Optimising Surface Characterisation of Gunshot Residue (GSR) Using X-ray Photoelectron Spectroscopy (XPS)


Scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS) is the most common method for the forensic analysis of gunshot residue (GSR); however, these techniques are unable to analyse the surface chemistry of GSR. This article discusses the use of X-ray photoelectron spectroscopy (XPS) in conjunction with SEM/EDS for precise and reliable characterisation of the fine fraction of GSR particles. Experimental results demonstrate that this approach allows for important information to be revealed regarding the surface composition and surface chemistry of GSR.
Firing a weapon triggers the combustion of both the primer and powder of the cartridge. The residue of the combustion products, called GSR, may be found on the skin or clothing of the person who fired the gun, on an entrance wound of a victim, or on objects at the scene of the discharge. The three main primer elements are lead (Pb) from lead styphnate, barium (Ba) from barium nitrate and antimony (Sb) from antimony sulphide [Frost, (1990)]. GSR consists of the products of combustion of these primer materials. Accurate detection and quantification of the three primer elements is of utmost importance in forensic science.

Computer-controlled scanning electron microscopy (CCSEM) has been traditionally used in forensic laboratories for the automated analysis of GSR. In addition, GSR particles generally range in size from 1 to 10 µm, although larger and smaller particles can be also formed. GSR particles usually have an outer layer of Pb surrounding an inner core of Sb and Ba. Particles that do not meet the specific compositional or morphological criteria are rejected as GSR.

The elemental composition of GSR particles may vary depending on the ammunition used. However, in cases when all three materials are detected, the particles under examination are flagged as a potential GSR particulate. Flagged particles that contain significant amounts of Pb, Sb and Ba are subsequently relocated for a live identification and a positive confirmation of GSR. Based on their composition and morphology, positive particles are classified as being either “characteristic of GSR” (when all three key elements are present) or “consistent with GSR” (when any two of the key elements are present). The element amounts are not taken into consideration for the classification of positive particles.

**GSR Characterisation**

XPS has emerged as a viable analytical technique, providing reliable characterisation of the surface chemistry of GSR particles to complement the findings of SEM/EDS studies. XPS combines qualitative with quantitative surface analysis capabilities and features a sampling depth of ≤ ~10 nm [Watts and Wolstenholme, (2003)]. The technique can detect all elements, except for hydrogen and helium, and has a detection limit of ~0.05–0.1 atomic percent for most elements. In addition to the elemental surface composition, XPS can also generate data about the oxidation state and chemical bonding, which cannot be obtained using other techniques [Watts and Wolstenholme, (2003)].
An additional advantage of XPS is that it can be used in conjunction with ion beam sputtering to produce in-depth compositional profiles and chemical state information. Nevertheless, this shortcoming is compensated by the fact that XPS can characterise the surface chemistry of small single particles. The typical spatial resolution of XPS (for example, 10 µm) limits the technique’s ability to analyse the surface chemistry of small single particles. This data may not be available in conjunction with ion beam sputtering to produce in-depth compositional profiles and chemical state information. Contrary to electron microscopy techniques, XPS offers limited spatial resolution and as a result it is sometimes not considered as a nanoscale analysis method. However, the technique is capable of analysing nanoparticle powders in considerable detail, generating information about elemental distributions, layer or coating structure and thickness, surface functionality, oxidation state and chemical bonding. This data may not be available from other methods [Baer and Englehard, (2010), Baer, et al, (2010)].

The typical spatial resolution of XPS (for example, > 10 µm) limits the technique’s ability to analyse the surface chemistry of small single particles. Nevertheless, this shortcoming is compensated by the fact that XPS can characterise the surface chemistry of aggregates of small particles or the larger individual particles that are often found in GSR [Schwoeble et al, (2010), Schwoeble et al, (2010)].

**Experimental**

The projectile and gunpowder were removed from a Federal brand 9-mm cartridge in order for primer-only GSR to be produced when the cartridge was discharged. The primer-only test, although lacking the exposure to high pressure found in a weapon, allows examination of a known primer and only that primer’s spent components. The cartridge was discharged through a 76 mm stainless steel tube placed directly over an alumina ceramic substrate that primer’s spent components. The cartridge was also analysed using a dedicated 200-kV STEM system (Hitachi HD-2300), which was equipped with an EDS system (Bruker), incorporating a 30 mm<sup>2</sup> silicon drift detector (SDD). The GSR powder was also analysed using a dedicated 200-kV STEM system (Hitachi HD-2300), which was equipped with a lithium-drifted silicon EDS system (Thermo Scientific).

**Table 1:** Surface compositions (atomic %) of a direct-deposit GSR sample on a ceramic substrate as determined by XPS before and after argon ion sputtering

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Sb</th>
<th>Ba</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>69.0</td>
<td>23.2</td>
<td>1.2</td>
<td>0.2</td>
<td>1.6</td>
<td>4.8</td>
</tr>
<tr>
<td>Argon ion sputtered 10 nm in-depth</td>
<td>63.2</td>
<td>26.2</td>
<td>0.5</td>
<td>0.6</td>
<td>5.8</td>
<td>3.7</td>
</tr>
<tr>
<td>Argon ion sputtered 20 nm in-depth</td>
<td>57.8</td>
<td>30.3</td>
<td>0.3</td>
<td>0.7</td>
<td>7.5</td>
<td>3.4</td>
</tr>
</tbody>
</table>

**Table 2:** XPS binding energies (eV) and chemical state assignments for a direct-deposit GSR sample on a ceramic substrate before and after argon ion sputtering

<table>
<thead>
<tr>
<th>XPS Peak</th>
<th>As-received</th>
<th>10-nm Argon Ion Sputter</th>
<th>20-nm Argon Ion Sputter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb 3d&lt;sub&gt;3/2&lt;/sub&gt;</td>
<td>539.7 Sb&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>539.3 Sb&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>539.4 Sb&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Ba 3d&lt;sub&gt;3/2&lt;/sub&gt;</td>
<td>780.2 BaO</td>
<td>780.1 BaO</td>
<td>780.2 BaO</td>
</tr>
<tr>
<td>Ba MNN</td>
<td>902.2</td>
<td>901.9</td>
<td>901.8</td>
</tr>
<tr>
<td>Pb 4f&lt;sub&gt;1/2&lt;/sub&gt;</td>
<td>138.6 PbO</td>
<td>138.3 + lower B.E. shoulder</td>
<td>138.3 + lower B.E. shoulder</td>
</tr>
</tbody>
</table>

The GSR deposit was prepared for electron microscopy analysis by first dispersing a portion of the material from the ceramic substrate in filtered isopropanol using ultrasonic agitation. A lacey Formvar/carbon substrate supported by the instrument manufacturer. In-depth elemental compositions were acquired at 2 kV. The ~900 nm in-depth compositional profiles and chemical state information. High-resolution XPS analyses were performed directly on one of the heavy GSR deposit areas shown in Figure 1 using a 200 µm X-ray spot size.

XPS survey spectra (0–1350 eV binding energy) were obtained to provide qualitative and quantitative elemental surface information. High-resolution XPS spectra were obtained for the major photoelectron peaks of all elements detected in the survey spectra to provide chemical state information. All binding energies were referenced to the main hydrocarbon C 1s peak = 285.0 eV. Surface composition results were calculated from the appropriate peak areas and relative elemental sensitivity factors supplied by the instrument manufacturer. In-depth elemental profile analyses were performed by sputtering with a 1 kV argon ion beam that was rastered over a 2 mm × 4 mm area. The reported sputtered depths were calibrated using a 100 nm SiO<sub>2</sub> on Si wafer standard reference material.

**Results and Discussion**

A secondary electron image of a typical GSR particle was acquired at 2 kV. The ~900 nm...
The 200 nm particle was identified as characteristic particles on the order of 50 nm dispersed around it. A STEM image of a 200 nm GSR particle with smaller internal structure observed in the bright-field STEM was visible in the STEM images. There was also little larger particles was such that no internal structure were also collected at 200 kV. The thickness of the GSR particles and the associated smaller particles were typically associated with the larger primary particle was confirmed as GSR following EDS analysis. Other primary particles that were confirmed as GSR by EDS ranged in size from ~400 nm to 1 µm. Numerous smaller particles (≤50 nm) were typically associated with the larger primary particles. Bright-field STEM (BF-STEM) images of GSR particles and the associated smaller particles were also collected at 200 kV. The thickness of the larger particles was such that no internal structure was visible in the STEM images. There was also little internal structure observed in the bright-field STEM images of the smaller particles. Figure 4 shows a BF-STEM image of a 200 nm GSR particle with smaller particles on the order of 50 nm dispersed around it. The 200 nm particle was identified as characteristic of GSR, whereas the smaller particles were only Pb-rich. As a result, the smaller particles could not be considered as GSR. Similar results were obtained for other particle aggregates with the larger particles (≥200 nm) usually being characteristic of GSR and the smaller particles being composed of Pb without Sb or Ba.

Figure 5 shows an XPS survey spectrum obtained for a 200 nm area on the GSR layer that was deposited on the ceramic substrate for the as-received sample. A survey spectrum following argon ion etching 10 nm into the surface is also illustrated. The XPS analysis represents an average surface composition over multiple GSR and associated samples of various sizes contained in the area under the irradiating X-ray spot. The qualitative and quantitative surface composition results are summarised in Table 1 for these two survey spectra as well as for the same area after argon ion sputtering 20 nm in-depth. The survey spectra indicated that the major elemental components detected by XPS in the GSR layer were C and O, together with small amounts of Pb, Sb, Ba and S. No Al from the alumina substrate was detectable, which indicates that the chosen analysis area was completely covered by GSR and that the thickness of the GSR layer was greater than the sampling depth of XPS.

Sulphur is a common component in GSR because the fuel used in ammunition primer is antimony sulphide (Sb₂S₃). The amounts of sulphur detected in the GSR sample in this study were too low to allow for an accurate chemical state assignment. However, a previous study indicated that sulphur can be present in GSR as sulphate and sulphide species [Schwoeble et al., (2010), Schwoeble et al., (2010)]. The surface concentrations of Sb and Ba increased relative to Pb with the sputtered depth. This finding is consistent with previous XPS results [Schwoeble et al., (2010), Schwoeble et al., (2010)] and indicates that, on average, GSR consists of particles with a Pb-rich surface layer and a Sb/Ba-rich core.

Pb 4f XPS spectra were obtained from GSR on a ceramic substrate sample as-received and after argon ion sputtering to depths of 10 nm and 20 nm. The Pb 4f XPS peak appears as a doublet (corresponding to the Pb 4f₇/₂ and Pb 4f₅/₂ electron energy levels) because of spin-orbit splitting for each chemical species present [Watts and Wolsethholm, (2003), Moulder, et al, (1992)]. The Pb 4f spectrum obtained for the as-received sample showed two main peaks, that is Pb 4f₇/₂ and Pb 4f₅/₂.

Three types of lead oxide are known to exist, namely PbO (Pb⁺), Pb₂O₃ (Pb³⁺) and PbO₂ (Pb⁴⁺). XPS can distinguish these three types because of chemical shifts in the Pb 4f binding energies for these different Pb oxidation states [Moulder, et al, (1992), Wagner, et al, (2003)]. The Pb 4f binding energies observed for the as-received GSR sample were characteristic of PbO [Schwoeble, et al, (2010), Moulder, et al, (1992)]. Weak shoulders at binding energies corresponding to Pb metal [Moulder, et al, (1992), Wagner, et al, (2003)] were observed on the low-binding-energy side of the main Pb 4f peaks for PbO after ion beam sputtering of the sample. The relative amount of Pb metal versus PbO increased slightly with the sputtered depth.

Figure 7 shows representative high-resolution Sb 3d, O 1s, Ba 3d and X-ray induced Ba MNN Auger spectra obtained for the GSR on a ceramic substrate sample after argon ion sputtering to a depth of 20 nm. No significant differences were observed between these spectra and those obtained for the as-received sample or the sample sputtered to a depth of 10 nm. The Sb 3d peak is normally the most intense peak observed in the XPS spectrum for antimony containing materials and this peak appears as a doublet (Sb 3d₅/₂ and Sb 3d₃/₂) because of spin-orbit splitting [Watts and Wolsethholm, (2003), Moulder, et al, (1992)]. The Sb 3d₅/₂ peak is the more intense peak in the Sb 3d doublet and hence would be the preferred peak for quantification purposes and for chemical state identification. However,
the Sb 3d_{5/2} peak is unfortunately completely overlapped by the intense O 1s peak in antimony/oxygen containing materials like GSR. Therefore, it is necessary to use the less intense Sb 3d_{3/2} peak for chemical state identification of antimony [Moulder, et al. (1992), Wagner, et al. (2003)].

Three oxides of Sb are known to exist, that is Sb_2O_3 (Sb^{3+}), Sb_2O_4 (Sb^{4+}) and Sb_2O_5 (Sb^{5+}). For the direct deposit GSR particulate examined in this study, the observed binding energies for the Sb 3d_{3/2} spectra were characteristic of Sb_2O_3 [Moulder, Schwoeble, et al. (1992), Wagner, et al. (2003)] on the as-received sample and both of the argon ion sputtered samples. There was no evidence for the presence of Sb metal or other Sb oxides in any of the Sb 3d_{3/2} spectra.

Representative high-resolution Ba 3d and X-ray induced Ba MNN Auger spectra were obtained for the GSR on ceramic sample after argon ion sputtering to a depth of 20 nm (Figure 7). It has been reported that assessing the chemical state of Ba can be rather difficult because of the small chemical shifts typically observed in the Ba 3d peaks between the metallic and oxide states [D’Uffizi, et al. (2002)]. However, the X-ray induced Ba MNN Auger peak exhibits distinct differences between the metal and oxide. In this study, the observed binding energies and peak shapes for Ba 3d and MNN Auger peaks were characteristic of BaO (the only known form of Ba oxide), where barium is in the Ba^{2+} oxidation state [Moulder, et al. (1992), Wagner, et al. (2003)]. Similar Ba XPS spectra were obtained for the as-received sample and for the sample that was argon ion sputtered to a depth of 10 nm. As was the case for Sb, there was no evidence for the presence of Ba metal in any of the Ba 3d spectra.

Conclusion
GSR analysis is a vital tool in forensic science, allowing for the identification of key crime suspects. XPS has been identified as a valuable method that can complement the more conventional CCSEM and EDS techniques, offering superior analytical capabilities for the surface characterisation of GSR. This powerful method surpasses the performance of traditional techniques, generating valuable information about the surface composition and surface chemistry of GSR.

References
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Brian’s research interests involve applications of surface analytical and microscopic techniques for industrial problem solving, product/process development, and the characterisation of complex materials. His expertise includes X-ray photoelectron spectroscopy (XPS or ESCA), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), and various other spectroscopic techniques. His technical experience includes the study of adhesion, corrosion, oxidation, and wetting phenomena; chemical and plasma modification of material surfaces; and the surface and microscopic characterisation of asbestos and associated minerals, catalysts, ceramics, glass and fiberglass, metals, oxides, paints and organic coatings, polymers, semiconductors, and vacuum-deposited thin film materials. Brian has served as an expert witness in litigation involving surface analysis methods.