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Characterisation of gunshot residue particles using self-consistent ion beam analysis

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ABSTRACT

Individual particles of gunshot residue were studied with particle-induced X-ray emission and backscattering spectrometry using a 2.5 MeV H^+ beam focussed to ~4 μm and self-consistent fitting of the data. The geometry of these spherical particles was considered in order to accurately fit the corresponding particle spectrum and therefore to quantify the trace element composition of these particles. The demonstrable self-consistency of this method allows the compositions of most residue particles to be determined unambiguously and with a higher sensitivity to trace elements than conventional methods.

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1. Introduction

Identification of gunshot residues found on suspects has challenged forensic scientists for many years [1]. Energy dispersive spectroscopy (EDS) on the scanning electron microscope (SEM) is used routinely by police authorities to identify gunshot residue, and it has been shown that SEM-EDS can be used to distinguish between some residues from different types of ammunition powders [2]. We have shown [11] that particle-induced X-ray emission (PIXE) with a microbeam is a more powerful technique to characterise such materials because of the much higher sensitivity to trace elements.

PIXE can be quantified absolutely without the use of standards, provided that the elemental composition of the material on the exit path of the X-rays is known, which is the case if the backscattered particle signal is collected and correctly analysed. However, until recently it has not been possible to analyse the photon and particle spectra self-consistently, that is, in an integrated code that uses the elemental specificity of the PIXE to overcome the poor mass resolution of the particle spectra, together with the compositional depth profile sensitivity of the particle spectra to correctly calculate the X-ray absorption on the exit path. In fact, the main PIXE codes cannot correctly calculate absorption where the same element is in multiple layers.

We use a new implementation of the DATTPIXE code [3] which has been incorporated into an open source C module LibCPIXE and integrated [4] into DataFurnace [5]; the latter is a *fitting* code using simulated annealing as a global minimisation algorithm as well as the local minimisation algorithms commonly used. DataFurnace has powerful facilities for handling multiple spectra simultaneously. The new PIXE/backscattering integrated code has been used to identify the corrosion product on a historic heliograph from 1827 [6], to quantify the pigment used on a 19th century reproduction of Frans Hals' *La Bohémienne* (1630) [7], and to determine the O content of nitric acid treated carbon nanotubes [8]. It has also been used to determine the position and composition of micro-inclusions in unexpected carbonaceous inclusions in impact glasses from the meteoritic impact crater near Mt. Darwin, Tasmania [9].

When a firearm is discharged, microscopic particles of gunshot residue (GSR) are deposited on the hands, clothing, skin and hair of the shooter. These GSR particles are condensation products of the high pressure, high temperature reactions that take place when a gun is fired, and are made up of material from various components of the gun including the primer, cartridge casing and the projectile. The particles range in size from a few nm to tens of microns in diameter and usually contain Pb, Ba and Sb.

Gunshot residues are frequently used in police casework to prove that a suspect has fired a gun, because the residues can remain on the clothing of the shooter for several days after the incident. However, suspects are often arrested by police officers who themselves may be contaminated with gunshot residue particles either from previous case work or from their own firearms. This

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leads to uncertainty over the origin of gunshot residue found on a suspect and a risk of assuming a false positive. This problem has come into the spotlight in the UK in the recent high profile case of Barry George, who was convicted of the murder of the television presenter Jill Dando, in which one particle of gunshot residue was found on his clothing. Defence lawyers have appealed by arguing that the gunshot residue was most likely to be contamination either from the arresting officers or from the analysis procedure. This has highlighted the need to be able to discriminate one type of gunshot residue over another.

Police authorities routinely use SEM-EDS to characterise gunshot residues. Forensic service providers in the UK have developed a classification scheme for gunshot residues, putting them into five broad categories in accordance with their elemental composition [10]. It follows that if gunshot residue found on a suspect falls in to the same category as gunshot residue generated by a firearms officer, the evidence is inconclusive. Therefore there is a clear need to further subclassify gunshot residues.

We have recently demonstrated [11] that microbeam PIXE is capable of detecting trace elements in gunshot residues that cannot be detected by SEM-EDS. We have shown that some residues, which fall into the same broad category of GSR in SEM-EDS terms, can be further sub-categorized using PIXE. It was concluded that quantitative treatment of the PIXE data would strengthen the discriminating power of the technique. A distinct advantage of PIXE over SEM-EDS is of course the ability to determine the major, minor and trace element concentrations in absolute terms.

Additionally, to properly demonstrate the validity of the technique it will be necessary to evaluate the uncertainties involved. This will follow only from a quantitative treatment of the PIXE data. In this work, we will show how such a treatment can be effected if the backscattering and PIXE spectra are analysed self-consistently.

2. Materials and methods

Gunshot residue samples were collected from shooters at Bisley Rifle Range, Surrey, England. Residues were collected from three different firearms: a pistol, a rifle 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 [1]. A Cu particle finder grid was placed on top of the stubs.

Gunshot residue particles were identified using a Philips XL30 scanning electron microscope. The same particles were located and analysed using a 2.57 MeV proton beam, focussed to ~4 μm [12]. PIXE spectra were obtained using a 146 eV 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 at a scattering angle of 155° and a solid angle of 50 msr. The backscattered particle image was used to locate the particles, together with the PbL X-ray map. Point spectra were taken for each of the particles.

3. Results and discussion

The RBS spectra (taken from a point at the centre of each of the samples) were found to vary considerably. This variation can be understood by considering the effect of the particle size on the spectrum. There are three different cases which give rise to different RBS spectra, depending on whether the beam is (a) larger (b) equivalent to, or (c) smaller in size compared with the sample, as shown in Fig. 1.

In Fig. 1(a), we consider an RBS spectrum from a particle (from the pistol) of similar size to the beam. There is a high energy signal coming from the particle (Pb:Ba:Sb) and a low energy signal which comes from the carbon substrate on which the particle sits. The atomic composition of the carbon substrate was determined from a point analysis to be C 8 O 1 Pb 0.001. It is interesting to note that there is a tailing of the low energy edge of the signal from the particle and a corresponding slope on the signal from the buried carbon substrate. This is because closer to the edges of the particle, the beam sees a thinner layer of particle above the substrate than it does at the centre of the particle. Standard non-Rutherford cross-sections are used for the C and O signals.

Using a simple simulator for the particle spectra (such as is in OMDAQ [13], routinely used for PIXE/RBS), it is difficult, if not impossible, to fit the backscattered particle spectrum because the ratio of particle: substrate that the beam "sees" varies with depth in accordance with the sample topography. However, using DataFurnace, which is routinely used to extract accurate depth profiles from particle spectra, the spectra can be accurately fitted, as shown in Fig. 1(a).

The PIXE data from this sample was fitted self-consistently with the particle spectrum, and the fit is shown in Fig. 1(b). DataFurnace does not handle the PIXE spectra directly: we rely on OMDAQ to

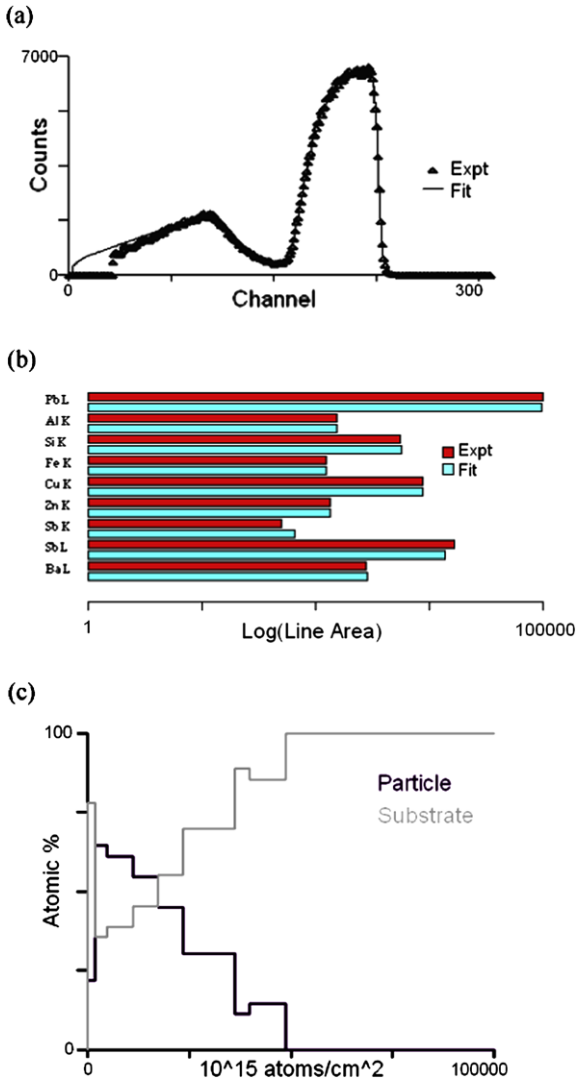


Fig. 1. (a) Fitted RBS spectrum (b) simultaneously fitted PIXE spectrum and (c) corresponding depth profile for a particle of a similar diameter to the beam.

extract characteristic line areas from the spectra, and DataFurnace fits these areas, as shown in Fig. 1(b). The data was fitted by allowing the proportion of substrate and particle to vary as a function of depth. The substrate was modelled as the molecule (C8 O1), and the particle was modelled as a single "molecule" of initial composition:

$$[\mathrm{Pb}, \mathrm{Al}, \mathrm{Si}, \mathrm{Fe}, \mathrm{Cu}, \mathrm{Zn}, \mathrm{Sb}, \mathrm{Ba}] = [760, 50, 40, 1, 23, 2, 47, 8]$$

where this composition was allowed to change during the fit. The resulting depth profile is shown in Fig. 1(c).

Note that this fit is very heavily constrained. Only two logical elements are permitted. The stoichiometry of the logical element ("molecule") that represents the GSR particle is allowed to vary during the fit to match the PIXE data. It is because the absorption which controls the interpretation of the PIXE spectrum is such a strong function of the depth profile that it is unfeasible to handle this type of data without a self-consistent treatment of the particle and photon spectra. But, given the assumptions imposed on the data, the fit is unambiguous. Moreover, the derived depth profile is apparently valid, since the fit is clearly good, and therefore the data are consistent with GSR particles of uniform composition.

We should also note that the model imposed on the data is of a flat layered structure. In the cases shown in Figs. 1 and 2 the sample is actually inhomogeneous laterally, and therefore the analysis is distorted. We neglect this here. It is worth pointing out that it is the proportion of the beam that overlaps the particle that gives the ratio of particle to substrate at the surface.

In Fig. 2(a), we consider the case where the particle is smaller than the beam spot size. The particle (from the rifle) that gave rise to the spectrum in Fig. 2(a) was approximately 3 μm in diameter, while the beam spot size was $\sim 4 \times 4$ μm. The spectrum shows a decrease in the signal coming from the particle and an enhancement in the carbon signal coming from the substrate, as would be expected for a small (i.e. thinner) particle. There is also a strong surface C signal (channel 162), coming from the area in which the beam is incident only on the substrate. Fig. 2 shows the fitted PIXE and RBS data for this sample and the corresponding depth profile. The depth profile shows that the particle is smaller (thinner) than the particle in Fig. 1.

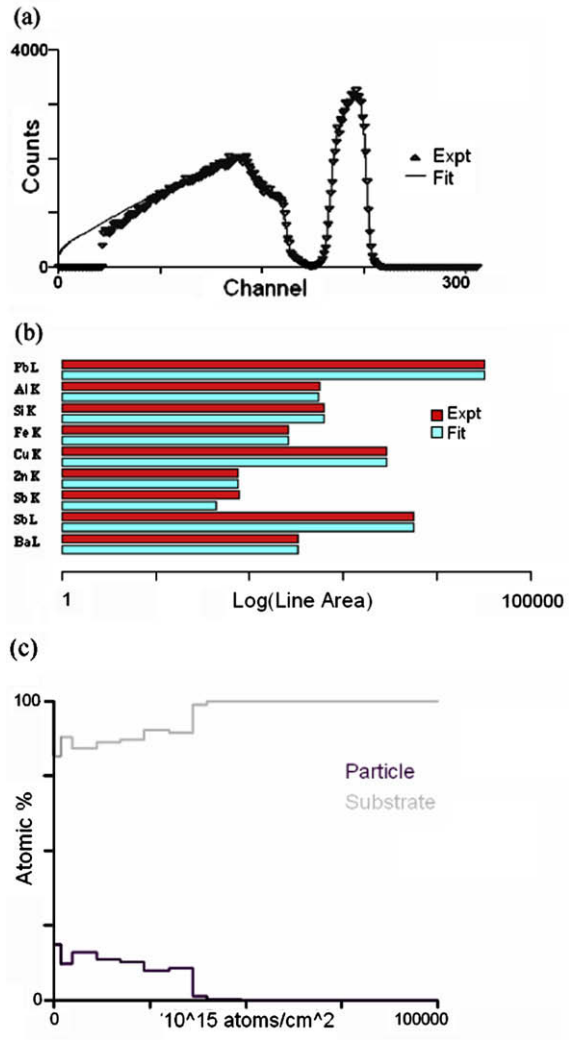


Fig. 2. (a) Fitted RBS spectrum (b) simultaneously fitted PIXE spectrum and (c) corresponding depth profile for a particle of a smaller diameter than the beam.

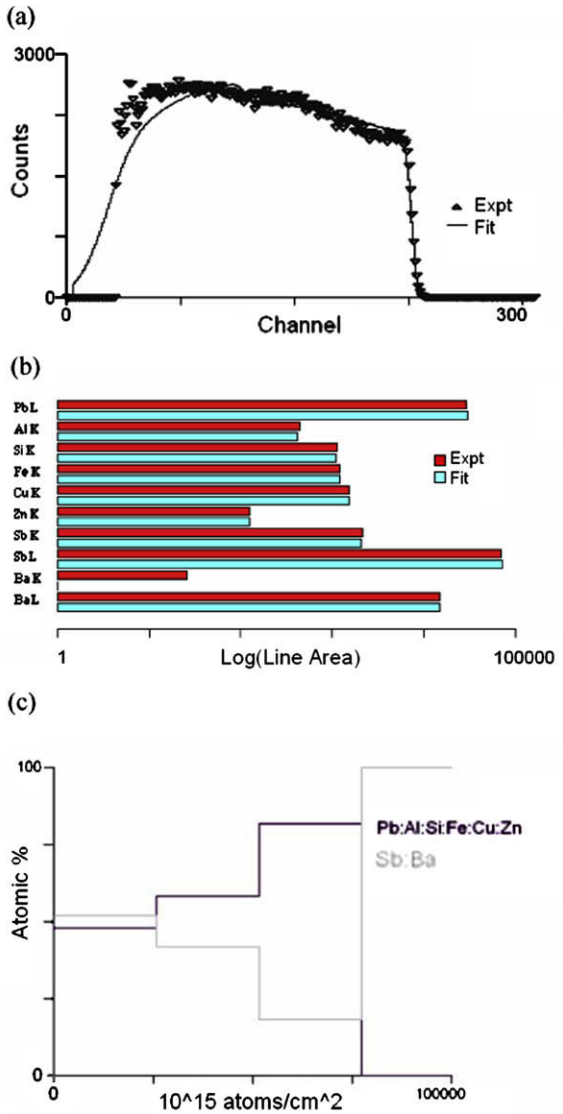


Fig. 3. (a) Fitted RBS spectrum (b) simultaneously fitted PIXE spectrum and (c) corresponding depth profile for a particle of a larger diameter than the beam. Note that the code does not attempt to fit the BaK line because it does not treat X-rays at this energy.

In Fig. 3(a), we consider the case where the particle is larger than the beam spot size. This particle (from the shotgun) is ~50 μm in diameter, and the spectrum comes from a spot on the centre of the particle. In this case, the substrate cannot be seen in the RBS spectrum because the sample is thick. In this analysis, the Pb was allowed to vary independently from the Ba and Sb signals with depth. This was necessary to fit the data, in contrast to the other samples. The resulting depth profile is shown in Fig. 3(c). However, the PIXE maps do not show any non-uniformity in the Pb L and Sb K signals. Additionally, it is known that Pb, having a significantly lower melting point than Sb and Ba, will often solidify as an outer shell in GSR particles [14]. The derived depth profile, in which the Pb signal increases with depth, is not consistent with this expected behaviour.

We propose that the spectrum of this particle is a strong function of its topography. For spherical particles, the surface presented to the beam is not flat, even when the particle is larger in diameter than the beam. This means that the calculated exit pathlength of both particles and photons is progressively overestimated as the interaction point is deeper in the sample. This has the effect that the low energy scattering is underestimated. The fitting software compensates for this by putting high mass particles deep in the sample, and distorting both the detector solid angles and the stoichiometry of the sample.

Therefore, although the fits are good the results are as valid as the model imposed on the data. We have assumed in this analysis that the particle composition is uniform and that the surfaces of the particles are flat. For small particles the assumption of a flat sample surface is a fair approximation (although the assumption of lateral homogeneity still distorts the interpretation), but for large particles it is clearly a poor approximation.

The analysis method used here assumes mixed layers of carbon and gunshot residue material, particularly for the small samples where at the surface the beam encompasses both the particle and carbon substrate. Of course the assumption of lateral homogeneity is false, since we actually have two discrete areas of different composition.

4. Conclusions

We have shown that spherical particles of gunshot residue can be successfully fitted by simultaneous treatment of the PIXE and backscattering data, thereby allowing the composition to be determined quantitatively. The fits are excellent for all sizes of particle, but for large particles the results are incredible. The extracted depth profiles in this case are clearly distorted by the spherical geometry, and must also distort the PIXE results. We conclude that compositions obtained in this way by PIXE will be distorted by this topography effect also for the small particles, although to a lesser extent, since the absorption is relatively small for small particles.

Accurate work must take account of particle shapes; but for this application, differences between particles that depend on such relatively small corrections cannot be used to reliably discriminate between GSR particles.

References

[1] F.S. Romolo, P. Margot, Forensic Sci. Int. 119 (2001) 195.
[2] Z. Brozek-Mucha, A. Jankowiczl, Forensic Sci. Int. 123 (2001) 39.
[3] M.A. Reis, L.C. Alves, A.P. Jesus, NIM B 109–110 (1996) 134.
[4] C. Pascual-Izarra, M.A. Reis, N.P. Barradas, NIM B 249 (2006) 780.
[5] C. Jeynes, N.P. Barradas, P.K. Marriott, G. Boudreault, M. Jenkin, E. Wendler, R.P. Webb, J. Phys. D: Appl. Phys. 36 (2003) R97.
[6] C. Pascual-Izarra, N.P. Barradas, M.A. Reis, C. Jeynes, M. Menu, B. Lavedrine, J.J. Ezrati, S. Röhrs, NIM B 261 (2007) 426.
[7] L. Beck, C. Jeynes, N.P. Barradas, NIMB 266 (2008) 1871.
[8] J.C.G. Jeynes, C. Jeynes, K.J. Kirkby, M. Rümmeli, S.R.P. Silva, NIM B 266 (2008) 1569.
[9] M.J. Bailey, K.T. Howard, K. Kirkby, C. Jeynes, Characterisation of Inhomogeneous Inclusions in Darwin Glass using PIXE/RBS/EBS, these Proceedings.
[10] Private Communication with LGC Forensics.
[11] M.J. Bailey, D. Cox, K.J. Kirkby, C. Jeynes, J. X Ray Spectrometry, in press, DOI: 10.1002/xrs.1142.
[12] A. Simon, C. Jeynes, R.P. Webb, R. Finnis, Z. Tabatabian, P.J. Sellin, M.B.H. Breese, D.F. Fellows, R. van den Broek, R.M. Gwilliam, Nucl. Instr. and Meth. B 219 (2004) 405.
[13] G.W. Grime, Science 109 (1996) 170.
[14] B. Cardinetti, C. Ciampini, C. D'Onofrio, G. Orlando, L. Gravina, F. Ferrari, D. Di Tullio, L. Torresi, Forensic Sci. Int. 143 (2004) 1.