Fingermarks, more than just a ridge pattern
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CHAPTER 11

COMPARISON OF DIFFERENT TECHNIQUES THAT ACQUIRE DONOR PROFILING INFORMATION FROM FINGERMARKS –

A REVIEW

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ABSTRACT

Fingermarks are one of the most important types of evidence that can be encountered at the scene of a crime. Since the unique ridge pattern of a fingermark can be used for individualization, fingermarks are a vital piece of evidence. However, individualization is not always possible, due to partial recovery or distortion of the ridge pattern or lack of a comparable fingermark in the database. Fortunately, fingermarks are composed of a wide variety of different components that originate from endogenous and exogenous sources. Detection and analysis of specific components in the fingermark can thus provide additional information about the fingermark donor. In this review we have summarized the types of information that can be obtained from fingermarks. Additionally, an overview is given of the techniques that are available addressing their unique characteristics and limitations. We expect that in the nearby future, donor profiling from contact traces, including fingermarks will be possible.
ABBREVIATIONS

ATR  Attenuated Total Reflectance  
DART  Direct Analysis in Real Time  
DESI  Desorption Electro Spray Ionization  
FT-IR  Fourier-Transform Infra Red spectroscopy  
GC  Gas Chromatography  
GLC  Gas-Liquid Chromatography  
HSI  Hyper Spectral Imaging  
IMS  Imaging Mass Spectrometry  
IR  Infra Red  
LC  Liquid Chromatography  
MALDI  Matrix-Assisted Laser Desorption/Ionization  
MS  Mass Spectrometry  
MSI  Mass Spectrometry Imaging  
PETN  Pentaerythritol nitrate  
PLS  Partial Least Squares  
PLS-DA  Partial Least Squares- Discriminant Analysis  
RDX  Hexahydro-1,3,5-trinitro-1,3,5-triazine  
SALDI  Surface-Assisted Laser Desorption/Ionization  
SERS  Surface Enhanced Raman Spectroscopy  
SIMS  Secondary Ion Mass Spectrometry  
ssDNA  Single stranded DNA  
THC  Δ9-TetraHydroCannabinol  
TLC  Thin Layer Chromatography  
TNT  2,4,6-trinitrotoluene  
TOF  Time-Of-Flight

1. INTRODUCTION

Fingermarks contain an enormous amount of undisclosed information on the donor of the mark. Secreted metabolites, proteins and peptides, but also exogenous components contain donor profiling information such as gender, blood group type, age, diet drug use and medical conditions [1-7]. The challenge lies in how to reliably retrieve this information from fingermarks as it is a minimal sample of complex origin.

The ability to obtain donor profiling information from fingermarks is not yet integrated in the crime scene investigation. With this review we would like to bring the possibility of using the chemical composition of a fingerprint to the attention of the forensic field. Additionally, the techniques that can be applied to obtain this information and their current developments will be discussed. In the discussion section, an overview of the type of information and the best suitable technique to obtain this type of information is schematically described.
2. FINGERMARKS AND THEIR COMPOSITION

The friction ridge skin present on the soles of our feet, palms of our hands and tips of our fingers and toes is composed of ridges and grooves. When touching a surface with the fingertip, a specific pattern is left behind and is called a fingermark [8]. The pattern of ridges and grooves contain material originating from sweat excreted via the pores, which are present on the ridges, but can also be contaminated with other material originating from touching different body parts and exogenous components, such as food, cosmetics and drugs [8]. Fingermarks can be used for individualization and thus identification purposes, based on the assumptions that no two fingermarks are identical, not even those of identical twins and that the friction ridge does not change over time, except in case of injury that affects the deeper layers of skin [9]. In crime scene investigation, the pattern of fingermarks has been used as an identification tool since the late 1900s [9].

Currently, fingermarks are only used for identification purposes, whereby the unique ridge pattern is used to discriminate between different donors. However, individualization of the fingermark is not always possible. The lack of a comparable fingermark in the database, a distorted fingermark or a badly developed fingermark all lead to the uselessness of this specific trace. Specific features of the ridge pattern can be used for donor profiling. Several studies have investigated the use of the ridge density for gender determination, in which the ridge density was found to be higher in female fingermarks compared to male fingermarks [10-12]. However, racial differences were observed in the mean value of ridge density within males and females, meaning that this method of ridge counting is not the golden standard for gender determination in multicultural populations [12].

Besides the unique ridge pattern, fingermarks are composed of a large variety of different chemical components, which originate from endogenous sources, but can also originate from materials present in the environment like food products and cosmetics [13]. An excellent review on the different components present in fingermarks has been described by Girod et al. [14]. In short, the major source contributing to the composition of fingermarks, is sweat. Sweat found in fingermarks can originate from the eccrine, sebaceous and/or apocrine glands. Eccrine glands are present all over the body and in highest density on the soles of the feet and palms of the hands. Therefore, eccrine sweat is the main contributor to the chemical components present in the fingermark. Inorganic compounds, including ammonia, sodium, phosphate, fluoride and chloride are secreted via the eccrine glands. Organic compounds, such as proteins, amino acids and lipids, can also be found in eccrine sweat [13]. Sebaceous glands are located in areas of the body containing hair follicles and are most abundant in the facial region. Sebaceous glands secrete sebum, an oily material. The glands are not present on the fingertips and soles of feet, but as human behavior involves touching the face and other skin areas containing sebaceous glands, sebum can be found in fingermarks. Sebum
components include triglycerides, squalene, wax esters, cholesterol and free fatty acids. The apocrine glands are highly distributed in the armpits and genital region and are the least studied glands, since contamination of apocrine secretion products with sebum complicates the study of the secretion products of apocrine glands [13].

Sweat is not the only source that contributes to the chemical composition of fingerprints. Environmental contaminants and endogenous body material, like saliva, can affect the composition of fingerprints. From all these components originating from different sources, donor profiling information can be obtained, that may aid in the forensic investigation. In cases where fingerprints are of poor quality, caused by smudging or distortion, or when no reference fingerprints are available for comparison, intelligence from fingerprints will be helpful during the crime scene investigation.

One of the materials that can provide additional information about the donor of the fingerprint is DNA. DNA can be found in fingerprints; however in most cases the amount of DNA is too low to ensure reliable DNA analysis. As DNA analysis is also destructive for the fingerprints, DNA analysis is seldom successfully performed on fingerprint traces [13].

3. DONOR PROFILING INFORMATION FROM FINGERMARKS

3.1 Gender
The fingerprints of men and women seem to differ in two ways: the ridges of men’s fingerprints are coarser and their marks appear to be greasier than those of women [10-12, 15]. Several studies have tried to determine the gender of the fingerprint donor based on the chemical composition of the fingerprint focusing on the fatty and oily components secreted via the sebaceous glands onto the skin. Nazarro-Porro et al. analyzed the presence and abundance of different fatty acids obtained from the skin surface using gas-liquid chromatography (GLC) [16]. They observed differences in the amount and composition of the skin surface lipids varying with the age and gender of the donor. A remarkable observation was that ∆9-type unsaturated fatty acids were found more often in fingerprints obtained from female than male donors. In another study, ten specific components were selected and analyzed using gas chromatography-mass spectrometry (GC-MS), including myristic acid, pentadecanoic acid, palmitic acid, palmitoleic acid, methyl palmitate, methyl palmitoleate, methyl stearate, oleic acid, stearic acid and cholesterol and their area ratios relative to squalene were calculated, as shown in figure 1. No significant difference could be observed between the average values of these components and gender. However, the average values of palmitic acid, palmitoleic acid, and oleic acid were slightly higher in fingerprints from males than females [17].

In a more recent study by Michalski et al. GC-MS was used to discriminate between gender and race focusing on the presence of fatty acids and their methyl esters, however no discrimination could be made between fingerprints from males and females [18].
They suggested to use a larger data set and a more comprehensive statistical treatment of the data to find possible relations between gender and race. Recently, matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS) in conjunction with the data analysis method partial least squares discriminant analysis (PLS-DA) was used by Ferguson et al. to discriminate between males and females, whereby they focused on peptides and small proteins present in the fingermark residue [1]. Promising results were obtained leading to gender discrimination between males and females with 67.5% to 85% accuracy. Interestingly, three biomarkers were identified that can probably be used for gender classification, namely SSL-29, and LEK-45 for males and DCD-1L for females [1].

As promising results were shown by Ferguson et al. obtaining gender information from fingermarks might be possible in the nearby future, probably resulting from a combination of the morphological aspects of the fingermark and the chemical composition of the fingermark [1, 10-12, 15].

3.2 Age of the donor
Two aspects of the fingermark change when the donor ages: the ridge groove pattern becomes coarser and the onset of puberty clearly influences the composition of the skin.
Ramasatry et al. investigated whether differences could be found in skin surface lipids obtained from children at birth and at an age of 17 [20]. Low cholesterol levels were found at birth, and were variable up to nine years. After nine years a decrease in cholesterol levels was observed. The inverse happened with wax esters, high levels of wax esters were measured at birth, then quite variable levels were found at early age, but after the age of six an increase in the level of wax esters was observed, which remained stable after the age of nine. In another study performed by Nazarro-Porro et al. skin surface samples were investigated on the levels of Δ9-type unsaturated fatty acids, including triglycerides, wax esters and sterols [16]. A maximum level of Δ9-type unsaturated fatty acids was found before puberty, then the level decreased, reaching a minimum at middle age and rose again with senescence. A general observation made by different fingerprint examiners was that children’s fingermarks disappear already after 24 hours, whereas fingermarks of adults are visible for longer [21]. The main difference in chemical composition between children’s fingermarks and adults’ is that the marks from children contain higher concentrations of volatile unesterified free fatty acids, whereas in adults’ marks higher concentration of more stable components, like long-chained fatty acid esters were found [3, 21-22]. This observation can be explained by the difference in activity of the sebum glands with increasing age. Since variation can be found in the sebum composition of individuals of different ages, Hemmila et al designed an approach to estimate the age of the fingerprint donor [3]. Spectroscopic analysis was performed on the fingermark residues using Fourier transform-infrared spectroscopy (FT-IR) followed by partial least square (PLS) regression using a constructed prediction curve. A good correlation was found between the FT-IR spectra predicted age and the actual age of the donors, specifically 92% with a root mean square error of 3.6 years.

FT-IR spectroscopy seems to be a promising technique to determine the age of the donor of a fingermark. The detection of volatile unesterified free fatty acids and long-chained fatty acids may result in a better estimation of the age of the donor. Also, other endogenous compounds like proteins and hormones are likely to provide additional information on the age of the donor [23-24]. However, the presence of hormones and the relation with age has not been studied in fingermark depositions, yet.

### 3.3 Diet

Eating behavior and diet of individuals is found to influence the body odor of humans [25-26]. Therefore, it is likely that specific components related to eating behavior can be found in the fingermark residue.

There is limited literature available on diet information obtained from fingermark residues. One study by Lambrechts et al. identified food metabolites using thin layer chromatography combined with fluorescence spectroscopy [2]. The goal of their study was to identify the fluorescent components responsible for the intrinsic fluorescence of
fingermarks. Two metabolites of chlorophyll, a plant pigment, were indicated to be the source of two characteristic red fluorescent spots found in the developed fingermarks. Pheophorbide A and pheophytin are both metabolites from chlorophyll. Chlorophyll can be found in green vegetables and the presence of chlorophyll metabolites in fingermarks may provide information about the donor’s diet [2]. In a study performed by Kuwayama et al. caffeine and its metabolites were detected in fingermarks after coffee intake [4]. Caffeine and its metabolites were chosen as a model for drug ingestion, since caffeine can be found in frequently consumed beverages, like coffee and tea. Caffeine and three metabolites, paraxanthine, theobromine, and theophylline were selected and were detected in fingermarks and blood samples using liquid chromatography mass spectrometry (LC-MS) [4]. Caffeine and paraxanthine, the major metabolite of caffeine, could be detected in fingermark residue, however the levels of theobromine and theophylline were below the lower limit of quantification. In the fingermarks of all three subjects the amount of caffeine and paraxanthine was larger after coffee intake, which is presented in figure 2 [4].

Figure 2. Amounts of caffeine and paraxanthine found in fingermarks before and after coffee intake. Average values and standard deviations were calculated of four measurements. Number sign # represents the value under the lower limit of quantification (LOQ). Dashed line shows the values obtained from fingermarks before coffee intake (subject B and C) or the LOQ (subject A). * significant difference of p<0.05 compared to values before coffee intake. This figure has been adapted and reprinted from Kuwayama K, Tsujikawa K, Miyaguchi H, Kanamori T, Iwata YT, Inoue H; Time-course measurements of caffeine and its metabolites extracted from fingertips after coffee intake: a preliminary study for the detection of drugs from fingerprints. Analytical and bioanalytical chemistry 2012:1-8 [4]. Copyright 2012, with permission from Springer.
For donor profiling to reduce the pool of donors, knowledge on the eating behavior of the last two days before depositing the fingermark might be helpful. However, up to now more research should be conducted on interesting food metabolites that could provide information on diet.

### 3.4 Personal habits

Knowledge on the use of hair gels, soaps, hand lotions and cosmetics will give a better understanding in the lifestyle and personal hygiene habits of the donor. Other interesting information that can be obtained from fingermarks is smoking habits and drug usage.

Different studies showed that cosmetic ingredients can be observed in contaminated fingermarks. Attenuated Total Reflectance (ATR)-ATR-FT-IR is a good technique for the study of oil in water or water in oil emulsions and the majority of the cosmetics contain these emulsions. Successful identification of different cosmetics was possible in fingermarks contaminated with face cream, body lotion, foundation and body butter using ATR-FTIR [27]. In fingermark residues from females certain levels of hydrocarbons, including tetracosane and octacosane, were found, which are likely to originate from cosmetics containing petroleum jelly. Also, levels of octylmethoxycinnamate were found using GC-MS. This substance is a commonly used ingredient in UV-B sunscreen or cosmetic penetration enhancers [5]. Differentiation between some endogenous fingermark and exogenous cosmetic ingredients is not possible, because they can originate from both sources. A large variety of fatty acids, which are commonly found in fingermarks are also present in cosmetics. Squalene and cholesterol are rarely found in cosmetics, but since they can be present in emollients and hair conditioning products, it is hard to determine whether their original source is intrinsic or exogenous [28]. Another contaminant, that is known to originate from lotions, hair products, body washes and tissues is the dimethyldioactadecylammonium ion, which was reported to be present in fingermarks and could be detected with MALDI-MSI [29].

Besides cosmetics and other hygiene products, drugs and their metabolites can be found in fingermark residues. To discriminate smokers from non-smokers in fingermarks, nicotine and its metabolite cotinine were suggested as markers for cigarette smoking. Nicotine is a component present in tobacco, which is metabolized in the human body to cotinine and other metabolites. Immunolabeling can be used to discriminate smokers from non-smokers using specific antibodies to cotinine [30-31]. However, nicotine and thus the metabolite cotinine can also be found in different foods, such as potatoes, tomatoes and cauliflower [32]. Our group tried to mimic the results presented by Hazarika et al., using immunolabeling. However, we were not able to obtain specific immunolabeling in fingermarks using the protocol described by Hazarika et al. [33]. We found that the magnetic particles used in these studies bound non-specifically to fatty components in the fingermark residue.
In another study on the discrimination of smokers versus non-smokers, it was found that the level of thiocyanate and benzoate, metabolites related to smoking behavior, were more pronounced in fingermarks from smokers than of non-smokers [34].

Other drugs and metabolites that have been identified in fingermarks are the heroin metabolite morphine and the major metabolite of cocaine benzoylecgonine [35]. Immunoassays can be used to detect these components. Besides the immunolabeling technique, also other techniques are available that are able to detect drug metabolites in fingermarks and sweat. GC-MS, Surface-assisted laser desorption/ionization mass spectrometry (SALDI)-MS and ATR-FT-IR can all be used to detect drug and their metabolites in fingermarks [7, 36-37]. Other, non-illegal drugs like aspirin and diazepam could be identified in contaminated fingermarks with FT-IR [37]. Figure 3 shows the detection of cocaine in cocaine spiked fingermarks using FT-IR [37].

Figure 3. A: Infrared spectral image (256 × 256 spectra) of cocaine contaminated fingermarks at 2893 cm⁻¹. B: Image of fingermark showing pixels at which cocaine was detected by searching against a cocaine reference. C: Spectra of varying quality detected in the image and the used reference spectrum of cocaine. This figure has been adapted and reprinted from Ng P, Walker S, Tahtouh M, Reedy B, Detection of illicit substances in fingerprints by infrared spectral imaging. Analytical and Bioanalytical Chemistry 2009, 394(8):2039-2048 [37]. Copyright 2009, with permission from Springer.
Table 1. Schematic overview of the type of donor information retrieved from fingermarks and the acquired technique

<table>
<thead>
<tr>
<th>Donor information</th>
<th>Suggested technique (currently available)</th>
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<tbody>
<tr>
<td>Gender</td>
<td>MALDI-MSI [1]</td>
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<tr>
<td>Age</td>
<td>GC-MS [21]</td>
</tr>
<tr>
<td></td>
<td>ATR-FT-IR [3]</td>
</tr>
<tr>
<td></td>
<td>HSI [22]</td>
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<tr>
<td>Blood group typing</td>
<td>Immunolabeling [43]</td>
</tr>
<tr>
<td>Diet</td>
<td>MALDI-MSI [44]</td>
</tr>
<tr>
<td>- Vitamins</td>
<td>DART-MS [45]</td>
</tr>
<tr>
<td>- Caffeine</td>
<td>DESI-MS [46-47]</td>
</tr>
<tr>
<td>- Nicotine</td>
<td>LC-MS [4]</td>
</tr>
<tr>
<td>- Amino Acids</td>
<td>ATR-FT-IR [7]</td>
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<tr>
<td></td>
<td>SERS [48]</td>
</tr>
<tr>
<td></td>
<td>HSI [49]</td>
</tr>
<tr>
<td></td>
<td>Immunolabeling [50]</td>
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<tr>
<td>Personal hygiene</td>
<td>MALDI-MSI [29]</td>
</tr>
<tr>
<td>- Hair gels</td>
<td>SIMS [41]</td>
</tr>
<tr>
<td>- Soaps</td>
<td>ATR-FT-IR [27]</td>
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<tr>
<td>- Hand lotions</td>
<td></td>
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<tr>
<td>- Cosmetics</td>
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<tr>
<td>Lifestyle</td>
<td>MALDI-MSI [51]</td>
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<tr>
<td>- Smoking habits</td>
<td>SALDI-MSI [36]</td>
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<tr>
<td>- Drug consumption</td>
<td>DART-MS [36, 45-47]</td>
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<tr>
<td>- Drug handling</td>
<td>DESI-MS [46-47, 52]</td>
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<td></td>
<td>GC-MS [47]</td>
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<tr>
<td></td>
<td>LC-MS [47]</td>
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<td></td>
<td>ATR-FT-IR [7, 37, 53]</td>
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<td>SERS [48, 54]</td>
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<td></td>
<td>HSI [49]</td>
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<tr>
<td></td>
<td>Immunolabeling [31, 35, 55-57]</td>
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<tr>
<td>Foreign substances</td>
<td>MALDI-MSI [42]</td>
</tr>
<tr>
<td>- Gunshot residues</td>
<td>SALDI-MSI [40]</td>
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<tr>
<td>- Explosives</td>
<td>DART-MS [40, 45]</td>
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<tr>
<td>- Condom traces</td>
<td>DESI-MS [47]</td>
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<td>SIMS [41]</td>
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<td></td>
<td>GC-MS [47]</td>
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<td></td>
<td>ATR-FT-IR [58-59]</td>
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<td></td>
<td>SERS [39, 54]</td>
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<td>HSI [37-38]</td>
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In most cases the fingermarks used for detection of drug metabolites were spiked with the metabolite of interest. To be relevant for the forensic field it is important in future studies to include fingermarks from drug users, since the amount and presentation of the drug metabolites in spiked fingermarks can differ from real, via the pores in the skin secreted drug metabolites in fingermarks.

Donor information on the hygiene status, smoking behavior and handling/usage of drugs provides a better insight in the lifestyle of the donor, which can be helpful in limiting the amount of possible donors. More research should be performed to find more interesting compounds that can be used to obtain this specific type of information.

3.5 Other foreign materials: Explosives, gunshot residues and condoms

The presence of compound related to explosives, gunshot residues and condoms in fingermark residues can provide important additional information on handlings of the donor. The relation between criminal activity with identity is helpful information in the forensic investigation.

Detection of gunshot residues in fingermarks can provide information on the handling of related items. In a controlled firing experiment, fingermarks of donors were investigated on the presence of compounds related to gunshot residues. An increased level of nitrite and nitrate was found in these fingermarks, however the typically gunshot residue species cyanate was only found to be mildly increased in fingermarks from donors, who fired guns compared to control fingermarks. Nitrite and nitrate may also originated from an increased sweat secretion during the activity of firing and should therefore be interpreted with special care [34].

Techniques that may provide information on the presence of gunshot residues and explosives are FT-IR, hyperspectral imaging, direct analysis in real time mass spectrometry (DART-MS), surface-assisted laser desorption/ionization-time of flight-mass spectrometry (SALDI-TOF-MS and C60+ secondary ion mass spectrometry (SIMS) [37-41]. One drawback of these studies is that the fingermarks used in these studies were spiked with the component of interest, which can contain a higher amount of the component and can thus deviate from real case examples.

Fingermarks that are contaminated with explosive residues, which can be associated with a planned bombing or actual bombing, are crucial in the forensic investigation [6]. The detection of explosive residues in fingermarks is possible and can be achieved using different techniques. One of the techniques that can be used to analyze contaminated fingermarks is HPLC. The explosive compounds, 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), pentaerythritol nitrate (PETN), chlorate and nitrate could be detected in contaminated fingermarks [6].
The detection of condom traces in fingermark residues has been shown by Bradshaw et al. [42]. MALDI MSI, MS/MS, Raman spectroscopy and ATR-FT-IR have been used to analyze fingermarks contaminated with condom traces. Condom specific polymers could be detected in the contaminated fingermarks. In some fingermarks, it was even possible to discriminate between condom residues originating from different condom brands/types. Information on the contamination of fingermarks with condom traces might be of additional value in the victim’s statement of sexual assault and can be used as additional intelligence in forensic cases [42].

Foreign substances can include a whole set of different compounds originating from various sources. However, more research should be performed on which compounds have enough discriminative power to use for donor profiling and which compounds provide interesting knowledge on for instance the handlings of the donor.

3.6 Donor profiling information
As described in the previous sections, various components, originating from endogenous and exogenous sources, can be detected in fingermark that provide additional information about the donor of the fingermark. In table 1 we have given a schematic overview of the techniques that can be used to obtain specific types of donor information. We expect however that much more information is present in fingermarks than presented in table 1. Since fingermarks are mainly composed of sweat originating from the body, including a large variation of different lipids, proteins, peptides and metabolites, information on the health status of individuals is assumed to be reflected in the chemical properties of the fingermark. Specific detection of biomarkers and the quantities of these biomarkers may provide additional information on the health status of individuals. This information will not only be useful in the forensic field, but can also of high value for the medical field.

4. TECHNIQUES
Recent developments in the forensic field have made it possible to detect, analyze and identify compounds in small traces, including fingermarks. Various techniques are available that can be used for the chemical analysis of fingermarks. However, up till now, the information that can be obtained from fingermarks with these techniques is not being used within forensic case work. In this section we will discuss the techniques that are able to provide information on gender, age, diet, and lifestyle of the donor and on the presence of foreign substances in the fingermark. Different types of mass spectrometry [6], spectroscopy and immunolabeling will be discussed.

4.1 Mass Spectrometry
Mass spectrometry (MS) can be used for the identification and relative quantification of sample material. There are three fundamental components involved in MS. An ionization source causing the ionization of the atoms present in the sample molecules. Once
ionized, ions pass the analyzer, which allows the separation of ions by their mass to charge ratio \((\text{m}/\text{z})\). As the ions come out of the analyzer they reach the detector which creates a mass spectrum in which the position of the peaks represents the \(\text{m}/\text{z}\) of the ions and the height or intensity of the peaks give information on the relative abundance of the ions [60-61]. There are different ionization methods including matrix-assisted laser desorption/ionization (MALDI), surface-assisted laser desorption/ionization (SALDI), direct analysis in real time (DART), desorption electrospray ionization (DESI) and secondary ion mass spectrometry (SIMS) [62]. Besides identification, characterization and quantification, MS can also be used for imaging, often abbreviated to IMS or MSI. Images can be created from individual mass spectra, where a mass spectrum is created for each pixel in the image, reflecting the chemical information and spatial information of the sample [62]. MS combined with imaging can be interesting for the analysis of fingerprints, since not only information about the chemical composition is obtained, but also information about the ridge pattern of the fingerprint.

4.1.1 MALDI-MS(I)

Matrix-assisted laser desorption/ionization (MALDI)- (time of flight) (TOF)- mass spectrometry imaging (MSI) is an ionization method that involves a matrix to enhance the desorption and ionization of the analyte of interest. The matrix is applied to the surface of the sample, thus the fingerprint. The matrix allows a good separation of the ions, since the number of matrix molecules exceeds those of the analyte, preventing the formation of clusters [36, 63-64].

In forensics, it is important that latent fingerprints can be visualized before analysis takes place. As most fingerprints found at crime scenes are invisible, they need to be detected before they can be collected and analyzed. One of the limitations of MALDI-MS was that the location of the fingerprint must be known, before MALDI-MS could be applied. Ferguson et al. developed a method that broadened the applicability of MALDI-MS in the forensic field [44]. Traditionally, the matrix exists of a chemical solution, which cannot be used as fingerprint developer. Therefore, Ferguson et al. introduced the two-step method in the forensic field, called the dry-wet method [44, 65]. Firstly, dry matrix material is applied to the fingerprint by dusting to allow the visualization of the fingerprint, comparable to the traditional powder. The powder is composed of small particles, that once applied to the fingerprint, makes it possible to obtain high resolution images of the developed fingerprints. Additionally, fingerprints can be lifted with lifting tape. The second-step involved in the dry-wet method is the classic-coat method, whereby an appropriate solvent solution is applied to the fingerprint. This dry-wet method is able to detect, lift and analyze fingerprints found at crime scene with MALDI-MSI. Fingerprints left on metal, wood, plastic and leather were all successfully detected, lifted and analyzed using the dry-wet method, as depicted in figure 4. Images of high resolution, 50 µm by 50 µm or even 20 µm by 20 µm, can be detected. However, the downside of this high resolution is that the acquisition time is more than 2 days, which is not fa-
A new kind of matrix was investigated by Francese et al. specifically curcumin. Curcumin can be used as a dual agent in the fingerprint development, since it can be used as a powder for the visualization of fingerprints and also appears to be a good matrix for MALDI-MSI for the analysis of drugs, lipids, peptides and proteins and thus can also be used in the dry-wet method.

Figure 4. The use of MALDI analysis performed on fingerprints deposited on different surfaces, visualized and analyzed using the dry-wet method developed by Ferguson et al. Fingermarks are left on a) glass b) metal c) wood d) plastic e) leather. R-CHCA was used as powder for the visualization of the fingerprints (a1-e1), which can also be used as a matrix for MALDI analysis. MS images of two endogenous components present in the fingerprint are shown (putative valine m/z 118 and oleic acid m/z 283) and an exogenous component (dimethylbenzylammonium ion m/z 304). Figure reprinted (adapted) with permission from (L. Ferguson, R. Bradshaw, R. Wolstenholme, M. Clench and S. Francese, Two-step matrix application for the enhancement and imaging of latent fingerprints, Anal. Chem., 2011, 83(14), 5585–5591) [44]. Copyright 2011, American Chemical Society.
4.1.2 SALDI-MS

Surface-assisted laser desorption/ionization-mass spectrometry (SALDI-MS) substitutes the matrix involved in MALDI-MS by an active surface. One advantage of this active surface is that the high background obtained with MALDI-MS in the region below the m/z of 700 is eliminated [67]. Instead of the matrix, particles are applied to the sample to act as ion emitters. The known substrates commonly used in SALDI-MS are carbon-based, semi-conductor-based or metallic-based particles [67]. As some of the commercial dusting powders in the forensic field are composed of these type of particles, it was suggested that developing fingerprints with these dusting powders still allows SALDI-MS analysis. Rowell et al. investigated nineteen commercial dusting agents and one new developed dusting agent in combination with SALDI-MS [36]. They found that three of the nineteen dusting powders were compatible with SALDI-MS, including black powder, magnetic iron powder and magnetic black powder. A new dusting powder composed of hydrophobic silica powder was the most effective powder as enhancer for SALDI-MS. This means, that fingerprints can be developed before SALDI-MS takes place, however in forensic practice a change in the use of dusting powders is required, since only three of the nineteen commercial powders are compatible with SALDI-MS [36].

Donor profiling information can be obtained using SALDI-MS. Rowell et al. were able to detect drugs and drug metabolites in spiked fingerprints and in the fingerprint residues of drug users, which had been developed and lifted [36]. This observation makes SALDI-MS an interesting technique to be used in the forensic field. Explosive residues can also be obtained from contaminated fingerprints [40]. SALDI-MS is a fast technique that has a nanogram sensitivity and is able to analyze samples at a high throughput [40, 67]. The surface on which the fingerprints are left has an effect on the resulting spectrum. Fingerprints lifted from plastics and analyzed with SALDI-MS showed lower signal intensities compared to other investigated surfaces, including laminated wood, paper, ceramic tile and metal cans [40]. As the surface can influence the analysis of the fingerprints, it is important to further investigate which surfaces are compatible with lifting and SALDI-MS analysis technique.

4.1.3 DART-MS

Direct analysis in real time – mass spectrometry (DART-MS) can be applied to detect chemicals on different surfaces without any sample preparation. The technique is based on interactions between electronic and vibronic excited-state molecules of the sample and atmospheric gases. The sample is exposed to a stream of excited gas, leading to the ionization of sample molecules. The gas flow can immediately be directed to a liquid or solid, meaning that no sample preparation is necessary [45]. The technique is minimally destructive, leaving the sample largely intact after DART-MS analysis [68].

One limitation of DART-MS is that it can only analyze small molecules up to 1 kDa [46, 69]. Detection of large proteins and molecules is not possible with this technique. The
technique can be used to detect drugs, drug metabolites and explosive residues in fingermarks. Although detection of explosives in fingermarks was possible, the sensitivity of the technique was limited compared to SALDI-MS. No detection of explosives was possible in lifted fingermarks using DART-MS, whereas SALDI-MS could detect explosives in the lifted fingermarks [36]. Food metabolites and spices can easily be analyzed with DART-MS, suggesting that dietary information can be obtained from fingermarks with this technique [45].

4.1.4 DESI-MS
Desorption electrospray ionization – mass spectrometry (DESI-MS), like DART-MS, is known as an ambient ionization technique. The technique can directly be applied to the sample of interest without any sample preparation. Unlike DART-MS, DESI-MS can be used to create a 2D chemical image of the sample [47, 70]. To ionize sample molecules, an electrospray is emitted to generate a spray of charged microdroplets directed towards the sample. Molecules are desorbed, ionized and directed into the MS system [46, 69]. DESI-MS is able to analyze both small and large proteins and molecules up to molecular weight of 66 kDa [46]. The sensitivity of DESI-MS is in nanograms and the spatial resolution is around 150 µm [71]. Molecules that are strongly bound to the surface, including porous surfaces, will cause analysis problems with DESI-MS, because these molecules cannot be desorbed.

Drug metabolites and explosives present in fingermarks can be detected with DESI-MS. Ifa et al. described the detection of drugs and explosives in fingermarks, followed by the development of the fingermark ridge pattern, as depicted in figure 5 [70]. Cocaine, the psychoactive compound of cannabis Δ9-tetrahydrocannabinol (Δ9-THC), and trinitrohexahydro-1,3,5–trazine (RDX, high explosive) could all be detected in fingermarks using DESI-MS [70].

4.1.5 SIMS
Secondary ion mass spectrometry (SIMS) uses a primary ion beam accelerated towards a sample to desorb the sample material. The primary ion beam interacts with the sample material, leading to the desorption and sputtering of secondary ions. These secondary ions are then extracted and analyzed by a mass analyzer [41, 71]. SIMS needs to be performed in high vacuum, meaning that volatile and fragile products are hard to analyze. SIMS enables imaging close to the nanoscale, resulting in spatial resolutions of about 100 nm [71]. Additionally, the sensitivity of this technique is quite high, namely in femtograms. Another advantage is that no sample preparation is needed. However, the surface on which fingermarks are left will influence the measurements. The best results are obtained on conductive and flat surfaces.

Sample consumption by SIMS is low as only the top monolayer is used for analysis, implying that the fingerprint can afterwards be used for other applications. Also, depth
profiles can be obtained, which can be to determine whether exogenous components are on the surface of the fingermark or are embedded in the ridge material. For instance, to determine whether a fingermark was placed before or after a document was written or printed [72]. Large proteins and peptides cannot be detected with SIMS [71].

Sisco et al. analyzed fingermarks with C60 SIMS, in which C60+ ions were used as primary ion source. They investigated the compatibility of SIMS with three different commercial available dusting powders, including black powder, fluorescent powder and magnetic powder. In all cases, spectra could be obtained from the fingermarks after applying the powder. The spectra remained mainly unchanged, however an increase in the relative signal intensity could be observed in the low ranges (0-150 m/z) of the spectra [41]. Figure 6 shows an image of a fingermark that has been visualized using SIMS. The SIMS image is compared with the optical image. This figure shows that SIMS can be used for the visualization of fingermarks.

4.1.6 Chromatography coupled MS

Chromatography can be used prior to MS. Chromatography techniques allow the separation of different components present in the sample. There are two commonly used chromatography techniques, including gas chromatography MS (GC-MS) and liquid chromatography MS (LC-MS). In general, two phases can be distinguished in chromatography, a stationary phase and a mobile phase. In GC-MS, gas is the mobile phase, samples are vaporized, separated and fractioned depending on their affinity with the gas or the column through which the vaporized components need to travel, which is called the stationary phase. In LC-MS, liquid is the mobile phase and separation occurs in a column containing the stationary phase. Both the mobile and stationary phase compositions can be adjusted depending on the affinity of the sample to either phase [64, 73-74].
GC-MS is a high sensitive technique in which fingermark components can be detected in nanogram levels. It is able to identify and quantify components of interest, however two major drawbacks are, first, volatile components cannot be analyzed and second, the technique is destructive as fingermarks need to be dissolved and vaporized for detection and analysis [75-77].

LC-MS is also a destructive technique as the fingermarks have to be dissolved before they can be analyzed. This technique is not limited to volatile components, but the sensitivity is lower than that of GC-MS. Both, GC-MS and LC-MS, have been used to study components present in fingermarks, mostly to study the abundance and distribution of lipids and amino acids in fingermarks of different donors.

Another chromatography technique is thin layer chromatography (TLC). This technique can also be used in combination with MS, and is able to provide additional information on components present in fingermarks. TLC is a simple separation technique that is able to run samples at the same time in parallel and can therefore be used as a fast screening technique. The technique is especially appropriate to separate low-mass organic compounds [78-79]. Compounds that have been separated with TLC can either be visualized directly, or after using a chemical reagent, like ninhydrin, Ehrlich's reagent or iodine vapor. After development of the TLC plates, to separate the compounds present in the sample, MS can be performed on the obtained spots. Most of the above mentioned

Figure 6 Comparison of SIMS fingermark image (A) to visual image (B). SIMS images were collected in negative mode using the signal from the palmitic acid ion. This figure has been adapted and reprinted from Sisco E, Demoranville LT, Gillen G: Evaluation of C60 secondary ion mass spectrometry for the chemical analysis and imaging of fingerprints. Forensic Science International 2013, 231(1-3):263-269 [41]. Copyright 2013, with permission from Elsevier.
techniques can be used in combination with TLC, including MALDI, SALDI and SIMS\cite{78-79}. For the detection of interesting compounds that provide information on the donor of the fingermark TLC is not often used. In a study performed by Lambrechts et al., fingermarks were directly placed on the TLC plates to separate the components present in the fingermarks\cite{2}. They indicated the presence of chlorophyll metabolites, which can be found in green vegetables, suggesting that information on the diet of a donor can be found in fingermarks\cite{2}.

4.2 Spectroscopy

In the forensic field, non-destructive techniques are of special interest for the investigation of fingermarks. As the pattern of the fingermark is of high value in forensic investigation, destruction or distortion of the pattern is unfavorable. A non-destructive and non-invasive technique to achieve additional information from fingermarks is spectroscopy\cite{55}. There are different spectroscopic methods available that can be used to characterize fingermarks. In most cases, the spectroscopic techniques are combined with Fourier transform\cite{60}. Fourier transform is a mathematical transformation that can be applied to the data to transform signal (raw data) into an actual spectrum.

4.2.1 Infrared spectroscopy

Infrared spectroscopy (IR) is based on the vibrations of atoms. Infrared radiation is used to pass through the sample. Depending on the characteristics of the molecules present in the sample, the incident radiation is absorbed at a particular energy, resulting in an absorption spectrum\cite{80}. The technique can be applied to almost any sample, such as powders, liquids, gases and surfaces, providing the proper sampling method is chosen\cite{80}. Because sample preparation is needed, the technique is not entirely non-destructive to fingermarks.

Traditional FT-IR is destructive to the sample, therefore attenuated total reflection (ATR)\cite{26} microscopy is introduced in conjugation with FT-IR, which is minimally destructive to the fingermark\cite{58}. No sample preparation is needed and the background interferences is reduced. In ATR a crystal is used that needs to be in contact with the sample during analysis, causing minimal disturbance of the investigated area. ATR-FT-IR allows for the visual examination of the sample using a microscope and subsequently performs the measurement at the appointed position. Particles of around 20 µm can be visualized and analyzed. Mou et al. used the ATR-FT-IR to distinguish natural fingermarks from fingermarks contaminated with particles of explosive material\cite{58}. Visual examination of the fingermarks with the microscope did not result in discrimination of these fingermarks, because the particles present in fingermarks have the same morphology as particles from explosives. However, differences in FT-IR spectra were obtained, resulting in the discrimination of natural fingermarks and fingermarks contaminated with the explosive. ATR-FT-IR affects the fingermark minimally. After detection, the particles are compressed and larger than before the measurement, but the ridge pattern of
the fingermark is not disturbed as the diameter of the ATR crystal is narrower than the ridge of the fingermark [58].

Depth profiling is also possible with ATR-FT-IR. Ricci et al showed that using a variable angle ATR accessory the imaging of fingermarks at different depths of penetration was possible [53]. Depth profiling can be used to distinguish overlapping fingermarks or determine the order of placement [53]. However, depth profiling using ATR-FT-IR to determine the order of placement of fingermarks is a time-consuming method as reconstruction of the images and data manipulation is necessary [59].

4.2.2 Raman spectroscopy
Raman spectroscopy (RS) is a non-destructive technique, whereby monochromatic light is applied to the sample, causing the inelastic scattering of light [54]. The obtained Raman spectrum is complementary to the IR spectrum. Instead of the absorption of light, the inelastic scattered photons are collected, which allows for the detection of analytes through media, even through glass. Cyanoacrylate fuming and powder do not hamper the Raman analysis of fingermarks [48, 55]. A drawback of the RS is that the Raman signal has a low intensity, due to the low cross-section of spontaneous Raman scattering. Additionally, fluorescence signal from the sample can interfere with the Raman spectrum. To avoid this interference near infrared excitation can be used instead of excitation in the UV region, which causes sample fluorescence [54].

After developing the fingermarks with powder and lifting the fingermarks, RS is still able to spectroscopically detect chemical components in fingermark residue. The choice of lifting tape is important, as some lifting tapes have a high background fluorescence that interfere with the Raman spectrum [48].

To improve the sensitivity of the technique, surface enhanced raman spectroscopy (SERS) can be used. Surface enhancement may result in the improvement of the Raman signal, due to the interaction of the analyte with a metal surface or nanostructure. Chemical enhancement may be achieved and the metal can be used to quench the fluorescent signal [81]. As the intensity of the peaks within the Raman spectrum is increased, more compounds can be detected at once. Nano- and picomolar concentrations can be detected with SERS, making it possible to detect ultra-trace amount of illicit drugs and explosive particles in fingermark residue [54]. Portable SERS is available and the system can be applied to multiple surfaces. However, SERS involves sample preparation as the metals or nanoparticles need to be applied to fingermarks, which might affect the fingermarks for further analysis.

4.2.3 Hyperspectral imaging
Hyperspectral imaging (HSI) is a technique that can be used to achieve both spatial and spectral information from the sample [38]. The hyperspectral camera is able to record visual and spectroscopic measurements simultaneously. Spectroscopic measu-
ments can be obtained by applying different regions of the electromagnetic spectrum, e.g. UV, visible, near-infrared, mid-infrared to the sample of interest. In these regions a wide range of spectroscopic measurements can be recorded by hyperspectral cameras, including absorption, transmission, reflectance, luminescence and Raman scattering. The spatial resolution of HSI is comparable to that of spectrographs [38]. An schematic overview of a HSI system is illustrated in figure 7.

HSI is a non-contact technique, needs no sample preparation and is therefore non-destructive to the sample material. The surface on which fingermarks have been left, however, might influence the measurements. A wide range of porous and non-porous materials are found to be compatible with HSI, although the background interference of some surfaces will cause problems. HSI can be performed in the field, since the HSI camera is portable. Data is recorded digitally, allowing the analysis of the data afterwards [38].

Infrared HSI was used to detect contaminants in fingermark residues. Fingermarks spiked, with ibuprofen, vitamin C, non-dairy creamer and/or sweetener were analyzed using infrared HSI. Spectral imaging demonstrated that specific components in fingermark residue could be detected using automated recognitions. A spectral library was used that compared the intensity and position of the peaks [49]. Raman HSI can be used to detect explosive particles in fingermarks [82]. However, it is not yet possible

Figure 7. Schematic overview of an hyperspectral analysis system. Figure adapted from Edelman et al [38]. This figure has been adapted and reprinted from Edelman GJ, Gaston E, van Leeuwen TG, Cullen PJ, Aalders MCG: Hyperspectral imaging for non-contact analysis of forensic traces. Forensic Science International 2012, 223(1–3):28-39[38]. Copyright 2012, with permission from Elsevier.
to analyze a whole fingerprint at once using infrared HSI and Raman HSI. Microscopic techniques need to be used to specifically detect suspicious particles in the fingerprint residue, which is hindered by the skin particles present in fingermarks.

4.3 Immunolabeling

Another technique to detect specific components in fingerprints is immunolabeling. This technique utilizes the specific properties of antibodies to bind to a specific epitope present on an antigen is used. Antigens, which can be proteins, peptides, hormones, food and drug metabolites can be found in the fingerprint residue. Immunolabeling involves sample preparation in which direct contact between the sample and different buffers is necessary. Depending on the surface, fingerprints are fixed and blocked to inhibit free sites that have the ability to react with the antibodies non-specifically. After blocking, a primary antibody is incubated on the fingerprint. If the antigen of interest is present, the antibody will bind to the antigen with a high-affinity. The excess of unbound antibodies is then washed away. The primary antibody can be conjugated, or “tagged”, to a visual enhancer, a fluorophore or enzyme, which allows the detection of the antigen. Instead of using a ‘tagged’ primary antibody, a secondary ‘tagged’ antibody can be applied to the fingerprint, which recognizes the primary antibody [33]. Immunolabeling involves different steps, which need to be performed in a laboratory. The minimum time of one labeling session can be half an hour, however in most cases, longer incubation times are used, which results in a labeling session of two to four hours. Nevertheless,
the method is non-destructive for the fingermarks, thus after immunolabeling, the fingermarks can be used for additional tests. Antibodies are highly sensitive and specific for their antigen, allowing the detection 1 ng to 10 pg of protein [83]. Immunolabeling cannot be applied on-site at the crime scene.

Immunolabeling can be applied to a large variety of forensic relevant surfaces, such as plastics, tiles, thermal paper and glass, as shown in figure 8 [84]. Several fingermark development techniques have been shown to be compatible with immunolabeling. Ninhydrin staining, powder dusting, indanedione-zinc treatment, physical development and different types of cyanoacrylate fuming can be used to visualize the fingermarks, subsequently immunolabeling can be applied to obtain donor profiling information from the fingermarks or to further develop the fingermark pattern [85-86]. Multiple components can be detected in one labeling session using primary antibodies conjugated to different visual enhancers, such as different fluorophores emitting at different wavelengths [33].

One of the first research groups who described the use of an immunogenic technique to obtain donor profiling information from fingermarks was Ishiyama et al. [43]. They were able to type the ABH-blood group type of fingermark donors using a mixed cell agglutination method, which can also be described as a type of sandwich method. With this method antibodies are used to detect the antigens present in the fingermarks, additionally an indicator cell was added that was able to react with the blood group type specific antibodies [43]. They continued their work, but instead of the determination of the blood group type, they tried to identify the drug metabolites, morphine and methamphetamine in sweat using an homogenous enzyme immunoassay [43]. Morphine and methamphetamine could both be detected in sweat, suggesting that these metabolites will also be present in fingermarks. Other research groups have shown that other drug metabolites can also be detected in fingermarks by immunolabeling. Cotinine, methadone, benzoylecgonine and tetrahydrocannabinol were detected in fingermarks, however in these studies proper control experiments were neglected [31, 35, 56, 87].

Instead of antibodies, aptamers can also be used. Aptamers are short single stranded nucleic acid oligo nucleotides, which can be single stranded DNA (ssDNA) or RNA. Aptamers can be chemically synthesized, whereas antibody production requires animals, which results in more batch to batch variation then the chemically synthesized aptamers [88-89]. Aptamers can be produced against any target, varying from small molecules to large complex mixtures. The shelf-life of aptamers is longer than the shelf-life of the less stable antibodies. However, the use of aptamers instead of antibodies is relatively new and has been introduced in the forensic field recently. Cocaine metabolites could be detected with aptamers conjugated to gold nanoparticles in fingermarks [57]. Thus, both antibodies and aptamers can be used to obtain donor profiling information from fingermarks.
**Table 2a Schematic overview of the different techniques with their advantages and disadvantages.**

*ND=not determined*

<table>
<thead>
<tr>
<th>Technique</th>
<th>Non-Destructive</th>
<th>Sample preparation</th>
<th>Detection limit</th>
<th>Imaging capability</th>
<th>Surface Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>MALDI-MSI [1, 29, 36, 44, 51, 63-65]</td>
<td>Minimally</td>
<td>Yes</td>
<td>fg</td>
<td>Yes</td>
<td>Non-porous</td>
</tr>
<tr>
<td>SALDI-MS [36, 40, 67]</td>
<td>Minimally</td>
<td>Yes</td>
<td>ng</td>
<td>Yes</td>
<td>Porous Non-porous</td>
</tr>
<tr>
<td>DART-MS [36, 45-46, 68-69]</td>
<td>Minimally</td>
<td>No</td>
<td>ng</td>
<td>No</td>
<td>Porous Non-porous</td>
</tr>
<tr>
<td>DESI-MS [46-47, 70]</td>
<td>No</td>
<td>No</td>
<td>ng</td>
<td>Yes</td>
<td>Non-porous</td>
</tr>
<tr>
<td>SIMS [41, 71-72]</td>
<td>No</td>
<td>No</td>
<td>fg</td>
<td>Yes</td>
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<tr>
<td>GC-MS [64, 73-77]</td>
<td>No</td>
<td>Yes</td>
<td>ng</td>
<td>No</td>
<td>None</td>
</tr>
<tr>
<td>LC-MS [64, 73-77]</td>
<td>No</td>
<td>Yes</td>
<td>ng</td>
<td>No</td>
<td>None</td>
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<tr>
<td>ATR-FTIR [53, 58-59, 80]</td>
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<td>No</td>
<td>ng</td>
<td>Yes</td>
<td>Non-porous</td>
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<tr>
<td>SERS [48, 54-55, 81]</td>
<td>Yes</td>
<td>No</td>
<td>pg</td>
<td>Yes</td>
<td>Porous Non-porous</td>
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<tr>
<td>HSI [38, 49]</td>
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<td>No</td>
<td>-</td>
<td>Yes</td>
<td>Porous Non-porous</td>
</tr>
<tr>
<td>Immunolabeling [33, 43, 56-57, 83-84, 86-89]</td>
<td>Yes</td>
<td>Yes</td>
<td>pg</td>
<td>Yes</td>
<td>Porous Non-porous</td>
</tr>
</tbody>
</table>
Table 2b Schematic overview of the different techniques with their advantages and disadvantages.
*ND=not determined

<table>
<thead>
<tr>
<th>Technique</th>
<th>Compatibility fingerprint developers</th>
<th>Limitations</th>
<th>Advantages</th>
</tr>
</thead>
</table>
| MALDI-MSI [1, 29, 36, 44, 51, 63-65] | No, only with special powder that can be used for visualization and as a matrix | • Vacuum conditions  
• Poor reproducibility  
• For each application most effective matrix needs to be investigated, time-consuming  
• Matrix can produce high chemical background interference | • Can be applied on lifted fingermarks  
• Portable |
| SALDI-MS [36, 40, 67] | Powder dusting | • Surface influences analysis | • Can be applied on lifted fingermarks |
| DART-MS [36, 45-46, 68-69] | ND | • Difficulty with background interference  
• Detection of explosives not possible in lifted fingerprints  
• Limited effective mass range (<1kDa) | • Can be applied on lifted fingermarks |
| DESI-MS [46-47, 70] | ND | • High effective mass range | |
| SIMS [41, 71-72] | Powder dusting | • High vacuum conditions | |
| GC-MS [64, 73-77] | ND | • Limited to volatile substances | |
| LC-MS [64, 73-77] | ND | • Less sensitive than GC-MS | |
| ATR-FTIR [53, 58-59, 80] | ND | • Difficulty with impure samples.  
• Not yet possible to analyze whole fingerprint at once | • Can be applied after lifting the fingerprints  
• Portable |
| SERS [48, 54-55, 81] | Powder dusting | • Not yet possible to analyze whole fingerprint at once | • Can be applied after lifting the fingerprints  
• Portable |
| HSI [38, 49] | ND | • Background interference | • Portable |
| Immunolabeling [33, 43, 56-57, 83-84, 86-89] | Powder dusting Ninhydrin Indanedione-Zinc Physical developer Cyanoacrylate | • Background staining  
• Not applicable at crime scene | • Can be applied on lifted fingermarks |
5. DISCUSSION
Although a number of techniques exist that allow the detection of specific components in fingermarks, none of these techniques are currently used during crime scene investigations. As described in this review, besides the ridge pattern additional interesting information can be obtained from fingermarks, such as gender, age of the donor, and whether they came in contact with drugs or explosives. Each described technique has its own advantages and disadvantages making it hard to select one of these as ultimate technique for donor profiling of fingermarks. Furthermore, the visualization of the ridge pattern also depends on the selected technique, adding an additional complication in the decision making process. In table 2a and b, a schematic overview is presented, discussing the techniques including their advantages and disadvantages.

The choice of technique depends on the type of information requested by the investigator. When no prior knowledge is available, the most interesting information will be the gender and age of the donor. If knowledge about the age of the donor is questioned, GC-MS and FT-IR seem to be the best suitable techniques since age estimation of the donor is not yet possible with the other described techniques. Given that GC-MS is a destructive technique and will destroy the fingermark for further analysis, FT-IR will probably be preferred over GC-MS. Gender determination is currently possible only with MALDI-MS, but as a few possible gender biomarkers are described in literature, including DCD-1L, SSL-29 and LEK-45, other techniques, such as immunolabeling, can probably also be used for gender determination [1]. Additionally, a combination of different techniques can be used to obtain more reliable results. Combining the chemical information with the ridge pattern will not only increase the amount of information obtained from the fingermark, but may also lead to other insights since the location of the components in the fingermark may provide intelligence in, for instance, the order of events.

When the donor of the fingermark is known, information like drug usage or handling of certain items, like explosives, might be interesting, which may help in the verification of testimonies. Almost all described techniques can be used to detect drugs and drug metabolites in fingermarks. The choice of technique will be depended on many factors such as the costs, time-effectiveness, destructiveness, sensitivity, specificity and reliability of the method. The circumstances in which the trace has been found, including the surface and the visibility of the trace, will also affect the choice of technique. As not all techniques can be used at the crime scene or directly on fingermarks that have been developed with a fingermark developer, the choice of the possible techniques that can be applied will be narrowed down.

There are several reasons why none of these techniques are implemented in the forensic field. One of these reasons is that there is still a gap between forensic research and the real forensic field. Another reason is, that none of the techniques has been properly validated for fingermark applications. Also, in most studies spiked fingermarks were
used to search for explosive residues or drug contamination. The amount of compound of interest is likely to be higher in the spiked fingermarks, than in real case examples. Additionally, many forensic investigators are not aware of the current developments concerning fingermark evidence. Crime scenes are now only searched for useful fingermarks for the identification process. These fingermarks need to be of good enough quality to use for the crime scene investigation. The amount of traces included in the crime scene investigation is therefore limited. In the Netherlands the average number of useful fingermarks recovered from crime scenes in 2005 was estimated to be 1.8 per latent print case file [90]. Donor profiling can be applied to each type of fingermark trace, including smudged fingermarks, distorted fingermarks and partial fingermarks. Of course, the techniques are not limited to fingermarks only, also other traces, including minimal contact traces, smears, blood, sperm and saliva can be analyzed with the described techniques.

Portable systems are preferred over laboratory work, however, moving the described techniques from the laboratory to the crime scene will be challenging. Portable systems are available, for instance portable HSI and portable RS. Fingermarks that are directly analyzed at the scene of crime are less likely to be exposed to contamination, get lost or get damaged during transport.

Environmental conditions and their effect on fingermark residues should be investigated. Temperature, humidity precipitation and light exposure will all affect the composition of the fingermarks, therefore, it is important to know under what conditions fingermarks can still be used for donor profiling. Upon aging of the fingermark chemical components present in the fingermark will be degraded or disturbed, which might hamper the analysis of the fingermarks.

The surface on which fingermarks are left can also be a limiting factor. In most studies the most appropriate surface has been studied, whereas in casework all conceivable surfaces are included, including non-porous, porous, colored and structured surfaces. As mentioned before, in most cases spiked fingermarks were used, whereas in crime scene investigations fingermarks can be composed of a large variety of components, including components that might hamper the chemical analysis. Additional research should focus on case examples and fingermarks that contain naturally secreted components. For instance, fingermarks donated by drug users should be included in drug-detection studies and compared to fingermarks donated by non-drug users.

**6. CONCLUSION**

Fingermarks contain a lot of information that can provide additional intelligence on the donor of the mark, which can be especially helpful when the identity of the donor is unknown and/or when fingermarks are smudged, distorted and not useful for identification. Donor profiling information from fingermarks includes information on
gender, age of the donor, contact with foreign substances and lifestyle. Different techniques are available that can be used to obtain these types of information. The advantages and disadvantages of each technique are described, varying from: destructive versus non-destructive; applicable to a large variety of surfaces versus applicable to only one surface; no sample preparation versus intensive sample preparation; sensitivity; analysis time and capability of imaging. Depending on what kind of information is questioned and in which specific circumstances the fingermark is found, the best suitable technique can be chosen. We expect that in the nearby future, donor profiling from contact traces, including fingermarks is a standard procedure included in the crime scene investigation.

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