



Unusual sources of Sn in GSR. An experimental study by SEM and IBA

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ABSTRACT

Gunshot Residue (GSR) produced by the discharge of a firearm often provides very useful information in criminal investigations in cases involving the use of firearms. Scanning Electron Microscopy equipped with an Energy Dispersive X-ray Spectrometer (SEM-EDS) is typically used worldwide to visualize micrometric particles constituting GSR and to analyse their elemental composition. The 2017 ASTM Standard guide for gunshot residue analysis by scanning electron microscopy/energy dispersive X-ray spectroscopy specifies that “Particles classified as characteristic of GSR will have one of the following elemental compositions: Lead, antimony, barium; Lead, barium, calcium, silicon, tin”. For the first time, the presence of an additional element, such as Sn, plays a key role in ASTM particle classification. It is known that some ammunitions, used for pistols, revolvers and rifles, contain tin foil discs for sealing the primer mixture into the cup, resulting in GSR particles containing Sn. The authors faced some cases in which Sn was unexpectedly found in GSR particles from a 0.22 Long Rifle derringer and from some 12 gauge shotguns. No tin foil discs are used in rimfire ammunitions and there is no published evidence of tin foil discs in shotshell ammunitions. Following a “case by case” approach, experimental research has been carried out to explain how Sn can be present in GSR particles when the last discharged cartridge also does not contain any Sn either in components and in the explosive charges.

Moreover, the use of Particle Induced X-ray Emission (PIXE) showed the capability to overcome overlap ambiguity of Sb and Sn peaks in the X-ray spectra, being a possible key issue in real shooting cases if Sn quantities are below the lower limit of SEM detection, especially when Sb is also present.

1. Introduction

Gunshot residue (GSR) is produced by the explosion of a cartridge used by a firearm. The inorganic GSR particles generated can be sampled from the shooters and analysed by Scanning Electron Microscopy coupled to Energy Dispersive X-ray Spectrometry (SEM-EDS), providing useful information in criminal investigations [1–3]. The majority of elements in GSR particles come from the primer mixture, but the cartridge case, the bullet, the propellant charge and the firearm itself contribute to their chemical composition. “The chemistry of ammunition components and the residues of firearms discharge is a vast landscape” [4]. In the nineteenth century the main priming explosive was mercury fulminate [5], a common primer mixture being mainly mercury fulminate, potassium chlorate and antimony sulphide. Their GSR consist of Sn, Sb, Hg, S, Cl and Cu accompanied by small amounts of Al, Si, Fe and Zn [6].

In 1928 Rheinisch-Westfälischen Sprengstofffabriken (RWS) developed

the first practical non-corrosive, non-mercuric (NCNM) primer, called SINOXID, replacing the former primers based on mercury fulminate and potassium chlorate with lead styphnate and tetracene. GSR particles from NCNM primers do not contain Hg but contain Pb. By the 50s the NCNM primer had shown such good stability that all US military small arms primers were converted to that type [7,8]. In 1997 Zeichner and Levin published a paper providing evidence for GSR particles containing Pb, Ba, Ca, Si and Sn, produced by 9 mm and 7.65 mm Sellier & Bellot (S&B - Czech Republic) ammunitions, where tin foil were used to produce primer cups [9]. For the 2017 ASTM Standard guide for gunshot residue analysis by scanning electron microscopy/energy dispersive X-ray spectrometry “Particles classified as characteristic of GSR will have one of the following elemental compositions: Lead, antimony, barium; Lead, barium, calcium, silicon, tin”. For the first time, the presence of additional elements, such as calcium (Ca), silicon (Si), and tin (Sn), plays a key role in ASTM particle classification. The presence of antimony (Sb) in GSR particles is explained by the use of Sb₂S₃ in primers with lead styphnate. The presence of barium

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Fig. 1. IGI Domino gas alarm Derringer pistol modified by barrel substitution.

(Ba) in GSR particles is explained by the use of $Ba(NO_3)_2$. According to Thornton other Sn sources in ammunitions are possible, because SnO_2 can be used in priming mixtures as burn rate modifier and, when metals used to produce projectiles are extracted from ores, “there may be trace concentrations of virtually any element”, including Sn [4].

The authors of the current work faced some cases in which Sn was unexpectedly found in GSR particles from a 0.22 Long Rifle derringer and from some 12 gauge shotguns also when the last discharged cartridge did not contain any Sn, both in components and in the explosive charges.

Beyond documenting unusual presence of Sn in some real shooting cases, the aim of the present paper is to explain, for the first time, a possible Sn source mechanism, by virtue of experimental work carried out following a “case by case” approach based on comparison of GSR [10,11]. We also demonstrate that the Particle Induced X-ray Emission technique (PIXE) can show superiority when Sn quantities in GSR particles are below the lower limit of SEM-EDS detection, including both cases with S&B or other Eastern Europe ammunition brands (MFS - Hungary, PPU - Serbia) from the civil market and with military ammunition in calibre $7,62 \times 39$ mm.

2. Casework experience

All the following analyses were carried out using both a FEI Quanta 400 ESEM tungsten scanning electron microscope, equipped with EDAX 10 mm^2 Si:Li detector and GSR XT software, and a Tescan field emission

Table 1

SEM-EDS results in the case involving the Derringer pistol. “Many” here stands for “at least 200 particles”.

| Suspect | |
|---|--|
| Sample | Particles of main interest |
| Right hand & wrist | 5 PbBaSb 1 PbSb, 1Sb, 7 Pb |
| Left hand & wrist | 2 PbBaSb 6 Sb, 7 Pb |
| Sweatshirt | 11 PbBaSb 2 PbBaSbSn 7 PbSb, 2 PbBa, 97Sb, 77 Pb |
| Derringer upper barrel | Many PbBaSb Many PbBaSbSn Many PbBa |
| Derringer lower barrel | Many PbBaSb Many PbBa |
| Fiocchi 0.22 Long cartridge case (found inside Derringer upper barrel) | Many PbBa |

| Known sources of GSR particles | |
|--------------------------------|---|
| Sample | Particles of main interest |
| Victim's shirt | Many PbBaSb 125 PbBaSbSn 126 PbSb, 63 PbBa, 4 Sb, many Pb |

scanning electron microscope, equipped with two Bruker 30 mm^2 silicon drift detectors and Tescan Trace GSR software, in the RIS Carabinieri in Parma (Italy).

2.1. Derringer pistol

In a first case, dated 2013, the population of particles found on the hands and on the sweatshirt of a suspect was compared with three sources of GSR particles: the shirt of the victim, an IGI Domino gas alarm Derringer pistol found on the suspect, modified by barrel substitution from the original 6 mm Flobert Blank calibre to 0.22 rimfire (Fig. 1), and a Fiocchi cartridge case calibre 0.22 Long (Fig. 2), found inside the upper barrel of the weapon. The analysis revealed on the suspect's sweatshirt 11 PbBaSb particles as well as 2 PbBaSbSn particles. Similar GSR populations were found on the victim's shirt, where many PbBaSb (“many” here stands for “at least 200 particles”) and 125 PbBaSbSn particles were detected, and on the Derringer upper barrel



Fig. 2. Fiocchi cartridge case calibre 0.22 Long.

Table 2
SEM-EDS results of the first case involving a shotgun (Pietro Beretta A300, 12 gauge). “Many” here stands for “at least 200 particles”.

| Suspect | |
|--|---|
| Sample | Particles of main interest |
| Right hand | - 4 PbSb, 2Sb, 21 Pb |
| Left hand | - |
| Hunting jacket | Many PbSb, 1 BaAl, 98 Sb, 69 Pb 9 PbBaSb 24 PbSb, 5 PbBa, 2 BaAl, 85 Sb, 127 Pb |
| Pietro Beretta A300 12 gauge semiautomatic shotgun | Many PbBaSb Many PbBaSbSn Many BaAl |
| Known sources of GSR particles | |
| Sample | Particles of main interest |
| Victim waistcoat | 35 PbBaSb Many PbSb, 4 PbBa, many Pb |
| Gualandi 12 gauge plastic wad | Many PbBaSb Many PbSb, many Pb |

Table 3
SEM-EDS results of the first case involving a shotgun (Vincenzo Bernardelli Roma 3, 12 gauge). “Many” here stands for “at least 200 particles”.

| Suspect | |
|--|---|
| Sample | Particles of main interest |
| Right hand & left hand | 23 PbBaSb 16 PbSb, 3 PbBa, 24 BaAl, 6 Sb, 171 Pb |
| Clothes (T-Shirt & jeans) | 108 PbBaSb Many PbSb, 4 PbSbSn , 12 PbBa, 36 BaAl, 31 Sb, many Pb |
| Vincenzo Bernardelli Roma 3 12 gauge SxS shotgun Right barrel - Muzzle | Many PbBaSb Many BaAl |
| Vincenzo Bernardelli Roma 3 12 gauge SxS shotgun Left barrel - Muzzle | Many PbBaSb Many BaAl |
| Vincenzo Bernardelli Roma 3 12 gauge SxS shotgun Right barrel - Breechface | Many PbBaSb Many PbBaSbSn Many BaAl |
| Vincenzo Bernardelli Roma 3 12 gauge SxS shotgun Left barrel - Breechface | Many PbBaSb Many BaAl |
| Known sources of GSR particles | |
| Sample | Particles of main interest |
| Victim jacket | Many PbBaSb Many PbSb, 8 PbSbSn , 26 PbBa, 66 BaAl, 1 Sb, many Pb |
| Nobel Sport Italia 12 gauge cartridge case Internal surfaces of the case | Many PbBaSb Many BaAl |
| Nobel Sport Italia 12 gauge cartridge case External surfaces of the case | Many PbBaSb 7 PbBaSbSn |

only, where many PbBaSb and **many PbBaSbSn** were detected. No evidence of Sn was detected in the GSR from the cartridge case found inside the same barrel, suggesting that the last round shot was not the source of Sn.

The SEM-EDS results are summarized in the following [Table 1](#).

2.2. Shotgun - 1st example

In a second homicide case, also dated 2013, the population of particles found on the hands, on the hunting jacket and inside a Pietro Beretta, model A300, 12 gauge, semiautomatic shotgun of a suspect, was compared with two sources of GSR particles: the waistcoat of the victim and a Gualandi plastic wad from a 12 gauge ammunition, found at the crime scene. The analysis revealed, on the suspect, many *consistent with* GSR particles (PbSb, PbBa, BaAl, Sb, Pb), together with 9 PbBaSb particles found on his hunting jacket. In a sample taken from the semiautomatic shotgun seized from the suspect, many PbBaSb and many BaAl particles were detected, together with **many PbBaSbSn** GSR particles. On the victim's waistcoat and on a Gualandi 12 gauge plastic wad found nearby the victim many PbBaSb, PbSb and Pb particles were detected, suggesting that the only round shot on the crime scene didn't contain any Sn. In this case, PbBaSbSn GSR particles were found in the shotgun barrel only.

SEM-EDS results are summarized in the following [Table 2](#).

2.3. Shotgun - 2nd example

In a third homicide case, dated 2017, the population of particles found on the hands, on the clothes (a T-shirt and a pair of jeans) and inside a Vincenzo Bernardelli, model Roma 3, 12 gauge, side by side (SxS) shotgun, was compared with two sources of GSR particles: the jacket of the victim and a Nobel Sport Italia 12 gauge cartridge case, removed from the right chamber of the weapon. The suspect admitted to being the shooter and claimed that he removed the Nobel Sport Italia 12 gauge cartridge case from the right barrel of the weapon immediately after the homicide and left it at the crime scene. The analysis revealed both *characteristic* and *consistent with* GSR particles on the hands of the suspect. Moreover GSR particles containing Sn (**4 PbSbSn**) were found on his clothes, with both *characteristic* and *consistent with* GSR particles.

In the sample taken from the SxS shotgun, seized from the shooter, many PbBaSb and many BaAl particles were detected, together with **many PbBaSbSn** GSR particles detected only in the sample taken from the breechface of the right barrel. On the victim's jacket, many PbBaSb and many *consistent with* GSR particles were detected, some of which contained Sn (**8 PbSbSn**). Inside the Nobel Sport Italia 12 gauge cartridge case many PbBaSb and BaAl particles were detected, suggesting that the only round shot at the crime scene did not contain any Sn. Some *characteristic of* GSR particles containing Sn (**7 PbBaSbSn**) were detected on the outer surfaces of the cartridge case.

The SEM-EDS results are summarized in the following [Table 3](#).

3. Materials and methods

An Ithaca Gun model 87, calibre 12 gauge, pump action shotgun was used for the shooting tests. Cartridges were 12 gauge S&B ammunition bought in Italy and 12 gauge MG2 Tungsten ammunition by Baschieri & Pellagri (B&P). B&P MG2 Tungsten cartridges were loaded with 35 g (11/4 oz.) of pellets (Ø 2.9 mm) of a Sn-coated W-Fe-Cu-Ni alloy bulk core. The shotgun was neither cleaned nor used between the shooting tests, with the B&P ammunitions and the swabbing.

GSR particles were collected from the shotgun breechface and chamber using cotton swabs, type 5100/SG/CS by Nuova Aptaca. Cotton swabs were soaked in ethanol before collection, to limit cotton fibre release when touching the adhesive carbon discs type C249/N by TAAB positioned on top of half inch aluminium stubs for GSR deposition.

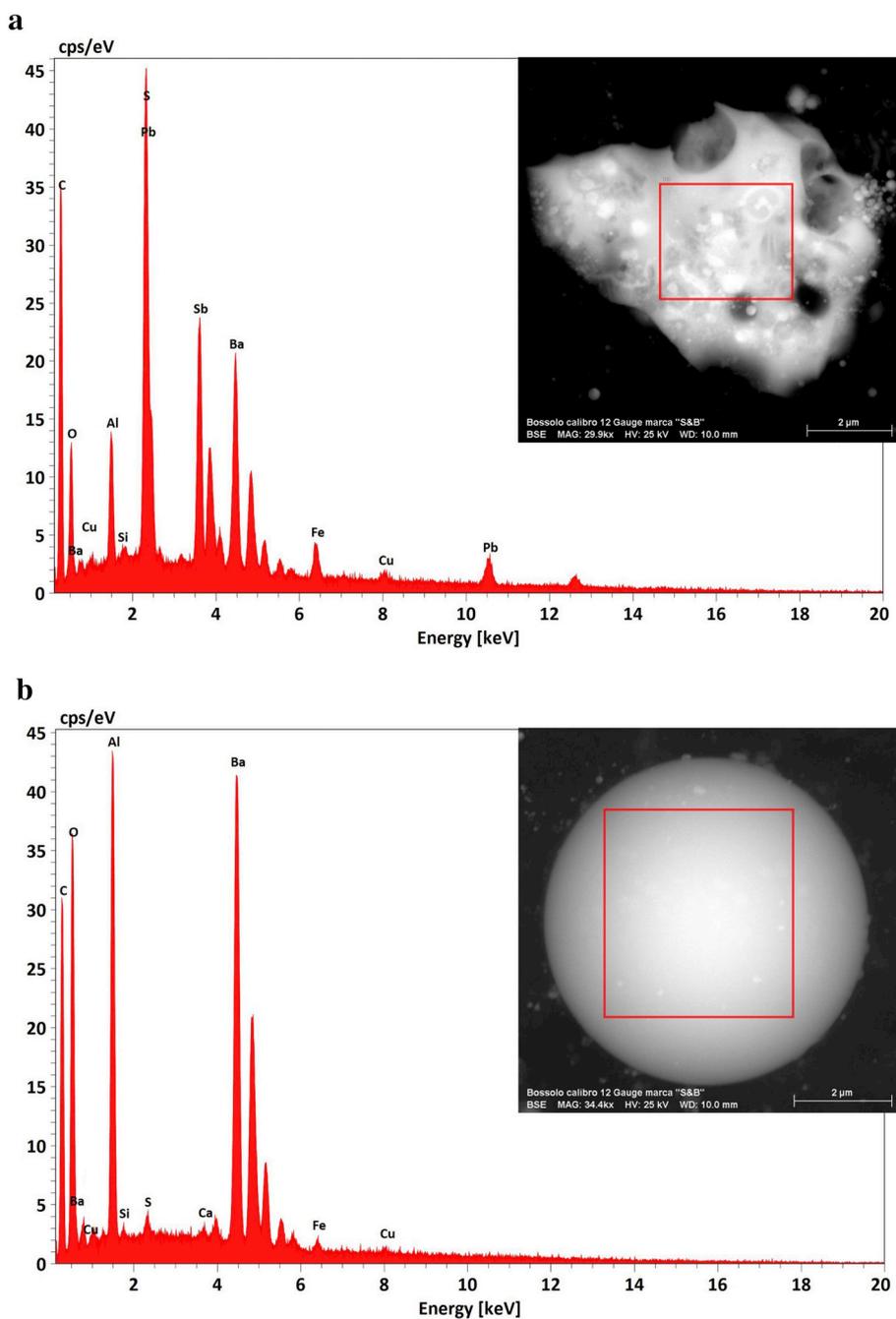


Fig. 3. Particles from the S&B 12 gauge ammunition. *Characteristic of GSR PbBaSbAl (a) and AlBa particle (b).*

Stubs were analysed both using a Quanta 400 W-SEM by FEI, equipped with a Si:Li SUTW detector by EDAX and GSR-XT software by Eastern Analytical and a Mira III FEG-SEM by Tescan equipped with two 30mm² SDD detectors by Bruker and Tescan Trace GSR software.

The positions were logged relative to indents created with a scalpel on the stubs and relocated using microbeam particle induced X-ray emission (PIXE) as per Christopher et al. [12]. PIXE spectra were generated using a 2.582 MeV proton beam with a beam current of 300 pA, focussed to a spot size of 2 × 2 microns. X-rays were detected using a 146 eV Si(Li) detector at a take-off angle of 45° with a 130 μm Be filter to exclude backscattered protons from the detector. Backscattered particle (EBS) spectra were simultaneously collected at a scattering angle of 155° and a solid angle of 50 msr. Energy calibration of μ-PIXE and EBS spectra was performed using the Pb-glass BCR-126A standard from the Institute for Reference Materials and Measurement, Geel,

Belgium. Relocation of particles in the ion beam was carried out using several ion-beam-induced secondary electron images at increasing magnification, together with the previously logged distances and SEM images to ascertain the general area of interest. For the highest magnification images, elemental X-ray maps (typically taking 1–2 min to generate) were used to find the exact location of each of the smallest particles.

4. Results of the shooting tests

Before the shooting tests, the breechface and the chamber of the Ithaca Gun shotgun were swabbed for GSR. In the samples taken from the shotgun, the only characteristic of GSR particles found were of PbBaSb type and no Sn-containing particles were found inside the gun.

During the shooting tests two 12 gauge S&B cartridges and two 12

Table 4
SEM-EDS results of the experiments before and after shooting. “Many” here stands for “at least 200 particles”.

| Before shooting | |
|--|---|
| Sample | Particles of main interest |
| Ithaca Gun 87 12 gauge pump action shotgun brechface - chamber | Many PbBaSb Many BaSb, many PbSb |
| After shooting (two B&P 12 gauge MG2 Tungsten rounds) | |
| Sample | Particles of main interest |
| B&P 12 gauge MG2 Tungsten Inner surfaces of the cartridge cases | Many PbBaSb Many BaSb, many PbSb |
| Ithaca Gun 87 12 gauge pump action shotgun brechface - chamber | Many PbBaSb 8 PbBaSbSn Many BaSb, many PbSb, 8 PbSbSn, |

gauge MG2 Tungsten cartridges by Baschieri & Pellagri were discharged and GSR samples were collected both inside the cartridge case and from the brechface and the chamber of the Ithaca Gun shotgun once again. *Characteristic of GSR particles from the S&B ammunition* were PbBaSb particles containing Al (Fig. 3a). Many spherical AlBa particles were also found in samples from the S&B ammunition (Fig. 3b). *Characteristic of GSR residues from the Baschieri & Pellagri ammunition* were PbBaSb particles only. In the sample taken from the shotgun after shooting, many PbBaSb characteristic of GSR particles and **8 PbBaSbSn** were found, together with **8 PbSbSn** consistent with GSR particles (Table 4).

B&P MG2 Tungsten pellet were analysed and the results are shown in Figs. 4, 5, 6 and 7. In Fig. 4 the SEM image and the EDS spectrum of the external surface of a pellet is presented. In Fig. 5, we present the

SEM image and the EDS spectrum of the cross section of a pellet. In Fig. 6, we present the SEM image and the EDS spectrum of the inner W spherules, visible at magnification about 50 times higher compared to Fig. 4 and Fig. 5. In Fig. 7, we present the SEM image and the EDS spectrum of the inner Fe-Cu-Ni alloy, visible at magnification about 50 times higher compared to Fig. 4 and Fig. 5.

5. Discussion

In the first case reported, the 11 PbBaSb particles and the 2 PbBaSbSn found on the suspect's sweatshirt gives a support at source level [13] of an involvement in a shooting with that pistol, where many PbBaSb and many PbBaSbSn were detected, and with that victim, wearing the shirt, where many PbBaSb (“many” here stands for “at least 200 particles”) and 125 PbBaSbSn particles were detected. This support is stronger, compared to a situation where Sn is not found in the GSR particles. It is interesting to discuss that no evidence of both Sb and Sn was detected in the GSR from the cartridge case found inside the upper barrel of the Derringer pistol, while many PbBaSb and many PbBaSbSn were detected inside the same upper barrel, suggesting that the last round shot was not the source of Sn. It is interesting to note that in this case the Derringer pistol used rimfire ammunition Fiocchi calibre 0.22 Long, found inside the upper barrel of the weapon. In this type of cartridge there is no primer cup and no need for any tin-foil, being the source of Sn found in GSR particles such as the ones formed in discharge of 9 mm and 7.65 mm Sellier Bellot [9]. We can thus explain the results as a “memory effect”, already known and published for some firearms but not for rimfire both ammunition and shotguns [14,15]. This situation is specially important because the IGI Domino gas alarm Derringer pistol found on the suspect was modified by substitution of the original 6 mm Flobert Blank calibre with a 0.22 rimfire smooth barrel, not leaving meaningful forensic information on the projectile.

In the second case, the many PbBaSbSn GSR particles found in the sample taken from the semiautomatic shotgun seized to the suspect did

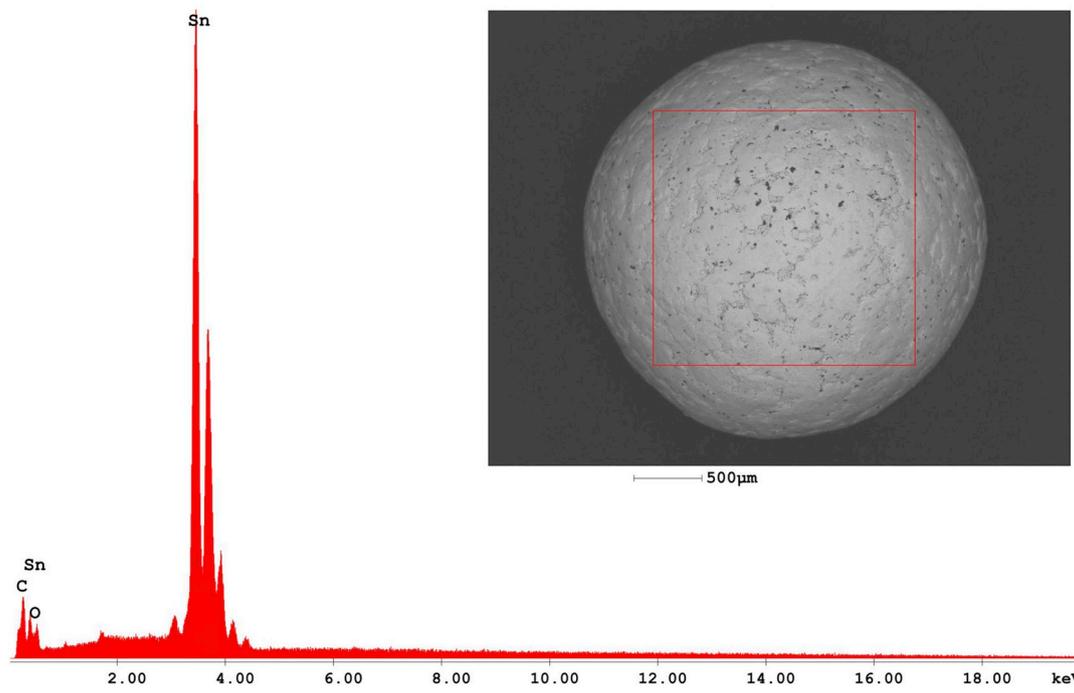


Fig. 4. SEM image and the EDS spectrum of the external surface of a pellet.

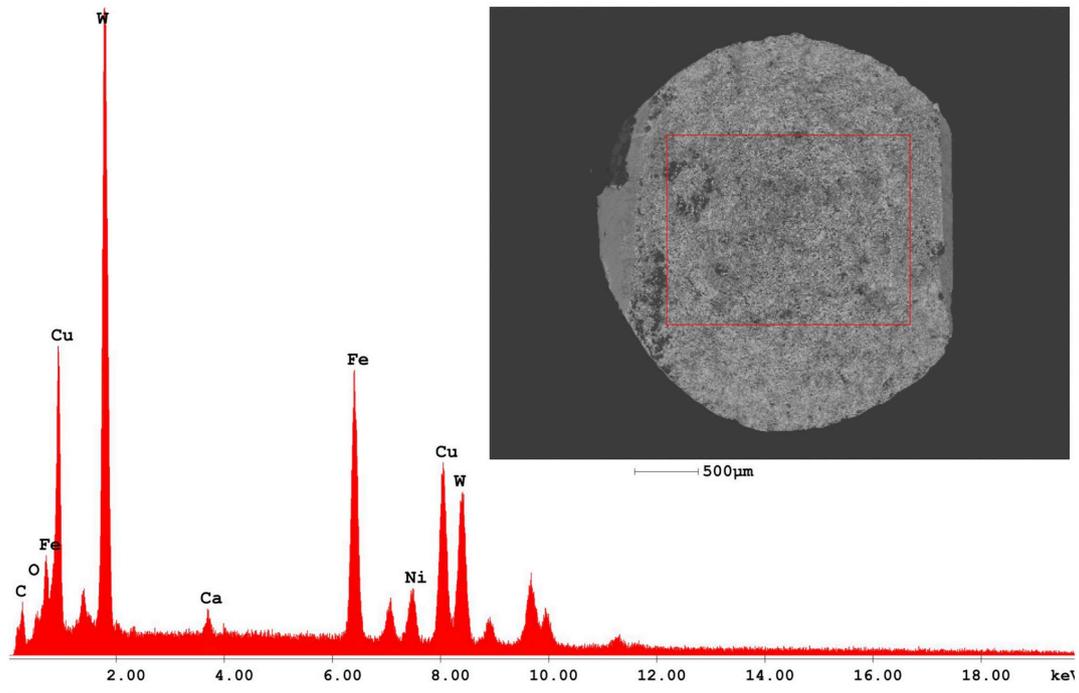


Fig. 5. SEM image and the EDS spectrum of the cross section of a pellet.

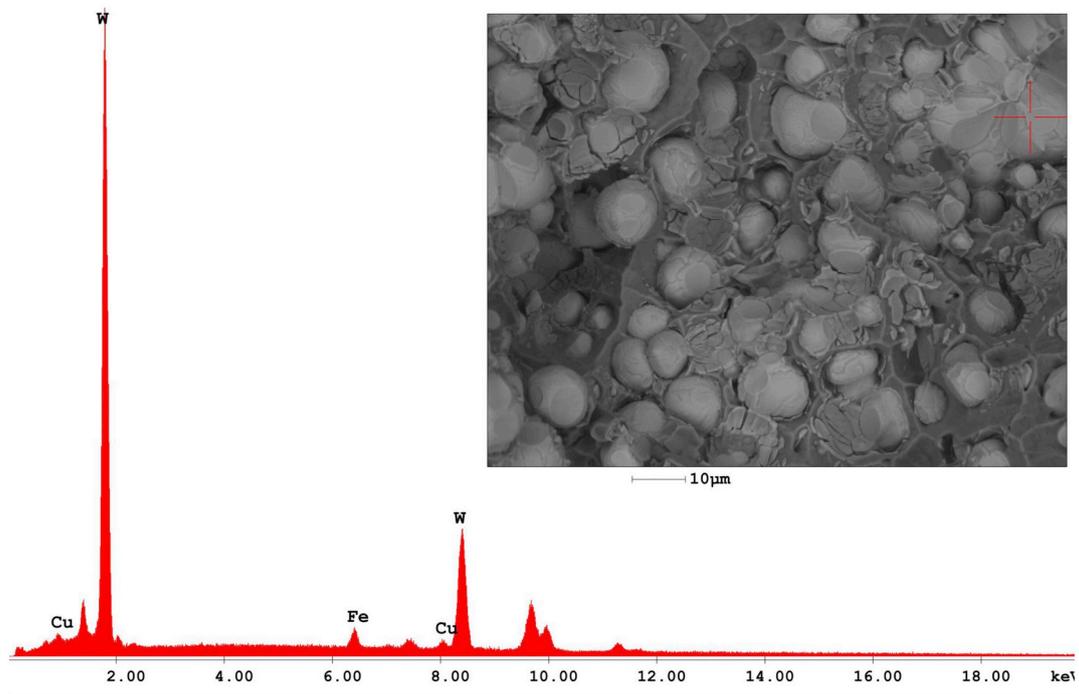


Fig. 6. SEM image and the EDS spectrum of the inner W spherules.

not find any correspondence with the population of particles found on the waistcoat of the victim and a Gualandi plastic wad from a 12 gauge ammunition found on the crime scene. In this case, the support is weaker, compared to a situation where Sn is found in the GSR particles on the victim and on the ammunition found on the crime scene but, as

far as we know, the finding of Sn in GSR particles from a shotgun was never reported.

In the third case, the analysis not only revealed both *characteristic* (23) and *consistent with* GSR particles on the hands of the suspect but also 4 GSR particles containing Sn on clothes, together with both

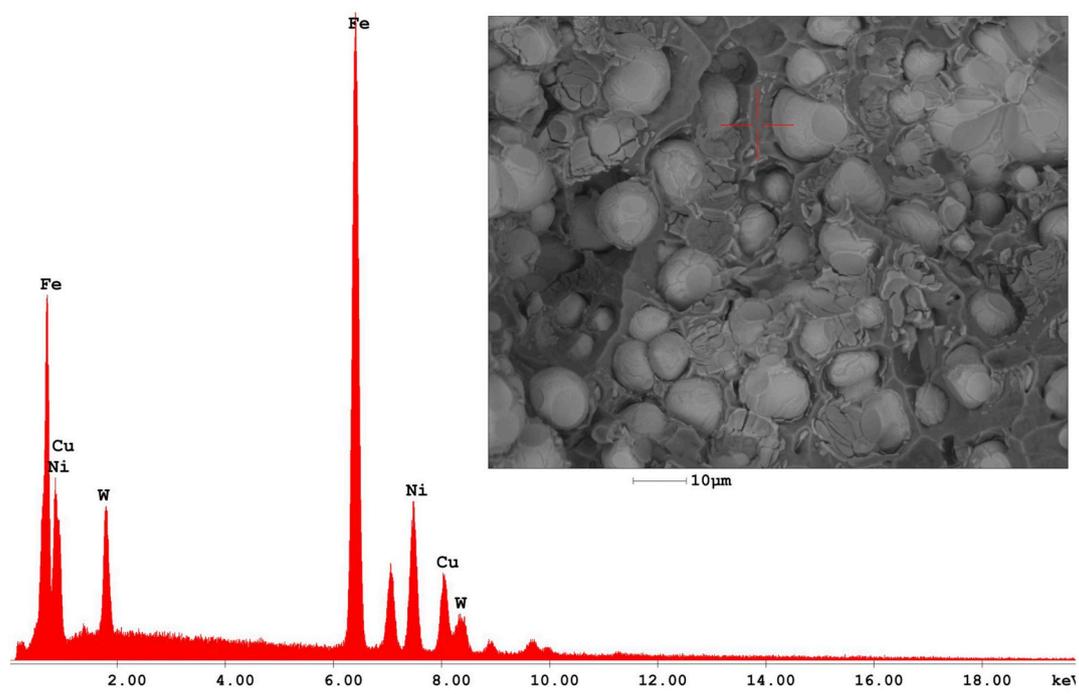


Fig. 7. SEM image and the EDS spectrum of the inner Fe-Cu-Ni alloy.

characteristic (108) and consistent with GSR particles. The interpretation of the populations of particles found gave a support at source level [13] of an involvement in the shooting, based on the 8 PbBaSbSn GSR particles on the victim's jacket, the many PbBaSbSn GSR particles in the sample taken from the breechface of the right barrel of the SxS shotgun seized from the shooter, and the 7 PbBaSbSn on the outer surfaces of the cartridge case.

The two cases involving 12 gauge shotguns were very peculiar because the last discharged cartridges did not allow the detection of any GSR particles contained on their internal surfaces. The examination of the forensic literature showed the need for experimental work to explain, for the first time, a mechanism to explain the presence of Sn in GSR particles from shotguns, following a “case by case” approach [10].

The examination of the pellets showed that in MG2 Tungsten ammunitions by Baschieri & Pellagri, tin is only present as metallic coating of the pellets, whose core is made of W spherules scattered into a Fe-Cu-Ni alloy. In leadless pellets for hunting, ammunition producers generally use a low atomic number alloy (Fe, $Z = 25$; Ni, $Z = 28$; Cu, $Z = 29$ in B&P MG2 Tungsten pellets) to lower the density of the main metallic pellet element (W, $Z = 74$ in this case) down to a desired value. Pellets are then coated with a mild metallic element as tin to prevent bore abrasion during shooting [16].

The results of the analysis of GSR particles swabbed from the breechface and the chamber of the Ithaca Gun shotgun (no Sn-containing particles) before shooting the ammunition with tin-coated W-Fe-Cu-Ni alloy bulk core pellets (12 gauge MG2 Tungsten ammunitions by Baschieri & Pellagri), from the inner surface of the cartridge case 12 gauge MG2 Tungsten ammunitions by Baschieri & Pellagri and from the breechface and the chamber of the Ithaca Gun shotgun after shooting the 12 gauge MG2 Tungsten ammunitions by Baschieri & Pellagri showed that the coating of the pellets made of Sn contributed to the

chemistry of GSR particles only in the barrel of the shotgun. Only in the sample from the breechface and the chamber **PbBaSbSn** and **PbSbSn** GSR particles were found. Our results are the first experimental demonstration of a source of Sn in GSR particles from shotguns.

One problem that can arise with identification of Sn in SEM-EDS is the overlap ambiguity between the Sn L lines and the K lines of Ca, K, as well as the L lines of Sb. This has the effect of lowering the detection limit for Sn in the presence of these elements. Fig. 8 shows the SEM picture of one particle recovered from the hands of a shooter (a) and its EDS spectrum (b), showing that the presence of Sn cannot be confirmed, due to line overlaps. The same particle was relocated in the ion beam using a relocation method developed previously [17] and characterised using Particle Induced X Ray Emission (PIXE). Due to the higher energy of the incident beam in PIXE, it is possible to excite Sn K lines, which are not excited by the electron beam in SEM-EDS. In Fig. 9 we show a PIXE spectrum for the same particle. Fitting of the PIXE spectrum using the GUPIX software confirms that Sn K is detected at $4 \times$ the limit of detection. In Fig. 10 elemental maps produced from the PIXE Ba L and Sn K lines demonstrate the location of Sn in the GSR particle. Therefore, PIXE can provide confirmation of Sn in GSR particles when SEM gives ambiguous results. SEM-WDS may be able to resolve Sn L and K K but SEM-WDS could be not sensitive enough to see this line above the Bremsstrahlung background.

An interesting observation here is the detection (using PIXE) of K K. This is not normally seen in GSR using SEM-EDS, presumably due to the low abundance in the particles and the comparatively high Bremsstrahlung background in this part of the spectrum. This creates its own problem, because Sn L and K K overlap, giving further ambiguity. However, a benefit of using PIXE is the ability to calculate the contribution of Sn L to this overlapped line, by using the Sn K line, for which there are no line overlaps. The PIXE software fitted $100 \times$ the

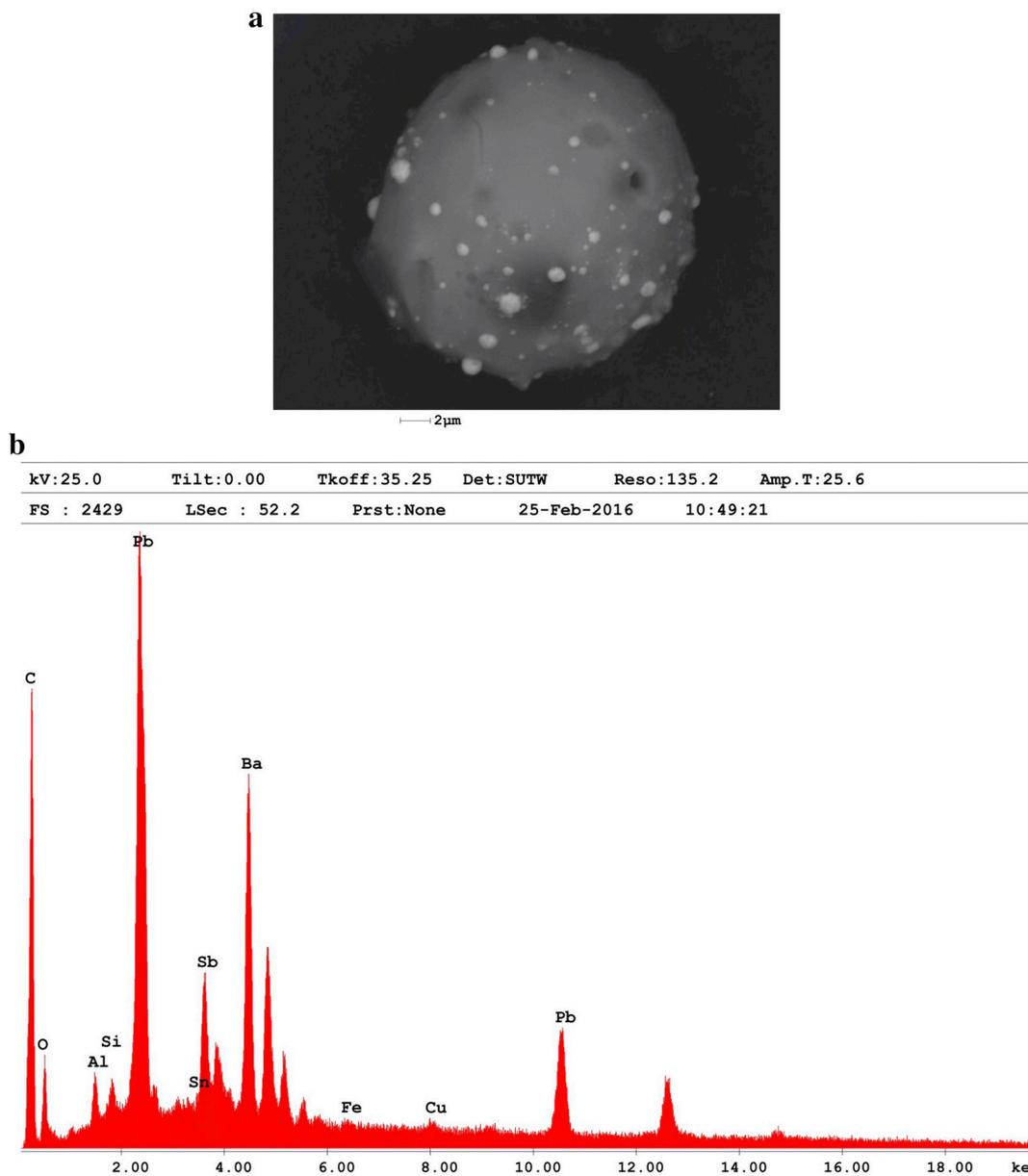


Fig. 8. SEM picture of one particle recovered from the hands of a shooter (a) and its EDS spectrum (b), showing that the presence of Sn cannot be confirmed, due to line overlaps.

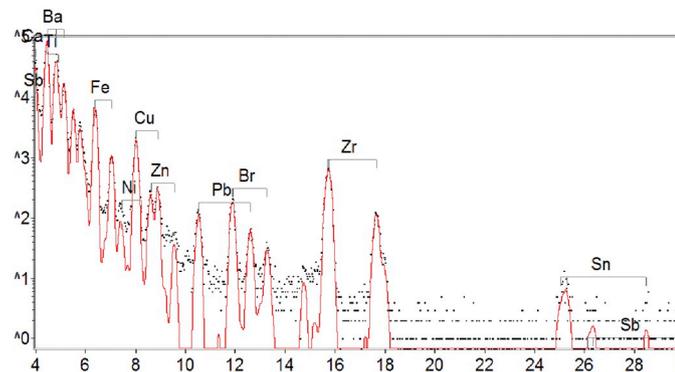


Fig. 9. Particle Induced X Ray Emission Spectrum, showing presence of Sn, Sb and Ba K lines.

LOD for K K and 10× the LOD for Sn L. Even using the improved sensitivity of SEM-WDS, it would be difficult to determine Sn L at this level, due to the Bremsstrahlung background.

6. Conclusion

The experiments carried out followed some cases in which Sn was unexpectedly found in GSR.

In the first case Sn is explained by a memory effect but it is the first time, as far as we know, from a rimfire ammunition.

The other two cases showed for the first time, as far as we know, that 12 gauge shotguns can produce GSR particles containing Sn, due to a memory effect. The Sn source mechanism was demonstrated by virtue of experimental work carried out using a shotgun and ammunition for hunting containing leadless pellets coated with Sn.

Finally we demonstrated that Particle Induced X-ray Emission

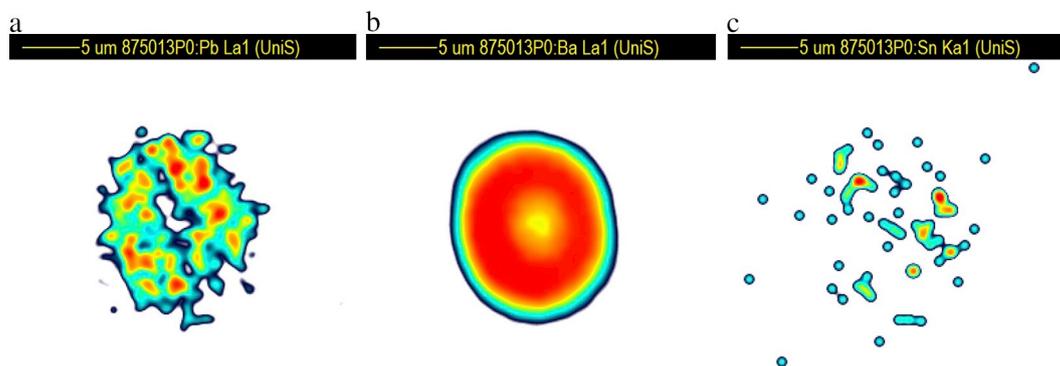


Fig. 10. PIXE maps showing the location of Pb (a), Ba (b), and Sn (c) in a particle from the hands of a shooter.

technique (PIXE) can help to overcome overlap ambiguity of Sb and Sn peaks in the X-ray spectra, providing key chemical information about GSR composition when Sn quantities in GSR particles are below the lower limit of SEM-EDS detection.

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References

- [1] O. Dalby, D. Butler, J.W. Birkett, Analysis of Gunshot Residue and Associated Materials - a Review, *J. Forensic Sci.* 55 (2010) 924–943.
- [2] American Society for Testing and Materials, E1588–17, Standard Practice for Gunshot Residue Analysis by Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy, Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA, USA, 2017.
- [3] The SWGGUN Guide for Primer Gunshot Residue Analysis by Scanning Electron Microscopy/Energy Dispersive X-Ray Spectrometry, last version dated Nov. 29th, 2011.
- [4] J.I. Thornton, The chemistry of death by gunshot, *Anal. Chim. Acta* 288 (1994) 71–81.
- [5] B.A. Bydal, Percussion primer mixes, *Associat. Firearms Tool Mark Exam. J.* 22 (1990) 1–26.
- [6] A. Zeichner, N. Levin, M. Dvorachek, Gunshot residue particles formed by using ammunition that have mercury fulminate based primers, *J. Forensic Sci.* 37 (1992) 1567–1573.
- [7] W. Matty, Primer composition and gunshot residue, *Associat. Firearms Tool Mark Exam. J.* 19 (1987) 8–13.
- [8] J.S. Wallace, Chemical aspects of firearms ammunition, *Assoc. Firearms Tool Mark Exam. J.* 22 (1990) 364–389.
- [9] A. Zeichner, N. Levin, More on the uniqueness of gunshot residue (GSR) particles, *J. Forensic Sci.* 42 (1997) 1027–1028.
- [10] F.S. Romolo, P. Margot, Identification of gunshot residue: a critical review, *Forensic Sci. Int.* 119 (2001) 195–211.
- [11] M.R. Rijnders, A. Stamouli, A. Bolck, Comparison of GSR composition occurring at different locations around the firing position, *J. Forensic Sci.* 55 (2010) 616–623.
- [12] M. Christopher, J. Warmenhoven, F.S. Romolo, M. Donghi, R. Webb, C. Jeynes, N.I. Ward, A new quantitative method for gunshot residue analysis by ion beam analysis, *Analyst* 138 (2013) 4649–4655.
- [13] R. Cook, I.W. Evett, G. Jackson, P.J. Jones, J.A. Lambert, A hierarchy of propositions: deciding which level to address in casework, *Sci. Justice* 38 (1998) 231–239.
- [14] S. Charles, B. Nys, N. Geusens, Primer composition and memory effect of weapons—Some trends from a systematic approach in casework, *Forensic Sci. Int.* 212 (2011) 22–26.
- [15] F.S. Romolo, A. Stamouli, M. Romeo, M. Cook, S. Orsenigo, M. Donghi, An experimental study about the presence of selenium in inorganic gunshot residues (GSR), *For. Chem.* 4 (2017) 51–60.
- [16] Baschieri, Pellagri, Personal communication, (2017).
- [17] F.S. Romolo, M.E. Christopher, M. Donghi, L. Ripani, C. Jeynes, R.P. Webb, N.I. Ward, Integrated Ion Beam Analysis (IBA) in Gunshot Residue (GSR) characterisation, *Forensic Sci. Int.* 231 (2013) 219–228.