

Distinction between the metals of various firearms by Scanning Electron Microscopy-Energy Dispersive X-Ray Analysis (SEM-EDX), micro X-Ray Fluorescence (μ -XRF) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

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ABSTRACT

There are currently over 600 million firearms in circulation throughout the world. Identification markings on firearms are often removed by drilling or grinding leaving metal swarf as evidence of serial number obliteration. The ability to demonstrate that recovered metal fragments originated from a firearm, and more specifically from a specific make and model of firearm, would be of significant investigative value.

Scanning electron microscopy – energy dispersive x-ray (SEM-EDX) spectrometry, micro – X-ray fluorescence (μ -XRF) spectrometry and solution based inductively coupled plasma mass spectrometry (ICP-MS) were used to provide an elemental association pattern, or chemical ‘fingerprint,’ for various metal sources including more than 80 firearms and various workshop steels.

Elemental analysis was effective at differentiating between steel originating from the firearms analysed and metals encountered in a typical workshop. The results also demonstrated that different metal alloys are employed in the manufacture of firearms. Principal component analysis followed by linear discriminant analysis of the principal component scores was an excellent method for determination of firearm make and showed potential for individual firearm discrimination.

The various techniques used in this study are compared and discussed in this paper. It is believed that elemental profiling may be used to augment traditional toolmark analysis, in particular for intelligence purposes .

BACKGROUND AND INTRODUCTION

Concern about the level of illicit firearm trafficking in Australia has risen in recent years. In general, weapons seized at crime scenes, and in routine policing, can be traced back to licensed Australian owners and arms importers [1]. The process of tracing a firearm relies on two integral elements; the marking of the firearm with a unique serial number, and the registration of this information. It is therefore a common practice for a criminal to obliterate this serial number. Serial number restoration techniques are well described in the forensic literature [2-5].

When a serial number on a firearm has been removed to below the area of plastic deformation, restoration of the original number is precluded, and in most cases, nothing more can be done to determine the origin of the firearm. It would be of significant investigative value if metal fragments recovered from a scene or adhering to a tool suspected of involvement in serial number obliteration could be shown to have originated from a firearm as opposed to other metal sources. The value of this information would be further increased if it were possible to show that this metal came from a specific make, or even model, of firearm. Similarly this would be useful in investigating suspected cases of firearm manufacture and could even be applied to non-firearms related cases such as vehicular serial number obliterations.

Few studies have involved the chemical analysis of steel from a forensic perspective. The research into elemental discrimination between metal from firearms is primarily concerned with analysing metal fragments generated during barrel shortening [6, 7]. The primary aim of this study was to assess the ability of three analytical methods available to the forensic scientist to differentiate between general workshop steels and metals commonly encountered in the manufacture of firearms. The secondary aim of the study was to assess the ability of each method to differentiate between metals from different makes and different models of firearms.

Essentially this study sought to evaluate and compare the use of SEM-EDX, μ -XRF and ICP-MS for their ability to chemically profile steel found at a crime scene, and compare this profile with that of other evidentiary samples. In order to achieve this,

Chemometric methods were used to process the multivariate data, which were then displayed graphically. Processing of the data generated ensured that the results of this study could be integrated into a computerised database. The use of visual plots addressed the need for the data to be presented in a manner that is comprehensible by the layperson and that may, ultimately, be presented in court.

MATERIALS AND METHODS

A total of 86 firearms from 20 different makers and 29 different models were selected, based on availability, as well as samples of steel known to be non-firearm related. Metal was removed from each of the sources by drilling as shown in Figure 1. A new drill bit was used on each occasion.

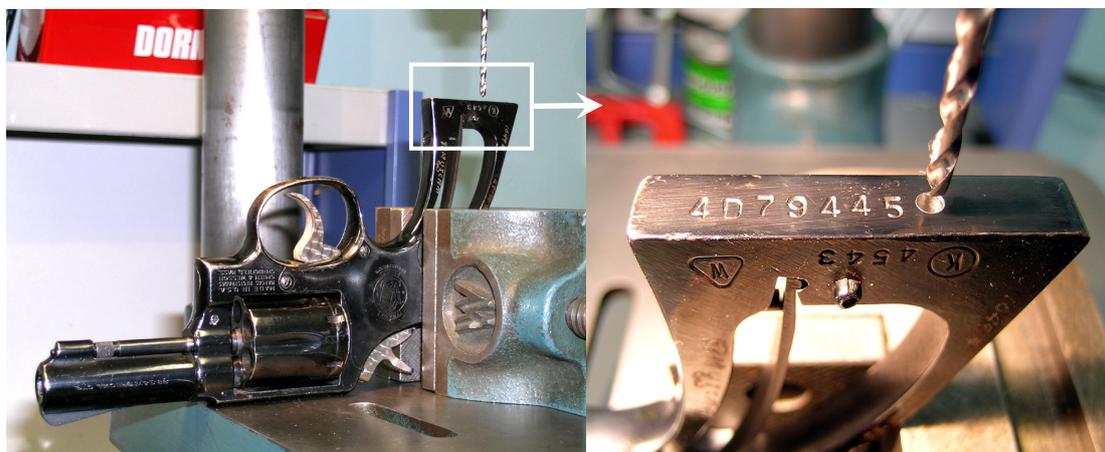


Figure 1 Sampling method

Analysis by SEM-EDX

A single piece of swarf from each sample was analysed using a Philips XL30 ESEM (FEI Company, Oregon, USA), coupled to an EDAX spectrometer with light element

x-ray detector (AMETEK, Philadelphia, USA). The SEM-EDX operating parameters are given in Table 1. Elements were manually identified in the spectrum. Standardless quantification of these elements was performed using computer software to calculate the results based on atomic number, absorption, and fluorescence (ZAF) correction. Analysis was repeated at three different locations on each sample and the mean response for each element detected in that sample was calculated.

Analysis by μ -XRF

A single piece of swarf from each sample was analysed using a Kevex Omicron X-ray Microfluorescence Spectrometer (Thermo Electron Corporation, Wisconsin, USA). The μ -XRF operating parameters are given in Table 2. For each sample a test spectrum was acquired and the sample position adjusted to achieve a dead time of as close as possible to, but not exceeding 50%. Elements present were manually identified in the spectrum. Standardless quantification of all elements detected was performed using the ASAP computer software to calculate the results based on ZAF correction.

Analysis by ICP-MS

0.0100 ± 0.0005 grams of swarf was weighed and placed in a centrifuge tube. 1.6mL of concentrated hydrochloric acid was added and heated at 75°C for twenty minutes or until no further sign of reaction. 0.2mL of concentrated nitric acid was added to the digest with continued heating until complete dissolution was observed. The solution was allowed to cool, 0.5mL of the digest taken, and diluted to 10mL with 1% ultra-pure nitric acid. The final solution was decanted into a 5mL screw top vial for analysis using a 7500ce ICP-MS (Agilent Technologies Inc., Melbourne, Australia)

equipped with an octapole reaction system (ORS) and integrated autosampler (I-AS). The operating conditions are listed in Table 3. An Agilent built peristaltic pump was used for sample introduction in conjunction with 1.02mm internal diameter Tygon tubing. ^{103}Rh was added as an internal standard through a t-piece. Twenty-seven elements were chosen for detection. Based on preliminary semi-quantitative results, elements that were substantially greater than the background were included.

Data Treatment

Chemometric analysis of the datasets via Principal Component Analysis (PCA), Cluster Analysis (CA) and Linear Discriminant Analysis (LDA) was conducted using Minitab[®] (Version 13.1 for Windows).

RESULTS AND DISCUSSION

In total, twenty-nine different firearm make and model combinations were examined. Twenty-one of these were able to be discriminated from mild steel samples by μ -XRF. Twenty-four firearm make and model combinations were distinguished from mild steel samples by SEM-EDX.

These differentiations were achieved by plotting the first three principal components of the element concentrations from groups of firearms of the same make and model, with those for mild steel. Examples are shown in Figures 2 and 3.

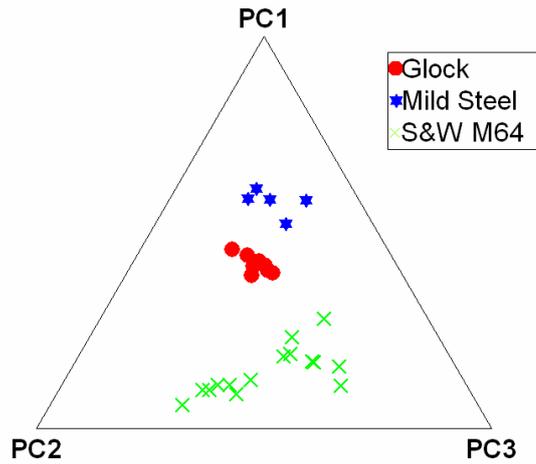


Figure 2 Ternary plot of first three PC for Glock pistols, mild steel, and Smith and Wesson Model 64 revolvers by μ -XRF

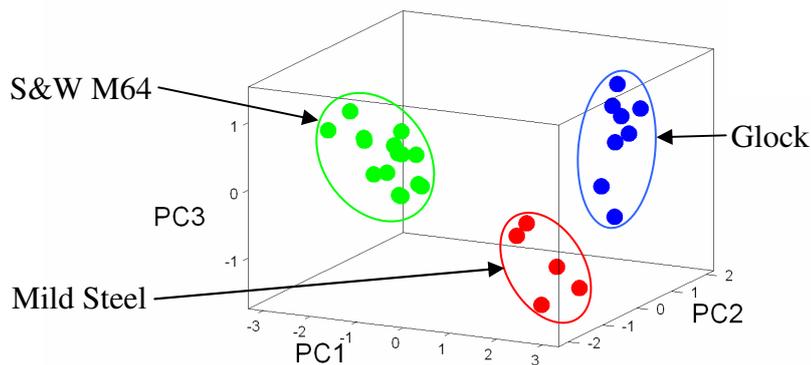


Figure 3 Three-dimensional plot of first three PC for Glock pistols, mild steel, and Smith and Wesson Model 64 revolvers by μ -XRF

Twenty-one of the twenty-nine make and model combinations were analysed by ICP-MS. Of these, nineteen were shown to have an elemental profile so unique that they could be reliably differentiated from each other. The results indicate that each of the three methods employed can be used to compare steel samples, and where there are

significant differences in composition, demonstrate that they are likely to have come from different sources.

This can be illustrated by a practical example. Consider a hypothetical case where metal swarf is located at a scene where illicit firearm manufacture or modification is suspected to have been undertaken. Two avenues of investigation are available within the context of this research. The principal components from the spectrometric analysis of the evidentiary sample(s) can be plotted against those from the suspected source of the metal or the same process can be used to compare the evidentiary swarf with known samples of mild steel. If the evidentiary sample proved indistinguishable from mild steel, and the firearms in question were known to be of a different composition, time could be better spent pursuing alternative lines of enquiry.

To relate this to the results from this study, if swarf were collected at a scene where it was suspected that illicit modifications had been carried out on the barrels from Glock pistols, the trace evidence should be compared with samples known to have come from the barrel of Glock pistols and with metals from other relevant sources. This is demonstrated in Figure 4 where a simulated evidentiary sample can be clearly distinguished from mild steel but not from the barrel material of other Glock pistols.

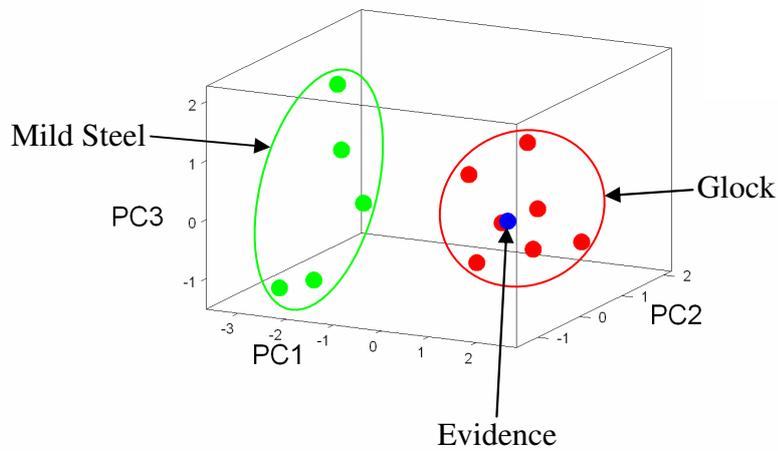


Figure 4 Comparison of a simulated evidentiary sample with known samples by μ -XRF

In cases where the principal components from an unknown sample do not coincide with those from a group of samples (that are known to be similar) it can be said that the samples are from different sources. However it must be emphasised that, using the techniques applied in this study, samples from two very different sources may be indistinguishable. For example, steel from Smith and Wesson Model 10 and Model 64 revolvers can be distinguished, while Model 10 revolvers cannot reliably be distinguished from mild steel.

A second situation encountered is where tools suspected of having been used in the obliteration of a firearm's serial number are seized. In cases where the toolmarks from the working edge of the tool remain, toolmark analysis can be used to show that a specific tool was used to undertake the obliteration. However, where a number of tools are suspected, or where no toolmarks remain, this can be difficult. This research

has demonstrated that a tool can be examined using the SEM, any adhering metal fragments located, and the method described applied to the trace evidence. This would form an excellent screening technique for subsequent toolmark analysis or effective class evidence that could be used to guide further avenues of investigation. If a tool is subsequently used to drill a hole in another material, traces from the previous material were found to be lost. This method of analysing particles adhering to tools is not compatible with μ -XRF analysis as x-ray emission from the metal of the drill bit, in addition to the sample, is unavoidable.

CONCLUSION

Each year firearms are recovered with serial numbers obliterated by an offender through drilling and milling. When this occurs existing forensic techniques are rarely effective in restoring the original number. Toolmark analysis has traditionally been used to provide a link between a firearm in question and the tool used to obliterate the serial number. This not only relies on the suspect tool being located but also on the working edge of the tool in question remaining unchanged since producing the toolmark. Metal particles and swarf generated during the removal of firearm serial numbers can be recovered at the scene and may be found adhering to the tool used in the offence.

This work utilised three accepted analytical techniques to analyse 104 metal samples from various sources, including eighty-six firearms. The multivariate data produced in each analysis was reduced in dimensionality using principal component analysis and the resulting data displayed in easily interpreted three-dimensional plots.

In total, 29 different firearm make and model combinations were examined. Twenty-one of these were able to be discriminated from mild steel samples by μ -XRF. Twenty-four firearm make and model combinations were distinguished from mild steel samples by SEM-EDX. Of the 21 makes analysed by ICP-MS 19 were shown to have an elemental profile so unique that they could be reliably differentiated from each other.

The superior detection limits of ICP-MS were shown to allow the greatest discrimination between samples where elemental concentrations were similar. However both SEM-EDX and μ -XRF were effective in discriminating between the majority of samples. The rapid, simple and non-destructive nature of these techniques may outweigh the benefits of solution based ICP-MS, depending on the nature of the investigation and laboratory resources. SEM-EDX has the added advantage of allowing trace evidence to be located and analysed *in situ* on tools.

The use of a technique such as laser ablation – inductively coupled - mass spectrometry (LA-ICP-MS), encompassing the increased sensitivity of ICP-MS, while retaining the ability to quickly and (semi) non-destructively target individual particles of trace evidence is being investigated in further research.

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TABLE 1 SEM-EDX operating parameters

| Parameter | Setting |
|------------------------------|------------------------------|
| Specimen chamber environment | HiVac |
| Accelerating voltage | 25 kV |
| Image mode | SEI |
| Magnification | 5000x |
| Working distance | 10mm |
| Spot size | 4.5 |
| Scan type | Full frame |
| Live acquisition time | 60s |
| Software | EDX Control Software V3.3 |

TABLE 2 μ -XRF operating parameters

| Parameter | Setting | |
|---------------------|------------------|---------------|
| Software | Kevex WinXRF | |
| Collimator | 300 μ m | |
| Spectrometer | Voltage | 12kV |
| | Current | 1.00mA |
| | Acquisition time | 600 s |
| | Atmosphere | vacuum |
| | Shaping index | 64 |
| | Range | 20keV |
| | Gain | 20 |
| | Channels | 4096 (5eV/Ch) |

| | | |
|------------------------|----------------------------|--------------|
| Pulse processor | Pulse pair resolution | 0.8 μ s |
| | Pulse optical inhibit | long |
| | Test signal | off |
| | Input | differential |
| | Slow discriminator enabled | on |
| | Pulse slope detect | on |
| | Fast amp pile-up reject | on |
| | Slow amp pile-up reject | off |

TABLE 3 ICP-MS operating parameters

| | |
|------------------------------|----------------------------------|
| <i>RF Power</i> | 1500 W |
| <i>RF Matching</i> | 1.82 V |
| <i>Gas Flow:</i> | |
| <i>Carrier Gas</i> | 0.95 L/min |
| <i>Make-up Gas</i> | 0 L/min |
| <i>Sample Depth</i> | 9 mm |
| <i>Nebulizer Pump</i> | 0.1 rps |
| <i>Reaction Cell:</i> | ON |
| <i>He Gas</i> | 4.5 mL/min |
| Peristaltic Pump program | |
| | <i>Before Acquisition</i> |
| Uptake speed | 0.20 rps |
| Uptake time | 30 s |