40 Semi-automatic pistol over a 30-minute period of drills. Immediately after the end of the session, the officer's hands were stubbed again. The collected stubs were analysed and gGSR particles were located using BSE-SEM and EDS analyses, as above. This ammunition was used because it has been found by us to contain glass frictionator within the primer mixture. Compared to rimfire ammunition the .40 calibre ammunition would subject GSR particles to higher temperatures and pressures within the cartridge and chamber during the firing process. The aim of this exercise was to recover gGSR particles consistent with what would be encountered in firearms casework, albeit a relatively extreme example, and consistent with particles on hands, as distinct from those collected *via* manual discharge or muzzle discharge. The particle selected for further analysis is shown in Figure 3.

SEM EDS Identification of GSR particles

All GSR samples collected in this study were collected using an aluminium pin stub covered in carbon adhesive (Tri-Tech Forensics Inc. North Carolina, USA.)

SEM EDS analysis of all samples was completed using an FEI Inspect F50 SEM-EDS system (FEI Inc., Oregon, USA), operating in Backscattered Electron Mode (BSE).

Particles were initially identified using GSR Magnum particle analysis system (FEI Inc., Oregon, USA). Exemplar spectra and elemental maps collected using TEAM Analysis Software (EDAX Inc., New Jersey, USA). Pre-FIB and post-FIB elemental and phase maps were collected using an accelerating voltage of 20 keV, a 30 µm aperture, a spot size of 6, an emission current of approximately 110 µA and a resolution of 128 eV. Analyses of regions of interest or 'spots' were initially undertaken on all samples; the samples were also mapped to check whether the glassy areas were reasonably homogeneous.

Sample Preparation by Focussed Ion Beam (FIB)

The instrument used for FIB was an FEI Helios Dualbeam Nanolab 600. Particles previously identified using the Inspect SEM were found using the SE or BSE SEM functionality on the Helios microscope. A backscattered electron top-down view (Figure 4, left), and a secondary electron view from a 52° stage tilt (Figure 4, right) is shown of a particle collected from the PMC Zapper ammunition in Figure 4. It should be noted that the particle is shown from two angles here.

A 2 µm thick layer of platinum was deposited over the region where the FIB was to operate with a platinum GIS. This serves to protect the sample, provide a conductive layer close to the milled area in order to minimise the 'theatre curtain' or 'waterfall' effect, which is a known FIB artefact, and it also provides a surface to which a probe can be welded for subsequent *in situ* manipulation [18]. After the platinum was deposited, troughs were sputtered around three sides of the region of interest using a Ga^+ LMIS at a beam current of up to 21 nA. An example of the troughs is shown in Figure 5.

Following this initial sputtering, lower current beams of 6.5 nA and then 2.8 nA were used to clean the surface of the slice. The bottom of the slice was milled in the same way, but at a 7° stage tilt, so that the milling was almost directly across the base.

The next step of the process involved welding a tungsten needle to the slice using the platinum GIS and a Kleindiek Nanotechnik Nano-manipulator. This was accomplished by aligning the tungsten needle with the slice, controlled by the nano-manipulator, using the two angles (ion image and SE image), and moving it into position so that it barely touched the deposited platinum layer on top of the slice. The GIS was then used to deposit a 1.5 µm thick layer joining the needle to the platinum layer. Finally, the last side of the slice (right side of slices in Figure 5, left) was sputtered, freeing the slice from rest of the particle. The slice was reviewed to verify that all sides had been milled clear, and then the stage was moved away from the needle. The slice was then welded to a copper holder, and the platinum attaching the needle to the slice was removed by sputtering with the GIS. The slice can be seen welded to the copper holder in Figure 6. When the specimen was placed under a transmitted light microscope it was possible to see through the central part of the thin slice that was excised, as is expected if it is a glass frictionator residue. For each slice prepared, optical microscopy was used to confirm that the particles were retained on the copper holder and had not been dislodged during the venting of the vacuum chamber or the inter-institutional travel.

Preparation for X-ray Spot Analyses and Mapping and SEM-EDS Analysis of FIB Slices

After optical examination using a light microscope, samples were prepared for further analysis by attaching the slice-holder to bare aluminium pin stubs using conductive carbon ink (Pasco Scientific Conductive Ink Dispenser PK–9031). Post-FIB SEM-EDS analyses were undertaken using the FEI Inspect F50 as detailed above.

The FIB-prepared particles were analysed by semi-quantitative EDS analysis and the results were compared to analysis of particles which had been prepared by solvent washes and mounting as described in [16].

A key question for research is whether the approach involving FIB sectioning of particles followed by elemental analysis is fit and practical for the forensic comparison purpose. In order to explore this question, glass frictionator fragments extracted from two cartridges taken from one box of Mexican Zapper and from 4 cartridges taken from three boxes of South Korean Zapper cartridges covering 3 batches (a duplicate selection was taken from one box chosen at random) were compared using SEM-EDX to a FIB-prepared slice of a gGSR fragment from a sample of PMC Zapper ammunition of origin unknown to the analyst.

ToF-SIMS Analysis of FIB-prepared slices of gGSR

ToF–SIMS experiments were performed using a Physical Electronics Inc. PHI TRIFT V nanoToF instrument equipped with a pulsed liquid metal ^{79} Au$^+$ primary ion gun (LMIG), operating at 30 keV energy. Experiments were performed under a vacuum of 5×10^{-6} Pa or better. 'Bunched' Au$_1$ settings were used to optimise mass resolution for the collection of SIMS spectra. 'Un-bunched' Au$_1$ settings were used were used to optimise the collection of image resolution.

The sample surface was sputtered for one minute, where required, to help dislodge surface contamination, and mass spectra were collected for two minutes.

ToF-SIMS was used to semi-quantitatively analyse the glassy region of each of the FIB-prepared slices of gGSR and extracted, polished frictionator specimens. Several measurements of each specimen were made, rastering 5 x 5 µm areas.

Results and Discussion

SEM-EDS analysis of FIB Slice – X-ray Spot Analyses and Mapping

SEM-EDS analysis was undertaken for all of the slices collected. Figure 7 shows a SE image of the particle from Winchester Power Point ammunition, and the regions that were analysed using EDS. From this figure, several distinct regions can be observed. On the left of each region is the copper holder to which the particle is attached (incorporating selected area 8), and then a platinum welding region which attaches the particle to the holder and protects the top of the slice (incorporating selected area 7, and the layer above area 2). A Pb and Ba crust from the outside of the particle is shown in selected areas 6, 2 and 3, and the glassy region is represented in areas 1, 4 and 5. The spectra generated in the regions were collated into Table 2, which shows that the different regions have specific compositions. Of particular note, is that calcium is not detected in the glass region, which suggests that it is a borosilicate. Following this, SEM-EDS mapping of the specimen was undertaken. The map (Figure 8) shows that the elemental composition of the glassy region was homogeneous, with neither Si, O, Al nor Na traces showing areas of varied intensity across the slice. Some elements observed in the slices are present due to the FIB process, and would not have been present in the original particle: Ga is an artefact from implantation from the LMIS; Pt was deposited to protect the particle and allow manipulation within the vacuum chamber; Cu was from the holder to which the particle is welded; and Al in regions 2, 3, 6 and 9 arises from the stub to which the holder is attached.

Two particles of PMC Zapper ammunition were similarly prepared from the PMC Zapper sample for which the country of origin was unknown to the researcher. The left panel of Figure 9 shows the BSE-SEM image of one of the slices, and the right panel shows the regions analysed.

The elements identified in each of these regions are shown in Table 3; the detection of calcium in the glass suggests that it is of the soda-lime type. The BSE image (Figure 9) shows variation in the glassy region of the particle slice, and this was largely supported by the observed elemental intensities. Unlike the previously sectioned particle, this example has a number of voids visible.

This particle was mapped using EDS to further investigate the homogeneity and composition of the particle interior. The map is seen in Figure 10, and shows various regions of compositional heterogeneity, including in the glassy region. There are two distinct phases visible in the glass structure via BSE, which was confirmed by the mapping. The lighter regions by BSE imaging, which corresponded to the pink phase in the map in Figure 10, indicate a higher incorporation of the heavy elements Pb and Ba. Similarly, the darker regions, which correspond with the blue phase, indicate a lower level of Pb and Ba incorporation (see Figure 11).

Finally, Figure 12 shows a SE image and a BSE image of the slice of the particle from Federal Premium centrefire ammunition (top-left and top-right). Of note is a particle embedded in the glassy region visible by both SE- and BSE-SEM. Three other phases are also clearly visible in the BSE image.

The elements present in each region, in approximate order of decreasing intensity, are shown in Table 4. The darkest region (Figure 12 - region 1) contained the glass elements Si O Al Na (which are indicative of borosilicate glass) and contained a small Cu-rich inclusion. The other regions contained Pb and Ba, with the Ba having higher intensities in region 3, and Pb having higher intensities in regions 2 and 4.

The single element maps shown in Figure 13 indicate that the particle is mainly glass, with a Pb/Ba enriched outer zone. It also shows that the silicon signal is fairly consistent across the core. The two inclusions observed in the glass from the BSE image exhibit higher concentrations of Pb, and the outer region of the glass shows that the Pb and Ba in the outer zone has implanted approximately 3-4 µm from every angle. The phase diagram shown in Figure 14, although not clearly showing the Pb nodules, does appear to highlight the homogeneity of the glass matrix in the particle.

It can be observed that in the first particle (the Winchester rimfire), only a very minor rim of the glass has had element (Pb/Ba) migration, in the Federal Premium (centrefire) particle, there has been migration of elements up to 2-3 µm into the glass, and in the PMC Zapper (rimfire) particle the migration has progressed into the centre of the particle. We hypothesise that during firing, the glass particles are present in a solid or semi-solid state while the other elements from the primer coalesce and cool around their outside to form gGSR. As the pressures generated during discharge may be very high (estimated to be approximately 35,000 psig for .40 Smith and Wesson cartridges [26] and approximately 24,000 psig for 0.22 calibre cartridges [27]) it is not surprising that migration of heavy metal primer residues into frictionator fragments takes place.

Particles showing these morphological/chemical characteristics are not likely to be produced by common environmental or industrial processes [6]. If such sources are rare then the detection of these particles could provide a valuable new capability for GSR examination, especially in shootings involving rimfire ammunition or when a residue collected involves a small number of particles that do not include the three key elements. Further work has been carried out in our laboratory to identify whether non-cartridge sources can produce particles resembling gGSR [17], and no such sources have been identified as yet.

Comparison of gGSR to extracted frictionator using SEM-EDS

After characterising these particles by SEM-EDS, it was of interest to investigate whether the pre- and post- firing residues could be linked, and whether particles from different sources could be differentiated. In our previous work [16], it was noted that frictionator particles from different brands of ammunition could be differentiated based on their elemental composition, but surprisingly, differentiation within the Winchester brand was not possible despite a large time-span (decades) in the manufacturing date of the cartridges sampled.

Unlike Winchester ammunition, PMC Zapper has previously been identified as having frictionator compositional variance within the brand [26], even to the extent that some batches contained borosilicate glass whereas other contained soda-lime glass. Therefore, there is the potential to demonstrate a link, or not, between gGSR and a putative source ammunition or between two deposits of gGSR, for example between deposits at two crime scenes or between deposits on a victim and deposits on a suspect.

The newer (Mexican) cartridges had at least two glass fragment populations within the individual cartridge (Figure 15), but as only one box was available it was not possible to determine the generality of this finding. Only one frictionator composition was observed within each cartridge of the South Korean variant and these compositions could not be distinguished using SEM-EDS (Figure 15). This Figure also displays the composition of the glass present in the FIB-prepared Zapper gGSR sample (the country of origin for which was not known to the researchers at the time) and it can be seen that its composition is different from both populations present in the Mexican examples of PMC Zapper. This difference can be established from the sodium, magnesium, potassium, calcium and tin concentrations. However, the FIB-prepared sample could not be distinguished from any of the South Korean samples using SEM-EDS, indicating that it may have been made in South Korea. After testing was complete, the origin of the FIB-prepared sample was revealed as South Korea, thus confirming the test indications. From the limited number of cartridges examined it appears to be the case that the composition of frictionator from the Mexican Zapper cartridges has greater variety than the frictionator from South Korean Zapper.

Comparison of gGSR to extracted frictionator using ToF-SIMS

The comparison of composition between gGSR collected from muzzle discharge and extracted frictionator samples for Winchester and PMC Zapper using ToF-SIMS are shown in Figure 16 and Figure 17, respectively. Figure 16 shows that the 99% confidence intervals for the relative intensities of the extracted and the FIB-prepared gGSR from Winchester ammunition overlap for every element, with the exception of Pb, which is present only in the FIB-prepared sample, indicating that it was most likely not incorporated during the firing process. Glass from Winchester ammunition has previously been observed to exhibit no significant variation between different batches, factories and ammunition types over the past several decades [16, 26]. The relatively low abundance of K and Ca indicate that the glass is of the borosilicate type.

Figure 17 shows a comparison of the compositions of the PMC Zapper gGSR slice and one of the South Korean PMC Zapper samples that were shown to be indistinguishable by SEM-EDS. The higher analytical power of ToF-SIMS allowed minor differences between the two glass samples to be observed with regards to Mg, Al, K and Na concentrations. Differences between the samples with regards to Cu and Pb were also observed, but these elements were only detected in the FIB-section. As this was phenomenon was also noted in the Winchester FIB-slice, the abundance of these elements is most likely connected to the deposition of other primer components onto the surface of the glass during discharge and/or FIB process and these elements were not used as a basis for discrimination.

Our previous work indicated that ToF-SIMS had a greater power of discrimination than SEM-EDS for comparing clean, extracted frictionator samples [16]. The results presented here support the relative powers regarding comparing sectioned gGSR particles with frictionator extracted from putative source ammunition.

Conclusions

gGSR particles are fragments of glass frictionator partially or completely covered with a heavy-metal crust derived mainly from other components of the primer. In other studies, we have not been able to find environmental sources of particles resembling gGSR. Therefore, the detection of gGSR in a case is potentially valuable evidence, especially in shootings involving 0.22 rimfire ammunition, which frequently contains glass frictionator but does not contain residues of antimony trisulfide. The purpose of the investigation described here was to explore methodologies for obtaining elemental profiles of the glass in gGSR as a means of associating particles with putative source ammunition or with other deposits of GSR (such as those arising from a different shooting). This article shows that it is feasible to obtain such profiles and thus presents an insight into the possibilities for a new forensic capability.

In order to obtain pristine samples of the frictionator core of gGSR particles for analysis, the particles were sectioned using a focussed ion beam (FIB) to expose a clean glass surface for examination. ToF-SIMS and SEM-EDS were used to generate semi-quantitative elemental profiles of glass from FIB-prepared slices for comparison with profiles generated from frictionator particles extracted from unfired cartridges.

The elemental profile of a FIB-sectioned gGSR particle from Winchester ammunition was found to be similar to previously obtained profiles for Winchester frictionator. This demonstrates the concept that gGSR can be compared to frictionator extracted from unfired ammunition. An additional demonstration of the concept was carried out using PMC Zapper ammunition. Even across a few ammunition samples, it was noted that frictionator from PMC Zapper ammunition manufactured in Korea showed more variation than that from Winchester, but Mexican PMC frictionator showed more variation than the Korean PMC Zapper. SEM-EDS was easily capable of discriminating elemental compositions of frictionator obtained from Winchester and PMC ammunitions and between Mexican PMC and Korean PMC. Using SEM-EDS the elemental profile of a FIB-section of a Zapper gGSR particle (not known to be of South Korean origin at the time of analysis) was found to resemble closely the profiles of frictionator extracted from a small population of South Korean PMC frictionator samples. ToF-SIMS was capable of achieving discrimination amongst all the extracted South Korean Frictionator samples and the section of gGSR, which supports our earlier finding that ToF-SIMS exhibits a higher discrimination power than SEM-EDS with regards to analysis of frictionator.

Processing of gGSR using a FIB is straightforward, if not a little slow, and as the unit is usually an accessory in an SEM; finding particles already detected by a traditional GSR search is quite simple. However, the equipment is not commonly available in forensic laboratories. Our earlier work used the ion beam in the ToF-SIMS to expose the glass core of particles by sputtering away primer encrustations prior to glass elemental profiling. Finding GSR particles using ToF-SIMS is more difficult than in a FIB-SEM, the ToF-SIM beam sputtered more slowly through the glass than using the FIB preparation method, and it did not allow particles to be lifted off of the stub. However, it was capable of sputtering sufficiently to obtain clean mass spectra of the glass (without Pb and Ba) so as to be comparable to pre-fired samples and could be used in casework.

In our laboratory we have now observed many samples of glass-containing gunshot residue particles; it has been noticed that a considerable proportion of particles have only a small fraction of their surface encrusted with heavy metal deposits. In particles such as these it is possible to acquire an elemental profile of the glass present very simply using SEM-EDS. Even though ToF-SIMS offers better discrimination than SEM-EDS, the latter can achieve a discrimination power of about 79%, which suggests that SEM-EDS may be the best initial test for rapid evaluation of whether a sample of gGSR may be associated with a particular source of ammunition or another deposit of gGSR.

SEM-EDS X-ray mapping was used to investigate elemental homogeneity within slices of gGSR and to determine whether primer-derived heavy metals migrate into the glassy matrix during firing. It was found that the frictionator samples are compositionally stable during firing, but it was also found that elements from the primer can migrate into the glass core of gGSR particles, which could affect the elemental profiles, but also be an indicator of the route of formation. This may indicate some mixing between molten metals, and glass during discharge of a firearm. Other than through the discharge of primer from a firearm or cartridge tool, such as a cartridge-operated nail gun, it is expected that sources of gGSR particles would be rare.

Although HMF ammunition was not specifically examined in this study, we have observed gGSR originating from a few brands. Therefore, a separate study is needed to determine whether there are environmental sources of glass-containing particles that resemble gGSR from HMF ammunition, such as glass with strontium-containing deposits on their surface, and whether there is compositional variance amongst the glass frictionators used in various brands of HMF ammunition.

This paper has assessed and compared several methods of analysing gGSR particles in order to add new information and capabilities to GSR analysis in forensic casework, and to further the fundamental understanding about the presence, formation, morphology and composition, and the potential use of these particles.

Declaration

The authors declare that they have no real or perceived conflicts or competing interests in publishing this manuscript.

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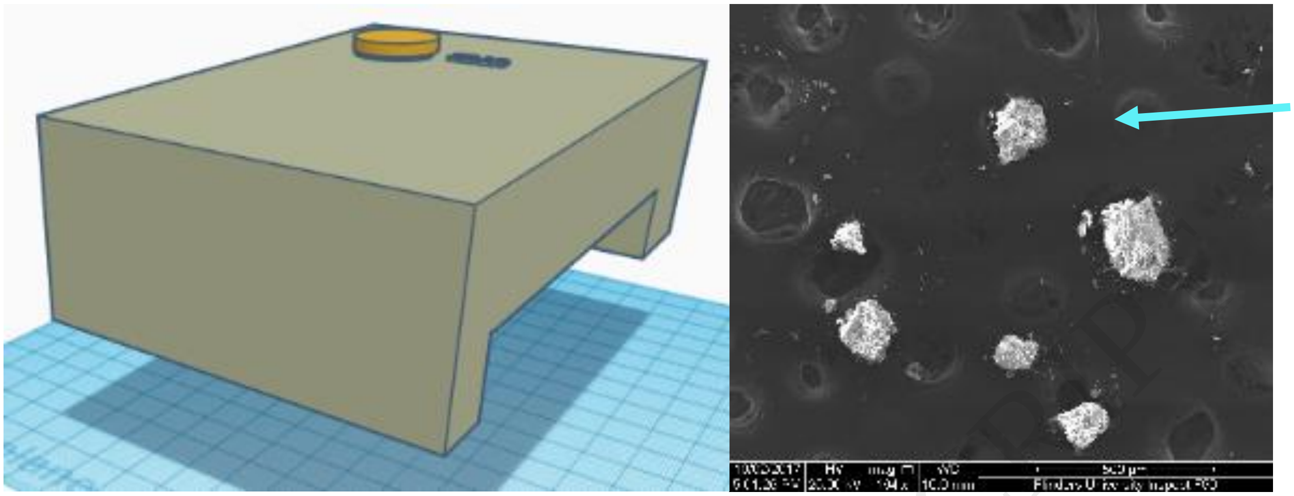

Figure 1: Left. Diagram of the aluminium holder designed to safely discharge disassembled ammunition cartridges, with a cartridge placed in the holder. The diameter of the hole through which the cartridge is place is smaller than the diameter of the cartridge case base but sufficient to allow cases to be inserted easily and removed after discharge. Right. Typical particles of Winchester Powerpoint GSR, the arrow indicates a particle that was later sectioned using the FIB.

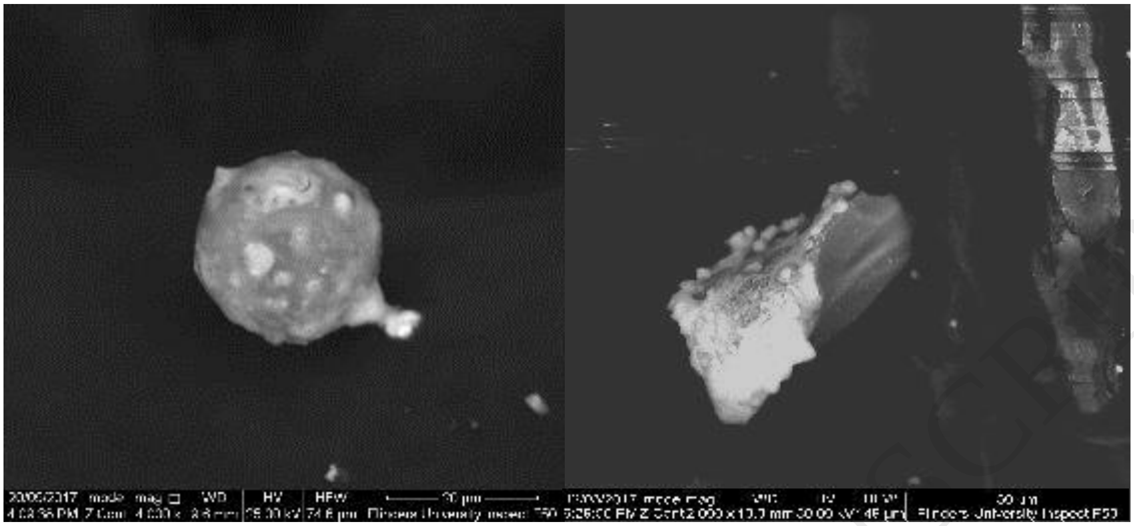

Figure 2: Particles collected from PMC Zapper ammunition that were sectioned by FIB, intended for further analysis. The left particle is the one for which analytical results are presented in this article.

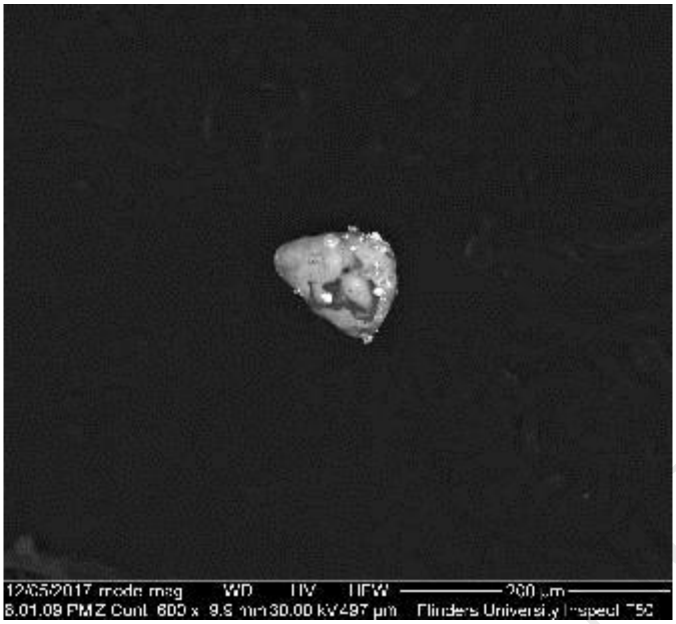

Figure 3: gGSR particle collected from Federal Premium (centrefire) particle from hands that was sectioned by FIB for further analysis

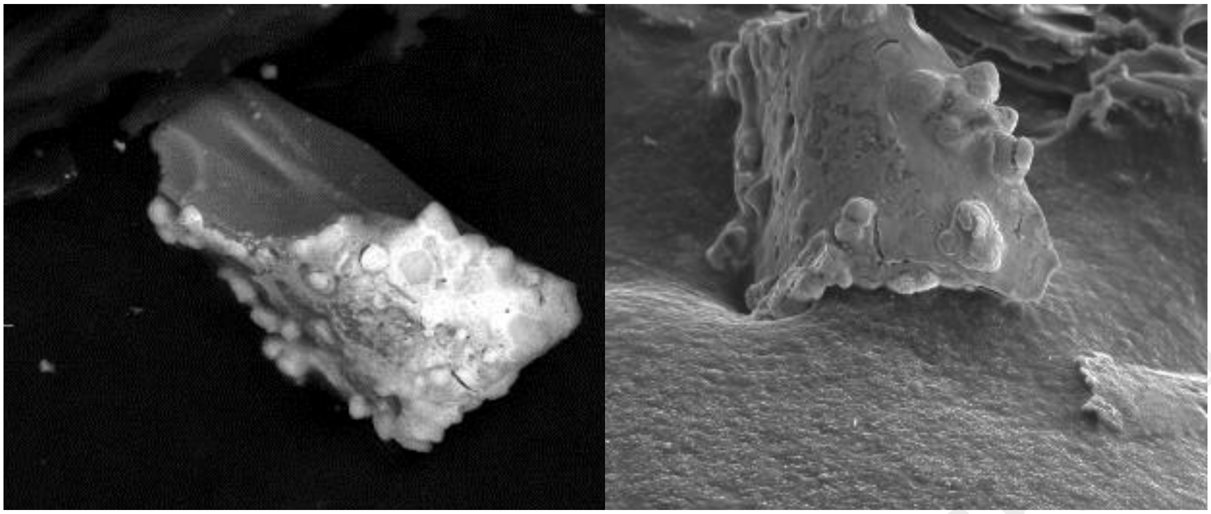

Figure 4: Top-down view (left) of gGSR particle from PMC Zapper taken using BSE-SEM-EDS on the FEI F50 instrument (note the typical glass choncoidal fracture evident), and an SE-SEM-EDS (right) image of the same particle taken at a 52° stage tilt and a clockwise rotation of about 45° on the FEI helios dualbeam nanolab 600 instrument.
n.b. The white arrow on the BSE image (Left) indicates the viewpoint for the SE image (Right). The view of the exposed glass is obscured by the bulk of the particle in the view on the right

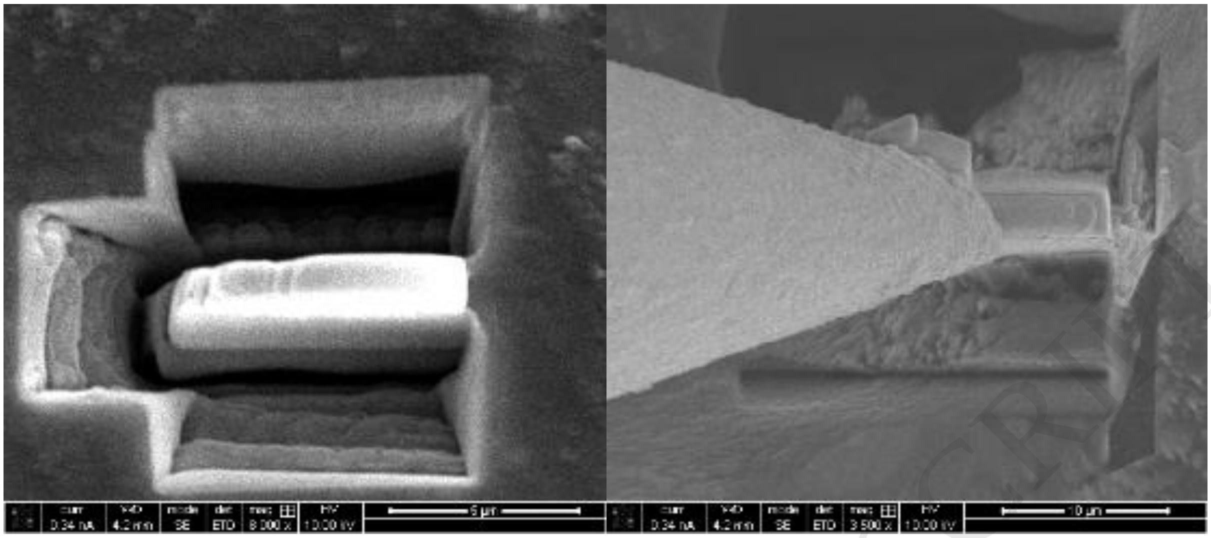

Figure 5: Troughs milled around the slice in the region of interest in a PMC Zapper gGSR particle (left) and needle from the nanomanipulator welded to top of the slice, to allow *in situ* transfer of it to a holder (right)

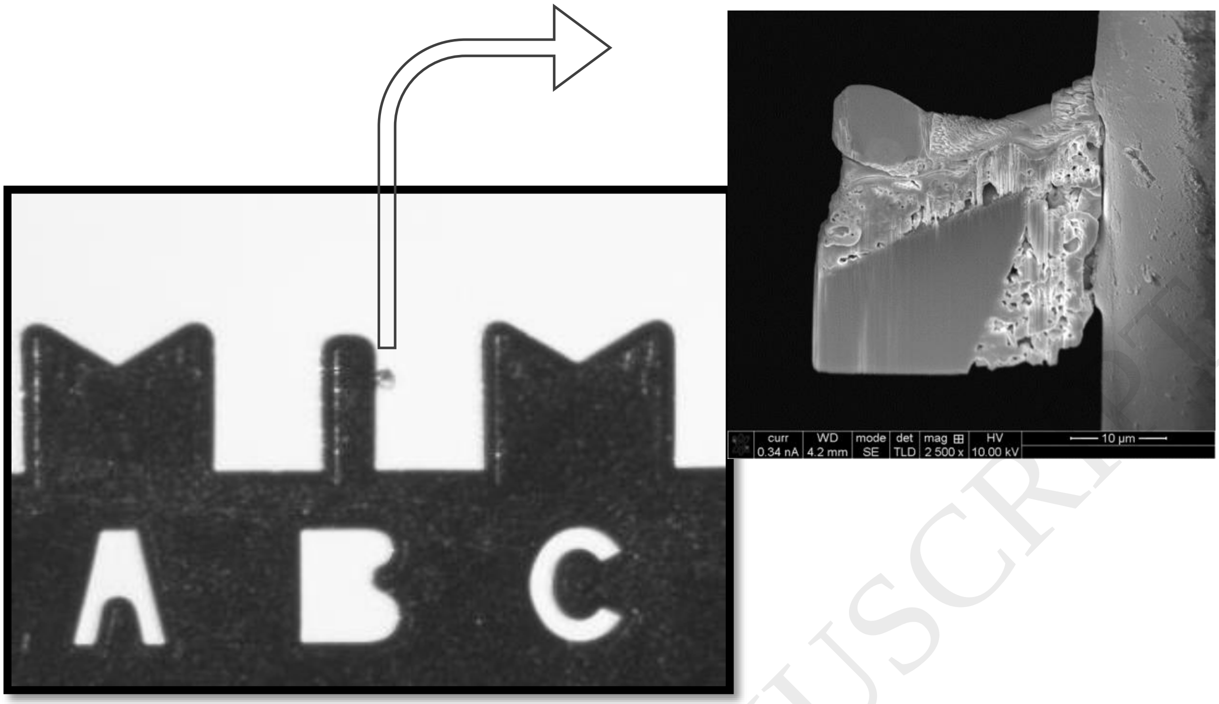

Figure 6: A slice of GSR welded to the copper peg (above the "B") of a sample holder. Inset is an electron photomicrograph image of the slice at 2,500 x magnification. Note that the specimen on the right is rotated about its vertical axis compared to the one on the left.

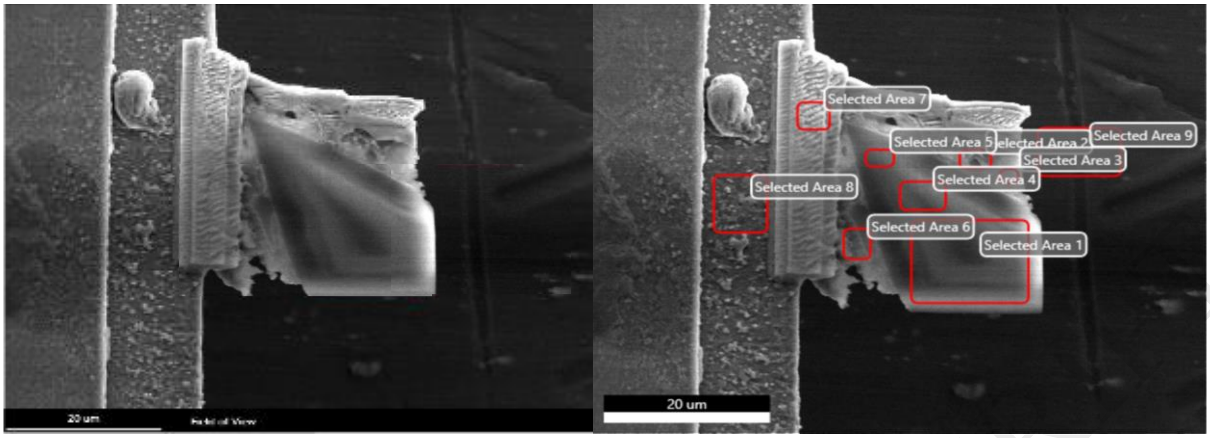

Figure 7: SE-SEM Image of a sliced Winchester Powerpoint particle showing clearly the glassy interior, and crusted exterior (left), and the 9 selected regions analysed by electron dispersive X-ray spectroscopy (right).

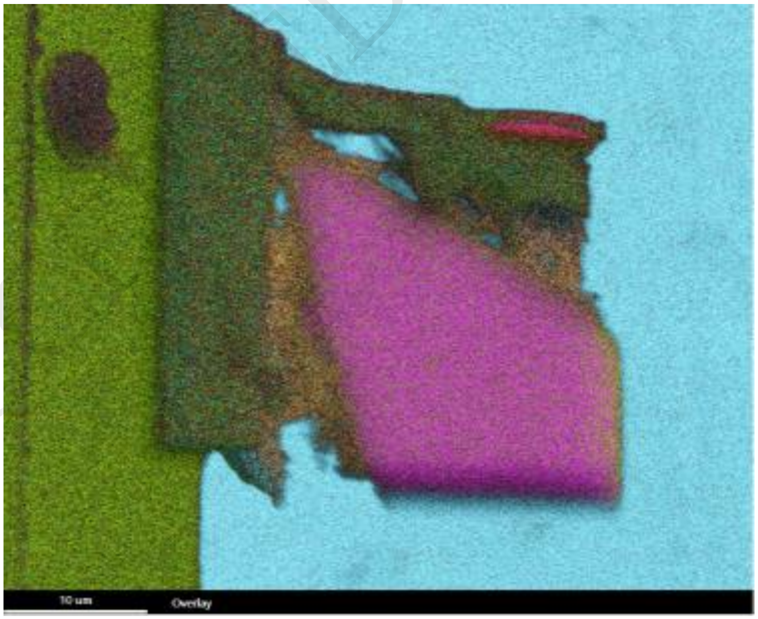

Figure 8: SEM-EDS mapping of particle sliced with a FIB. Overlay of elements showing Cu (lightest green, sample holder), Pt (dark green, weld and coating), Pb (brown-yellow, primer residue) and Si (pink, glass, area also contained significant O, Na), and Al (blue, stub surface)

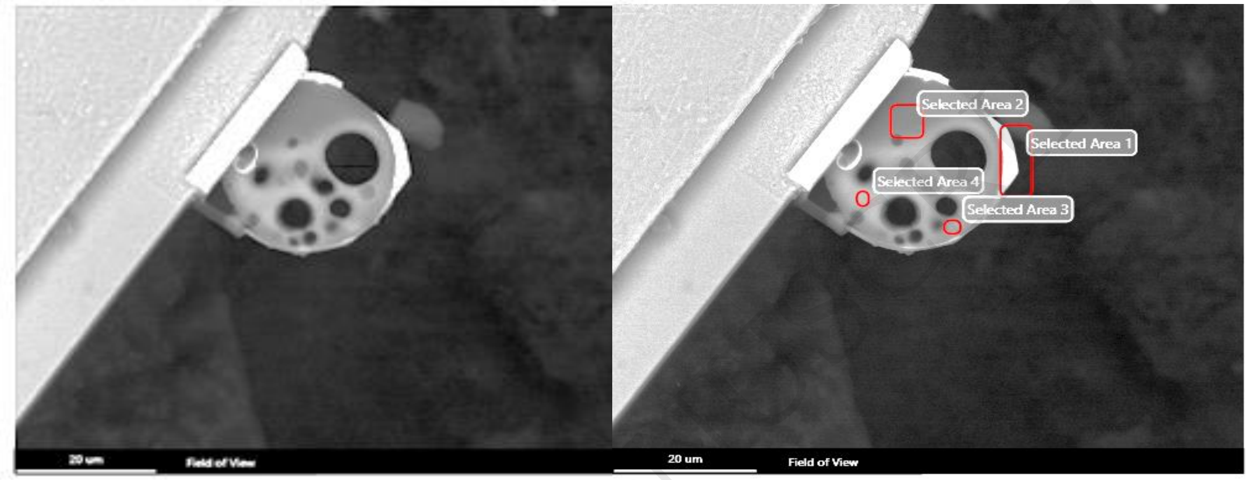

Figure 9: Left BSE image showing the various regions and voids in the PMC Zapper particle, and right, the regions examined via EDS analysis.

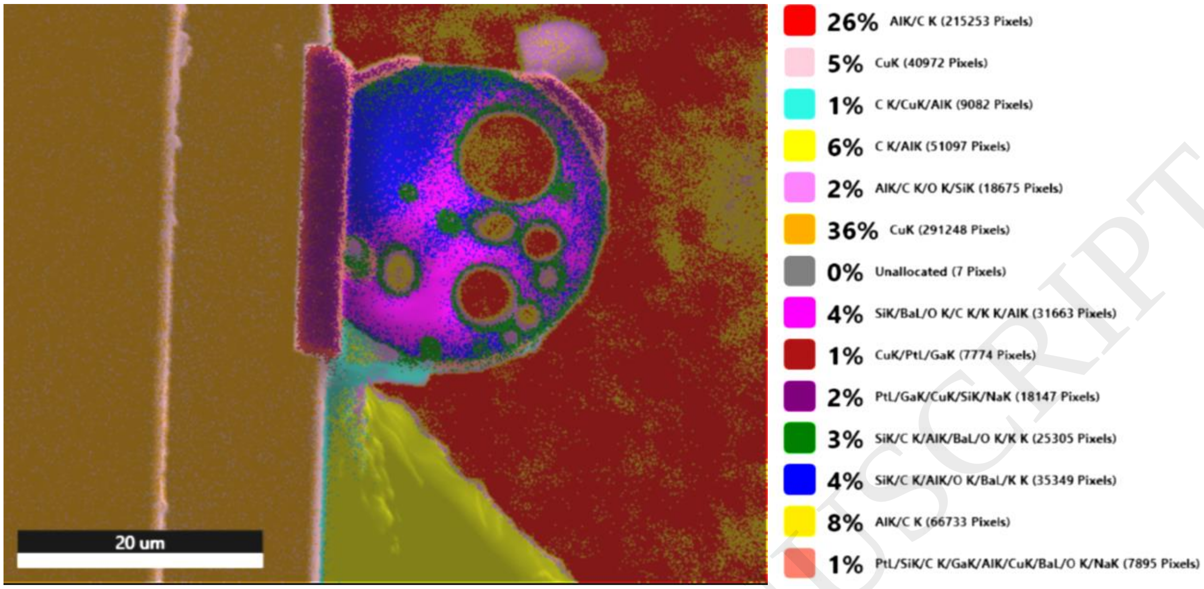

Figure 10: Map showing overlay of phases found by SEM-EDS mapping of a particle of PMC Zapper sliced open using FIB

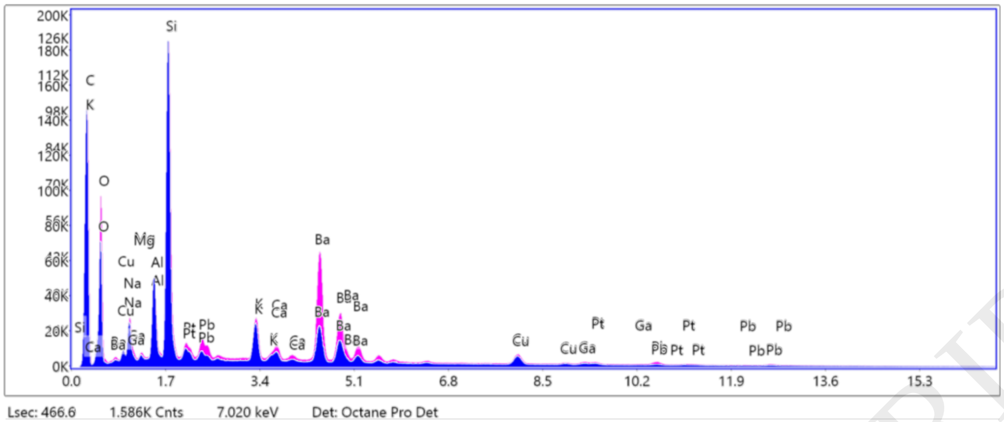

Figure 11: EDS spectra of the 2 glassy phases from the slice of PMC Zapper, the blue region showing less incorporation of Pb and barium, and the pink region showing a greater incorporation of Pb and Ba into the glass

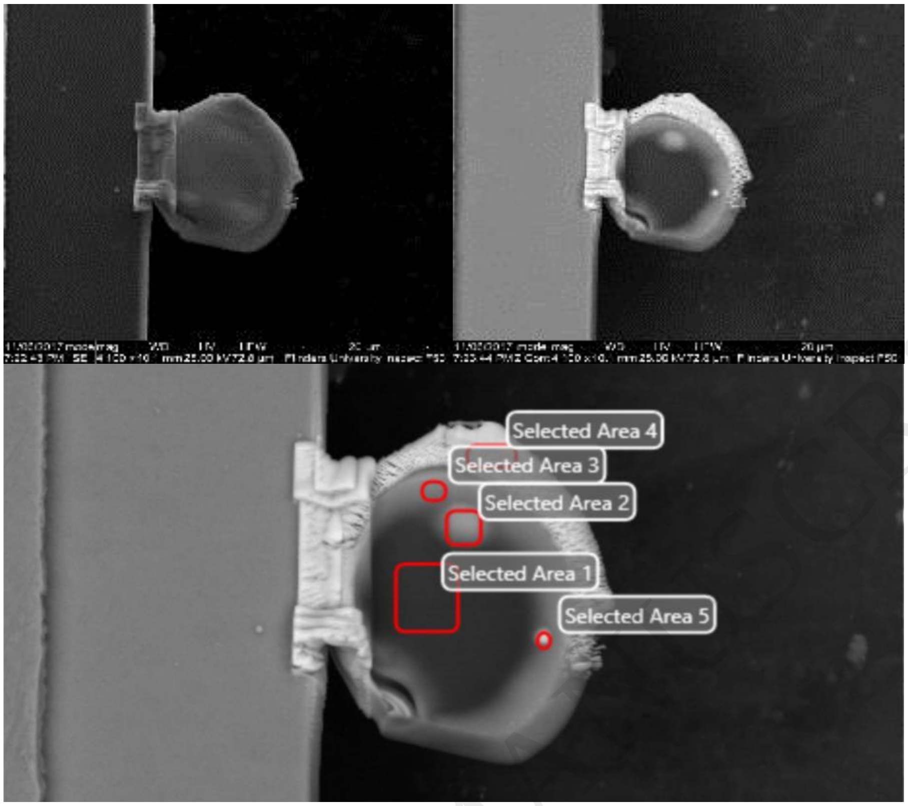

Figure 12: SE-SEM image showing the sliced particle from the Federal Premium (centrefire) particle (top left), showing two regions, a core and a crust. BSE image (top right) showing four distinct regions in the core, and an outer rim with Pb and Ba incorporated, Diagram (bottom) labelling the various regions of the particle examined corresponding to the compositions listed in Table 4.

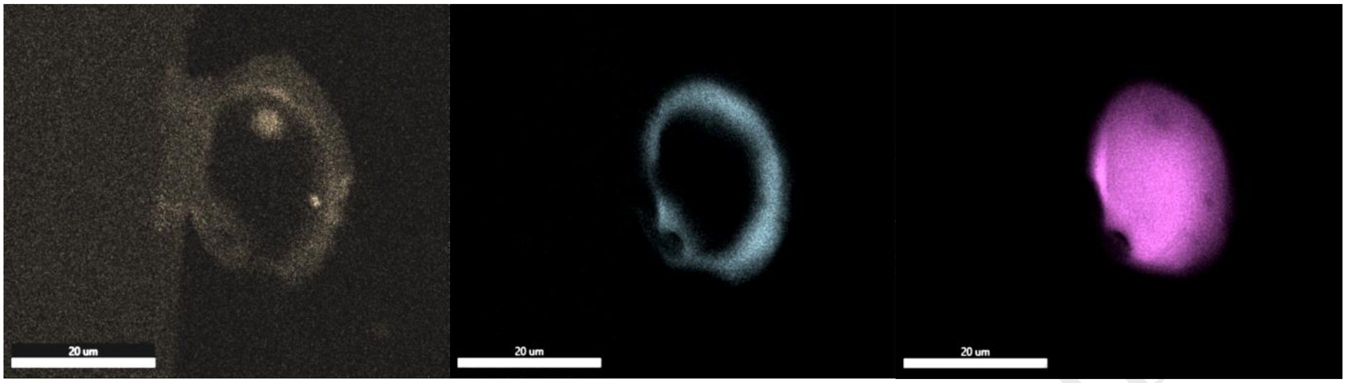

Figure 13: Single element maps of particle of Federal Premium (centrefire), showing a silicon containing glassy core (right), with incorporated Pb nodules (left), and a Pb/Ba incorporation on the outer rim of the particle (Ba, centre).

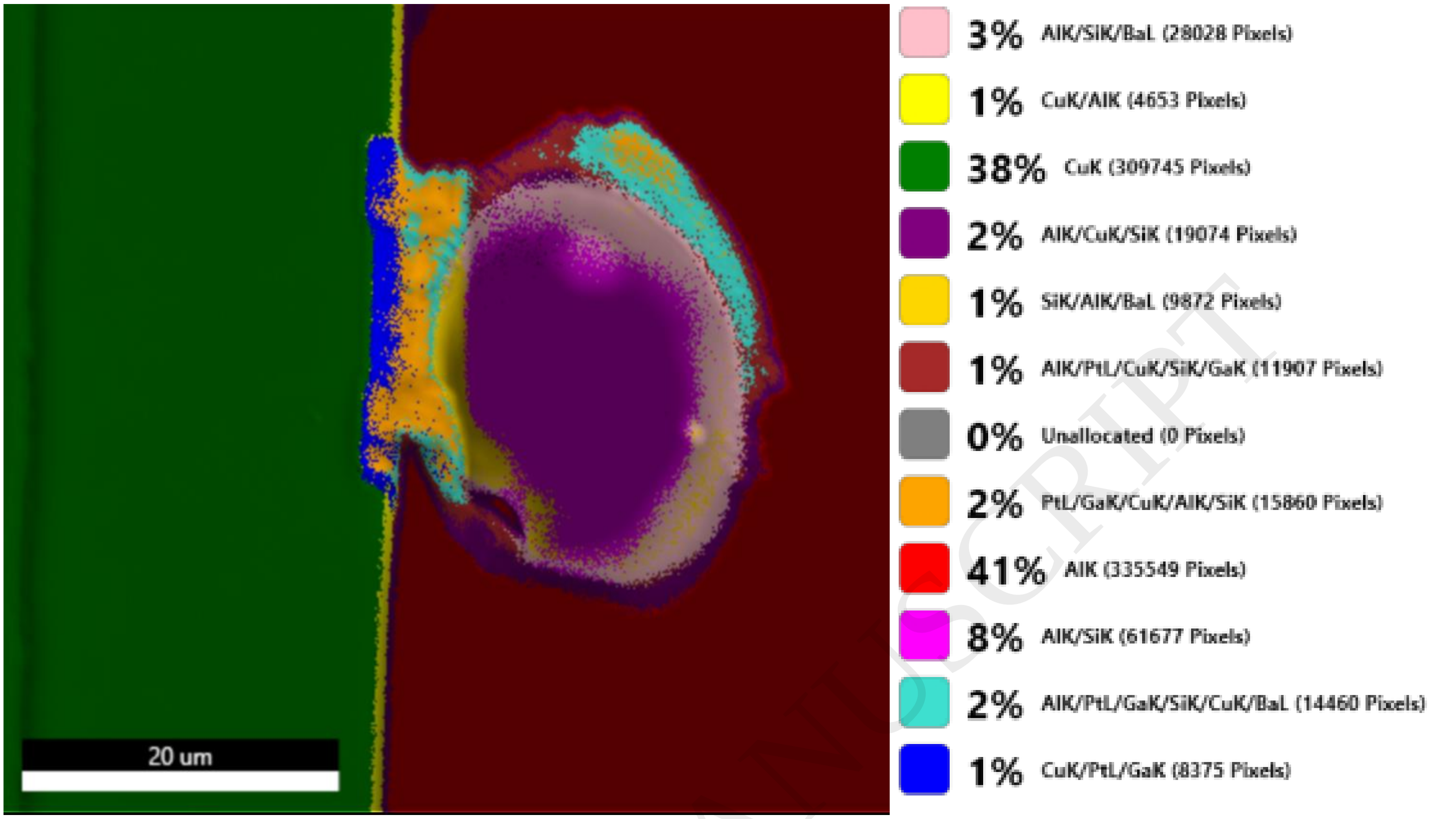

Figure 14: Phase overlay diagram of SEM-EDS map of Federal Premium centrefire ammunition sliced open using FIB

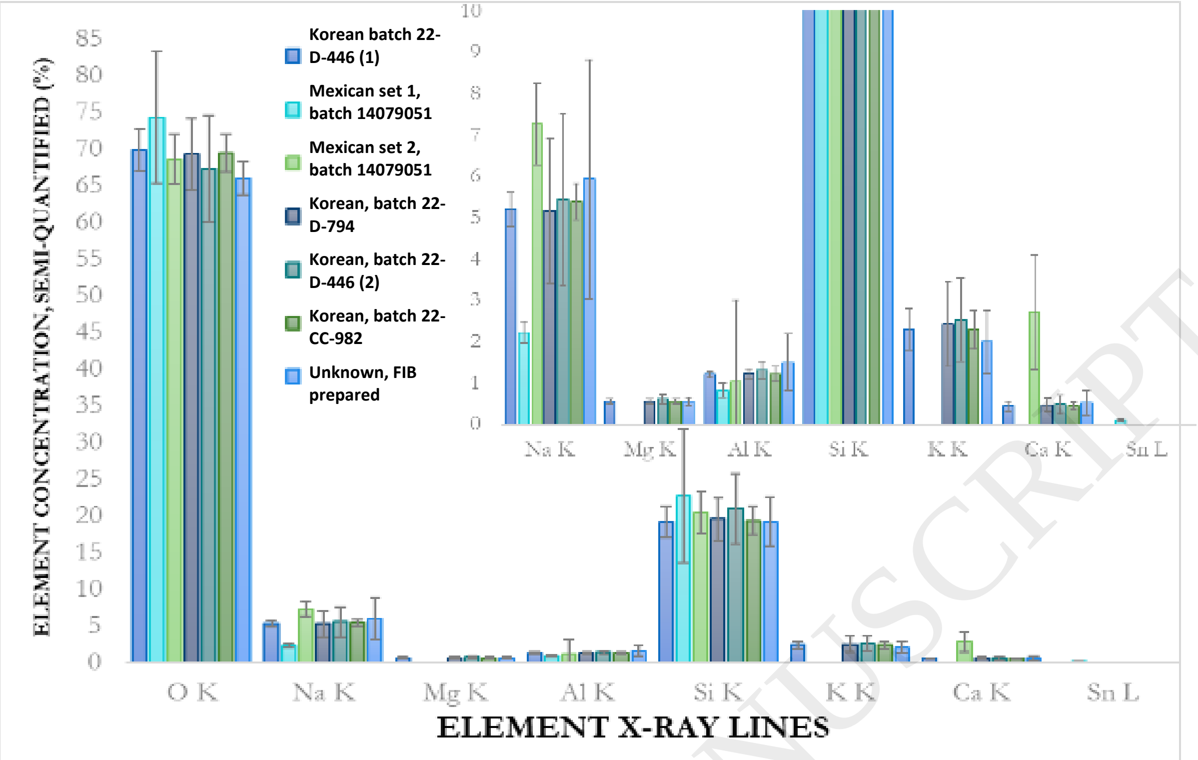

Figure 15: SEM-EDS comparison of glass frictionator fragment populations from PMC Zapper samples of various manufacture and a gGSR particle from a PMC Zapper particle of unknown manufacture. It is important to note that the two populations of Mexican frictionator present originated from one cartridge, where all other samples represent separate cartridges. Inset: a close-up of the low concentration elements. X-axis shows the X-ray lines for each element used for quantitation.

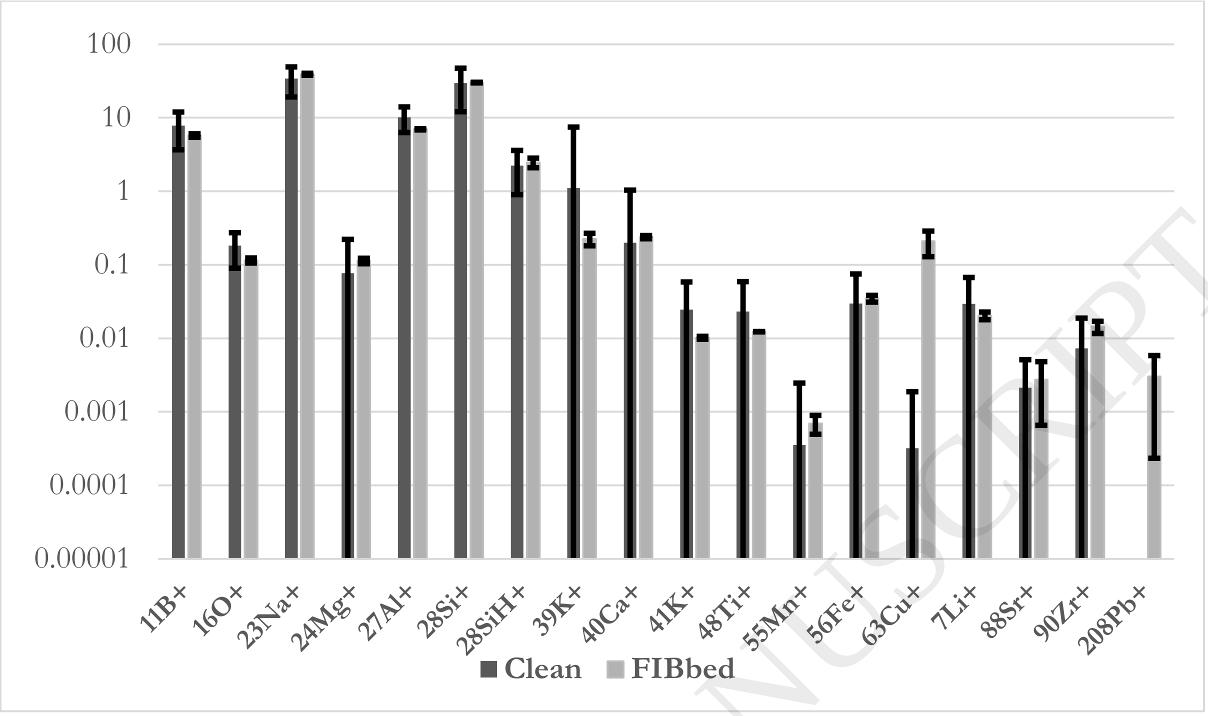

Figure 16: Mean intensities of fragments ±3σ, as a percentage of total counts of, comparing extracted frictionator and FIB-prepared gGSR samples from Winchester

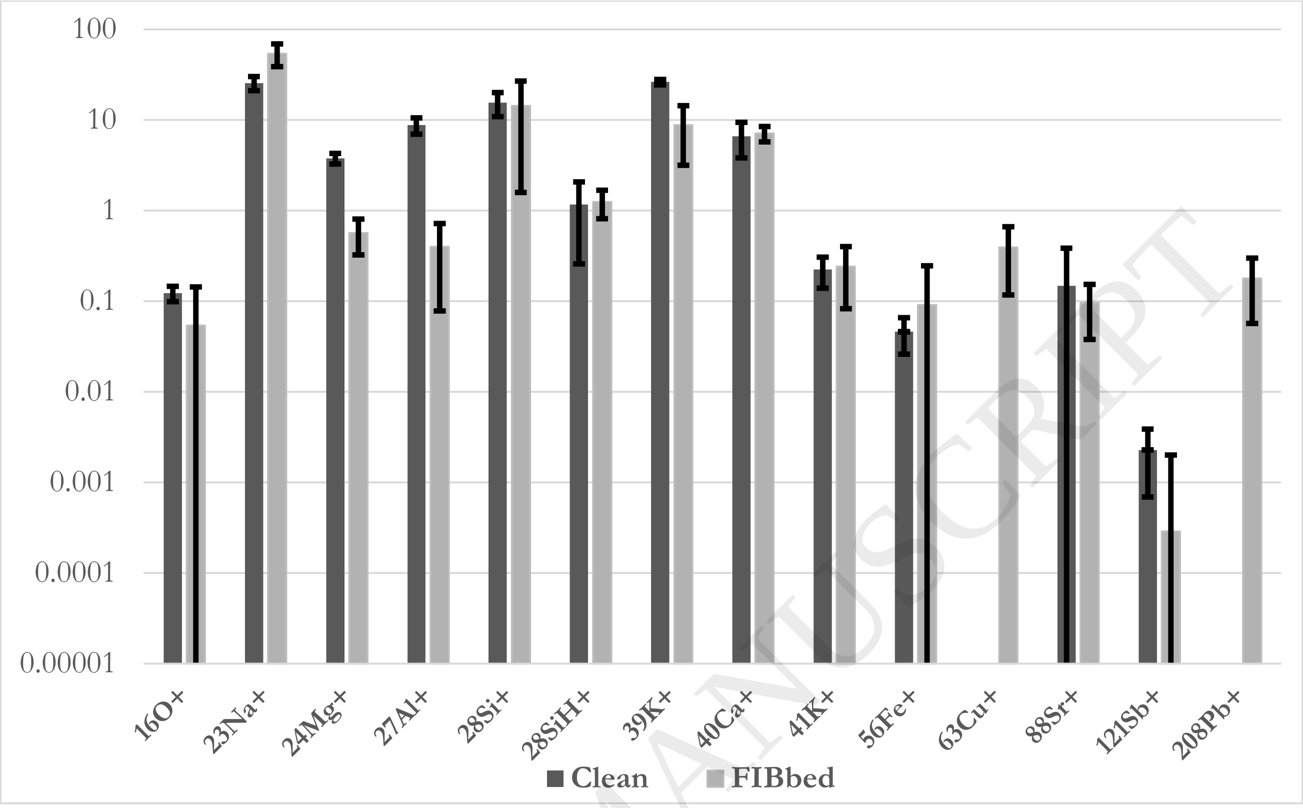

Figure 17: Mean intensities of fragments ±3σ, as a percentage of total counts, comparing extracted frictionator and FIB-prepared gGSR samples from PMC Zapper

Table 1: Inorganic compounds associated with primer GSR and their functions, with compounds in bold being reported as the most common for 0.22 calibre [5, 15]

Function	**Compound**
Oxidizer	**Barium nitrate** Barium peroxide Lead nitrate Lead peroxide
Initiator	**Lead styphnate** Lead azide* Mercury fulminate*
Fuel	**Calcium silicide** Lead thiocyanate Powdered zirconium Powdered aluminium antimony sulfide#
Sensitizers	**Tetrazene** Pentaerythritol tetranitrate Trinitrotoluene
Frictionator	Antimony sulfide Calcium silicide **Ground glass**

*historical # common for ammunitions other than 0.22

Table 2: Elements present in a Winchester Powerpoint ammunition slice, by region, organised by intensity.

Region	Elements Present (in approximately descending order of intensity)
1. Glass Region (1)	Si O Al Na
2. Crust	Al Pt Si Pb O Ga Ba
3. Thin Crust Region	Al Pb Ba O Si Cu
4. Glass Region (2)	Si O Al Na
5. Glass Region (3)	Si O Al Na
6. Crust-Glass Interface	Al Pb Si Pt O Ga Ba Cu
7. Platinum Cap	Pt Ga Cu (trace)
8. Sample Holder	Cu
9. Background (Al pin stub)	Al Cu (trace)

Table 3: Elements present in the particle of PMC Zapper ammunition, divided by region and then ordered approximately in decreasing intensity

Regions	Elements Present (in approximate order of decreasing intensity)
1. Platinum Cap	Al Pt Ga
2. Glassy region (1)	Si O Al Na K Ba Cu Ca Mg
3. Glassy region (2)	Si Al O Na Ba K Ca Cu Mg Pb
4. Glassy region (3)	Si O Ba Al Na K Pb Ca Mg Cu

Table 4: Elements present in the various regions of the particle slice from Federal Premium centrefire ammunition

Regions	Elements Present (in approximate order of decreasing intensity)
1. Glassy region (1)	Al Si O Cu Na
2. Glassy region (2)	Al Si O Pb Cu Ba Na
3. Glassy region (3)	Al Si O Ba Pb Cu Na
4. Platinum Cap	Pt Al Ga Cu
5. White spot in glassy region 2	Al Si O Pb Ba Cu Na