Alternative Strategies for Friction Ridge Detail Recovery from Ballistic Evidence

Georgios Christofidis

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Declaration of Originality

I, Georgios Christofidis, certify that I have written this PhD thesis. This original work is my own, except as specified in the references. All the information and literature sources utilised, have been specified throughout this manuscript. I further attest that neither this thesis nor the original work contained herein, has been previously submitted for a degree or for part of the requirements for a degree.

Georgios Christofidis

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Abbreviations

ATR-FTIR: Attenuated Total Reflectance – Fourier -Transform Infrared Spectroscopy

AFT-FTIR: Aerosol Flow Tube - Fourier -Transform Infrared Spectroscopy

CAST: Centre for Applied Science and technology

CCD: Charged Coupled Device

CL: Confidence Limit

DCS: Digital Capturing System

DFO: 1,8-Diazafluoren-9-one

DNA: Deoxyribonucleic Acid

ESA: Europium strontium aluminate

FTIR: Fourier – Transform Infrared Spectroscopy

GC/MS: Gas Chromatography-Mass Spectrometry

GSR: Gun Shot Residue

IFRG: International Fingerprint Research Group

ISO: International Standardization Organization

LED: Light Emitting Diode

LC-MS/MS: Liquid Chromatography- Mass Spectrometry/Mass Spectrometry

MALDI-MSI: Matrix-Assisted Laser Desorption Ionization—Mass Spectrometry Imaging

MALDI-MSP: Matrix-Assisted Laser Desorption Ionization – Main Spectra Profile

MMD: Multi Metal Deposition

MSD: Mass Selective Detector

NIR: Near Infrared Radiation

PBS: Pharmacy and Biomolecular Sciences

PCA: Principal Component Analysis

PEDOT: Poly (3, 4-ethylenedioxythiophene)

PLS-DA: Partial Least Square – Discriminant Analysis

RUV-VIS: Ultraviolet Radiation- Visible

SEM: Scanning Electron Microscopy

SERS: Surface-Enhanced Raman Spectroscopy

SIM: Single Ion Monitoring

SKP: Scanning Kelvin Probe

SMD: Single-Metal Deposition

SOP: Standard Operating Procedures

SPSS: Statistical Package for the Social Sciences

S&W: Smith and Wesson

TIC: Total Ion Count

TLC: Thin Layer Chromatography

UV-C: Ultraviolet light type C

VMD: Vacuum Metal Deposition

VSC: Video Spectral Comparator

Abstract

Fingermarks are one of the most important and frequently encountered pieces of evidence in a crime scene. Ballistic material may also be recovered from a crime scene where firearms have been involved. The current recovery rate of identifiable fingermarks on ballistic evidence is quite low. The study herein aims to improve the knowledge base in relation to the enhancement of fingermarks on ballistic surfaces by employing various fingermark enhancement techniques that have been underutilised, while also using Gas Chromatography - Mass Spectrometry and a new fingermark deposition protocol to further strengthen our understanding of mark enhancement. A quick and cost-effective Gun Blue protocol with exceptional results on unfired ballistic material that had been exposed to a variety of environmental conditions and some well enhanced fingermarks (from various donors) on cartridges fired by different firearms is studied and proposed as a routine police casework technique.

Vacuum metal deposition, a technique that was mostly visited for enhancing marks on plastic surfaces, is revisited for mark enhancement on ballistic material. The results of 2 different studies with different donor pools, showcase the suitability of the technique for brass surfaces and fired brass cartridge cases with a wide range of donors (20), while also being effective on older fingermarks (2 months old). Our results show the potential of VMD to be a used in police routine casework, when the surface in question is brass.

The use of Gas Chromatography - Mass Spectrometry lead to the identification and quantification of compounds that are able to withstand the extreme conditions of firing, and thus providing information on which fingermark enhancement methods would be the best candidates for fired cartridge cases. Squalene, palmitic acid and cholesterol were the compounds that were most consistently present in the fingermark samples, while also being less affected by the time elapsed after deposition. Our findings in this chapter explain the favourable results Gun Blue enhancement generated on old fingermark samples.

An artificial fingermark was created as a way to generate reproducible fingermarks by loading the fake fingermark with a precise amount of compounds found in fingermarks prior to each deposition. Our preliminary results demonstrate

the additional advantage of this protocol, which is the potential it has to pinpoint, which compounds facilitate fingermark enhancement for different development methods. This could result in a better understanding of all fingermark enhancement methods and therefore could lead to improved recovery rates of fingermarks.

1. Introduction to Fingermarks-Chemical Profile and Further Considerations

Abstract:

Fingermarks have a key role in criminal investigations and are the most commonly used form of evidence worldwide. This chapter describes the characteristics, topography and composition of fingermark residue as being a multifactorial structure with a very large number of constituents coming from different sources. The initial composition (corresponding to the composition of the mark right after deposition) to the aged composition (corresponding to the evolution/degradation of the initial composition over time) can vary greatly depending on the circumstances/conditions. This review highlights variations in composition due to donor characteristics and environmental variables whilst giving the reader the necessary background information to obtain a better understanding of fingermark research and this PhD thesis in its entirety.

Introduction

Fingermarks are considered one of the most valuable types of physical evidence recovered from a crime scene [1,2]. It has never been shown that two individuals share the same fingermarks. Subsequently, fingermarks can be used for identification purposes [3-4]. Three types of distinctive features can be recognized in the fingermark identification process. The first type, level one features, is the macro detail of the ridges. Arches, whorls, loops, and/or a combination of the aforementioned groups, as shown in figure 1. Level two features include characteristic details, called minutiae and include the more specific appearance of the ridges (see figure 1, second row). A line unit or dot is a short fragment between two ridges, whereas a line-fragment is a bit longer than a line-unit. Endings are defined as the place where a ridge ends abruptly. The location where a ridge is split into two ridges is called a bifurcation. An eye or island is formed by two opposing bifurcations [5]. Level two features have

sufficient discrimination power and can therefore be used in the identification process. The last characteristics, the level three features, include scars, pores and line shapes (Figure 1) [3-4]. Level three features are also described as unique and immutable and can therefore be used in the identification process [4].

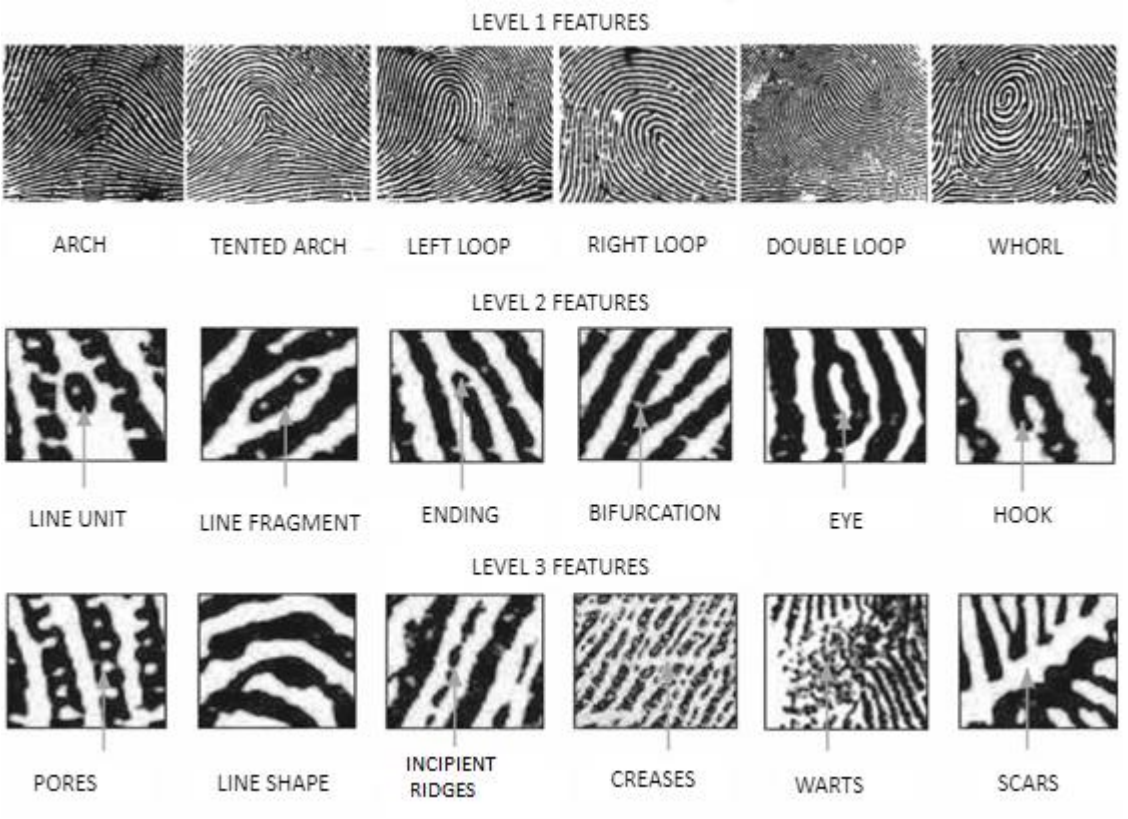

Figure 1. The different features found in fingermarks [3]

Most of the fingermarks found at crime scenes are classed as latent (invisible to the naked eye) and need development before the ridge pattern can be visualised. A variety of fingermark development techniques are available, including physical, chemical and luminescent techniques, such as powder dusting, ninhydrin spraying and cyanoacrylate fuming [6].

The best suitable method for the visualisation of latent fingermarks is determined by the substrate upon which the fingermark is deposited [6]. The selection of a suitable technique depends on different factors, such as the expected composition of a fingermark, the ability of the chosen technique to be used in tandem with other techniques, and the nature of the substrate. A developed and recovered fingermark, however does not always lead to the identification of a donor.

A limiting factor (apart from the quality of the enhanced fingermark) can also be the current availability of fingerprints registered in databases. The main challenge in fingermark studies is the highly variable (in terms of compounds) content of fingermarks [4], which makes the establishment of a standardised approach for their development/visualisation a very difficult task. Previous research on fingermark composition has focused on optimizing existing fingermark visualisation methods or on the development of novel visualisation methods [5-10]. Additionally, both the effect of time and donor-specific characteristics (*i.e*. gender, diet) and their implications on fingermark composition have been previously studied and their findings are critically examined in this Chapter [11-17].

1.2 Fingermark composition

Sweat secretions comprise a large part of fingermarks and contain mostly organic compounds [21]. In addition, a mixture of compounds from the dermis and epidermis, along with metabolites, traces of drugs/medication, and extrinsic components such as grease, dirt, make-up, oil, remnants of food and nicotine metabolites, and even traces of explosives and gunshot residue [22-27] make fingermarks a very challenging physical evidence for analysis. The complexity of analysing fingermark composition increases even more when factors as donor variability and time of deposition, are taken into consideration.

Fingermark composition is generally divided in two phases [4, 21]. The deposition phase, which consists of the compounds left on a substrate immediately after contact. The aged state, which consists of the deposition phase compounds but also of compounds created/emerged after deposition occurred. These two phases are influenced by different factors, as highlighted on Figure 2. Specifically, the deposition composition is affected by donor characteristics such as race, gender, diet, age, health and any deformations/scars [14, 28, 29] on the fingertips of the donor. The circumstances under which the deposition occurred, also plays a role, this includes the nature of the contact of the donor with the substrate (angle of contact, amount of pressure exerted etc.). Environmental conditions and lastly the nature of the substrate (porous, non-porous) are also important.

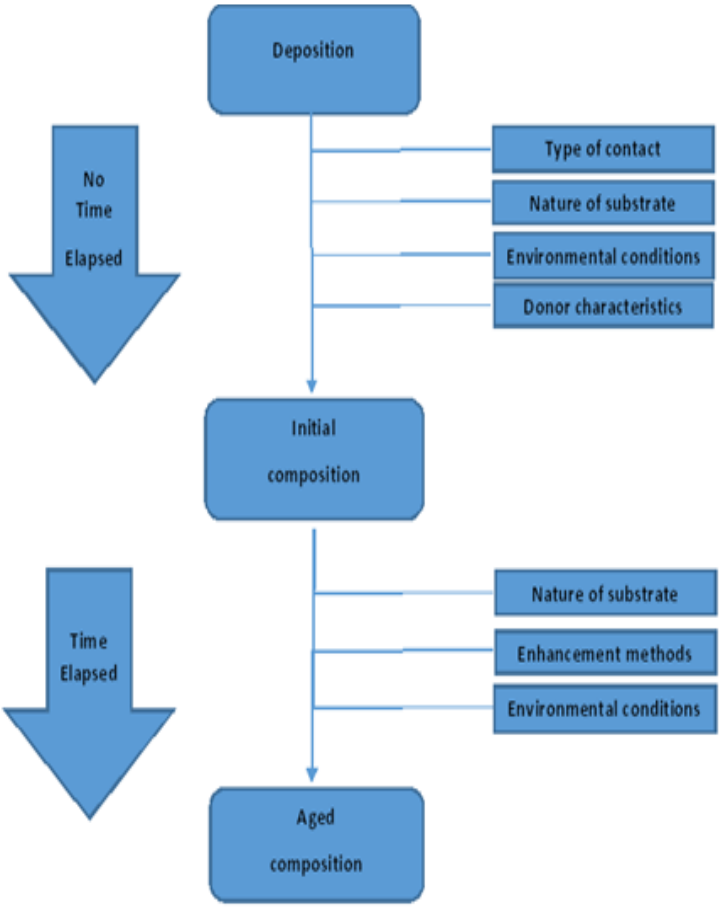

Figure 2. Factors influencing fingermark composition before and after deposition occurs, scheme adapted from [4].

The aged state (of a fingermark) is influenced by the time elapsed after deposition. Some compounds increase in concentration (*i.e*. protein oxidation products) while others are depleted (*i.e.* squalene) after a certain time threshold [30, 31]. Environmental conditions and the nature of the substrate play a significant role as well, as these factors can have a dramatic influence on the composition of fingermarks (*e.g.* photo-oxidation reactions)[21] . For example, certain amino acids and proteins are better retained when a fingermark is deposited on to a porous material and kept under dark conditions. This information is of importance for some enhancement techniques such as development of latent fingermarks with Ninhydrin[32]. Previous research on metallic surfaces suggested that humidity at 80% is beneficial for the development of fingermarks with cyanoacrylate fuming[33]. The final step of an aged composition, is the composition of a fingermark, after an enhancement method has been applied to it.

There are 3 main glands to be found throughout the human body, the eccrine, apocrine and sebaceous glands, each different gland produces sweat that has some different components.

Eccrine glands are present in every part of the body, but they appear in larger numbers in the palms and soles areas. Apocrine glands are found in the armpits and in the genital area (also known as axillary regions). Sebaceous glands are mostly present in the hairy areas of the body (head, face) but may also be found in the scalp[34].

As far as fingermark composition is concerned, the sebaceous and eccrine glands are usually the glands that contribute to their composition. Nevertheless, there is always a chance that the apocrine glands may contribute to a fingermark's composition. According to Farkaš R. [35], the secretions from the

apocrine glands are primarily rich in proteins, rather than being rich in oily substances (*i.e*. wax esters). Iron has also been reported in apocrine sweat.

Different compounds are detected in sweat originating from sebaceous glands (Table 1) and eccrine glands (Table 2). Fatty acids, glycerides, wax esters, are some of them, along with squalene and cholesterol, all of which have been previously identified [31].

Table 1. Compounds of eccrine origin in fingermark residue (table adapted from [4])

Compounds	**Quantity (per fingermark)**	**Reference**
Proteins	384 µg	[36, 37]
Polypeptides	-	[3, 38-41]
Lactic acid	9-10 µg	[34]
Chloride	1-15 µg	[42]
Amino acids	0.2-1 µg	[43, 44]
Urea	0.4-1.8 µg	[45]
Sodium	0.2-6.9 µg	[46]
Potassium	0.2-5 µg	[47]
Ammonia	0.2-0.3 µg	[47]
Ammonium	5.13mM	[46]
Phenol	0.06-0.25 µg	[46, 47]
Calcium	0.03-0.3 µg	[46, 47]
Sulphide	0.02-0.2 µg	[47]
Magnesium	1.67 µM	[46]
Choline	-	[48]
Uric acid	150 µM	[46, 47]
Vitamins	-	[49]
Creatinine	-	[46, 47]

Table 2. Compounds of sebaceous origin in fingermark residue (table adapted from [4])

Compounds	Quantity (per fingermark)	Literature
Free fatty acids	37.6%	[11, 30, 43, 45, 50]
Wax esters	25%	[3, 11, 51]
Diglycerides		[3, 11, 51]
Triglycerides	21%	
Monoglycerides		
Cholesterol esters		[52]
Squalene	14.6%	[11, 31, 53, 54]
Squalene oxidation products	-	
Cholesterol	3.8%	[11, 13, 55-57]

1.3 Organic compounds

Due to the abundance of organic compounds in fingermarks, numerous attempts have been made in identifying and quantifying these compounds in fingermarks. This endeavour is not always easy due to the often low concentration of proteins in a fingermark sample. Although, when it comes to compounds excreted from eccrine glands, research [43, 44] shows that proteins and amino acids are the largest group of compounds present in a fingermark.

Amino acids are easier to detect and quantify compared to proteins and are of great interest for forensic purposes, as they play a key role for visualisation methods of latent fingermarks. The persistent nature of amino acids especially on a porous substrate has assisted their study. The majority of the amino acids identified in fingermarks was by means of extraction using different solvent systems(*e.g*. a sodium hydroxide, ethanol, and pyridine system), derivatisation and then by employing GC/MS [43]. The presence of some amino acids and proteins was inferred by performing TLC on fingermarks and then checking the fluorescence spectra of the stains which were developed and comparing them

with literature spectral data [16]. Serine is (usually) the most abundant amino acid (Table 3 and Figure 3) found in fingermarks[53, 58] but that is not always the case for all fingermarks, as compounds like glycine and ornithine have been reported to be present in similar amounts [43].

Vitamins have also been found in fingermarks (as was shown on Table 1). Riboflavin (vitamin B2) is likely to be a major contributor to a fingermark's fluorescence, and pyridoxal (vitamin B6) and thiamin (vitamin B1) are also likely to be part of fingermark residue[15]. Urea and uric acid have also been reported in fingermarks.

Table 3. Amino acids present in sweat based on [59,60,61,62], table adjusted from [21]

Amino acids (Relative Abundances)	**Hadorn et al. [59]**	**Hamilton[60]**	**Oro et al.[61]**	**Croxton et al.[62]**
Serine	100	100	100	100
Glycine	54	67	59	42
Ornithine	45	32	45	-
Aspartic acid	11	22	22	25
Theonine	9	17	18	-
Histidine	13	17	14	-
Valine	10	12	9	10
Leucine	7	10	10	7
Isoleucine	6	8	8	8
Glutamic acid	12	8	5	8
Lysine	5	10	-	-
Phenylalanine	5	7	5	5
Tyrosine	5	6	5	-
Cysteine	-	-	-	5
Proline	-	-	-	7
Asparagine	-	-	-	25

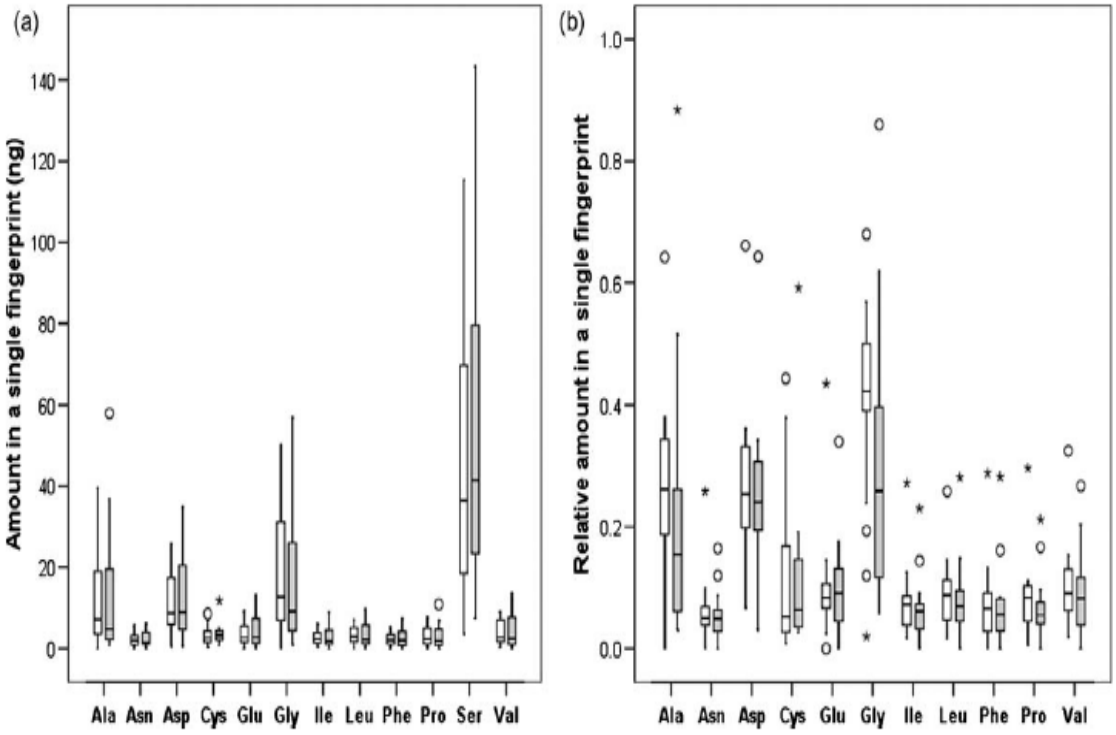

Figure 3. Amino acid content in fingermarks. (a): amino acids shown in nanograms, (b): in relation to serine. The shaded boxes represent fingermarks rich in sebaceous sweat while the non-shaded boxes represent fingermarks poor in sebaceous sweat. [62]

Although in the studies of Hadorn et al.[59], Hamilton[60] and Oro et al[61], ornithine was the third most abundant amino acid, quantification was not possible in the study by Croxton et.al[62] due to its inconsistent behaviour. This difference could be attributed to the different sampling procedures.

Fatty acids

All analytical techniques used in previous studies have shown that fatty acids (Table 4) are present in abundance in all fingermark samples. The concentration of fatty acids in a fingermark sample fluctuates over time, which is something that will be examined further in this chapter. Table 4 provides a summary of the fatty acids identified and quantified in fingermarks.

Table 4. Fatty acids in fingermarks. Cn: carbon number, DBn: number of double bonds

Fatty acids(Cn:Dbn)	**ng**	**Literature**
Octanoic acid (8:0)	-	[43]
Nonanoic acid (9:0)	-	[51, 63]
Decanoid acid (10:0)	68	[43]
Tridecanoid acid (13:0)	21-69	[51]
Myristoleic acid (14:1)	10-428	[51]
Myrisctic acid (14:0)	16-712	[64]
Pentadecenoic acid (15:1)	-	[51]
Pentadecanoic acid (15:0)	23-720	[51, 65]
Palmitoleic acid (16:1)	0-4326	[66]
Palmitic acid (16:0)	75-1637	[51, 65]
9-Hexadecanoic acid (16:1)	-	[67]
Margaric acid (17:0)	6-316	[67]
Heptadecanoid acid (17:1)	8-450	[67]
Linoleic acid (18:2)	33-277	[43, 67]
Oleic acid (18:1)	32-1675	[65]
Petroselenic acid(18:1)	-	[29]
Stearic acid (18:0)	22-904	[65, 68]
Nonadecanoic acid (19:0)	-	[69]
Eicosanoic acid (20:0)	9-43	[70]
Heneicosanoic acid (21:0)	-	[65, 68]
Docosanoic acid (22:0)	-	[53, 70]
Tricosanoic acid (23:0)	-	[53, 70]
Tetracosanoic acid (24:0)	18-69	[53, 69, 70]

Squalene

Squalene has been the subject of many fingermark studies [3, 30, 31, 55, 71, 72]. It is a triterpene (C_3H_{48}), steroid precursor. Squalene is one of the compounds that is repeatedly found in fingermarks despite the expected inter- and intra-donor variations. Quantification of squalene was possible in previous research [30], along with identification of some of its oxidation products (hexanedioic, pentanedioic acid). Additionally, intermediate products were identified such as epoxides, ketones and squalene hydroperoxides. Polymerisation with squalene as a parent compound has also been reported in one study [30]. Identification of high and low molecular weight products was possible.

Cholesterol

Cholesterol is also frequently found in fingermarks. This compound is secreted by the sebaceous glands and it is the most abundant sterol in the human body[34]. Cholesterol has also been quantified and reported to decrease in concentration with time, which makes it a strong candidate for a reference substance when it comes to estimating the age of deposition of a fingermark[11]. Cholesterol has been reported to interact with the fatty acid and triglyceride content of fingermarks, but this phenomenon needs further examination [73]. Lastly, susceptibility to oxidation has been observed, along with some esterification processes[56, 72, 73].

1.4 Inorganic compounds

The inorganic components of fingermarks (Tables 5, 6) are less explored compared to their organic counterparts. This is mainly due to their smaller representation in a fingermark sample. Despite their smaller quantity, valuable information could be extracted by the inorganic components of a fingermark. Previous research has suggested that a slight decrease in the concentration of chloride occurs[42], although this decrease is not substantial, it could potentially be monitored in tandem with the other decreases that occur in the organic constituents of a fingermark, in order to develop a potential age estimation method. Other research using ion chromatography, showed that the detection (and even quantification) of anionic energetic material is possible even in fingermarks processed with the usual visualisation methods[74]. This finding could be of importance when trying to detect traces of explosive material in one's fingermarks.

Table 5. Inorganic constituents of fingermarks [21,75]

Compounds	**Quantity (per fingermark)**
Nitrite	0.5 ng/mL
Cyanate	0.4 ng/mL
Chlorate	1.3 ng/mL
Nitrate	1.1 ng/mL
Thiocyanate	2.6 ng/mL
Perchlorate	4.4 ng/mL

Table 6. Inorganic constituents of eccrine sweat

Compounds	**Quantity**	**Literature**
Chloride	3.5 g/L	[21, 75]
Sodium	3.3 g/L	[21, 75]
Potassium	0.2 g/L	[21, 75]
Iron	3.5 g/L	[21, 75]
Calcium	0.002 g/L	[21, 75]
Sulphate	0.0010 g/L	[21, 75]
Phosphate	0.0014 g/L	[21, 75]
Fluoride	$6{,}9 \times 10^{-6}$ g/L	[21, 75]
Bromide	35×10^{-6} g/L	[21, 75]
Iodide	0.85×10^{-6} /L	[21, 75]
Magnesium	traces	[21, 75]
Zinc	traces	[21, 75]
Copper	traces	[21, 75]
Cobalt	traces	[21, 75]
Lead	traces	[21, 75]
Manganese	traces	[21, 75]
Molybdenum	traces	[21, 75]
Tin	traces	[21, 75]
Mercury	traces	[21, 75]

1.5 Extrinsic components

Another layer of complexity in fingermarks comes from the presence of extrinsic components such as drugs, food contaminants, cosmetics residue (face or body cream, perfume), gunshot residue, explosives and nicotine and cotinine (nicotine is a compound found in cigarettes and cotinine is its metabolite)[24, 25, 27, 74, 76]. Although from a purely scientific point of view the presence of extrinsic components might be useful to investigate, for example, if cotinine is found in fingermark residue then we know the donor is a smoker, and that additional information could help identifying a perpetrator. However, in routine casework this information is rarely helpful. This might be also the reason behind the lack of extensive research available, when it comes to these kinds of substances.

Nevertheless, the methods that provide further intelligence relating to the donor of fingermarks have been studied, due to some added benefits they can provide, such as the consolidation of the evidential value of fingermarks, and the ability of these methods to be used on smudged fingermarks.

Specifically, in cases where explosives where used by the donor, a custom made micro ATR-FTIR has been utilised and it was shown that a successful identification of explosive compounds is feasible with this minimally invasive method[77].

Detection of drugs and their metabolites was proven to be feasible even in fingermarks that were visualised with one of the conventional methods (*i.e.* cyanoacrylate fuming)[78]. The metabolites did not seem to interact/react with the fingermark enhancement technique nor create any issues in the extraction of the fingermark. This finding might strengthen the use of donor profiling techniques in real cases.

1.6 Changes in fingermark composition with time

The changes of fingermark composition with time is a topic that has been extensively examined, but due to its complexity definitive or conclusive results for fingermark age estimation have not been yet obtained. The added benefits of acquiring insights on how time affects the reaction mechanisms and kinetics in a fingermark, are, having the ability to develop better enhancement techniques for fingermarks (since it will be known which compounds are targetable in an aged fingermark sample), and also developing a reliable and robust fingermark age estimation method.

Loss of Water content

Originally, it was believed that fingermarks consisted of around 98% water[12]. Further research showed that most latent fingermarks weigh somewhere around 4 to 10 μg and over the course of few weeks this weight drops 30% to 80% from its original value. This decrease in weight is mostly caused by the evaporation of water but other volatile compounds are also evaporated. The main issue from a forensic point of view is that the loss of water is reducing the success of development methods due to the to the reduced reaction surface area, which is caused by the absence of water and the rise of organic compounds which form a layer that may hinder further reactions[67].

Changes in Organic compound composition

Amino acids and proteins display a relative stability over time. Amino acids have been also found to produce some other compounds with time. Research [21] suggests that the nature of the substrate plays a role in the preservation of amino acids and proteins over time. For example a very porous substrate can preserve a print longer due to the fact that a lot of print material will be protected from environmental factors by being inside the substrate's pores.

Changes in Fatty acid composition

Saturated fatty acids have been found to remain stable over time[79]. Nevertheless, this is not the case for short chain fatty acids, which show an increase in their concentration over the period of 15 days after deposition. It is inferred that this increase is linked with the breakdown of wax esters/glycerides that are also present in a fingermark [79]. After the initial increase in unsaturated fatty acids, a decrease was observed which could possibly be attributed to the degradation of those compounds. In general, due to the lack of an active functional group, saturated fatty acids remain for a longer duration in a fingermark compared to their unsaturated counterpart[80]. Unsaturated fatty acids have been observed to decrease with time. Chain reaction processes form compounds like aldehydes and ketones from the available fatty acids[81].

Changes in wax ester composition

The lack of an active functional group makes wax esters a group of compounds that remains mostly unchanged with time. Research [51] has shown this property of wax esters might be a helpful to estimate the age of fingermarks by including the ratio of a certain wax ester along with squalene and cholesterol. Nevertheless, extensive research still has to be done about wax esters and their degradation products.

Changes in squalene concentration

Squalene has been extensively studied [11, 31]. Most studies report a rapid decrease over time, and usually within a week squalene is completely absent from a fingermark sample[31]. This decrease is also dependent upon the surface the fingermark is developed on. Squalene forms degradation products from normal oxidation but also from photo oxidation[54, 72]. Studies have shown that fingermarks stored under dark conditions can preserve (up to a certain extent) their squalene content for up to 33 days[31].

Changes in cholesterol concentration

Cholesterol also shows a decrease in concentration over time[11]. The decomposition of cholesterol seems to be connected to the presence of fatty acids and triglycerides meaning that the cholesterol decomposition products can vary depending on the availability of the aforementioned compounds [57]. Cholesterol has been found to form a large number of oxygenation products, which can differ depending on the general health of the donor [56].

1.7 Changes in Fingermark composition due to environmental factors

The most studied and frequent environmental conditions are: Temperature, humidity, exposure to light, dust, exposure to air currents, contamination by the atmosphere and contamination from nearby surfaces/materials [82].

Temperature

An increase in the temperature of the environment leads to a faster depletion of the water content of fingermarks[83]. Under extreme heating conditions certain degradation products of amino acids have been reported to arise (*i.e.* maleimide), additionally Harper et al. (83) report a gradual degradation in all amino acids they tested starting from 100°C. This degradation could be the reason behind the reduced effectiveness of development methods that target amino-acids, when the fingermarks were exposed to heat prior to development [84]. Urea, and esters were found to decompose faster at higher temperatures [38, 39].

Humidity

Humidity appears to be an important factor when it comes to enhancing fingermarks. Cyanoacrylate fuming has been examined and found to be more efficient when the humidity inside the development chamber is 80%. An explanation of this phenomenon could be that the polymerisation which occurs in the ridges of the fingermark is facilitated by the presence of water molecules [85, 86]. Other enhancing methods like DFO, ninhydrin and indanedione have been examined in different humidity conditions, and the results showed that humidity is not impacting the development of fingermarks [87].

Exposure to light

Several authors have found decomposition mechanisms in fingermarks, which appear to be light dependent [30, 88]. Decomposition of squalene has been largely attributed to photo-oxidation mechanisms; its concentration was significantly decreased after 2 weeks when the fingermark sample was left under light. Squalene decomposition also occurs when a fingermark sample is left under dark conditions, but to a lesser degree. Cholesterol and other fatty acids also decomposed in fingermarks that were kept under light conditions [30, 88].

1.8 Fluctuations in fingermark composition due to deposition conditions and substrate nature

The following can all affect the composition of a fingermark: The pressure and the duration of the contact, the amount of time since the donor had washed his/her hands[89, 90]. Moreover, the areas of the body recently touched prior to deposition, the substrate on which the deposition took place can all have an effect on the composition of a fingermark. The nature of the substrate can help the preservation of some compounds (paper has been reported to preserve amino acids). On the other hand, a non-porous substrate (*i.e*. metal) usually makes a fingermark sample more prone to damage, due to the greater availability of the fingermark's constituents to extrinsic factors.

Other aspects that may contribute to the alteration of the chemical composition of a fingermark sample are the dimension of the fingermark deposited and the time of day that the fingermark was deposited, but research so far is inconclusive. The finger that was used to deposit the fingermark appears to have an effect in the composition [91]. Specifically, in a previous study [21], the left hand fingers, deposited a smaller amount of chloride compared to right hand, and the middle fingers, index, and thumb showed the same tendency. This observation can be due to the fact that most people are right handed and lose more secretions from their right hand since it is the hand that is used most of the times. The same is true for the fingers that are most frequently used.

1.9 Inter and Intra donor variation in fingermark composition

Gender

Various research has been done in an attempt to determine differences in the composition of fingermarks that are due to the different gender of the donor. Michalski et al. used GC/MS and focused on fatty acids and their abundance in different samples[29]. No discrimination was possible, although Asano et al. [14] using the same method reported a difference in the levels of fatty acids between men and women, with men having a slightly larger amount on average. Croxton et al. used also GC/MS and focused on the amino acids found in fingermarks and found that fingermarks deposited by female donors had slightly larger amount of amino acids, with the main difference being on the levels of asparagine[53]. Apart from GC/MS, MALDI-MSP along with partial least squares method discriminant analysis (PLS-DA) was used by Ferguson et al. on a large database compared to the other articles (40 samples for males and 40 samples for females). In that study the focal point was small proteins and peptides with the success rate on identification of the gender of the donor was 67-85% (depending on the criteria assigned for gender identification)[92].

Personal tendencies

Drug metabolites can be identified in sweat, and fingermarks but the specificity of this method remains to be examined. A study [93] focusing on metabolites of nicotine tried to discriminate between fingermark donors who were smokers and non-smokers. The marker that was used was cotinine (metabolite of nicotine). The choice of nicotine/cotinine as target metabolite seems to be problematic since these are compounds that can be acquired from other sources (*i.e*. tomatoes).

Immunolabelling has been used by many different research groups in an attempt to detect specific drug metabolites, but these methods lack reproducibility. Van Dam et al. [93] have tested immunolabelling methods developed by their group and have found that in most cases these methods are usable even in fingermarks that were chemically enhanced. Apart from drugs, medication can also be traced by its metabolites. Lorazepam (anxiety treatment drug) was detected in stacked fingermarks within 2 hours after administration with LC-MS/MS. Ingredients of cosmetics in fingermarks have been identified with AFT –FTIR for different types of cosmetics [93].

Traces of explosives and gunshot residue

Gilchrist et al.[25] have tried detecting anions that are specific to gunshot residue but the results did not indicate a clear increase of the target anions in all cases, although there is indication that with an improved method, an increase could be observed. A major problem with identifying gunshot residue compounds on fingermarks was that up until recently there was not an established gunshot residue- only group of organic compounds. As a result, even if detection of suspected GSR is successful in fingermarks, the outcome was still disputable. However, recently there seems to be a consensus on what would be classified as organic gunshot residue compounds [94, 95]. Mou et al.[77] was able to distinguish fingermarks with explosive traces on them from natural fingermarks using custom made micro AFT-FTIR.

1.10 Morphological alterations with time

De Alcaraz-Fossoul et al.[96] observed in a sample size of around 30 fingermarks a change in the topography of the fingermarks with time. Regardless of the lighting and in most cases the substrate a ridge drift was observed. The analyses showcased that the position of a single ridge was changed while the surrounding ridges remained the same. This ridge drift change has to be born in mind when comparing fingermarks. Furthermore, fingermarks by the same donor tended to present the same dissimilarities with time and the effect was localized in a certain area of the fingermark. This finding may have an effect on the criteria of fingermarks comparison.

In another study[97] by the same author fingermarks were studied upon their alterations through time (under different environmental conditions, and on different substrates). The most common ones are also determined in a different study[98] are:

- Diffusion of fingerprint components on the surface
- Loss of adhesivity to the enhancing powders
- Narrowing of the fingermark ridges
- Loss of continuity along the fingerprint ridges
- Decreasing number of minutiae

Difference in contrast between ridges and furrows with time has been reported again [99], but the authors believe more research is needed to reach conclusions and connect this finding with age estimation of the deposition of a fingermark.

1.11 Summary & Conclusion

The overall findings of this review of the literature, highlight the complexity of fingermark residue research, and why it is hard to establish a concrete set of rules when it comes to defining the age of a mark, the age and gender of the donor, or the activities of the donor prior to the deposition of the mark. However, with the current body of research available scientists and forensic practitioners have been made aware of the most common compounds that are expected to be present in fingermark residue and how they can fluctuate depending on factors like sunlight and age (among others). A focal point of future exploration regarding the compounds found on fingermarks would be a thorough study on how all environmental factors (even extreme ones) can affect the aged composition of a fingermark on multiple substrates, since the current body of data seems to have many contradicting points (mainly due to the inherent variability of fingermarks). Moreover, there appears to be no information regarding the fingermark components that can withstand extreme heat, gas blowback etc. This can be valuable knowledge, since sometimes fingermarks can be recovered on fired cartridge cases and more rarely on bullets. Once these components are identified, a fingermark enhancement method could be tailored to develop these types of fingermarks.

Lastly, there are many fingermark enhancing methods, which are currently used routinely in police casework, but their underlying mechanisms are partially understood. This issue can be tackled by improving our knowledge concerning the constituents of the fingermarks, and subsequently these fingermark enhancement methods could be further improved.

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2. Detection of Fingermarks on Metallic Surfaces: A Literature Review

Abstract:

There are many different fingermark visualisation techniques available, and the choice of methodology employed may be dependent on the surface type. This comprehensive review of the scientific literature evaluates the methodologies of fingermark enhancement methods that are applicable to metallic surfaces; optical, physical, chemical, and physicochemical methods are critically discussed. Methods that are currently used and those that have the potential to reduce the cost and time required to process evidence and increase the recovery rates are considered and are assessed against the Centre for Applied Science and Technology (CAST) and the International Fingerprint Research Group (IFRG) guidelines. The use of chemical imaging techniques in particular has increased the potential to recover fingermarks of sufficient quality for identification purposes. Presently, there appears to be a lack of detailed research pertaining to validation and thorough casework studies for fingermark enhancement techniques.

Introduction

Fingermark casework is still the most common casework for forensic scientists despite the increase in use of DNA [1] to identify/exonerate suspects via bodily fluids [2]. The ridge patterns found in fingermarks are permanent and can be used to individualise or exclude suspects from an investigation.

Detection of fingermarks on metallic surfaces will be dependent upon the compounds remaining from the fingermark residue. Several detailed reviews have already been published on fingermark composition, but none of them has focused on fingermarks deposited on metallic surfaces [3, 4].

Metallic surfaces are also commonly encountered in crime scenes and are ubiquitous in the environment. Surfaces such as the door of a car, objects like handles, weapons, and tools are usually made of steel. Cartridge cases are frequently recovered from crime scenes and are usually made of brass or nickel [5]. There are a number of different techniques that can be applied to a surface to visualise latent fingermarks. The selection of a suitable technique depends on different factors, such as the expected composition of a fingermark, other techniques that would have to be used, and the nature of the substrate. In this review, the focus will be on fingermarks deposited on metallic surfaces, and the optical, physical, chemical, and physicochemical visualisation techniques that can be used for detection of fingermarks on these surfaces.

The U.K. Home Office's grading -system (Table 1) is considered when assessing the quality of the development of fingermarks of all the different enhancement methods. It should be noted that the assessment of the quality of fingermark development was performed by the author, based only on the data that were disclosed in each different study. Moreover, the majority of the scientific papers included in this review studied fingermark development under laboratory conditions and thus may not replicate the "real" conditions seen in actual casework.

Table 1. Fingermark grading system [6]

Grade	Criteria
0	No ridge detail visible
1	Weak development; evidence of contact but no ridge details
2	Limited development; about 1/3 of ridge details are present but probably cannot be used for identification purposes
3	Strong development; between 1/3 and 2/3 of ridge details; identifiable finger mark
4	Very strong development; full ridge details; identifiable finger mark

Additionally, in order to provide extra information about the stage of the fingermark study of each individual paper examined in this review, the International Fingerprint Research Group (IFRG) guidelines will be introduced and used when reviewing a study. Specifically, there are four main research phases in fingermark research [7]:

- Phase 1 (Pilot Study) involves initial pilot or proof of concept investigations of novel fingermark detection methods (reagents or techniques) or major modifications to existing methods. These projects are often the domain of universities and dedicated government research facilities.

- Phase 2 (Optimization and comparison study) is a more detailed investigation and evaluation of a method. The optimization of relevant parameters is generally a first step in this phase. The relative performance of the new or modified method then needs to be compared to that of established operational techniques and the performance of the method across a number of variables (substrates, donors, and

ageing periods, *e.g.*) assessed under reasonably controlled conditions. Consideration may also be given to how the new method performs in sequence with relevant routine detection techniques. Phase 2 projects may be undertaken by universities, government research facilities, or operational casework facilities.

- Phase 3 (Validation) studies are designed to introduce successfully optimized techniques to more realistic, pseudo operational scenarios using simulated casework material. This phase is a rigorous evaluation of the performance of the new technique against current methods in order to assess suitability for potential operational use. The position of the new method in relevant detection sequences must also be thoroughly tested as part of the validation. Phase 3 research may be done by universities or government research agencies but should at least be undertaken in close collaboration with an operational casework facility.

- Phase 4 (Operational, evaluation, and casework trials) focuses on eventual casework implementation via inclusion into standard operating procedures (SOPs). Phase 4 must be under taken as a live casework trial by an operational facility intending to introduce the method. For accredited facilities, Phase 4 evaluations should be undertaken in a manner that will facilitate the subsequent formal method validation processes required to meet relevant international standards (*e.g.*, ISO 17025). A typical Phase 4 project includes the assessment of a new technique across a large number of cases—and possibly across a large number of laboratories in the case of national agencies or geographically broad jurisdictions—during a designated trial period. During this period, the performance of the new technique is compared to the performance of current methods. For studies undertaken across multiple locations, the ambient laboratory conditions can differ significantly and may affect the results. If this can be an issue, it is recommended that the temperature and humidity in each laboratory and storage conditions be recorded. If field-based methods are being evaluated, environmental conditions should be recorded to determine if these may be impacting on the results achieved. This information can be invaluable for assessing and documenting the robustness of a new technique.

The IFRG guidelines also discuss parameters such as number of donors, substrates, donation variables for each study phase and assessment methodologies [7].

2.1 Optical Fingermark Development Methods

Optical fingermark development methods can detect a fingermark without the use of any other chemical enhancement technique. This is possible by exploiting the different optical behaviour of the fingermarks compared to the substrate they are deposited on [8]. The advantage of these methods is that they can provide information about the composition and the morphology of a fingermark simultaneously. These already established fingermark visualisation techniques revolve around exciting certain compounds present in the latent fingermark in a narrow range of wavelengths and then detecting the data at one specific wavelength. Chemical imaging can analyse an image into its component colours at many different wavelengths quantitatively. This feature enables the forensic examiner to discriminate usable information from a background interference pixel-by-pixel. Unwanted interference including fluorescence, texture, and colours can be efficiently minimised, leading to a detailed fingermark image. Although these techniques may be considered complex, there is no relevant literature available on simpler optical methods in relation to metallic surfaces.

Infrared Reflection/Infrared Imaging

Infrared imaging is a process in which the (latent) fingermark and the surface upon it is deposited are illuminated with infrared radiation and the outcome is captured by an infrared sensitive viewing system. When a substrate is illuminated, the substrate obtains a light colour while the fingermark has a black/dark colour [8]. It is a nondestructive procedure that can provide information about the morphology and the composition of a fingermark on almost any surface (except for substrates that absorb infrared light). The visualisation of the fingermark is also dependent on the fingermark itself and on whether other enhancement techniques have been used

prior to infrared imaging. For instance, a fingermark deposited on a metallic surface which is untreated (the fingermark) or can be enhanced with deposition of a metal-containing powder is an ideal candidate for this method. Fourier transform infrared spectroscopy (FTIR) imaging has the added benefit of obtaining better images of the fingermarks using various data analysis techniques (*i.e*., principle component analysis — PCA)[9]. Additionally, information about other compounds (drugs, explosives) present on fingermarks can be gathered using this technique but only in cases where the deposition happened on a flat metal substrate (aluminium coated slides) or on a substrate where the fingermark can be easily lifted [10]. Finally, Tahtouh et al. [11] in their study state that this method is also relatively fast, reporting that an experienced user can develop a fingermark within 4 hours.

Ultraviolet Reflectance Spectroscopy

Fingermarks absorb the largest part of incident visible light, while reflecting the largest part of ultraviolet light, a phenomenon, which can be exploited especially on smooth non-porous surfaces. This method is especially helpful for fingermark detection on surfaces that have multiple colourations and thus many visual disruptions (*i.e*., aluminium can).

One disadvantage of this technique is that it damages the DNA present in fingermarks. Gibson et al. state that although the different UV detection procedures can visualise fingermarks, only a small percent around 7–14% of these fingermarks will be of a Home Office's grade 3 or 4 [12]. Additionally, the visualisation quality depended on the illumination angle, which can vary when dealing with different samples and different substrates. The UV-C radiation wavelength range used was from 100 to 280 nm, and the systems evaluated were as follows: a UV-C-sensitive, back-thinned CCD and camera system, RUVIS (reflected ultraviolet imaging system), which is a UV-C-sensitive image intensifier (254 nm) and a flatbed scanner fitted with a UV-C light source. UV reflection has also been used sequentially with specially modified

cyanoacrylate. A pilot study by Khuu et al. [13] using one-step luminescent cyanoacrylates, where the authors used a VSC 6000, has shown some potential, but further work is still needed.

Fluorescence

Recent research has demonstrated excellent visualisation (without damaging the DNA present in a fingermark) [14] on many different metallic substrates (stainless steel sheets, aluminium foil) can be achieved when using a near-infrared (NIR) radiation source at 980 nm for excitation of latent fingermarks that have been powdered with NaYF4:Yb, Er upconversion nanoparticles. One limitation of this research is that it was only tested with one donor of fingermarks [14]. The efficacy of this technique is yet to be determined on a wider range of metallic surfaces. Another study by King et al. [15] capitalizing on fluorescence yielded good results on metallic surfaces (such as metals used for aerosol cans). A modification of a cuprorivaite fingermark powder was used (by applying with a brush rotationally), and the image was captured with modified Nikon D810 with the IR filter removed. The excitation wavelength applied was 780 nm and took the form of a 9 x 780 nm LED array, fitted with an 800 nm short-pass filter. Despite the reasonable donor pool in this study [10], the focus was mainly on non-metallic surfaces (banknotes, plastics), which means more data are required before drawing any conclusions.

Surface Enhanced Raman Imaging

Connatser et al. [16] used surface-enhanced Raman spectroscopy (SERS) imaging in an attempt to visualise eccrine latent fingerprint that would otherwise remain undetected (due to exposure to heat or other degrading factor). For their experiments, they also used an artificial fingermark solution, which was made after evaluating all the methods that were available, and creating a single optimized solution. The solution consisted of a large amount of the known components of eccrine sweat. Chemical imaging of fingermarks was based upon the hydrocarbon bond from skin oils at 2900 cm^{-1}. Imaging was successful on high contrast surfaces (including metals). In the same study, a sebaceous fingermark with drug remnants on

it was used and successfully detected. Raman imaging and IR imaging could be used in tandem as they complement one another, but in order for SERS to be used in practice a lot more research has to be done, specifically with a large donor size and the optimization of the enhancement methodology.

Song et al. [17] also used SERS to detect specific biomolecules in latent fingermarks. In their study, they used the aromatic ring vibrations to detect the molecules and obtain clear SERS photos of the fingermarks. Although in this study the experiments were not performed on a metal substrate, the potential of Raman imaging is clearly demonstrated and the added benefit (compared to fluorescence) is that the spectral bands are narrower allowing for a more precise assignment to the bonds. A performance table (Table 2) provides a summary of the optical methods discussed in this section. Although in some of the studies examined in this section the surfaces and items that were included resembled items that can be encountered in crime scenes, the lack of a large number of donors and fingermarks aged for different time limits makes the classification of the research as phase 1 according to IFRG guidelines.

Table 2. Summary of optical fingermark enhancement methods

Technique	Destructiveness	Evaluation of Enhancement Quality	Limitations	Strengths	Literature
Infrared reflection	Nondestructive	Home Office's grade 3–4 can be achieved	Works better when one knows where to look for latent fingermarks. Only a few studies available	Information of other exogenous substances can be obtained (*i.e.*, drugs)	8-10

Continuation of Table 2 page 52

Technique	Destructiveness	Evaluation of Enhancement Quality	Limitations	Strengths	Literature
Ultraviolet reflection	Nondestructive	Home Office's grades can be achieved but not consistently	DNA on fingermarks can be damaged Process might be harmful for the user of the method	Applicability on a wide range of substrates	12, 18
Fluorescence	Nondestructive	Home Office's grade 3–4 can be achieved	Pretreatment of the sample might be needed. Only a few studies available	Achieves the best visualisation compared to other optical techniques	14, 15
Raman Imaging	Nondestructive	Home Office's grade 3–4 can be achieved	Only a few studies with artificial fingermarks available Pretreatment is necessary for high-quality visualisation	Information of other exogenous substances can be obtained (*i.e.*, drugs)	16

2.2 Physical Methods

Physical methods are usually methods that employ solid-state reagents, and in most cases, the fingermarks are not significantly altered.

Powder Methods

The powders used for developing latent fingermarks at a crime scene adhere preferentially to specific components of the fingermarks. The concept of these methods is quite simple: application of the powder to the surface of interest and observation and monitoring of the progress of the deposition [8]. With "fresh" fingermarks, the powder adheres to the aqueous components. In aged fingermarks, the adhesion happens mostly due to the fatty acids and other greasy substances present in sebaceous sweat [19].

Powder methods can be divided into four categories: metal flake, granular, magnetic flake, and magnetic granular. Each has different advantages and disadvantages (work better on different surfaces, etc.). A general rule for powders is that they can be detrimental for further analysis and that the forensic practitioner must know which powder to use on each surface. An advantage of powder use is that their application is simple; thus, no extensive training is needed. All of them are routinely used in casework for developing fingermark on metallic surfaces (*i.e.*, car doors) [20]. Bandey [20] states that studies have been conducted to find out the suitability of each powder on different (metallic) surfaces. Specifically, brass flake powder should be used on smooth silver surfaces. Aluminium flake powder can also be the powder of choice for certain smooth metal surfaces as it is easy to apply and gives good contrast. Black granular powder can be used on smooth surface only, while the black magnetic powder can also be used on textured surfaces. This study illustrates that there is not one powder that is deemed the most effective across all surfaces, including metals. Recently, with the advances in nanotechnology, hybrid (inorganic and organic) powders are being developed, with the ultimate goal of creating a powder that can develop high quality fingermarks in the majority of the cases, despite the variation in the fingermark itself (in terms of compounds), and the substrate it is deposited on.

Silica-Based Nanoparticles

From 2008 and onwards, silica-based composites for the development latent fingermarks were developed and studied. In the work of Liu et al. [21], Eu^{+3} was entrapped in a SiO_2 matrix and a series of different sensitizers was used with 1,10-phenanthroline providing the best results in an array of substrates by dusting. J. Dutta et al. [22] modified latent fingermarks with columnar thin films consisting of SiO_2 and CaF_2. The procedure involved depositing the columnar films with the physical vapour deposition technique and then spin coating with rhodamine 6G solution. Fingermarks on non-porous substrates were developed with this method. Luminescent nanophosphors embedded in silicate matrix have been synthesized and tested on aluminium foil and demonstrated that fingermarks of seven days old could be developed. Another group of composite compounds are the porous phosphate heterostructures. These developing powders are made of zirconium phosphate on silica galleries. PPH-S-CdS nanocomposite was used to developed latent fingermarks on a steel surface successfully [23]. Although the silica-based nanoparticles seem to adhere well on the ridges of fingermarks on various substrates (including aluminium and steel), their visualisation is achieved by exploiting their optical properties (light absorption, photoluminescence), and that is not always feasible in surfaces that their background luminescence is strong.

Lanthanide-Based Powders

Europium strontium aluminate (ESA) phosphors have revealed long afterglow properties. Liu et al. [21] examined their use in substrates that may fluoresce themselves using ESA phosphors and UV-lighting and development of fingermarks was achieved on a range of surfaces. Favourable results were achieved on aluminium foil for both fresh and a few-day-old fingermarks. Saif [24] examined the use of Ln^{3+}:$Y_2Zr_2O_7/SiO_2$ (Ln^{3+}=Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+} or Pr^{3+}) for development of fingermarks also on aluminium foil with Terbium (Tb^{3+}) powder found to be the most effective.

The use of this method might be detrimental for DNA evidence examination, which means that it needs to be performed after all DNA related methods in a sequential treatment. Despite the fact that only one donor was used in both studies, the method seems promising, due to its low-cost, low-risk nature along with its fast and successful development of fingermark.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy has some advantages compared to optical microscopy. Information about the morphology and the composition (when SEM with Energy Dispersive X-Ray Analysis is used) of the sample can be obtained at the same time and textured substrates that are not transparent can be examined. However, SEM may not be the best method for analysing a large bulk of samples, due to the difficulty of locating accurately the area of interest (in our case the area of the latent fingermark). SEM works best with a pretreated mark (*i.e.*, cyanoacrylate) [25] because this way the area of interest becomes easy to visualise. Fingermarks on a wide range of metallic surfaces (brass, copper, steel, aluminium, stainless steel foils) have been studied and visualised with SEM along with their interactions with the substrates (corrosion) [5, 26].

Scanning Kelvin Probe

A metallic surface is scanned with a vibrating gold wire probe measuring the Volta potential of the surface and latent fingermarks are scanned by observing the differences in Volta potentials where the fingermarks are deposited. When fingermarks are deposited on metallic surfaces, usually corrosion or insulation occurs, resulting in a different Volta potential compared to the regions of the surface where no fingermarks are deposited [8,27]. The whole procedure can take hours to complete but the advantage is that the fingermarks remain intact. Another limiting factor of this method is that the shape of the object/surface under analysis has to be relatively simple for this method to work effectively. Williams et al. [27] have demonstrated in their study that this method has potential in detecting eccrine fingermarks (Figure 1), and fingermarks on metallic (*i.e.*, iron) surfaces that were previously cleaned/rubbed or polished.

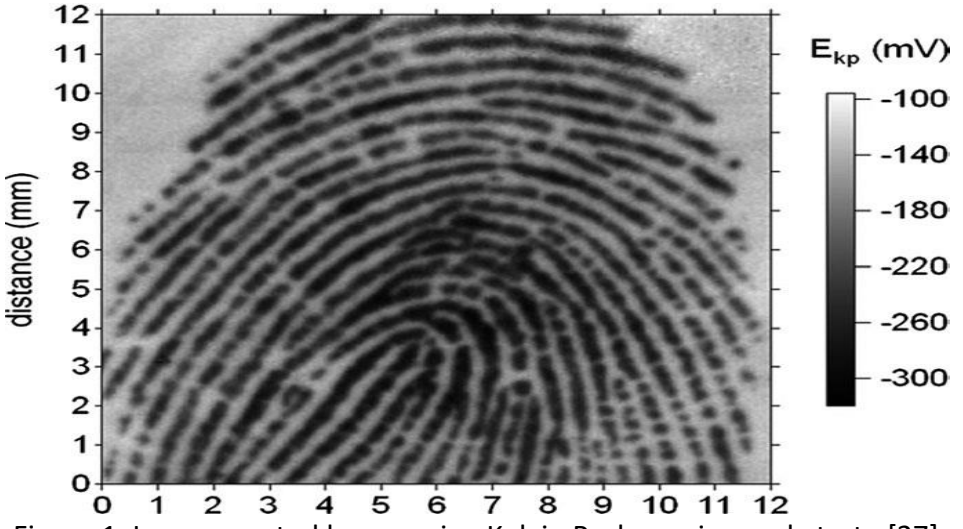

Figure 1. Image created by scanning Kelvin Probe on iron substrate [27].

Matrix-Assisted Laser Desorption Ionization—Mass Spectrometry Imaging (MALDI-MSI)

Matrix-assisted laser desorption ionization—mass spectrometry (MALDI-MS) is an established technique when it comes to analysing human tissue due to its specificity and speed of analysis. The added benefit of MALDI-MSI compared to MALDI-MS is the ability to extract information about the distribution of compounds in a sample. When MALDI-MSI is used for fingermarks, no other sample preparation has to be performed except for the application of the matrix solvent. Using a matrix, the different constituents of the sample can be extracted into the matrix solvent with the help of a laser beam. The laser constantly changes position and a mass spectrum is acquired in each position during the analysis to ensure homogeneity and to capture a precise image of the fingermark and its chemical composition [8]. It has to be noted here that MALDI-MSI can be used after a standard enhancement method (*i.e.*, superglue) has been used first as Bradshaw et al. and Wolstenholme et al. report in their studies [28,29]. Moreover, Wolstenholme et al. demonstrated the versatility of MALDI-MSI as a stand-alone method for fingermark visualisation in a range of substrates, including aluminium foil [29]. Despite the promising results on aluminium foil, research on more metallic substrates is required to be able to perform a thorough assessment of this technique.

Time of Flight—Secondary Ion Mass Spectrometry (ToF-SIMS/ SIMS)

Bailey et al. [30] demonstrated the improvement in ToF-SIMS can offer in cases where the conventional methods produce unsatisfactory results, although the number of donors and substrate was not large (with aluminium foil being the only metallic one). A disadvantage of ToF-SIMS is that the use of vacuum has been proven to alter the composition of fingermarks (a reduction in the lipid composition of a fingermark) [31], which can be detrimental for a reliable analysis, since the original content of compounds is altered.

Thermal Development

Most of the research concerning thermal development in the literature studies the development of fingermarks on paper [32]. However, Wightman et al. [33] used this technique to develop fingermarks on metallic surfaces, namely brass, aluminium, and steel, which are materials used for ammunition casings. They used a low thermal mass furnace and acquired favourable results especially for the brass samples that were heated at 200°C (Figure 2). The effect of time of deposition was also tested, and encouraging results were also obtained. However, only three donors were included in this study and further research is needed to produce reliable results. Moreover, this method is destructive and a lot of donor-specific information could be lost when it is employed.

Figure 2. Fingermark thermally developed on brass surface.

Metal-Containing Nanoparticles and Small-Particle Reagents

Metal-containing nanoparticles are also used for the enhancement of latent fingermarks. These reagents rely on their affinity with the oily part of latent fingermarks and can be classified as powdering methods. ZnO was studied by Choi et al. [34] on its effectiveness as a fluorescent pigment on aluminium foil, and favourable results were produced when using long wave UV light for visualisation. Rohatgi et al. [35] created a suspension powder consisting mostly of zinc carbonate hydroxide monohydrate and successfully enhanced fingermarks up to 25 days old on wet aluminium foil, while achieving high-quality development on fingermarks that were 6–15 days old. The applicability of this technique to other metallic surfaces needs to be given further attention.

Vacuum Metal Deposition

The presence of fingermarks is detected by the different rate of metal growth on the surface. This is a sensitive method, which employs metal evaporation and exploits the difference in the rate of deposition on a surface with disturbances (*i.e.*, fingermarks). A high vacuum chamber is needed for this method. Wetted surfaces and surfaces that have been exposed to high temperatures are not problematic when this technique is used. Gold/zinc vacuum metal deposition is the most effective option in a wide range of substrates. First gold is deposited to form a thin film; this deposition facilitates the visualisation of the marks. Gold diffuses in the areas where fatty components of the fingermarks are present. When zinc is deposited, it condenses in the areas where the non-diffused gold is (Figure 3).

Lately, vacuum metal deposition has been successfully used for the visualisation of fingermarks on fired cartridge cases [36] but still needs to be studied further before it can become a standard casework procedure.

Figure 3. Fingermark developed with vacuum metal deposition (gold/zinc) on brass surface.

A performance table (Table 3) provides a summary of the physical methods discussed in this section. In general, the studies examined in this section fall into the Phase 1 IFRG category (with the exception of the powdering techniques) and fail to place on a higher phase due to the lack of a higher number of substrates examined and donors employed or the lack of “natural” fingermarks. However, that does not necessarily mean that the examined methods shown here cannot progress to a higher phase.

Table 3. Summary of all physical methods

Techniques	Destructiveness	Evaluation of Enhancement Quality	Limitations	Strengths	Literature
Powder methods	Destructive	Usually a Home Office's 3–4 grade can be achieved	Can be detrimental for further analyses The examiner must know which powder to choose	Simple application, Minimal training needed	14, 21, 34
Scanning Electron Microscopy	Nondestructive	A high grade fingermark can be visualised	Usually better after the fingermark has been enhanced with other method	Morphology and composition of fingermark can be obtained	5, 25, 26
Scanning Kelvin Probe	Nondestructive	A high grade fingermark can be visualised	A flat surface is preferable	Can enhance fingermarks that have been wiped off. Can enhance eccrine fingermarks	27
MALDI-MSI	Destructive	A high grade fingermark can be visualised	Fingermark Requires pretreatment	Can work as a sequential or stand-alone technique	28, 29

Continuation of Table 3 page 62

Techniques	Destructiveness	Evaluation of Enhancement Quality	Limitations	Strengths	Literature
ToF-SIMS	Potentially destructive	Usually a Home Office's 3–4 grade can be achieved	Relatively unexplored	Has shown applicability in many substrates	30, 37
Thermal development	Destructive	Mediocre results most of the times	Detrimental to further fingermark analyses	Older fingermarks could be visualised	33
Metal-containing nanoparticles/small-particle reagents	Destructive	Usually a Home Office's 3–4 grade can be achieved	Often extra illumination with UV light is needed	Also applicable on older fingermarks	34, 35
Vacuum metal deposition	Destructive	Usually a Home Office's 3–4 grade can be achieved	Competent Personnel is needed	Can be applied on wetted surfaces	8, 38, 39

2.3 Chemical Methods

In the chemical development processes, the fingermarks are usually treated with an aqueous reagent and their composition may be altered.

Acid Dyes

Acid dyes target the proteins or protein-rich compounds that are present in blood and give a coloured or fluorescent background. This is a method that has to be used in sequence with other fingermark enhancing techniques when a bloody metallic item is examined [8]. Barros et al. [40] tested several acid dyes (as a part of a sequential treatment) on painted aluminium and were able to develop/enhance bloody fingermarks. It is not clear; however, how many of the developed fingermarks were of identifiable quality. Additionally, their donor pool consisted of only 3 donors.

Cyanoacrylate Fuming

Farrugia [41] performed a comparative study on metallized plastic films, to find out the effect of cyanoacrylate fuming under vacuum. This method is performed in a fuming cabinet. It is noteworthy that eccrine fingermarks produce the best results since the polymerisation produces fibrous noodle-like deposits on the ridges. Sebaceous fingermarks form different sphere-like structures [8, 42]. The main advantage of this method is that it can be effectively used in almost all surfaces and it is not time-consuming (20–30 min). However, often an extra enhancement of fingermarks is required after superglue fuming; additionally, this method is significantly hindered when the surface is wetted.

A modification of cyanoacrylate, Lumicyano™ (Figure 4), which is a fluorescent reagent, was studied by Prete et al. [43]. Results on aluminium foil showed that Lumicyano™ could enhance fingermarks slightly better than the two-step method of cyanoacrylate and Basic Yellow 40. Khuu et al. [13] evaluated the performance of commercially available fluorescent cyanoacrylate compared with the conventional Cyanobloom-Rhodamine 6G method. Slightly better enhancement was achieved overall with the majority of the fluorescent cyanoacrylate methods. Greater enhancement was achieved specifically on polystyrene substrates and also on older fingermarks where Cyanobloom-Rhodamine 6G was underperforming. However, in both studies the number of donors was not high [3,4]; thus, no definitive conclusions can be drawn yet. Although, cyanoacrylate fuming is routinely used in police casework and thus it has the potential to be considered for a phase 4 IFRG study, the articles examined in this section will be ranked as phase 1 study mostly due to the lack of donors included in each study.

Figure 4. Fingermark developed with Lumicyano™ (left) and normal cyanoacrylate (right) on brass surface.

Patination Fluid and Gun Blue

Patination fluid consists of selenium dioxide and nitric acid. A black patina is developed when patination fluid is applied to metallic surfaces leaving the latent fingermark intact. The process is time- and cost-efficient, but can be harmful due to the formation of selenious acid when selenium oxide is dissolved in water, and additionally, unfavourable results were obtained on aluminium surfaces. James et al. have studied this process on cartridge cases of brass and found promising results especially with sebaceous fingermarks [44]. In their study, they also had a stable development time of 90 sec per sample, which can be an advantage compared to the Gun Blue method, where the development time seems to be highly variable and user specific. This study was a proof-of-concept study and only one donor provided fingermarks; thus, only limited data currently exist on the efficacy of these fluids.

Gun blue is a solution consisting of selenious acid, nitric acid, cupric sulfate, and water. When applied on a metallic surface, which has latent fingermarks present, the surface becomes dark blue while the part of the surface where the fingermarks are deposited, remains unstained due to the presence of fatty components (Figure 5).

Figure 5. Fingermark on a cartridge case developed using Gun Blue

Gun blueing develops fingermarks rapidly and is a cost-efficient procedure, but it has not been yet fully studied and has a questionable success rate on latent fingermarks [8]. However, research so far using this technique has produced inconsistent results, possibly due to the use of different commercial products and different dilutions of those products used in each different study. Gun blueing appears to be the best approach when one needs an enhancement method for latent fingermarks deposited on surfaces made of brass (brass cartridge cases were mostly used in studies). Other advantages of this method are that it can be used as a part of a sequential fingermark (*i.e.*, Superglue-Gun Blue) treatment; therefore, a better development can be achieved and that it has shown promising results even for corroded and fired cartridge cases [45–48]. The application of this and other techniques to enhance fingermarks on cartridge cases is discussed separately.

Palladium Deposition

Deposition of palladium onto metallic (copper, brass, bronze) surfaces occurs leaving the area where the latent fingermark is deposited, intact; thus, a negative fingermark is developed. The article with the latent fingermark is immersed in a solution and subsequently washed with water to halt the reaction (Figure 6).

Figure 6. Fingermark developed with palladium chloride on brass surface.

Palladium deposition is a method not yet fully explored, although preliminary research has shown some potential [49]. Dominick et al. [46] compared sequential cyanoacrylate (CA) and palladium deposition to sequential cyanoacrylate, gun blueing and Basic yellow 40 and found that the number of fingermarks that were successfully developed was similar. An advantage of CA and palladium deposition was that the fingermarks were developed after 1 day while the other method needed 2 days. However, the cost of palladium chloride makes this method less cost-efficient than others.

Development by Electrolysis

Nizam et al. [50] in their study found favourable results when using short electrolysis times (5 min) and a 37% HCl as solvent. However, developing fingermarks on the fired cases proved to be challenging with only one of four cases yielding sufficient detail, while fingermarks in all of the unfired cases were successfully developed. When the time between deposition of fingermarks and development increased, there was a decrease in ridge detail developed, with absolutely no ridge detail developed after seven days. This was a proof-of-concept study as only one male donor was utilised.

Development by Aqueous Electrolytes

Jasuja et al. [51] examined the development of eccrine and sebaceous fingermarks on metallic surfaces. The experiments were carried out by immersion (10–20 min) of the metal substrate with the latent fingermark, in solutions of variable pH. In some instances, a second metallic surface (without latent fingermarks) was immersed in the solution to accelerate the reaction. Favourable results were obtained on most surfaces. Aluminium, zinc, copper, and brass were some of the surfaces examined, for some metals slight acidic solutions gave off the best development while others needed a more basic environment. However, Jasuja et al. [51] have used their own grading scale, with grade 3 being somewhere between a grade 2 or 3 compared to the Home Office's grading system, with the ideal grade for an identification by the Home Office's standards being 3 or higher. Nevertheless, the effectiveness of this method was proven, since 10 different donors were utilised for this study and "older" fingermarks of 10 days old were successfully developed. This method can develop fingermarks fast while keeping the cost low. An example of the enhancement aqueous electrolytes can achieve is shown in Figure 7.

Liu et al. [52] investigated how this method performs on fired and unfired cartridge cases using an adaptation of the technique used by Jasuja et al. [51]. For the unfired cases, sufficient development was possible for the vast majority of them; however, only a few samples (4 of 60) were successfully developed on fired cases. It appears that the heat and friction during the shooting have a detrimental effect on the fingermarks. Liu et al. also suggests that the longer a fingermark is deposited on a case, the better its visualisation will be due to the greater corrosion time allowed. In this study, the immersion time of the cases was 24 h, which is significantly longer than that reported by Jasuja et al. [51] (10–180 min). This could have played a role in the quality of the fingermarks that were developed.

According to IFRG guidelines, the studies examined here can be considered as phase 2, although a higher phase seems within reach since fired cartridge cases were also examined.

Figure 7. Fresh sebaceous fingermark on brass developed by aqueous electrolytes (8M NaOH).

A performance table (Table 4) provides a summary of the chemical methods used for fingermark detection. Although destructive, these techniques do appear to be able to provide fingermark detection of a high quality. Using the IFRG guidelines, with the exception of the studies on the aqueous electrolytes methods which can be ranked as phase 2 the majority of the methods discussed in this section can be regarded as phase 1 studies. Cyanoacrylate fuming is extensively used in casework; however, the research examined in this review has been phase 1 or 2.

Table 4. Summary of chemical fingermark enhancement methods

Technique	Destructiveness	Evaluation of Enhancement Quality	Limitations	Strengths	Literature
Acid dyes	Destructive	Usually a Home Office's 3–4 grade can be achieved	Has to be used with other enhancement methods Not thoroughly explored method	Can enhance fingermark contaminated with blood	8
Cyanoacrylate fuming	Destructive	Usually a Home Office's 3–4 grade can be achieved	Can be problematic in wet surfaces.	Can be used almost in all substrates	41, 43, 53
Gun blueing	Destructive	Usually a Home Office's 3–4 grade can be achieved	Still relatively unexplored	Enhances the substrate thus leaving the fingermark intact for further enhancement	45, 46, 54
Palladium deposition	Destructive	Usually a Home Office's 3–4 grade can be achieved	Still relatively unexplored	Has shown potential for developing fingermarks on fired cartridge cases	46, 49
Patination fluid	Destructive	Some of the samples gave off high-quality fingermarks	Still relatively unexplored (only one study available)	Simplicity of use	44

Continuation of Table 4 page 71

Technique	Destructiveness	Evaluation of Enhancement Quality	Limitations	Strengths	Literature
Electrolysis	Destructive	Usually a Home Office's 3–4 grade can be achieved	Only one study available	Enhancement was successful in one fired cartridge case	50
Aqueous electrolytes	Destructive	Usually a Home Office's 3 grade can be achieved	Only two studies available	Successful with older fingermarks and in many metallic substrates	51, 55

2.4 Physicochemical Methods

Electrostatic Enhancement

Exploiting the corrosion that occurs even under ambient conditions when fingermarks are deposited on a metallic surface (brass, aluminium, steel), Bond et al. [56, 57] applied electrical potential to metal-containing deposited fingermark and subsequently applied black powder to it. The black powder was applied with the help of spherical beads, which were rolled back and forth on the substrate. The conducting black powder was found to adhere on the corroded areas of the surface, thus assisting visualisation. This technique was found to be useful when conventional techniques produced a grade 1 or 2 fingermark. When used sequentially, the fingermarks developed improved to a 3–4 grade. This is one of the few studies that included a large pool of donors (forty) and the results can be regarded as reliable. Nevertheless, the method was not effective when used on aluminium and steel surfaces.

Multi Metal Deposition (MMD)

Multi metal deposition is a two-step metallic deposition. Colloidal gold is deposited, after the pH of the environment is adjusted, the amino and fatty acids of fingermarks become charged making it possible for the colloidal gold particles to be deposited on to them. After the initial gold deposition silver is deposited, which is selectively reduced and a dark brown colour is obtained. Conventional MMD is ideal for developing fingermarks on nonporous surfaces, but the method failed to produce favourable results on dark surfaces [8].

Recently, a modification on MMD was studied on aluminium foil [58]. In this study instead of using silver, ZnO was deposited after the initial gold deposition. ZnO-based structures have luminescent capabilities, which can tackle the dark substrate visualisation problem. In the case of aluminium foil, reverse deposition happens (the gold and ZnO nanoparticles have greater affinity with the aluminium foil rather than the fingermark). This irregularity does not appear to hinder the visualisation of the fingermark (Figure 8) and the method appears to work very well on aluminium foil, but no other metallic surface was tested in this study. Finally, only three donors were used in these experiments.

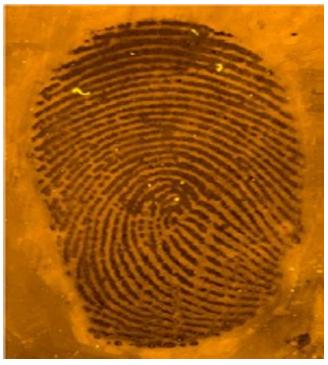

Figure 8. Fingermark developed with MMD/ZnO on aluminium foil under 300–400 nm excitation light [58].

Single-Metal Deposition (SMD)

Single-metal deposition is an improvement of MMD. Gold particles are used both for the deposition and for enhancement steps. SMD can develop more samples in one solution bath, without any major detriment on the quality of the fingermarks while also enhancing 50% more fingermarks than MMD. Newland et al. [59] reported producing grade 2 fingermarks (Figure 9) when using SMD on aluminium foil (among others), adding also that the method does not seem to be hindered by the environmental conditions (*i.e.*, heat). One disadvantage of the method would be the increased use of gold, which can be costly. SMD compared to other enhancement methods remains a tedious method that requires keeping constant the pH value of

the gold bath, and creating nanoparticles of the suitable size. Therefore, trained personnel will be necessary to achieve optimal results.

Figure 9. Fingermark on aluminium foil developed with single-metal deposition [59].

Deposition of Electrochromic Films

A conducting polymer is deposited on the surface of interest. A negative fingermark is developed when using this method since latent/superglued fingermarks act as protection and deposition only occurs on the background. After deposition, the sample is placed in a second solution resulting in a change of colour in the polymer (decided by the examiner) depending upon what the best contrast would be. An advantage of this method is the ability to develop fingermarks on an array of metal substrates such as bronze, brass, lead, copper, and nickel, all metals used for cartridge cases. The main disadvantages of this method are its destructive nature since further enhancement after applying this method is not possible, and the fact that it requires highly trained personnel to be able to carry out this process. Sapstead et al. [60] studied the insulating effect fingermarks have on metallic surfaces using electro-oxidation of copolymers on stainless steel films and improvement of the visualisation of the negative fingermark based on film colour, composition, and topography.

This was a proof-of-concept study, but the authors reported the visualised fingermarks to be grades 3–4.

Beresford [61] achieved similar results using polyaniline films on stainless steel plates, and it was equally effective on both old and fresh fingermarks. The method was tested with only one donor, but a range of fingermarks was produced under different sweat inducement times and deposition pressure. However, only 40% were usable for forensic purposes. Brown et al. [62] studied the enhancement of fingermarks with poly(3,4-ethylenedioxythiophene) also known as PEDOT. Different donors and different deposition times were used in this research to assess the efficacy of the method; additionally, the samples were also enhanced with one of the already established techniques to obtain a better understanding on which cases electrochromic deposition is superior to the other methods. The method achieved over 50% successful enhancements and specifically for samples of seven days old, the success rate was 60%. The results demonstrate that this method can be complementary to the superglue method due to its superiority in substrates where superglue was unsuccessful. Brown et al. [62] believe that this method could become a staple of fingermark visualisation due to its relatively low-cost (similar to a cyanoacrylate development chamber) and relatively easy development technique.

Electrodeposition of Metal Nanoparticles

When a fingermark is deposited on a metallic surface, it can act as an insulator to an electrodeposition process. Deposition of metal nanoparticles happens only on fingermark-free areas, thus obtaining a negative image of the fingermark with high contrast. Qin et al. [63] examined this method on a range of substrates and achieved high-quality enhancement of fingermarks on both eccrine and sebaceous deposits (Figure 10). Additionally, this method is faster (only five minutes deposition time) than MMD methods that require multiple bath immersions of the samples.

Despite the promising results, this was a proof-of-concept study and only one donor was utilised.

Figure 10. Fingermark developed with the electrodeposition of metal nanoparticles method [63].

Zhang et al. [64] used a similar method with the difference being the use of silver and copper particles. They achieved development of grades 3–4 for their fingermarks in an array of metallic surfaces (Figure 11), and they also underline that for each different metallic surface a different deposition time and potentiostatic parameters were ideal. Aged fingermarks of identifiable quality were also developed using this method from three different donors.

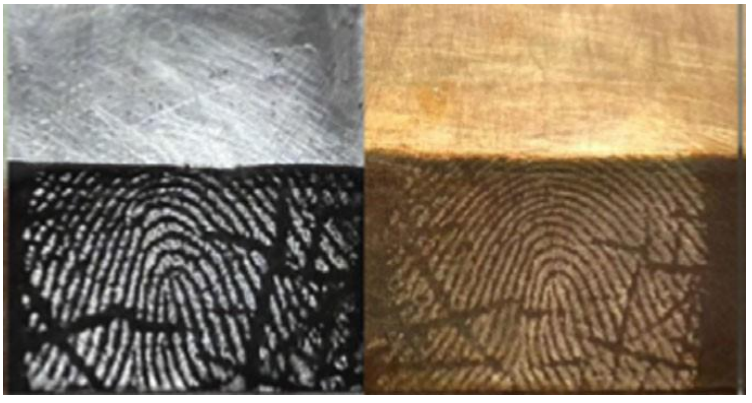

Figure 11. Electrodeposition of metal nanoparticles on different metal surfaces (left: zinc, right: copper) [64].

A performance table (Table 5) summarizes the physicochemical methods used for fingermark detection. According to IFRG guidelines, all the studies examined in this section can be classified as phase 1 studies.

Table 5. Summary of physicochemical fingermark enhancement methods

Technique	Destructiveness	Evaluation of Enhancement Quality	Limitations	Strengths	Literature
Electrostatic enhancement	Destructive	Converted to Home Office's grade 2–3	Effective in a few metallic surfaces	A large donor pool was tested Effective when conventional techniques failed	56
Multi metal deposition	Destructive	Usually a Home Office's 3–4 grade can be achieved	Proven applicability only on aluminium foil.	Potentially works well on most metallic surfaces	65, 66
Single-metal deposition	Destructive	Usually a Home Office's 3–4 grade can be achieved	Trained personnel needed	Enhancement is not hindered by environmental conditions	59
Deposition of electrochromic films	Destructive	Usually a Home Office's 3–4 grade can be achieved	Trained personnel needed	Complementary to cyanoacrylate fuming	62
Electrodeposition of metal nanoparticles	Destructive	Usually a Home Office's 3–4 grade can be achieved	Trained personnel needed	Successful enhancement for eccrine and sebaceous fingermarks and in many metallic surfaces	63

2.5 Ammunition/Cartridge Cases

Several studies have focused on achieving fingermark enhancement on cartridge cases. In some of them, a comparative study is performed between fired and unfired cartridge cases. Dominick et al. [46] studied six different methods for the development of fingermarks on unfired cartridge cases. With the exception of powder suspension, the rest of the methods performed well, with cyanoacrylate-palladium and cyanoacrylate- Gun blueing-Basic Yellow 40 giving the best results. Girelli et al. [45] examined many sequential treatments like cyanoacrylate-gun blueing, cyanoacrylate powders and achieved high-quality enhancement (grade 3–4) on both metal discs and unfired cartridge cases. Liu et al. [52], in their study, successfully recovered identifiable fingermarks on unfired cartridge cases with electrolyte deposition in a variety of pH ranges. Williams et al. [27] also achieved visualisation of fingermarks on unfired brass cartridges with a scanning kelvin probe. Generally, it could be concluded that visualisation of fingermarks on unfired cartridge cases will be achievable in the majority of instances.

However, in a crime scene it is more likely that fired cartridge cases will be recovered, and thus, optimizing the recovery process of a fingermark from fired cartridge cases is of crucial importance. Development of fingermarks appears to be significantly more difficult on fired cartridge cases due to the heat and the friction of the expanded case against the barrel of the gun while it is being fired [67]. Such processes are likely to degrade or chemically alter any remaining print residue. Contamination with gunshot residue and associated material may also be present on the cases after the firing of the projectile, which might be problematic for some development of any surviving fingermarks. In certain firearms (submachine guns, pistols), it is believed that a part of the fingermark material is damaged during the loading/ reloading phase [68].

Girelli et al. [45] also studied the development of fingermarks on fired cartridge cases. The results show that the most efficient methods on unfired cases (cyanoacrylate-Gun blueing, cyanoacrylate-Basic Yellow 40) were the most efficient on the fired cases as well. However, the recovery was of a much poorer quality, acquiring fingermarks of Home office grade 3 in <20% of the cartridge cases examined. To fully understand the inhibiting factors contributing to the added difficulty of fingermark enhancement on fired cartridges, the authors tried to pinpoint the cause by heating metal discs prior to enhancement and loading and unloading the cartridges. In both instances, development of fingermarks was successful indicating that there are other factors during the firing process that affect the fingermark recovery, such as the blowback of the hot gasses produced from the burning of the propellant powder, or some by-products of the propellants that adhere to the surface of the cartridge and hinder visualisation. Although Girelli et al.'s [45] study approaches the subject as close to real crime scene samples as possible and included many cartridge cases (n=100), the small number of donors (2) makes the drawing of conclusions difficult. Nizam et al. [50] used electrolysis only, which successfully developed fingermarks in 1 of 4 spent cartridge cases, and used only one donor. Additionally, other parameters of the method itself were not optimized (voltage, catalyst). Palladium deposition was one of the methods that has also yielded results on fired cartridges. Migron et al. [49] achieved partial development of fingermarks on fired cartridges while using palladium deposition; however, partial development has limited forensic value. Leintz et al. [69] tried an optical approach in their study. A reflected UV imaging system was employed in an attempt to visualise the corrosion pattern from the sweat included in the fingermark, which has been proven to be detectable [57] even after a fingermark has been wiped off from the surface. However, this attempt did not result in high-quality enhancement possibly due to the monochromatic wavelength source of the RUVIS system.

2.6 Summary & Conclusion

The complexity of visualizing a fingermark that has been exposed to various environmental factors becomes greater if one takes into account the alterations that occur on to the substrate, especially when dealing with metallic substrates (corrosion, change of texture).

In terms of choosing and investing in a fingermark visualisation/enhancement method, chemical imaging techniques seem like the ideal technique for forensic applications due to their nondestructive nature. However, they can incur higher costs than other development techniques. A more realistic approach would be to focus on validation studies on enhancement techniques like palladium deposition, gun blueing, development with patination fluid and/or aqueous electrolytes. All of the aforementioned techniques have shown their potential for fingermark development on metallic surfaces in proof-of-concept studies and in some cases partial development on fired cartridge cases and other metallic surfaces has been achieved. These techniques are simple to apply and their cost is minimal, which means that they could be incorporated into standard operating procedures in police laboratories once they have been validated.

Lastly, although (as pointed out in Chapter 1), there have been studies with regards to the chemical composition of fingermarks and the changes observed with time, the substrate used in this type of studies is usually not a metallic one. It would be interesting to see the effect a metallic substrate has to an aging fingermark when compared to non-metallic substrates. This knowledge could then be a newfound tool in the ongoing quest of improving fingermark enhancement methods (in this case on metallic substrates).

2.7 References

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3. The Use of Gun Blue to Enhance Fingermark Ridge Detail on Ballistic Material

Abstract:

Brass cartridge cases are the most common type of cartridge case found at crime scenes, but it is not always feasible to obtain identifiable fingermarks on these cartridges. This chapter evaluates the effectiveness of gun blue as an enhancement method on fingermarks that were deposited on brass metal discs and left to age (2, 7, 14, and 30 days) under different environmental conditions, namely, under dark conditions, under ambient light, and outdoors. Ten different donors (5 males, 5 females) were employed for this chapter, and their fingermarks (60 per donor) were enhanced with gun blue solution (50% v/v). It was possible to enhance aged fingermarks (natural and groomed) that had been deposited on the brass metal discs to an identifiable level, with the fingermarks left outdoors being the most challenging to enhance. The feasibility of enhancing fingermarks on fired brass cartridges shot from different firearms was also assessed.

Introduction

When someone touches a surface friction ridge detail may be deposited on to this surface. This fingermark ridge detail frequently requires enhancement in order to visualise it. Due to the rise of firearm offences in United Kingdom and the low recovery rate of fingermarks[1] from ammunition, some research groups[2, 3] have tried to develop a better protocol of fingermark recovery from ammunition. In a paper by Girelli et al.[3] it was demonstrated that using Gun Blue as a single enhancement method can lead to recovery of second level detail on fired cartridge cases (although the recovery rates where less than ideal). Morrissey et al.[4] in their study demonstrated that fingermarks of sufficient quality for identification purposes can be obtained even on fired cartridge cases, however only 1 (female) donor was employed in their experiments. Thus, there remains a need to further evaluate the efficacy of such methods for fingermark enhancement.

Most of the commercial Gun Blue reagents contain selenious acid, cupric salt, nitric acid and may also contain phosphoric acid, zinc and ammonium salt. Gun Blue is a reagent used for the patination of metallic surfaces (equation 1) which helps to protect the surface from scratches and oxidation.

$$H_2SeO_3 + 4H^+ + 4e^- \longrightarrow Se + 3H_2O \qquad \text{Equation 1[4]}$$

It has been observed however, that when a greasy, waxy or oily component is present on a metallic surface then the application of Gun Blue does not stain this area. It is suspected that the aforementioned components act as a protective layer, not allowing Gun Blue to react with the metallic surface that lies beneath. This phenomenon is the reason why latent fingermarks (which may contain greasy, waxy and oily components) can be developed when using Gun Blue. The majority of previous studies used Gun Blue as a part of sequential treatments and reported unsatisfactory fingermark development when Gun Blue was used independently [5, 6, 7]. It is noteworthy the studies mentioned earlier report that the protocols they used were not standardised and that may have hindered fingermark development.

The aim of this chapter is to determine whether Gun Blue can be used as a standalone development technique to enhance fingermarks deposited by various donors, which had been left to age under various environmental conditions on a ballistic brass surface. The effect of environmental conditions in this case is two-fold: The conditions can alter the compound content of the fingermarks, (specifically the eccrine components of the fingermarks seem to be more sensitive to degradation than their sebaceous counterparts) but also the substrate (ballistic brass) itself, potentially creating further implications regarding fingermark enhancement [5]. The possibility of developing identifiable fingermarks with the use of Gun Blue as the only enhancing

method on fired brass cartridge cases, is also examined. Some of these aforementioned parameters have been examined in previous studies but in this chapter the number of donors is extended and an attempt to standardise the development protocol is discussed. Differences in male and female donors are examined, since contradictory studies have been published [8-11] regarding the differences (or similarities) in compounds (and/or compound ratios) in fingermarks from male and female donors. A successful development technique using Gun Blue, would provide an efficient, cost effective methodology with excellent sample throughput.

3.1 Materials & Methods

Ballistic brass metal discs (3x3 cm, www.metalsheets.co.uk) were chosen for the initial experiment, their elemental analysis showcased that they can be regarded as an equivalent of brass cartridge cases (65% Cu, 35% Zn). The discs were washed with warm water and detergent (Decon 90 5%v/v, Fischer Scientific, UK), rinsed with ethanol and left to dry in the open air. The donors rubbed their hands on their foreheads and clenched their hands prior to depositing one (''groomed'') fingermark from their right thumb on each disc. The donors applied light pressure on the surface for 3 seconds. Ten different donors were used for this chapter, 5 males and 5 females of different ethnicities and of a median of 28 years to assess the reliability of the method. Each donor deposited 60 fingermarks (1 fingermark per disc, not a depletion series). Furthermore, monitoring of the effect of ageing and environmental conditions on fingermark development with Gun Blue was performed. From the total of 600 fingermarks from all 10 donors three equally numbered (200) sub groups were created and were kept constantly under dark in cardboard containers, ambient light and directly exposed to outdoor conditions (average monthly temperature was 8°C with 13 days of average 37 mm rainfall) for 2,7,14 and 30 days. As a point of reference fingermarks developed directly after deposition were obtained from all the donors (5 fingermarks per donor). Statistical analysis of the grades assigned on fingermarks was performed in Excel, using the Chi-square test of independence after converting the grades from numbers to nominal data (either identifiable or non-identifiable).

Moreover, eight donors in total were used in another experiment assessing Gun Blue's enhancing ability when dealing with natural fingermarks. The donors washed their hands with commercial soap and water 30 minutes prior to depositing the print, and then resumed their normal daily routine [12]. This protocol was followed in order to get a type of print that would resemble the ones found on crime scenes. Each donor deposited one print onto 12 separate discs. The fingermarks were then divided into 6 groups of two. One group of fingermarks were tested immediately (fresh), another after 7 days and another after 14 days. The storage times were chosen based on what the fingermark literature suggests, and the duration of the project [12, 13]. The other three groups of fingermarks were subject to being stored in the dark, under ambient light and outside, each for 7 days before the application of Gun Blue. Two groups of the natural fingermarks were also subject to alternating ambient light and dark conditions (12 hours each) in order to simulate crime scene conditions.

In order to evaluate Gun Blue's effectiveness on developing fingermarks on fired cartridge cases, three experiments were performed. Due to the UK legislation regarding firearms and ammunition it was not possible to have all experiments on the same day, with the completion of experiments subject to the availability of the ammunition, the shooters' and the donors'. In the first one, one male donor deposited groomed fingermarks (the same type of fingermarks as in the initial experiment) on 20 cartridge cases (7.62mm Bisley Target -1 per case) which were cleaned using the same protocol as described above. The cartridges were shot using a single shot bolt-action rifle. The fired cartridges were developed the following day (approximately 12-16 hours after firing). In the second experiment, two male donors deposited six groomed fingermarks each, one on each cartridge case (Winchester .45 ACP) (a total of 12 fingermarks) and they were fired using a .45 Glock pistol. For the third experiment, four donors (2 males and 2 females) deposited a mix of natural and groomed fingermarks on a total of 20 rounds of ammunition (Winchester .38 Special, J.S.P.) which were fired with a .38 S&W revolver 5 days after the fingermarks had been deposited. These cases were then developed within 2 hours after firing.

Gun Blue Protocol

The Gun Blue solution consisted of 50% Birchwood Casey Perma Blue solution and 50% distilled water. Each metal disc was immersed into the Gun Blue solution and held by using tweezers. The timer was started upon the whole contact of the metal disc with the solution. The discs were constantly observed and once ridge detail of sufficient quality was visible, the metal disc was removed from the solution and placed in to a beaker of distilled water for a few seconds to halt the reaction. The immersion times were recorded.

Ridge detail evaluation

The ridge detail was examined and given a grade as detailed in Table 1. All grading carried out was done by examining the mark on the casings using a magnifying fingerprint glass. The photographs of all impressions were used for this purpose. (taken with a NIKON D750, Camera mode: Manual, Shutter Speed: 1/250, Aperture: Wide open (f/1.4), ISO: 3200, White Balance: Auto WB, Autofocus: AI-Servo, Drive Mode: Continuous, Metering: N/A, Image Quality: raw) Independent grading was also conducted by a second examiner. Any differences in grades on certain fingermarks were later discussed and agreed upon.

Table 1: Outline grading scheme used for assessment of developed marks, adapted from [10].

Grade	Criteria
0	No ridge detail developed
1	No clear pattern or ridge flow, with few or no characteristics disclosed. Cannot be used for identification purposes.
2	Pattern or ridge flow is disclosed; however, characteristics are not clear throughout the whole impression. May possibly be used for identification purposes.
3	Pattern and/or ridge flow is disclosed with clear characteristics throughout. Identifiable ridge detail.

3.2 Results & Discussion

Development time

Morrissey et al. [4] reported that the average development time was 32 seconds. In this chapter, which included a larger sample and a variety of donors, the development times differ (from 20 to 120 seconds) depending upon the time interval between the deposition of the fingermark and development (Figures 1a-1f). The fingermarks deposited were groomed fingermarks, which means that their content in fatty components are higher than in other type of fingermarks [13] making them the best candidate for an enhancement method like Gun Blueing. Any time differences that may occur could be due to inter-donor and intra-donor variability (most likely due to the different amount of sebaceous material contained in each fingermark), different age and storage conditions of the fingermark samples [12,13]. As it can be seen from the graphs (Figures 1a&1c), in some of those aged samples that had been left under dark and ambient light (especially for those that had been left for 2 days) the development time actually drops with age. This phenomenon may indicate a reduced water content and better ‘’protection’’ of the substrate with the remaining oily/greasy components [14].

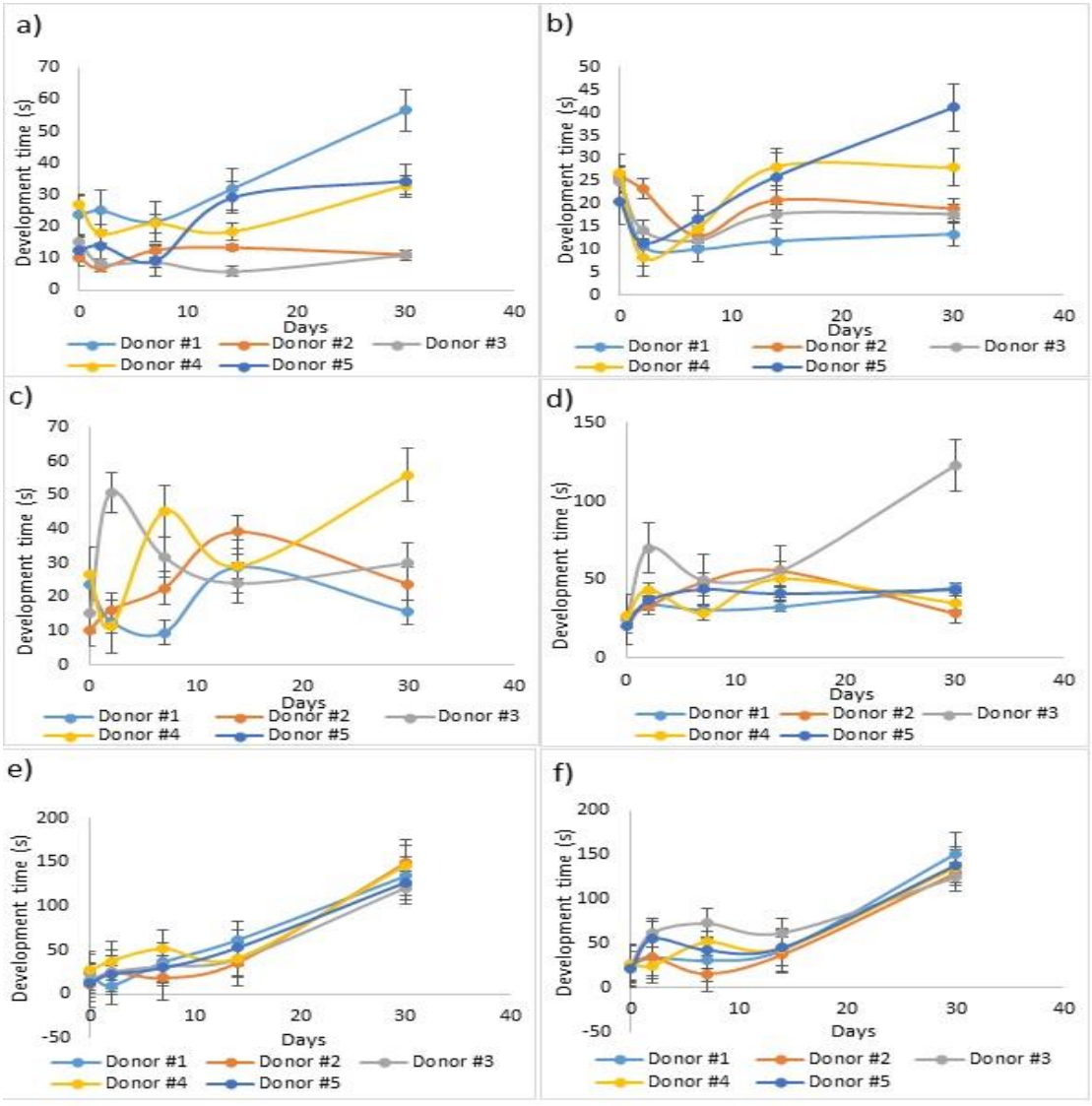

Figure 1. Average development times of aged groomed fingermarks a) male donors under dark conditions. b) female donors under dark conditions. c) male donors under ambient light conditions. d) female donors under ambient light conditions. e) male donors under outdoor conditions. f) female donors under outdoor conditions. The error bars represent the standard error. Each graph point is a sample size of n=5.

Generally, fingermarks on the brass discs which were kept under dark conditions were developed faster than the ones that where left under ambient light and outdoors. The brass discs that were left outdoors required the longest development time (Figures 1e&1f), and produced unexceptional results which seems logical due to their exposure

to environmental conditions (rain, wind) that may have removed or altered a lot of the fingermark residue that was initially deposited on the discs. This would allow greater exposure of the brass substrate for reaction with the Gun Blue, thus producing poorer fingermark development. This lack of fingermark residue seems to be the reason why the trends observed in the graphs 1e and 1f are more homogeneous compared to the other graphs. The less fingermark residue is available the lower the chance of different response to a fingermark enhancement method.

The fingermarks which were left under dark conditions did not show a clear trend of an increasing development time as they aged. On the contrary, increased development times were observed on aged fingermarks that were left under ambient light and outdoors. Dark conditions appear to decelerate the degradation process of the more oily substances in fingermarks [5].

Groomed fingermarks on brass metal discs

Ridge detail enhancement was successful in the vast majority of the samples, as shown in Figure 2 where the fingermarks were enhanced immediately after deposition.

Figure 2. Groomed Fingermark from a male (left) and female (right) donor developed immediately after deposition

Examples of fingermarks that were enhanced 2 days after deposition are shown in Figure 3. Due to the short ageing period and the high sebaceous content in the

deposited impressions, almost all fingermarks were enhanced succesfully regardless of the storing conditions.

Figure 3. Fingermarks from male donor developed after 2 days under dark conditions (left), under ambient light (middle), and 2 days outdoors (right)

Fingermarks of identifiable quality were also developed 7 days after deposition (Figure 4). At this time interval no noticeable drop in fingermark enhancement was observed.

Figure 4. Fingermarks from a female donor developed after 7 days under dark conditions (left), under ambient light (middle), and 7 days outdoors (right)

Identifiable fingermarks were also obtained even after the enhancement was performed 14 and even 30 days after deposition. However, the quality of the enhanced fingermarks was much lower (on average) for the ones that were left outdoors (Figures 5&6).

Figure 5. Fingermarks from a female donor developed after 14 days under dark conditions (left), under ambient light (middle), and 14 days outdoors (right)

Figure 6. Fingermarks from a male donor developed after 30 days under dark conditions (left), under ambient light (middle), and 30 days outdoors (right)

As it can be seen from the Figures 5 and 6, the samples that were left outside show signs of corrosion.

However, this is not necessarily a drawback. Wightman et al. [16] in their study demonstrated that a fingermark deposited on a metal surface can cause the surface to become preferentially corroded in the furrows of the fingermark thus making (sometimes) the latent fingermark visible without any further enhancement.

In other instances, the fingermark residue is just removed/degraded after sufficient days of exposure to outside conditions, rendering any successful enhancement highly unlikely (Figure 7).

Figure 7. The change in enhancement quality of fingermarks left outdoors from the same donor affected by the time elapsed. From left to right: 2 days old, 7 days old, 14 days old, and 30 days old.

Overall, the enhancement achieved on the majority of the fingermarks was for most of them up to an identifiable level. In most cases even 3rd level detail was present (even second level detail is enough for identification). Due to the frequent rain in the UK, a lot of the fingermark residue was likely washed away, making enhancement a much more difficult task. Had the rain occurrences been less frequent, higher enhancement grades would have been achieved for the fingermarks left to age outdoors.

Ridge detail evaluation

An overall distribution of the grades assigned to enhanced fingermarks is depicted on Figure 8.

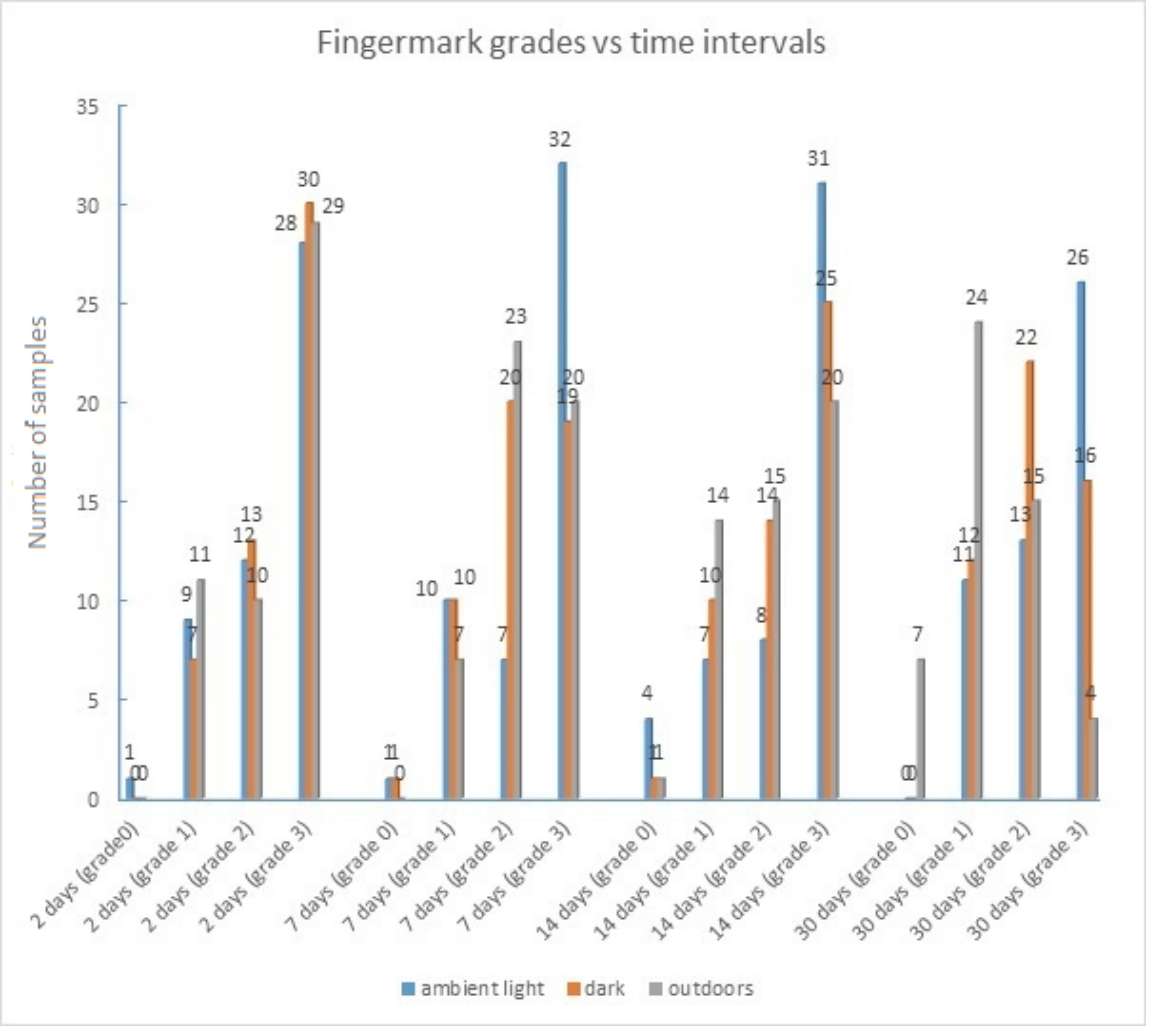

Figure 8. The cumulative grading of all fingermarks (n=600) from all donors divided by time elapsed since deposition and environmental condition.

As a general observation, it can be seen from Figure 8 that darkness, ambient light and time elapsed under dark and ambient light conditions, does not hinder, the enhancement of fingermarks significantly. When it comes to the samples left outdoors to age, it is difficult to assess what causes the most degradation to the fingermark

residue due to the uncontrolled nature of the conditions. We can only speculate that the constant fluctuations of temperature, humidity, wind and sunlight[17] make the enhancement of fingermarks that had been left more than 14 days to age, a difficult task to achieve.

It has to be noted that all of the samples were exposed to wet and sunny (UV radiation) conditions at least once before developing them and that exposure to rain may have caused diffusion [16, 17, 18] of their components and subsequently lowering the quality of the development by altering the original fingermark ridge detail pattern. From the brass discs that had been left outdoors to age, identifiable fingermarks could also be obtained, but mostly up to 14 days after deposition. In some cases, identifiable fingermarks were also obtained from samples that had been left to age for 30 days, but for far fewer samples (19 out of 50) compared to the brass discs that had been left under dark (38 out of 50) and ambient light (39 out of 50) conditions. It can be concluded that the proposed time ranges would be the following: 10-30 seconds for fingermarks left indoors up to 1 month, 20-60 seconds for fingermarks that have been left exposed to outdoor conditions up to 2 weeks, and lastly for fingermarks that have been left outdoors for 1 month 100-150 seconds.

Statistical analysis after converting the grades of the fingermarks to nominal data (either identifiable or non-identifiable) showed that the difference between the fingermarks left outside for 30 days and the ones indoors for 30 days was significant Chi-square (1, N=400, p value ~0.0001). It was also determined there was no significant difference between the samples that were left under dark and ambient light conditions (again for 30 days) Chi-square (1, N=400, p value ~.812).

An assessment into whether the gender of the donor plays a role in the quality of the enhancement was undertaken. Previous studies [18-20] suggest that fingermark residue from males has a larger amount of oily/greasy components than the ones from females. It seems that our results confirm this previous finding. From the total

number of 300 samples deposited by female donors, 202 were enhanced to an identifiable level. For male donors the number of samples that were enhanced to an identifiable level was 250 out of 300. It was also observed that when development times exceeded a certain time limit (usually 120s) that led to unidentifiable fingermark development (possibly due to the lack of greasy/oily compounds). Our statistical computations indicated that indeed there is a significant difference in the quality of the enhancement between males and females (enhancement with Gun Blue worked better on fingermarks from male donors).The data was converted from interval data (0, 1, 2, 3) to nominal data (Identifiable or non-identifiable fingermark) Chi-square, (1, N=600, p value~0.0001).

Natural fingermarks on brass discs

As shown in Figure 9, some of the discs were enhanced and identifiable fingermarks were developed.

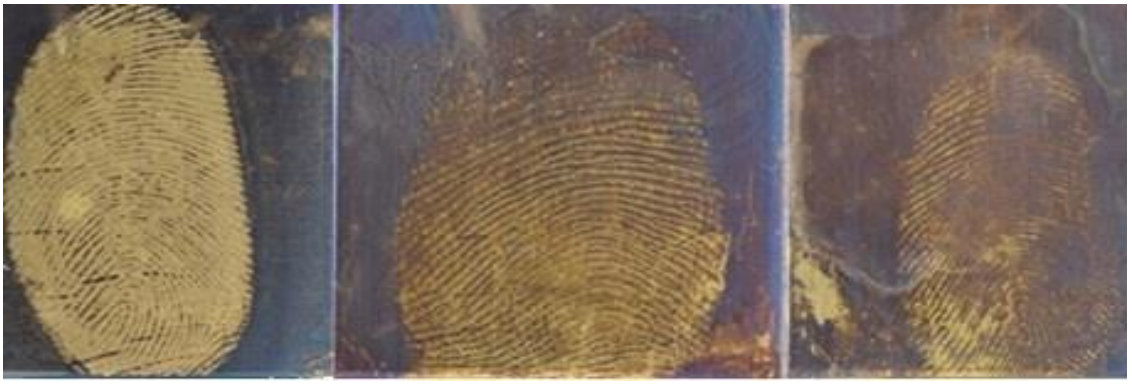

Figure 9. Identifiable fresh natural fingermarks from male (middle) and female (left and right) donors

However, some of the natural fingermarks were not developed to an identifiable grade. Lower quality of development on natural fingermarks compared to the groomed ones is to be expected due to their lower level of fatty components

[8,13,21,22,23].An overall grading of our results on natural fingermarks on brass discs is shown in Table 2.

Table 2. Fingermark grades of natural fingermarks on brass discs

Condition Subjected	**Grade 3**	**Grade 2**	**Grade 1**	**Grade 0**
Fresh	7	5	4	0
7 days old (alternating between dark and ambient light)	3	1	11	1
14 days old (alternating between dark and ambient light)	2	2	5	7
Light (1 week old)	3	1	6	6
Dark (1 week old)	3	1	7	5
Outdoors (1 week old)	3	2	6	5

It is clear that the 'fresh' condition group gave the best development overall, but this would be expected as they were developed immediately after deposition. The 14 days

old group performed the poorest overall with only 2 sets of fingermarks being grade 2 and above.

Clearly, the number (n = 96) of natural fingermarks developed here is not large enough to perform any meaningful statistical analysis, however it has been shown that Gun Blue can work on fingermarks with a development time ranging from 20 to 42 seconds [4] and that fresh natural fingermarks are more likely to be developed up to an identifiable level.

Fired cartridge cases

The most favourable results were acquired from a male donor who deposited groomed fingermarks on cartridges that were fired from single shot bolt-action rifle (Figures 10&11). However, only 1 out of 20 was of identifiable quality (grade 2).

Figure 10. Fired cartridge case 7.62mm (single shot bolt-action rifle). Identifiable groomed fingermark from a male donor. The red arrow indicates a very clearly defined second level feature (ridge ending).

Figure 11. Fired cartridge case 7.62mm (single shot bolt-action rifle). Groomed fingermark from a male donor. Suitable for identification purposes due to the low number of second level features.

A trend was also observable when looking at the developed fingermarks on cartridges fired from a single shot bolt-action rifle, the quality of the ridges was much lower near the head (which is the base, on the opposite end of the bullet) of the cartridge, this might indicate that the gas blowback affects primarily that part of the cartridge when this particular gun is used.

Almost all of the cartridges fired from the single shot bolt-action rifle showed 3 or 4 level 2 characteristics on average meaning that they can potentially be used for elimination purposes.

However, it was noted several cases only developed minimum ridge detail as shown in Figure 12.

Figure 12. Fired cartridge case 7.62mm (single shot bolt-action rifle). Groomed fingermark from a male donor. Almost all levels of features are absent.

It is notable that some ridge detail from female donors was also developed from cartridges that were fired with a .38 S&W revolver. Only 1 out of 20 fingermarks was close to an identifiable grade, but ridge detail was obvious in the majority of them (Figures 13-15). Out of all 12 cartridges fired with a .45 Glock, none of them showed any ridge detail development.

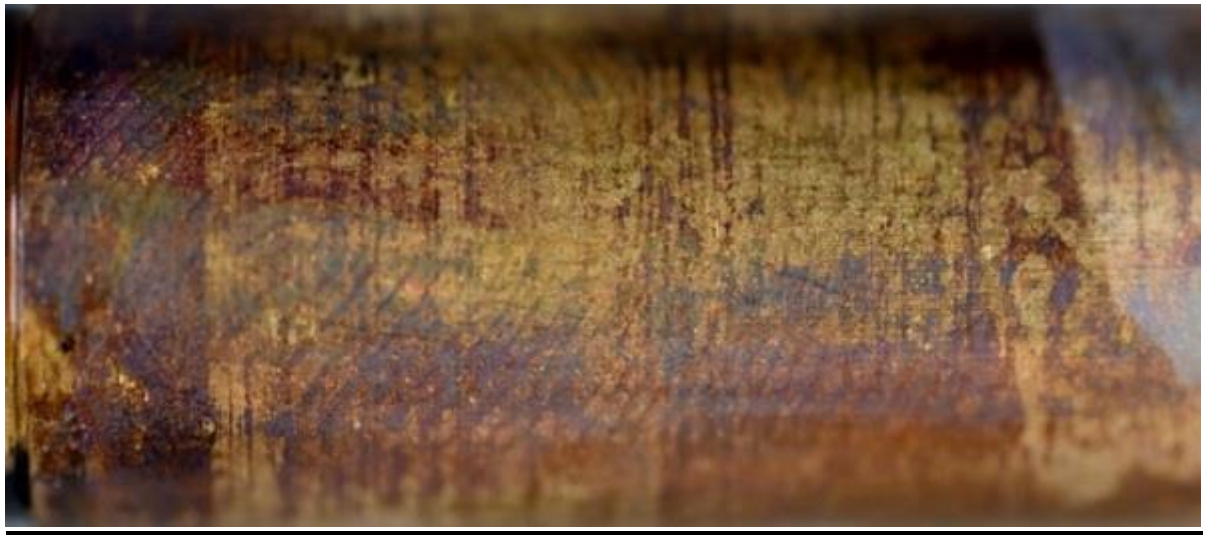

Figure 13. Fired cartridge case (.38 S&W revolver). Natural fingermark from a female donor. Clear level one features are present but fewer second level.

Figure 14. Fired cartridge case (.38 S&W revolver). Natural fingermark from a female donor

Figure 15. Fired cartridge case (.38 S&W revolver). Groomed fingermark from a female donor

It appears that the type of weapon used for firing the cartridges can have a detrimental effect on the development of fingermarks with Gun Blue. Specifically, it seemed that cartridges fired from the single shot bolt-action rifle and the .38 S&W revolver showed overall better quality of development than the ones discharged with the .45 Glock. This finding agrees with that reported by Bentsen et al. [24] when it comes to revolvers. However, our sample size is not large enough to draw any rigid conclusions. Gun Blue can develop fingermarks on fired cartridge cases under a controlled environment but with a low success rate when it comes to producing identifiable fingermarks (grade 2&3). It may be more likely that it could help develop fingermarks suitable for elimination purposes, which is still information that can aid an investigation.

Overall, Gun Blue was shown to develop natural and groomed fingermarks from different donors and on fired cartridge cases while offering a very fast and cost-effective way of developing fingermarks.

3.3 Summary & Conclusion

After a consideration of the results from all donors and from different environmental conditions, certain tendencies of the enhanced groomed fingermarks were observed. Firstly, it has been demonstrated that in the majority of cases, groomed fingermarks that had been left to age up to one month under dark and ambient light can be successfully enhanced to an identifiable grade (>2) using the Gun Blue protocol on brass surfaces. However, the heavily sebaceous nature of the fingermarks used for this part of the study, do not allow extrapolation of the conclusions to casework fingermarks. Natural fingermarks (most likely to be found in casework) may be less resilient to outside conditions or other degrading factors (in our study, temperature, humidity, air currents, different light level and UV radiation, substrate corrosion played a part in fingermark degradation) [25].

Moreover, it has been shown that there is no standard optimal development time that can be recommended; however, there are suggested time ranges for this method depending on the circumstances. The development time is generally 10-30 seconds for fingermarks left indoors up to 1 month, 20-60 sec for fingermarks that have been left outdoors up to 2 weeks and, lastly, 100-150 sec for fingermarks that have been left outdoors for 1 month.

This research demonstrates that Gun Blue can be effective with a variety of donors and that it can be used for groomed fingermarks that have been deposited up to 30 days prior to enhancement even under outdoor conditions. Moreover, the potential of developing natural fingermarks on brass discs under different environmental conditions and time intervals was also showcased.

The use of Gun Blue as a standalone technique can develop fingermarks (groomed and natural) suitable for identification purposes on fired cartridge cases. Finally, the effects of the firearm used on the success of recovery of fingermarks is considered. A single shot bolt-action rifle and revolver produced the best results. It was also observed that the richest fingermark area was usually around the middle of the cartridge, contradicting the finding of previous research [3] where the fingermark was almost intact near the head of the cartridge.

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4. Vacuum Metal Deposition: A Preliminary Study

Abstract:

In order to assess the efficacy of vacuum metal deposition (VMD) as a technique to develop fingermarks on ballistic metallic surfaces, a preliminary study using six donors (three male & three female) was conducted. Using a sequential metal deposition process, two metal combinations were studied—gold/zinc and silver/zinc. Results indicate the potential of this technique, by developing identifiable fingermarks on brass metal discs aged from a few days up to more than a month old. As the development of fingermarks on fired (brass) cartridge cases is an area of interest, a further study was conducted where a total of 20 fingermarks were deposited on cases. After firing, second level fingermark characteristics were successfully observed on cartridge cases highlighting its potential as a fingermark enhancement method for ballistic brass materials. Further work is required to fully evaluate the VMD process and its reliability as a fingermark enhancing method on ballistic surfaces.

Introduction

Vacuum metal deposition (VMD) is a fingermark enhancement technique that is used in police casework (1), but is a relatively unexplored technique in relation to metallic surfaces. It is a thin-film deposition technique in which a source metal is vapourised in a vacuum, in order to coat a substrate. The technique has been long established in the industrial application of metal coatings for articles such as mirrors [1]. The use of VMD as a tool for the forensic enhancement of latent fingermarks was first proposed in 1968 [1]; however, a substantial number of years passed before it would be considered as a viable enhancement technique. VMD was initially introduced in the forensic field to detect fingermarks on paper [2] and was then optimized to be fully operational in the late 1970s. The method involves placing the item to be treated inside the deposition chamber, which is sealed/operated at a high vacuum, typically

larger than 3×10^{-4} mbar. The chamber contains tungsten boats for the containment and heating of the selected metal to be deposited and a window to allow the operator

to monitor and control the deposition process [1,3]. The most commonly used metals in the VMD treatment of latent fingermarks are gold/zinc, gold is applied first, followed by zinc [1]. After the vapourisation of gold, gold atoms cluster together forming agglomerates, which may penetrate some constituents of the fingermark residues (Figure 1). Zinc is then vapourised, which preferentially deposits on the exposed gold agglomerates [4] rather than on areas where these are embedded in the latent fingermark deposit. The zinc is binding to the fingermark furrows and not the ridges of the print (Figure 1). The fingermark developed is a negative one with the furrows covered by the gold and zinc appearing gray. Positive development of fingermarks can also occur. It is thought that positive development occurs in samples where the fingermarks are rich in fatty components or other contaminations (*i.e.*, grease) [5,6]. Other metal sequential deposition protocols for VMD can also include silver/zinc, sterling silver, copper/zinc and copper. The metal combinations studied here are considered to be the most utilised [5–8].

One of the greatest advantages of VMD includes its versatility, including its suitability for a wide range of substrates, including wetted ones [2]. VMD is also ideal to use as a sequential treatment, as it does not damage any DNA that may be present in fingermarks [8] (since it targets the metallic substrate and not the fingermark itself), and works well with other conventional fingermark enhancement techniques such as cyanoacrylate fuming [6, 8]. Drawbacks of VMD include the cost of the equipment and that the quality of enhancement relies upon the experience of the operator to determine the optimum time at which the process should be halted to prevent overdevelopment of fingermarks. The cost of the deposition metals is minimal due to the minute quantities needed for each process. Over recent years, studies have focused on using VMD on fabrics [7–9] with some success. The introduction of polymer banknotes in some countries has sparked a resurgence in VMD research, in an attempt to enhance fingermarks on this difficult surface [9].

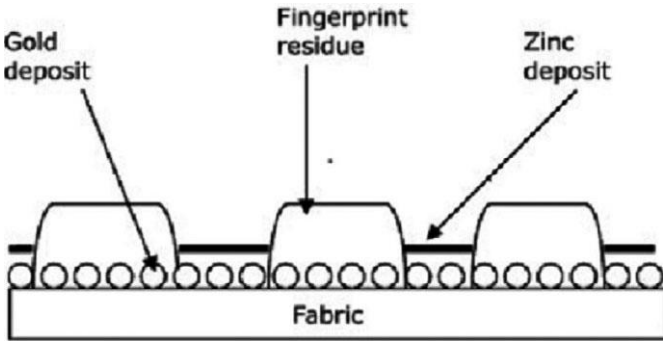

Figure 1—Visualisation of fingermarks and grab impressions on fabrics. (Part 1: gold/zinc vacuum metal deposition) [7].

Table 1—Outline grading scheme used for assessment of developed marks [18] adapted from [6].

Grade	**Criteria**
0	No ridge detail enhanced
1	Few ridge detail enhanced; unidentifiable mark
2	Pattern or ridge flow is enhanced, but with unclear characteristic. Possibility for identification purposes. Mark can be used for exclusion purposes.
3	Pattern and/or ridge flow is enhanced with clear characteristics throughout. Identifiable ridge detail.

The motivation behind this research stems from the lack of studies on employing VMD on metallic surfaces as a standalone technique and also the scarcity of reliable techniques for the development of fingermarks on fired cartridge cases [10]. A study by Fraser et al. [11] showcased the increased efficacy of VMD compared to cyanoacrylate fuming on smoother almost nonporous fabrics (such as nylon); however, this finding might hold true for metallic surfaces also (which are nonporous surfaces). The only peer-reviewed literature studies using VMD for metallic surfaces were by Dafydd et al.[12] and Tiwari et al.[13]. In the former study, they used Scanning Kelvin probe in conjunction with VMD for latent fingermark visualisation, while in the latter the authors focused on optimizing the deposition protocols for fingermark enhancement on aluminium surfaces.

This preliminary study addresses utilization of gold/zinc and silver/zinc protocols for the enhancement of latent natural fingermarks on brass metal discs, while also exploring the potential of the method for groomed fingermarks on fired brass ammunition, a topic of great interest for forensic examiners.

4.1 Materials & Methods

Fingermark Deposition

Six donors were employed for the first part of this study (3 male, 3 female), and written consent was acquired after the purpose of this study was explained. Ethical approval was granted for this study by the Liverpool John Moores University ethics committee (17/PBS/002). The criteria for this preliminary study was achieving a balance between male and female donors since it has been debated that the gender of the donor can play a role in the composition of fingermarks (in some studies male donors tended to have higher concentration of fatty components in their fingermark residue) and consequently in their enhancement [14,15]. The age of the donors was between 25–30 years old, within this age limit there were no particular differences observed in fingermark composition [14]. The donors were asked to wash their hands

with soap and water and resume their normal daily routine for 30 min before depositing any fingermarks as it is the standard procedure for generating natural fingermarks [16,17]. The donors' daily normal routine revolved around desk-based work using a computer. The deposition was performed by placing simultaneous fingermark impressions from the right thumb across two brass metal discs. This was done to ensure the same fingermark was examined with the two metal deposition protocols as proposed by Sears et al. [16]. The discs (3x3 cm) had been previously cleaned with 5% v/v Decon 90 solution, followed by ethanol and left to air dry. Each donor deposited 12 full fingermarks (which is an adequate number for a preliminary study [17]) which were divided into four even groups according to the number of days they were left to age before development (2, 7, 14, 35 days old), the aforementioned time ranges were chosen based on fingermark research and guidelines in the literature [16,17]. The discs were stored under dark and dry conditions, with temperatures ranging from 15– 20°C. The process consisted of loading the brass disc or bullet cases onto the "metal hood" of the chamber, before adding a 2-5mm 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 ($3x10^{-4}$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.

The simultaneous natural fingermark impressions were treated with two different vacuum metal deposition protocols, namely gold/zinc and silver/zinc. Each run on the VMD lasted approximately 10 minutes, with the duration (of each run) varying slightly between samples due to inherent donor variability (although sample fingermark deposition and collection protocols for all donors was the same).

The apparatus used for all experiments was a VMD900 Metal Deposition System from West Technology. Blank cleaned discs were run with VMD to assess any deposition

artefacts on the brass surfaces which may affect any fingermark evaluation. No impact on the results was noted.

Brass cartridge cases (.38 Special) were cleaned with a 5% v/v Decon 90 solution and ethanol. Each donor (two male, two female -male and female donors 1 and 2 from the initial brass discs study) deposited a single groomed fingermark on five cartridges (groomed procedure same as for natural marks including rubbing of forehead and nose areas as per IFRG guidelines) [17]. The cartridges were fired using a .38 Smith and Wesson (S&W) revolver. This weapon was chosen due to the larger case surface area of the ammunition enabling full fingermark deposition and discharged 5 days after the deposition of the fingermarks (the shooting time was based on the availability of the firearms services). The loading and collecting of the cartridges were completed while wearing gloves. In this instance, groomed fingermarks on cleaned cartridge cases were employed to increase the chances of fingermark residue adhering on the cartridge after firing. The employment of groomed fingermarks is considered acceptable for pilot studies [17].

Ridge Detail Grading

Developed prints were graded according to the scheme given in Table 1 [18]. All gradings were carried out by examining the mark on the casings using a magnifying fingerprint glass. The photographs of all impressions were taken with a NIKON D7100: Camera mode: Manual, Shutter Speed: 1/250, Aperture: Wide open (f/1.4), ISO: 3200, White Balance: Auto WB, Autofocus: AI-Servo, Drive Mode: Continuous, Metering: N/A, Image Quality: raw were also used for this purpose. No enhancement photo software was used. Independent blind grading conducted by a second trained fingerprint examiner was undertaken. Both were graded independently and both set of grades were in agreement. All fingermarks were labeled with an alphanumeric code to prevent potential bias and to protect the donors' privacy. In all photos, no scale was used due to the known dimensions of the objects and due to the fact that the photos were not used to compare the size of the items.

4.2 Results & Discussion

One male (male donor 1) donor of the total 6 donors (Figure 2a,b) produced fingermarks that were of identifiable quality throughout all of the different ageing time intervals. One female donor (female donor 1; Figure 2c, d) deposited fingermarks that could not be developed by either deposition protocol.

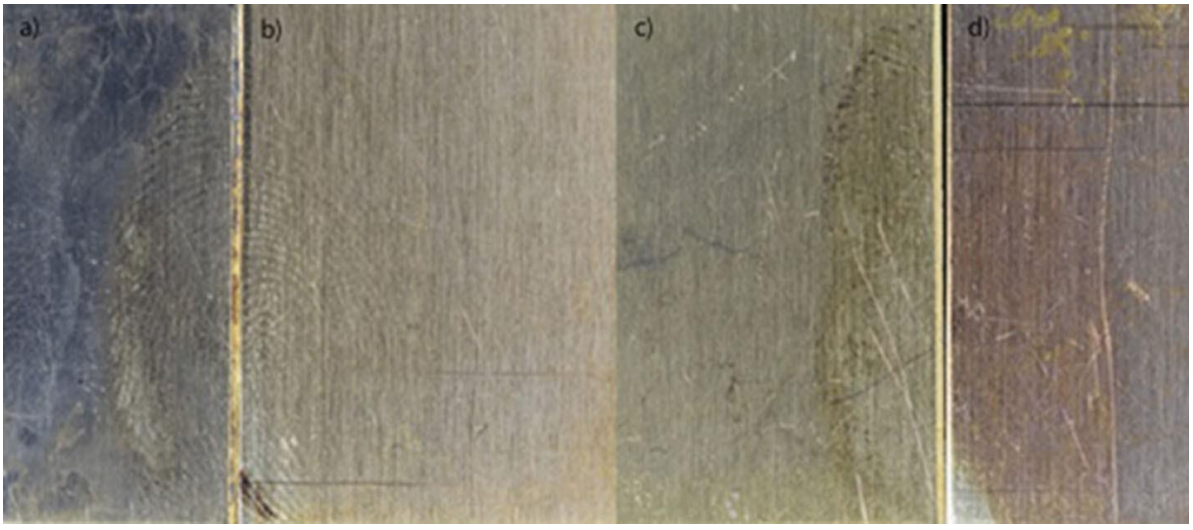

Figure 2. Simultaneous natural fingermarks on brass discs developed 2 days after deposition: Male donor 1 (a): gold/zinc (b): silver/zinc. Female donor 1 (c): gold/zinc (d): silver/zinc

Fingermarks from male donor 2 were more receptive toward the silver/zinc metal deposition protocol (Figure 3b). Female donor 3 mostly produced “empty” fingermarks but in some cases ridge detail enhancement was achieved (Figure 3d).

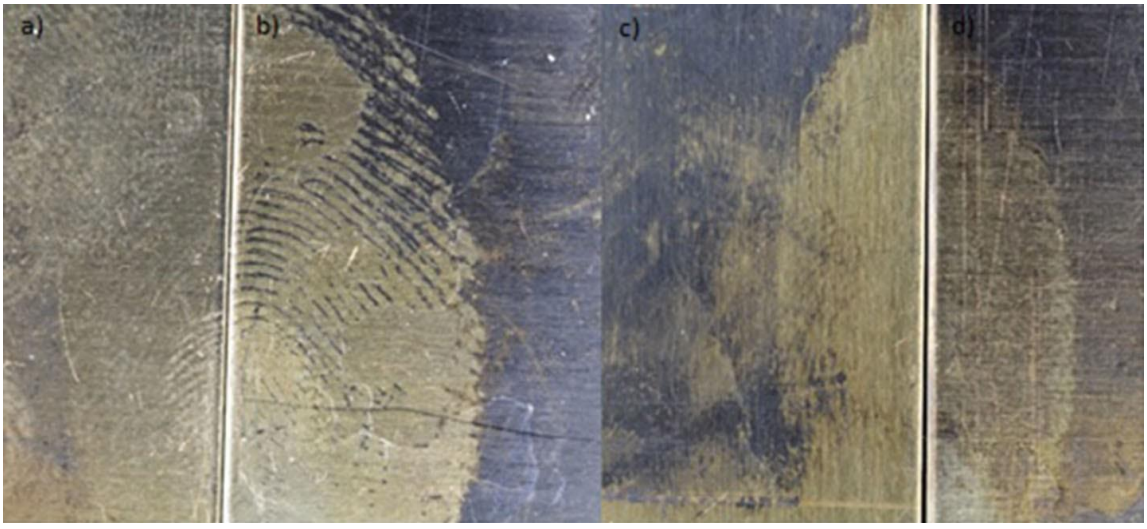

Figure 3. Simultaneous natural fingermarks on brass discs developed 7 days after deposition: Male donor 2 (a): gold/zinc (b): silver/zinc. Female donor 2(c): gold/zinc (d): silver/zinc.

Male donor 3 mostly produced “empty” fingermarks but in some cases some ridge detail enhancement was possible (Figure 4b). In these instances, it could be inferred that fingermarks from certain donors (female donor 1 and male donor 3) may not be ideal for the VMD.

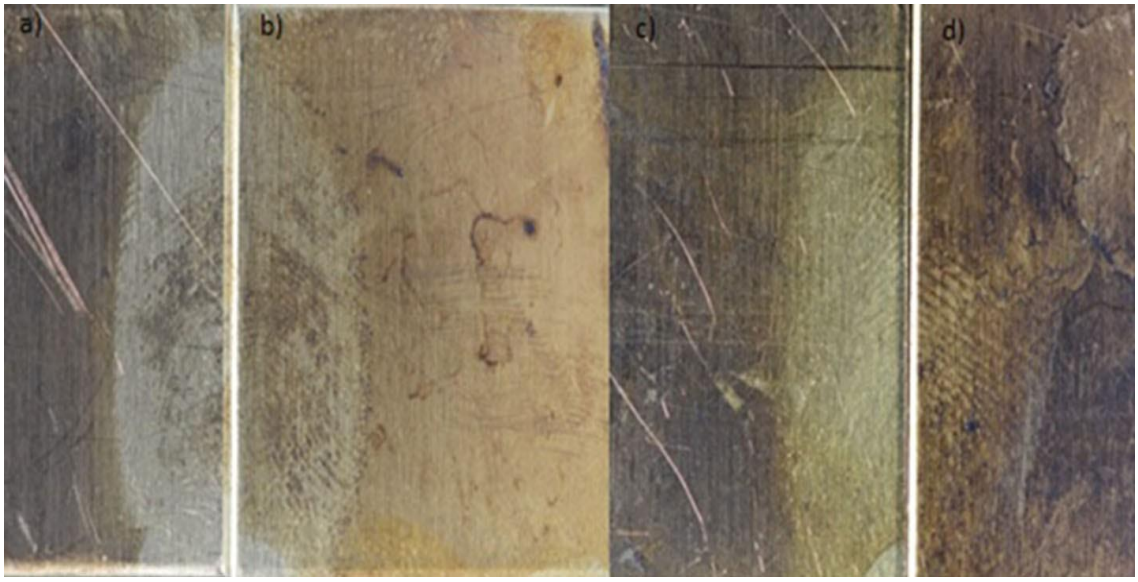

Figure 4. Simultaneous natural fingermarks developed 14 days after deposition: Male donor 3 (a): gold/zinc (b): silver/zinc Female donor 2 (c): gold/zinc (d): silver/zinc.

Female donor 3 had not produced an identifiable fingermark on earlier time intervals; however, at 35 days an identifiable fingermark (Figure 5d) was developed. It seems that the effect of time on fingermarks might be complex, meaning that a fresh fingermark will not necessarily be developed any easier than an older fingermark when VMD is used.

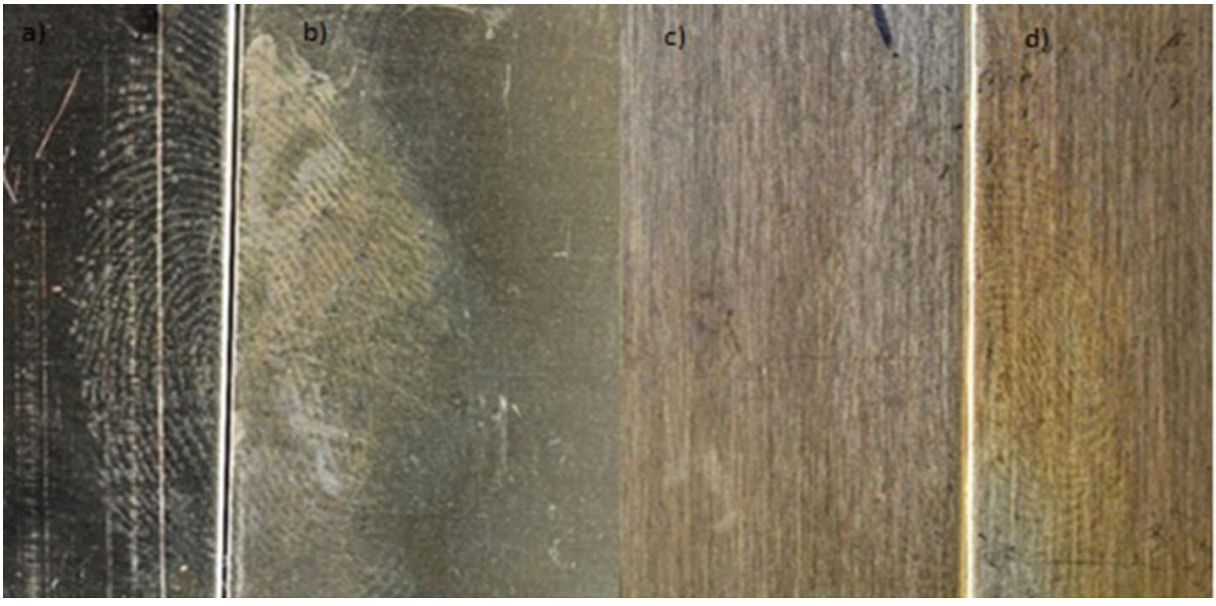

Figure 5. Simultaneous natural fingermarks developed 35 days after deposition. Male donor 1: (a): gold/zinc (b): silver/zinc Female donor 3: (c): gold/zinc (d): silver/zinc.

Fingermarks which contained second level detail—ridge characteristics were developed on fired cartridge cases (Figure 6a,b,c). The fingermarks were deposited 5 days prior to firing the cartridge. Out of 20 fingermarks, only 3 (deposited from male donor 1, the same donor as in the brass discs experiment) displayed some sort of second level characteristics when enhanced. Although the sample size was small, it indicates that there is a possibility to enhance fingermarks that would be of a quality high enough to perform identification of a suspect.

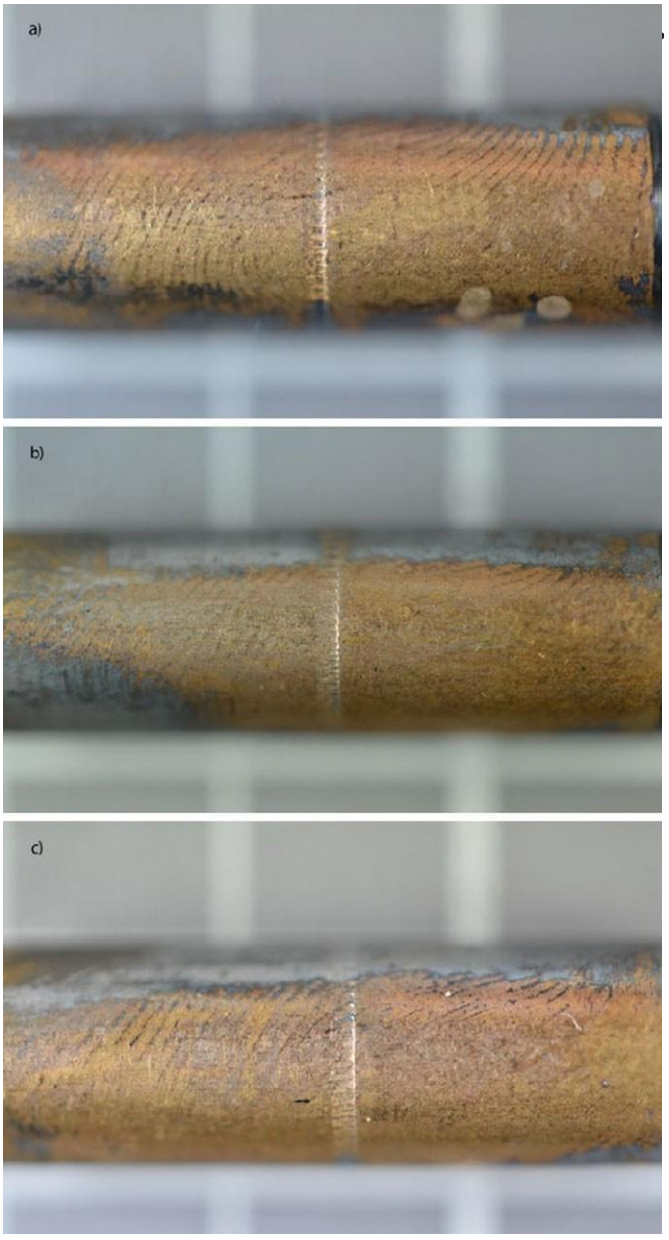

Figure 6. Groomed fingermark by a male donor (male donor 1) on 3 separate cartridge cases (a, b, c) developed with silver/zinc 1 day after firing.

Below (Tables 2 and 3) the grading of the fingermark developed on brass metal discs using two different metal deposition, protocols can be seen.

The fingermark grades data were checked for normality (using the Kolmogorov–Smirnov test) and it was found that it does not follow a normal distribution (as expected when using a nonlinear scale).

Table 2. Evaluation of natural half fingermarks on brass metal discs developed with gold/zinc.

Donors	**Grades Day 2**	**Grades Day 7**	**Grades Day 14**	**Grades Day 35**
Male donor #1	1,2,1	0,1,1	1,2,3	3,3,3
Male donor #2	1,2,1	1,1,0	1,0,1	0,0,0
Male donor #3	1,0,1	0,0,0	1,1,1	0,0,0
Female donor #1	0,0,0	0,0,0	0,0,0	0,0,0
Female donor #2	0,0,0	0,0,0	0,0,0	0,2,0
Female donor #3	0,1,0	0,1,0	0,0,0	1,0,0

Table 3. Evaluation of natural half fingermarks on brass metal discs developed with silver/zinc

Donors	Grades Day 2	Grades Day 7	Grades Day 14	Grades Day 35
Male donor #1	1,1,1	2,1,1	1,2,2	1,3,1
Male donor #2	1,1,1	0,0,0	2,0,1	0,0,0
Male donor #3	1,0,0	1,1,1	2,2,1	0,0,0
Female donor #1	0,0,0	0,0,0	0,0,0	1,0,0
Female donor #2	0,0,1	0,0,0	0,0,1	1,1,2
Female donor #3	0,0,0	0,1,0	0,1,0	3,0,0

The grades of fingermarks developed with gold/zinc and silver/zinc were divided in to two groups and tested with a Mann–Whitney test. The result shows that there is no significant difference ($p \sim 0.4$, confidence interval 95%) in the quality of developed fingermarks when using one of the two metal deposition protocols.

Table 4 shows the grades of the fingermarks deposited on fired cartridge cases using silver/zinc, based on the results from the brass disc experiments.

Table 4. Evaluation of groomed fingermarks on fired brass cartridge cases developed with silver/zinc.

Donors	Grades
Male donor #1	1,2,1,1,0
Male donor #2	0,0,0,0,1
Female donor #1	0,0,0,0,0
Female donor #2	0,0,0,0,0

As a general remark regarding the quality of enhancement of the fingermarks that were enhanced with VMD, it can be inferred that the time of deposition does not really follow a linear relationship with the quality of enhancement. In other words, an ''older'' fingermark

will not necessarily yield worse enhancement and vice versa. This phenomenon is particularly evident on Table 3 where the 35 days old fingermarks were enhanced to identifiable levels more times than the 2 days old ones. When it comes to developing fingermarks on fired cartridge cases, the expected unexceptional enhancement was achieved (as shown on Table 4) suggesting that the degradation from firing can be for the vast majority of fingermarks a very hard obstacle to tackle.

4.3 Summary & Conclusion

The work described here indicates that successfully enhancing latent fingermarks on a flat brass surface with VMD depends on the donor of the fingermark. Out of 6 donors, only one male donor produced fingermarks that could be developed to an identifiable level throughout all the different time intervals. The overall quality of the fingermarks developed by male donors and by using the gold/zinc and silver/zinc protocol seems to be higher and statistically significant than the fingermarks from female donors (Mann– Whitney p ~ 0, confidence interval 95%), but the lack of data due to low donor numbers limits the value. The statistical analysis of fingermarks developed by gold/zinc and silver/zinc show that overall, there is no significant difference in the quality of the enhanced fingermarks. However, it should be noted that certain donors responded better to one of the two metal deposition protocols, namely male donor 3 and female donor 3 produced identifiable fingermarks with the silver/zinc deposition protocol. Fingermarks that were aged up to 35 days were only identifiable when developed from male donor 1, and female donor 3. Further work is recommended to assess the ageing process of fingermarks in relation to VMD enhancement. The results on fired cartridge cases shot by a .38 S&W revolver demonstrate that VMD is capable of producing fingermarks that have second level characteristics (bifurcations, ridge endings etc.). When applied to casework, such detailed fingermark development may prove problematic due to the degradation of the fingermark residue on a cartridge case that would make the development of a clear ridge detail pattern more challenging. Moreover, the use of VMD processes impacting on other evidence types needs to be considered (*e.g.*, case striation marks). This study has also shown that

natural and groomed fingermarks from certain donors can be enhanced successfully using this technique. In terms of the compounds that are present in fingermarks and could be facilitating their enhancement when using VMD, both eccrine and sebaceous components are to be considered, especially since it has been reported [12] that eccrine prints of good quality can be developed with VMD.

4.4 References

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5. Vacuum Metal Deposition Enhancement of Friction Ridge Detail on Ballistic Materials

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 was recovered. Lastly, an attempt to understand which fingermark components are facilitators of VMD enhancement was made. Fingermark residue was extracted from brass discs 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 one plays in VMD enhancement.

Introduction

The majority of friction ridge detail 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 friction ridge detail [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 friction ridge detail from potentially corroded surfaces, unlikely to react with any contaminants, and able to develop friction ridge detail 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 calibers of ammunition. This 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 process currently recommended by the Centre for Applied Science and Technology (CAST) for use on smooth non-porous items, is a sequential treatment of cyanoacrylate fuming, followed by Basic Yellow (BY40) fluorescent dye [6]. This generally involves heating cyanoacrylate 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 friction ridge detail, the structure of which helps to scatter light and trap subsequent fluorescent dye molecules. The exhibits are then dyed with ethanol-based BY40 before viewing under an appropriate light source to allow the visualisation of the marks [7].

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 novel techniques which aim to improve the recovery of friction ridge detail 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 [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 novel techniques, Gun Blue appears most likely to be developed further; however, the technique is limited to metallic surfaces and requires further evaluation and optimization 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 SG 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 (Figure 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 [24] and has shown success on several notoriously difficult substrates such as polymer banknotes and fabrics [25, 26]. Unlike SG fuming, VMD can also be used on exhibits that have previously been wet [27], and is recommended for aged marks [6].

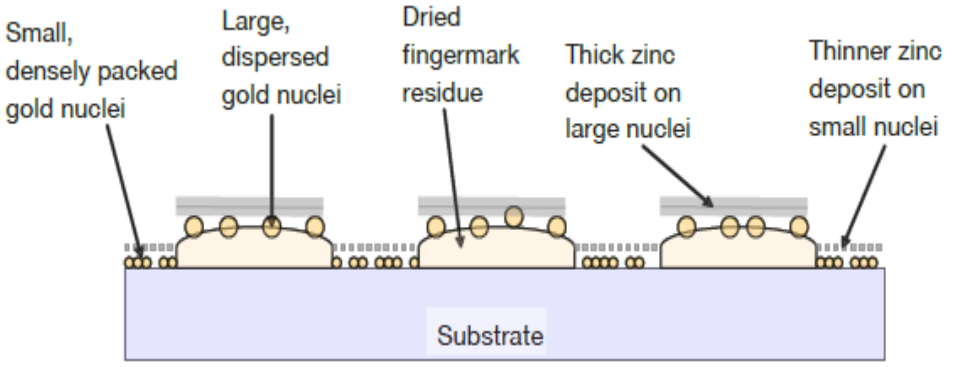

Figure 1: The process by which zinc deposits only on the background surface leaving transparent ridges [6]

Whilst there is little specific research into the use of VMD on metallic surfaces, particularly regarding ballistic evidence, Tiwari et al. [28] 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 friction ridge detail 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 [29]. 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 [30]. The study does however show that VMD enhancement occurs successfully on a variety of metals including brass [29].

Research is now focusing 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 friction ridge detail on ballistic brass discs, and produce second level friction ridge detail 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 friction ridge detail on ballistic evidence.

This chapter aims to further investigate the use of VMD for the recovery of friction ridge detail 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 enhancement is made, by pinpointing the compounds that are the major contributors of VMD enhancement.

5.1 Materials & Methods

Fingermark collection

Initial Phase brass discs

The same ballistic brass discs were used in this chapter along with the same cleaning protocol as described in an earlier VMD chapter (4.1). Additionally, each disc was labelled to show, the donor, age of mark and VMD treatment (Figure 2). A total of 40 discs were prepared for each donor to provide five repeats for each of the ageing categories: a day, a week, a month and two months.

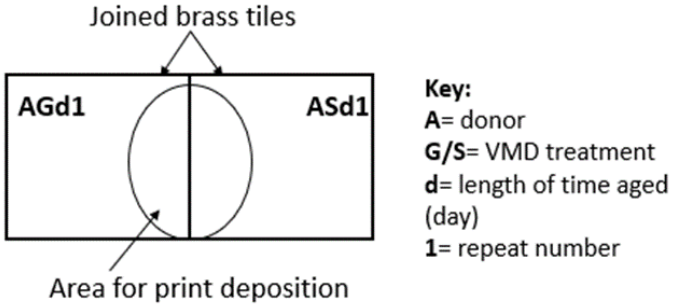

Figure 2: Diagram of brass disc set-up for donation

10 male donors and 10 female donors were selected from volunteers, labelled A to T. Three were of an ethnic minority background. The proportions of the sample population were based on a stratified sample from the latest census data, using as many variables as was practicable [31]. 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 generalized. The resulting sample contained 20 donors of unknown quality, representing an age range from 19-56, and a variety of job types from office work to laboratory work.

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 minutes prior to donation [32]

During the collection they were instructed to press their right thumb across the join of each pair of disc for three seconds. In between each deposition donors rubbed their fingertips together to redistribute the fingermark residues and help to prevent depletion. The discs were kept in secure storage, akin to where evidential items are kept before treatment.

Brass Bullet Cases

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

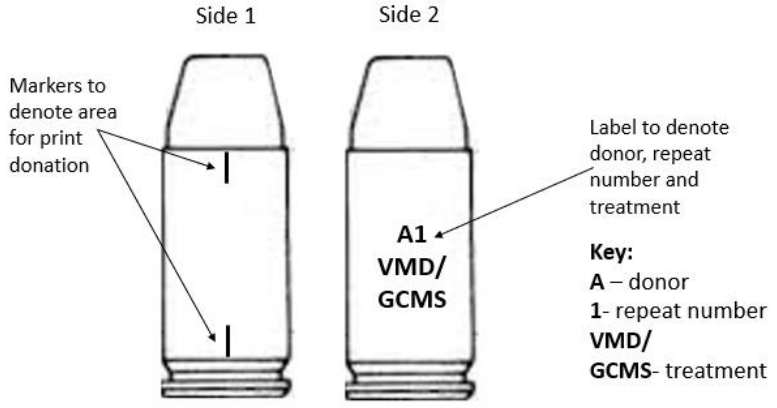

Figure 3: 9mm brass cartridge labelled for fingermark donation.

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 again collected and donors received the same instruction as above in the previous section.

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

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, donor fingermark residue was subjected to GCMS analysis.

Ballistic brass discs were prepared as stated above. Instead of being joined together individual discs were labelled as shown below (Figure 4), three were prepared for each donor. 9mm brass bullet cases were also prepared as stated above, again three per donor, as shown in Figure 3.

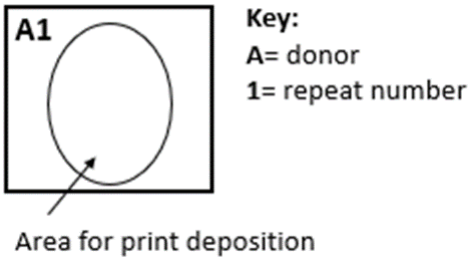

Figure 4: Brass disc labelled for fingermark donation.

Natural prints were again collected following the aforementioned methodology. The same six donors selected in the brass bullet cases section, based on the quality of their enhanced fingermarks, were used for continuity and to ensure a range of donors were tested.

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 same procedure as described in Chapter 4.1 was used.

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 100mm 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 optimized lighting.

The photographed marks were initially graded using the standard Centre of Applied Science and Technology [6] (CAST) scheme (Table 1). This consisted of examining each photographed mark individually with an eyeglass. When referring to the fingermarks enhanced on brass discs 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 person (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.

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

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

Fingermark compositional analysis

GC/MS instrumentation and conditions

Chromatographic analysis was performed with an Agilent Technologies 7890A network GC system, equipped with an Agilent 7683 Series auto sampler. An Agilent J&W Scientific HP5-MS UI (30 m x 0.25 mm x 0.25 µm) column was used. Helium was used as the carrier gas (1mL/min), the injection volume was 1 µL, with a solvent delay of 3.6 minutes. 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 minutes and finally with a ramp of 4°C/min up to 310°C for 8 minutes. The total run time was 46 minutes. The GC was coupled with an Agilent 5975B Inert MSD system using electron impact (EI) ionization. The scan range was set from 40 to 500 m/z. The transfer line between the column and the MS was kept at 280°C. The method was adapted from[33].

Fingermark extraction

5 mL of MeOH (Sigma-Aldrich, UK) was used to extract the fingermark residue from the fired cartridge/metal disc by slightly agitating the beaker for 2 minutes. Then the solution was evaporated to dryness under nitrogen and reconstituted using 100 microliters of MeOH. An extra 2.5 microliters of hexadecane (Merck, UK) (transferred from a 1%v/v hexadecane/MeOH solution) were added as the internal standard.

Data analysis

Principal component analysis on the fingermark chromatographic data was performed by using the OpenChrom (Lablicate 2018) open source software. The Chromatograms were modified in Microsoft Excel.

5.2 Results & Discussion

VMD Process

Enhancement Procedure

The initial work undertaken for this chapter 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 initialization period before use and a shut-down period after treatments, these were found to be on average 43.86 ±0.70 minutes (n=7) and 39.00 ±4.34minutes (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 minutes in total, with the pump-down time making up 62% of that time, and development by metal deposition only 19% (see Table 2). 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.

Table 2: Showing the time taken for each stage of a VMD treatment, along with standard deviation and standard error of the mean (n=65)

	Average Time (minutes)	**SD (minutes)**	**SE (minutes)**
Pump-down	6.83	1.78	0.22
Development	2.05	0.72	0.09
Vent	2.15	0.51	0.06

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. Figures 6 and 7 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.

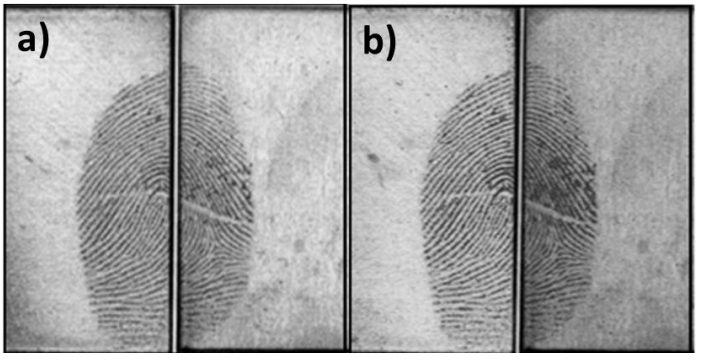

Figure 5: Fingermark deposited by female donor A and developed by VMD: **a)** initial photograph after enhancement **b)** same mark re-photographed after 80 days.

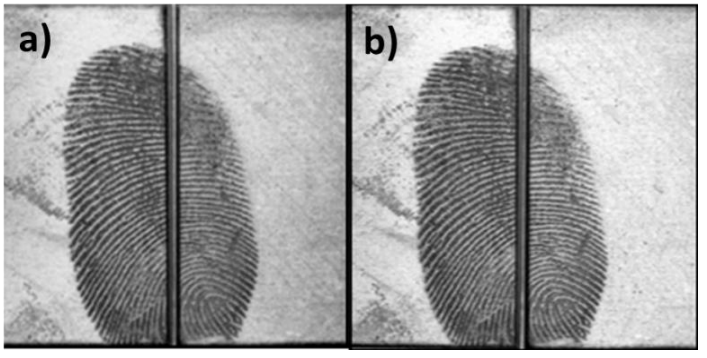

Figure 6: Fingermark deposited by male donor M and developed by VMD: **a)** initial photograph after enhancement **b)** same mark re-photographed after 80 days.

The marks of the above donors were also wiped 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 friction ridge detail 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.

Brass Discs

VMD Treatments

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 ageing 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 Figures 7 and 8 which display a similar pattern of development grades regardless of the VMD treatment. This is further illustrated below (Figures 9-14) 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 (Figure 14, 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 Figure 14c, 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.

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

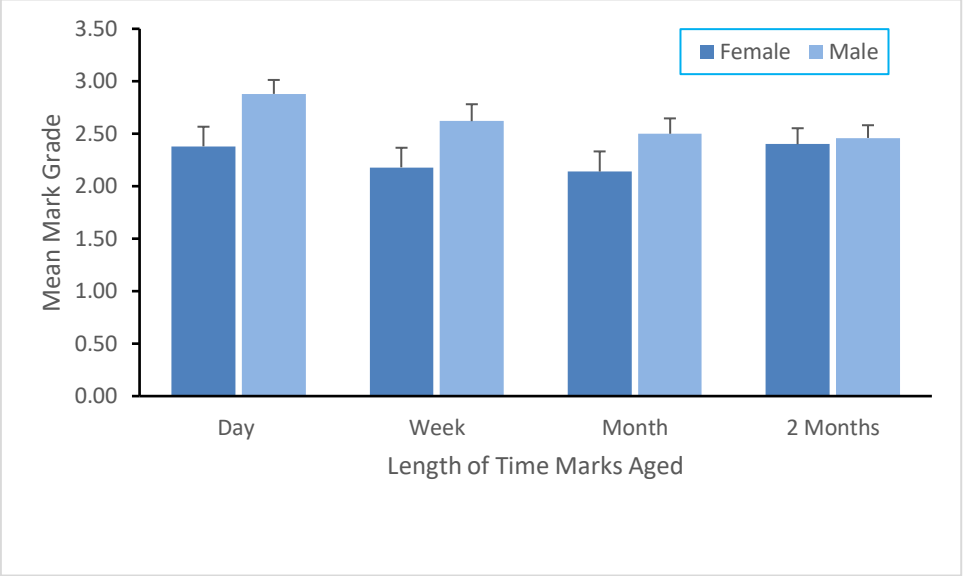

Figure 7: Histogram showing the mean average grades of female and male participants (n=50) at each age interval from one day to two months, when treated with gold/zinc VMD.

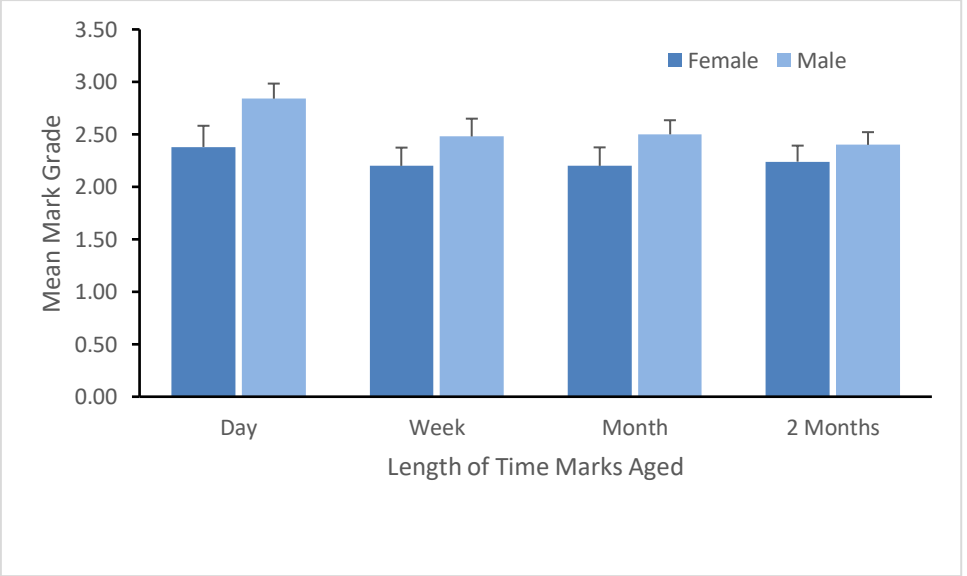

Figure 8: Histogram showing the mean average grades of female and male participants (n=50) at each age interval from one day to two months, when treated with silver/zinc VMD.

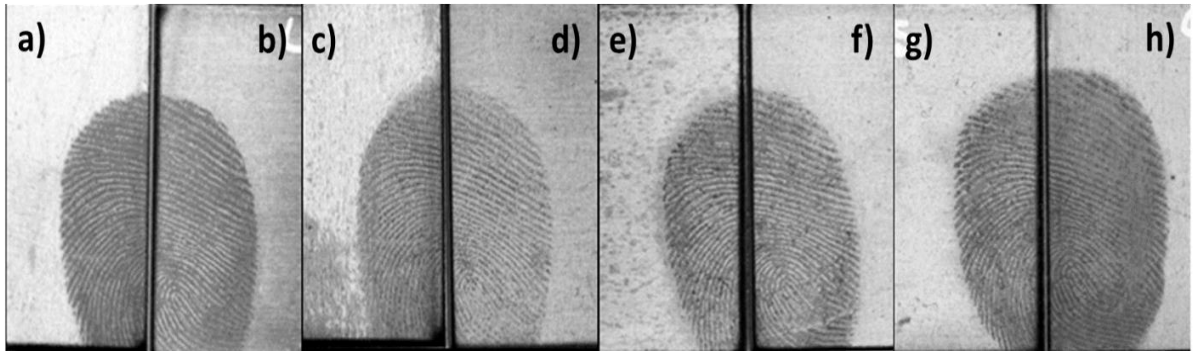

Figure 9: Fingermarks of donor L, identified as a good quality male donor: **a)** mark one day aged and treated with gold/zinc VMD **b)** mark one day aged and treated with silver/zinc VMD **c)** mark one week aged and treated with gold/zinc VMD **d)** mark one week aged and treated with silver/zinc VMD **e)** mark one month aged and treated with gold/zinc VMD **f)** mark one month aged and treated with silver/zinc VMD **g)** mark two months aged and treated with gold/zinc VMD **h)** mark two months aged and treated with silver/zinc VMD

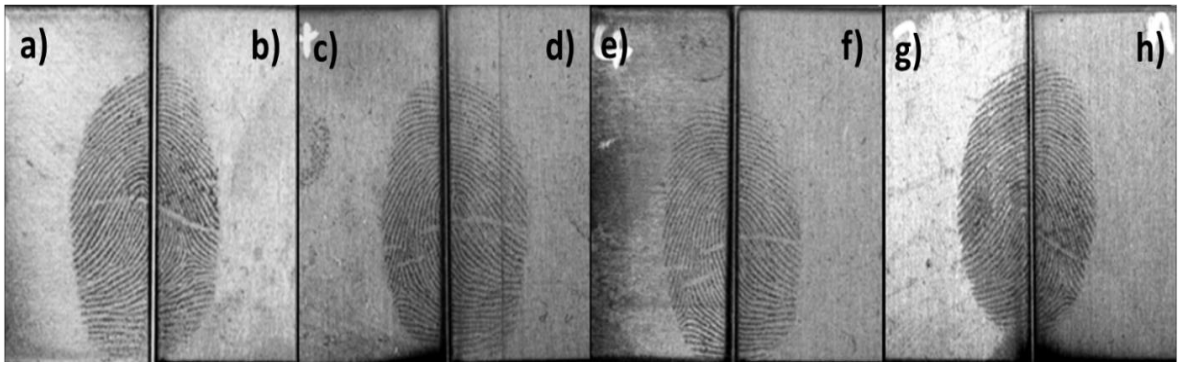

Figure 10: Fingermarks of donor A, identified as a good quality female donor: **a)** mark one day aged and treated with gold/zinc VMD **b)** mark one day aged and treated with silver/zinc VMD **c)** mark one week aged and treated with gold/zinc VMD **d)** mark one week aged and treated with silver/zinc VMD **e)** mark one month aged and treated with gold/zinc VMD **f)** mark one month aged and treated with silver/zinc VMD **g)** mark two months aged and treated with gold/zinc VMD **h)** mark two months aged and treated with silver/zinc VMD

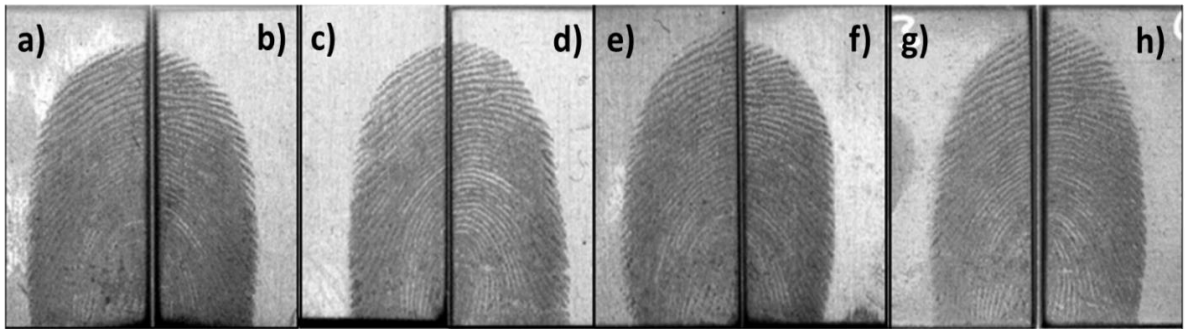

Figure 11: Fingermarks of donor Q, identified as a medium quality male donor: **a)** mark one day aged and treated with gold/zinc VMD **b)** mark one day aged and treated with silver/zinc VMD **c)** mark one week aged and treated with gold/zinc VMD **d)** mark one week aged and treated with silver/zinc VMD **e)** mark one month aged and treated with gold/zinc VMD **f)** mark one month aged and treated with silver/zinc VMD **g)** mark two months aged and treated with gold/zinc VMD **h)** mark two months aged and treated with silver/zinc VMD

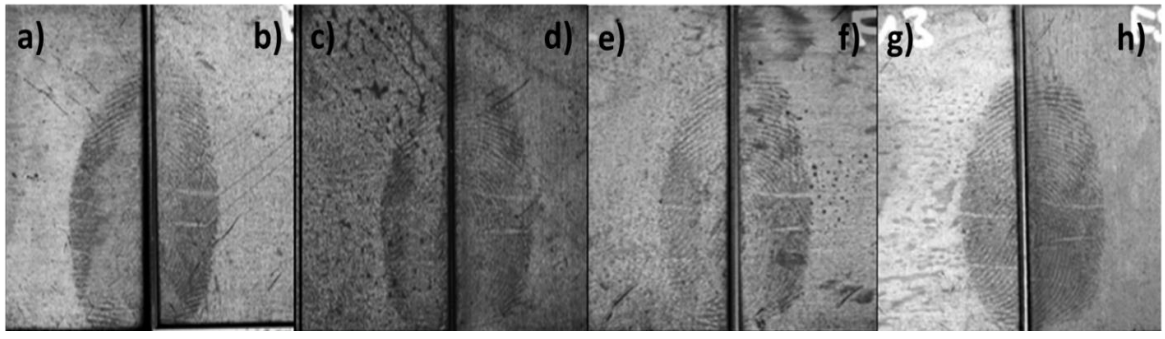

Figure 12: Fingermarks of donor F, identified as a medium quality female donor: **a)** mark one day aged and treated with gold/zinc VMD **b)** mark one day aged and treated with silver/zinc VMD **c)** mark one week aged and treated with gold/zinc VMD **d)** mark one week aged and treated with silver/zinc VMD **e)** mark one month aged and treated with gold/zinc VMD **f)** mark one month aged and treated with silver/zinc VMD **g)** mark two months aged and treated with gold/zinc VMD **h)** mark two months aged and treated with silver/zinc VMD

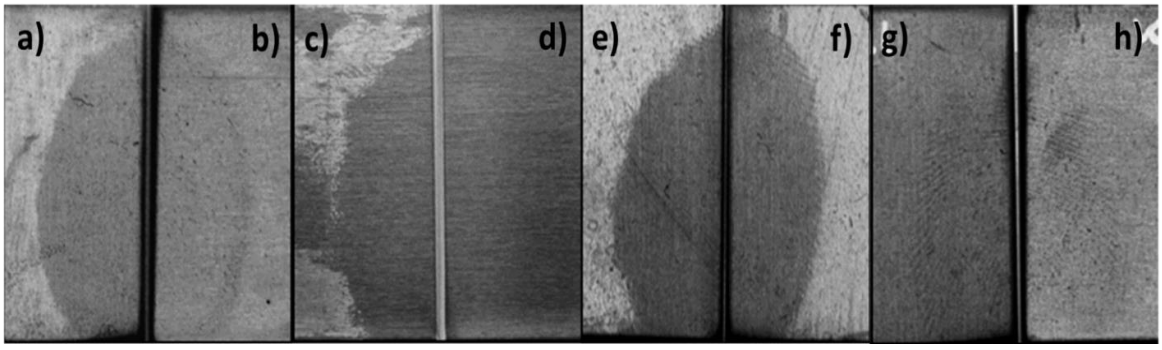

Figure 13: Fingermarks of donor K, identified as a poor quality male donor: **a)** mark one day aged and treated with gold/zinc VMD **b)** mark one day aged and treated with Silver/Zinc VMD **c)** mark one week aged and treated with gold/zinc VMD **d)** mark one week aged and treated with silver/zinc VMD **e)** mark one month aged and treated with gold/zinc VMD **f)** mark one month aged and treated with silver/zinc VMD **g)** mark two months aged and treated with gold/zinc VMD **h)** mark two months aged and treated with silver/zinc VMD

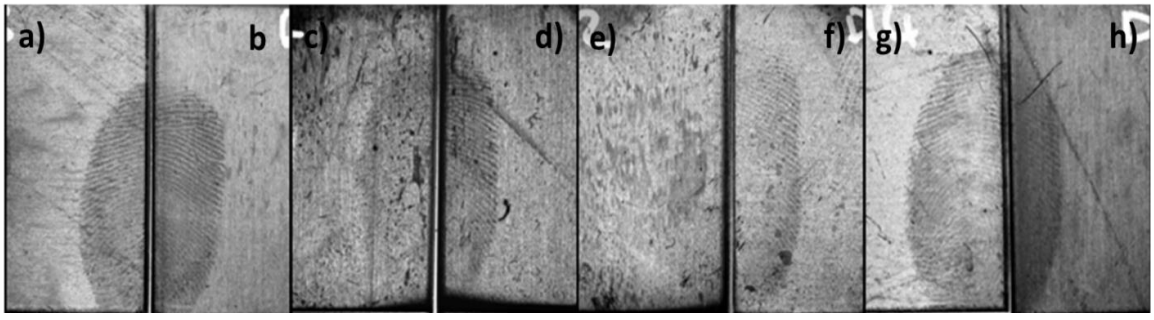

Figure 14: Fingermarks of donor D, identified as a poor quality female donor: **a)** mark one day aged and treated with gold/zinc VMD **b)** mark one day aged and treated with silver/zinc VMD **c)** mark one week aged and treated with gold/zinc VMD **d)** mark one week aged and treated with silver/zinc VMD **e)** mark one month aged and treated with gold/zinc VMD **f)** mark one month aged and treated with silver/zinc VMD **g)** mark two months aged and treated with gold/zinc VMD **h)** mark two months aged and treated with silver/zinc VMD

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), illustrated by figures 7 and 8 which show minor variation in the mean grades produced over each of the age categories. Comparison of the developed fingermarks above (Figures 9-14) 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 ageing. 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 ageing, which may explain the consistency in grades throughout the different ageing 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 ageing or VMD treatment, some donors showed greater variation in the quality of their marks (figures 15 and 16). 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 figures 9-14), interestingly the small amount of grade inconsistency appears to be more prominent with the poor quality donors ((*e.g.* Donors D and K,) figures 15 and 16)).

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].

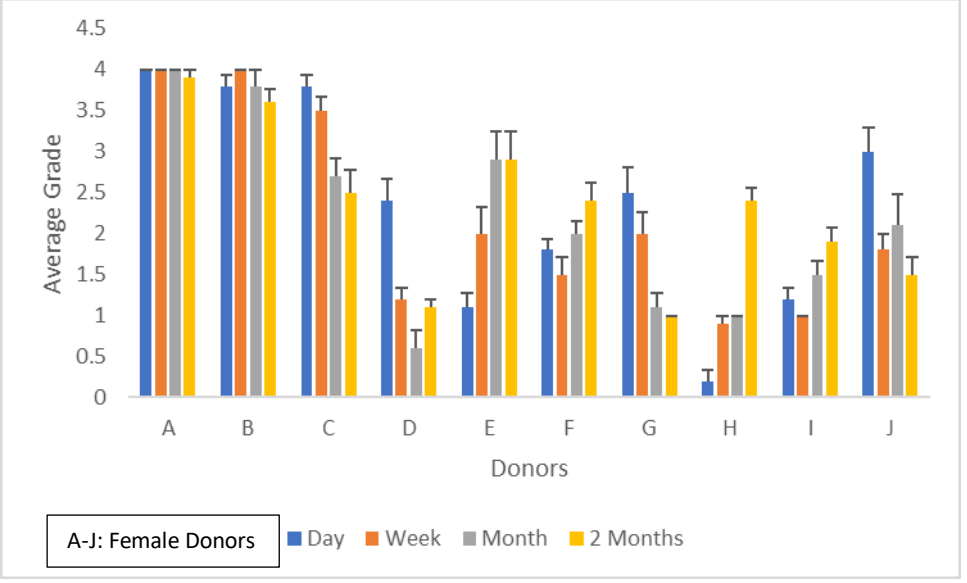

Figure 15: Histogram showing the mean average grades of female donors for each of the ageing periods (n=5)

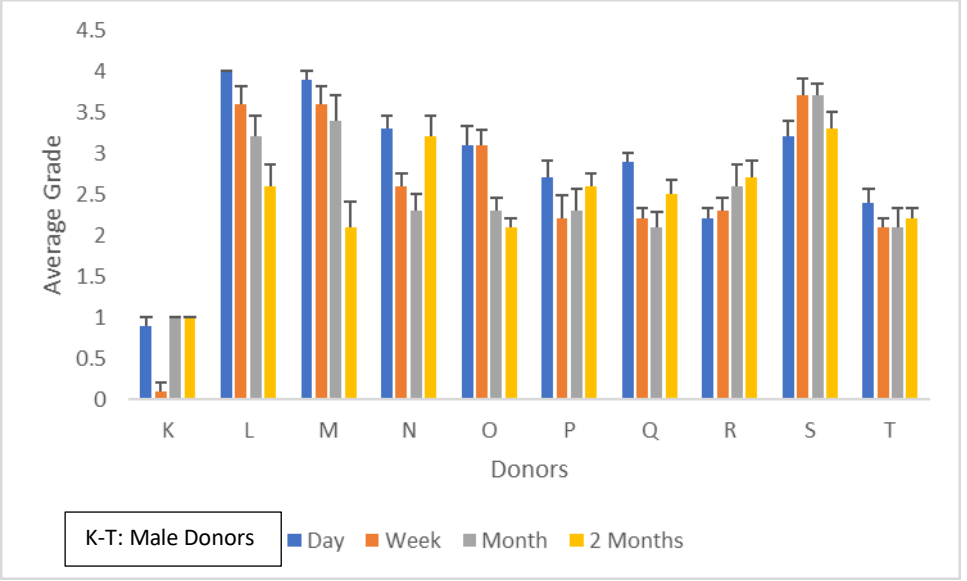

Figure 16: Histogram showing the mean average grades of male donors for each of the ageing periods (n=5)

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 (figures 7 and 8). 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 figures 15 and 16).

Both the male and female groups of participants consisted of a similar age range, 22-56 and 19-55 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 theorized 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 [34]. 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 their higher average grade, as a greater area of the surface is covered by friction ridge detail and therefore the likelihood of usable areas remaining after degradation is increased. Differences in the quality of marks left by female and male donors have been briefly noted in other literature [3, 28], however their sample sizes were small, often only containing one female donor, making it difficult to generalize the reliability of this finding.

Fired cases

Of the 18 fired 9mm bullet cases only five showed clear signs of friction ridge detail being enhanced (Figure 17). 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 discs. In contrast to the brass discs where a large part of the fingermark developed, at best only a fraction of the fingermark was developed on the bullet cases. This would make it highly unlikely that the friction ridge detail enhanced would be usable for identification, although some ridge characteristics were discernible (Figure 17b and e)

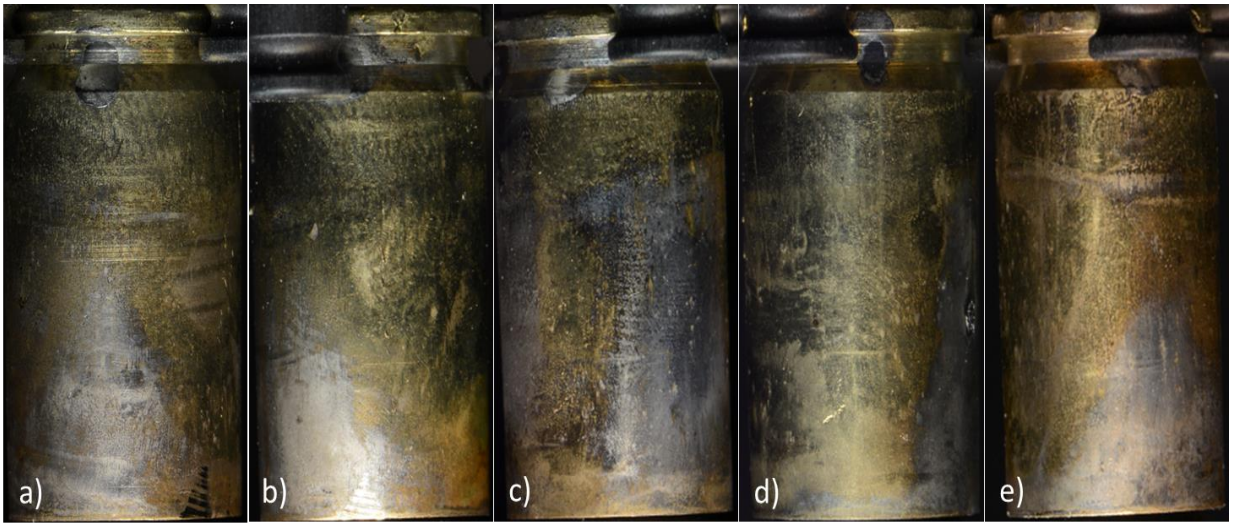

Figure 17: Showing all five bullet cases with enhanced friction ridge detail: **a)** donor A (good quality female donor) repeat 1 of 3 **b)** donor A (good quality donor) repeat 2 of 3 **c)** donor D (poor quality female donor) repeat 1 of 3 **d)** donor L (good quality male donor) repeat 2 of 3 **e)** donor Q (medium quality male donor) repeat 1 of 3

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 9mm 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 friction ridge detail 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 [35] brass discs were heated to first 63°C - the maximum external temperature recorded for a 9mm casing immediately after firing- and then

200°C, 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 gases [3]. This is illustrated by Nizam et al. [14] who when treating fired cases found that zinc oxide formed on the surface obscuring friction ridge detail. 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, 36]. Whilst it is likely that several aspects of the firing process play an important role in the degradation of fingermarks, the results of this chapter suggest that contaminants from the firing process have had the most impact. Regions of the fired cases displayed zinc overdevelopment which appeared to preferentially aggregate onto areas of contaminant from the firing process resulting in a shiny silver covering much of the casing and obscuring friction ridge detail that lay beneath. This occurred on all of the treated casings, and can be seen in Figure 17 - particularly a),b),c) - where further friction ridge detail 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 9mm casings is related to their small size and reaction with contaminants (*e.g.* propellants) on the surface.

The GC/MS analysis of the fingermark constituents of the donors, yielded some of the expected peaks of squalene (27.136 min.), methyl stearate (16.805 min.), stearic acid (16.538 min.), palmitic acid (14.828 min.), methyl tetradecanoate (12.763 min), most of which can be seen in donor A's (good female donor) chromatogram (Figure 18). The same substances have been found in fingermarks in other studies [37-39]. The Internal standard was eluted at 11.3 min. (not shown).

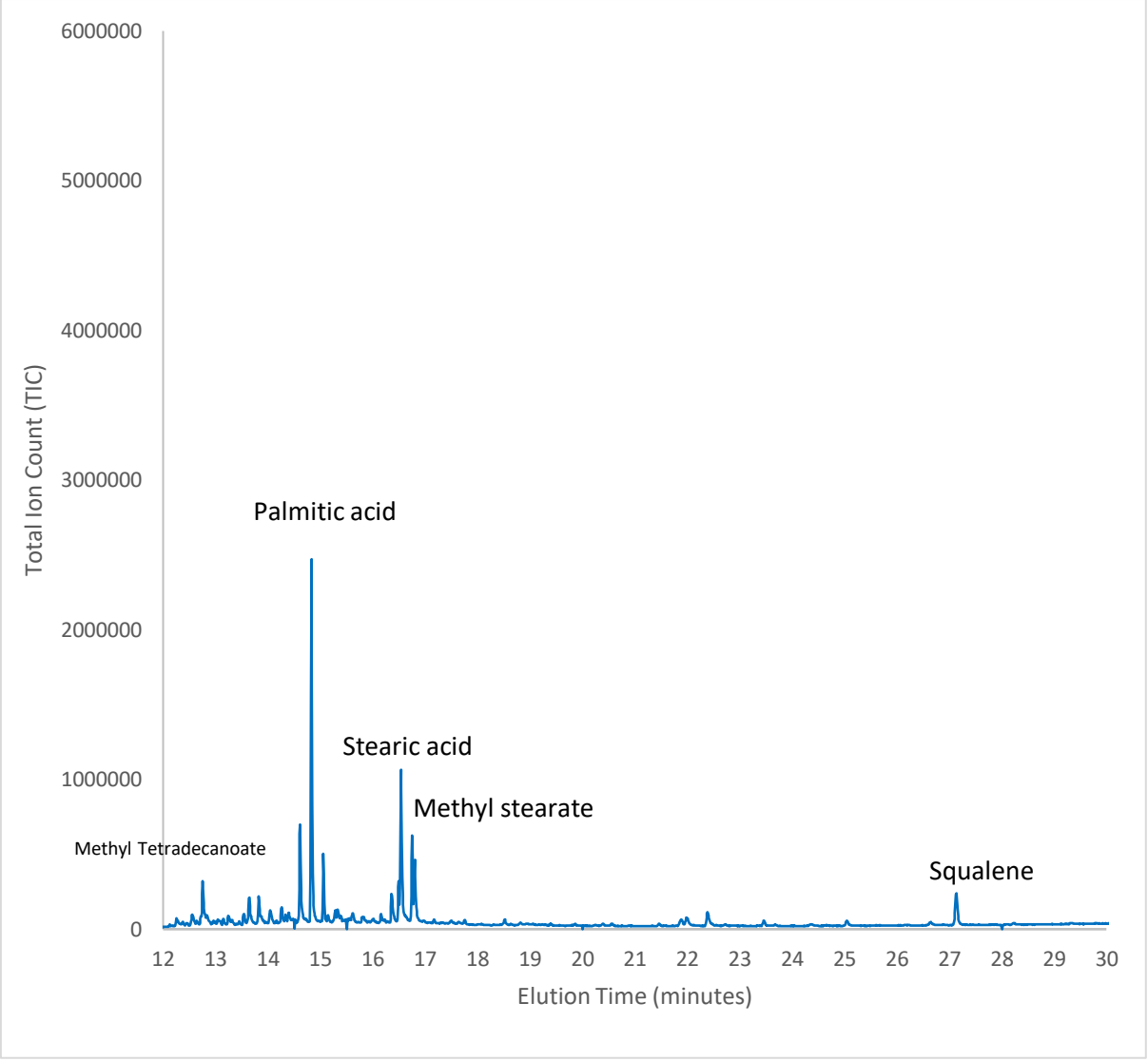

Figure 18. Chromatogram of a good female donor (A). Fingermark extracted from a brass disc

Interestingly, the aforementioned compounds seem to withstand the firing process, which is evident in Figure 19. 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 throughout the chromatogram have emerged which correspond to compounds commonly found in propellants [40], suggesting that propellant contamination remains on the cartridge surface after firing.

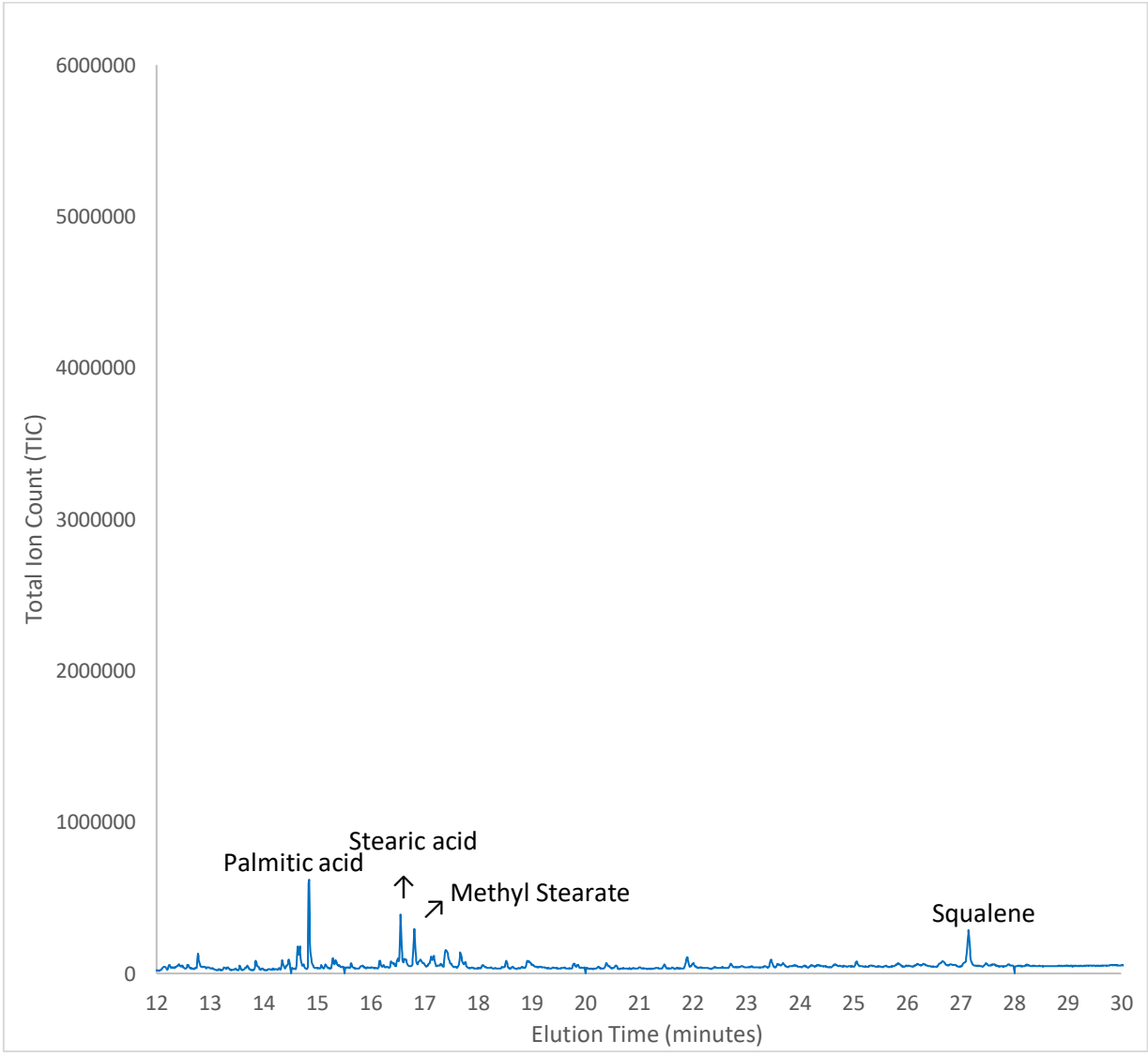

Figure 19. Chromatogram of a good female donor (A). Fingermark extracted from a fired cartridge

Donor A produced the most samples with recoverable friction ridge detail from fired cartridge cases, and the highest graded marks on brass discs, suggesting that the profile of the fingermark constituents yielded are those most likely to produce recoverable friction ridge detail. The profile produced by donor L – also a "good" donor with recoverable friction ridge detail from fired cases - showed similar peaks supporting this theory. However, an additional fingermark component of pentadecanoic acid (13.834 min.) was also detected in donor L's metal disc samples (Figure 20).

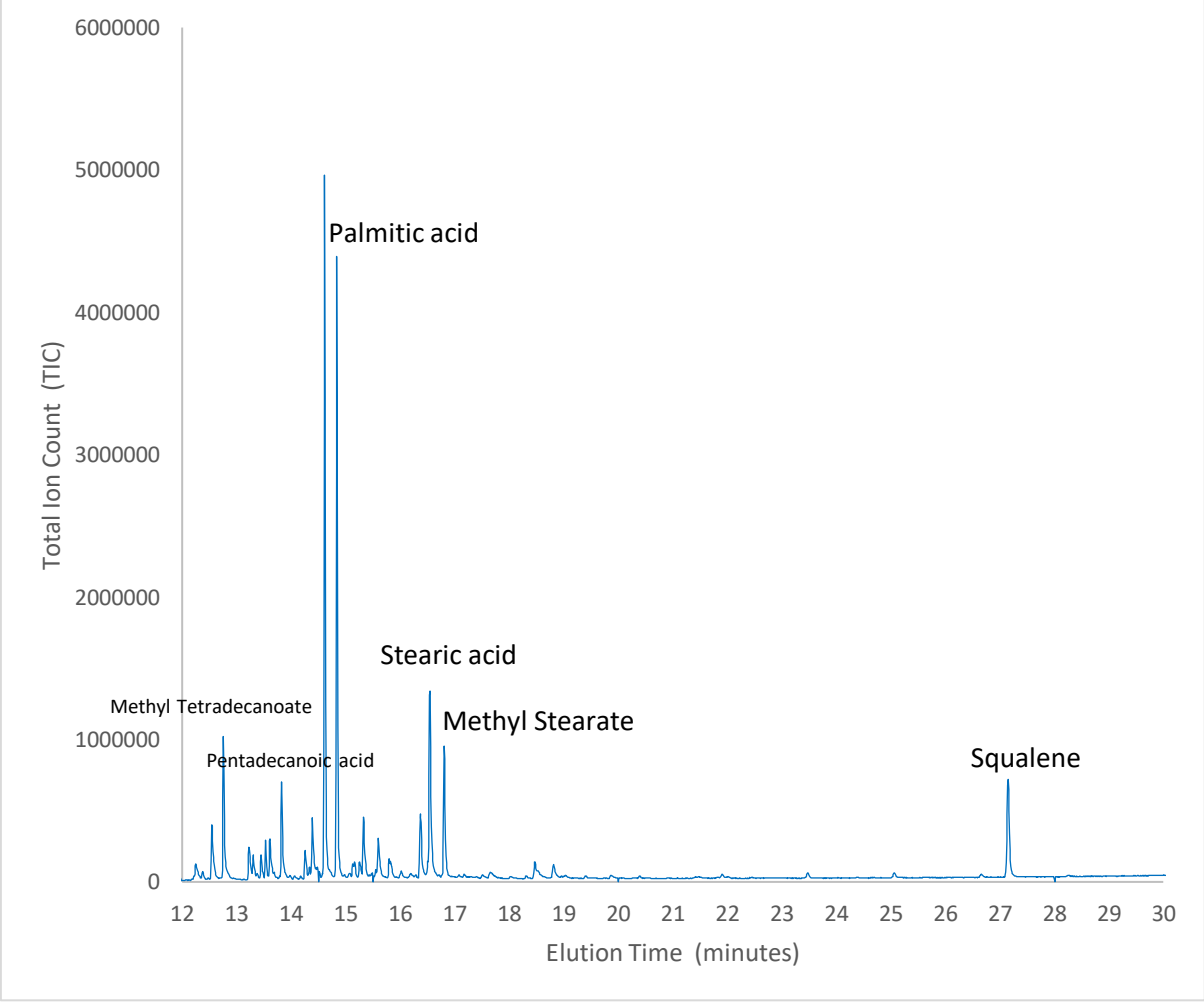

Figure 20. Chromatogram of a good male donor (L). Fingermark extracted from a metal disc.

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 (figures 21&22) show the presence of Palmitic acid, Stearic acid,and Methyl stearate. Interestingly and unexpectedly, one of the fired cases from donor D (female poor donor) exhibited some friction ridge detail enhancement after VMD treatment. Although both good donors (A and L) managed to produce at least one casing with recoverable friction ridge detail after firing, only one of the medium donors (Q) produced any enhanced friction ridge detail. Therefore, it appears additional compounds may be playing a role in VMD enhancement, possibly constituents of eccrine sweat, which were not investigated in this chapter.

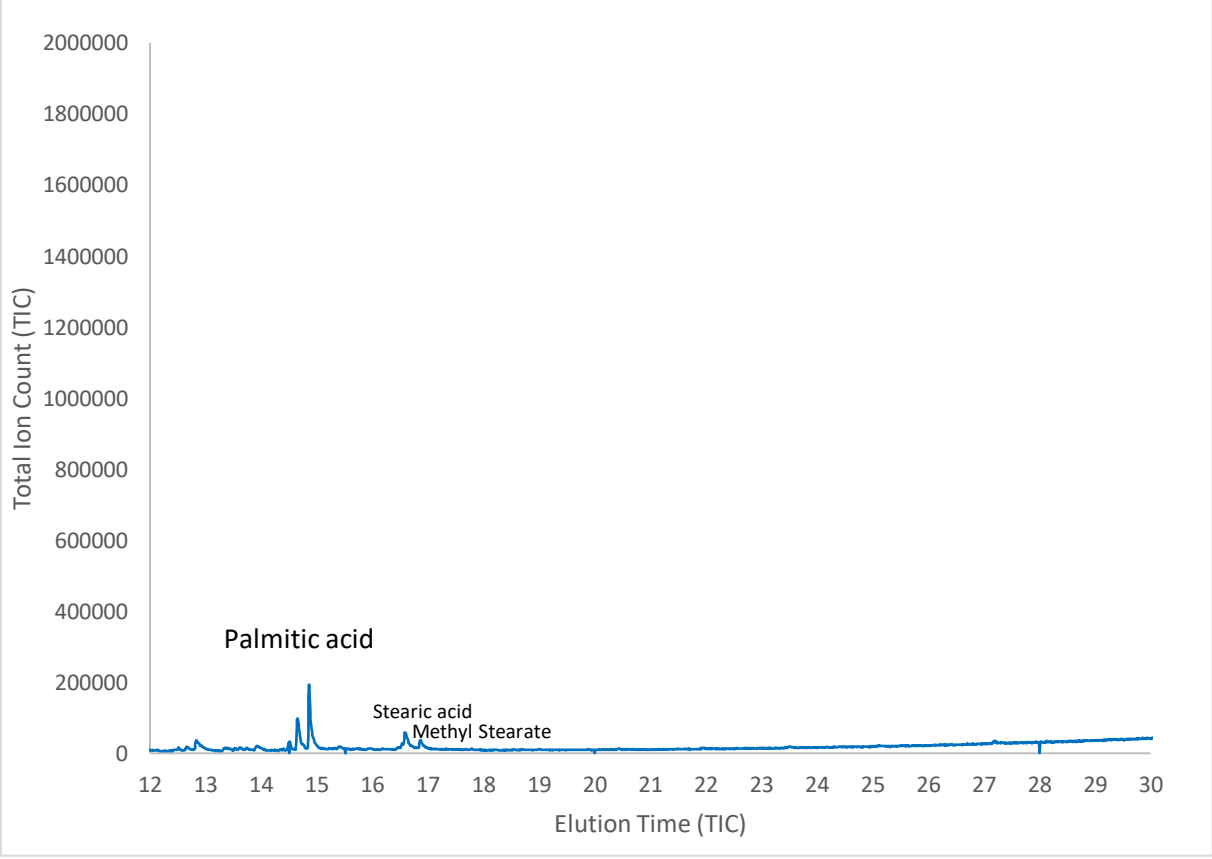

Figure 21. Chromatogram of a poor female donor (D). Fingermark extracted from a metal disc.

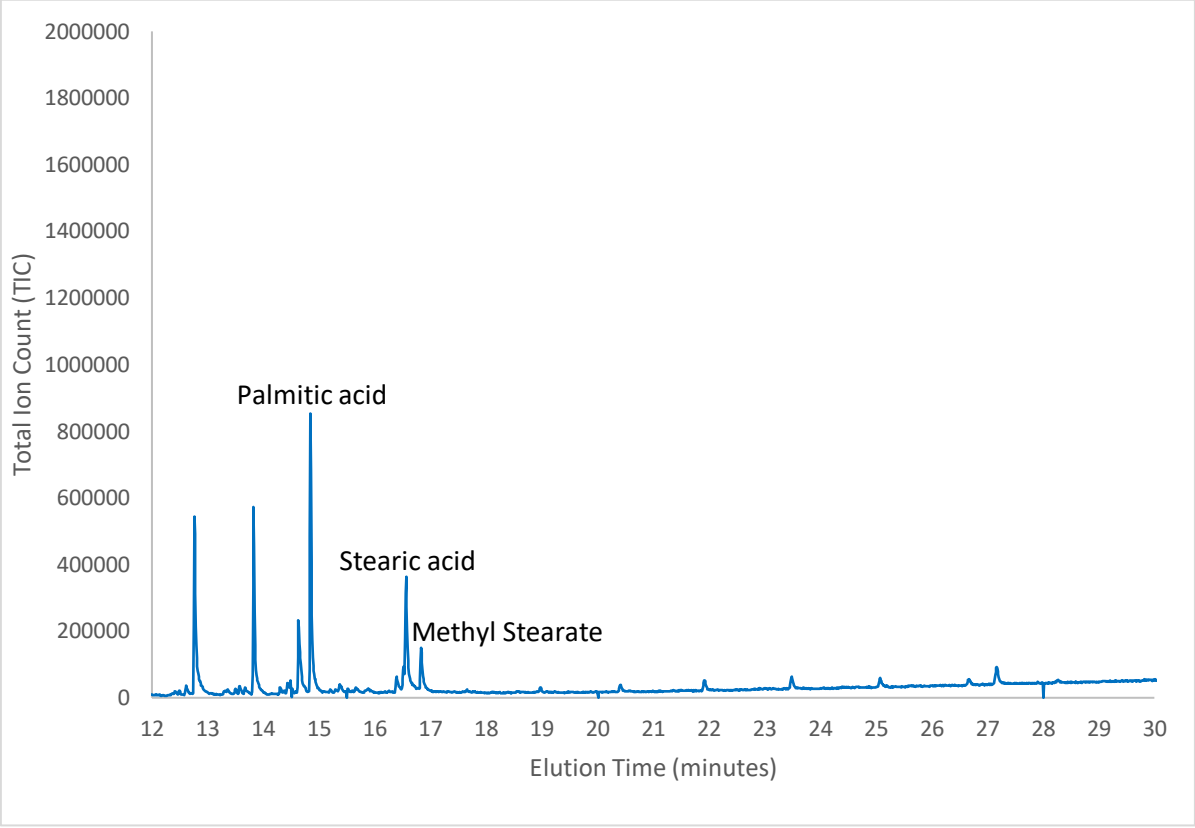

Figure 22. Chromatogram of a poor male donor (K). Fingermark extracted from a metal disc.

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 conclusions about the role of squalene in VMD enhancement since, friction ridge detail was recovered from fired cartridge case of Donors D and Q, who were a ‘‘poor’’ and “medium” donors respectively, with low relative abundance of squalene.

Principal Components Analysis (PCA)

An inter-donor variability study was carried out (Figure 23) to investigate any similarities/differences between donors (in terms of compounds, compound ratio, or compound absence) that could elucidate the VMD enhancement mechanism.

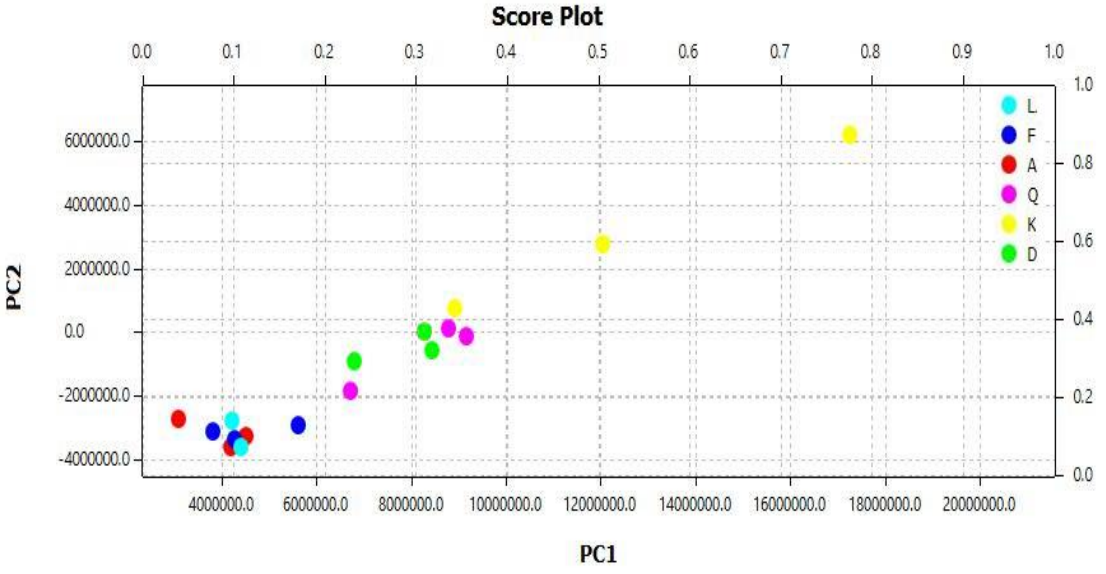

Figure 23. PCA based on the Area under Curve chromatographic data from fired cartridge cases

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, their factor loading scores were 75% and 25% respectively. There also appears to be a relatively close correlation between donor F’s (medium female donor) chromatograms, resembling what is seen with the “good” donors. The internal standard peak was not included in the PCA analysis, and normalization was performed automatically by the software.

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.

Overall, some expected patterns are present, such as the close relationship of the chromatograms for donors A and L, backed up by the recoverable friction ridge detail 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 the aforementioned clustering can be partially explained from the low number of fatty components that were recovered from the samples –especially from ‘’medium’’ and ‘’poor’’ donors.

5.3 Summary & Conclusion

This chapter shows that both gold/zinc and silver/zinc VMD treatments are effective methods of developing friction ridge detail 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 ageing 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 friction ridge detail 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 friction ridge detail enhancement with VMD.

Friction ridge detail 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 friction ridge detail. On small rounds where it is likely that only a partial fingermark will be deposited, such as the 9mm used here, the likelihood of the development of identifiable friction ridge detail is reduced. However, the limited enhancement seen here, and the promising results seen on brass discs, suggest that viable enhancement may be possible on larger caliber cases, if the original fingermark is of good quality and contains compounds which facilitate friction ridge detail enhancement.

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6. Chemical Profile of Fingermarks on Cartridge Cases/Ballistic Material: Effect of Firing and Ageing

Abstract:

A series of small scale studies up to 5 donors were conducted in order to elucidate the effect of the firing process and ageing of a fingermark residue on ballistic material. Nickel and brass fired and unfired cartridges were used throughout the study, along with brass discs. A .38 revolver S&W and .45 Glock semi-automatic pistol were used to assess if the choice of handgun plays a role in the degradation of fingermark residue. The firing of cartridges appears to have a significant impact on the abundance of the sebaceous compounds regardless of the handgun used. However, some of the fingermark residue constituents (squalene, palmitic acid, stearic acid) are detectable on the cartridge surface after firing, in relative abundances ranging from 30 - 80 % lower than their pre-firing values. Fingermarks that were deposited on brass discs and stored under dark conditions up to a month do not seem to undergo any significant changes in terms of sebaceous compound loss. Further research is required to obtain more consistent quantification of the compounds found in fingermark residue by standardising a fingermark deposition and extraction protocol.

Introduction

Fingermarks are an essential piece of evidence that can reveal a wealth of information. Currently, there is existing scientific literature regarding the compounds found in fingermark residue, the information that the compound content of a mark can provide, such as: donor characteristics (age, gender, items that were recently handled), and the alterations that happen within the fingermark residue due to time, nature of substrate and environmental conditions[1-3].

An extensive number of studies regarding fingermarks so far have shown that obtaining reproducible results in regards to compound quantification can be an almost impossible feat, even when the donor of the fingermarks is the same.

Weyerman, Koenig and Frick in their studies [4-6] çonclude that the inter- and intra-donor variation remained high even for samples that were collected and processed on the same day. Additionally squalene, which is a major component of fingermarks from all donors was the one with the highest variability.

A more recent study by Dorakumbura et.al[7] focused on the effects of sampling procedure on the reproducibility of intra-donor quantification on squalene. In their study, favourable results were obtained when the deposition force was controlled. They also found the least variation in squalene within samples from the same donor when they used sebum rich fingermarks; however this type of fingermarks are not crime scene representative.

Most studies to date, have focused on identifying the fingermark compounds that are usually found in most donor's fingermark residue, while others have tried to establish the effect of time on fingermark residue, if any new compounds are formed or if other compounds are lost[8, 9]. The knowledge regarding fingermark residue alterations on cartridges that had been subjected to firing remains relatively untapped compared to the plethora of studies pertaining to the effect of environment and time on fingermark constituents.

Some research groups have studied the efficacy of different enhancement techniques on fired cartridge cases [10-16]. Such techniques included Superglue Fuming, Gun Blue, palladium chloride, Amino Acids, Vacuum metal deposition, and Electrodeposition. The majority of results were unimpressive. Moreover, the focal point of the aforementioned studies was mostly to demonstrate that the enhancement technique of choice could provide some enhancement on fingermarks of fired cartridge cases and not necessarily attempt to explain why this is possible, which is something that can lead to further improvement of the effectiveness of the fingermark enhancement technique at hand.

The analytical methodology discussed in this chapter, aims to identify and quantify the substances present in fingermark residue that can withstand the firing process and be

retained on a fired cartridge. Additionally, two different guns will be employed a .38 revolver and a .45 Glock, since it is expected that the firing process will vary depending on the gun type and subsequently have a different impact on the fingermark residue. Lastly, the chemical profile of fingermarks left to age on brass ballistic material will be obtained in order to identify any changes in the compound content of the mark's residue due to ageing.

This information can be useful to forensic practitioners, since it will identify which are the compounds that can be targeted by a suitable fingermark enhancing technique (after the firing of a cartridge).

6.1 Materials & Methods

Experiment 1, 2 and 3

Solvents and standards

Methanol (Sigma- Aldrich) was used as an extracting medium, hexadecane (Merck UK) and squalene (Sigma-Aldrich) were used as standard solutions.

GC/MS instrumentation and conditions

Experiment 1 and 2

Chromatographic analysis was performed with an Agilent Technologies 6890N network GC system, equipped with an Agilent 7683 Series auto sampler. An Agilent J&W Scientific HP5-MS UI (30 m x 0.25 mm x 0.25 µm) column was used. Helium was used as the carrier gas, the injection volume was 1 µL, with a solvent delay of 3.6 minutes. 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 minutes and finally with a ramp of 4°C/min up to 310°C for 8 minutes. Total run time was 46 minutes. The GC was coupled with an Agilent 5975B Inert MSD system using electron impact (EI) ionization.

The transfer line between the column and the MS was kept at 280°C. The method was adapted from [5].

Experiment 3

Everything was same as in experiments 1 and 2 but the oven temperature was slightly altered in the ending stage: Initially at 80 °C, then with a ramp of 10°C/min to 230°C for 2 minutes , then a ramp of 6°C/min was used for 8 minutes for up to 290°C and finally a ramp of 320°C/min up to 310°C for 2 minutes. Total run time 48 minutes.

Print deposition

Experiment 1

Natural and groomed fingermarks (produced as suggested by the IFRG guidelines and relevant literature)[17, 18] were employed for this chapter. One fingermark (either groomed or natural) per cartridge case (Winchester .38 special, nickel) was deposited. The donors were asked to keep the finger on the cartridge for 3 seconds.

Experiment 2

Same as Experiment 1 with the exception of the cartridge case type which was a Howitzer 9mm luger, brass.

Experiment 3

Natural and groomed fingermarks were collected from 5 donors on brass metal discs (1 mark per disc). One fingermark (either groomed or natural) per brass metal disc was deposited. The donors were asked to keep their finger on the cartridge for 3 seconds.

Sample preparation

Experiment 1

5 mL of MeOH was used to extract the fingermark residue from the cartridge by placing them inside a beaker and slightly agitating the beaker for 2 minutes. Then the solution was dried out under nitrogen and reconstituted using 100 microliters of MeOH. An extra 15 microliters of hexadecane (transferred from a 0.1%v/v hexadecane/MeOH solution) were added as the internal standard.

In total 5 donors (3 male, 2 female) deposited 100 fingermarks (50 natural, 50 groomed), 1 fingermark per cartridge. Half of the cartridges (25 natural and 25 groomed marks) were fired while the other half was left unfired.

Experiment 2

Same as experiment 1. An extra 2.5 microliters of hexadecane (transferred from a 1%v/v hexadecane/MeOH solution) were added as the internal standard. In total 4 donors (3 male, 1 female) deposited 80 fingermarks (40 natural, 40 groomed), 1 fingermark per cartridge which were all fired. An extra number of 40 marks (20 natural and 20 groomed) were deposited from the donors on cartridges that were left unfired.

Experiment 3

Same as experiment 1.In total 5 donors (3 male, 2 female) deposited 45 groomed fingermarks and 45 natural fingermarks, 1 fingermark per brass metal disc.

6.2 Results & Discussion

Experiments 1, 2 and 3

Although previous research [5, 19, 20] suggests that a wide range of compounds were detected using this method, within our sample and donor pool, only a few were identified consistently. Specifically, squalene at 27.4 min, cholesterol at 32 minutes, stearic acid at 16.7 minutes, and at 15.5 min palmitic acid (Figures 1&2). Single ion monitoring was also employed in order to minimise the irrelevant peaks obtained from the propellant that would persist on the cartridge cases after firing, which were peaks that correspond to what the gunshot residue literature reports[21]. In some

groomed fingermarks, the peak of methyl tetradecanoate at 12.8 minutes and also the peak of pentadecanoic acid at 13.9 minutes were observed (Figure 3).

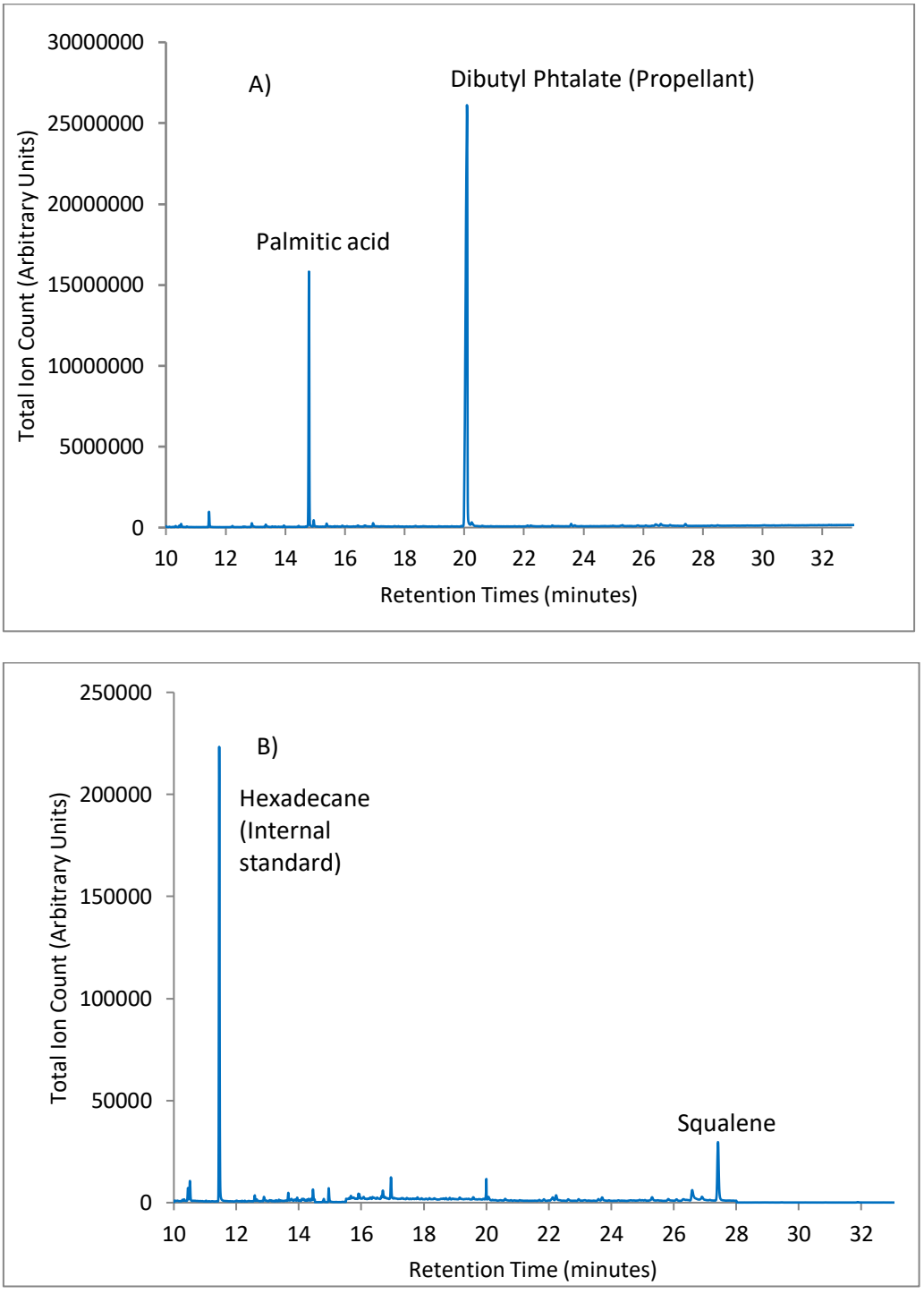

Figure 1. A): TIC Chromatogram of natural fingermark residue and TIC for a male donor on an unfired cartridge B): SIM Chromatogram of natural fingermark residue for a male donor on an unfired cartridge

Due to its presence in almost every sample, squalene (elution time 27.5 min) was used to quantify the losses that occur on fingermark residue during the firing process, as it seemed that there was a drop in squalene abundance on fired cartridge cases (figure 2).

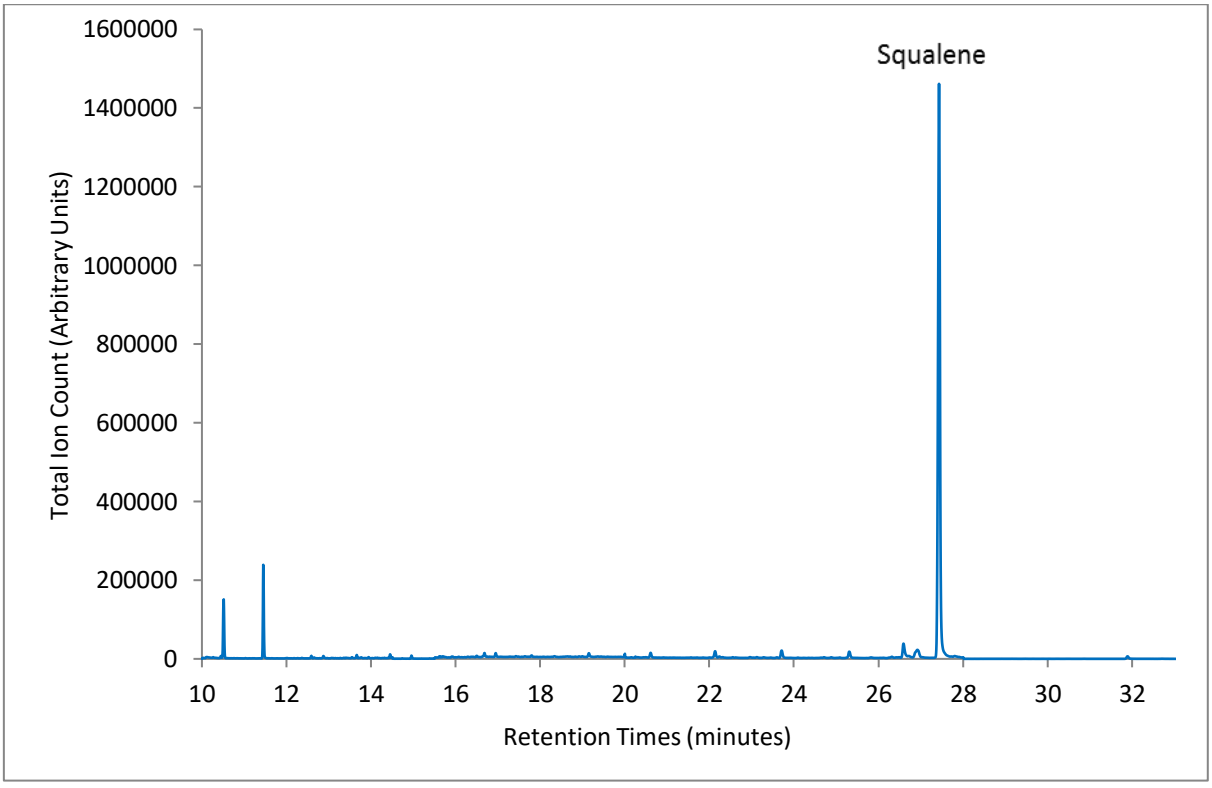

Figure 2. Chromatogram of a natural fingermark on an unfired cartridge case from a female donor..

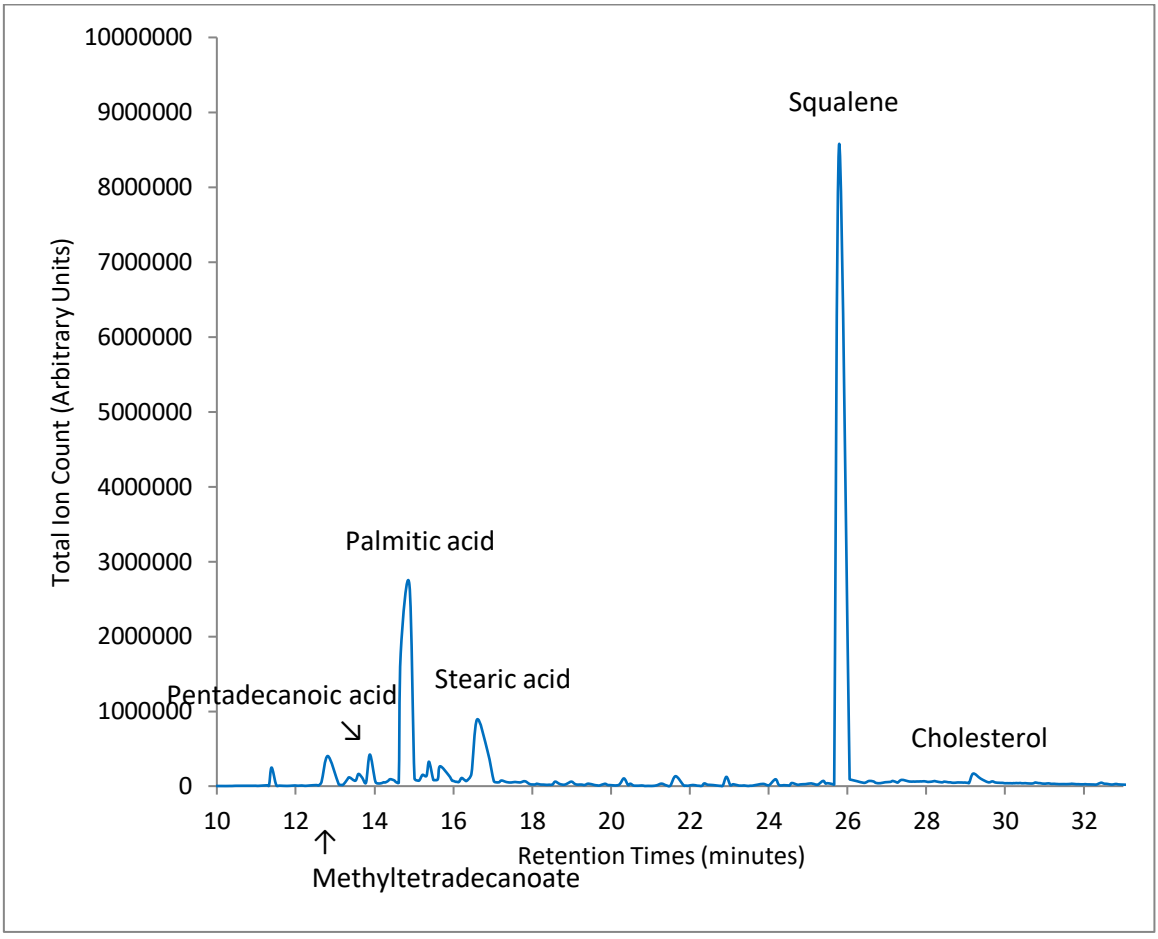

Figure 3. Chromatogram of a groomed fingermark (1 month old) on a brass disc from a male donor

Quantification of squalene loss

Experiment 1

The standard solution that were employed for quantification purposes generated the following figure (Figure 4)

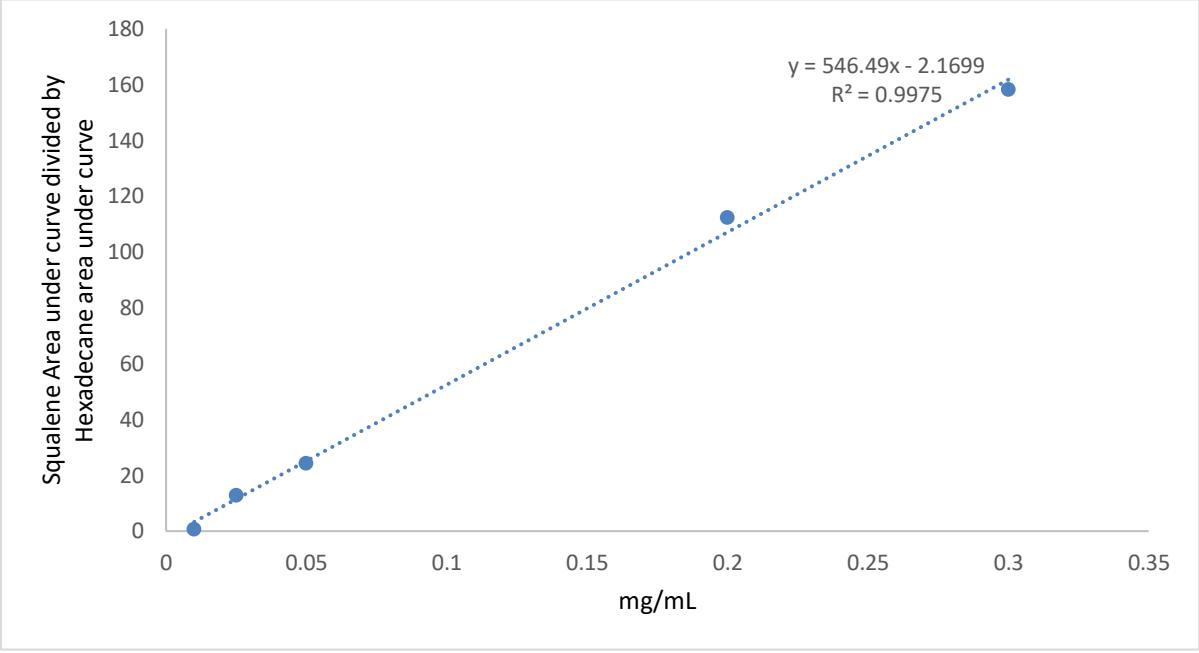

Figure 4. The experiment 1 trend line formed by squalene area under curve with the internal standard of hexadecane included.

The Tables 1 and 2 showcase the squalene loss due to firing (.38 Revolver). The values were calculated according to figure 4.

Table 1. Groomed Fingermarks (average squalene values per donor)

Donors	**Groomed Unfired AUC SQ/I.S.**	**Groomed Fired AUC SQ/I.S.**	**Percentage of squalene lost due to firing**
MD1	0.023	0.007	70%
MD2	0.029	0.008	77%
MD3	0.016	0.009	56%
FD1	0.013	0.008	61%
FD4	0.005	0.004	25%

Table 2. Natural Fingermarks (average squalene values per donor)

Donors	**Natural Unfired AUC SQ/I.S.**	**Natural Fired AUC SQ/I.S.**	**Percentage of squalene lost due to firing**
MD1	0.030	0.006	80%
MD2	0.032	0.006	83%
MD3	0.026	0.007	77%
FD1	0.013	0.004	70%
FD4	0.022	0.005	78%

To check the significance of squalene reduction on fired cartridge cases the data was checked for normality (Kolmogorov-Smirnov) and it was found that it does not follow a normal distribution. Consequently, a non-parametric test was used (Mann-Whitney). The data was separated into four groups, the first group contained the area under curve of squalene on unfired cartridges (natural) and the second group contained the area under curve of squalene on fired cartridges (natural). The Mann-Whitney (a= 0.05) test performed on those two groups showed that the firing of the cartridges has a significant effect on the quantity of squalene present on a fired cartridge case. The other two groups were formed by groomed prints, one group contained the unfired cartridges and the other contained the fired ones. Again, the Mann-Whitney test showed that the effect of firing was statistically significant on the quantity of squalene extracted from the fired cartridge cases.

Experiment 2

A new set of standards were measured for experiment 2, which generated a trend line similar to figure 4 (shown previously). Tables 3 and 4 depict the amount of squalene loss due to firing (.45 Glock). The values were computed according to a trendline similar to Figure 4.

Table 3. Groomed Fingermarks (average squalene values per donor)

Donors	**Groomed Unfired AUC SQ/I.S.**	**Groomed Fired AUC SQ/I.S.**	**Percentage of squalene lost due to firing**
MD1	0.033	0.031	1%
MD2	0.033	0.022	33%
MD3	0.017	0.013	26%
FD4	0.016	0.013	19%

Table 4. Natural Fingermarks (average squalene values per donor)

Donors	**Natural Unfired AUC SQ/I.S.**	**Natural Fired AUC SQ/I.S.**	**Percentage of squalene lost due to firing**
MD1	0.041	0.017	59%
MD2	0.017	0.014	10%
MD3	0.029	0.015	53%
FD4	0.046	0.011	76%

The significance of squalene loss was checked the same way as in experiment 1 with a Mann-Whitney test. The results reached significance, meaning that firing (with a .45 Glock) has a significant impact on the abundance of squalene.

Experiment 3

There were not any major fluctuations in the compounds found in the fingermark residue of all donors despite the fact that the samples were aged up to a month. The Mann-Whitney test on the area under curve of squalene of fresh samples vs the aged samples, produced results that did not reach significance. The most likely scenario is that the storage conditions which were ambient (20°C) and dark were ideal for the preservation of the marks.

Analysis of Variables

Experiment 1

Variable analysis (using the same software and process as in Chapter 5) demonstrated that the Chromatograms of fired and unfired cases do not share many similarities as it can be seen from their separation in the following figure (Figure 5). Orthogonal partial least square method was used for the analysis. The peaks attributed to propellants were excluded from the analysis, and the focus was solely on the compounds that originated from the donors of the fingermarks. Component 1 (PC1) was palmitic acid and component 2 (PC2) was squalene. Overall, the analysis showed that distinction is possible between fired and unfired cases even when the peaks attributed to propellants are not taken into account, this is due to the complete loss of some of the fatty acids (*e.g.* pentadecanoic acid), and the significant decrease (which conversely means a decrease in the area under peak) of other mark constituents (*e.g.* squalene).

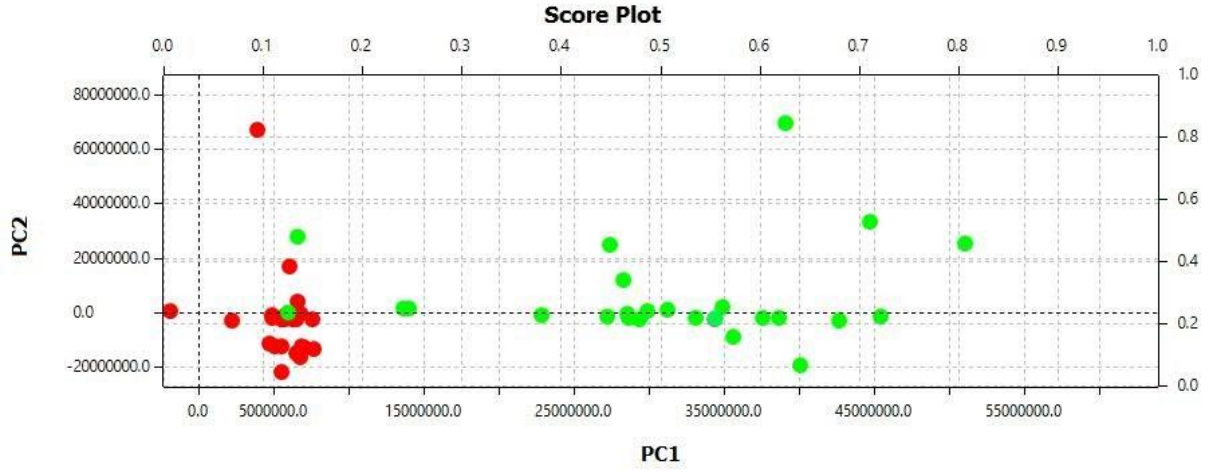

Figure 5. Fired natural fingermarks (red) vs unfired natural fingermarks (green). All donors included

Experiment 2

The process that was used for Experiment 1 was used for Experiment 2 as well; as it can be seen from figure 6 there is a clear distinction between fired and unfired cases, which is again due to the loss of the same fingermarks constituents that were lost due to firing in Experiment 1.

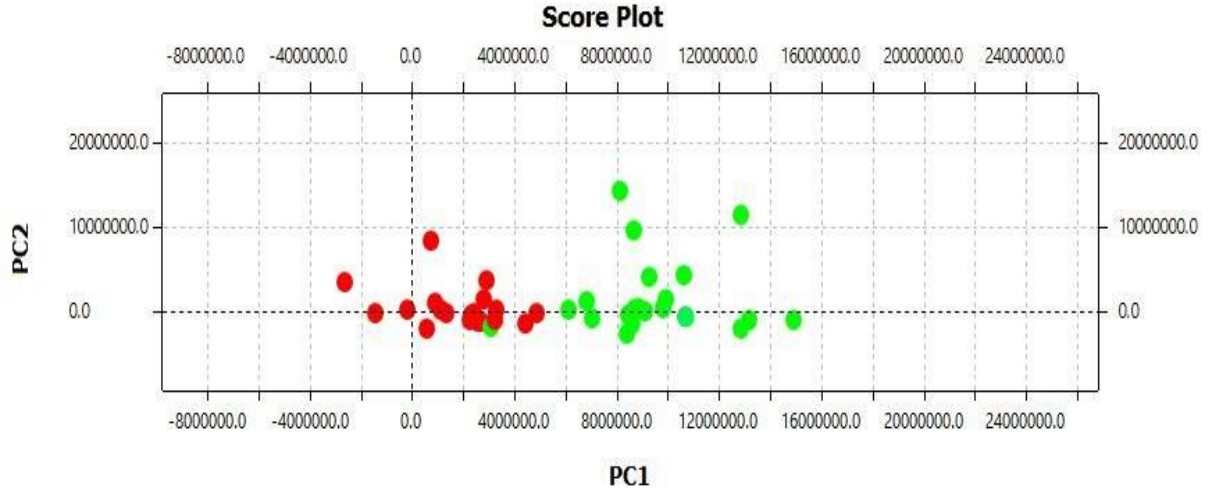

Figure 6. Fired natural fingermarks (red) vs unfired natural fingermarks (green). All donors included

Experiment 3

Variable analysis on experiment 3 yielded a good separation (figure 7) between Groomed and Natural marks, which is to be expected due to the much higher abundances of the two principal components (squalene and palmitic acid) on groomed marks.

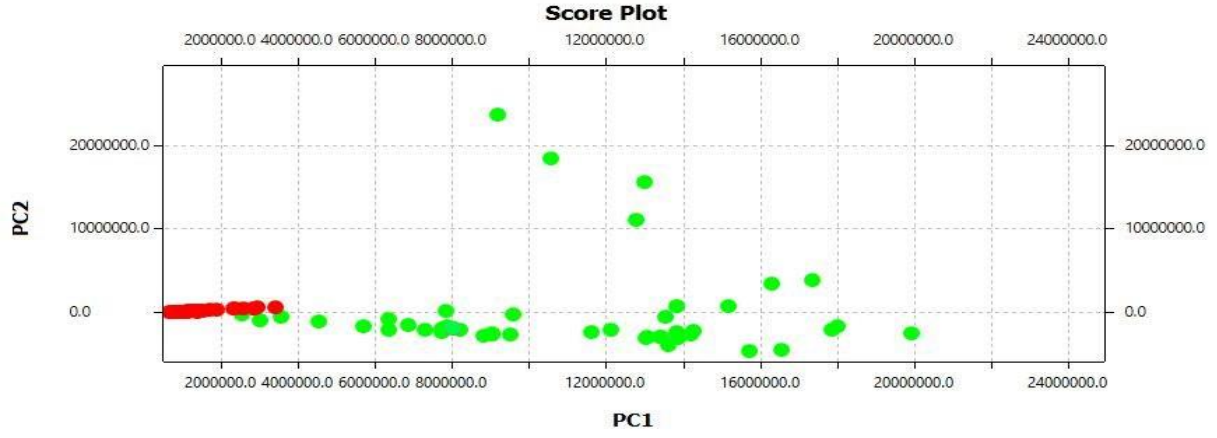

Figure 7. Natural marks (red) vs Groomed marks (green). All donors included.

The natural marks that were left to age for up to a month do not seem to undergo any major changes. The analysis shows that the chromatograms of the marks that were analysed immediately after deposition are quite similar to the ones analysed a month later (Figure 8).

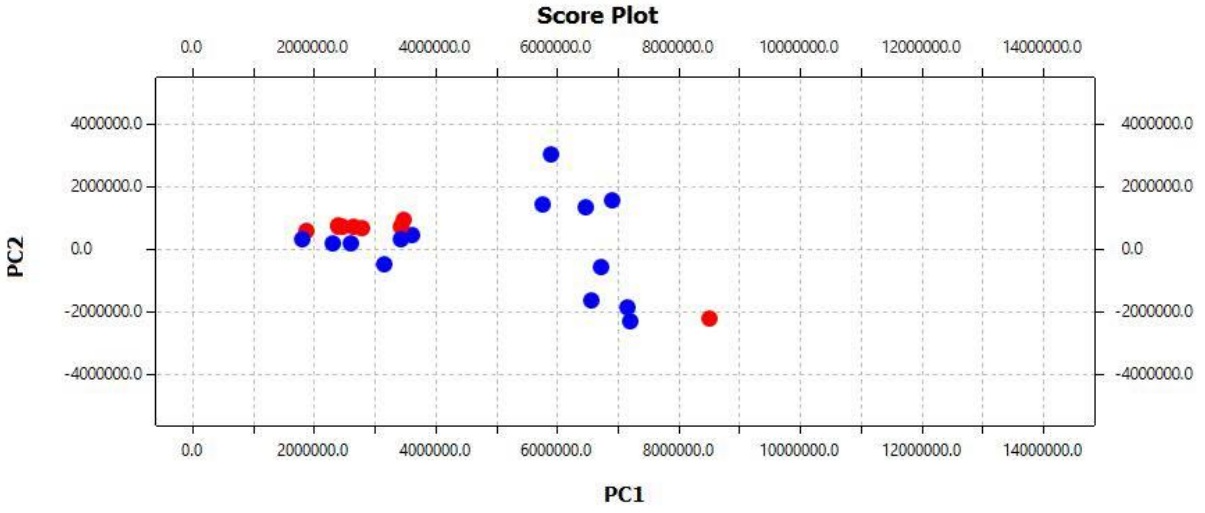

Figure 8. Natural fresh marks (red) vs Natural marks 1 month old (blue). All donors included.

Similar to natural marks, groomed marks do not seem to be altered by ageing, as shown in the following graph were fresh and older samples are clustered together (Figure 9).

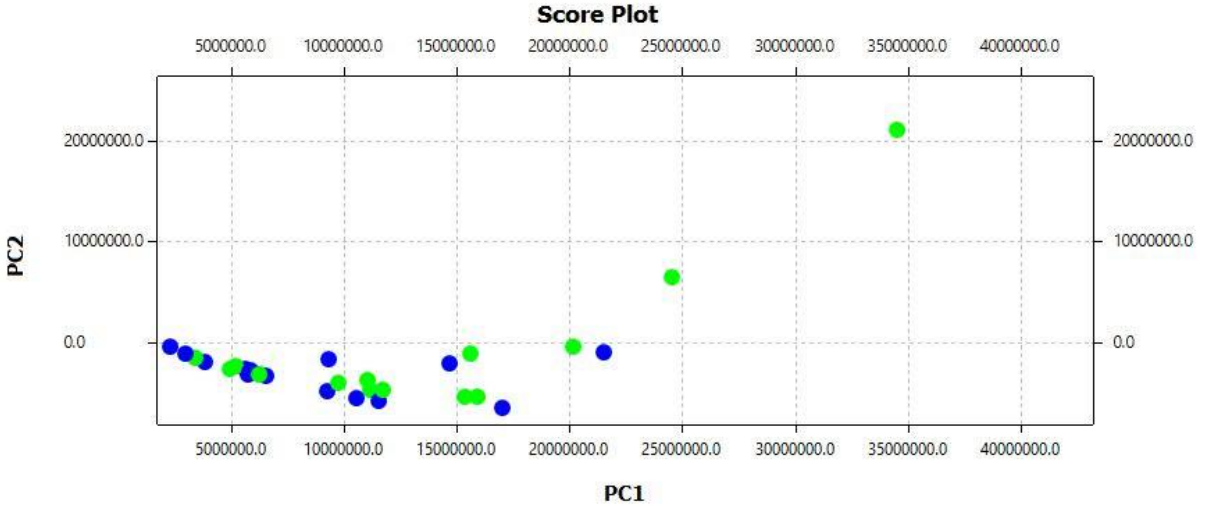

Figure 9. Groomed fresh marks (green) vs Groomed marks 1 month old (blue). All donors included

The concentration of the compounds found in fingermark residue and quantified are not necessarily the actual concentration on the cartridge due to losses that happen during the extraction of the residue from the cartridge[22]. An alternative approach would be to incorporate a mix of extracting solvents that would be more efficient and possibly extract more fatty compounds. Additionally, it appears that the compounds found on the sebum are not really affected by ageing when they are kept under dark indoor conditions. Our results on brass discs showcase the persistence of these compounds, and the fact that fingermark enhancement methods that rely on these compounds will be effective even when the fingermark residue has been aged. It has to be taken into consideration that the storage conditions in this experiment were ideal for the preservation of fingermark residue. Had the samples been kept outdoors, the degradation of the mark residue would have been noticeable.

Moreover, the intra-donor variance of the samples was apparent throughout the study despite having a 3-second deposition protocol. A step forward would be to use a weighing scale, which would help the donors deposit their print using a standardised amount of pressure in every individual deposition. This protocol was proven to reduce variability when compound quantification of mark residue is the goal[7].

Another important part is the overall number of donors, with the great inter- and intra-variability of fingermark samples the employment of as many donors as possible will always be of great importance and could help mitigate the ''damage'' from the inherent randomness of the mark samples.

The findings in this section are in agreement with the fingermark enhancement results that were discussed and presented in the previous chapters. Specifically, our assumption that the major contributors of Gun Blue enhancement (after achieving great fingermark enhancement on samples that were more than a month old) are the oily and greasy components of fingermark residue holds true. Since squalene and other fatty acids seem to be present on the surfaces of the discs even after a long period of time, and of course, even after the firing of a cartridge.

Forensic practitioners should be aware that when dealing with evidence that may contain aged fingermarks or have been degraded (due to environmental exposure, firing), the ideal fingermark enhancement methods would be the ones that target or they are facilitated by the presence of the compounds discussed above.

6.3 Summary & Conclusion

The process of firing cartridges appears to cause alterations on the fingermark residue, regardless of the firearm employed. This is an expected outcome due to the high temperatures that are reached (even for a brief moment) and the gas blowback that takes place within the barrel of the gun, combining with the potential friction between the case and the barrel. These issues could explain the difficulty of enhancing friction ridge detail on fired cartridge cases no matter the enhancement method of choice. The analysis of variables was able to differentiate between fired and unfired cases; however, no differentiation was observed when the samples were separated by gender or by donor, which is a finding that agrees with the results of previous research [1, 4]. The results obtained in this chapter show a big decrease in the abundance of the three most prevalent sebum components: squalene, palmitic acid and stearic acid on fired cases, and also that other compounds (such as cholesterol or pentadecanoic acid) become undetectable. Nevertheless, the findings demonstrate the persistent nature of the aforementioned compounds (squalene, palmitic acid and stearic acid) and thus it should be taken into account when one wants to perform fingermark enhancement on a fired cartridge case. An extra consideration for future study would be to focus on the eccrine part of the fingermark. Although it is unlikely that the majority of this part would withstand the firing process, it would be interesting to know if any compounds from that part can play a facilitating role in fingermark enhancement.

Finally, different types of guns have a very different effect on the mark residue and it would be interesting to know how it fluctuates from firearm to firearm, especially for the ones that are commonly encountered in crimes.

6.4 References

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7. Elucidation of Fingermark Enhancement Mechanisms: A Novel Approach Utilising an Artificial Fingermark

Abstract:

A study was undertaken wherein a new methodology for understanding the mechanisms behind fingermark enhancement methods is proposed and tested. Artificial fingermarks made from liquid rubber, cast on the thumbs of 2 donors (1 male and 1 female) are used throughout this chapter, and depending on the fingermark enhancement method, different fingermark constituents are loaded on the artificial fingermark. The marks deposited by the artificial fingermark show great similarity with the actual marks deposited from the donors. Lactic acid and histidine appeared to be major facilitators of superglue enhancement whereas sebaceous components such as squalene seem to aid the Gun Blue and palladium chloride enhancement. Overall, the results obtained showcase the potential of this new methodology and its ability to provide more scientific knowledge on popular fingermark enhancement methods which are currently used in Police casework (*i.e.* superglue fuming), but also on other methods that are currently underutilised such as Gun Blue and palladium deposition. Further research on other fingermark enhancement methods would be the next step in order to fully assess the efficacy of this new methodology.

Introduction

The enhancement of fingermark friction ridge detail along with the information enclosed [1-4] in the constituents of a fingermark can offer a wealth of information, which can be beneficial during an investigation. Fingermarks can be viewed as a complex matrix of different components. This exact property is enabling many interactions (physical and chemical) between a fingermark and a developing medium. Fingermark residue is rich in different kinds of compounds, an average fingermark usually contains sebaceous and eccrine sweat secretions. Eccrine glands are present

throughout the human body, most of the times they share the same area with the other glands of the human body (sebaceous, apocrine). However, on the surfaces of the hands, the only glands to be found are the eccrine ones. Conversely, sebaceous glands can be found on the areas of the face and the hair, which explains the presence of compounds produced by the sebaceous glands in fingermarks. Apocrine glands are also another type of glands found in the human body (armpits, genital area) but are outside the scope of this chapter.

Identification of the eccrine and sebaceous compounds found on fingermarks has been performed with a plethora of methods [2, 5-10], and an overview of the compounds present in fingermarks can be seen in the following table (Table 1).

Table 1. Constituents of fingermarks adapted by [11]

Source	**Inorganic**	**Organic**
Eccrine glands	Chlorides	Amino acids
	Metal ions	Urea
	Ammonia	Lactic acid
	Sulphate	Sugars
	Phosphate	Creatinine
		Choline
		Uric acid
Sebaceous glands	-	Glycerides
		Wax esters
		Sterol Esters
		Squalene
Apocrine glands	Iron	Proteins
		Carbohydrates
		Cholesterol

It has been reported that fingermark residue may also include contaminants such as cosmetics, food residue, and even drugs and gunshot residue [12-14]. Therefore, it would be a difficult task to define which (latent) fingermark compounds are the facilitators of their enhancement, when a fingermark is successfully enhanced with any of the available fingermark enhancement methods.

Research regarding the elucidation of reactions mechanisms of fingermarks with developing media such as Superglue, Physical developer, and Solvent black 3 has been completed [15-20]. In these studies the most common approach involves the use of spot tests, in other words a spot (with varying concentration) is made by using a compound commonly found in fingermarks (*e.g.* squalene) and then, this spot is exposed to the developing medium and the interaction is recorded. Microscopy has also been employed for the same purpose[15-20].

Another approach is to use solvent washes on fingermarks [18], which in theory would remove many of the compounds. For example if Dichloromethane is used as a washing agent then the sebaceous part of the fingermark would be eliminated leaving only the eccrine part available to interact with the developing medium. Comparisons of natural, groomed and eccrine fingermarks in order to assess if the eccrine or sebaceous part is the main contributor of the reactions was also another one of the methodologies that have been used in the literature [19].

The aforementioned methodologies can provide significant knowledge regarding the chemical interactions taking place during the enhancement of a fingermark. Spot tests although very selective/specific do not guarantee that the same mechanism will take place in the fingermark residue, while the solvent washes, and natural vs eccrine fingermark comparisons do not assure complete detachment of the eccrine from the sebaceous part of the fingermark and vice versa.

In this chapter a new methodology is demonstrated, in which the above-mentioned difficulties are successfully tackled and 3 different developing reagents are used, namely Gun Blue, palladium chloride, and cyanoacrylate fuming (Superglue). Superglue is the most widely used of the three in police casework, and studies regarding its mechanism have already been conducted [15, 21-25].

7.1 Materials & Methods

Liquid latex rubber

An artificial fingermark was created by spreading liquid latex rubber evenly on the donor's (2 donors: 1 male, 1 female) left and right thumb, and then after the application the liquid latex was dried using an air dryer. The resulting latex cast was a mirror image (in terms of ridge detail) of the donor's thumb (Figure 1).

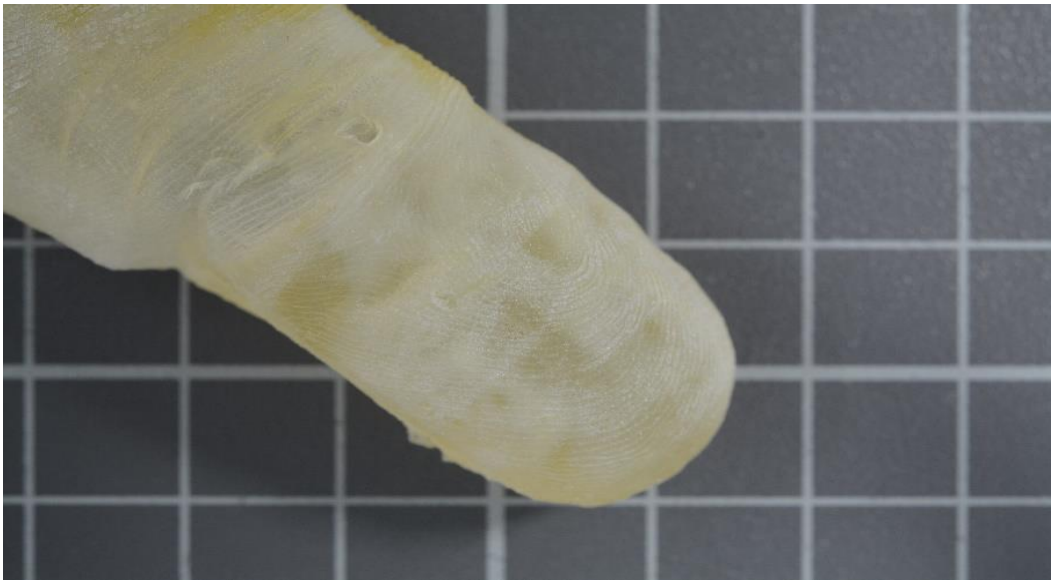

Figure 1. One of the artificial fingermarks made from latex rubber that was used in this chapter

In order to minimise the variation of each deposition, the index finger of the individual performing the deposition was inserted in the cast, and subsequently a weighing balance was used to regulate the force exerted throughout each deposition. The force chosen throughout our experiments was set at 400 grams for 3 seconds. Before each deposition the artificial fingermark was loaded with the desired substances using a pipette. The amount of each substance was kept in a range of what can actually be found on an average fingermark[26], and each deposition was made in triplicate. Lastly, the development of the deposited fingermarks was performed at different times (immediately after deposition, two days old and seven days after deposition), to account for the effect of fingermark ageing as well[27, 28].

Fingermark constituents

Squalene, palmitic acid, lactic acid, and histidine were the compounds of interest (Figure 2). The compounds chosen for this chapter were based on their abundance in actual fingermarks[26] , but also what previous research has indicated as major contributors in fingermark enhancement[15, 29]. The substrates chosen were Ballistic brass (for Gun Blue and $PdCl_2$) and Plastic (for Superglue). These substrates were chosen due to their already known suitability when using the fingermark enhancement techniques that were earlier discussed [24, 30-35].

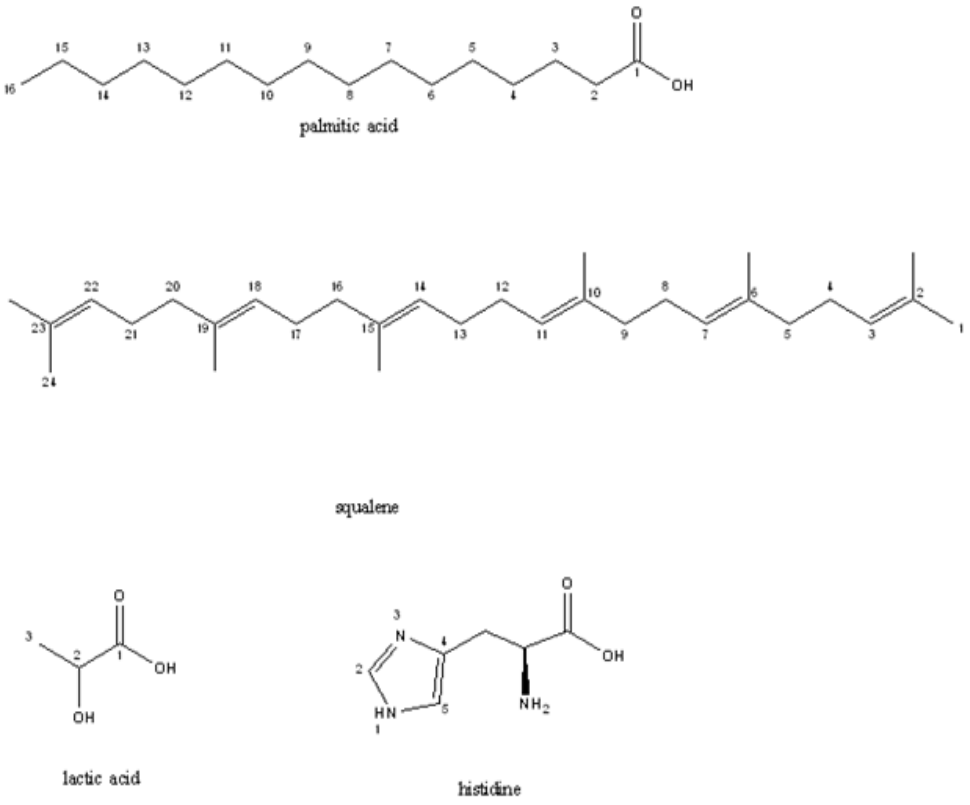

Figure 2. The main fingermark constituents used in this chapter

Fingermark enhancement techniques

In this proof of concept study, the goal was to specify which compounds facilitate each fingermark enhancement method by introducing one compound at a time and assessing its contribution. Gun blueing, palladium chloride and cyanoacrylate fuming have been selected as the fingermark enhancing techniques, which is a good combination of techniques where there is no previous research on them regarding their mechanism of enhancement (Gun blueing, palladium chloride) except for a study where it was inferred that Gun Blue performed better on natural and groomed fingermarks compared to eccrine ones [29].

Fingermark evaluation

The scoring system (Table 2) used for this chapter is similar to the CAST guidelines[25], however it has to be clarified that the goal of the scoring here is not to differentiate between identifiable and non-identifiable fingermarks. The goal is to give an indication on how much the inclusion of a compound aids to fingermark enhancement. Therefore, even a fingermark graded with ''1'' can be considered as helpful in the endeavour of identifying the constituents that facilitate fingermark enhancement. All grading was carried out by a fingerprint expert with 25 years of experience in forensic fingerprint casework.

Table 2. The scoring system for fingermark enhancement

Score	**Level of detail**
0	No enhancement
1	Weak enhancement; No ridge details
2	Limited enhancement; 1/3 ridge details visible
3	Strong enhancement; more than 1/3 and up to 2/3 of ridge details visible
4	Excellent enhancement; full or almost full ridge detail

7.2 Results & Discussion

Firstly, to establish how the actual fingermarks of the donors look after enhancement with Gun Blue and $PdCl_2$, the donors deposited fingermarks on brass discs, which were immediately developed (Figures 3&4)

Figure 3. Actual right and left thumb fingermarks from male donor developed immediately after deposition with Gun Blue.

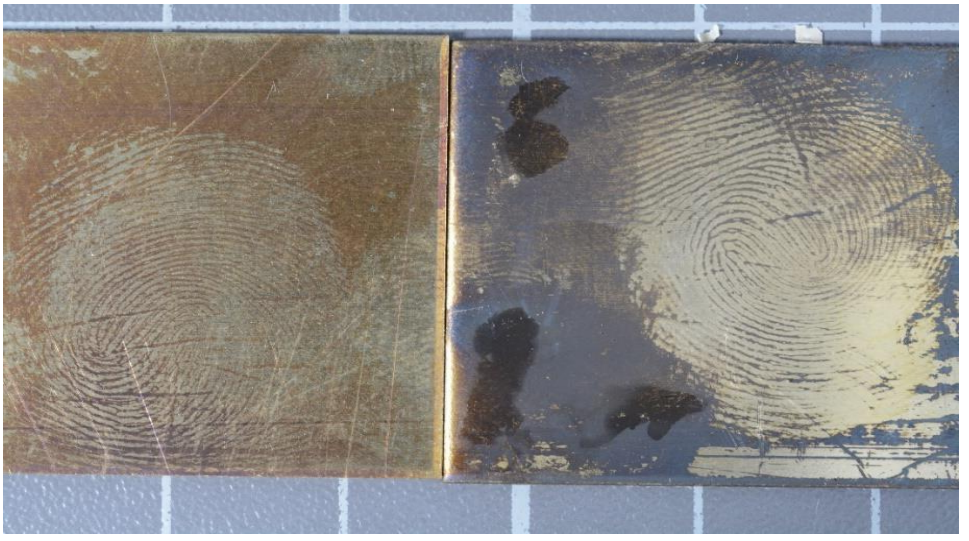

Figure 4. Actual right and left thumb fingermarks from female donor developed immediately after deposition with Gun Blue.

Although in some areas the ridge detail is not fully visible, the quality of the enhancement is sufficient (>2) for identification purposes.

Subsequently, the artificial fingermark was loaded with sebaceous content from one of the donor's (by rubbing the donor's finger with the artificial fingermark); in an attempt to demonstrate that indeed, the artificial fingermark has the ability to produce identical fingermarks when similar constituents with the actual fingermarks are loaded onto it. The result (Figure 5) shows that the fingermark ridge detail is of comparable quality to the actual fingermark (although the enhanced mark is a mirror image of the original mark)

Figure 5. Artificial fingermark (mirror image of the right thumb) from male donor loaded with the actual sebaceous components from the donor, developed immediately after deposition with Gun Blue

The marks enhanced immediately after deposition with Gun Blue show many second level characteristics. Both donors produced a few marks of identifiable quality (figure 6)

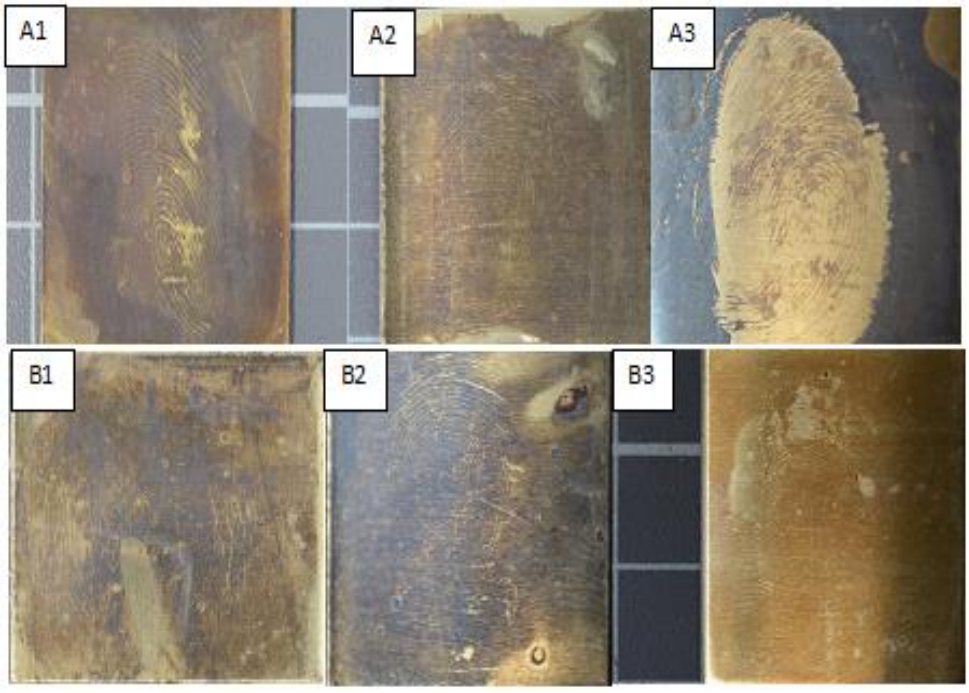

Figure 6. Artificial fingermarks from male donor (A1-3) and female donor (B1-3), developed immediately after deposition with Gun Blue. A1,B1: fingermark loaded with squalene, A2,B2: Fingermark loaded with palmitic acid, A3,B3: fingermark loaded with squalene and palmitic acid.

Palladium chloride produced similar results with Gun Blue for the fingermarks enhanced immediately after deposition for both donors (Figure 7)

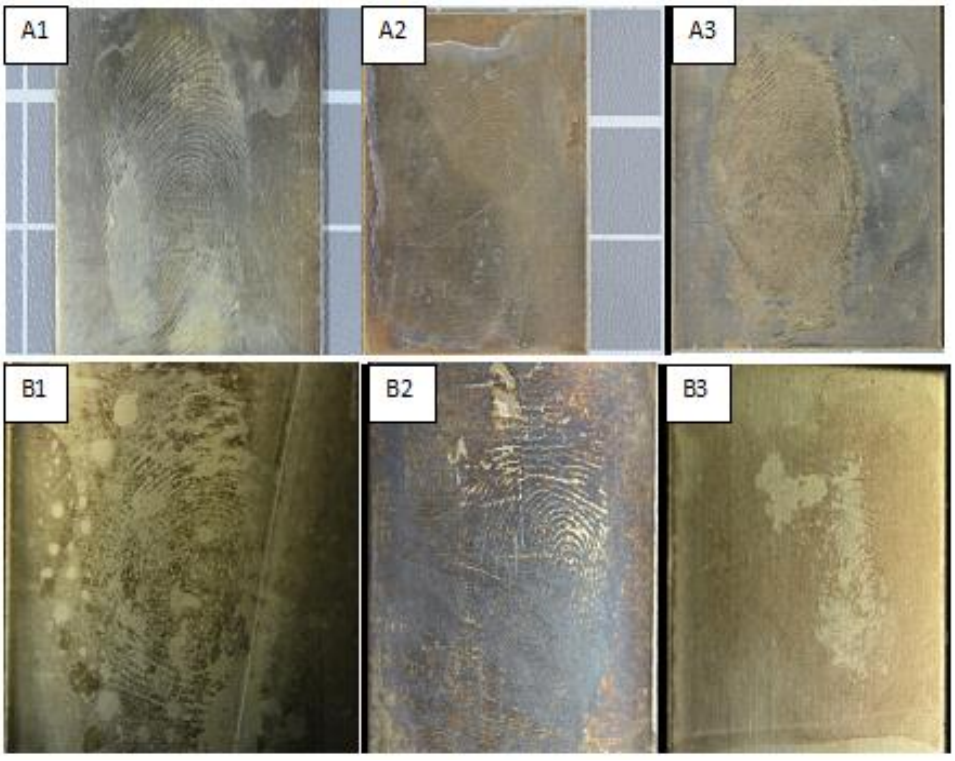

Figure 7. Artificial fingermarks from male donor (A1-3) and female donor (B1-3), developed immediately after deposition with palladium chloride. A1,B1: fingermark loaded with squalene, A2,B2: Fingermark loaded with palmitic acid, A3,B3: fingermark loaded with squalene and palmitic acid.

Identifiable marks were also enhanced with Gun Blue two days after deposition although the male donor seems to produce better results (Figure 8).

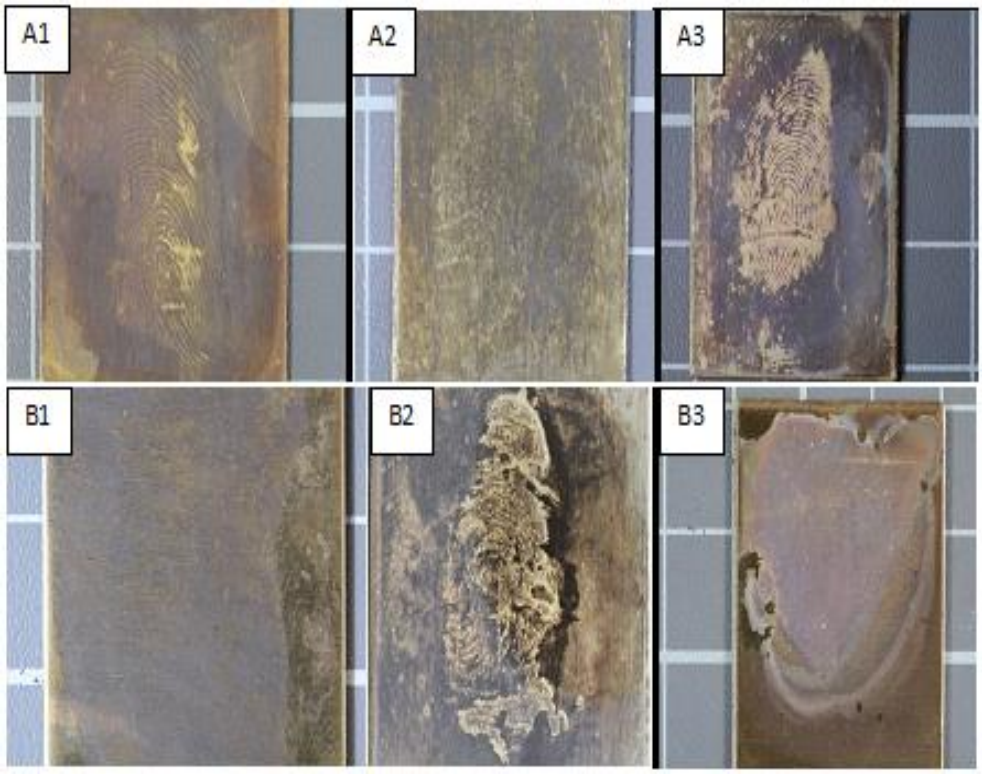

Figure 8. Artificial fingermarks from male donor (A1-3) and female donor (B1-3), developed two days after deposition with Gun Blue. A1,B1: fingermark loaded with squalene, A2,B2: Fingermark loaded with palmitic acid, A3,B3: fingermark loaded with squalene and palmitic acid.

Mixed results were obtained from $PdCL_2$ enhancement two days after deposition of the marks, with the fingermark ridge detail from the male donor being clearer (Figure 9).

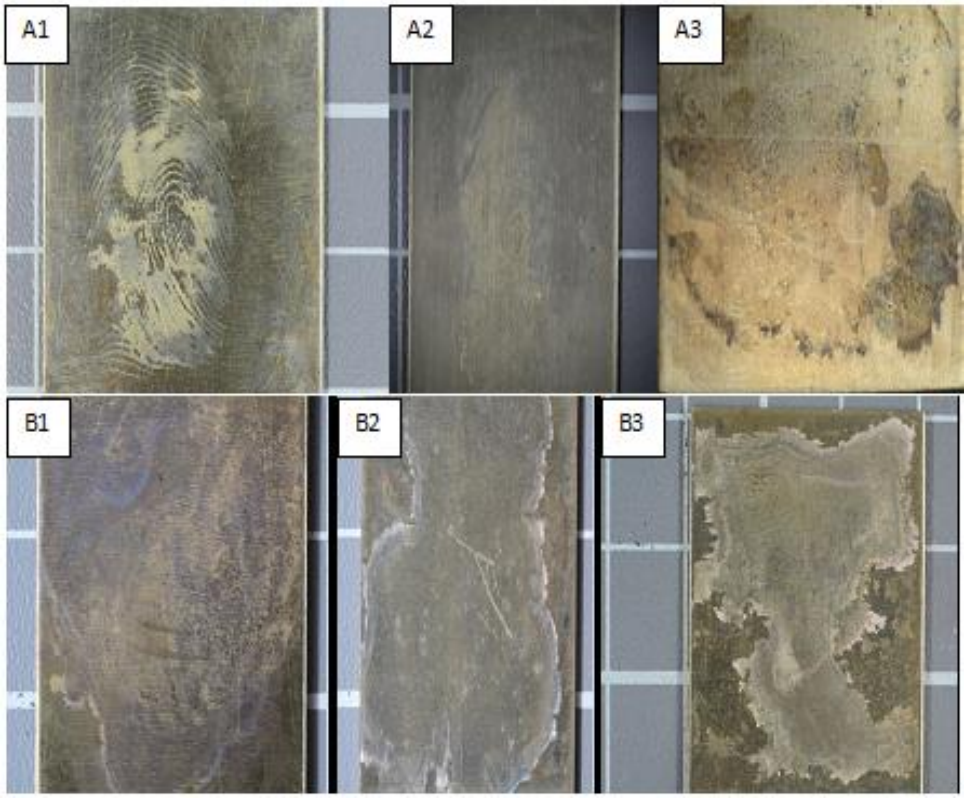

Figure 9. Artificial fingermarks from male donor (A1-3) and female donor (B1-3), developed two days after deposition with palladium chloride. A1,B1: Fingermark loaded with squalene, A2,B2: Fingermark loaded with palmitic acid, A3,B3: fingermark loaded with squalene and palmitic acid.

The marks enhanced seven days after deposition with Gun Blue have a lot of second level characteristics (bifurcations, line-units, endings) but only for the male donor (figure 10).

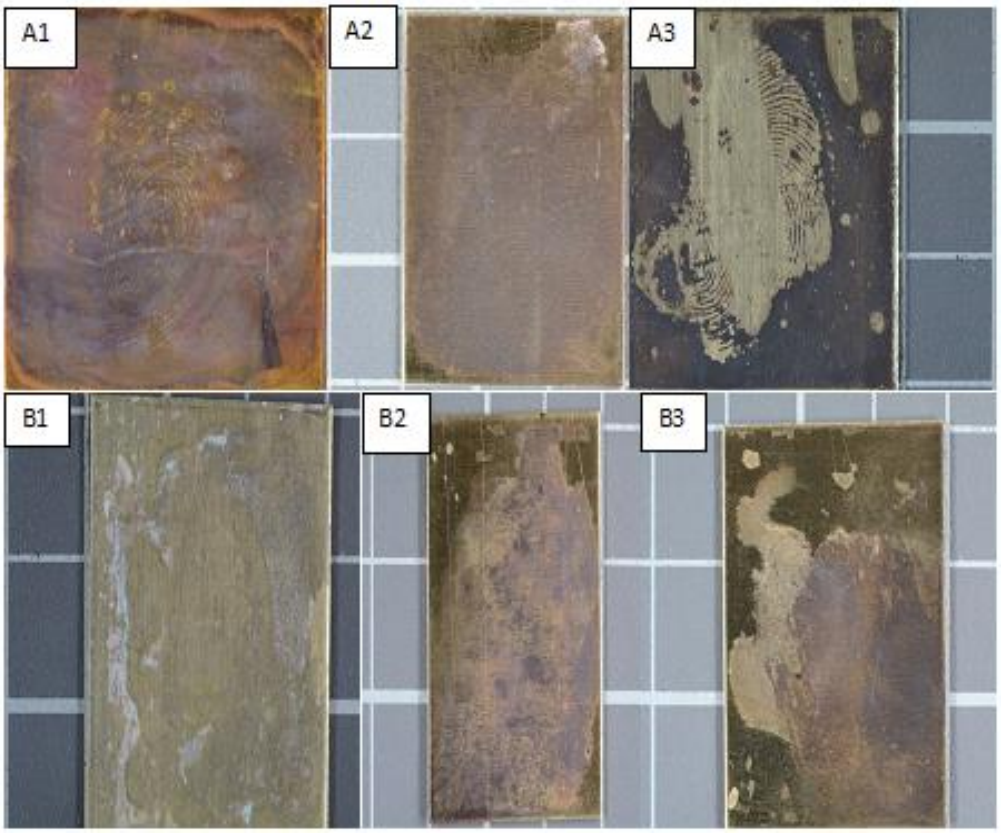

Figure 10. Artificial fingermarks from male donor (A1-A3) and female donor (B1-B3), developed seven days after deposition with Gun Blue. A1,B1: Fingermark loaded with squalene, A2,B2: Fingermark loaded with palmitic acid, A3,B3: Fingermark loaded with squalene and palmitic acid.

Compared to the results obtained with $PdCL_2$ for the samples enhanced 2 days after deposition, the enhancement for the seven days old marks is superior, although no identifiable mark was developed (Figure 11).

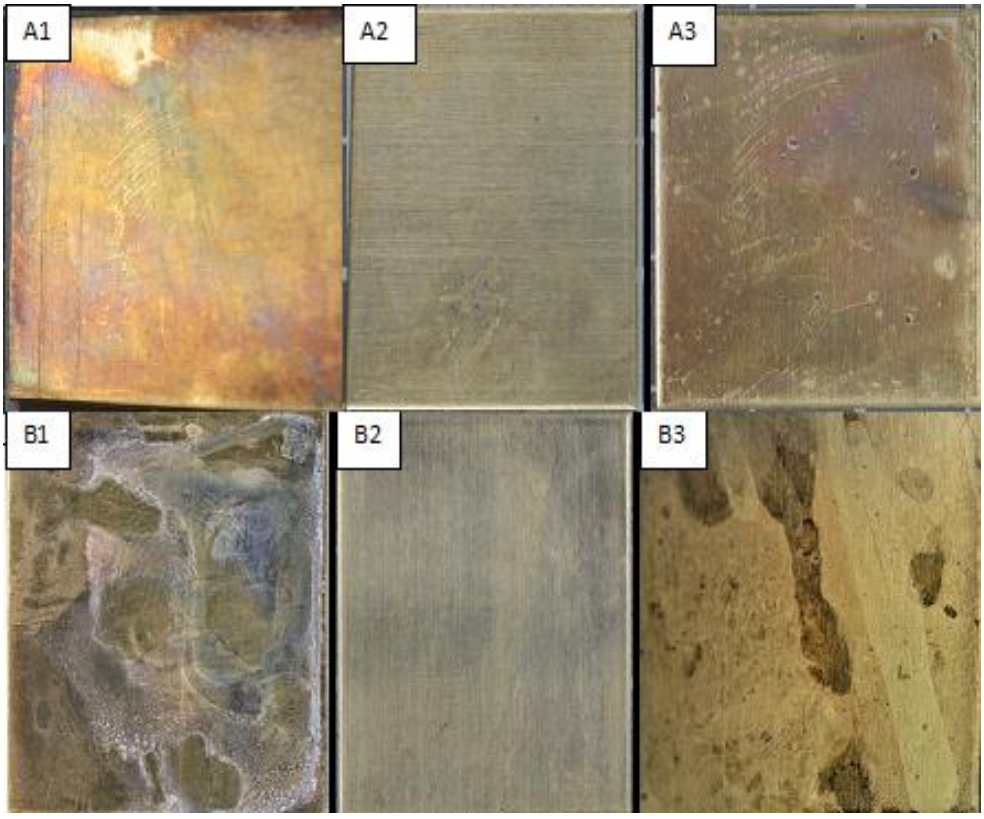

Figure 11. Artificial fingermarks from male donor (A1-3) and female donor (B1-3), developed seven days after deposition with palladium chloride. A1,B1: Fingermark loaded with squalene, A2,B2: Fingermark loaded with palmitic acid, A3,B3: Fingermark loaded with squalene and palmitic acid.

The artificial marks loaded with eccrine-only components did not result in enhanced marks of good quality (Figure 12), a finding which supports the literature indicating that the sebaceous component of fingermarks are the main contributor to Gun Blue and $PdCL_2$ enhancement.

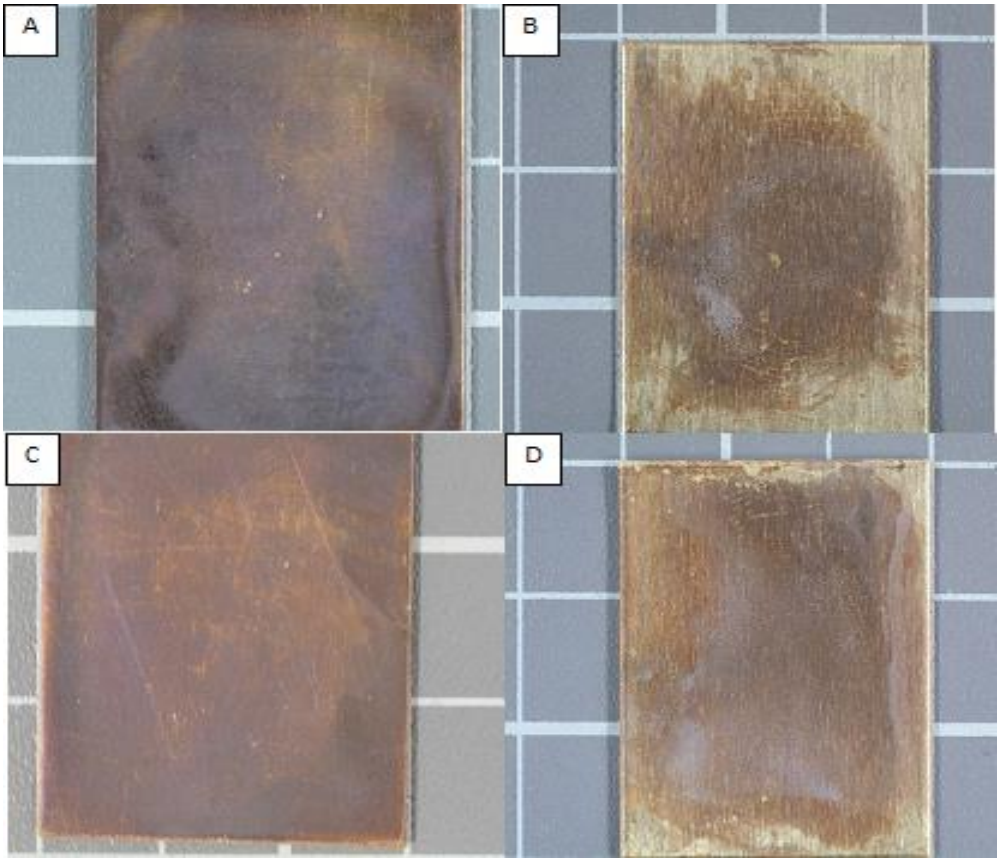

Figure 12. Artificial fingermarks loaded with eccrine components and developed immediately after deposition. A: Fingermark from female donor developed with $PdCl_2$. B: Fingermark from female donor developed with Gun Blue. C: Fingermark from male donor developed with $PdCl_2$. D: Fingermark from male donor developed with Gun Blue.

A similar approach to the Gun Blue and $PdCl_2$ experiments was undertaken with Superglue. Initially the eccrine fingermarks of the two donors were developed, as a reference point (Figures 13&14).

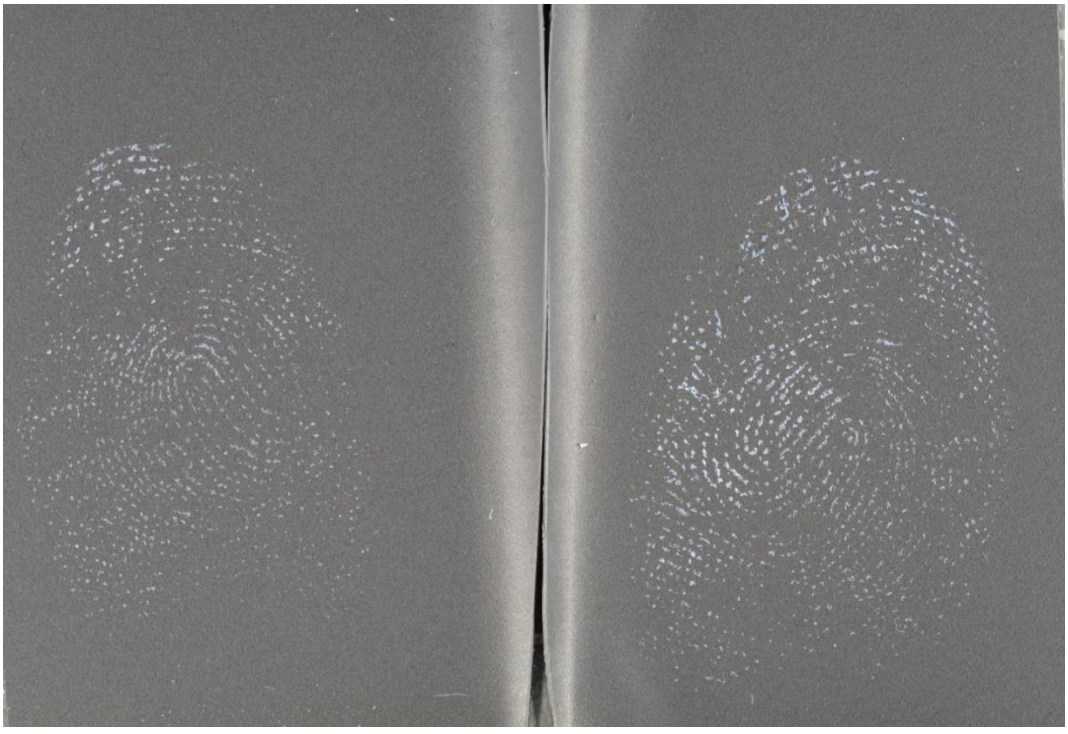

Figure 13. Actual right and left thumb eccrine fingermarks from female donor developed immediately after deposition with Superglue fuming.

Figure 14. Actual right and left thumb eccrine fingermarks from male donor developed immediately after deposition with Superglue fuming.

In this enhancement method, the expected result is different from the results with Gun Blue and $PdCL_2$, due to the eccrine part of fingermarks being the main facilitator of superglue fuming enhancement (Figure 15).

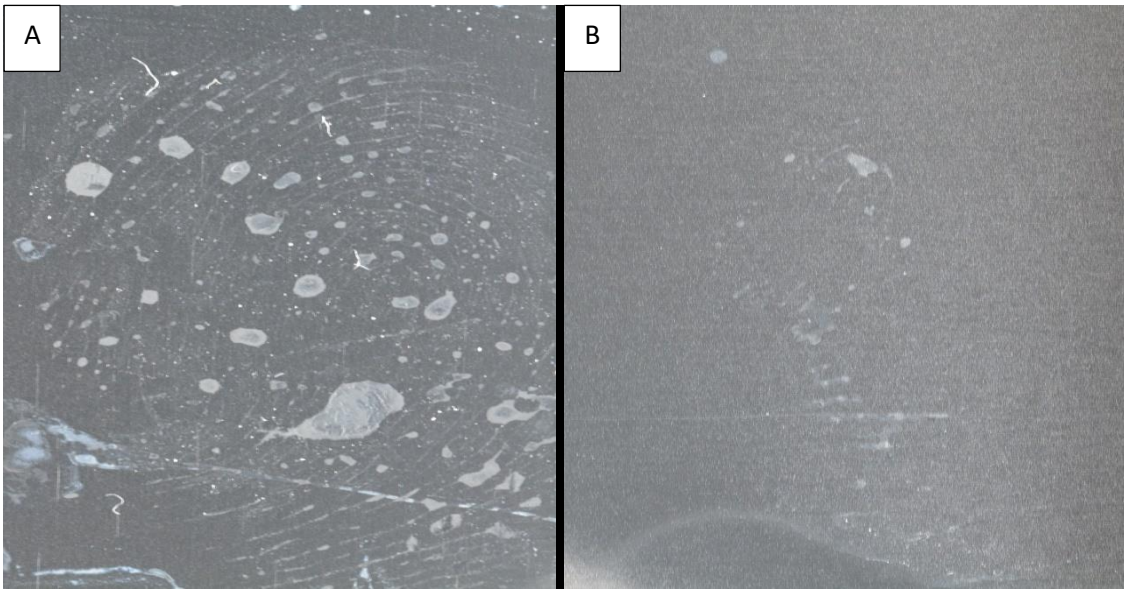

Figure 15. Artificial fingermarks on plastic surface from male donor developed immediately after deposition with Superglue. A: Fingermark loaded with serine, glycine, alanine, histidine in water. B: Fingermark loaded with squalene, palmitic acid, cholesterol, and methyl palmitate.

Initially, lactic acid was used as the only component on the artificial fingermark. Lactic acid has been suspected to be one of the primary contributors/initiators for superglue enhancement.

It seems that lactic

acid acts as a foundation for superglue development, the characteristic white colour of the fingermarks is missing possibly due to the lack of amino acids (Figure 16).

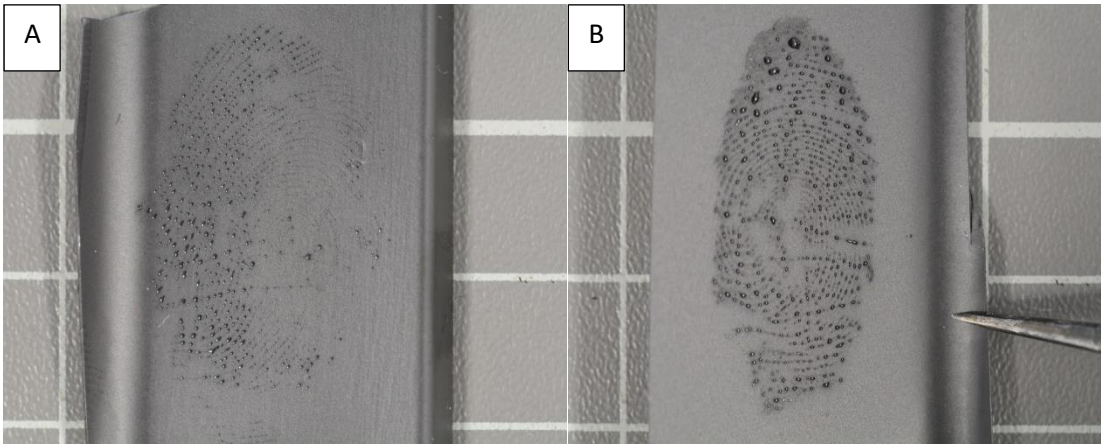

Figure 16. Artificial fingermarks on plastic surface from both male (A) and female (B) donors loaded only with lactic acid and developed immediately after deposition with Superglue.

With serine being the most abundant amino acid in fingermarks, it was deemed necessary to test if it aids mark enhancement by adding it alongside lactic acid. The fingermarks that were enhanced, appear as if serine did not have a positive effect on them. The lack of the characteristic white ridges is apparent (Figures 17&18)

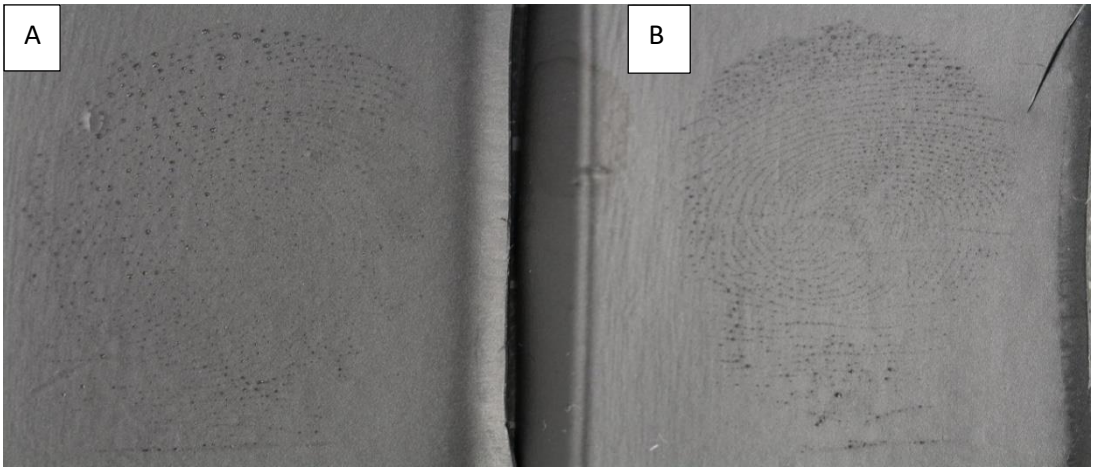

Figure 17. Artificial fingermarks on plastic surface from both male (A) and female (B) donors loaded with lactic acid and serine, developed immediately after deposition with Superglue.

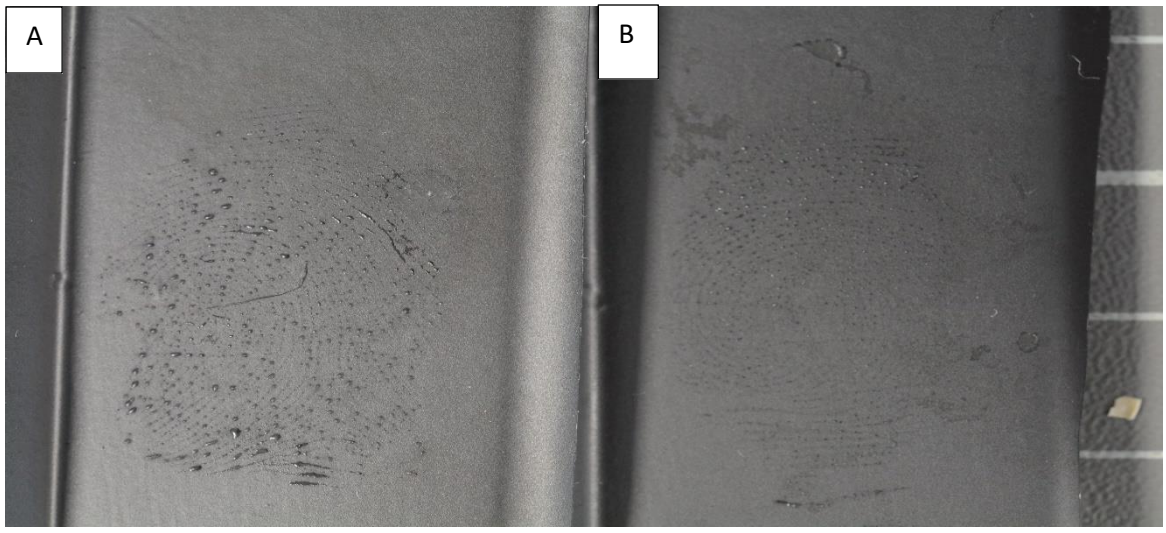

Figure 18. Artificial fingermarks on plastic surface from both male and female donors loaded with lactic acid and serine, developed immediately after deposition with Superglue.

Another compound (alanine) that was suspected to be a facilitator of fingermark enhancement according to previous research, did not lead to the changing of the colour of the ridges to white (Figure 19), indicating that probably another amino acid (or compound) might be the contributor of the white colour on the ridges.

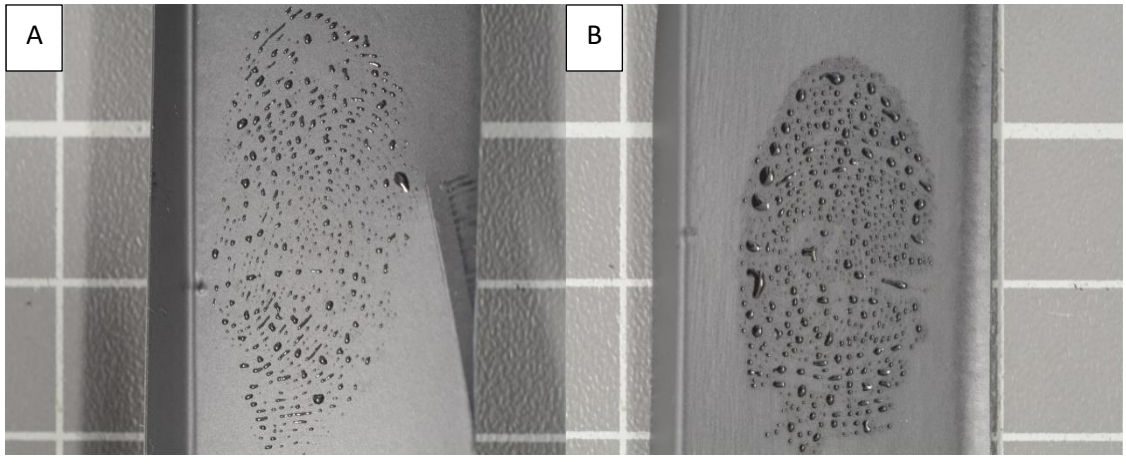

Figure 19. Artificial fingermarks on plastic surface from both male (A) and female donors (B) loaded with lactic acid and alanine, developed immediately after deposition with Superglue.

After the addition of histidine to the previous mixture, the characteristic white colour found in actual fingermarks developed with Superglue could be observed (figure 20).

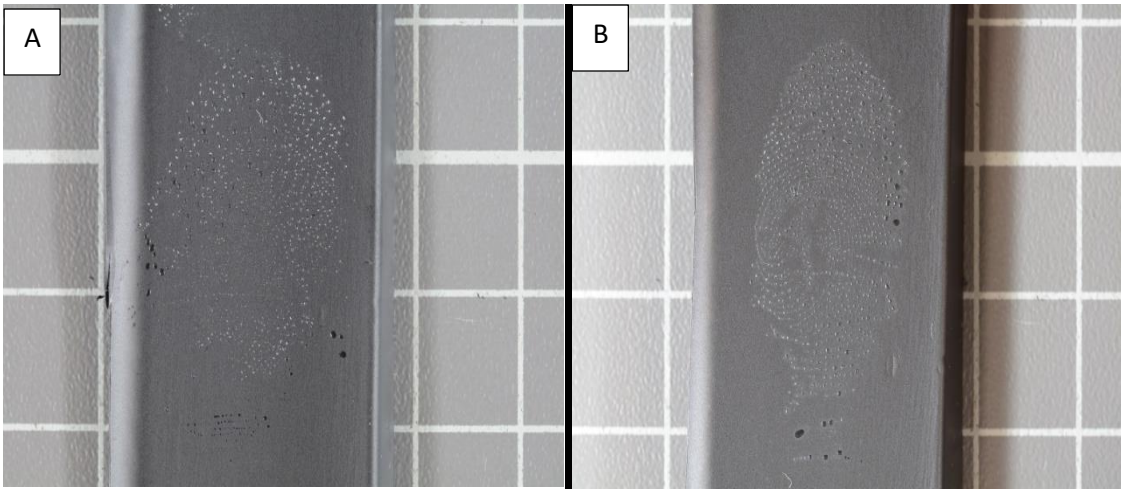

Figure 20. Artificial fingermarks on plastic surface from both male (A) and female (B) donors loaded with lactic acid, histidine and alanine, developed immediately after deposition with Superglue.

It appears that the characteristic white colour is a result of histidine and alanine interaction since it could not be observed in the mixture of lactic acid, histidine, serine (Figure 21).

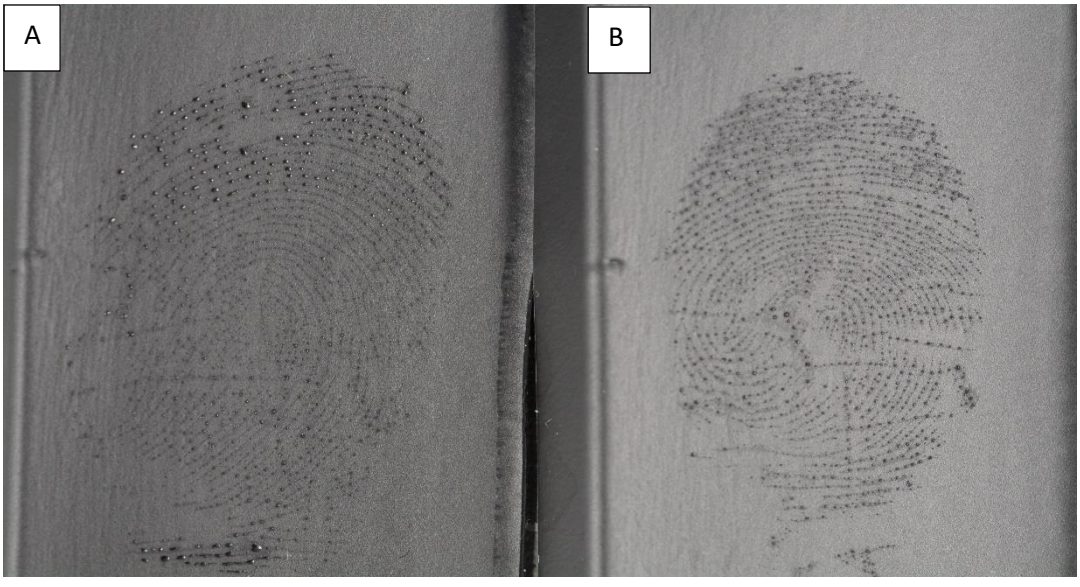

Figure 21. Artificial fingermarks on plastic surface from both male (A) and female (B) donors loaded with lactic acid, histidine and serine, developed immediately after deposition with Superglue.

When a mixture of lactic acid and histidine is used, the ridges developed were white (Figure 22), but they were not as clear as in the lactic acid, histidine, alanine mixture.

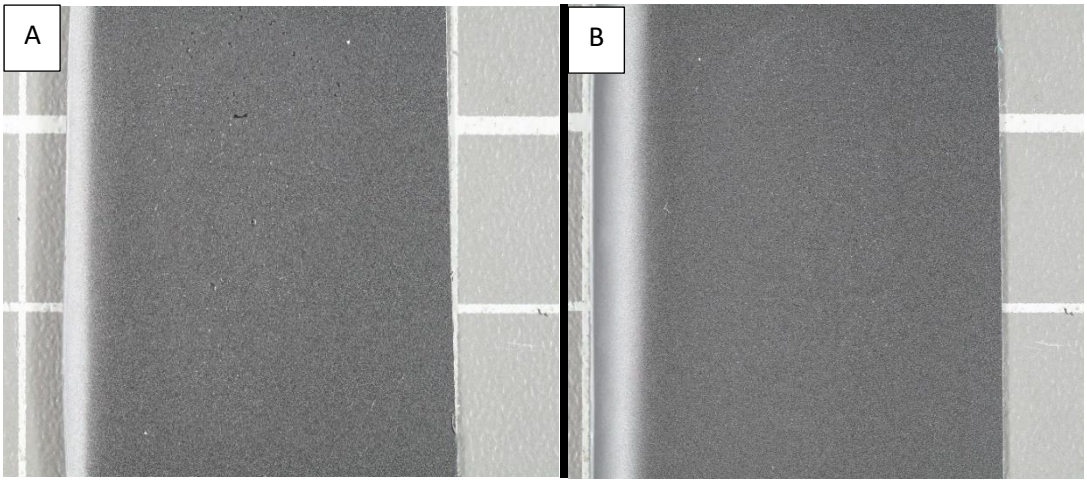

Figure 22. Artificial fingermarks on plastic surface from both male (A) and female (B)donors loaded with lactic acid and histidine, developed immediately after deposition with Superglue.

Similar or potentially even better results (in terms of detail) were observed with the same mixture but the development was performed 2 and 7 days after mark deposition (Figures 23,24 &25).

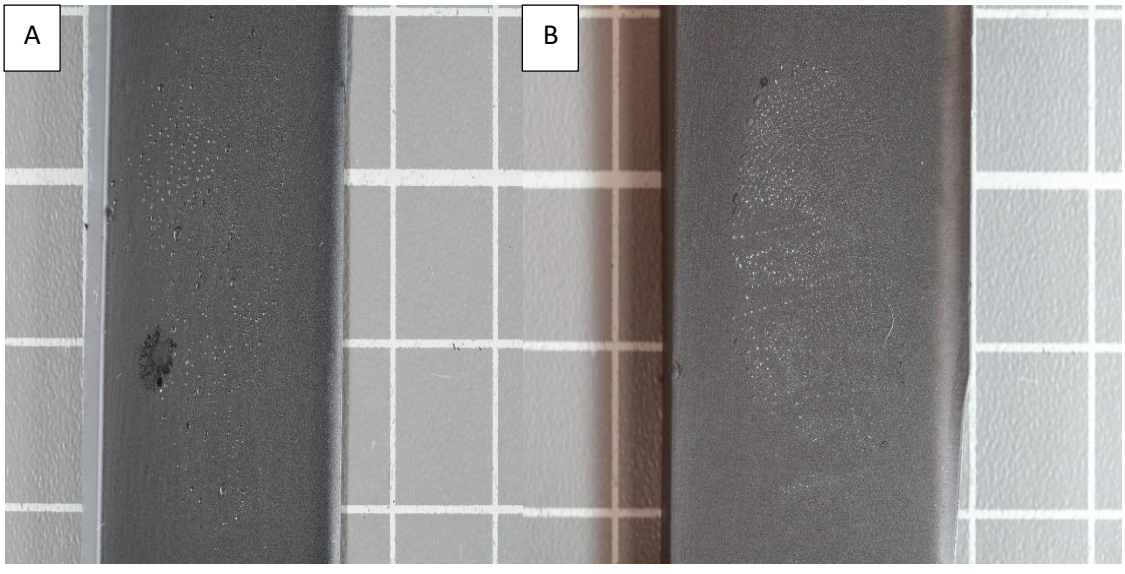

Figure 23. Artificial fingermarks on plastic surface from both male (A) and female (B) donors loaded with lactic acid and histidine, developed 2 days after deposition with Superglue.

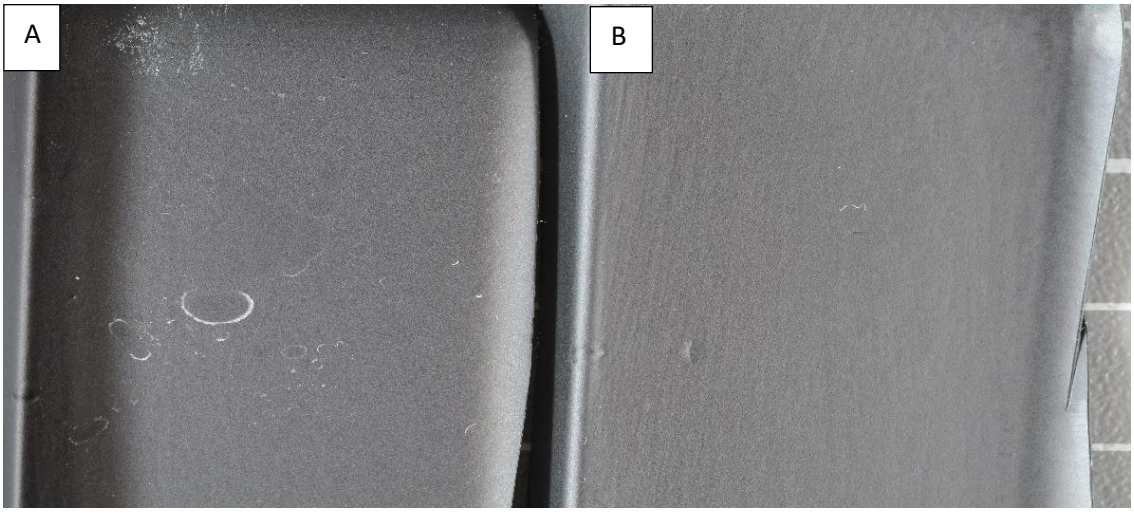

Figure 24. Artificial fingermarks on plastic surface from both male (A) and female (B) donors loaded with lactic acid and histidine, developed 2 days after deposition with Superglue.

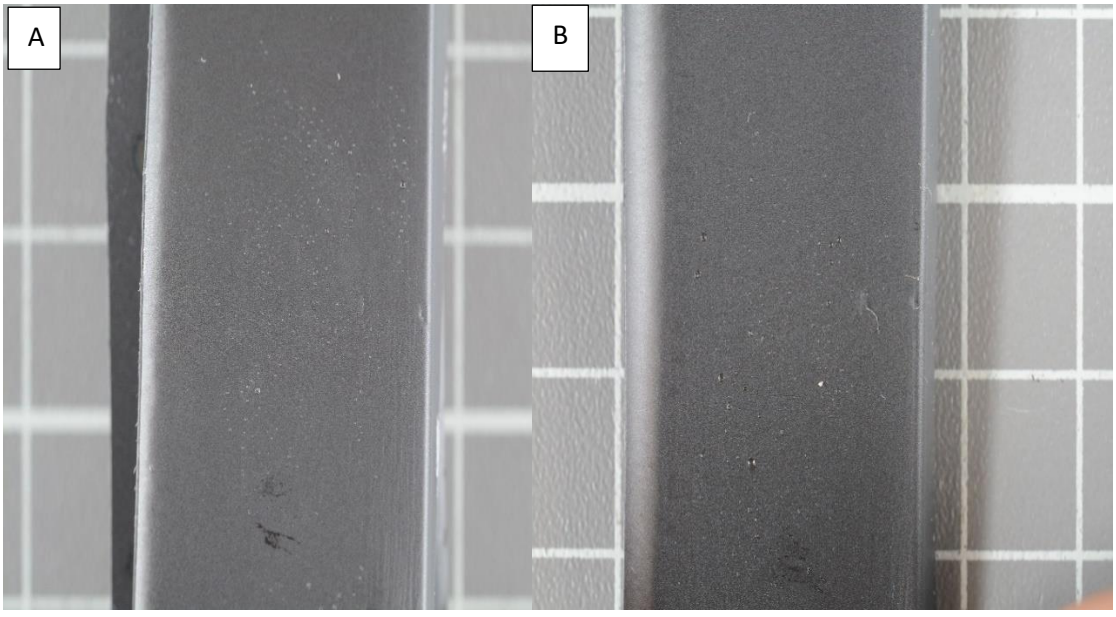

Figure 25. Artificial fingermarks on plastic surface from both male (A) and female (B) donors loaded with lactic acid and histidine, developed 7 days after deposition with Superglue.

Further proof of the minute contribution of the other amino acids found on fingermarks was observed after using a mixture of valine, asparagine, arginine, and lysine using the same quantities as for every other amino acid. Although in reality, the quantities of these compounds are much less, compared to the other amino acids and lactic acid found on the average fingermark, this approach ensures that the amount of compounds is not affecting the results.

The following tables (Tables 3-13) show the overall fingermark enhancement grades that were achieved for the artificial marks from both donors, for all 3 fingermark enhancement methods and also for all different ages.

Table 3. Male donor squalene and palmitic acid

Days since deposition	**Gun Blue**	**$PdCl_2$**	**Superglue**
0	0,1,2	0,1,1	0,0,0
2	1,0,2	1,0,1	0,0,0
7	2,1,0	0,0,0	0,0,0

Table 4. Male donor squalene

Days since deposition	**Gun Blue**	**$PdCl_2$**	**Superglue**
0	0,3,1	2,1,3	0,0,0
2	0,1,0	0,0,1	0,0,0
7	0,2,3	1,1,0	0,0,0

Table 5. Male donor palmitic acid

Days since deposition	**Gun Blue**	**$PdCl_2$**	**Superglue**
0	1,2,2	1,2,2	0,0,0
2	0,1,2	0,1,1	0,0,0
7	0,0,0	0,0,0	0,0,0

Table 6. Female donor squalene and palmitic acid

Days since deposition	Gun Blue	$PdCl_2$	Superglue
0	2,0,0	0,1,0	0,0,0
2	0,0,0	0,0,0	0,0,0
7	0,0,0	1,0,2	0,0,0

Table 7. Female donor squalene

Days since deposition	Gun Blue	$PdCl_2$	Superglue
0	2,1,1	2,1,0	0,0,0
2	0,0,0	0,0,0	0,0,0
7	0,0,0	0,0,1	0,0,0

Table 8. Female donor palmitic acid

Days since deposition	Gun Blue	$PdCl_2$	Superglue
0	1,2,0	0,1,0	0,0,0
2	0,1,0	0,0,0	0,0,0
7	0,0,0	0,0,0	0,0,0

Table 9. Male donor serine, glycine, alanine

Days since deposition	Gun Blue	$PdCl_2$	Superglue
0	1,0,0	0,0,0	0,0,1
2	0,0,0	0,0,0	0,0,2
7	0,0,0	0,0,0	0,0,0

Table 10. Male donor lactic acid

Days since deposition	Gun Blue	$PdCl_2$	Superglue
0	0,0,0	0,0,0	3,3,3
2	0,0,0	0,0,0	2,3,2
7	0,0,0	0,0,0	1,1,3

Table 11. Male donor lactic acid and histidine

Days since deposition	Gun Blue	$PdCl_2$	Superglue
0	0,0,0	0,0,0	3,3,3
2	0,0,0	0,0,0	2,3,2
7	0,0,0	0,0,0	1,1,3

Table 12. Female donor lactic acid

Days since deposition	Gun Blue	$PdCl_2$	Superglue
0	0,0,0	0,0,0	3,3,3
2	0,0,0	0,0,0	1,3,0
7	0,0,0	0,0,0	1,1,3

Table 13. Female donor lactic acid and histidine

Days since deposition	Gun Blue	$PdCl_2$	Superglue
0	0,0,0	0,0,0	3,3,3
2	0,0,0	0,0,0	2,3,2
7	0,0,0	0,0,0	1,1,3

Although oily substances are known to be less vulnerable to ageing or degradation (*e.g.* oxidation), our results indicate that when using the artificial fingermark, some of the sebaceous marks were not adequately enhanced in a few instances (Table 11-13). Whereas the 7 days old marks loaded with eccrine compounds were enhanced to an identifiable level (Tables 5-7). The successful enhancement on the ''older'' eccrine marks can be partially be explained due to the storing conditions; which were ideal for the preservation of the eccrine components (dark indoor conditions eliminate photo degradation/oxidation and any unexpected removal of fingermark residue). The unsuccessful enhancement of the sebaceous marks could potentially be attributed to uneven distribution of the oily components on the artificial fingermark. Any degradation due to ageing or environmental conditions seems highly unlikely.

Scanning Electron Microscopy (SEM) was employed to establish if there are any differences in the formation of polymers, depending on the compounds with which the artificial fingermark was loaded (Figure 26). A gold coating was sputtered onto the samples prior to any analysis. The apparatus was a SEM-EDX FEI Quanta 200 and all the relevant settings can be seen on the bottom of each SEM picture (Figures 26-29).

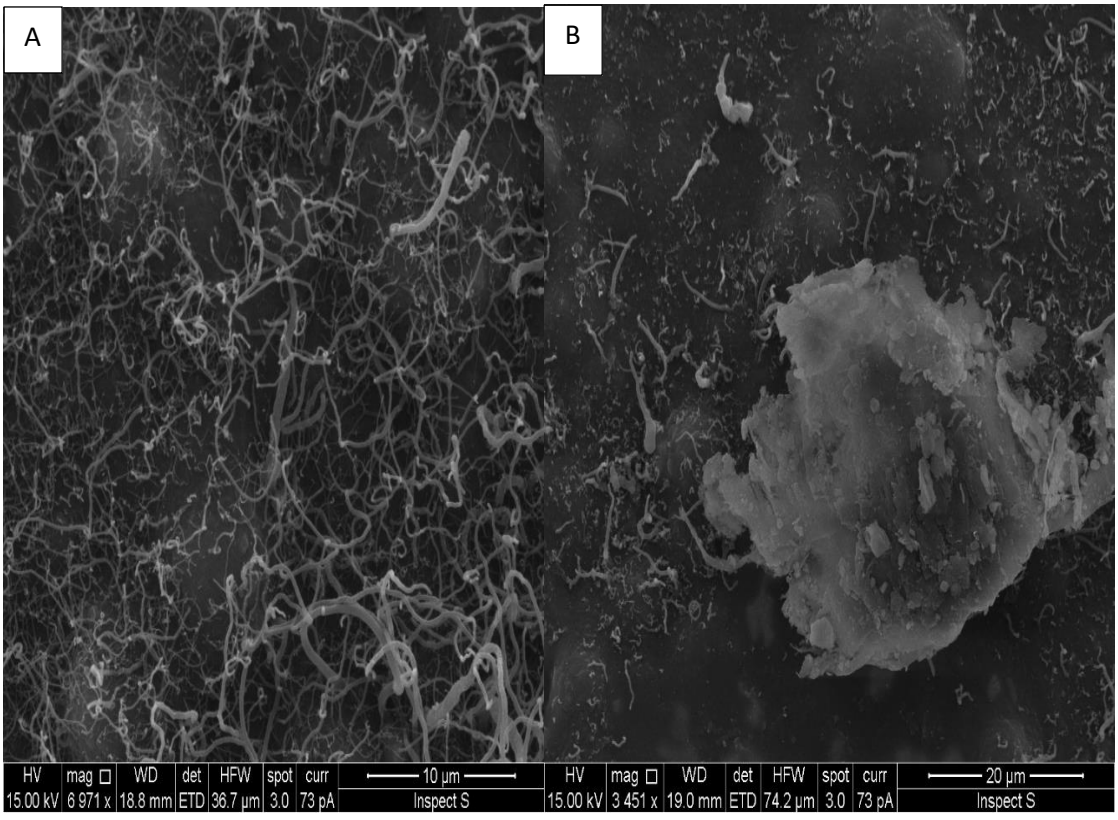

Figure 26. SEM pictures of Natural fingermark, both noodle-like structure (A) and blobs (B) were observed, with the noodle-like structure being prevalent

It is noteworthy that the actual eccrine fingermark created noodle-like shapes with superglue (Figure 27), whereas the artificial print loaded with lactic acid and histidine resulted in blob-like (spherical) particles (figure 28), with no other shapes to be found.

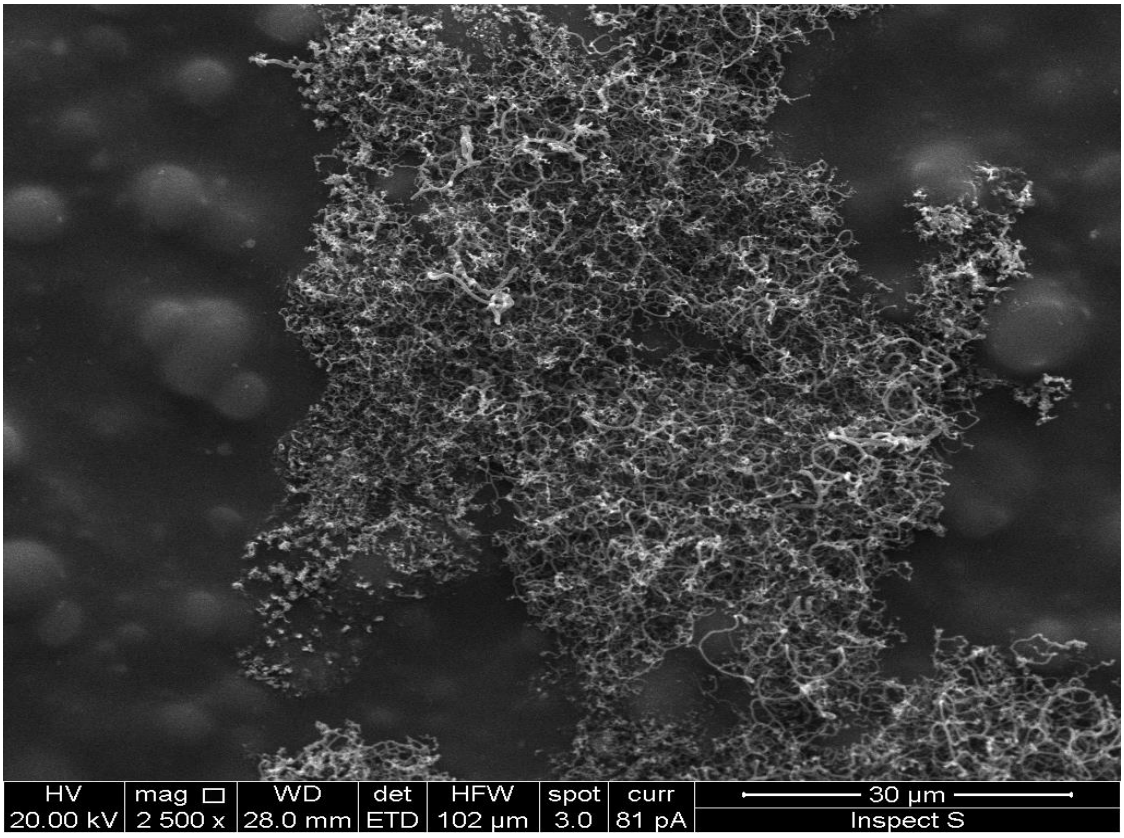

Figure 27. SEM image of the ridges an actual eccrine print from male donor

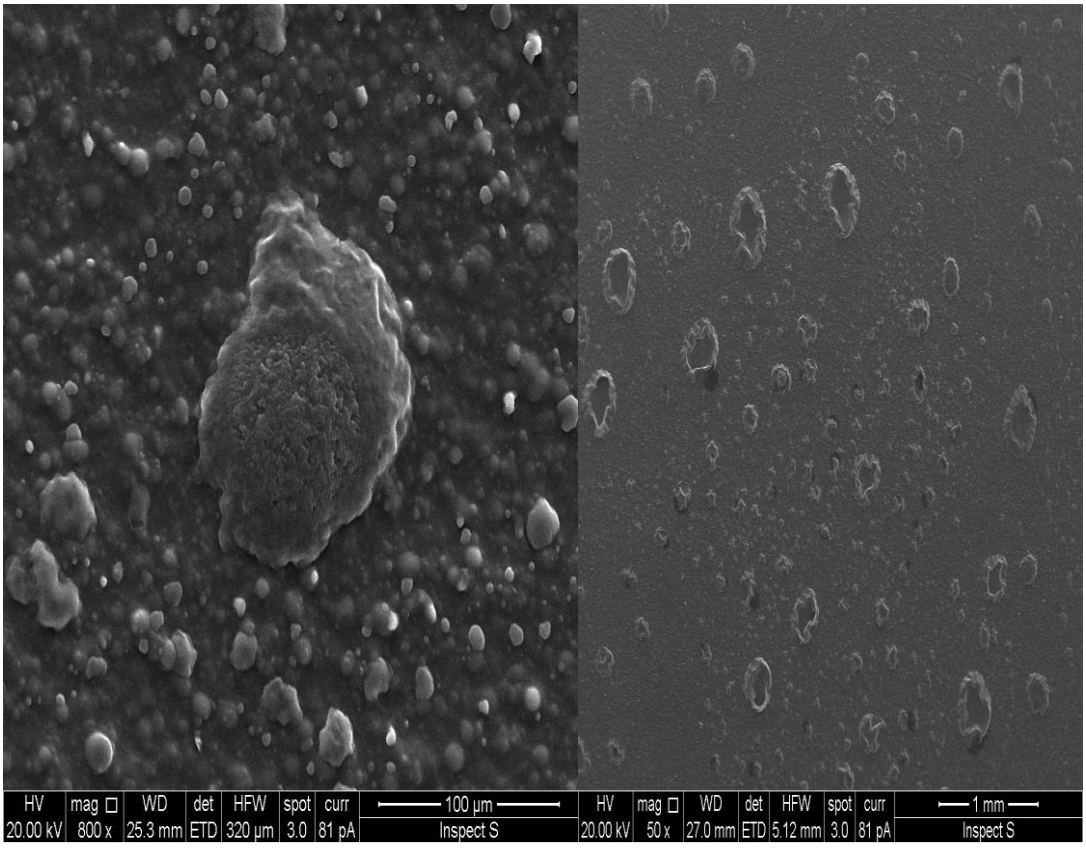

Figure 28. SEM images of the ridges of artificial prints loaded with lactic acid and histidine

The SEM images on the artificial fingermark that was loaded only with amino acids did not show any particular formations (Figure 29)

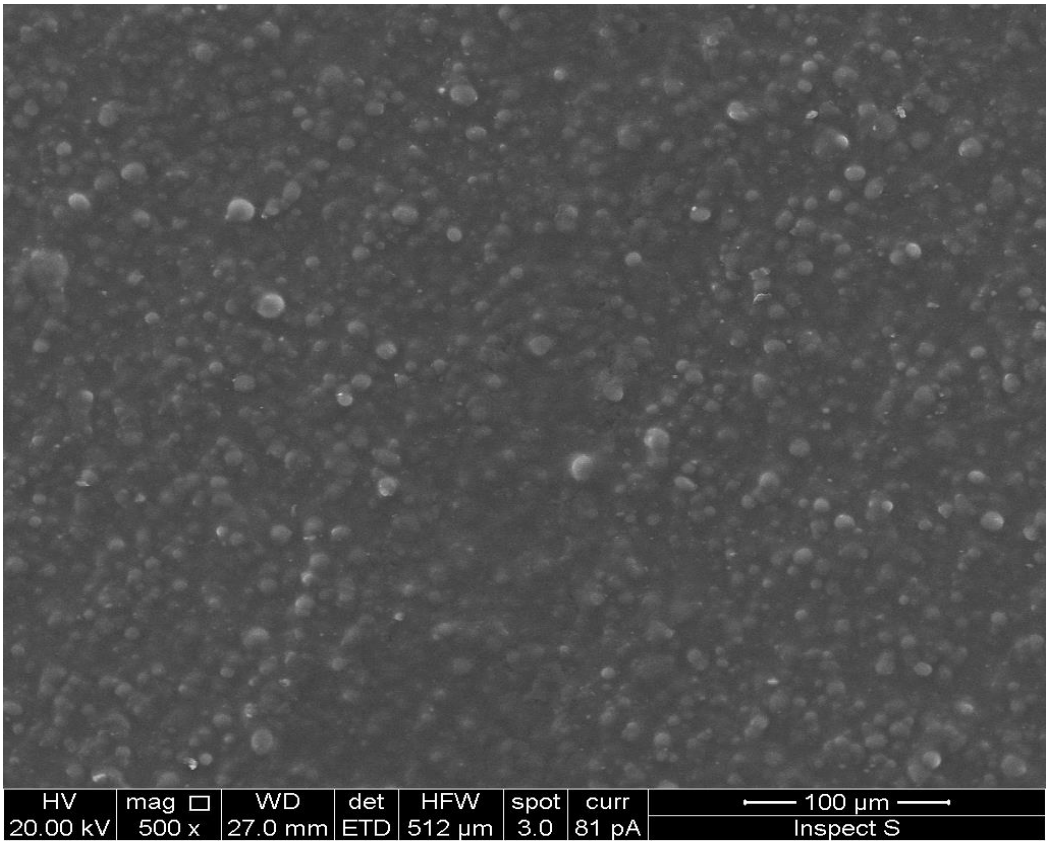

Figure 29. SEM image of the ridges of an artificial print loaded with amino acids and developed with superglue

7.3 Summary & Conclusion

By using the proposed methodology, identification of the contribution of each individual fingermark constituent to each enhancement technique was possible. It was also displayed which part of the fingermarks (eccrine, sebaceous) was the primary contributor for each enhancement method. The sebaceous part was mainly the facilitator for Gun Blue and $PdCl_2$ enhancement, as it has been speculated in previous research [29]. It appears that the eccrine components of the fingermark were the driving force behind superglue enhancement, as it was also demonstrated in previous research [15]. Histidine, was not considered one of the key constituents for superglue enhancement, however in this chapter the importance of histidine was demonstrated, since it seems that the characteristic white ridges of fingermarks developed with superglue are due to the presence of histidine. Lastly regarding the Superglue

mechanism, it appears that the actual fingermarks have a different mechanism that leads to their enhancement compared to the artificial ones with lactic acid and histidine, although both marks looked similar, SEM showed that the polymer formation on the ridges is different. For Gun Blue and $PdCl_2$ it could be inferred that the compounds used in this chapter were acting as a protective layer on the surface of the brass discs, allowing deposition of Selenium and Palladium only on the furrows of the fingermark. Moreover, squalene appeared to be more impactful than palmitic acid, indicating a better ability to confine the developing medium on the furrows of the deposited fingermark, this property is due to the more hydrophobic nature of squalene compared to palmitic acid, which has a –OH group. The employment of SEM images provided additional information regarding the mechanisms taking place, while also making clear that there is an additional process/mechanism that occurs during the development of actual eccrine/natural fingermarks compared to the artificial marks (loaded with histidine and lactic acid). This can be observed by the lack of the noodle-like structures and the presence of only the blob-like formations in the artificial fingermarks. The consensus of the scientific literature [15, 36, 37] seems to be that cyanoacrylate polymerisation happens on the ridges of the mark and is an anionic polymerisation caused by the excess of carboxylate groups (due to amino acids) and also the presence of amine groups.

An additional way to use the artificial fingermark would be the possibility of intentionally creating a fingermark that would be considered as a fingermark donated by a ‘’poor’’ donor, following that, an effort could be made to alter the parameters of the enhancement technique (*e.g.* humidity, time of development) of choice until a satisfactory fingermark development is achieved. This strategy would improve our understanding of the enhancement technique while also making it more efficient.

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8. General Discussion & Conclusion

8.1 Introduction

The aim of this PhD project was mainly to develop new protocols that can be beneficial for the enhancement of fingermark ridge detail on fired cartridge cases. The newly developed/optimised methods could then be used as a basis for new fingermark enhancement protocols in routine police casework. After the initial stage of studying the available literature and writing a detailed literature review on the subject, it was apparent that there was a knowledge gap in the areas of: Gun Blue deposition, vacuum metal deposition, and on the chemical profiling of fingermarks on fired cartridge cases. Additionally, our understanding of how and why certain fingermark enhancement method work could be strengthened. The body of work presented in this thesis has progressed our understanding in all the aforementioned areas.

8.2 Gun Blue Deposition

Enhancement of fingermarks with Gun Blue has all the necessary characteristics of an ideal technique for forensic purposes which are low cost, short development times and simplicity of use. Our results showcased the great efficacy of the method in enhancing ‘‘groomed’’ aged fingermarks from male and female donors that had been exposed to outdoor conditions. However, unimpressive results were achieved for natural fingermarks. Additionally, when it comes to fired cartridge cases it was shown that it is much more rare to obtain an identifiable natural fingermark compared to a groomed one, and that the type of cartridge and gun can have an effect on fingermark enhancement. Obviously, the larger the cartridges case the higher the chances of getting an identifiable fingermark. When it comes to the type of gun used, favourable results were obtained from bolt-action single shot rifle and from a .38 revolver. Overall, it cannot be confidently stated that Gun Blue enhancement is superior to the methods that are the staples right now in police casework, but this cost-effective technique still has a place in the forensic scientist’s toolbox.

8.3 Chromatography

GC/MS was used in order to identify the fingermark compounds that persist on the cartridge surface after firing. Our results determined that squalene, palmitic acid and stearic acid are the compounds that are most likely to be present on the cartridge surface. Therefore, it is more likely to achieve enhancement of fingermarks on fired cases when one chooses a method that either interacts with these compounds or is facilitated by their presence. Moreover, it was it was shown that the majority of fingermark residue is degraded when the cartridge is fired, and that is the main contributory factor to the difficulty in the enhancement of fingermarks on a fired cartridge.

8.4 Vacuum Metal Deposition

Of the studies conducted within this PhD project, the gold/zinc and silver/zinc deposition protocols were both effective for fingermark enhancement. The ageing of the marks did not appear to cause any major issues on the quality of the enhancement. Overall, the original quality of the mark seems to be the most important factor that will determine the quality of fingermark enhancement. The enhancement of fingermark ridge detail on fired brass cases has been shown to be possible; however, none of the developed fingermark were of an identifiable grade.

Favourable results are expected if the ammunition used for enhancement is larger in size, such as a cartridge used in shotguns. A full fingermark can be more easily deposited, both on the metallic and the plastic surfaces of this type of cartridges. When it comes to police routine casework, it might be preferable to utilise the silver/zinc protocol due to relatively lower cost. Recently tabletop models of VMD have been developed, greatly reducing the time, and cost while also achieving the same quality (or even better) of mark enhancement. VMD could be incorporated as a standard procedure in casework, since literature now suggests that it is an effective method for a variety of surfaces, and not really affected by ageing of a sample, which

compares favourably with other established methods (*e.g.* superglue fuming).Our analysis of the fingermark compounds that play a facilitating role in VMD enhancement showed that generally a donor who is considered as an overall good donor, will most likely produce better results with VMD. Squalene, palmitic acid, stearic acid were the most consistent compounds throughout our donor pool, so they must be one of the primary contributors in the enhancement. However, that does not mean that other compounds are not also involved, additional consideration is required regarding the eccrine part of fingermarks.

A further exploration of the sebaceous part of the fingermarks can be revisited, with potentially using a different substrate instead of brass discs, and even experimenting with different extraction solvents [1] which would yield a more complete fatty components profile from all the donors. Quantification of compounds, could also be one of the next steps in understanding how the VMD enhancement mechanism works. For example, two donors that are classified as ‘’good’’ and ‘’poor’’ for VMD could deposit fingermarks on a ballistic surface, and then the fingermarks can be extracted, chromatographically analysed (GC/MS and/or LC/MS) and their differences could be enlightening. The caveat with this approach would be that deposition, extraction and analysis of the samples must be done with great focus on reproducibility, meaning that the deposition of the marks must occur with identical pressure [2] and duration. The extraction must have the same duration for every sample, and ideally the same exact instrumentation settings must be kept throughout the experiment. This would assure less variability in the results (apart from the inherent variability of fingermarks), which in turn would allow for the drawing of much more accurate conclusions.

8.5 Artificial Fingermark/Reproducible Fingermark deposition

As demonstrated in the relevant chapter this new methodology can offer a greater understanding of most fingermark enhancement methods, due to the ability to load the artificial fingermark with the exact amount of compounds that are deemed as important. Moreover, it is a step closer to depositing reproducible fingermarks. The results obtained in this chapter, identify the key compounds in enhancement methods such as Gun Blue, palladium deposition and Superglue Fuming. Specifically for Superglue Fuming the importance of histidine in fingermark enhancement is a completely novel finding. However, there still seems to be a difficulty with creating reproducible fingermarks due to the inherent variability in the deposition of fingermarks. A step further could be the use of one the fingermark press rigs that have been reported in literature [3].

8.6 Self-Assessment/Future Ideas

Overall, in the studies presented herein, novel concepts have been explored and critically discussed, however there is still a lot room for improvement. Specifically for the first chapter (chemical profile of fingermarks), a more complete review could include more studies from journals that are not solely forensic related. Perhaps more details regarding the chemical reactions of fingermark related constituents could have been found there.

On the second chapter, although the literature available on fingermark enhancement on metallic surfaces is not particularly rich, a better qualitative comparison of fingermark enhancement methods could have been done. Statistical analysis of the results on a specific metallic surface throughout the body of available literature could have given off the enhancement method that performed better most of times.

When it comes to the Gun Blue study, more emphasis could have been placed on natural fingermarks. The majority of the fingermarks used were groomed marks and this lead to better fingermark enhancement overall. This however, does not necessarily reflect real crime scene fingermark enhancement. Additionally, the use of GC-MS would have been ideal in identifying critical fingermark components that aid Gun Blue enhancement.

The vacuum metal deposition studies were well designed and followed the principles of reproducible fingermark research. One drawback would have to be the equipment itself, since the model of the VMD used in both studies was a relatively old one (a mid-90's model), and since then the equipment's capabilities have improved dramatically. Moreover, a greater availability of the VMD donor pool on the chromatographic analysis would have allowed for more concrete conclusions regarding the elucidation of VMD's enhancement mechanism.

On chapter 6, a more focused approach on the alterations of the constituents by environmental conditions could have been easily followed. Fingermark samples could have been kept in very low temperatures and/or subjected to very high temperature for a certain time. This type of experiments are scarce on the current body of literature, and could help when it comes to the fingermark enhancement of this type of fingermarks.

Lastly, on the artificial fingermark study, there must still be room for improvement when it comes to the texture/detail of it. The formulation of the liquid latex used could have an impact on the ridge detail, and more experiments with that goal in mind need to be performed to find the ideal one. Additionally, specifically regarding the experiments on superglue fuming, the inclusion of a few more amino acids (such as glutamic acid) could have provided a clearer picture of superglue's enhancement mechanism.

8.7 References

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[3] H. Reed, A. Stanton, J. Wheat, J. Kelley, L. Davis, W. Rao, A. Smith, D. Owen, S. Francese, The Reed-Stanton press rig for the generation of reproducible fingermarks: Towards a standardised methodology for fingermark research, Sci & Justice, 2016; 56(1):9-17

9. Appendices

Publications:

Chapter 2: Christofidis, G., Morrissey, J. and Birkett, J.W. Detection of Fingermarks—Applicability to Metallic Surfaces: A Literature Review. J Forensic Sci, 2018;63:1616-1627

Chapter 3: Christofidis, G., Morrissey, J. and Birkett, J. W. Using Gun Blue to Enhance Fingermark Ridge Detail on Ballistic Brass. J Forensic Identific, 2019;69(4):431-449

Chapter 4: Christofidis, G., Morrissey, J. and Birkett, J.W. A Preliminary Study on Vacuum Metal Deposition as a Standalone Method for Enhancement of Fingermarks on Ballistic Brass Materials. J Forensic Sci 2019;64:1500-1505

Chapter 5: Submitted to Forensic Science International