Article Title: The forensic exploitation of fingermark chemistry: a review

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Abstract

The substances deposited from the fingertip onto a surface during contact between them represent a highly complex range of chemicals that can be exploited in a variety of ways in a forensic investigation. An overview is given of the multitude of chemicals that have been detected in fingermarks, including those occurring in endogenous sweat, metabolites of ingested substances, and exogenous substances picked up on the fingertip. Changes in chemistry that may occur between deposition of the fingermark and its subsequent forensic analysis are discussed, with particular reference to the ways in which these changes have been considered as a means of dating fingermarks. The ways in which fingermark enhancement reagents utilise the different chemicals present to reveal ridge is reviewed, together with how different classes of chemical can be sequentially targeted to optimise the number of fingermarks recovered. A field of increasing interest is the use of advanced analytical techniques incorporating mass spectrometry and imaging capability to simultaneously obtain additional contextual information about the donor of the mark whilst visualising the fingermark ridge pattern. Examples are given of how such information can be applied in forensic investigations. It is concluded that an extensive 'tool kit' of fingermark enhancement

processes is already available to utilise the different chemicals present, and the advances that can be made in this field using conventional approaches are limited. There is, instead, significant potential to utilise analytical techniques to forensically exploit the chemical information within fingermarks but there are also significant barriers to their implementation in this way.

Keywords: Fingermark chemistry, fingermark enhancement, forensic exploitation, mass spectrometry, chemical imaging, lifestyle

Graphical/Visual Abstract and Caption
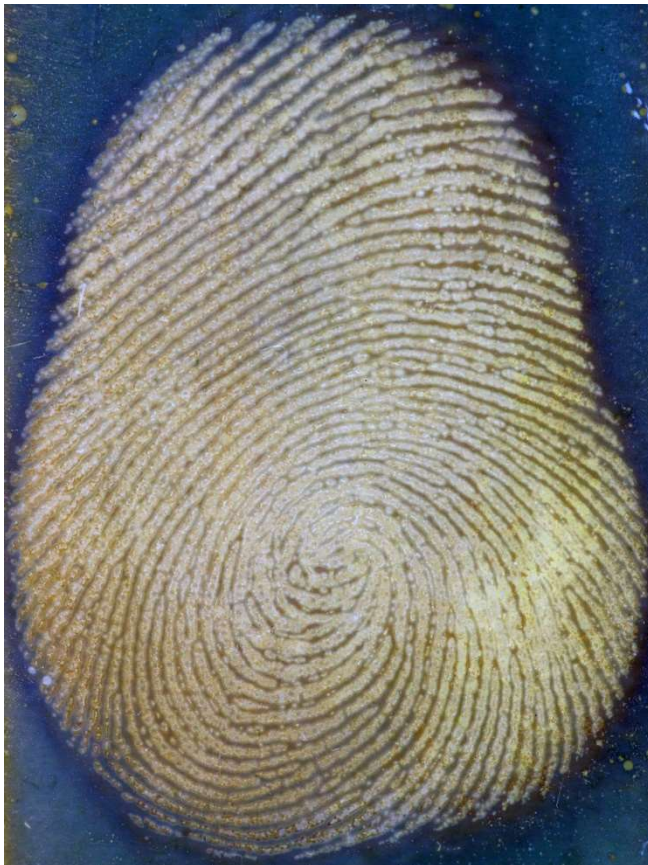
A sebum-rich thumb mark deposited on a glass slide and developed using silver vacuum metal deposition. The mark shows the Level 1, Level 2 and Level 3 detail used for fingerprint comparison and identification. The differences in colour in the ridges indicate variations in thickness and composition of the substances deposited.

1. INTRODUCTION

There is evidence that the use of fingerprints for the identification of an individual, either for civil or criminal purposes, has been considered in some form for over 2000 years (Barnes, 2011). The comparison of a mark left by an individual at a crime scene with sets of reference prints taken under controlled conditions is a cornerstone of forensic investigation, first being proposed in 1880 (Faulds, 1880). Following the generation of classification systems for fingerprint patterns (Galton, 1892) and filing systems enabling databases to be searched (Henry, 1901), fingerprint comparison and

identification has been successfully employed for over 120 years. The fact that fingerprint patterns are 'unique' (to the best of scientific knowledge) and persistent throughout life makes them a powerful identification tool. Indeed, the term 'fingerprint' is widely used across many other branches of science, for example, the mid-infrared spectrum of organic substances is often referred to as a form of chemical "fingerprint" because it is sufficiently characteristic to a particular substance to enable it to be identified.

In criminal investigations the focus is on locating marks that may have been left by the suspect at the crime scene. These can be of three principal types; a positive mark where material is transferred from the fingertip to the surface, a negative mark where the fingertip removes material (e.g. dust) from the surface, or a 'plastic' mark where the fingertip leaves a permanent impression in a soft substance such as putty. The classification of a positive mark can be further divided into a 'patent' mark where the material transferred is readily visible to the eye (e.g. mud, ink), or a 'latent' mark where the material transferred cannot typically be readily seen by eye and needs further enhancement to be seen.

The chemistry of the material transferred from the finger to the surface is important to the visualisation of the contact trace. This is because chemical substances present can be utilised by a range of processes that either convert a latent mark into one that is visible or assist in further enhancing the pre-existing detail in a patent mark. The chemical development of fingermarks was observed as early as the 1860s (Quinche & Margot, 2010) and was already being explored in a more focused way in the 1920s (Mitchell, 1920), with a range of chemical processes targeting different constituents being proposed for use.

In the forensic community, there is some debate over the exact definition of the terms *fingerprint* and *fingermark*. Here, we define a **fingermark** to be a trace that is on a surface at a crime scene. For a fingermark, the circumstances of deposition are unknown. Once the fingermark has been developed and photographed, the ridge patterns are normally compared to an inked **fingerprint**, given by a known donor. In contrast to a fingermark, a **fingerprint** can deposited under controlled conditions – for example by controlling the contact time, pressure and cleanliness of both the finger and the surface. In this review, a fingermark refers to a mark deposited in an uncontrolled manner by an unknown donor, whereas a fingerprint is deposited in a controlled manner by a known donor.

This review will focus on the material that is ultimately transferred from the fingertip to the surface to form a fingermark. It will consider how this highly complex chemistry can be utilised by a wide range of chemical reagents, and by advanced analytical techniques in combination with imaging capabilities, to reveal the fingermark ridge detail and additional information contained within it.

2. FINGERMARK CHEMISTRY

Before progressing to a discussion of the composition of the material that may be transferred during contact, it is necessary to consider the quantity of material that is actually transferred. There have been few studies that address this important aspect.

Early work focused on estimations of the mass of a single fingermark or examining the loss of mass over time due to drying of the sample and evaporation of water (Cuthbertson and Morris, 1972;

Scruton et al., 1975; Darke and Wilson, 1977). However, it was not possible to extrapolate the mass of a single latent fingermark using the approaches proposed at that time. In 2008 a study determined the mass of a single natural latent fingermark collected on a non-porous substrate using a microbalance with a readability of 0.1 µg (Croxton, 2008). Fingermark mass was found to range between 0.33 and 29.00 µg (mean 7.40 µg, s.d. 7.46 µg, n = 55 fingermarks from seven donors). Over a 24 hour period a loss in mass was observed for some fingermarks, as well as an increase in mass in others. The latter was thought to be due to hydration of the fingermark due to the presence of hygroscopic constituents. Additionally, Bright et al. (2013) observed that fingermarks that were placed into a vacuum system lost around 26% of their mass - equivalent to 5 weeks ageing under ambient conditions.

Watkinson (2018) found that the chemical composition of sequential fingermarks from the same individual, donated under controlled conditions can be reproducible. The variability in the mass of fingermark depositions was found to vary by up to 100% within donors. However, if a donor washed their hands prior to depositing a fingermark, the variability in deposited mass reduced to 21%. Additionally, it was found that the chemical composition of sequential depositions was also relatively reproducible, provided hands were washed prior to providing a fingermark.

It is now well known that the composition of latent fingermarks is complex. Latent fingermarks consist of chemical contributions from a number of natural sources, predominantly the eccrine and sebaceous glands, in varying relative amounts with minor contributions at times from the apocrine sweat glands and the epidermis (Table 1). Contributions from external sources such as cosmetics, hair and tobacco products and any other contaminant the fingertips may come into contact with, further increase the complexity. This complexity, however, provides the opportunity for latent fingermarks to be exploited for information about the donor and/or their habits.

Table 1: Summary of endogenous latent fingermark residue constituents and their sources

Source	Organic constituents	Inorganic constituents
Eccrine sweat	Amino acids (e.g. serine, glycine, ornithine, alanine, aspartic acid); Creatine; Creatinine; Enzymes (e.g. esterases, proteolytic enzymes); Glucose and other reducing sugars; Glycogen; Lactic acid and lactate; Peptides (e.g. dermicidin, cathelicidin LL-37); Phenol; Proteins (e.g. albumin, cathepsin D, immunoglobulins (IgG, IgA, IgD, IgE), keratins 1 and 10); Pyruvic acid and pyruvate; Urea; Uric acid; Vitamins (e.g. ascorbic acid, choline, folic acid, niacin, riboflavin)	Ammonia; Bicarbonate; Bromide; Chloride; Fluoride; Iodide; Metal ions – major (e.g. calcium, iron, potassium, sodium) and trace (e.g. cobalt, copper, lead, magnesium, zinc); Phosphate; Sulphate; Sulphide; Water
Sebum		Alcohols; Fatty acids (e.g. palmitic, palmitoleic, oleic, stearic, myristic acids); Fatty acid alkyl esters (e.g. palmitic acid methyl ester, stearic acid methyl ester);

		Glycerides (e.g. mono-, di- and triglycerides); Hydrocarbons (saturated and unsaturated); Squalene; Squalene degradation products (e.g. squalene epoxides, squalene hydroperoxides); Sterols (e.g. cholesterol); Sterol esters (e.g. cholesterol esters); Wax esters (e.g. myristyl myristate, palmityl palmitoleate, stearyl palmitate)
Epidermal lipids		Fatty acids; Glycerides; Proteins (e.g. cathepsin D, keratins 1 and 10); Sterols (e.g. cholesterol); Sterol esters (e.g. cholesterol ester)
Apocrine sweat	Androgenic steroids; Carbohydrates e.g. glycogen; Carboxylic acids; Proteins; Sterols e.g. cholesterol	Ammonia; Iron; Water

2.1 Eccrine sweat

Since eccrine sweat glands are the only glands found on the palmar region of the hand and fingers, eccrine sweat is often the predominant endogenous component of latent fingermark residue. Water is typically a very high proportion of eccrine sweat with the remainder consisting of a mixture of water-soluble organic compounds and inorganic salts (Table 1). There can be great variation in eccrine sweat composition between donors and within a donor over time, although there are common constituents.

The predominant organic components of eccrine sweat are amino acids and proteins. Amino acid concentration has been reported to be between 0.30 and 2.59 mg L^{-1} with individual amino acids present in different relative abundances (Hansen and Joullié, 2005). Serine, glycine and alanine are the most abundant. Threonine, leucine, tyrosine, isoleucine, lysine, phenyalanine, methionine and cystine are also present but in decreasingly lower amounts. Quantitative studies of deposited latent fingermarks using a variety of analytical techniques have found comparable amino acid profiles to eccrine sweat (Croxton et al., 2010; Atherton et al., 2012; De Puit et al., 2014; van Helmond et al. 2017).

A variety of other ninhydrin-positive substances have been identified in eccrine sweat (such as cysteic acid, methionine sulphoxide and glucosamine (Liappis and Hungerland, 1973), as well as proteins including albumin, cathepsin D, dermicidin, immunoglobulins (IgG, IgA, IgD and IgE), keratins 1 and 10, and antimicrobial proteins and peptides (O'Neal, Page and Remington, 1967; Nakayashiki, 1990; Flad et al., 2002; Murakami et al., 2002; Drapel et al., 2009). Other organic compounds reported in eccrine sweat include glucose, pyruvic and lactic acid, urea, uric acid, creatinine, creatine and ammonia (Bleay, Croxton & de Puit, 2018).

The protein component of latent fingermarks has also been studied (Ferguson et al., 2012; Song et al., 2012; Oonk et al., 2018). Dermicidin, the most abundant protein in eccrine sweat, was targeted

by immunolabelling and revealed a "dotted" fingermark ridge pattern (van Dam et al., 2013). Ferguson et al. (2012) demonstrated that the use of matrix assisted laser desorption/ionisation mass spectrometry (MALDI MS) could detect many other peptides and protein species, including dermicidin, and psoriasin. By using MALDI MS imaging (MSI), a similar dotted dermicidin molecular image could be provided albeit at lower resolution (200 μm x 200 μm) (Francese, 2015) (Figure 1)
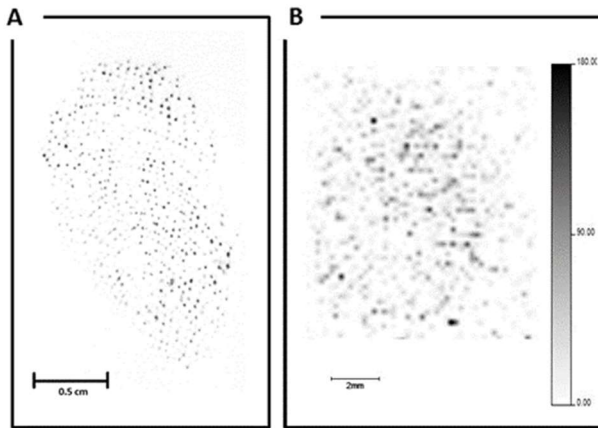

Figure 1. Fingermark images generated by dermicidin peptide. A: immunolabelled dermicidin-generated image of an eccrine mark; B: MALDI MSI image of dermicidin at m/z 4918. (A) was Reprinted/adapted from Forensic Science International, 232/1-3, van Dam A, Aalders MC, van de Braak K, Hardy HJ, van Leeuwen TG, Lambrechts SA, Simultaneous labelling of multiple components in a single fingermark, 173-9., Copyright (2013), with permission from Elsevier; (B) Adapted and reprinted from Francese, S. (2015). Techniques for fingermark analysis using MALDI MS - a practical overview. In R. Kramer (Ed), Advances in MALDI and laser induced soft ionisation mass spectrometry. Springer. Copyright 2016

The most abundant inorganic salt is chloride (predominantly as sodium chloride) with bromide, iodide and fluoride also found. Chloride concentration, in particular, varies greatly with a number physiological factors including anatomical site, sweat rate and dietary and water intake (Rothman, 1954; Olsen, 1972) and has also been shown to vary in latent fingermarks between donors (Cuthbertson, 1969). Other inorganic components found in eccrine sweat include copper, manganese, magnesium, phosphorous, iron and calcium. The spatial distribution of elemental constituents from both endogenous and exogenous sources has been studied in latent fingermarks (Worley et al., 2006; Bailey et al., 2013; Thandauthapani et al., 2018; Boseley et al., 2019).

2.2 Sebaceous sweat

Sebum is the secretory product of the sebaceous gland which is found in varying abundance in different anatomical sites. They are most abundant on the scalp and face but absent from the palms of the hands and fingers. Sebum does, however, contribute to latent fingermark residue to varying degrees as a result of the fingertips coming into contact with other parts of the body. The composition of sebum is highly complex and highly variable between individuals. Sebum, together with epidermal lipids, contribute to skin surface lipids which have been extensively studied due to the ease with which samples can be collected. Fatty acids, squalene, wax esters and triglycerides are the major components of sebum (Downing and Strauss, 1974; Downing et al., 1977). Sebaceous

glands are stimulated by androgens and as such their activity varies with age, affecting the skin surface lipid composition as a consequence. Sebum composition is also affected by pathological conditions (e.g. acne), environmental conditions (e.g. temperature and ultraviolet (UV) irradiation) and microbial colonisation.

Free fatty acids can make up between 16-33% of skin surface lipids and arise from both sebum and epidermal lipids. Palmitic acid (hexadecanoic, C16:0) is the most abundant, followed by palmitoleic acid (*cis*-9-hexadecenoic, C16:1) and oleic acid (*cis*-9-octadecenoic, C18:1). Myristic (tetradecanoic, C14:0), stearic (octadecanoic, C18:0) and linoleic (*cis*-9,12-octadecadienoic, C18:2) acids are also abundant (Nicolaides, 1974; Boniforti et al., 1973; Nazzaro-Porro et al., 1979). Wax esters make up 20-27% of skin surface lipids and are produced exclusively by the sebaceous glands, as well as squalene (2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexaene), a cholesterol intermediate forming 10-15% of skin surface lipids. Sterols and sterol esters are also found in skin surface lipids, predominantly arising from the epidermal lipids, with cholesterol (cholest-5-en-3β-ol, 0.7-2.4%) and cholesterol ester (2-3.3%) being the most abundant. Other organic components of skin surface residue include carboxylic acids, short-chain alcohols, aldehydes, alkane, alkenes ketones, aromatic amides, amines and heterocyclics.

The lipid composition of latent fingermarks has been well studied largely due to the ease of analysis of most components. Good correlation has been found between the lipid composition of deposited latent fingermarks and skin surface lipids. The relative composition can vary depending on variables such as amount of contact between fingertips and other parts of the body and thus the level of sebum-contamination picked up. As such inter- and intra-donor variation has been demonstrated in many studies (Archer et al., 2005; Croxton et al., 2010; Weyermann et al., 2011; Bailey et al., 2012; Emmerson et al., 2011; Ferguson et al., 2013; Dorakumbura et al. 2019; Frick & Weyermann, 2019; O'Neill et al., 2020). The substrate has been shown to affect the amount of material deposited (Weyermann et al., 2011). The method of fingermark extraction and sample preparation can also affect the quantitative data collected for different constituents (Kim et al., 2019).

2.3 Apocrine sweat

Apocrine sweat can be found in latent fingermarks as a result of contamination of the fingertips from touching axillary regions of the body (namely the armpit and genital areas) but is not usually a major constituent. Proteins, ammonia, carbohydrates, ferric ions, cholesterol and androgen steroids are the main constituents (Saga, 2002). Since the apocrine sweat glands are not active until puberty, contribution to latent fingermarks will vary with age (Robertshaw, 1991; Saga, 2002).

2.4 Skin cells and epidermal lipids

Epidermal lipids arise predominantly from stratum corneum cells and together with sebum, form the skin surface lipids as outlined above. The epidermal contribution is relatively constant for different anatomical sites, whilst that of the sebaceous glands varies due to gland density variation (Rothmann, 1954; Downing and Strauss, 1974). Epidermal lipids consist of large amounts of sterols, sterol esters, glycerides and phospholipids (Downing and Strauss, 1974; Downing et al., 1977). Epidermal lipids contribute to latent fingermarks as a consequence of the fingertips touching other parts of the body and/or migration of material from the back of the hand.

In addition to epidermal lipids, it is expected that skin cells will also be shed from the fingers and palms in addition to being picked up on the fingers during contact with other parts of the body. Skin cells are more likely to be sloughed from the fingers during contact with rough surfaces and may be more forcefully pulled from the fingertip on contact with adhesive surfaces (Jones et al., 2010). It has also been shown that the quantity of skin cells shed from the palmar region varies, with higher densities of skin cells shed from the fingertips than from the palm (Oleiwi et al., 2015).

2.5 DNA

There are multiple sources of DNA in fingermarks, the principal one being skin cells as discussed above. However it has also been shown that there also are significant quantities of cell-free nucleic acids in sweat (on average 11.5 ng of DNA in 1 mL of cell-free sweat) and these are of a suitable length for standard DNA profiling (Quinones & Daniel, 2012).

2.6 Contaminants (exogenous substances) and metabolites

In addition to the wide range of substances that occur naturally within a fingermark, there are also a countless number of substances that can be picked up on the hand through daily tasks, and also others that will be excreted as metabolites following the ingestion of other substances. Although the balance of natural substances present in a fingermark will vary according to factors such as diet, physical exertion, time of day etc., exogenous substances and metabolites have greater potential to provide additional contextual information about the donor.

Figure 2 shows a series of images of fingertips with different types of contaminant present.
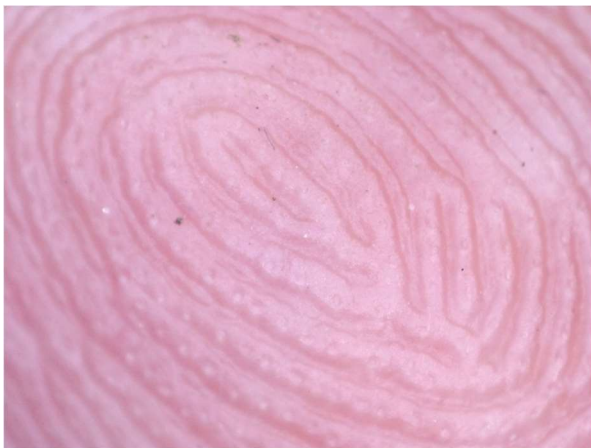
a)   b)

c)   d)

Figure 2. Micrographs (x10) of a fingertip, a) clean fingertip, b) contaminated with traces of blood, c) residues from peeling an orange, and d) residues from eating corn chips

The examples given above are only some of the materials that may be found and providing an exhaustive list is not possible here. Blood is probably the most significant contaminant that may be encountered in a fingermark at a crime scene. Some of the other significant contaminants and metabolites that have been detected within fingermarks by different research groups, using a wide range of analytical techniques, are summarised in Tables 2-4 below.

Table 2: Summary of drugs, pharmaceutical and illicit, and their metabolites that have been detected within fingermarks

Drugs [metabolites]	Reference
Amphetamines: Amphetamine, methamphetamine, 3,4-methylenedioxyamphetamine, 3,4-methyl enedioxymethamphetamine(Ecstasy);	Day et al. (2004a); Day et al. (2004b); Szynkowska et al. (2009); West & Went (2009); Szynkowska et al. (2010); Clemons et al. (2013); Groeneveld et al. (2015); Muramoto et al. (2015); Skriba & Havlicek (2018); Souza et al. (2018); Hudson et al. (2019)
Aspirin	Day et al. (2004a); Day et al. (2004b); West & Went (2008); Ng et al. (2009); Banas et al. (2012); Banas et al. (2014); Sundar & Rowell (2014); Sundar & Rowell (2015)
Barbital	Day et al. (2004a); Day et al. (2004b);
Benzodiazepines: Diazepam, flunitrazepam, lorazepam [3-*O*-glucuronide], nitrazepam	Day et al. (2004a); Day et al. (2004b); Goucher et al. (2009); Ng et al. (2009); Moule et al. (2017)
Caffeine [paraxanthine. theobromine, theophylline]	Day et al. (2004a); Day et al. (2004b); West & Went (2008); Ng et al. (2009); Bradshaw et al. (2012); Clemons et al. (2013); Kuwayama et al. (2013); Sundar & Rowell (2014); Sundar & Rowell (2015); Watkinson (2018)

Chlorpheniramine	Kuwayama et al. (2014)
Cocaine [benzoylecgonine, methylecgonine, ecgonine methyl ester, norcocaine]	Day et al. (2004a); Day et al. (2004b); Hazarika et al. (2008); Ng et al. (2009); West & Went (2009); Hazarika et al. (2010); Clemons et al. (2013); Li et al. (2013); Bradshaw & Francese (2014b); Sundar & Rowell (2014); Bailey et al. (2015); Groeneveld et al. (2015); Muramoto et al. (2015); Sundar & Rowell (2015); van der Heide et al. (2015); Yang et al. (2015); Bradshaw et al. (2017); Costa et al. (2017); Ismail (2018); Lauzon and Chaurand (2018); Skriba & Havlicek (2018); Costa et al. (2019b); Fowble and Musah (2019); Hudson et al. (2019)
4-hydroxybutanoic acid (GHB)	West & Went (2008); Ricci & Kazarian (2010)
Ibuprofen	Grant et al. (2005); Ricci et al. (2006); West & Went (2008); Kuwayama et al. (2014)
Ketamine	West & Went (2009)
Mephedrone [nor-mephedrone]	Czerwinska et al. (2020)
Nicotine [cotinine]	Leggett et al. (2007); Hazarika et al. (2009); Benton et al. (2010a); Benton et al. (2010b); Boddis & Russell (2011); Lim et al. (2013); Groeneveld et al. (2015); Yang et al. (2015)
Opiates: Codeine, dihydrocodeine, heroin (diacetylmorphine) [morphine, 6-monoacetylmorphine], methadone [2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP)], noscapine	Day et al. (2004a); Day et al. (2004b); Ricci et al. (2006); Hazarika et al. (2008); Jacob et al. (2008); West & Went (2008); Rowell et al. (2009); Hazarika et al. (2010); Lim et al. (2013); Kuwayama et al. (2014); Sundar & Rowell (2014); Groeneveld et al. (2015); Muramoto et al. (2015); Sundar & Rowell (2015); Bailey et al. (2016); Ismail (2018); Lauzon & Chaurand (2018); Skriba & Havlicek (2018); Hudson et al. (2019)
Paracetamol	Day et al. (2004a); Day et al. (2004b); Ricci et al. (2006); West & Went (2008); Ng et al. (2009); Sundar & Rowell (2014); Sundar & Rowell (2015)
Procaine	Kaplan-Sandquist et al. (2014); Kaplan-Sandquist et al. (2015)
Quetiapine (antipsychotic drug)	Costa et al. (2019)
Sympathomimetics: Methylephedrine [ephedrine], pseudoephedrine	Kaplan-Sandquist et al. (2014); Kuwayama et al. (2014); Kaplan-Sandquist et al. (2015); Fowble and Musah (2019)
Terbinafine (antifungal drug)	Lim and Seviour (2012)
9-Tetrahydrocannabinol (THC) [11-nor-9-carboxy-Δ⁹-tetrahydrocannabinol , tetrahydrocannabinolic acid]	Hazarika et al. (2008); Ifa et al. (2008); Groeneveld et al. (2015); Lauzon and Chaurand (2018); Hudson et al. (2019)

Verapamil	Yagnik et al. (2013)

Table 3: Summary of cosmetic and personal products that have been detected within fingermarks

Cosmetic/personal product or constituent	Reference
Bug spray	Hinners et al. (2018)
Condom lubricants	Bradshaw et al. (2011, 2012, 2013a), Mirabelli et al. (2013)
Cosmetics e.g. foundation	Ricci & Kazarian (2010)
Cosmetic products e.g. face cream, hand/body lotion, body butter, serum cream and their constituents (e.g. dimethylbenzylammonium and dimethyldioctadecylammonium ions)	Hartzell-Baguley et al. (2007); Wolstenholme et al. (2009); Ricci & Kazarian (2010); Bradshaw et al. (2013b); Lauzon & Chaurand (2018); Yang et al. (2019)
Hand sanitisers, antibacterial wipes/detergents	Bradshaw et al. (2011); Bradshaw et al. (2013b); Bradshaw & Francese (2014b); Bradshaw et al. (2017), Chadwick et al. (2017)
Hair products	Wolstenholme et al. (2009); Bradshaw et al. (2013b)
Sunscreen	Hartzell-Baguley et al. (2007); Hinners et al. (2018); Zheng et al. (2019)

Table 4: Summary of explosive and gunshot residue traces that have been detected within fingermarks

Explosive / Gunshot residue trace	Reference
Ammonium nitrate	Emmons et al. (2009); Mou and Rabalais (2009); Ng et al. (2009); Tripathi et al. (2011); Fernandez de la Ossa et al. (2014)
C4	Emmons et al. (2009); Banas et al. (2014)
Chlorate and perchlorate	Gilchrist et al. (2012); Love et al. (2013)
DNT (2,4-dinitrotoluene)	Abedlhamid et al. (2011); Lucena et al. (2013); Malka et al. (2013)
Gunshot residues e.g. barium, cyanate, lead, nitrite, nitrate, strontium	Szynkowska et al. (2010) ; Gilchrist et al. (2012); Love et al. (2013); Pluháček et al. (2018)
HMX (cyclotetramethylene-tetranitramine (High Melting eXplosive))	Emmons et al. (2009); Tripathi et al. (2011); Rowell et al. (2012)

MNT (mononitrotoluene)	Abedlhamid et al. (2011)
Nitroglycerin (TNG)	Rowell et al. (2012)
PETN (pentaerythritol tetranitrate)	Emmons et al. (2009); Ng et al. (2009); Tripathi et al. (2011); Banas et al. (2012); Rowell et al. (2012); King et al. (2013); Lucena et al. (2013); Banas et al. (2014);
Potassium nitrate	Malka et al. (2013); Figueroa et al. (2017)
Pyrodex	Gilchrist et al. (2012); Love et al. (2013); Gallidabino et al. (2019)
RDX (1,3,5-trinitro-1,3,5-triazine (Royal Demolition eXplosive)	Ifa et al. (2008); Chen et al. (2009); Emmons et al. (2009); Tripathi et al. (2011); Banas et al. (2012); Rowell et al. (2012); King et al. (2013); Lucena et al. (2013); Kaplan-Sandquist et al. (2014); Kaplan-Sandquist et al. (2015); Fowble and Musah (2019)
TATP (triacetone triperoxide)	Rowell et al. (2012)
Tetryl (*N*-methyl-*N*-(2,4,6-trinitrophenyl)nitroaniline)	Rowell et al. (2012)
Trinitrobenzene	Mou and Rabalais (2009)
TNT (2,4,6-Trinitrotoluene)	Mou and Rabalais (2009); Abedlhamid et al. (2011); Banas et al. (2012); Rowell et al. (2012); King et al. (2013); Lucena et al. (2013); Banas et al. (2014); Kaplan-Sandquist et al. (2014); Kaplan-Sandquist et al. (2015)

3. POST-DEPOSITION CHANGES IN FINGERMARK CHEMISTRY

The previous sections describe the composition of the material that is deposited in the fingermark at the point of initial contact. It is recognised that this composition will almost immediately begin to change. Interactions between the fingermark, the environment and the surface occur over the period of time between deposition and recovery through a series of interactions that can be defined by the 'Triangle of Interaction' (Baniuk,1990; Sears et al., 2012). As a consequence, it is likely that several of the compounds initially deposited in the fingermark, depending on how chemically labile and susceptible they are, will no longer be present by the time the item it has been deposited on is treated in a laboratory.

Several studies have explored the influence of different environmental factors (light, ultraviolet radiation, heat, humidity and time) on the changes in the chemical composition of a fingermark, and some have proceeded to investigate the impact of those chemical changes on its subsequent

development. Although research has been conducted into the effect of more extreme environments such as chemical decontamination (Wilkinson, 2005; Zuidberg et al., 2014), elevated temperatures (Richmond-Aylor et al., 2007) and exposure to ionising radiation (Hoile et al., 2010), those studies examining variables across ranges typical of a specific ambient environment are most relevant for the vast majority of situations encountered in casework.

A summary of published research into compositional changes during fingermark ageing was produced by Cadd et. al (2015), and there have been several subsequent publications that build on knowledge in this area. The changes in the sebaceous constituents of fingermarks appear to have received more attention (Olsen, 1987; Wolstenholme et al., 2009; Weyermann et al., 2011; Fritz et al.., 2013; Girod et al., 2015; Muramoto et al., 2015; Frick et al., 2016; Reed et al.., 2016; Szaboova et al., 2017; O'Neill & Lee, 2018; Kim et al., 2020; Dorakumbura et al., 2020), possibly because these have been shown to be more affected by environmental exposure. These constituents also ionise easily, facilitating their analysis by mass spectrometry. Olsen (1987) found that exposing fingermarks to temperatures above ambient and observing the corresponding thin layer chromatograms indicated that free fatty acids, cholesterol and squalene decreased to levels below their limits of detection over the period of hours/days in that order. Several other researchers have observed a decrease in the level of squalene, which is initially abundant in sebaceous sweat. Archer et al. (2005) observed that loss of squalene was more rapid when fingermarks were exposed to light compared to storage in the dark, suggesting a photodegradation mechanism. In a subsequent study Mountfort et al. (2007) proposed a progressive oxidation process from the squalene, squalene epoxide and squalene monohydroperoxide present at the time of deposition to the final product squalene pentahydroperoxide, with squalene found to be absent after 7 days.

Ultraviolet radiation has been observed to have a greater impact on certain fingermark constituents than visible light. It has been shown (Dennis & Shibamoto, 1989; Yeo & Sibamoto, 1992) that squalene will decompose to formaldehyde and malonadehyde on exposure to ultraviolet radiation and that this degradation is more rapid for shorter wavelengths. Goode et. al (1979) observed that exposure to ultraviolet radiation was detrimental to subsequent fingermark visualisation using radioactive bromine and this may be associated with a ultraviolet-induced breakdown of squalene, thought to be the principal target for this process. This was consistent with previous observations by Gray (1978) indicating ultraviolet radiation had most impact on unsaturated compounds and had a detrimental effect on their development using iodine fuming.

On the whole eccrine constituents appear less affected by light or ultraviolet radiation although it has been found (De Paouli et al., 2010) that lactic acid can degrade by a photochemical reaction when exposed to artificial sunlight. Urea and amino acids were found to be unaffected by the same exposure conditions.

Cuthbertson & Morris (1972) monitored changes in the concentration of urea and chloride in fingermarks over a period of approximately 8 months. They found that although the chloride concentration appeared to be constant over this period, there did seem to be a significant reduction in urea.

4. UTILISATION OF CHEMICAL CHANGES IN FINGERMARKS FOR DATING PURPOSES

It has been proposed by several groups of researchers that the changes that occur in fingermark chemistry over time may be useful in establishing a timeline for its deposition.

The focus of these studies has primarily been the sebaceous constituents of fingermarks, although in operational casework these would generally be expected to be less abundant than eccrine sweat. Weyermann et al. (2011) used GC-MS to consider whether the use of squalene/cholesterol ratios within fingermarks could be used as a potential means of dating and this approach was subsequently refined further using the same technique by Koenig et al. (2011) with the addition of the wax ester content into the calculations. Szaboova et al. (2017) employed GC-MS to also propose the use of squalene content, in this case in a ratio with pentadecanoic acid, as a means of dating fingermarks. Girod et al. (2016) adopted a more holistic approach using principal component analysis on the lipid fraction in the fingermark but ultimately concluded that other factors such as substrate and intra-donor variability had a significant effect on results and made accurate dating by this method difficult.

Other researchers (Muramoto et al., 2015) employed Secondary Ion Mass Spectrometry (SIMS) imaging and used the rate of diffusion of sebaceous constituents on a silicon water surface to give an approximate time since deposition. However, later results obtained by O'Neill et al. (2018) using Matrix Assisted Laser Desorption Ionisation Mass Spectrometry Imaging (MALDI MSI) showed a strong influence of the substrate on diffusion rates, making the use of such models problematic.

Wolstenholme et al. (2009) were the first authors to employ MALDI in Profiling and Imaging modes (MALDI MSP and MALDI MSI) to closely monitor oleic acid and its degradation products. Here, the intention was to pinpoint age on the basis of the relative abundance changes of inter-relating species. MALDI MSI has also been used to visualise the reaction products formed between atmospheric ozone and the triglycerides in sebaceous sweat directly on the ridge pattern (Pleik et al. 2018, Hinners et al. 2020). It has been suggested that characteristic reaction products are formed that can be tracked over time and seem relatively independent of fingermark donor across the small pool of donors tested to date.

A review of chemical mass spectrometry imaging methods for fingermark imaging has recently been conducted by Francese and Bradshaw (2020). This highlights the challenge and complexity of age determination studies; it is extremely difficult to address all the interrelated factors influencing the correct determination/prediction of the age of a mark in a single study. In addition, the use of groomed (sebum-rich) fingermarks in many such studies is an unrealistic representation of crime scene marks and does not provide a true evaluation of method sensitivity.

The eccrine constituents of fingermarks have also been evaluated for dating purposes. It has been proposed (van Dam et al., 2014; van Dam et al., 2016) that the fluorescence of the amino acid tryptophan and its progressive breakdown to its fluorescent derivatives indoleacetic acid, harman, norharman and xanthurenic acid can be used as a means of estimating time since deposition. All of these substances have slightly different emission and absorption spectra. As tryptophan breaks down and the ratio between the original amino acid and its derivatives changes there is a shift in the position of the combined fluorescence emission peak and the authors propose this can be related to the age of the fingermark.

Following from the first fingermark protein maps generated by Ferguson et al. (2012) and Patel et al. (2015), via non-destructive MALDI MS based approaches, a destructive proteomic approach to fingermark dating had been explored by Oonk et al. (2018) via Liquid Chromatography tandem Mass Spectrometry. These authors investigated whether any of the proteins identified exhibited a response to ongoing environmental exposure that could be used in fingermark age estimation. It was proposed that dermcidin (the abundance of which decreased over time) and four keratin proteins (the abundance of which increased with time) offered potential for development of an ageing model. However, validation of any such model necessitates use of natural marks, multiple donors, a range of environmental conditions and surfaces of deposition individually and in combination.

Another chemical change that is being evaluated for dating purposes is racemisation of amino acids (van Helmond et al., 2020). In this approach the progressive, naturally occurring conversion of the L-stereoisomer of the amino acid into the D-stereoisomer was explored for a series of amino acids (histidine, serine, threonine, alanine, proline, methionine and valine). Of these, the D/L-serine ratio appeared to exhibit a potentially significant change over time although it is recognised that the effect of many other environmental factors that may affect results such as pH and temperature would need further study.

The corresponding physical changes that occur in fingermarks during ageing have been studied by several researchers (Thomas & Reynoldson, 1975; Moret et al., 2015; Dorakumbura et al., 2016; De Alcarez-Fossoul et al., 2018.) and in some cases have been proposed as aids to fingermark dating although more detailed consideration of this is beyond the scope of this review.

5. UTILISATION OF FINGERMARK CHEMISTRY IN MARK ENHANCEMENT

5.1 Eccrine sweat

Because eccrine glands are the only glands present on the surface of the palm and the fingers, it is anticipated that the major component of any latent mark will be eccrine sweat. As a consequence, the majority of processes in widespread use tend to utilise the chemicals found in this component. The ways in which some of the principal constituents of eccrine sweat have been utilised in fingermark enhancement are outlined below.

5.1.1 Water

Water is the principal solvent for the other chemicals found within eccrine sweat. Although eccrine sweat contains 98% water, the content deposited in a latent fingermark has been a subject of recent debate with Kent (2016) suggesting it may be as low as 20% and subsequent studies (Keisar et al., 2019) indicating that a range of 20-70% is realistic.

Water is utilised by fingermark visualisation processes in a variety of ways. It is one of the substances that promotes adhesion of particles to the fingermark during the application of powders, and the effectiveness of many powders will decrease as the mark dries out and water is lost. For this reason, the practice of 'huffing' (re-humidifying the fingermark with warm, humid air) is sometimes used to increase fingermark recovery when powdering older marks (Montgomery et al., 2012).

Water is also essential to achieving optimum results using the cyanoacrylate (superglue) fuming process. Water can act as a weak base to initiate polymerisation of cyanoacrylate monomer vapour to form polycyanoacrylate on the fingermark ridges. Lewis et al. (2001) demonstrated that cyanoacrylate fuming of older, eccrine marks where water content had been lost by evaporation resulted in lower quality fingermarks. Many commercial fuming chambers incorporate a humification stage to re-introduce water to the fingermark ridges prior to fuming. Paine et al. (2011) demonstrated that a humidity range of between 75 and 90% was required for optimum enhancement of both eccrine and sebaceous marks. It was also seen that the humidity level used influenced the morphology of the polycyanoacrylate deposit formed. Alternative approaches such as pre-treatment with acetic acid, ammonia (Wargacki et al., 2008) and methylamine (McLaren et al., 2010) have been proposed to improve the quality of developed marks in situations where deposits have dried out and water has been lost.

Water has been shown to enhance the results obtained from iodine fuming (Almog, Sasson & Anati, 1979). Almog proposed two interaction mechanisms that may bind the iodine into the fingermark, a dipole-induced dipole interaction between iodine and water molecules, and the partial transfer of electrons from the water (Lewis base) to the iodine (Lewis acid) to produce a loosely bound charge transfer complex. The loss of water, as marks dry out, may be a contributing factor to the reduction observed in the effectiveness of iodine fuming in the development of fingermarks more than a few days old (Goode & Morris, 1983).

5.1.2 Amino acids

Amino acids are the most abundant constituents of eccrine sweat. They are also the most important chemical target for development of fingermarks on porous surfaces such as paper. Because amino acids are larger molecules than urea and sodium chloride and can also interact with the cellulose chains in the substrate (Spindler et al., 2011; Spindler et al., 2015), they do not generally migrate from the site of initial deposition unless exposed to high humidity or fully immersed in water. Fingermarks on paper can therefore be detected using amino acid reagents many years after deposition unless exposed to such adverse conditions (Bleay et al., 2019).

A wide range of amino acid reagents have been used for fingermark visualisation, some adapted from existing colorimetric tests and others synthesised specifically for fingermark applications. The first reagent proposed for fingermark development was ninhydrin (Oden & von Hofsten, 1954). The reaction of ninhydrin with a range of amine-containing substances to form the characteristic Ruhemann's Purple product had been noted as early as 1910 (Ruhemann, 1910). Oden and von Hofsten recognised that there were sufficient amino acids in fingermarks to make ninhydrin useful for fingermark visualisation. The initial formulation has been subsequently refined to increase sensitivity and reduce flammability (Morris et al., 1973) and to minimise the impact on other forensic analyses such as document examination. The reaction mechanism between amino acids and ninhydrin has been extensively studied, for example by Joullié et al. (1991), and in most cases is expected to proceed to the characteristic purple reaction product. However, the reaction rate may vary for different amino acids and in some cases the reaction may stop at different coloured intermediate compounds. The reaction rate (and the effectiveness of the process for fingermark development) can be accelerated by the addition of a controlled amount of water and elevated

temperature (Linde, 1975). Humidified ovens are generally used for development to provide these conditions in a controlled manner.

A range of other amino acid reagents have been considered for fingermark development with the objective of improving on the sensitivity achieved with ninhydrin. It was recognised that the use of a reagent giving a fluorescent reaction product may improve the limit of detection and the first of these compounds to be investigated were fluorescamine and *o*-phthlaldehyde (Lee & Attard, 1979). Although shown to give potential improvements in sensitivity over ninhydrin, the practicality of these reagents is limited by the use of optical brighteners in modern papers which fluoresce under the same irradiation conditions as the developed fingermark and obscure it.

The development of lasers and high intensity light sources with output in the visible region of the spectrum made the use of other fluorescent amino acid reagents feasible, including NBD chloride (4-chloro-7-nitrobenzofurazan) (Warrener et al., 1983). It was also observed that marks developed using ninhydrin could be post-treated with salts of zinc and cadmium (Lennard et al., 1987) to produce a fluorescent product and increase the number of marks detected.

Modifications of ninhydrin have been another focus of research, with many analogues produced and evaluated including 5-methylthioninhydrin (Almog et al., 1992), 5-methoxyninhydrin (Lennard et al., 1986) and benzo[f]ninhydrin (Almog et al., 2000). Of all of these analogues, 5-methylthioninhydrin (5MTN) has proved most useful.

The introduction of 1,8-diazafluoren-9-one (DFO) in the early 1990s (Grigg et al., 1990) provided an amino acid reagent that was both more sensitive than ninhydrin and also provided a fluorescent reaction product. DFO became recognised as the most effective amino acid reagent for fingermark visualisation until 1,2-indandione was later proposed for this purpose (Hauze et al., 1998). The results initially obtained using 1,2-indandione were variable, but the incorporation of zinc chloride into the formulation produced a reaction that was more consistent (Spindler et al., 2009) and it is now generally recognised that 1,2-indandione formulations with zinc chloride are the most effective amino acid reagents currently available.

Attention has also been given to 'dual action' reagents where the developed marks are both coloured and fluorescent, including genipin (Almog et al., 2004) and 5MTN with additions of zinc chloride (Almog et al., 2008). Although such reagents may have niche applications, they have been found to generally be less effective than ninhydrin in developing coloured marks, and less effective than DFO or 1,2-indandione in developing fluorescent marks (Porpiglia et al., 2012).

It should also be noted that the reagent 4-dimethylaminocinnemaldehyde (DMAC) also reacts with amino acids when applied to fingermarks as a vapour (Brennan et al., 1995) and this has been proposed as a method for development of fingermarks on thermal papers without removing the text.

The reaction between the amino acid and the reagent produces a product that is either coloured (e.g. ninhydrin), fluorescent (e.g. DFO, 1,2 indandione), or both (e.g. genipin, 5-MTN). In some cases the reaction product may be independent of the amino acid contributing to the reaction (e.g. the Ruhemann's purple for ninhydrin) and in others the reaction product retains some character of the

individual amino acid (e.g. genipin). Of all of the reagents investigated the most widely used are ninhydrin, 1,2 indandione and DFO.

The application of a single amino acid reagent does not result in exhaustion of all amino acids present. Several studies (Salama et al., 2007; McMullen & Beaudoin, 2013; Marriott et al., 2014; and Bleay et al., 2019) and operational experience have demonstrated that sequential use of amino acid reagents (ninhydrin after DFO or 1,2 indandione) will develop additional marks. The progressive consumption of amino acids during sequential treatment has been studied using mass spectrometry (Mangle, Xu & de Puit, 2015) which confirms that a significant proportion of the amino acid fraction remains available for reaction if a second reagent is applied.

Amino acids may also contribute to the detection of latent fingermarks by fluorescence examination. Some naturally occurring amino acids in eccrine sweat (tyrosine, tryptophan and phenylalanine) are fluorescent (Teale & Webber, 1957) and this may enable fingermarks to be detected during examination with high intensity light sources. However, the fluorescence contribution from amino acids is likely to be low in comparison with other contaminants that may be present. The potential use of the change in fluorescence spectra associated with progressive degradation of tryptophan as a method to date fingermarks has already been discussed in this review.

Finally, it has been suggested (Wargacki et al., 2007) that the carboxylate functional group of the amino acid alanine may be another contributor to the initiation of cyanoacrylate polymerisation in the superglue fuming process.

5.1.3 Urea

Urea is relatively abundant in eccrine sweat but there have been few development techniques that have utilised it. A formulation of DMAC in solution (Goode & Morris, 1983) produced fingermark development without the need for heating. The reaction between DMAC and urea in an acidic environment formed a magenta-coloured Schiff base. The process was relatively quick and did not require specialist equipment such as ovens, but operationally DMAC was ineffective because many marks developed on older exhibits were diffuse without clear ridge detail. The small size of the urea molecule means that it can migrate more easily from the point of deposition, contributing to this issue. The process is no longer used.

5.1.4 Sodium chloride

The sodium chloride content of fingermarks can be utilised for their development by using the silver nitrate process. When sodium chloride is exposed to a solution of silver nitrate, a reaction can occur between the chloride constituent and silver nitrate to form insoluble silver chloride. Silver chloride is a light sensitive compound and on subsequent exposure to light the silver is reduced to its metallic form, darkening the fingermark sufficiently for it to be seen.

Cuthbertson (1969) used the silver nitrate process extensively in studies of the chloride content in latent fingermarks and it is still occasionally used in casework. The main limitation is that chloride ions are small and relatively mobile, and rapid diffusion of ridge detail can occur on exposure to high humidity environments.

Sodium chloride in fingermarks may also act as an initiator of corrosion on certain metal surfaces and several methods have been proposed that visualise fingermarks by detecting the corrosion signatures that they have produced (Williams et al., 2001; Bond, 2008; Wightman & O'Connor, 2011).

The sodium and potassium ions present in eccrine sweat have also been successfully used as a means of visualising fingermarks on both porous and non-porous surfaces (Bailey et al., 2010; Bailey et al., 2013). Secondary Ion Mass Spectrometry (SIMS) has a spot size of < 1 μm, providing high resolution images of fingermarks sufficient to reveal the pore structure. The technique has been reported to image fingermarks deposited on paper, metal and plastic surfaces before or after development with cyanoacrylate (Bailey et al., 2013). A high resolution map of potassium ion distribution obtained by SIMS is shown in Figure 3.

Figure 3. Chemical Imaging of a fingermark: Time of Flight (TOF) SIMS image of potassium (K^+) in a fingerprint deposited on brass, showing third level detail.

5.1.5 Sodium lactate

Studies conducted by Wargacki et al. (2007) indicated that the lactate in constituent of fingermarks was another initiator of the polymerisation reaction during cyanoacrylate fuming and that ultraviolet degradation of lactate may contribute to the drop in effectiveness of this process on older fingermarks (Wargacki et al., 2008)

5.1.6 Proteins and peptides

In 2009 Drapel et al. demonstrated the feasibility of detecting keratin 1, keratin 10 and cathepsin-D in eccrine sweat using antibody tests but this has not subsequently resulted in practical methods. An immunolabelling method using tagged antibodies has also been developed as a developer targeting dermicidin, (van Dam et al., 2013a, 2013b) and this is closer to practical implementation. The distribution of dermicidin in fingermarks can also be mapped directly using analytical techniques such as MALDI MSI (Francese, 2015), as illustrated in Figure 1.

Although it has been shown that there are diverse methods that target different eccrine sweat constituents for fingermark enhancement, there are still many constituents of eccrine sweat (e.g. the carboxylic acid functionality of amino acids, vitamins and lactic, uric and pyruvic acids) that are not specifically utilised. However, such substances are typically less abundant and less stable, hence there may be limited benefit in basing novel development reagents on them.

5.2 Sebaceous secretions

Although expected to be less abundant than the eccrine component, there will generally be some sebaceous material present in fingermarks and several reagents have been employed to react with constituents of sebum.

The first reagent proposed primarily for reaction with the fats in fingermarks was osmium tetroxide (Mitchell, 1920) which reacts across the unsaturated carbon double bonds present in several of the compounds present. However, the toxicity of this reagent means that it is no longer considered for operational use.

5.2.1 Squalene

Squalene is one of the most abundant sebum constituents, although it is lost relatively quickly from the fingermark. It is thought to be one of the principal targets for the iodine fuming process, and the rapid loss of squalene is another reason proposed for the poorer performance of iodine fuming on older fingermarks. One mode of interaction may be a reaction across the double bonds (Popolan-Vaida et al., 2014) but this may not account for the intense brown colour observed when spots of squalene are exposed to iodine vapour and simple absorption of iodine into the fats may also be a factor. Oil Red O has also been shown to strongly stain squalene (Salama et al., 2007).

5.2.2 Cholesterol

Cholesterol is another sebaceous constituent that is heavily stained by Oil Red O (Salama et al., 2007) and has also been shown to be strongly stained by basic violet 3 and basic violet 2 (Garrett & Bleay, 2013). In the case of basic violet 3 and basic violet 2 the stained cholesterol test spots also exhibited strong fluorescence.

5.2.3 Fatty acids

The range of fatty acids present in sebum have been shown to vary in their interactions with the reagents used for fingermark enhancement. Salama et al. (2007) found that Oil Red O produced strong staining on palmitic, stearic, and to a lesser extent myristic acids, but did not significantly stain palmitoleic or oleic acids. Garrett & Bleay (2013) observed strong staining of hexanoic acid by an ethanol-based solvent black 3 formulation, and of decanoic, dodecanoic, eicosanoic acids by a 1-methoxy-2-propanol-based solvent black 3 formulation. Basic violet 3 was seen to strongly stain docosanoic acid (Garrett & Bleay, 2013).

Oleic acid has also been proposed as a substance that can be used in printing a test strip for quality control testing of the physical developer process (Kupferschmid et al., 2010).

5.2.4 Triglycerides

Some of the triglycerides present in fingermarks may also be stained by fingermark reagents. These include staining of tristearin by Oil Red O (Salama et al., 2007) and glyceryl tripalmitate and glyceryl tristearate by basic violet 3.

Other sebaceous substances exhibiting strong interactions with fingermark reagents include cholesterol palmitate (Salama et al., 2007), stained by Oil Red O, cholesteryl acetate (Garrett & Bleay, 2013), stained by solvent black 3 and giving strong fluorescence with basic violet 3, and cholesteryl benzoate (Garrett & Bleay, 2013) which gave strong fluorescence with basic violet 3.

5.2.5 Mass Spectrometry Imaging of sebaceous constituents

The compounds found in sebaceous secretions can also be effectively used to produce images of fingermarks when chemical imaging by mass spectrometry is employed. Desorption Electrospray Ionisation Mass Spectrometry Imaging (DESI MSI) was the first technique to be used to generate molecular maps of sebaceous constituents (Ifa et al., 2008); MALDI MSI has subsequently been used to generate fingermark images of fatty acids, diacyl and triacylglycerols at sufficient spatial resolution (up to 100*100 μm) for *minutiae* to be observed (Wolstenhome et al., 2009; Ferguson et al., 2013), though cutting edge instrumentation can image a mark with much higher lateral resolution (10* 10 μm). Similarly, the literature reports the use of silver-assisted LDI (AgLDI) Imaging to generate fingermark images at similar resolutions (Lauzon et al.,2017).

Figure 4 presents an example of fingermark images generated by DESI, MALDI, and AgLDI MS Imaging.

MALDI MS used in imaging mode has been a particularly prolific technique in generating images of lipids and a non-exhaustive list is reported in Bailey et al. (2012) and Ferguson et al. (2013). In addition, Ferguson et al. (2013) report that the application of the dry-wet method of matrix deposition greatly improves the ridge pattern clarity continuity when generating lipid molecular images.
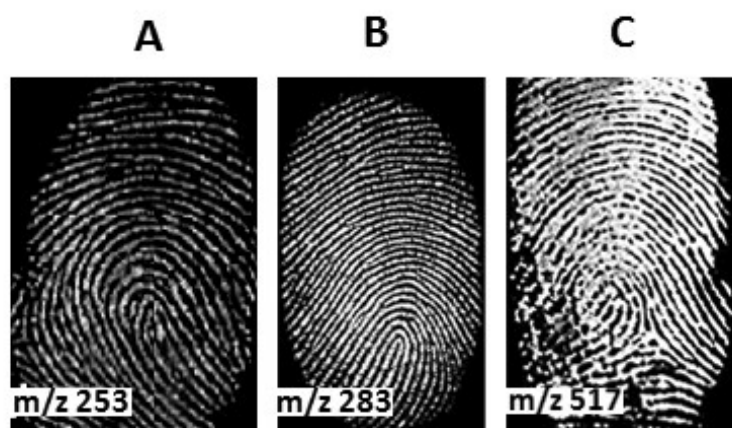

Figure 4 Chemical Imaging of fingermarks by mass spectrometry. (A) DESI MS image of cis-hexadecanenoic acid (m/z 253) from a groomed fingermark on glass (Ifa et al. Science 2008); (B) MALDI MS image of oleic acid (m/z 283) on an aluminium slide (Ferguson et al. 2013); (C) AgLDI image of squalene (m/z 517), in a latent fingermark on a lifting tape after dusting with green fluorescent powder and silver sputtering (Lauzon et al., 2017). Panel A is from Ifa et al. (2008), with permission from The American Association for the Advancement of Science; panel B is adapted from Ferguson et al. (2013) Journal of Mass Spectrometry with permission from John Wiley and Sons; panel C is adapted from and Lauzon et al. (2017) with permission from John Wiley and Sons .

5.3 Sebaceous and eccrine emulsions

There remain some fingermark development processes for which the mechanism of deposition is not fully understood, and combinations of eccrine and sebaceous constituents may be required for development to occur. The most researched of these processes is physical developer, the most effective process that can be used on porous surfaces that have been wetted. The most comprehensive studies into the constituents targeted by physical developer have been conducted by de la Hunty et al. (2015a, 2015b). These demonstrated that, when spots of sebaceous constituents (fatty acids, cholesterol and squalene) were treated with physical developer, only cholesterol was found to promote deposition of silver. However, when natural marks were treated with reagents containing solvents that dissolve fats, physical developer stopped working. It was shown that physical developer could selectively deposit at positions associated with the position of eccrine pores but did not develop purely eccrine fingermarks, possibly because of the water-based solutions used dissolving these constituents. A synergistic effect between eccrine and sebaceous constituents was proposed with a protective layer of non-water soluble material protecting eccrine constituents that promote deposition of silver from solution.

It is possible that a similar combination of sebaceous and eccrine material may be required for optimum performance of the powder suspensions process (Downham et al., 2017). Atherton (2013) used a number of analytical techniques (GC-MS, IC and FT-IR spectroscopy) to determine the amount of select eccrine (amino acids, inorganic ions) and sebaceous (fatty acids, squalene) constituents in latent fingermarks and whether there was any correlation with the quality of powder suspension development. However, no correlation was found for the constituents studied.

In some cases, the chemistry of the fingermark deposit is not necessarily important, but the fact that it differs from the substrate it has been placed upon is. The most significant process that works in this way is vacuum metal deposition, where it has been shown that the nucleation of the metal clusters that delineate the fingermark is controlled by surface characteristics. Monolayers of fatty constituents present on the surface in fingermarks can be detected by this method (Thomas, 1978) but eccrine constituents will also affect nucleation characteristics. The ability of vacuum metal deposition to detect a broad range of chemically different contaminants was demonstrated by Gaskell et al. (2013).

5.4 Ingested substances and metabolites

Although several studies of fingermark composition have shown that several metabolites can be detected by various analytical techniques, they have been under-utilised as a means of visualising fingermarks. A notable exception to this has been the work of Leggett et al. (2007) and Hazarika et al. (2009). Hazarika et al. used magnetic particles functionalised with anti-cotinine antibody and a fluorescent marker to selectively develop the fingermarks of smokers. The magnetic powders were applied in a standard powdering process and became bound to the cotinine antigen present in sweat. The process was capable of distinguishing between the fingermarks of smokers and non-

smokers but the development was confined to the regions immediately around the eccrine pores and would not be a feasible method for developing continuous ridge detail.

In the following years, mass spectrometry proved to be a better approach for detecting and mapping metabolites in fingermarks due to both higher sensitivity and the opportunity to use an untargeted approach which does not require *a priori* knowledge of the molecular target (which is otherwise necessary for the selection of the appropriate antibody). In mass spectrometry, this application, detection and mapping of metabolites is again less likely to produce full images of fingermarks because these constituents tend to be concentrated around eccrine gland openings resulting in 'dotty', discontinuous ridges (unlike the more uniform distribution observed for sebaceous constituents). However, redistribution of such constituents may occur during contact (e.g. with the face) enabling continuous ridges to be imaged. Analysis of these species is more likely to generate contextual information about donor lifestyle (e.g. medication and diet).

In 2008-2009, the group of Jickells et al. (Jacob et al., 2008; Goucher et al., 2009) found that the prescription medications lorazepam and methadone, alongside their metabolites, could be detected in fingerprints using liquid chromatography mass spectrometry (LC-MS). The authors used creatinine normalisation to account for differences in biomass deposition, and the elimination profile of lorazepam could be observed through a pooled sample corresponding to set of fingerprints. Whilst the LC-MS approach provides excellent selectivity, a limitation is the destructive nature of the analysis and lack of spatial information.

In 2012 Bradshaw, Rao et al. demonstrated the ability to detect and map caffeine in a fingermark from a donor that had drunk coffee within 30 minutes prior to fingermark deposition, by using MALDI MSI. Caffeine was detected both intact and as fragments at m/z 195.1 and 138.0 respectively. This compound can be excreted in urine and in larger part in sweat (Kovacs et al. 1998), or metabolised into paraxantine, theophylline and theobromine. Whilst these metabolites were not detected in that instance, caffeine was truly an excretion product due to the study design which prevented any caffeine contamination of the fingertips. Subsequently, metabolites of caffeine have been observed in fingerprint residues using chromatographic approaches (Kuwayama et al., 2013; Watkinson, 2018) and have been found to relate to ingestion of caffeine.

Groeneveld et al. (2015) devised a MALDI base mass spectrometric method to detect and map a total of seventeen drugs of abuse and metabolites (including amphetamine, methylbenzoylecgonine (cocaine), diacetylmorphine (heroin), Δ 9-tetrahydrocannabinol (cannabis, Δ 9-THC), 3,4-methylenedioxy-methamphetamine (ecstasy, MDMA), methylenedioxyamphetamine (MDA), ecgonine methyl ester (EME), benzoylecgonine (BZE), 6-acetylmorphine (6-MAM), morphine (MOR), 11-nor-9-carboxy-THC (THCA) and methadone) demonstrating that it was possible to detect both the parent drug and the corresponding metabolites within the same analysis from mocked up fingermarks. Findings from these studies showed that it was possible to obtain molecular images of drugs and metabolites in fingermarks for concentrations as little as 0.19 ng.cm^{-2} though some species exhibited a poorer ionisation efficiency and could be detected but not sufficiently to enable reconstruction of the fingermark ridge pattern.

One traditional limitation of mapping drugs or metabolites in fingermarks using mass spectrometry approaches is the time required per analysis (around 2-3 hours for a full fingermark), although advanced systems have demonstrated the potential to bring this down to 10 minutes. In 2015

Bailey, Bradshaw et al. used DESI and MALDI in a profiling mode (non-imaging analysis) to rapidly detect cocaine and metabolites in the fingermarks of a small number (n=4) of drug users in a timeframe of ~2 minutes per sample.

Costa et al. (2019b) developed a (destructive) methodology for detecting cocaine use from a whole fingermark using paper spray mass spectrometry and applied it to 239 fingermarks collected from patients attending a drug rehabilitation centre. It was possible to develop fingermark ridge detail with silver nitrate to reveal ridge details prior to mass spectrometry analysis. In general, there was good agreement between fingermark and oral fluid testing results for cocaine, with a 99% detection rate and 2.5% false positive rate. Paper spray mass spectrometry, as well as LC-MS has also been deployed for the detection of antipsychotic medications and their metabolites. The approach of Costa et al. (2019b) may be forensically useful for marks on paper recovered from scenes of crime, for example to profile a donor, or to show whether or not a donor was taking medication at the time of an offence. For the latter, more data on the elimination profile of antipsychotics is needed.

Although the detection of these metabolites in fingermarks using the reported mass spectrometry techniques is reliable, it is important to highlight that source level attribution is not enough to establish culpability or infer suspect activities. There remains the question of how metabolites (and contaminants) have ended up in someone's fingermarks. In fact, secondary transfer or environmental contamination could be alternative explanations.

To this end, Costa et al. (2017) Ismail et al. (2018), Costa et al. (2019a) and Jang et al. (2020) have explored significance of detecting cocaine and heroin in fingermarks. If hands can be washed prior to deposition of a fingermark, the detection of metabolites of drugs of abuse can be used to confirm that a drug has been used. In contrast, where hands are not washed (as in the case of crime scene fingermarks), fingermarks from drug use and drug contact could not be distinguished.

The increasing sensitivity of analytical techniques, and in particular of mass spectrometry means that caution must be taken when providing contextual information from the detection of both forensically interesting metabolites and contaminants in fingermarks.

5.5 Skin cells

The staining of epithelial cells by basic violet 3 is a long-recognised technique in histological staining, with the basic dye binding to negatively charged molecules on the surface of the cell and other materials such as polysaccharides that may be present. The fact that skin cells can be shed from the fingertip results in them being more abundant on substrates such as adhesive tapes, for which basic violet 3 is one of the recommended development processes.

There has also been an increased interest in the use of dyes for the detection of latent DNA and these have also been used to visualise the skin cells that may be shed in fingermarks (Haines et al., 2015; Kanokwongnuwut et al., 2018a; Kanokwongnuwut et al., 2018b; Kanokwongnuwut et al., 2019). In some circumstances there may be sufficient skin cells shed to be able to visualise the flow of the ridges.

5.6 Contaminants

5.6.1 Blood

As discussed above, the number of contaminants that may be present on a fingertip during deposition of a mark is limitless, but for practical purposes the one that is of most interest is blood. Certainly the detection of blood is crucial in major crimes for a number of reasons. Blood indicates that a violent event has actually occurred and blood pattern analysis helps consequently to establish the dynamics of the crime. Blood is also a source of numerous other information about the individual that has shed it. First and foremost, DNA would establish the identity of the person (if matched to an available reference) or the provenance of blood other than human. Blood groups are also recoverable and this is valuable intelligence in the absence of a DNA match to narrow down the pool of suspects. Finally, blood may host metabolites indicating the presence of drugs and medications as well as potential disease biomarkers. Such contextual information could greatly inform investigations. MALDI MS Profiling and Imaging have been proposed as techniques elucidating much of the important intelligence mentioned above (Bradshaw et al., 2014a; McBean et al., 2015; Deininger et al., 2016; Park et al., 2019).

Like all other body fluids, blood has a complex chemistry. There are two main constituents, plasma and blood cells. Approximately 55% of the blood volume consists of plasma, which contains several substances that are also found in eccrine sweat including amino acids, urea, inorganic salts, metabolites and proteins. The remaining 45% is formed of red blood cells, white blood cells and platelets. All contain proteinaceous materials with the white blood cells providing a source of DNA, and the red blood cells containing the protein haemoglobin (which gives blood its red colour).

Different aspects of this chemistry can be utilised to enhance faint traces of blood. Because blood contains many amine containing compounds, all of the amino acid reagents are capable of developing fingermarks in this contaminant. (Moore et al., 2009; Bossers et al., 2011) The intensity of reaction observed with blood is typically greater than is seen with latent fingermarks because there are more amine-containing substances present within blood. The drawback with using amino acid reagents as a blood enhancement technique is the lack of specificity – latent fingermarks will be developed in addition to marks in blood, and other biological matrices such as semen also contain amino acids and proteins which could react with ninhydrin.

An approach that is often adopted when enhancing faint traces of blood is to target the protein constituents that are present in both the plasma and blood cell fractions. A range of acid dyes have been proposed for this purpose including acid black 1 (Godsell, 1963, Sears et al., 2000), acid violet 17 (Sears et al., 2001), acid violet 19 (Theeuwen et al., 1998), Coomassie Blue (Norkus and Noppinger, 1986) and acid yellow 7 (Sears et al., 2005). All of these dyes rely on the proteins being first fixed in some way, either dehydrated using heat or methanol, or precipitated using 5-sulphosalicylic acid. The dye then selectively stains the proteins, and excess unbound dye molecules are removed with a wash solution. These dyes are all sensitive to faint traces of blood because there are many proteins present, however they have limitations in that they are not specific to blood and can give false positive reactions with a wide range of other protein-containing substances (Cadd et al., 2016).

Greater specificity to blood can be obtained by the use of peroxidase reagents where the oxidation reaction from a colourless to a coloured form is catalysed by the haem molecule present in haemoglobin. The earliest chemicals proposed for this application (benzidine and o-tolidine) have been found to be carcinogenic and are no longer used. However, there are still a broad range of peroxidase reagents that have been adapted to enhancement of fingermarks in blood. These include 3, 3', 5, 5'-tetramethylbenzidine (TMB) (Holland et al., 1975; Garner et al., 1976), diaminobenzidine (Allman & Pounds, 1989), leuco crystal violet (Bodziak, 1996), leuco malachite green (Cox, 1991) and fluorescein (Cheeseman & DiMeo, 1995). The increased specificity of the reagents (targeting just the haem molecule within blood) means that they are less sensitive than the protein stains because there is less material available to react. Despite this increase in specificity, there are still some substances such as vegetable peroxidases and some metals (e.g. iron) that can produce a false positive reaction (Cox, 1991; Prestamo & Manzano, 1993).

Further improvements in specificity for the detection of traces of blood have been achieved by the use of tagged nanoparticles (Frascione et al., 2012). In this approach a magnetic nanoparticle is tagged with antibodies specific to human blood. This results in a magnetic powder that can be applied to fingermarks using conventional magnetic applicators and allowed to incubate and bind with the blood antigens before excess powder is removed.

In terms of blood detection, while presumptive tests are quick and easy, they are prone to false positives due to their lack of target specificity. Confirmatory tests are possible remotely but they are destructive and do not disclose blood provenance unless serological tests are performed. MALDI MS imaging was proposed first in 2014 (Bradshaw et al.) as a much more reliable technique to ascertain the presence of blood due to the ability to specifically measure haemoglobin and haem in a single analysis.

In their work Bradshaw et al. demonstrated using MALDI MSI that: (i) it was possible to detect haemoglobin and haem on the ridge patterns of marks, even in a long depletion series where the blood was no longer visible (ii) that both molecules could be detected in fingermarks previously treated with ninhydrin and acid black 1, and in a suspected crime scene bloodstain previously subjected to the Kastle-Meyer test and that (iii) haemoglobin protein sequences are sufficiently different to detect animal provenance within human, bovine and equine bloodstains that had been analysed.

Patel et al. (2015) adopted a proteomic approach yielding multiple blood specific protein signatures from haemoglobin and other proteins which enabled the discrimination of mixed provenance blood sources (a difficult task if mixed DNA required resolving). These signatures were then exploited by Deininger et al. (2017) to reconstruct molecular images of fingermarks deposited in blood. Kamanna et al. (2017) also used a proteomic approach concentrating on haemoglobins only to differentiate and map blood signatures from human and a range of Australian native mammals. Kennedy et al. (2020) have subsequently validated the proteomic approach developed by Patel et al. (2015) by MALDI MS on a total of 71 blind samples (stains and fingermarks) demonstrating that blood can be detected and discriminated from other biofluids and biofluid unrelated matrices. Semen markers were also detected in stains and in fingermarks, during this study. The technique was used to reliably determine the provenance when human, bovine, porcine and chicken samples were presented in a blind test.

5.6.2 Skin care products & cosmetics

A large class of possible contaminants is derived from day care products, including soaps, hand sanitisers, hair products and cosmetics. Many of these are either applied using the hands or applied to the hands so it is unsurprising that traces of them may be detected within fingermarks.

Chadwick et al. (2017) investigated the impact of the use of hand sanitisers on the subsequent effectiveness of fingermark enhancement processes. They found that alcohol-based sanitisers had no observable effects, however when non-alcoholic sanitisers were used an increase in the quality of developed marks was observed when amino acid reagents were used. This was attributed to the presence of benzalkonium chloride (alkyldimethylbenzyammonium chloride), the active ingredient in such sanitisers, as a contaminant in fingermarks.

At least two substances found in antibacterial wipes/gels, detergents and hair products have also been detected, identified and mapped using MALDI MSI (Bradshaw et al., 2011; Bradshaw et al., 2013). The alkyldimethylbenzyammonium chloride ion (as proposed by Chadwick et al. above) and the closely related dimethyldioctadecylammonium ion at m/z 304.3 and 550.6 respectively, are frequently detected and reported in many MALDI MSI based publications on fingermark analysis. They have a very good ionisation efficiency and as such very often yield high quality ridge detail when the technique is used in the imaging mode.

However, much analytical attention must be paid to these or any other substances if they are used to provide contextual information. For example, alkyldimethylbenzyammonium chloride has the same nominal m/z as cocaine (304 Thomson units). As such there is a risk to either overlook the presence of cocaine or to claim it when the individual had simply performed a personal hygiene action. The use of tandem mass spectrometry is always recommended to confirm molecular identification and Bradshaw & Francese (2014b) have suggested an identification approach that combines tandem mass spectrometry and imaging.

Hinners et al. (2018) have also employed MALDI MS Imaging to detect, visualise and source attribute active ingredients from insect sprays and sunscreens, as well as food oils, alcohols, and citrus fruits.

5.6.2 Grease

Another contaminant that can occasionally be of relevance in operational environments is 'grease'. A range of different oils and greases can be encountered, and the composition of the contamination will vary according to the whether the origin of the material is foodstuffs and cooking material, mechanical lubricants, or cosmetics and wash products. Gaskell et al. (2011) conducted a study of the effectiveness of a range of reagents on contaminants from 'kitchen', 'garage' and 'bathroom' environments. This found differences between the types of contaminant that were strongly developed by each of the reagents used. An iodine solution gave intense development of sugar-containing substances such as cola, lager, cider, red wine, orange juice, ketchup and cough syrup, in addition to moisturiser, engine grease and Swarfega hand cleaner, although effectiveness on many of the drinks residues decreased as the marks aged. Basic Violet 3 was shown to stain vegetable oil spread, used cooking oil, sun cream, anti-seize compound, Swarfega, used engine oil, and its effectiveness on olive oil, sunflower oil and mayonnaise increased as marks aged.

Solvent Black 3 and Natural Yellow 3 both produced strong staining on butter, vegetable oil spread, lard, mayonnaise, hand cream, used cooking oil, lipstick, engine grease, with solvent black 3 also giving good results for red wine, orange juice, ketchup, cough syrup, WD40, Swarfega, sun cream, and moisturiser. Four of these contaminants (olive oil, butter, vegetable oil spread and hand cream) were subsequently used by Cadd et al. (2011) in comparative trials of the effectiveness of solvent black 3 formulations.

The study by Gaskell et al. also demonstrated that white powder and black powder suspension formulations were more effective than any single lipid reagent across the broad range of contaminants studied. These processes were effective because in most cases they targeted the latent fingermark constituents in preference to the contamination. It was also seen that in a real scenario where the nature of the contamination is unknown, there may be merit in sequential application of reagents that target different classes of 'greasy' contaminant.

5.6.4 Condom lubricants

Amongst other possible contaminants, condom lubricants are those relating to either consensual sexual activity or sexual assault. As such, their detection and mapping may provide circumstantial evidence which may become corroborative of the victim/defendant's statements or of other evidence such as the packet of condoms from which the lubricants have originated, found at the victim/defendant's premises. The crime and analytical scenarios are those according to which the individual wearing/using the condom would have contaminated their fingertips with the viscous matrix (lubricants) wetting the condom itself. Upon contact with a surface, a fingermark would be transferred containing the condom lubricants. MALDI MS has been used in both profiling and imaging mode to detect and visualise condom lubricants from a range of condoms (Bradshaw et al., 2011; Bradshaw et al., 2013a). Crucially, the visualisation of lubricants generates molecular images of the fingermark thus linking the biometric information with the circumstances of the event under investigation.

Lubricants are complex matrices made up many different substances including polymers. These compounds ionise particularly well in MALDI and many types of polydimethylsiloxane-based and polyethylenglycol-based polymers as well as the spermicidal nonoxynol-9 and co-polymers were detected within the seven condoms investigated by Bradshaw et al. (2013a). Mirabelli et al. (2013) used desorption electrospray ionization mass spectrometry (DESI) to detect compounds in condom lubricants in the lower *m/z* range (50-1000 and 50-2000) and determined the presence of low molecular weight polymers (nonoxynol-9, polyethylene glycol, and polydimethylsiloxane) and small additive molecules including N-methylmorpholine, N-octylamine, N,N-dibutyl formamide, and isonox 132 in condoms. Molecular images of the condom contaminated marks were also generated.

Every condom and condom brand showed a unique "polymeric fingerprint" as condom lubricants are always made up of mixtures of different polymers and both 2013 studies showed it was possible to distinguish amongst them. However, it is important to create a reference database of condom lubricant polymer spectra for each analytical technique being used if this is to be validated for practical use.

It was observed (Bradshaw et al., 2013a) that fingermark images could still be obtained after 3 months from the deposition of the "condom contaminated" fingermark, demonstrating persistence

of this particular contaminant. This is particularly important in rape cases where, for various reasons, the victim may not immediately report the crime to the police.

5.6.5 Explosives, gunshot residue and metal ions

Other contaminants of forensic significance that may be found in latent fingermarks include explosives residues, gunshot residues, and metal ions from the handling of metal articles such as weapons and an overview of different studies and the species that have been detected is given in Table 4.

These species have been little utilised in the visualisation of fingermarks, although their distribution on the hands can be mapped to provide potentially important operational context. It has been recognised that metal ions can transfer into the sweat on the hands when metal items are held, and the 3-(2-pyridyl)-5, 6-diphenyl-1,2,4-triazine (PDT) complexing agent has been proposed for the detection of iron ions transferred during the handling of firearms (Almog & Glattstein, 1997). However, this method requires the impression to be developed in situ by the reagent being sprayed directly onto the hand. Bleay et al. (2014) have subsequently shown that metal ions present on the hand can be transferred from the hand onto other surfaces within the fingermark residues, and demonstrated the simultaneous detection and mapping of copper and lead ions in a finger/palm print taken from the hand using a gelatin lifter. Rubeanic acid was used as the development reagent in this case.

6. UTILISATION OF FINGERMARK CHEMISTRY IN SEQUENTIAL TREATMENT

It has been demonstrated that various individual constituents, or classes of them, can be targeted by a range of different chemical development processes. The fact that the use of a single chemical development reagent can leave a substantial proportion of the chemicals deposited in the fingermark still available for reaction means that it is possible to use a series of processes in sequence to maximise recovery rates.

Studies in the 1970s and 1980s resulted in processing sequences being proposed for several surfaces encountered operationally (Goode & Morris, 1983; Kent, 1986). The sequences iodine – ninhydrin – silver nitrate and ninhydrin – physical developer were established for use on porous surfaces, however the subsequent introduction of methods such as cyanoacrylate fuming and metal toning of ninhydrin necessitated further systematic study. This was first addressed by Lennard & Margot (1988), who considered techniques established at the time in terms of whether they were thought to develop eccrine or sebaceous deposits. They proposed revised fingermark processing sequences that incorporated the use of fluorescent dye stains and lighting techniques, such as episcopic lighting, into appropriate points in the sequence.

In general, the processing sequences that have been proposed follow a logical order of processes. The first stage is to use non-contact, non-destructive processes (e.g. visual examination and fluorescence examination) which leave chemical constituents unaffected, followed by vapour phase processes or dry powders that have minimal impact. Finally, liquid-based chemical enhancement processes can be used, with organic solvent-based formulations typically being used before aqueous formulations because they are generally less destructive. By using this progressive approach it is

possible to use sequences of chemical/physical processes and continue to develop additional marks at each stage (Bandey, 2014).

This can be shown schematically in the overview of fingermark constituents shown in Figure 5 and the example of how these different constituents can be utilised in sequential processing (in this case for porous surfaces) given in Figure 6.
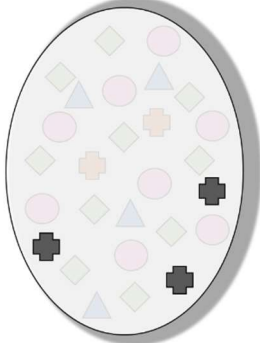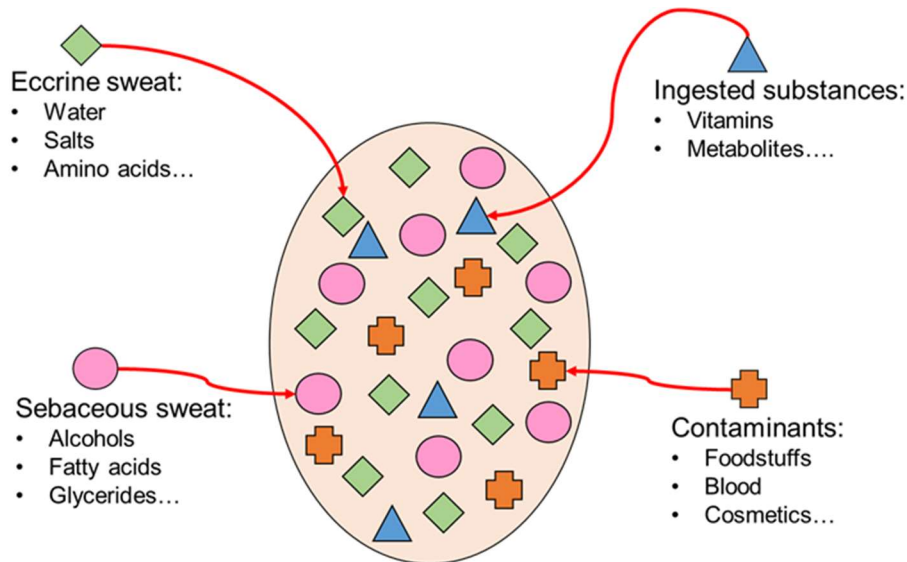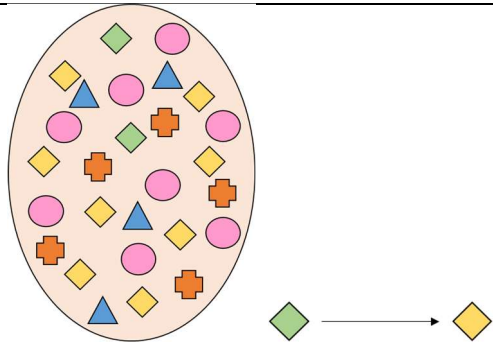
Figure 5. A schematic diagram of a fingermark showing the different constituents present.
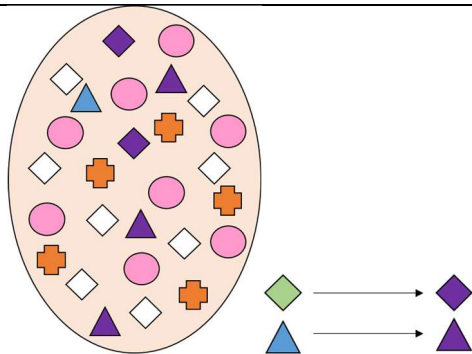
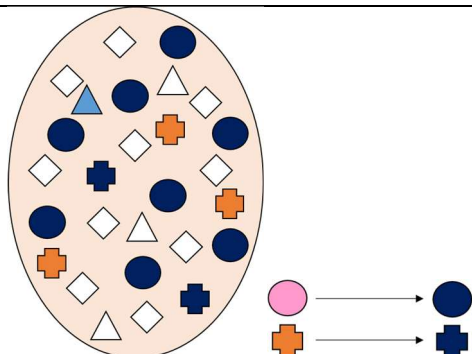| Fingermark schematic	Sequential processing stage
	Visual examination: Examination of the mark using white light at different angles may reveal marks. Some contaminants in the fingermark (e.g. blood, mud) may absorb light, and the fingermark may reflect or scatter light differently to the surface providing contrast.
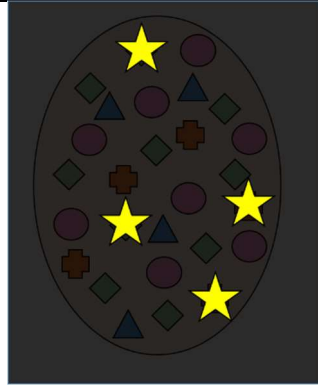
	Fluorescence examination: Examination using a high intensity light source such as a laser may cause certain naturally occurring fingermark constituents (e.g. tryptophan) and some contaminants to fluoresce.
	Amino acid reagent 1: Application of an amino acid reagent such as 1,2 indandione (IND) or 1,8 diazafluoren-9-one (DFO) produces a reaction with amino acids in the fingermark. The reaction product gives marks that are fluorescent. The reaction does not necessarily go to completion, or react with all amino acids present.
	Amino acid reagent 2: Application of a second amino acid reagent such as ninhydrin. Ninhydrin reacts with the residual amino acids in the fingermark and potentially with other constituents such as steroids. This reaction produces marks that are coloured and may reveal additional fingermarks.
	Sebaceous or sebaceous/eccrine reagent: Physical Developer and/or Oil Red O can be used to interact with the sebaceous constituents remaining in the fingermark and also with some fatty contaminants. This interaction produces marks that are visible.

There may still be substances left in the fingermark that can either be used to enhance it (e.g. mapping distribution of reaction products or unreacted substances) or to provide useful contextual information. Analytical techniques such as MALDI and SIMS may be useful in this application.
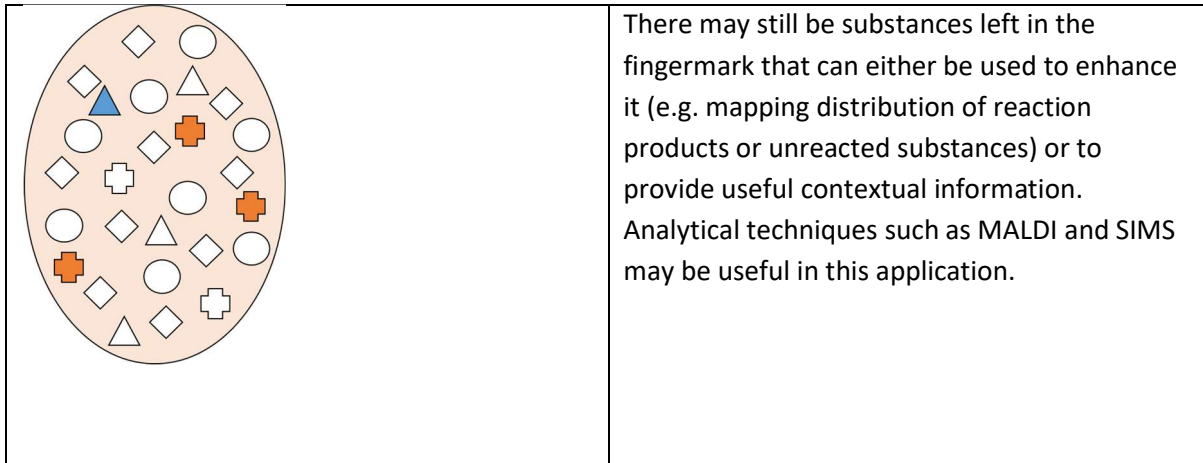
Figure 6. A schematic representation of a processing sequence on porous surfaces

Studies into processing sequences are less commonly reported than those that compare the effectiveness of single processes. Sequential studies on porous surfaces have been reported by Salama et al. (2007), McMullen et al. (2013), Marriott et al. (2014) and Bleay et al. (2019). All these studies confirm that the most effective sequence for developing fingermarks on porous surfaces is 1,- indandione (previously DFO) followed by ninhydrin, and finally physical developer. Oil Red O can be incorporated into these sequences, and indeed McMullen et al. have shown that it can be effective in developing additional marks when used in sequence after 1,2-indandione and ninhydrin. However, the choice of solvent used in the reagents can affect which processes remain effective. Salama et al. observed that when petroleum ether was used as the solvent for 1,2-indandione and ninhydrin, many of the constituents targeted by Oil Red O were dissolved and Oil Red O was ineffective when used subsequently. The 1,2-indandione and ninhydrin formulations used by McMullen et al. used alternative solvents (HFE 7100) which did not have the same detrimental impact. Marriott et al. looked at the incorporation of a lipid reagent, Nile Red, into processing sequences but observed that the increased benefit over the 1,2-indandione – ninhydrin – physical developer sequence was minimal. Bleay et al. looked at the potential benefit of using a blue toner to further enhance the silver marks produced by physical developer and found that this process could produce a significant increase in the number of marks visualised.

There are fewer studies into sequences for non-porous surfaces and those reported have focused on a subset of the wide range of substrates encountered. Downham et al. (2012) looked at sequences for polymer bags and packaging, and found that the process found most effective in equivalent studies in the mid-1980s (vacuum metal deposition) had become effective than both cyanoacrylate fuming with Basic Yellow 40 (BY40) staining and the powder suspensions process. This was attributed to an increase in the recycled polymer content of packaging material and guidance on processing such surfaces was changed accordingly (Bandey, 2014). Basic violet 3 continued to develop a small percentage of additional marks when used at the end of a sequence after all of these processes.

A comparison of different processing sequences was necessitated by the introduction of polymer banknotes in several countries. The first of these studies (Jones et al., 2003) was conducted on Australian banknotes and found a sequence of visual and fluorescence examination, cyanoacrylate

fuming, vacuum metal deposition followed by fluorescent dye staining to be most effective. A similar study on Canadian polymer banknotes (Lam et al., 2014) came to a similar conclusion. A study on UK banknotes was conducted and reported by Downham et al. (2018). A sequence using black magnetic powder followed by powder suspensions was found to be the most effective sequence using established processes whilst a sequence including novel infrared fluorescent powders also showed promising results.

It is recognised that however effective these processing sequences may be, it is probable that a proportion of the marks present may still go undetected. An alternative approach for porous surfaces was explored by Jaber et al. (2012), who used 'reverse development' using gold and silver nanoparticles to selectively darken the paper background, revealing any fingermarks present visible as white outlines. Because the paper composition will be constant but the fingermark composition variable, it was hoped that selectively developing the paper background may reveal more of the fingermarks present.

As illustrated in Figure 6 and discussed in previous sections, mass spectrometry-based techniques with imaging capability may have a role in revealing additional ridge detail, even after full processing sequences involving conventional developers have been applied. Due to its nature, mass spectrometry is a multiplexed technique. This means that it can detect hundreds to thousands of compounds in one analysis in both a targeted and untargeted approach. In theory, if a conventional development technique targets a certain class of compounds and these compounds are no longer detectable because they have already reacted, mass spectrometry has to ability to target other classes of compounds. For example, cyanoacrylate fuming generates a white polycyanoacrylate deposit on fingermarks. It can be hypothesised that whilst higher molecular weight species such as peptides and proteins could be trapped within the intricate polymer network, lower molecular weight species such as lipids could be available for detection. This has been demonstrated by Groeneveld et al. (2015) who were able to detect and image drugs, metabolites and fatty acids in fingermarks after both cyanoacrylate fuming and vacuum metal deposition.

The range of mass spectrometry techniques available differ in terms of the compounds they are most suited to detect. For example, while SIMS can target, amongst other species, electrolytes, MALDI cannot. Conversely, while MALDI is capable of detecting high molecular weight peptides and proteins, SIMS cannot. It is necessary to take these differences into consideration if selecting mass spectrometry methods to 'fill in' ridge detail at the end of a processing sequence.

Both MALDI, and to a lesser extent, SIMS, have demonstrated that they can detect and image compounds that remain after full processing sequences, and/or can be used to reveal more information than conventional development processes.

MALDI MSI has been shown capable of revealing additional ridge detail in fingermarks previously processed using VMD, cyanoacrylate fuming and BY40 dye staining (Groeneveld et al., 2015), powders, ninhydrin, acid black 1 (Bradshaw et al. 2013b; Bradshaw et al., 2014, Patel et al.., 2016), acid yellow 7, leucocrystal violet (Kennedy et al., 2020) and indandione. Even when a specific compound or classes of compounds have been targeted by conventional techniques, these species do not become automatically unavailable for detection using MALDI. Bradshaw et al. (2014) have demonstrated that it is possible to detect and image intact haemoglobin in marks previously enhanced with acid black 1 whilst Patel, Cicatiello et al. (2015) have been able to detect a variety of

blood specific proteins in a 9 year old acid black 1 enhanced palm print on a tile. The same capability is retained if ninhydrin is used. Francese (2019) showed that it was possible to detect haemoglobin in a mark on fabric developed 32 years previously using ninhydrin, via a MALDI based proteomic approach.

TOF-SIMS also has the potential to produce images of fingermarks in situations where conventional reagents do not. Bailey et al. (2013) demonstrated how TOF-SIMS could be used to enhance the quality of ridge detail in marks only partially developed by conventional reagents. The authors showed examples of enhanced visualisation of ridge detail by SIMS on marks previously developed on aluminium foil using cyanoacrylate fuming/BY40. SIMS also produced images of fingermarks on glass that had been buried in soil and marks deposited on the handle of a hand grenade, both of which could not be developed conventionally. Similarly, Thandauthapani et al. (2018) have shown that SIMS can be effective in detecting ridge detail on stainless steel knife blades where cyanoacrylate fuming has proved to be relatively ineffective. However, the latter examples discuss the use of SIMS as an alternative to conventional processes rather than used to enhance detail at the end of a sequence. Unpublished research indicates that SIMS does have potential to be used in this way, but further work is required to identify compatibility with other processes.

7. UTILISATION OF FINGERMARK CHEMISTRY TO OBTAIN ADDITIONAL CONTEXTUAL INFORMATION

Due to their specificity and sensitivity, mass spectrometry techniques are able to exploit the molecular make up of fingermarks to provide contextual information. A good example is illustrated by Bradshaw et al. (2017) in the application of MALDI MSI to operational police casework. A suspect accused of harassment had been apprehended and tested positive for cocaine abuse. MALDI MSI was performed on the powdered fingerprint recovered from the interior side of a PVC window frame on a tape lift. The analyses, performed 26 days after fingermark recovery, confirmed cocaine abuse but also detected a unique metabolite named cocaethylene, indicative of simultaneous consumption of cocaine and alcohol. It is important to note that during the police interview the suspect had denied alcohol consumption and had he not confessed just before the court hearing, the complete information on his state of mind would have not been obtained without employing MALDI MSI.

Hinners et al. (2018) have also employed MALDI MS Imaging to detect, visualise and source attribute active ingredients from bug sprays and sunscreens, as well as food oils, alcohols, and citrus fruits. The determination of the presence of these and other compounds that are picked up on the fingertips may reveal lifestyle information that could potentially inform investigations. In their work the authors suggest that while one compound may be insufficient to provide reliable contextual information, the simultaneous determination of multiple compounds from different sources (for example from consumer products, foods, and alcohols) may give important insights into a person's lifestyle.

Another example in which non-destructive methods can be used first followed by methods that exploit the molecular make-up of the fingermark still available to provide contextual information has been reported by Bradshaw et al. (2013a). Although the following may not routinely occur, a scenario in which "condom-contaminated" marks are searched and photographed first using

specialised lights, followed by tape lift and analysis by ATR-FTIR and by a second lift subjected to MALDI MSI analysis to complement (if necessary) the biometric information and provide additional contextual evidence, is shown to be possible (Figure 7).
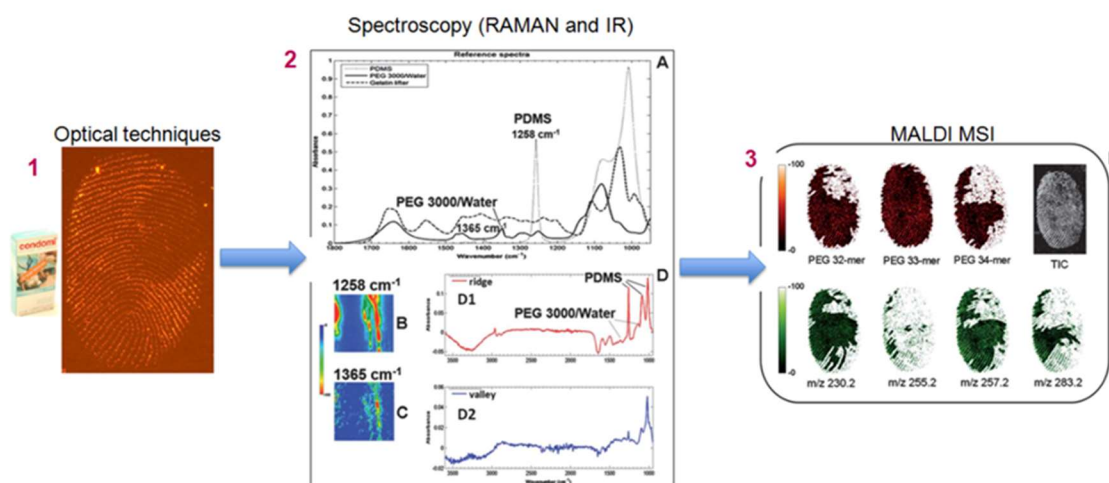

Figure 7. Combined specialised light- ATR-FTIR imaging-MALDI MSI analysis of a Condomi Max Love contaminated fingermark. (1). Fluoresence image of the mark using laser illumination at a wavelength of 532 nm and an orange viewing filter (cut-on 549 nm). (2) A shows the reference FTIR spectra of vinyl PDMS (at 1258 cm^{-1}) and PEG 3000 (at 1365 cm^{-1}) superimposed with the spectrum of a BVDA gelatin lifter. Panels B and C show the ATR-FTIR image of PDMS at 1258 cm^{-1} and the ATR-FTIR image of PEG at 1365 cm^{-1} present on the same ridges of a Condomi Max Love contaminated fingermark selected region. Panel D shows two ATR-FTIR spectra from the ridge (D1) and the valley (D2) (high and low concentration of the two polymers respectively). (3) MALDI MS images of 32-mer, 33-mer and 34-mer PEG ion signals, the complete ridge pattern provided by the image of the total ion current (TIC), as well as a small sample of the many fatty acids detected. Adapted from Bradshaw, Wolstenholme et al. (2013) with permission from The Royal Society of Chemistry.

Mass spectrometry-based techniques have also been investigated for their potential to add context to a forensic timeline. A question that is sometimes posed when fingermarks are developed on an incriminating document is whether the paper was handled before or after the incriminating content was present. This issue has been addressed by several researchers using SIMS (Bailey et al., 2010; Bright et al., 2012, Attard-Montalto et al., 2013; Attard-Montalto et al., 2014), with the general approach being to identify signals from chemical species unique to both the ink and fingermark components. It has been demonstrated that it is possible to discriminate between the 'ink over fingerprint' and 'fingerprint over ink' scenarios using both imaging and depth profiling modes prior to development of the fingermark. However, use of a chemical reagent to develop the fingermarks can lead to redistribution of constituents and makes discrimination more difficult. The most comprehensive study of this type (Attard-Montalto et al., 2014) found that the ability to discriminate the order of fingermark and ink was influenced by printing method and fingermark development technique used. Discrimination was best on laser printed documents with fingermarks developed using iodine fuming or 1,2 indandione.

It should also be noted that chemical differences between fingermarks from different donors have also been used to separate and image overlapping fingermarks (Bradshaw et al., 2012). In this case the technique used was MALDI MSI.

Conclusion

The chemistry of the residue that is deposited in fingermarks is highly complex, and compositional analysis has detected hundreds of different substances that may be present. This is despite the fact that the amount of material that may be deposited is minimal, of the order of micrograms. The chemical composition has traditionally been exploited in a forensic context by a range of different reagents that target different constituents of the fingermark. The suite of processes that have been proposed for fingermark enhancement are highly effective, with high sensitivities for the most abundant constituents and the capability to be used sequentially to maximise the number of fingermarks recovered. Although not all constituents present are currently exploited for visualisation, there is probably minimal, if any benefit in seeking developers specific to any constituents not already specifically targeted if increases in overall effectiveness are required.

The future directions for the exploitation of fingermark chemistry are the synthesis of developers with increased specificity to a constituent or contaminant of particular interest (e.g. tagged nanoparticles that bind to specific metabolites or body fluids), and the use of analytical techniques to characterise and spatially map the substances present. The potential of MS-based techniques to contribute to improved biometric information as well as to contextual information is vast.

From a solely identification perspective, MS imaging techniques are crucially capable of "filling in the ridge detail gaps" after the application of conventional processes and there is therefore a potential role for such techniques as a final sequential process in a serious crime investigation. However, the main area of anticipated growth is their potential to provide additional contextual information (e.g. about substances handled, lifestyle, potential pathologies from the detection of medications etc.) simultaneously with the provision of the biometric information (imaging) or beyond identification (profiling). Such intelligence can be used to inform and steer the investigations faster and potentially with savings to the public purse. For this reason the research must have a dynamic focus to keep up with the ever increasing number of possible contaminants (such as newly synthesised drugs, medications or changing molecular composition in day care products or others); this would also require that the protocols that are available will need to be constantly tested against new substances. Capabilities are always accompanied by limitations and drawbacks and each MS Imaging technique will have their own.

It is also important to mention that different MS instrumentation, employing the same MS technique, may perform vastly differently within the protocols available. The authors believe that this issue will need to be addressed as part of the validation of these techniques, the requirements for which may change depending on the particular criminal justice system environment and judicial systems. The validation process should also encompass the elucidation of the impact and the extent to which MS techniques affect subsequent processes for extraction of additional biometric or biological information. Whilst some studies have been published and others are in progress, much of this knowledge is presently missing and is required to allow appropriate positioning of these

processes in the forensic workflow of fingermark visualisation, identification, and for use as a source of further biological information.

Another challenge for operational implementation of such methods is the need to create comprehensive reference databases for the contaminants of operational interest. One such example relates to the creation of a condom lubricant mass spectral libraries discussed earlier in the "Contaminants" section. The generation of libraries of this kind is often regarded as a "repetitive exercise" and does not attract funding from research bodies.

Finally, there is a need for the technology that enables detection and analysis of this complex chemistry to be made as accessible as possible, whether by miniaturisation to make equipment portable, developing simple interfaces to make operation straightforward, or automation of complex analyses. The closer such techniques can be brought to the 'operational' environment, the more widely they can be utilised. The points above describe significant barriers to these techniques realising their full operational potential and all require collaborative and international approaches if they are to be overcome.

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