Trace Element Profiling of Gunshot Residues by PIXE and SEM-EDS: A Comparative Study

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Abstract
We critically compare particle induced X-ray emission (PIXE) on the ion microprobe with scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) for the characterisation of gunshot residues (GSR). Samples of gunshot residue from several different firearms were collected. Individual particles of GSR were analysed by SEM-EDS using a 30keV electron beam focussed to ~10nm and PIXE using a 2.5MeV proton beam focussed to ~4 microns. PIXE revealed trace or minor elements undetectable by SEM-EDS, and could discriminate GSR indistinguishable by SEM-EDS.

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Introduction
In order to demonstrate that a suspect in a criminal investigation has fired a weapon, police authorities routinely take swabs from the clothing, skin and hair of the suspect and use electron microscopy to search for gunshot residue (GSR) particles on the swabs. These particles are condensation products of the high temperature, high pressure reactions that occur when a firearm is fired and are known to be deposited at the crime scene and on the shooter [1]. The particles are made up of material from the primer, bullet, bullet jacket, cartridge casing and the gun barrel, are spherical, and are of the order of a few microns in diameter. There are several types of particle that are characteristic of gunshot residue, including those containing Pb, Ba and Sb [2].

In case work, it is highly desirable to be able to discriminate GSR from different sources to rule out possible contamination and to strengthen the link between a suspect and a crime scene. It is known that GSR varies in composition and morphology in accordance with the type of firearm that has produced it. The UK Metropolitan Police have developed a categorisation system for gunshot residues, putting them in 35 different categories in accordance with their morphology and chemical composition. It is accepted that the chemical composition of GSR is a better indicator of its provenance than morphology [3], [5]. The technique of choice amongst police institutions for the analysis of GSR is scanning electron microscope energy dispersive X ray spectrometry (SEM-EDS) since the technique is widely available, relatively cheap and can be automated. EDS also offers the advantage of imaging the particles as well as determining their chemical composition, and is non-destructive.
Despite the success of EDS in many cases to categorise GSR particles, it remains impossible to discriminate between certain types of residue. Analysis methods with a higher sensitivity to trace elements could provide a means for discriminating between residues that look similar under EDS analysis. Particle induced X-ray emission (PIXE) using MeV proton beams is sensitive to trace elements, unlike SEM-EDS which has orders of magnitude larger bremsstrahlung background, as shown in Figure 1. PIXE has previously been used to characterise gunshot residues, but on a broad beam, limiting the sensitivity to the individual particles, and leaving the analysis vulnerable to contamination [4]. In this work we use microbeam PIXE to image individual particles of gunshot residue, to investigate whether PIXE can be used to further sub-categorise GSR samples.

An additional advantage of PIXE over SEM-EDS is that the technique is quantitative and absolute. This is because the backscattered particle spectrum (collected simultaneously with the PIXE spectrum) comes almost entirely from single scattering events (unlike SEM-EDS) and can therefore be readily analysed to determine the matrix composition of the sample and its variation with depth. Thus the absorption of the exiting X rays can be accurately calculated where there is no prior knowledge of the sample composition, or where it varies with depth. It is known that gunshot residue particles are often non-uniform in composition [3] and therefore fully quantitative analysis of such particles by SEM-EDS is difficult.

Another significant difference between PIXE and SEM-EDS is the interaction volume from which the X-rays are generated. This is particularly significant in the case of particles of the size and morphology to be considered here. For SEM-EDS, the electron beam is scattered laterally through the sample, resulting in a pear-shaped interaction volume whose precise dimensions are determined by the beam energy and the sample composition. For PIXE, the heavier proton beam is not so easily deflected and therefore the interaction volume is cylindrical with a diameter given by the spot size of the ion beam, and therefore both the excitation and absorption probabilities are much easier to calculate with PIXE.

**Materials and Methods**

Gunshot residue samples were collected from shooters at Bisley Rifle Range, Surrey, England. Residues were collected from four different firearms: a pistol, 2 rifles and a shotgun. The pistol residue was obtained by swabbing the shooters’ hands with an SEM stub. The other residues were collected by shaking the spent cartridge cases onto respective SEM stubs. Both methods have been used in previously published work for the collection of gunshot residue [6] [7]. A Cu particle finder grid was placed on top of the stubs.

The particles were located using a Philips XL30 scanning electron microscope, fitted with an EDAX EDX system. The beam energy was 30keV and the detector was a 133eV Si(Li) UTW (ultra-thin window) detector with a take-off angle of 45°. Individual GSR particles were located and imaged using BSE image. Roughly 10 particles per sample were studied. 10 minute spectra (on average) were recorded. The spectra were fitted using the EDAX software package [ref??].
After the SEM-EDS analysis, the same particles were located and analysed using a 2.5MeV proton beam, focussed to ~4microns [8]. PIXE spectra were obtained using a 146eV Si(Li) detector at a take-off angle of 45° with a 130 μm Be filter to exclude protons from the detector. Backscattered particle spectra were simultaneously collected. The backscattered particle image was used to locate the particles, together with the PbL X ray map, as shown in Figure 2. Point spectra were taken for each of the particles. The spectra were fitted using the software code OMDAC [8b] (which implements GUPIX [9]).

Results

The elemental composition determined by SEM-EDS of particles from the shotgun and from the pistol residues are shown in Figure 3. For each of the samples, the intra-sample variance is large, particularly for the major elements Pb, Ba and Sb, in accordance with previous studies, where particles of varying composition have been found in GSR [10]. The intra-sample variance of the minor elements, S, K, Fe and Cu is somewhat lower. No S is detected in the pistol residue, whereas a small amount (<10wt%) is detected in the shotgun residue. The average K and Cu content of the pistol residue is higher than for the shotgun residue. Small traces of Fe (~1at%) are detected in the shotgun residue but not in the pistol residue.

Figure 4 shows the elemental composition determined by SEM-EDS of particles from the residues of Rifle 1 and Rifle 2. Both rifle residues contain Al and Si, which is not detected in the shotgun or pistol residues. There is no significant difference in the detection of the other elements.

PIXE analysis of the particles was carried out to investigate whether further discrimination between the particles could be obtained. In Figure 1, a typical PIXE spectrum from the GSR particles is plotted together with a typical SEM-EDS spectrum. The figure clearly shows how the bremsstrahlung background of the SEM-EDS limits the sensitivity to trace elements. In this particular case this permits the detection of elements such Fe and Zn that are not detected by SEM-EDS. A further advantage of the PIXE technique is that the K lines of the heavier elements (Sb, Sn, Ba) are excited. This offers a significant advantage in reducing both the ambiguity caused by the overlap of the Sb, Sn and Ba L lines, and topography effects, since the absorption of the higher energy X-rays is less.

Figure 5 shows the elemental composition determined by PIXE for the particles from the residues of the shotgun and the pistol. PIXE detects small quantities of a number of different elements (including Sn, Al, Si, Cl, Ca, and Zn) that are not detected by SEM-EDS. It is known from previous studies that certain gunshot residues can contain these elements [2]. In agreement with the SEM-EDS measurement, the measured K content of the pistol residue is higher than for the shotgun residue. The measured Cl content is also higher for the pistol residue. However, a very clear discriminator between the particles is Sn, which is not detected by SEM-EDS. Sn is found in the pistol residue but is completely absent in the shotgun residue.

Figure 6 shows the elemental composition determined by PIXE for the particles from the residues of Rifle 1 and Rifle 2. The data shows a higher content of Sn in the
particles of Rifle 1 compared with Rifle 2. The Ca content of Rifle 2 is on average higher than Rifle 1, although this is subject to considerable intra-sample variation.

Discussion

The shotgun and pistol residues could be discriminated by SEM-EDS. Additionally, low levels of Sn were observed by PIXE in the pistol but not in the shotgun residues, allowing further discrimination between the particles.

For the two rifle residues, no significant difference is detected by SEM-EDS. With PIXE, Sn was detected in most of the particles from the residue of Rifle 1 but not in most of the particles for Rifle 2. However, to discriminate unequivocally between these residues either a greater number of particles need to be studied or the results should be treated quantitatively (or both). As discussed previously, quantitative results from such samples are not available by SEM-EDS, which anyway lacks the sensitivity to measure either the SnL line (due to the low signal/noise ratio) or the SnK line (due to low excitation cross-section). For the present work, the PIXE data (like the SEM-EDS data) has been treated only semi-quantitatively.

However, a major benefit of the PIXE technique, as mentioned previously, is the ability to treat the spectra quantitatively, using the backscattered particle spectra. GUPIX does not allow accurate quantification of PIXE spectra from samples which are inhomogeneous in depth. This is now possible with the DataFurnace code [11], but is considered outside the scope of the present work.

Conclusion

We have shown that PIXE detects trace and minor elements in GSR particles that are not detected by SEM-EDS. We have shown that PIXE can be used to strengthen the discrimination between different sources of GSR by also studying these elements. We have shown a case in which SEM-EDS cannot discriminate GSR from two different sources. These results indicate that PIXE could be used to discriminate between sources that look the same under SEM-EDS. Quantitative treatment of the data is necessary and this work is in progress.

References

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Figure 1: Comparison of typical SEM-EDS and 2.5MeV proton PIXE spectra obtained for the GSR samples
Figure 2. Typical X-ray and backscattered particle images for the GSR particles using 2.5MeV protons

(a)

(b)

Figure 3: SEM-EDS results for (a) the shotgun residues and (b) the pistol residues
Figure 4: SEM-EDS results for (a) Rifle 1 residue and (b) Rifle 2 residue
Figure 5: Minor element composition determined by PIXE for (a) shotgun residue (b) pistol residue
Figure 6: Minor element composition determined by PIXE for (a) Rifle 1 (b) Rifle 2