

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

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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.



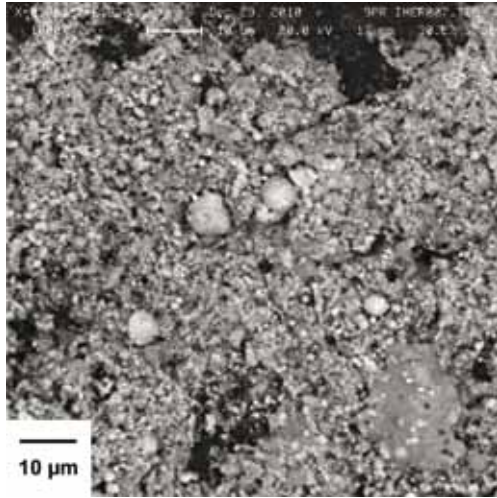


Figure 1: BSE Image of the direct-deposit GSR layer on a ceramic substrate

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 styphanate, 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

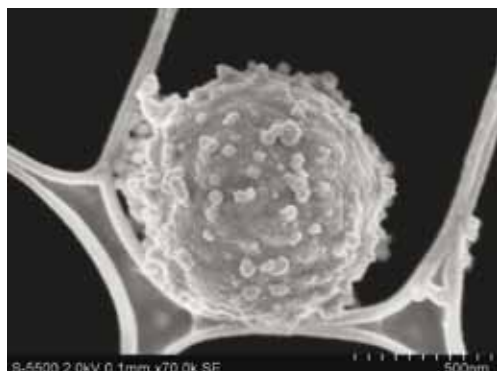


Figure 2: Secondary electron image of a typical GSR particle showing associated smaller particles

[Schwoeble and Exline, (2000), Wolten *et al*, (1977), Tillman, (1987), White and Owens, (1987) DeGaetano and Siegel, (1990)]. For the purposes of this analysis, SEM sample stubs coated with a conductive adhesive have been typically used to collect GSR samples from a crime suspect's hands and/or clothing. Energy-dispersive X-ray spectroscopy (EDS) has been employed extensively to provide fast screening of large populations of

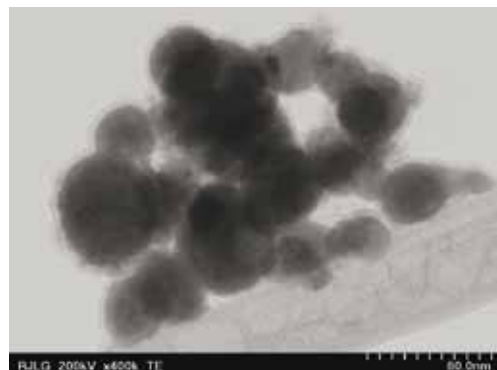


Figure 3: Bright-field STEM (BF-STEM) images of a GSR particle and associated smaller particles dispersed on a lacey carbon grid.

particles in the size range of ~1–10 μm for the presence of combinations of Pb, Sb and Ba. However, CCSEM is not sensitive enough to generate data for low concentrations of particles (much less than 1 μm), while also being unable to analyse the surface chemistry of the GSR particles.

GSR particles also take on characteristic morphologies [Schwoeble and Exline, (2000)]. In general, they are spherical in shape; however, irregularly shaped particles may also be produced.

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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 Wolsetholme, (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 Wolsetholme, (2003)].

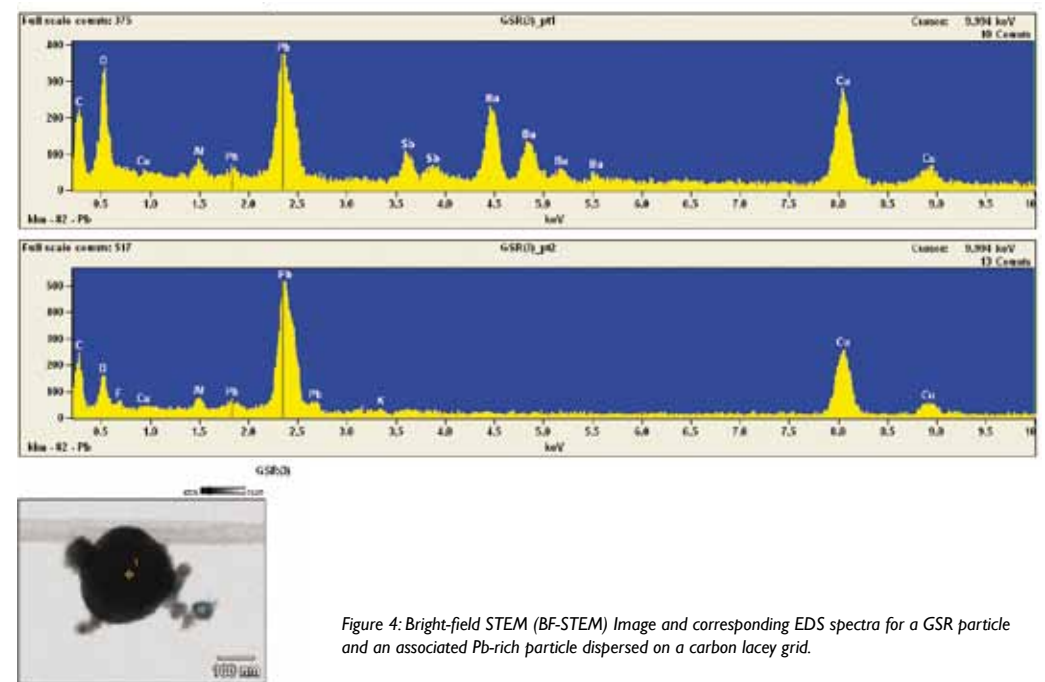


Figure 4: Bright-field STEM (BF-STEM) Image and corresponding EDS spectra for a GSR particle and an associated Pb-rich particle dispersed on a carbon lacey grid.

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.

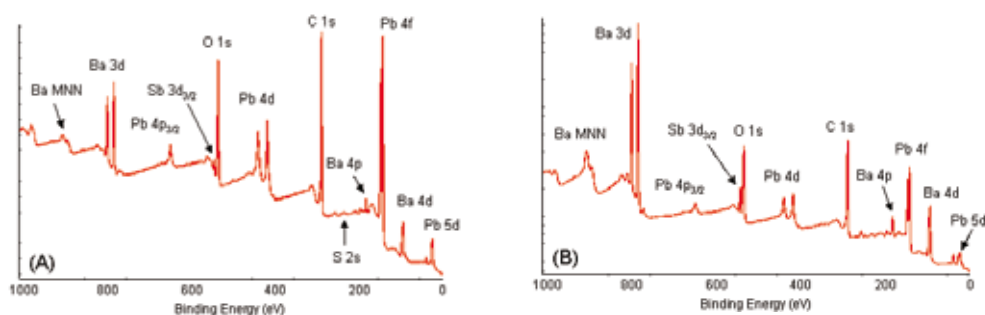


Figure 5: XPS survey spectra for a direct-deposit GSR layer on a ceramic substrate: (A) as-received and (B) after argon ion sputtering 10 nm in-depth

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. 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

| Sample | C | O | S | Sb | Ba | Pb |
|------------------------------------|------|------|-----|-----|-----|-----|
| As-received | 69.0 | 23.2 | 1.2 | 0.2 | 1.6 | 4.8 |
| Argon ion sputtered 10 nm in-depth | 63.2 | 26.2 | 0.5 | 0.6 | 5.8 | 3.7 |
| Argon ion sputtered 20 nm in-depth | 57.8 | 30.3 | 0.3 | 0.7 | 7.5 | 3.4 |

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.

| XPS Peak | As received | | 10-nm Argon Ion Sputter | | 20-nm Argon Ion Sputter | |
|----------------------|---------------------|--------------------------------|-----------------------------|--------------------------------|-----------------------------|--------------------------------|
| | Binding Energy (eV) | Chemical State Assignment | Binding Energy (eV) | Chemical State Assignment | Binding Energy (eV) | Chemical State Assignment |
| Sb 3d _{3/2} | 539.7 | Sb ₂ O ₃ | 539.3 | Sb ₂ O ₃ | 539.4 | Sb ₂ O ₃ |
| Ba 3d _{5/2} | 780.2 | BaO | 780.1 | BaO | 780.2 | BaO |
| Ba MNN | 902.2 | | 901.9 | | 901.8 | |
| Pb 4f _{7/2} | 138.6 | PbO | 138.3 + lower B.E. shoulder | PbO + Pb metal | 138.3 + lower B.E. shoulder | PbO + Pb metal |

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

of 2 cm dia. The direct-deposit discharge produced a relatively dense layer of GSR particulate of various sizes and shapes on the ceramic substrate surface. The backscattered electron (BSE) image shown in Figure 1 was obtained using a SEM instrument (R) Lee Instruments).

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 a TEM grid was then dipped in the solution and the sample was air-dried and further dried on a hot plate at 70°C for 20 minutes. The GSR sample was characterised using a high-resolution field emission SEM analyser (Hitachi S-5500) with scanning transmission electron microscopy (STEM) capabilities. The analysis was performed at 2 kV to obtain surface morphology information and at 10 kV to obtain elemental maps. The high-resolution field emission SEM instrument was equipped with an EDS system (Bruker), incorporating a 30 mm² 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).

XPS analyses were performed on an XPS instrument (Thermo Scientific K-Alpha), with a

typical base pressure of 2 × 10⁻⁹ mbar in the analysis chamber. The analyser utilises a monochromatic Al Kα X-ray source and a low-energy electron/argon ion flood gun for sample charge compensation. The X-ray spot size on the instrument can be varied as necessary from 30 - 400 µm. The entire ceramic substrate was inserted into the system and 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 SiO₂ 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

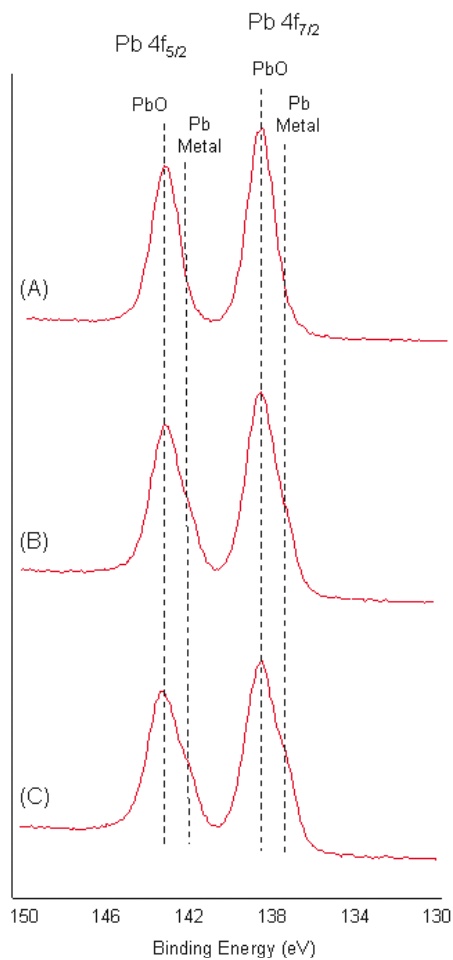


Figure 6: High resolution Pb 4f XPS spectra for a direct deposit GSR layer on a ceramic substrate: (A) as-received; (B) after 10 nm argon ion sputter; and (C) after 20 nm argon ion sputter.

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 particles 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 (Sb_2S_3). 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.

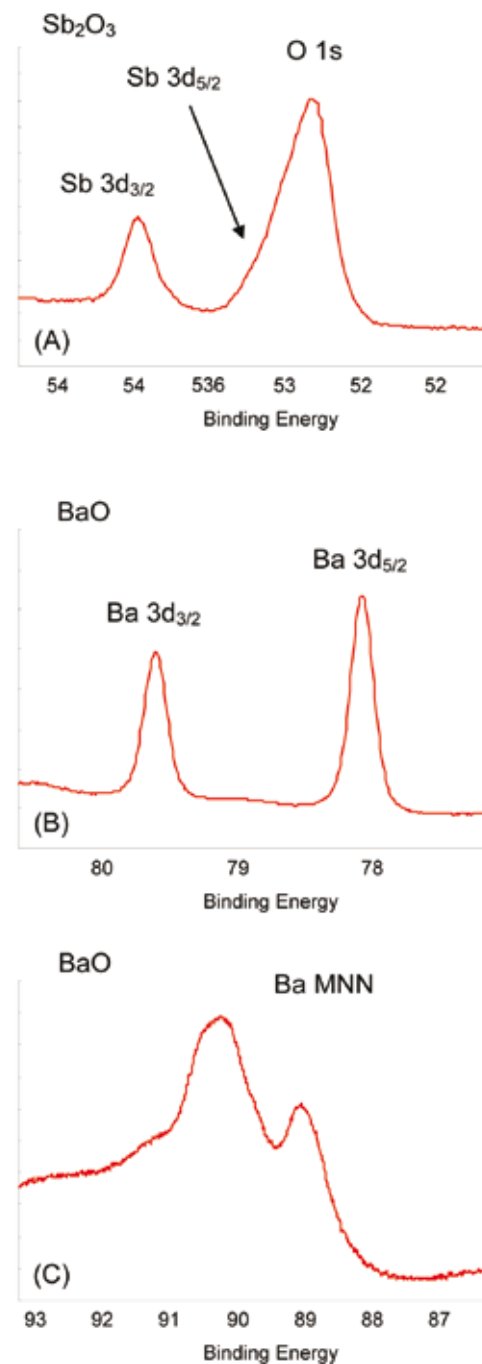


Figure 7: High resolution XPS spectra for a direct deposit GSR layer on a ceramic substrate after a 20 nm argon ion sputter: (A) Sb 3d and O 1s region; (B) Ba 3d region, and (C) X-ray induced Ba MNN Auger region.

Binding-energy information for the main XPS peaks for Pb, Sb and Ba, as well as for the corresponding chemical state assignments of these elements, are

summarised in Table 2. High-resolution Pb 4f 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 4f_{7/2} and Pb 4f_{5/2} electron energy levels) because of spin-orbit splitting for each chemical species present [Watts and Wolsetholme, (2003), Moulder, *et al.*, (1992)]. The Pb 4f spectrum obtained for the as-received sample showed two main peaks, that is Pb 4f_{7/2} and Pb 4f_{5/2}.

Three types of lead oxide are known to exist, namely PbO (Pb²⁺), 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 3d_{5/2} and Sb 3d_{3/2}) because of spin-orbit splitting [Watts and Wolsetholme, (2003), Moulder, *et al.*, (1992)]. The Sb 3d_{5/2} 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 Sb₂O₃ (Sb³⁺), Sb₂O₄ (Sb⁴⁺) and Sb₂O₅ (Sb⁵⁺). For the direct deposit GSR particulate examined in this study, the observed binding energies for the Sb 3d_{3/2} spectra were characteristic of Sb₂O₃ [Moulder, 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'Uffiz, 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 Ba²⁺ 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.

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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.