Contents lists available at ScienceDirect

Forensic Science International

journal homepage: http://ees.elsevier.com

Vacuum metal deposition enhancement of friction ridge detail on ballistic materials

Jessica N. Pollitt [a,b], George Christofidis [a], Joanne Morrissey [c], Jason W. Birkett [a,*]

[a] The School of Pharmacy and Biomolecular Sciences, Liverpool John Moores University, Liverpool, L3 3AF, UK
[b] Merseyside Police Forensics Laboratory, Merseyside Police Head Quarters, Canning Place, Liverpool, L1 8JX, UK
[c] School of Life Sciences, Faculty of Science & Engineering, Anglia Ruskin University, Cambridge Campus, East Road, Cambridge, CB1 1PT, UK

ARTICLE INFO

Article history:
Received 29 October 2019
Received in revised form 9 October 2020
Accepted 14 October 2020
Available online xxx

Keywords
Forensic science
Vacuum metal deposition
Friction Ridge detail
Ballistics
Fired cartridge cases
Fingermarks

ABSTRACT

The efficacy of Gold/Zinc and Silver/Zinc vacuum metal deposition (VMD) protocols were assessed as stand-alone methods of fingermark enhancement on ballistic brass materials. The results demonstrate the effectiveness of VMD enhancement on a large pool of donors (n = 20), with potentially identifiable marks recovered for the majority of donors, including samples aged up to two months. Of the 20 donors a subset of six donors were selected to assess the capability of VMD enhancement on brass fired cartridge cases, from which some friction ridge detail (FRD) was recovered. Lastly, an attempt to understand which fingermark components are facilitators of VMD enhancement was made. Fingermark residue was extracted from brass tiles and fired cartridge cases before analysing chromatographically (GC–MS). Although some key components were indicated, further evaluation of all fingermark components is needed to draw firm conclusions as to the role each plays in VMD enhancement.

1. Introduction

The majority of friction ridge detail (FRD) deposited on evidence requires some form of enhancement to visualise. The most suitable process varies depending on a number of factors including the surface type – generally porous or non-porous – and environmental exposure. Therefore, a robust and diverse range of treatments must be available to allow the selection of the most appropriate process.

Ballistic evidence, commonly recovered from firearms incidents, often consists of fired brass bullet casings which require additional consideration when selecting a treatment [1]. The effects of the metal surface and firing process must be taken into account, and likely contribute to the current low recovery rates of FRD [2].

The firing process itself is thought to be the main cause of fingermark deterioration on ballistic evidence, with the casing undergoing several processes, which could contribute to weathering of the surface, or changes to the fingermark residues. These include: abrasive friction, the blowback of hot gasses, high temperatures, contamination from the propellant by-products and the process of loading the cases [3].

Due to conflicting opinions regarding the most prominent method of degradation from the firing process, and specific aspects of metallic surfaces, multiple factors must be considered when determining the most effective technique for use on ballistic evidence. Suitable techniques must be: highly sensitive, able to recover degraded FRD from potentially corroded surfaces, unlikely to react with any contaminants, and able to develop FRD on curved surfaces evenly.

Metallic items can be classified as smooth non-porous surfaces; however, unlike the majority of similar substrates they are often reactive and curved or intricately shaped. The reactivity of metals leaves them prone to weathering, especially when exposed to outdoor conditions, affecting the surface of the object and potentially the ability to recover fingermarks [4]. The enhancement of bullet casings is likely to be further affected by the relatively small surface area and high curvature of common calibres of ammunition. This, together with the effect of loading action can result in partial or overlapping fingermarks being deposited, it may also mean less residue is present and therefore, deterioration may have more impact on the results obtained [3]. Curvature can also lead to difficulty in ensuring even treatment, as well as increased difficulty in visualisation [3,5].

The approved processes commonly in operational use on smooth non-porous items, are a sequential treatment of cyanoacrylate (CA) fuming, followed by fluorescent dye [6]. This generally involves heating CA to 120 °C within a specially designed chamber, maintained at approximately 80% relative humidity. This results in the formation of a white "noodle-like" polymer on any present FRD, the structure of which helps to scatter light and trap subsequent fluorescent dye molecules. The exhibits are then dyed before viewing under an appropriate light source to allow the visualisation of the marks [7].

* Corresponding author.
E-mail address: j.w.birkett@ljmu.ac.uk (J.W. Birkett)

https://doi.org/10.1016/j.forsciint.2020.110551
0379-0738/

Although well-established, there are limitations to this method, some of which seem to have particular effects on metallic substrates. Relative humidity must be carefully maintained within its optimum range, too high will result in irreversible overdevelopment, and too low cause changes to polymer structure affecting its efficiency [8]. Furthermore, exposure to humidity in this range may instigate the formation of electrolyte films on metals which may impact on development [4]. The heating process, which may also increase the rate of corrosion on metals, can result in uneven development within the chamber, a particular concern with bullet casings, which are highly curved, and of small size [3].

This has led to the development of several techniques which aim to improve the recovery of FRD from metallic substrates and fired cartridge cases. These have included the development of aqueous electrolytes [9], electrochromic films [10–13], electrolysis [14], electrostatic development [5] and Gun Blue (GB) [15,16]. Although there are a variety of positive attributes to all these techniques, most also have problematic characteristics likely to prevent them from becoming widely used in laboratories. Of these techniques, GB appears most likely to be developed further; however, the technique is limited to metallic surfaces and requires further evaluation and optimisation to determine its effectiveness.

Another possible technique for application to metallic and ballistic exhibits is Vacuum Metal Deposition (VMD) [17]. VMD is an approved technique for non-porous substrates, already in use by several police forces worldwide [6,18]. It was first used operationally in the 1970s and is often reported as being more sensitive than CA fuming, particularly on aged marks or those exposed to adverse environmental conditions [19].

VMD involves evaporation and deposition of a variety of metals, most commonly gold or silver, followed by zinc, within a high vacuum chamber [20]. The initial metal forms a thin film across the entire surface made up of small clusters of the metal atoms. Although this film is evenly distributed across the background surface, the fingermark residues present enclose the clusters in the areas where ridges have been deposited. The bonding energy of zinc, which is subsequently deposited, is so small that it requires preferred sites to nucleate and grow, in this case the accessible clusters (Fig. 1). This causes the background surface to become plated with zinc whilst the ridges remain transparent forming a "negative print" [19]. Monometallic VMD processes are also available, most commonly using silver. These appear to follow a similar development process, however they rely on contrast between the initial background film and the areas covered with residues, rather than having the added contrast of a zinc layer [21].

A major strength of VMD is its sensitivity and versatility of application. The majority of literature focuses on the use of VMD to recover fingermarks from a variety of plastic substrates [19,22,23], as this has previously been the main operational use for the technique. However, it was originally investigated as a means of treating porous substrates

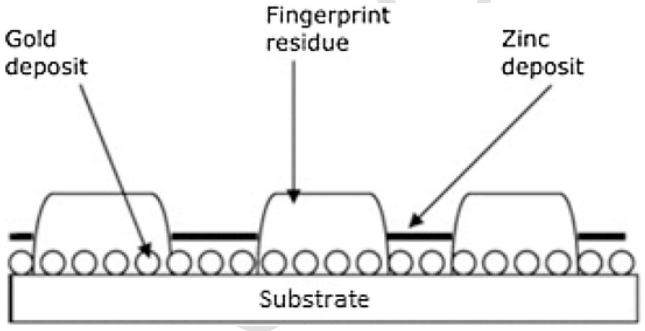

Fig. 1. The process by which zinc deposits only on the background surface leaving transparent ridges [26].

[24] and has shown success on several notoriously difficult substrates such as polymer banknotes and fabrics [25,26]. Unlike CA fuming, VMD can also be used on exhibits that have previously been wet [27], and is recommended for aged marks [6].

Whilst there is little specific research into the use of VMD on metallic surfaces (with the exception of a very recent comparative study by [28]), particularly regarding ballistic evidence, Tiwari et al. [29] have proven its applicability on rough aluminium surfaces, with a reported 70 % success rate. VMD was chosen as the most suitable technique due to the large surface inhomogeneity. Despite this, and the use of different zinc compounds during the treatment, the VMD reaction appeared to occur as normal on the metallic surface. However, the study reported no grading or comparable analysis of the FRD developed, so it is unclear as to the quality of the fingermarks produced.

In an investigation into the use of Scanning Kelvin Probes (SKP) to detect latent fingermarks, VMD was used on metal substrates in order to improve the contrast in Volta potential between the surface and areas insulated by fingermark residue [30]. Although the ability to use these two techniques in conjunction is of interest it is unlikely to become commonplace due to the time and cost implications of using SKP, and the difficulties using this technique on curved surfaces [31]. The study does however show that VMD enhancement occurs successfully on a variety of metals including brass [30].

Research is now focussing more specifically on the use of VMD for ballistic evidence. A recent study by Christofidis et al. [20] found that both Gold/Zinc and Silver/Zinc VMD were able to enhance potentially identifiable FRD on ballistic brass tiles, and produce second level FRD on cartridge cases after firing. Although the study used only six donors, the results indicate that VMD may be an effective technique for the development of FRD on ballistic evidence.

This study aims to further investigate the use of VMD for the recovery of FRD from ballistic evidence using a large donor pool (n = 20) representative of UK's population, with focus on a ballistic brass surface and fired brass bullet cases. Additionally, an attempt towards understanding the mechanism behind VMD FRD enhancement is made, by pinpointing the compounds that are the major contributors.

2. Materials and methods

2.1. Fingermark collection

2.1.1. Initial phase brass tiles

Ballistic brass tiles (3 cm × 3 cm, 65 % Cu, 35 % Zn, www. Metalsheets.co.uk) were prepared for fingermark deposition by removing the protective acetate layer, cleaning with ethanol and air drying. Several randomly selected tiles were then subjected to VMD treatment as blanks; these yielded no FRD indicating that the tiles were free from previous contamination.

The remaining tiles were joined together in pairs to enable fingermarks to be deposited across the join and each half subjected to a different VMD process. Each tile was then labelled to show, the donor, age of mark and VMD treatment (Fig. 2). A total of 40 tiles were prepared for each donor to provide five repeats for each of the four aging categories: a day, a week, a month and two months.

10 male donors and 10 female donors were selected from volunteers, of these three were of an ethnic minority background and were labelled A to T. The proportions of the sample population were based on a stratified sample from the latest census data, using as many variables as was practicable [32]. The aim being to ensure that data collected was as representative of the UK population as possible and that the results could therefore be appropriately generalised. The resulting sample contained 20 donors of unknown quality, representing an age range from 19 to 56, and a variety of job types from office work to laboratory work.

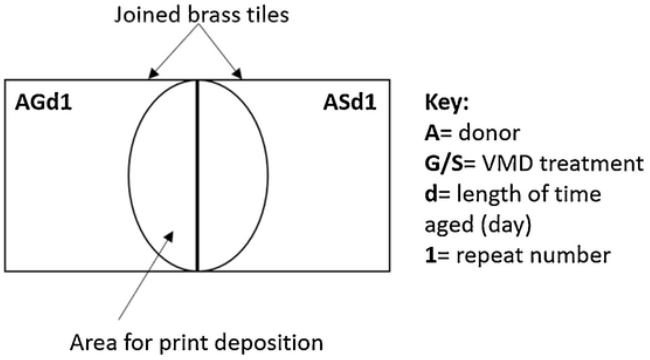

Fig. 2. Diagram of brass tile set-up for donation.

Each donor deposited all 20 of their repeat marks at the same time. Natural prints were collected and, as such, the donors were asked to wash their hands in soap and water and resume their normal activities for approximately 30 min prior to donation [33]. During the collection they were instructed to press their right thumb across the join of each pair of tiles for three seconds. In between each deposition donors rubbed their fingertips together to redistribute the fingermark residues and help to prevent depletion. The tiles were kept in secure storage, akin to where evidential items are kept before treatment.

2.1.2. Brass bullet cases

Brass metal case bullets (FIOCCHI, 9 mm LUGER, 123 grain) were cleaned down using ethanol and left to air dry. They were then labelled as shown in Fig. 3 to denote the donor and the repeat number.

Six of the previous donors were selected based on the quality of the fingermarks enhanced in the initial phase. A male and female good quality, medium quality and poor quality donor. Natural prints were collected and donors received the same instruction as above in section 2.1.1.

The cartridges were then loaded, fired and collected by gloved firearms personnel.

2.1.3. Sample collection for compositional analysis

In order to identify key chemical constituents in donors fingermarks, and to assess any changes in chemical composition due to the effect of firearms discharge, fingermark residue was subjected to GC-MS analysis.

Ballistic brass tiles were prepared as stated above in Section 2.1.1. Instead of being joined together individual tiles were labelled to show the donor and repeat number. Three were prepared for each donor. 9 mm brass bullet cases were also prepared as above in Section 2.1.2, again three per donor, as shown in Fig. 3.

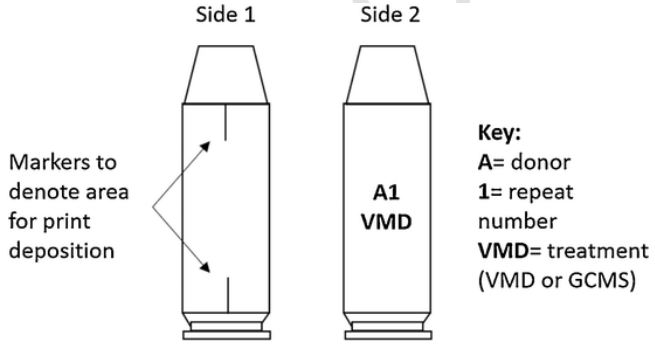

Fig. 3. 9 mm brass cartridge labelled for fingermark donation.

Natural prints were again collected following the previous methodology (Section 2.1.1). The same six donors selected in Section 2.1.2, were used for continuity.

2.2. VMD treatments (gold and silver)

VMD treatments were carried out using a VMD900 system (West Technology Systems Limited), in accordance with the local Police Forensic Laboratory standard procedure (FEL-SOP-007 v.2.0) and ISO17025 guidelines.

The process consisted of loading the brass tiles or bullet cases onto the "metal hood" of the chamber, before adding a 2–5 mm section of gold or silver wire to an evaporation boat found in the base of the chamber. A second evaporation boat contained zinc, the amount of which must be monitored after each treatment. The chamber was sealed and pumped down to a high vacuum (3×10^{-4}mbar or higher), before the metals were sequentially evaporated by the operator through the application of an electric current. The development was monitored and controlled by the operator through a portal window.

Where the brass tiles were subjected to either Gold/Zinc or Silver/Zinc VMD treatment dependant on their assigned category, only Gold/Zinc VMD treatments were carried out on the bullet cases. This decision was made based upon results from the initial phase and the availability of materials for this secondary investigation.

2.3. Fingermark analysis and evaluation

Developed marks were photographed by a specialist from the local Police Forensic Imaging Unit using standard procedure for forensic casework. The DCS4 Capturing System (Foster and Freeman) consisting of a Nikon D800 and 100 mm macro lens was used, with a focal length of 4.0 and an aperture of F16. All images were taken using a one-to-one scale under optimised lighting.

The photographed marks were initially graded using the standard Centre of Applied Science and Technology (CAST) scheme (Table 1) by the first author (who carried out the experimental aspects of the study). This consisted of examining each photographed mark individually with an eyeglass. When referring to the fingermarks enhanced on brass tiles each half was considered as a separate mark due to the separate treatments. To avoid any confirmation bias, independent blind grading, was conducted by another author (a trained fingermark examiner with 23 years of police casework experience) on a randomly selected sample of marks (n = 80). All fingermark grades from both examiners were in agreement.

Non-parametric statistical analysis, in the form of Wilcoxon signed rank, Mann Witney U and Kruskal Wallis H tests, were carried out using SPSS (v24). Subsequent data analysis was carried out using Microsoft Excel (2016).

Table 1
CAST grading scheme for the assessment of developed fingermarks [6].

Grade	Detail Visualised
0	No evidence of a fingermark
1	Some evidence of a fingermark
2	Less than 1/3 clear ridge detail
3	Between 1/3 and 2/3 clear ridge detail
4	Over 2/3 clear ridge detail

2.4. Fingermark compositional analysis

2.4.1. GC–MS instrumentation and conditions

Chromatographic analysis was performed with an Agilent Technologies 7890A network GC system, equipped with an Agilent 7683 Series autosampler. An Agilent J&W Scientific HP5-MS UI (30 m x0.25 mm x0.25 μm) column was used. Helium was used as the carrier gas (1 mL/min), the injection volume was 1 μL, with a solvent delay of 3.6 min. Splitless mode was set for the injections, along with a 40 mL/min at 0.75 min purge flow. Inlet temperature was set at 250 °C, the oven temperature was: Initially at 80 °C, then with a ramp of 10 °C/min to 230 °C for 2 min and finally with a ramp of 4 °C/min up to 310 °C for 8 min. The total run time was 46 min. The GC was coupled with an Agilent 5975B Inert MSD system using electron impact (EI) ionisation. The transfer line between the column and the MS was kept at 280 °C. The method was adapted from [34]. The following standard compounds were purchased from Sigma-Aldrich: Squalene, palmitic acid, stearic acid, methyl stearate, methyl tetradecanoate, pentadecanoic acid.

2.4.2. Fingermark extraction

5 mL of MeOH was used to extract the fingermark residue from the fired cartridge/metal tile by agitation of the beaker for 2 min. Then the solvent was evaporated to dryness under nitrogen and reconstituted using 100 μL of MeOH, with the addition of 2.5 μL of hexadecane (transferred from a 1 % v/v hexadecane/MeOH solution) as the internal standard.

2.4.3. Data analysis

Principal component analysis on the fingermark chromatographic data was performed by using the OpenChrom software. The area under curve was taken into account for all peaks with the exception of the internal standard peak. The internal standard was used in all samples.

Table 2
Average time required for various stages of the VMD process (n = 65).

	Average Time (minutes)	SD
Pump-down	6.83	1.78
Development	2.05	0.72
Vent	2.15	0.51

3. Results and discussion

3.1. VMD process

3.1.1. Enhancement procedure

The work undertaken for this study involved carrying out 65 full VMD processes to allow for the compilation of data to aid in ascertaining a standardised VMD process. The VMD system requires an initialisation period before use and a shut-down period after treatments, these were found to be on average 43.86 ± 0.70 min (n = 7) and 39.00 ± 4.34 min (n = 4) respectively. The treatment process itself consists of three stages: the time taken for the pumps to reach a suitable high vacuum once the chamber has been loaded and sealed (pump-down time); the development time where the metals are deposited onto the substrate; and the time taken to vent the chamber so that it can be opened again. On average each treatment took 11 min in total, with the pump-down time making up 62 % of that time, and development by metal deposition only 19 % (see Table2). The low variation in the time taken to develop marks, regardless of donor or VMD method, indicates that multiple items can be treated at once in the chamber (see Table 2). However, only a brass substrate was used during these experiments, different substrates may have an effect on the development time required.

3.1.2. Mark persistence

The fingermarks of two donors were selected at random from the earliest treatments for re-evaluation. The purpose of which was to determine if marks developed by VMD on a brass surface would fade over time. Figs. 4 and 5 clearly show no difference in the clarity or detail of the marks over time indicating that over the period of 80 days there has been no fading. There was no difference in the grades given to the marks at re-evaluation and those initially received.

The marks of the above donors were also wiped after 80 days, first with a dry cloth and then with a damp cloth to establish print permanence. Rubbing with the dry cloth caused some minor fading, however the FRD detail was still clearly discernible with no overall impact to the quality of the mark. The addition of a cleaning reagent removed further detail, although faint ridges could still be seen.

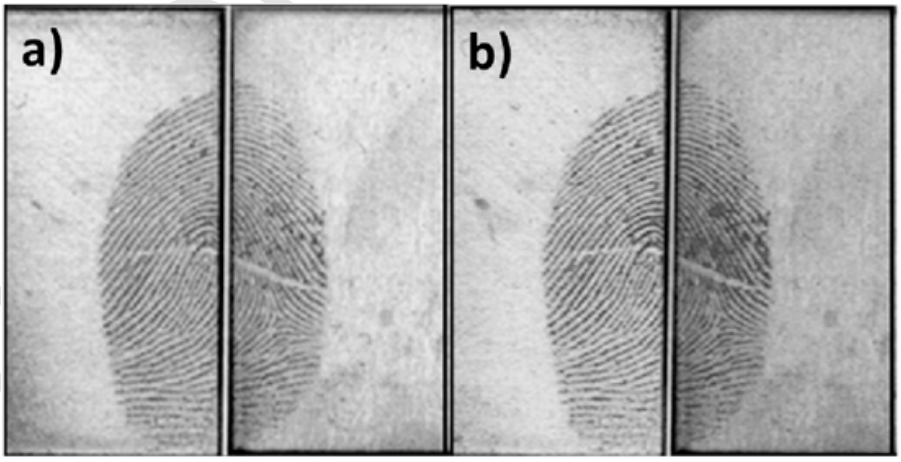

Fig. 4. Fingermark deposited by female donor A and developed by both Gold/Zinc (left tile) and Silver/Zinc (right tile) VMD **a)** initial photograph after enhancement **b)** same mark re-photographed after 80 days.

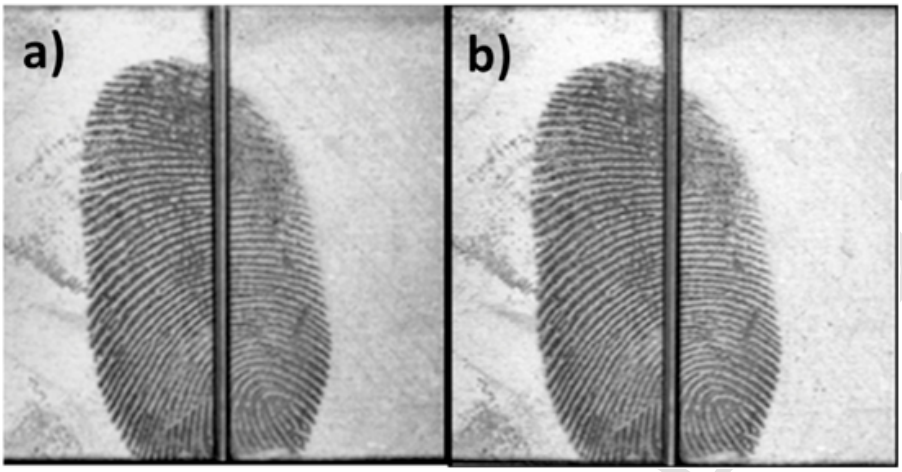

Fig. 5. Fingermark deposited by male donor M and developed by both Gold/Zinc (left tile) and Silver/Zinc (right tile) VMD : **a)** initial photograph after enhancement **b)** same mark re-photographed after 80 days.

3.2. Brass tiles

3.2.1. VMD treatments (metal deposition)

No significant difference was found between the Gold/Zinc and the Silver/Zinc VMD treatments for any of the groups of marks in the different aging categories at either the 99 % or 95 % CL (Wilcoxon Signed-rank for Gold/Zinc and Silver/Zinc comparison of day aged, week aged, month aged and two month aged marks respectively: $z=-0.33$, $p = 0.74$; $z=-0.86$, $p = 0.39$; $z=-0.33$, $p = 0.74$; $z=-1.47$, $p = 0.14$), as can be seen in Figs. 6 and 7 which display a similar pattern of development grades regardless of the VMD treatment. This is further illustrated below (Figs. 8–13) where it can clearly be seen that a comparable amount of development occurred on each half of the fingermarks. With the possible exception of the week aged and month aged marks deposited by donor D (Fig. 13, c–f), where more detail appears to be developed on the half of the mark treated by Silver/Zinc VMD. Whilst there appears to be some contaminant present particularly shown in Fig. 13c, potentially obscuring development, this pattern was seen throughout with this donor. It is therefore more likely that the cause was due to uneven pressure during donation, supported by the lack of this trend in the other donors.

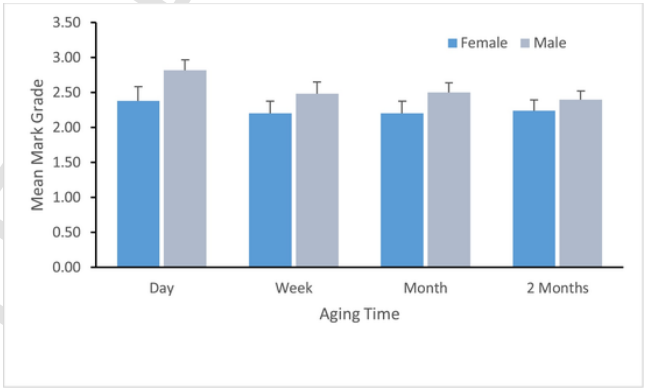

Fig. 7. Bar chart showing the mean average grades of female and male participants (n = 50) at each age interval from one day to two months, when treated with Silver/Zinc VMD.

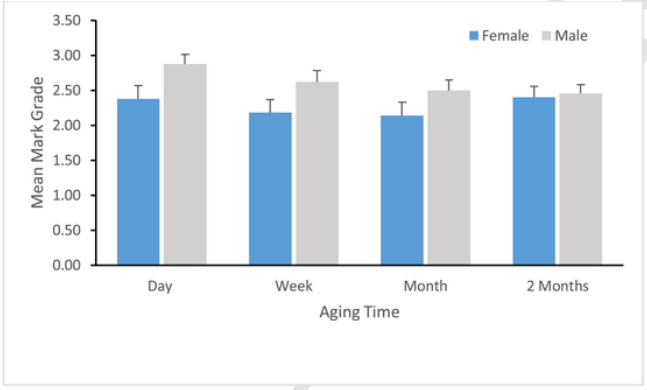

Fig. 6. Bar chart showing the mean average grades of female and male participants (n = 50) at each age interval from one day to two months, when treated with Gold/Zinc VMD.

This suggests that similar bonding occurs between the gold or silver atoms and the brass surface, resulting in analogous film structure and thus comparable development. Jones et al, determined that the film structure of the initial metal is dependent on how the bonding between the atoms compares to the bonding with the surface. The relationship alters the shape and size of the clusters and thus the effectiveness of

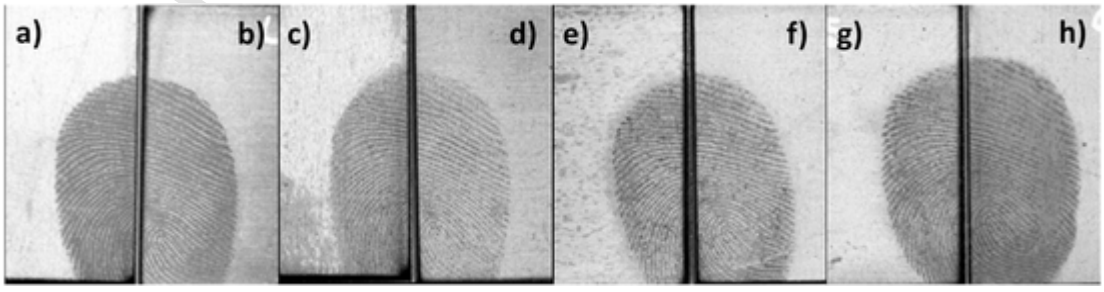

Fig. 8. Aged fingermarks of donor L (good quality male donor) treated with Gold/Zinc and Silver/Zinc VMD respectively. **a,b)** one day **c,d)** one week **e,f)** one month **g,h)** two months.

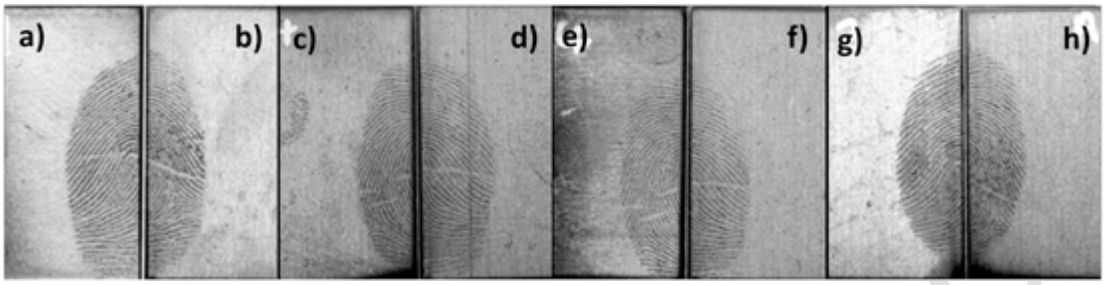

Fig. 9. Fingermarks of donor A(a good quality female donor) treated with Gold/Zinc and Silver/Zinc VMD respectively. **a,b)** one day **c,d)** one week **e,f)** one month **g,h)** two months.

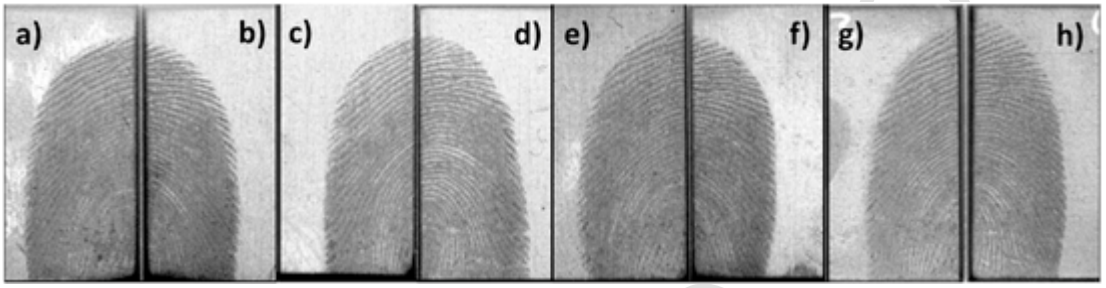

Fig. 10. Fingermarks of donor Q (a medium quality male donor) treated with Gold/Zinc and Silver/Zinc VMD respectively. **a,b)** one day **c,d)** one week **e,f)** one month **g,h)** two months.

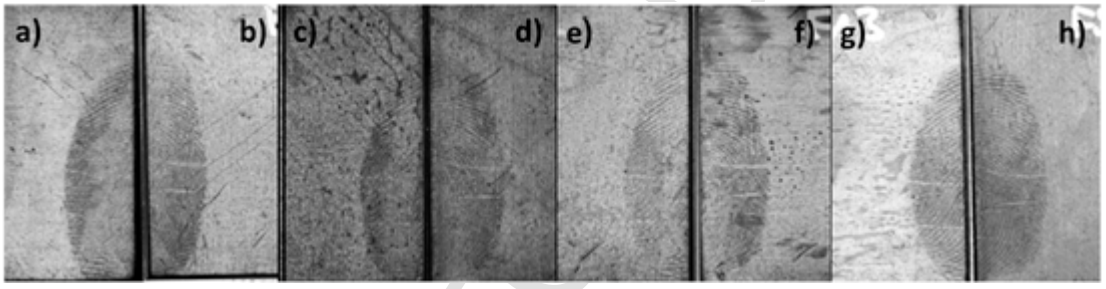

Fig. 11. Fingermarks of donor F (a medium quality female donor) treated with Gold/Zinc and Silver/Zinc VMD respectively. **a,b)** one day **c,d)** one week **e,f)** one month **g,h)** two months.

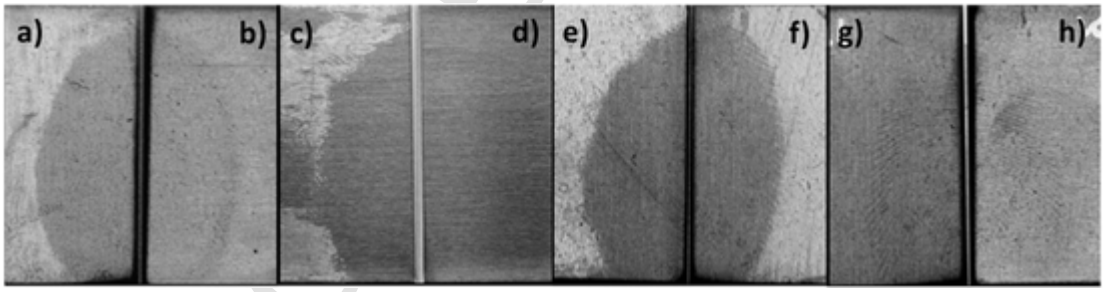

Fig. 12. Fingermarks of donor K (a poor quality male donor) treated with Gold/Zinc and Silver/Zinc VMD respectively. **a,b)** one day **c,d)** one week **e,f)** one month **g,h)** two months.

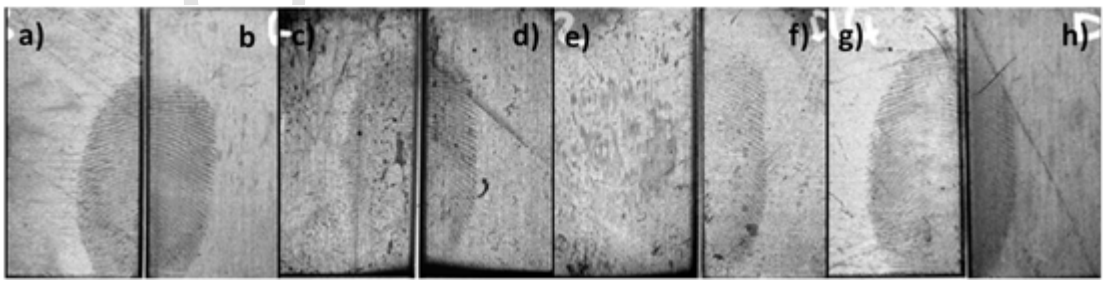

Fig. 13. Fingermarks of donor D (a poor quality female donor): treated with Gold/Zinc and Silver/Zinc VMD respectively. **a,b)** one day **c,d)** one week **e,f)** one month **g,h)** two months.

zinc deposition [19,22]. It would seem that gold and silver interact/bond with the brass substrate in a corresponding way. Therefore, the choice of metal deposition should be made based on contrast and availability of materials rather than any difference in performance.

3.2.2. Aged marks

Similarly, the amount that the print was aged had no significant impact on its development at either 99 % or 95 % CL (Kruskal Wallis tests for comparison across mark age groups of female Gold/Zinc marks, male Gold/Zinc marks, female Silver/Zinc marks and male Silver/Zinc marks respectively: $H(3) = 1.99$, $p = 0.58$; $H(3) = 6.44$, $p = 0.09$; $H(3) = 0.70$, $p = 0.87$; $H(3) = 6.62$, $p = 0.09$). This is illustrated by Figs. 6 and 7 which show very little variation in the mean grades produced over each of the age categories. Comparison of the developed fingermarks above (Figs. 8–13) also emphasizes this, similar levels of detail and development can be seen across the aged groups for each donor.

This provides further support for the sensitivity of VMD development [19,22], and its appropriateness for use on aged or degraded marks. In a study into the effects of vacuum conditions Bright et al. [23] found fingermarks lose around 26 % of their mass when exposed to a vacuum, equivalent to approximately five weeks of aging. The degradation caused by the VMD treatment itself indicates that the fingermark residue components involved in the reaction are likely to be those that are resistant to aging, which may explain the consistency in grades throughout the different aging conditions. However, these vacuum effects would need to be considered if planning sequential treatments, as some techniques that perform poorly on aged marks may not be suitable after VMD.

Whilst overall grades remained consistent regardless of aging or VMD treatment, some donors showed greater variation in the quality of their marks (Figs. 14 and 15). This could be a result of the donation procedure, by which a smudged or badly deposited repeat mark could have impacted the average for that time period. Generally, the grades were consistent enough to classify the donors as providing good, medium or poor quality fingermarks (see Figs. 8–13), interestingly the small amount of grade inconsistency appears to be more prominent with the poor quality donors ((e.g. Donors D and K,) Figs. 14 and 15). This suggests that the quality of the donor is the main contributing factor for consistency and quality of development as described by Girelli et al. [3]. Other work [23] reported that further exposure to vacuum conditions led to the loss of specific lipids such as tetradecanoic and pentadecanoic acid. Therefore, the fingermarks of donors who produce large quantities of these components may not develop effectively thus producing the poor-quality marks. Their study also exposed marks to a higher vacuum and a longer time than during a VMD treatment, meaning that vacuum effects in our study may not be as prevalent [20,23].

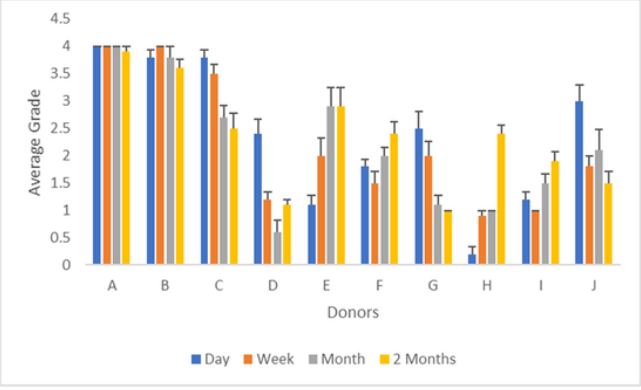

Fig. 14. Bar chart showing the mean average grades of female donors for each of the aging periods (n = 5).

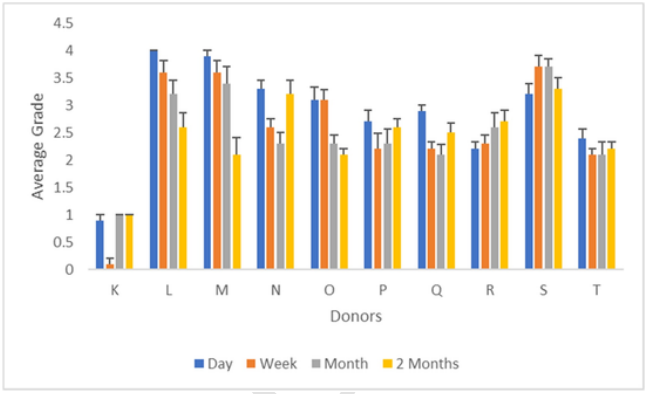

Fig. 15. Bar chart showing the mean average grades of male donors for each of the aging periods (n = 5).

3.2.3. Male and female donors

A comparison between male and female donors did show a significant difference for development times up to one month at the 95 % confidence limit only (Mann-Whitney for male and female comparison of day aged, week aged, and month aged marks respectively: $z = -2.26$, $p = 0.02$; $z = -2.34$, $p = 0.02$; $z = -2.06$, $p = 0.04$). The exception to this being for marks aged for two months (Mann-Whitney test for male and female comparison of two-month aged marks $z = -0.92$, $p = 0.36$) which were not significantly different at either CL (Figs. 6 and 7). Although the variation between male and female donors is small, it still poses an interesting question as to the cause. The average grade of male donors was marginally higher at 2.59 ± 0.05 (n = 400), compared to 2.27 ± 0.06 (n = 400) for female donors. However, the standard deviation of female marks was higher at 1.26 compared with males at 1.02, indicating that there was greater variation in fingermark grades for the female donors than the males (see Figs. 14 and 15). Both the male and female groups of participants consisted of a similar age range, 22– to 56 and 19 to 55 respectively, which should account for any impact of age on donation. However, the average age of male participants was slightly higher at 40.8 ± 3.51 (n = 10), compared to 34.9 ± 4.00 (n = 10) for females.

It has been theorised that many lifestyle factors such as diet and occupation have an impact on fingermark deposition. It therefore stands to reason that the use of skin or hair products and makeup may also be highly influential factors [35]. With a greater variety of these products targeted at the female population, it could be that their use within our sample contributed to the greater variation in grades. The generally larger surface area of male fingermarks could potentially contribute to a higher probability of recovering detail. With a greater area of the surface covered by FRD the likelihood of usable areas remaining after degradation is increased. However, this relates more strongly to the recovery of identifiable marks and it is unclear as to whether this could contribute to a difference in grades which are analysed proportionally. Differences in the quality of marks left by female and male donors have been briefly noted in other literature [3,27], however their sample sizes were small, often only containing one female donor, making it difficult to generalise the reliability of this finding.

3.3. Fired cases

Of the 18 fired 9 mm bullet cases only five showed clear signs of FRD being enhanced (Fig. 16). Where enhancement was visible, the ridges generally appeared well contrasted, although they lack some of the clarity seen in the initial phase experiments on brass tiles. In contrast to the brass tiles where a large part of the fingermark developed, at best only a fraction of the fingermark was developed on the bullet

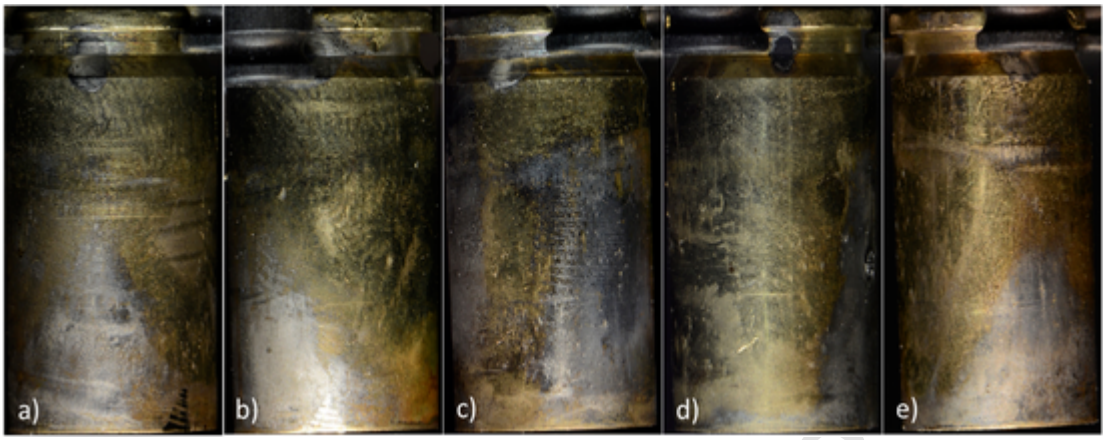

Fig. 16. Showing all five bullet cases with enhanced FRD: **a)** donor A (good quality female donor) repeat 1 of 3 **b)** donor A (good quality donor) repeat 2 of 3 **c)** donor D (poor quality female donor) repeat 1 of 3 **d)** donor L (good quality male donor) repeat 2 of 3 **e)** donor Q (medium quality male donor) repeat 1 of 3.

cases. This would make it highly unlikely that the FRD enhanced mark would be usable for identification, although some ridge characteristics were discernible (Fig. 16b and e)

It is likely that there are several contributing factors to this reduction in development. Firstly, - and perhaps most predominantly – the small size and high curvature of the 9 mm bullet casings reduce the area which comes into contact with the finger. This means it is likely that only a partial fingermark was deposited in the first place, reducing the chances of enhancing an identifiable mark. Furthermore, any degradation of a partial mark is likely to have far greater impact on what FRD can be developed and whether it is then identifiable.

Increased degradation of the fingermark and weathering to the surface is known to be caused by specific aspects of the firing process. Abrasive friction – a form of physical force - occurs between the cartridge and chamber wall as the bullet expands. Similarly, the blowback of hot gasses is thought to wipe away some of the fingermark and increase friction in the chamber [3]. High temperatures (up to 2000 °C) involved in the firing process are also mentioned as a contributing factor in several studies [2,14]. However, in Girelli's study [36] brass tiles were heated to first 63ºC - the maximum external temperature recorded for a 9 mm casing immediately after firing- and then 200ºC, and no prevention of fingermark visualisation was found. They suggested that temperature did not sufficiently reproduce the effects of firing and is unlikely to be one of the main factors affecting fingermark degradation. It is also likely that contamination of the surface occurs due to propellant by-products deposited during the blowback of hot gasses [3]. This is illustrated by Nizam et al. [14] who when treating fired cases found that zinc oxide formed on the surface obscuring FRD. This was likely to be due to a reaction with contaminants from the firing process.

Although previous studies have listed abrasive friction or the blowback of hot gasses as the primary cause of deterioration, there is a lack of consensus as to the most influential factor [3,37]. Whilst it is likely that several aspects of the firing process play an important role in the degradation of fingermarks, the results of this study suggest that contaminants from the firing process have had the most impact. Regions of the fired cases (both in the presence and absence of developed FRD) displayed zinc overdevelopment which appeared to preferentially aggregate onto areas of contaminant from the firing process resulting in a shiny silver covering over much of the casing, obscuring FRD that lay beneath. This occurred on all of the treated casings, and can be seen in Fig. 16 - particularly a),b),c) - where further FRD has been lost.

Previous study into the weathering of metal substrates found that brass was relatively resistant, showing no signs of coarse pitting to the surface [4]. In addition, the initial phase of this study demonstrated that age and vacuum related deterioration of the fingermarks had no impact on the development using VMD. This supports the theory that VMD enhancement should be relatively unaffected by many aspects of the firing process, and that the lack of viable enhancement seen on the fired 9 mm casings is related to their small size and reaction with contaminants (e.g. propellants) on the surface.

3.4. Fingermark residue composition

The GC–MS analysis of the fingermark constituents of the donors from a single fingermark, yielded some of the expected peaks of Squalene (27.14 min.), Methyl Stearate (16.81 min.), Stearic acid (16.54 min.), Palmitic acid (14.83 min.), Methyl tetradecanoate (12.76 min), most of which can be seen in donor A's (good female donor) chromatogram (Fig. 17a). The same substances have been found in fingermarks in other studies [38–40]. The internal standard was eluted at 11.3 min (not shown).

Interestingly, the aforementioned compounds seem to withstand the firing process, which is evident in Fig. 17b. As anticipated, their relative abundance is lower, due to a part of them being lost by the high temperatures reached during firing and the gas blowback within the barrel. Additionally, some extra peaks (phthalates) throughout the chromatogram have emerged which correspond to compounds commonly found in propellants [41], suggesting that propellant contamination remains on the cartridge surface after firing and their relative abundances can vary greatly from sample to sample.

Donor A produced the most samples with recoverable FRD from fired cartridge cases, and the highest graded marks on brass tiles, suggesting that the profile of the fingermark constituents yielded are those most likely to produce recoverable FRD. The profile produced by donor L – also a "good" donor with recoverable FRD from fired cases - showed similar peaks supporting this theory. However, an additional fingermark component of pentadecanoic acid (13.85 min.) was also detected in donor L's metal tile samples (Fig. 18a). Within the available donor pool for chromatographic analysis, pentadecanoic acid was not found in any other donor.

In some samples a number of components mentioned earlier were not detectable. Samples from donors classified as ''poor'' showed no Squalene and Methyl tetradecanoate, while the rest of the fingermark constituents were less abundant. This could be an indication that the combined presence of these compounds facilitates the enhancement of fingermarks by VMD.

Additionally, the ''poor'' donors D and K (Figs. 18b and 19) show the presence of Palmitic acid, Stearic acid,and Methyl stearate. Interestingly, one of the fired cases from donor D (female poor donor) exhib-

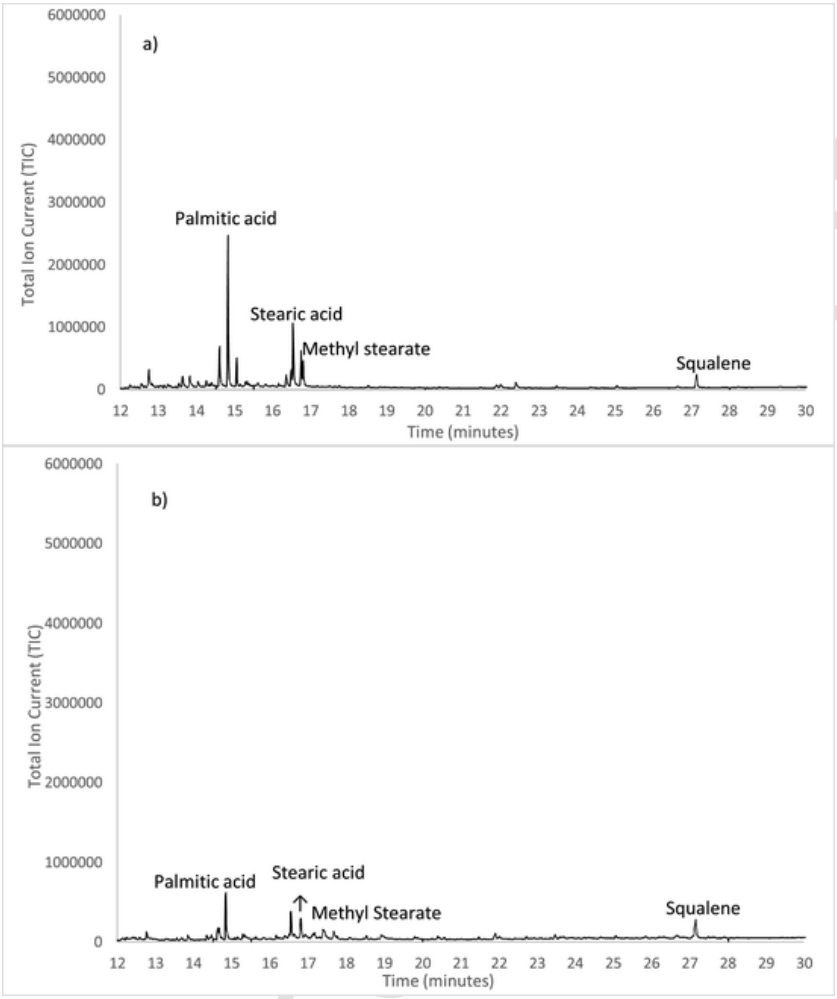

Fig. 17. Chromatogram (fingermark extract) of a good female donor (A) extracted from: a) brass tile; b) fired cartridge case.

ited some FRD enhancement after VMD treatment. Although both good donors (A and L) managed to produce at least one casing with recoverable FRD after firing, only one of the medium donors (Q) produced any enhanced FRD. Therefore, it appears additional compounds may be playing a role in VMD enhancement, possibly constituents of eccrine sweat, which were not investigated in this study.

The analyses demonstrated that Palmitic acid and Stearic acid were the most prevalent compounds for our donor group with Squalene being the third most prevalent. Palmitic and Stearic acid are more likely to withstand firing, compared to Squalene (or at least appear more abundant after firing).

Moreover, within the samples of donors A and L (classified as ''good'' donors) a greater quantity of Squalene was found relative to other donors. It is difficult however, to draw any rigid conclusions about the role of Squalene in VMD enhancement since, FRD was recovered from fired cartridge case of Donors D and Q, who were ''poor'' and "medium" donors respectively, with low relative abundance of Squalene. Therefore, a likely scenario is that the presence of squalene has a positive impact on FRD enhancement but it is not the prime contributor.

3.4.1. Principal Components Analysis (PCA)

An inter-donor variability study was carried out (Fig. 20) to investigate any similarities/differences between donors (in terms of compounds, compound ratio, or compound absence) that could elucidate the VMD enhancement mechanism.

The results depict a closer clustering of the donors that were classified as ''good'' (donors A and L) in comparison with the other donors. Principal Components 1 and 2 were identified as Palmitic acid and Stearic acid. There also appears to be a relatively close correlation between donor F's (medium female donor) chromatograms, resembling that seen with the "good" donors.

In contrast, the chromatograms of donors Q, K and D appear quite different, hence the greater distance from the clustering of A, L and F. Whilst the results are expected for donors Q and K (medium and poor donors respectively), as the other poor donor D was expected to be clustered with K. The lack of this cluster could be related to the variation seen in the average grades produced by donor D, or may indicate different underlying reasons for poor development seen with each of these donors.

Overall, some expected patterns are present, such as the close relationship of the chromatograms for donors A and L, backed up by the recoverable FRD on their fired cartridges. However, a clearer distinction between all the donors was expected, with distinct clusters for "good", "medium" and "poor" donors. The lack of this can be partially explained from the low number of fatty components that were recovered from the samples –especially from ''medium'' and ''poor'' donors. With regards to the recovery of fatty components, this could potentially be attributed to the solvent (MeOH) that was used. This together with possible contaminant co-extraction from the firing procedure (e.g. benzyl butyl phthalate. nitrocellulose) may impact on the efficacy of the extraction of the compounds of interest. Additionally, research [42]

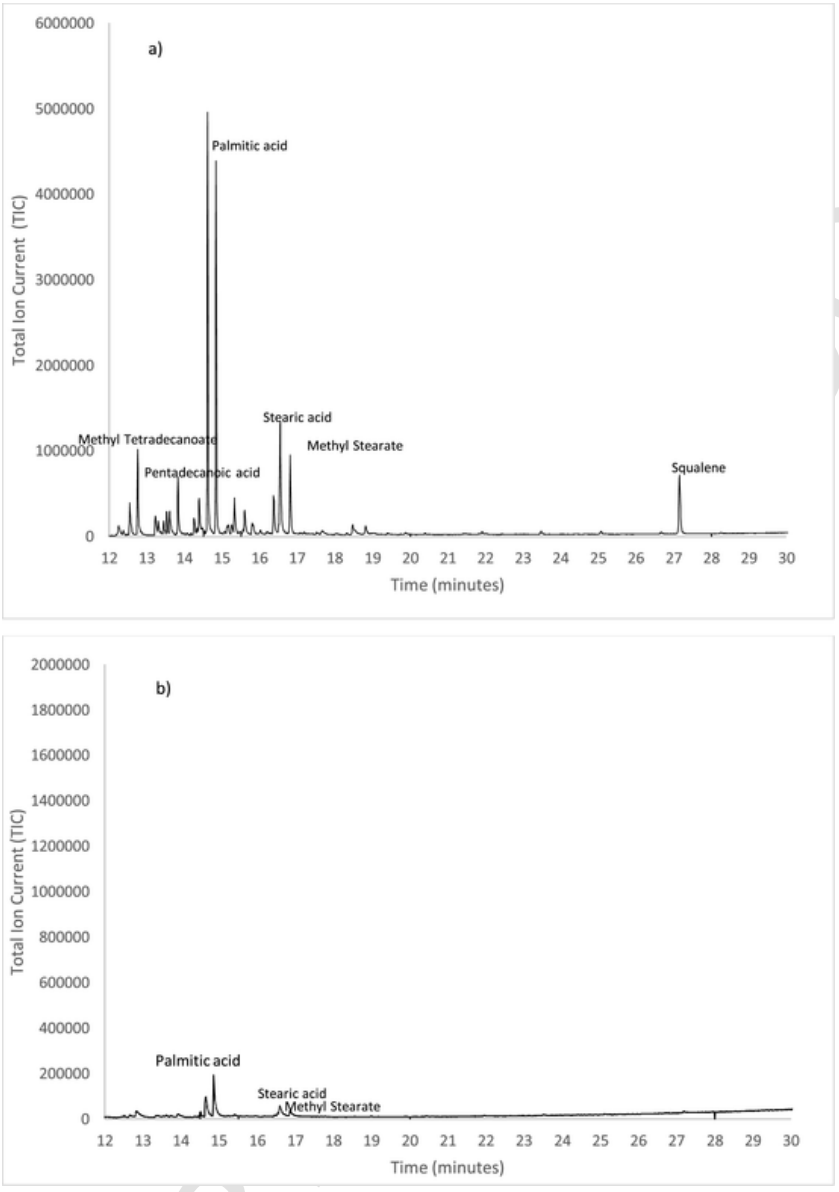

Fig. 18. a)Chromatogram (fingermark extract) of a good male donor (L). Fingermark extracted from a metal tile b)Chromatogram (fingermark extract) of a poor female donor (D). Fingermark extracted from a metal tile.

shows that results can vary greatly and that each individual fatty component interacts differently with different solvents.

4. Conclusion

This study shows that both Gold/Zinc and Silver/Zinc VMD treatments are effective methods of developing FRD on a ballistic brass surface. The treatment appears to be unaffected by the age-related deterioration of marks, with donor grades remaining relatively consistent for both male and female donors at all mark aging intervals. This finding suggests that the quality of the original print will determine the level of enhancement achieved, rather than an aspect of the VMD mechanism.

Although some variation was observed between the grades achieved by male and female donors (at the 95 % CI), the difference was marginal and potentially explained by lifestyle factors or inherent variability of fingermarks and their deposition, which would affect any development technique. It seems therefore that VMD, regardless of which deposition process is selected, is a highly effective technique for FRD enhancement on ballistic brass surfaces, particularly for aged samples.

Analysis of the fingermark compounds that play a facilitating role in VMD enhancement showed that generally a donor with a greater content of Squalene, Palmitic acid, and Stearic acid will produce better results when enhanced by VMD. These compounds also resisted degradation after the firing process. Additional work identifying all fingermark compounds (sebaceous and eccrine) and their degradation processes is recommended to further elucidate the mechanisms/ compounds responsible for FRD enhancement with VMD.

FRD from donors with these preferential components were also enhanced on fired brass cases. Although, VMD reaction with contaminants from the firing process obscured areas of the surface restricting the amount of visible FRD. On small rounds where it is likely that only a partial fingermark will be deposited, such as the 9 mm used here, the likelihood of the development of identifiable FRD is greatly reduced. However, the limited enhancement seen here, and the encouraging results seen on brass tiles, suggest that viable enhancement may be possible on larger calibre cases, if the original fingermark is of good quality and contains facilitatory compounds.

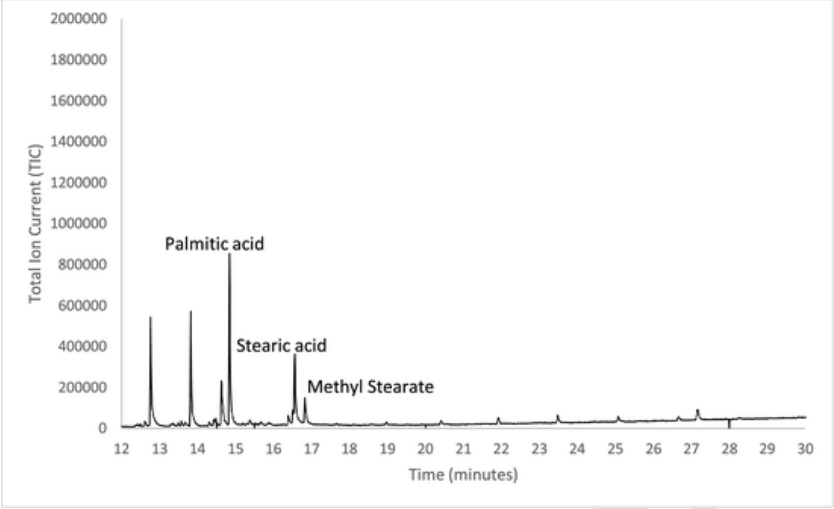

Fig. 19. Chromatogram (fingermark extract) of a poor male donor (K). Fingermark extracted from a metal tile.

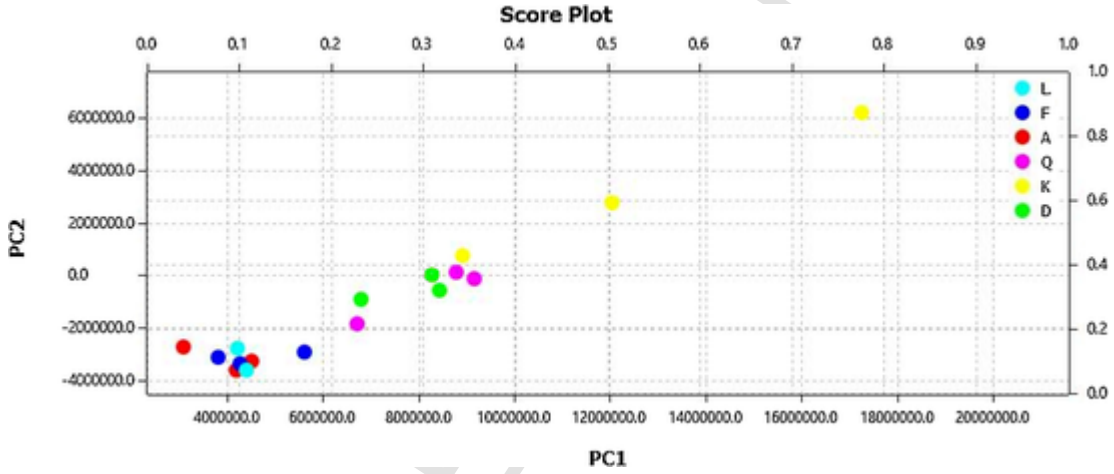

Fig. 20. PCA based on the Area under Curve chromatographic data from fired cartridge cases.

Authorship contributions

All Authors contributed fully in categories 1 (design and data acquisition), 2 (manuscript drafting), 3 (manuscript approval).

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgements

The authors would like to thank the School of Pharmacy and Biomolecular Sciences at Liverpool John Moores University for research funding through the Faculty of Science Ph.D Studentship Scheme, and Merseyside Police for access to the VMD.

References

[1] R.M. James, M.J. Altamimi, The enhancement of friction ridge detail on brass ammunition casings using cold patination fluid, Forensic Sci. Int. 257 (2015) 385–392.
[2] S. Liu, M. Pflug, R. Hofstetter, M. Taylor, The effect of pH on electrolyte detection of fingermarks on cartridge cases and subsequent microscopic examination, J. Forensic Sci. 60 (1) (2015) 186–192.
[3] C.M.A. Girelli, M.A. Vieira, K. Singh, A.G. Cunha, J.C.C. Freitas, F.G. Emmerich, Recovery of latent fingermarks from brass cartridge cases: evaluation of developers, analysis of surfaces and internal ballistic effects, Forensic Sci. Int. 290 (2018) 258–278.
[4] M. Pitera, V.G. Sears, S.M. Bleay, S. Park, Fingermark visualisation on metal surfaces: an initial investigation of the influence of surface condition on process effectiveness, Sci. Justice 58 (5) (2018) 372–383.
[5] J.W. Bond, Visualization of latent fingerprint corrosion of metallic surfaces, J. Forensic Sci. 53 (4) (2008) 812–822.
[6] Centre for Applied Science and Technology (CAST), Centre for Applied Science and Technology Fingermark Visualisation Manual, 2nd edn., Home Office Centre for Applied Science and Technology, Sandridge, St. Albans, 2014.
[7] K.J. Farrugia, J. Fraser, L. Friel, D. Adams, N. Attard-Montalto, P. Deacon, A comparison between atmospheric/humidity and vacuum cyanoacrylate fuming of latent fingermarks, Forensic Sci. Int. 257 (2015) 54–70.
[8] M. Paine, H.L. Bandey, S.M. Bleay, H. Willson, The effect of relative humidity on the effectiveness of the cyanoacrylate fuming process for fingermark development and on the microstructure of the developed marks, Forensic Sci. Int. 212 (1–3) (2011) 130–142.
[9] O.P. Jasuja, G. Singh, J. Almog, Development of latent fingermarks by aqueous electrolytes, Forensic Sci. Int. 207 (1–3) (2011) 215–222.
[10] Y. Zhang, M. Zhang, Q. Wei, Y. Gao, L. Guo, X. Zhang, Latent fingermarks enhancement in deep eutectic solvent by Co-electrodepositing silver and copper particles on metallic substrates, Electrochim. Acta 211 (2016) 437–444.
[11] A.L. Beresford, A.R. Hillman, Electrochromic enhancement of latent fingerprints on stainless steel surfaces, Anal. Chem. 82 (2) (2010) 483–486.
[12] G. Qin, M. Zhang, Y. Zhang, Y. Zhu, S. Liu, W. Wu, et al., Visualizing latent fingerprints by electrodeposition of metal nanoparticles, J. Electroanal. Chem. 693 (2013) 122–126.
[13] R.M. Sapstead, N. Corden, A. Robert Hillman, Latent fingerprint enhancement via conducting electrochromic copolymer films of pyrrole and 3,4-ethylenedioxythiophene on stainless steel, Electrochim. Acta 162 (2015) 119–128.
[14] F. Nizam, W. Knaap, J.D. Stewart, Development of fingerprints using electrolysis: a technical report into the development of fingerprints on fired brass cartridge cases, J. Forensic Identific. 62 (2) (2012) 129–142.

[15] J. Morrissey, J. Larrosa, J.W. Birkett, A preliminary evaluation of the use of gun bluing to enhance friction ridge detail on cartridge casings, J. Forensic Identific. 67 (3) (2017) 313–322.
[16] A. Dove, Fingerprint development on cartridge cases through the electrodeposition of gun blue, J. Forensic Identific. 67 (3) (2017) 391–409.
[17] G. Christofidis, J. Morrissey, J.W. Birkett, Detection of fingermarks—applicability to metallic surfaces: a literature review, J. Forensic Sci. 63 (6) (2018) 1616–1627.
[18] T. Kent, G.L. Thomas, T.E. Reynoldson, H.W. East, A vacuum coating technique for the development of latent fingerprints on polythene, J. Forensic Sci. Soc. 16 (1976) 93–101.
[19] N. Jones, M. Stoilovic, C. Lennard, C. Roux, Vacuum metal deposition: factors affecting normal and reverse development of latent fingerprints on polyethylene substrates, Forensic Sci. Int. 115 (1–2) (2001) 73–88.
[20] G. Christofidis, J. Morrissey, J.W. Birkett, A preliminary study on vacuum metal deposition as a standalone method for enhancement of fingermarks on ballistic brass materials, J. Forensic Sci. (2020) Last accessed: 31/07/19, doi:10.1111/1556-4029.14052.
[21] D. Philipson, S. Bleay, Alternative metal processes for vacuum metal deposition, J. Forensic Identific. 57 (2) (2007) 372–383.
[22] N. Jones, D. Mansour, M. Stoilovic, C. Lennard, C. Roux, The influence of polymer type, print donor and age on the quality of fingerprints developed on plastic substrates using vacuum metal deposition, Forensic Sci. Int. 124 (2–3) (2001) 167–177.
[23] N.J. Bright, T.R. Willson, D.J. Driscoll, S.M. Reddy, R.P. Webb, S. Bleay, et al., Chemical changes exhibited by latent fingerprints after exposure to vacuum conditions, Forensic Sci. Int. 230 (1–3) (2013) 81–86.
[24] P. Theys, New technique for bringing out latent fingerprints on paper: vacuum metallisation, Int. Criminal Police Rev. 23 (1968) 106–108.
[25] R.P. Downham, E.R. Brewer, R.S.P. King, V.G. Sears, Sequential processing strategies for fingermark visualisation on uncirculated £10 (Bank of England) polymer banknotes, Forensic Sci. Int. 288 (2018) 140–158.
[26] J. Fraser, K. Sturrock, P. Deacon, S. Bleay, D.H. Bremner, Visualisation of fingermarks and grab impressions on fabrics. Part 1: gold/zinc vacuum metal deposition, Forensic Sci. Int. 208 (1–3) (2011) 74–78.
[27] R. Steiner, A. Bécue, Effect of water immersion on multi- and mono-metallic VMD, Forensic Sci. Int. 283 (2018) 118–127.
[28] S.M. Bleay, P.F. Kelly, R.S.P. King, S.G. Thorngate, A comparative evaluation of the disulfur dinitride process for the visualisation of fingermarks on metal surfaces, Sci. Justice 59 (6) (2019) 606–621.
[29] A. Tiwari, I. Alaoui, S. Guddala, Enhanced visualization of latent fingermarks on rough aluminum surfaces using sequential Au and Zn/ZnS/ZnO depositions, J. Forensic Sci. 63 (4) (2018) 1275–1281.
[30] H. Dafydd, G. Williams, S. Bleay, Latent fingerprint visualization using a scanning kelvin probe in conjunction with vacuum metal deposition, J. Forensic Sci. 59 (1) (2014) 211–218.
[31] G. Williams, N. McMurray, Latent fingermark visualisation using a scanning Kelvin probe, Forensic Sci. Int. 167 (2007) 102–109.
[32] Office, for, National, Statistics Census:Key Statistics and Quick Statistics for Local Authorities in the United Kingdomhttps://www.ons.gov.uk/peoplepopulationandcommunity/populationandmigration/populationestimates/datasets/2011censuskeystatisticsandquickstatisticsforlocalauthoritiesintheunitedkingdompart12011Last accessed: 20/08/19
[33] International Fingerprint Research Group (IFRG), International Fingerprint Research Group guidelines for the assessment of fingermark detection techniques, J. Forensic Identific. 64 (2) (2001) 174–200.
[34] A. Koenig, A. Girod, C. Weyermann, Identification of wax esters in latent print residues by gas chromatography-mass spectromertry and their potential use as aging parameters, J. Forensic Identific. 61 (6) (2011) 652–676.
[35] V.G. Sears, S.M. Bleay, H.L. Bandey, V.J. Bowman, A methodology for finger mark research, Sci. Justice 52 (3) (2012) 145–160.
[36] C.M. Girelli, B.J. Lobo, A.G. Cunha, J.C. Freitas, F.G. Emmerich, Comparison of practical techniques to develop latent fingermarks on fired and unfired cartridge cases, Forensic Sci. Int. 250 (2015) 17–26.
[37] S. Wiesner, E. Springer, U. Argaman, A closer look at the effects of the shooting process on fingerprint development on fired cartridge cases, Neurim, International Symposium on Fingerprint Detection and Identification, 167, 1995, pp. 161–178.
[38] A. Girod, R. Ramotowski, C. Weyermann, Composition of fingermark residue: a qualitative and quantitative review, Forensic Sci. Int. 223 (1–3) (2012) 10–24.
[39] S. Cadd, M. Islam, P. Manson, S. Bleay, Fingerprint composition and aging: a literature review, Sci. Justice 55 (4) (2015) 219–238.
[40] A.A. Frick, G. Chidlow, S.W. Lewis, W. van Bronswijk, Investigations into the initial composition of latent fingermark lipids by gas chromatography–mass spectrometry, Forensic Sci. Int. 254 (2015) 133–147.
[41] E. Goudsmits, G.P. Sharples, J.W. Birkett, Recent trends in organic gunshot residue analysis, Trends Analyt. Chem. 74 (2015) 46–57.
[42] S.J. Cadd, L. Mota, D. Werkman, M. Islam, M. Zuiderg, M. de Puit, Extraction of fatty compounds from fingerprints for GCMS analysis, Anal. Methods 7 (2015) 1123–1132.