

Composition of fingerprint residue: a qualitative and quantitative review

Abstract

This article describes the composition of fingerprint residue as being a complex system with numerous compounds coming from different sources and evolving over time from the initial composition (corresponding to the composition right after deposition) to the aged composition (corresponding to the evolution of the initial composition over time). This complex system will additionally vary due to effects of numerous influence factors grouped in five different classes: the donor characteristics, the deposition conditions, the substrate nature, the environmental conditions and the applied enhancement techniques.

The initial and aged compositions as well as the influence factors are thus considered in this article to provide a qualitative and quantitative review of all compounds identified in fingerprint residue up to now. The analytical techniques used to obtain these data are also enumerated.

This review highlights the fact that despite the numerous analytical processes that have already been proposed and tested to elucidate fingerprint composition, advanced knowledge is still missing. Thus, there is a real need to conduct future research on the composition of fingerprint residue, focusing particularly on quantitative measurements, aging kinetics and effects of influence factors. The results of future research are particularly important for advances in fingerprint enhancement and dating technique developments.

Keywords: fingerprint, fingerprint, review, composition, aging, influence factors

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1. INTRODUCTION

The composition of skin and perspiration originating from the eccrine secretory glands has already been studied extensively for medical and dermatological purposes [1-6]. However, the information provided in these studies is not sufficient for the forensic scientist working in the field of fingermarks. In fact, the chemical composition of fingermark residue differs qualitatively and quantitatively from the general chemical composition of sweat, because it contains a complex mixture of compounds coming from different glands and not exclusively from the eccrine ones. Numerous contaminants can also be present such as cosmetics, food residue or drugs and their metabolites. Furthermore, in practice, a forensic scientist will never collect fingermarks right after deposition. Therefore, chemical, physical and biological alterations over time will also affect the fingermark residue left on surfaces during a crime and hence modify its initial composition.

Many forensic studies have thus been carried out in order to gain a better knowledge about the precise nature of fingermark residue and its modification over time. These studies concentrated on the chemical characterization of fingermarks, but focused on three distinct objectives:

- 1) The development and/or the improvement of enhancement techniques [1,7-35]
- 2) The development of fingermark dating techniques [13-14,20-21,36-49]
- 3) The capacity to distinguish between people using their personal characteristics (e.g., age, gender) [8,50-52] as well as extrinsic components found in their fingertip secretions (e.g., drugs) [7,9,53-62]

Despite these numerous studies, there has been no recent overview covering the chemical composition of fingermarks since the last review was published in 2001 [17]. Therefore, the present article aims to provide an up-to-date review of the literature regarding the qualitative and quantitative analysis of compounds identified in fingermark residue. Recent developments and improvements in analytical instrumentation and increasing interest on this topic during the last decade have lead to a better understanding of fingermark chemistry. This paper will thus begin with a preliminary definition of fingermark composition and then continue with a detailed description of the compounds identified in fresh fingermark residue originating from different sources (initial composition). The aging of fingermarks will then be considered (aged composition), as well as the variability of the composition due to influence factors. Finally, perspectives in the field of chemical analysis of fingermark residue will be outlined.

2. FINGERMARK COMPOSITION

Numerous analytical techniques have been proposed and tested to elucidate fingermark composition, resulting in an expensive and complex combination of analytical procedures. However, despite the large amount of research carried out on this topic, advanced knowledge has not been achieved yet, mainly because of the technical difficulty of the needed analyses. In fact, determining the composition of fingermark residue is an analytical challenge because of its complex and multifaceted nature, which can be described as a system gathering different states over time as follows:

- 1) **The initial composition:** This corresponds to the transferred fingermark residue immediately after the contact between the finger and a substrate. All compounds having been identified in fingermark residue are taken into consideration.
- 2) **The aged composition:** This corresponds to the evolution of the initial composition over time. Products emerging over time in fingermark residue are also considered.

The two states of the chemical composition of fingermarks are highly variable, because of numerous **influence factors**. When considering fingermark composition, it is therefore necessary to take into account the combination of initial and aged compositions, as well as the role of influence factors (Figure 1).

(Figure 1)

The complexity of the fingermark composition is well illustrated by the difference in effectiveness of fingermark enhancement techniques applied on fresh or old fingermarks. For example, the efficiency of physical developer is known to be higher on aged fingermarks than on fresh ones [63]. While this observation highlights the fact that the composition between fresh and aged fingermarks significantly differs, no fundamental knowledge about specific compounds responsible for this difference is available yet. Among other things, such knowledge would help understand reaction pathways of enhancement techniques, such as physical developer.

Differences in the enhancement quality between adult and children's fingermarks were also observed. In fact, enhanced fingermarks of children seem to be generally of poorer quality than those of adults, due to chemical differences of fingermark residue [16,25,64-65]. The age of the donor is thus one example of influence factors affecting the chemical composition of fingermarks and making it complex (see section 2.3 for more details).

The following sections describe the qualitative and quantitative information available in the literature regarding the initial and aged fingermark composition as well as the different influence factors affecting this composition.

2.1. INITIAL FINGERMARK COMPOSITION

The initial composition of fingermark secretions is a mixture of numerous substances originating from three sources: (1) epidermis, (2) secretory glands in the dermis and (3) extrinsic contaminants. The compounds that have been previously identified in fingermark residue are described below and classified according to their origin.

2.1.1. Compounds from the epidermis

The epidermis is the outermost layer of the skin, which is made of epithelium (tissue formed from cells very densely packed together), divided into distinct strata (layers) (Figure 2). The horny layer (stratum corneum) is the most external layer of the epidermis and is composed of dead cells regularly eliminated through the continuous desquamation process needed for skin renewal [66-68]. During this process, cells migrate through the epidermis from the basal layer (stratum basale) towards the surface in approximately 30 days. Different proteins are expressed during desquamation [31,67,69-74], which could then be transferred to fingerprint residue during contact between the horny layer and a substrate.

(Figure 2)

Only one study identified proteins actually expressed during the desquamation process in fingerprint residue [31]: keratins 1 and 10 (56 and 64 kDa) and cathepsin D (the 48 and 52 kDa forms). This study used sodium-dodecyl-sulfate polyacrylamide gel electrophoresis (SDS-PAGE) coupled with WESTERN blotting to identify proteins and peptides. The overall protein content was estimated at 384 µg per trace, but no detailed quantitative information was obtained for the specific proteins.

In addition to the desquamation process, the purpose of the horny layer is to form a barrier, which protects the underlying tissue from infections, dehydration, chemicals and mechanical stress. This protective role is mainly assured through the hydrolipidic film covering the horny layer. The lipid compounds comprising this film are glycerides and fatty acids (65%), cholesterol (20%), and sterol esters (15%). These compounds are mainly synthesized by the keratinocytes in the granular layer (stratum granulosum), but can also come from the sebum secreted by the sebaceous glands [66-68,75]. Details regarding these compounds are discussed below in the section addressing compounds from the sebaceous secretory glands.

2.1.2. Compounds from the dermis

The dermis is the bottom layer of the skin and contains – among others constituents – five million secretory glands including apocrine, eccrine and sebaceous, whose secretions reach the skin surface through epidermal pores [76]:

- Apocrine glands are found in the genital, breast, inguinal and axillary regions. The compounds emanating from these glands were the subject of only a few studies [22,77-78]. No study has directly discussed their contribution to fingerprint secretions. This lack of details may be due to the technical complications generated through contamination emanating from the eccrine and sebaceous glands and also to the fact that apocrine gland secretions generally play a minor role in fingerprint composition because of their localization. They may however be significant in crimes of a sexual nature [17].
- Eccrine glands are present all over the body without any exceptions and thus play an important role in fingerprint composition. The main constituent of their secretions is water (99%), but many other inorganic and organic compounds have also been identified.
- Sebaceous glands are found all over the body except on the hands and feet. These glands secrete sebum, which is a major component of fingerprint composition. As hands and feet are free from sebaceous glands, sebum is transferred onto fingertips only after contact with other parts of the body (e.g., face and hair).

Numerous publications have studied the compounds secreted by the eccrine and sebaceous glands for dermatological or medical purposes [1-6,68,79-84], but only a few focused on the ones generated by these glands and identified in fingerprint residue. Thus, the sections below summarize relevant information about compounds clearly identified in fingerprint residue.

A. *Compounds from eccrine glands*

(Table 1)

The proteins/polypeptides represent the most abundant group of compounds from eccrine origin present in fingerprint residue (Table 1). However, only a small number of proteins were actually identified in these residues until now. SDS-PAGE was used to identify albumin, keratins 1 and 10 and cathepsin D in fingerprint residue [31,85]. The presence of dermcidin, a peptide playing a protective antibacterial role in eccrine secretions, was additionally identified in fingerprint secretions through immunodetection reactions [31]. Studies using Fourier transform infrared (FTIR spectroscopy) and FTIR-imaging also observed the presence of proteins, but without identifying or quantifying them [8,10,27,50,54].

More exhaustive studies regarding proteins in fingerprint residue were never carried out until now because of the difficulty of such analyses due to low sample concentration (fingerprint residue has a very low protein content) and high background interferences [91-92]. Advanced mass spectrometry techniques with careful sample preparation may yield detailed results in the future, but these techniques are particularly time consuming and costly [93-94].

On the contrary, amino acids in fingerprint residue have been quite thoroughly studied using several different analytical techniques, the oldest one being thin-layer chromatography (TLC) and the most recent being laser desorption ionization techniques alone (LDI) or assisted by a surface (surface assisted LDI, i.e., SALDI) coupled with a time-of-flight mass analyzer (TOF) and mass spectrometry (MS) or imaging mass spectrometry (IMS) (Table 1). This interest for amino acids in forensic science is probably due to the fact that they are target compounds for routine detection techniques used on porous surfaces, such as ninhydrin, 1,8-diazafluoren-9-one (DFO) and indanedione [14].

Many of these amino acids were identified using the following protocol: extraction using different solvent systems (e.g., sodium hydroxide, ethanol, and pyridine), derivatization (e.g., with ethyl chloroformate) and analysis using gas chromatography coupled with mass spectrometry (GC/MS) [11-12,19,45]. Chemical imaging using Raman, FTIR and mass spectrometry (using laser desorption ionization, i.e. LDI) was successfully used to identify fingerprint amino acid composition as well [8,33,35]. However, no quantitative data are available yet. Results were presented as serine ratios (Table 2), with serine being the most abundant amino acid in fingerprint residue (Figure 3).

(Table 2)

(Figure 3)

Concerning lactic acid, this compound was identified and quantified in fingerprint residue through analysis conducted with GC/MS [12,17,45] and high performance liquid chromatography (HPLC) [86]. Infrared microspectroscopy [10] and Raman imaging [33] also allowed for its identification. The sodium salt of lactic acid was also identified through infrared microspectroscopy, but without quantification [10].

Phenol, uric acid and creatinine were all identified in sweat and in fingermark residue through flame photometry in the late 1960s and reported in the last review of fingermark composition [17]. No other studies seem to have focused on the analysis of phenol in fingermark residue, probably because of its very low concentration. On the contrary, uric acid was also identified and quantified using HPLC analysis [86] and creatinine was identified through Raman spectroscopy [33].

Concerning vitamins, a study using laser-assisted thin layer chromatography identified B-complex vitamins in fingermark residue, in particular riboflavin. This compound seems to be responsible for the fluorescence observed in fingermark residue under laser illumination (argon laser, 488-514.5 nm excitation wavelengths) [41]. Choline, a water-soluble essential nutrient usually grouped within the B-complex vitamins, was also identified in fingermark residue using flame photometry [17].

Urea was identified and quantified using GC/MS [12,45,89]. This compound was also identified using Raman imaging [33] and Fourier transform infrared (FTIR) spectroscopy using the attenuated total reflection mode (ATR) [8].

Finally, the following inorganic compounds of eccrine origin were also identified and quantified in fingermark residue: chloride, sodium, potassium, ammonia, calcium, sulphide, magnesium (Table 1). The chloride components of fingermarks are targeted by the silver nitrate method, which is a fingermark enhancement technique used for nearly 150 years especially on paper and untreated wood [14]. The other inorganic compounds identified in fingermark residue are mostly inert compounds (low reactivity and high stability over time) and are therefore not typically targeted for forensic applications [17].

B. Compounds from sebaceous glands

(Table 3)

Many compounds of sebaceous origin were also identified in fingermark residue (Table 3). Squalene, wax esters, triglycerides and phospholipids are the main constituents of sebum produced by the sebaceous glands. Other glycerides, cholesterol, cholesterol esters and free fatty acids are also contained in sebum, but originate mainly from the epidermis (hydrolipidic film).

Free fatty acids represent the most abundant group of lipid compounds identified in fingermark residue using different analytical techniques, the more recent being laser desorption ionization techniques (LDI) assisted by a matrix (matrix assisted LDI, i.e. MALDI) or by a surface (surface assisted LDI, i.e., SALDI) and desorption electrospray ionization (DESI) coupled with mass spectrometry (MS) or imaging mass spectrometry (IMS) (Table 3). The identified fatty acid species are enumerated in Table 4 and molecular structure examples are presented in Figure 4 [11,15,25,37].

(Table 4)

(Figure 4)

Wax esters were also identified in fingermark residue but have generally not been detailed. Only one study identified specific wax esters in fingermark residue but did not provide quantitative data (Table 5) [46]. Wax esters are the result of an esterification between a fatty

acid and a fatty alcohol. The involved fatty acids are linear and frequently contain double bonds. On the contrary, the involved fatty alcohols are mostly saturated. It is interesting to note that these fatty alcohols were never identified in the lipids on the surface of the skin; this may indicate that bacteria are unable to hydrolyze wax esters [95]. In fingerprint residue, wax esters composed of fatty acids and fatty alcohols containing 14 or 16 carbon atoms were the most commonly encountered [46] (Figure 5).

(Table 5)

(Figure 5)

Triglycerides are [esters](#) derived from [glycerol](#) and three [fatty acids](#) (Figure 6). These compounds are also present in fingerprint residue, but have been the focus of only a few studies (Table 3). Recently, a study using laser desorption/ionization time-of-flight mass spectrometry (LDI/TOF-MS) established a list of triglycerides found in fingerprint residue [48] (Table 6). However, as isomeric triglycerides have the same mass, exact identification could not be determined based only on the m/z value obtained through LDI/TOF-MS. Table 6 reports the m/z of the molecules that were conclusively identified through further tandem MS/MS experiments (fragmentation) [48].

(Figure 6)

(Table 6)

Squalene (Figure 7) is the precursor of many steroids including cholesterol and has been very frequently identified in fingerprint residue using quite simple analytical techniques such as thin-layer chromatography (TLC) as well as more advanced techniques such as electrospray ionization (ESI) and liquid chromatography atmospheric pressure chemical ionization (LC-APCI) coupled with mass spectrometry (MS) (Table 3). However, the absence of squalene from adult fingerprint residue left on porous filter papers was also reported, even if this absence seems to be an exception [25]. This compound contains six double bonds and is ramified, giving this molecule a high capacity to react and degrade (Figure 7). This is the reason why oxidation products of squalene were identified in fresh fingerprint residue using GC/MS [25], ESI/MS and LC-APCI/MS [28] as well as FTIR spectroscopy [8,10,27]. These oxidation products are mainly squalene (SQ) hydroperoxides, in particular squalene monohydroperoxide (SQ-[OOH]) (main oxidation product) and SQ-[OOH]₅. Squalene epoxides were also identified [28].

(Figure 7)

Cholesterol (Figure 8) is the most abundant sterol in animal tissues (Table 3). While the sebaceous glands do not normally secrete it, it is contained in sebum. It seems that cholesterol enters into the sebum through blood circulation and through the plasma. Cholesterol identified in fingerprint residue is probably from sebum and epidermal origin [17].

(Figure 8)

2.1.3. Contaminants

In addition to compounds coming from the epidermis and secretory glands, fingerprint residue also contains many contaminants, such as food residue, dust and/or bacteria spores [17].

Cosmetics, like hair products, perfume residue, face or body creams were also quite often identified in fingerprint residue using GC/MS [19,25,37,46]. It should be noted that cosmetics

can be difficult to differentiate from intrinsic fingermark residue, because they may contain lipid compounds that are also naturally present in fingermark secretions, for example, fatty acids (e.g., palmitic acid) or wax esters (e.g., myristyl myristate).

Nicotine contamination was also identified in fingermark residue through surface assisted laser desorption ionization-time of flight (SALDI-TOF) mass spectrometry [96]. The aim of this study was to evaluate if the presence of nicotine in fingermark residue could be used to assess the donor's smoking habits. It was observed that active cross-contamination from a smoker to a non-smoker could occur through handshakes and that passive cross-contamination was also possible through contact with surfaces. However, when comparing the peak intensities, these cross-contaminations occurred at lower levels than the direct contamination due to contact with nicotine during smoking.

Different chemical imaging techniques were proposed for the development of new enhancement techniques for latent fingermarks based on the detection of exogenous materials (illicit drugs, explosives, gunshot residue, aspirin, diazepam and caffeine). FTIR and Raman spectral imaging [53,59,62] as well as time-of-flight secondary ion (TOF-SI) [56] and desorption electrospray ionization (DESI) mass spectrometry (MS) were used to analyze these exogenous substances [61]. However, such applications have a limited usefulness in practice because they do not correspond to routine casework. In fact, cases where a suspect does have enough of these contaminants on his hands are not common and these circumstances are not often known beforehand. Therefore, it is quite unrealistic to propose such techniques to visualize fingermarks in routine cases, even without taking into account that such technologies are not portable and quite expensive. However, it should be noted that future developments of these applications might to some extent have relevance for terrorism investigations.

Finally, drugs (e.g., sulfonamides, L-dimethylamphetamine) have also been identified in eccrine sweat with concentrations being proportional to plasma levels. Aided by their low ionization processes, these drugs seem to enter the eccrine glands through simple diffusion. Furthermore, the metabolite of L-dimethylamphetamine was also found to be secreted in eccrine sweat after consumption of L-dimethylamphetamine [97-98]. Thus, the fingermark residue can probably also contain drug traces due to the consumption of such substances and their integration into the metabolism.

2.2. AGED FINGERMARK COMPOSITION

Like all materials, fingermarks undergo modifications over time (i.e., they age). Thus, the aged composition of fingermarks can be defined as resulting from the chemical, biological and physical processes occurring over time on the initial composition of fingermarks.

Aging can follow many different pathways at varying rates [99]. Alteration and/or disappearance of the initial compounds will occur over time in a continuous process involving a large number of phenomena such as degradation, metabolism, drying, evaporation, migration, oxidation or polymerization.

Several studies on the aging of the initial composition of fingermarks were carried out to gain a better understanding of those mechanisms and their kinetics. These studies mainly concentrated on the aging of amino acids, proteins, fatty acids, squalene, cholesterol and wax esters but were carried out with the following different practical objectives:

- 1) The development and/or improvement of enhancement techniques [8,10,13-17,25,29,34,50]
- 2) The development of fingerprint dating techniques [13-14,17,36-37,49]

The general effect of aging on eccrine fingerprint residue is the loss of water, with water being the main constituent of palmar eccrine sudation [25,38]. In fact, a study reported a loss of 85% of the fingerprint weight over a two-week timeframe and presumed that it was primarily due to the loss of water [25].

Concerning the effect of aging on amino acids, a study on the development of ninhydrin analogues for the visualization of fingerprints highlighted the general stability of amino acids over time. In fact, this study showed that old fingerprints could still be developed on paper with amino acid visualizing reagents [100]; the given explanation is that the amino acids have an affinity for cellulose and can thus remain stable for long periods of time, principally on paper substrates. However, Cuthbertson observed that over a period of 236 days, the amino acid content of a fingerprint left on paper decreased from $0.083 \mu\text{g}/\text{cm}^2$ to $0.046 \mu\text{g}/\text{cm}^2$ [87]. These results tend to suggest that the amino acids are not fully stable over time, but that their concentration still remains high enough to be detected with amino acid visualizing reagents.

Similar observations were also made for proteins present in fingerprint residue. A study on the enhancement of fingerprints using antibody reactions with albumin showed that good quality enhancement was obtained on both fresh and old fingerprints (up to 130 days) [85]. These observations were explained by the stability of the albumin on paper. Another study using FTIR also observed the stability of certain acidic salts, like lactic acid [10].

Concerning chloride and urea concentration in fingerprint residue over time, Cuthbertson observed that, over a period of 236 days, the chloride content was constant (change from $0.223 \mu\text{g}/\text{cm}^2$ to $0.217 \mu\text{g}/\text{cm}^2$ observed, but not significant) and the urea content from $0.083 \mu\text{g}/\text{cm}^2$ to $0.028 \mu\text{g}/\text{cm}^2$ (significant) [87].

However, only limited data exists at present regarding the general behavior of other fingerprint eccrine compounds over time, such as phenol, choline, uric acid, vitamins and creatinine.

The aging of sebaceous compounds is mainly illustrated by their qualitative and quantitative decrease over time, principally squalene, cholesterol and fatty acids [13,15,25,37]. These compounds undergo significant degradation as a function of time, resulting in the production of new constituents, mostly small oxidized molecules [15,25,37]. Squalene, being the precursor of steroids, can degrade through microbial processes, resulting in degradation products such as epoxide, ketones, alcohols and hydroperoxides through reaction with oxygen. These reactions end with the formation of molecules in fully oxidized forms (hexadioic and pentadioic acids). Short fatty acids were mostly observed in old fingerprints and long fatty acids mainly in fresh fingerprints; the authors thus concluded that short fatty acids were derived from the long ones [15]. Cholesterol also degrades upon aging. Cholestadiene or cholestenones are possible degradation products, but were not clearly identified in aged fingerprint residue [25].

Another project (never published) was undertaken at the Savannah River Technical Center (SRTC) in cooperation with the United State Secret Service (USSS) to study fingerprint compounds and their changes over time [17]. Efforts were directed at on the characterization of the degradation products formed over time (principally hydroperoxides) to determine if any of these compounds could be targeted by enhancement techniques. Standard lipids were used as samples (not natural fingerprints) and they were derivatized before being analyzed by GC/MS. Hydroperoxydes were measured using iodine/starch testing and chemiluminescence. The SRTC found that unsaturated compounds are rapidly degraded even under cool, dark storage conditions. Concerning the aging of squalene samples, it was observed that after one month of exposure to ambient conditions, 10% of each sample was composed of hydroperoxides.

The hardening of fingermarks over time was also observed. This phenomenon seems mainly due to the loss of moisture and to the transformation of unsaturated moieties to saturated molecules. These saturated molecules have a more orderly crystal structure, which leads to a more crystalline surface in older fingermarks. This consolidation process of the surface of fingermark residue is similar to that of “drying oils” observed in many natural products. This process causes the materials to darken and thicken on exposure to air, which results in the emergence of a type of varnish [25].

Concerning the aging of inorganic compounds, it was observed that the silver nitrate enhancement technique based on the chloride ions available in fingermark residue is considerably less effective on old fingermarks. This observation is due to the diffusion of chloride through the substrate over time [14,39]. The shape and size of this diffusion pattern was studied by Angst and proposed as a fingermark dating parameter in the early 1960s [39]. However, this technique is highly dependent on the storage conditions of the substrate and the conclusions are mainly subjective and based on the examiner’s experience. This is probably the reason why this dating technique was not studied further.

Additional data in the literature regarding the aging of fingermark residue was generally linked to environmental conditions, particularly with respect to sebaceous components. This information is thus presented in the next section, where the discussion focuses more particularly on the influence factors causing the greatest variability in fingermark residue composition.

2.3. VARIABILITY OF FINGERMARK COMPOSITION: INFLUENCE FACTORS

As described in the preceding sections, fingermark aging occurs over time and this modifies the *initial composition* to give a subsequent state referred to as the *aged composition*. Additionally, many influence factors affect the initial and aged composition of fingermark residue, thus resulting in a very complex and variable matrix.

The variability of fingermark composition is the result of two major successive stages leading to the initial and aged composition (Figure 9):

- 1) **Transfer** leads to the creation of the initial composition through the deposition of a fingermark on a surface. The residue transferred depends on different influence factors, which can be classified into three categories: the *donor characteristics* (e.g., diet, age, gender), the *deposition conditions* (e.g., deposition pressure, contact duration) and the *substrate nature* (porous, semi-porous and non-porous). These factors may be significantly different from fingermark to fingermark, and thus lead to variability in initial composition.
- 2) The **elapsing time** between the transfer of a fingermark on a surface (initial composition) and its discovery results in the emergence of the aged composition. During this elapsed time, three types of factors influence the aging process, leading to variability among the aged composition: the *substrate nature*, the *environmental conditions* and the *enhancement techniques* used to visualize latent marks. Thus, the variability of the aged composition is the addition of the variability of the initial composition (starting point of the aged composition) with the variability of the influence factors occurring over time.

(Figure 9)

The influence factors are particularly important to explain the complexity of fingerprint composition. More information is given in the following sub-sections, based on research that mentions the extent of influence of different factors on the initial and aged fingerprint composition [8,10,14-17,25,29,32,34,36-37,46,49-52,64,96,100-112].

2.3.1. Donor characteristics

The donor characteristics include age, ethnic origin, medication, psychological state, health, metabolism and diet as well as external parameters such as contact with other products such as drugs, food or cosmetics [17,25,37,46,96,109,105-106,110-112].

Studies showed that the **age** of the donor influences fingerprint residue [10,16,25,50-51,64,110-111]. Secretions from children were observed to disappear much more rapidly after deposition on a surface than those of adults. This phenomenon was explained in the literature by the fact that residue from children mainly contains aqueous saline compounds and fewer free fatty acids. These compounds are very volatile and thus disappear quickly. The residue from adults, on the contrary, includes squalene, cholesterol, large fatty acid esters, wax esters and glycerides. These compounds are far less volatile and thus persist on substrates [10,16,25,50,64-65]. Interestingly, residue from adolescents show a very inhomogeneous pattern: some adolescents yielded fingerprints that are only composed of eccrine related compounds, others appeared to secrete sebaceous components in the same way as adults, while some others showed a high amount of cholesterol, even higher than in adult residue. These variations were explained by the maturation process occurring in adolescent metabolism [25,82,84]. In fact, the so-called “puberty” begins at different ages for each adolescent – sometimes with several years’ difference between individuals – what may explain the large variability observed in their secretions. Based on these observations, it is probably possible to predict the onset of “puberty” based on the analysis of the lipid compounds secreted from an individual.

Concerning the inorganic compounds available in fingerprint residue, it is interesting to note that the chloride amount in fingerprint residue is inversely proportional to the age of the donor: the chloride amount decreases as the age of a person increases [34].

The differences in fingerprint composition due to age were investigated in studies aimed at determining the age of a person based on the chemical composition of their fingerprint residue as analyzed by FTIR [50-51]. These studies highlighted that the spectra of children and adults’ fingerprints differed when considering the lipid composition. It was thus proposed to construct calibration curves with combinations of lipid compounds to then infer the age of a person (within 4 years) [51].

The influence of **gender** has also been studied. However, contradictory results were obtained. In fact, Asano [52] and Cuthbertson [34] concluded that no significant differences can be identified in fingerprint residue between males and females (concerning respectively the lipid compounds and the chloride ions), while Buchanan [16] and Hartzell-Baguley [89] highlighted that some compounds (e.g. urea, fatty acids) may be useful to differentiate between genders. In her article, Buchanan explains that differences could be due to the different metabolism processes concerning glands and hormones, which are mainly illustrated by differences in the position of double bonds in the unsaturated fatty acids.

It has also been observed that **diseases and medications** may significantly influence the recovered fingerprint residue. For example, concerning the lipid composition, a person affected by acne has a higher amount of fatty acids and squalene than an otherwise healthy person [17]. However, when this hormonal disorder was treated (e.g. with an anti-acne cream), these compounds were observed to decrease dramatically [46].

Contact with different products, for example drugs or cosmetics, can affect the fingerprint composition, as these products have been identified in fingerprint residue [53,56,59,61-62,96]. Donor habits (e.g., drug consumption) thus influence the composition of fingerprint residue. Contact with food will also influence the composition of the fingerprint residue. No precise study on this influence was reported in the literature, but this parameter was taken into account in published casework [109,112]. Concerning cosmetics, some lipid constituents of commonly encountered products (e.g., face creams and hair gels) have been identified in fingerprint residue [15,17,19,25,46].

Finally, no study has focused on the effect of the **ethnic origin, psychological state or diet** on the composition of fingerprint residue. However, Jones mentions these parameters as factors to be considered when preparing fingerprint samples for comparative chemical studies, because they can affect the fingerprint composition [106].

The above subsection describes the different donor characteristics influencing the fingerprint composition and causing large qualitative and quantitative variability. However, it is unclear if this variability is sufficiently large and reproducible so that the composition can be considered unique, i.e., that each person has their own specific and unique fingerprint composition. However, the study of human body odors and the capacity of dogs to recognize these scents give some indications about this question.

Some very interesting studies highlight the fact that human scent is so variable among individuals, that each human has specific sweat odor patterns that animals such as dogs can detect and even individualize and that can also be analytically differentiated [113-117]. The body odors of humans have been classified in the literature into the three following groups: “primary odor” (genetically based constituents staying stable), “secondary odor” (endogenous constituents influenced by diet and environment) and “tertiary odor” (exogenous constituents, e.g., soaps and perfumes) [113-114]. It seems that dogs principally base their individualization of humans on the “primary odor”. However, tests showed that properly trained dogs are also able to discriminate correctly scents of monozygotic twins, i.e., individuals who are genetically the same, using secondary and tertiary odors [115]. The compounds detected and used by dogs to individualize humans have yet to be clearly identified. Research on human odor composition concluded that human scents are mainly comprised of eccrine and sebaceous secretions as well as scents coming from the microbial degradation of these secretions [113]. One study on the identification of the compounds emanating from human hands has resulted in a list of more than 300 compounds using thermo-desorption (TD) coupled with a GC/MS analysis [117,116]. A more recent study focused on the volatile secretions coming from human hands identified 63 different compounds using solid-phase microextraction (SPME) coupled with GC/MS analysis [113-114]. The compounds identified in these studies are: carboxylic acids, alcohols, aldehydes, hydrocarbons, amides/amines, esters, halides, heterocyclics, ketones, sulfides and thiol/thioesters/sulfonyls.

Numerous compounds have thus already been identified in human body odors. The capacity of dogs to differentiate between individuals based on these compounds supports the hypothesis that human scents are individual, as analytically studied in the publications of Curran [113-

114]. As the compounds identified in human scents are similar to those found in fingerprint residue, it may be hypothesized that the composition of fingerprint residue is also individual.

2.3.2. Deposition conditions

The deposition conditions refer to the pressure, the contact duration, the time of day (e.g., morning, afternoon, night), the dimension of the fingertip area in contact with the substrate, the finger itself and the washing of the hands [11,19,34,37,106-107].

The **pressure** and the **contact duration** between the fingertip and a surface influence the initial composition of fingerprints [106-107]. In fact, a study revealed that the greater the pressure exerted, the stronger the coloration of fingerprints with ninhydrin [107]. The authors concluded that this increase in coloration may be due to a higher amount of transferred compounds.

The influence of the **time of the day** on fingerprint composition was also studied (morning versus afternoon), but this factor seemed to have no significant influence over the initial chemical composition [52]. However, the time of the day could have an influence on the composition of fingerprint residue because of some metabolism aspects. In fact, as mammalian metabolism is mainly regulated through circadian control, i.e., clock-controlled processes roughly corresponding to 24-hour cycles, and thus the rhythmic expression and activity of different compounds can differ during the day [118]. These differences could thus be observed in compounds forming the fingerprint residue.

The **dimension of the fingertip area** being in contact with the substrate could also influence the composition of the fingerprint residue. However, only one study seems to have studied this parameter and concluded that the differences between fingertip dimensions were not significantly correlated with the amounts of squalene and cholesterol measured [37].

One study on the chloride amount found in fingerprint residue showed that the **finger** itself seems also to be a parameter influencing the fingerprint composition [34]. Two main observations were made: (1) the fingers of the left hand left fingerprint residue that contained larger amount of chloride than the fingers of the right hand and (2) the thumb, index and middle fingers gave fingerprints containing significantly smaller amount of chloride than the ring and little fingers. The author suggests that these observations can be explained by the fact that most people are right handed and thus use this hand more than the left one and that they use their thumb, index and middle fingers more than the ring and little fingers. Therefore, the most commonly used fingers lose their secretions because of frequent contact with different surfaces, while the less used fingers can build up and keep larger amount of secretions before coming into contact with a surface.

The **washing of the hands** was not precisely reported in the literature, but is however listed as a possible influence factor when preparing fingerprint samples for comparative chemical studies [106]. In fact, emulsification of the lipid compounds can occur when washing hands with soap and water. A decrease of the concentration of these compounds on the fingertip surface will then occur and thus modify the fingerprint composition.

2.3.3. Substrate nature

The influence of the substrate on the fingerprint composition is dependent upon the porosity of the substrate and its capacity to retain compounds. This will in turn be dependant upon its texture, physico-chemical structure, curvature, temperature, electrostatic forces and surface free energy (related to surface tension). The physico-chemical processes occurring on the surface and inside the substrate are thus of great importance and a study concluded that the more porous the surface was, the higher the adhesion forces were and thus the more the fingerprint compounds migrated into the substrate [101]. It was also observed that the depth of penetration of the residue in the substrate was proportional to the support porosity; the more porous the substrate was, the more significant the penetration. The same study measured the mean penetration depth as being between 40-60µm [102]. The paper surface free energy is another factor influencing the penetration depth of fingerprint residue into paper. In fact, while paper with low surface free energy reacts rather in the same way than non-porous surfaces (good enhancement quality with cyanoacrylate fuming, low residue penetration), paper with higher surface free energy shows the same behavior than porous surfaces (good enhancement quality with amino acid visualizing reagents, significant residue penetration) [124]. The different types of substrates are summarized in table 7.

(Table 7)

The initial amount of squalene and cholesterol on different substrates was studied [37]. It was observed that these amounts were higher for both compounds on microfilter paper, normal paper and polyvinylidene difluoride (PVDF) paper than on glass surfaces. The behavior of some lipids in fingerprint residue was also reported in the same study. The concentration of squalene decreased very rapidly over the first day and could not be detected after seven days on glass (non-porous). On the contrary, its diminution was significantly slower on filter paper (porous) because squalene was still detectable after 30 days. The same tendencies were observed for cholesterol; its diminution was slower on filter paper than on glass. Another study on the chloride available in fingerprint residue reported the same observations; fingerprints left on a non-porous surface (aluminium foil) contain less chloride than fingerprints left on a porous surface (filter paper) [34].

These results support the observations described above [101].

Finally, it is also important to note that the adhesive forces are inversely proportional to temperature. In fact, when touching or holding different objects, the lipid fingerprint compounds stick to the surfaces because, in most cases, those objects are cooler than the human fingertip [101].

2.3.4. Environmental conditions

The relevant environmental conditions include humidity, light exposure, temperature, dust, rain, condensation, friction, air circulation and contaminants present in the atmosphere or on adjacent materials or surfaces [36].

Exposure to high **temperatures** was tested and FTIR analyses showed that the higher the temperature, the more rapid the ester degradation. Furthermore, small molecules appeared and were identified as volatile degradation products [8,10]. High temperatures also have a significant influence on amino acids in fingerprint residue [29,32]. Degradation of amino acids into smaller molecules was observed to occur faster when the temperature increased than at a stable room temperature. The degradation process for urea in fingerprint residue was also found to accelerate through exposure to high temperatures [8]. On the contrary, acid salts were

much more resistant to high temperature; after heating at 70°C for 72 hours, their presence could still be observed through FTIR analysis [10].

Exposure to **light** is another factor that was observed to influence the composition of fingermarks. Squalene, for example, was observed to disappear much faster when exposed to light than in the dark. On the contrary, for saturated fatty acids, an increase was observed up to 20 days followed by a decrease below the initial amounts for fingermarks exposed to light as well as stored in the dark [15,32]. These observations can probably be explained by the breakdown of triglycerides into fatty acids by bacteria causing first an increase in fatty acids followed then by a decrease when triglycerides have been completely broken down.

In dark conditions with no airflow, a temperature of 20-25°C and a relative humidity of 40-80%, the compounds containing double bonds (e.g., squalene, palmitic and oleic acid) appeared to substantially decrease both qualitatively and quantitatively over one month, the main loss occurring during the first week. The saturated compounds (e.g., palmitic and stearic acid), the wax esters and cholesterol decreased as well, but slowly. Moreover, saturated acids with low molecular weight also appeared to increase over time, originating from the oxidation products of squalene and some fatty acids (e.g., nonanoic, hexadecanoic and pentadecanoic acids) [37].

Other studies observed the negative influence of **electron beam irradiation** [103] and **formaldehyde** (used for biological agent decontamination) [104]. These studies were carried out to assess the influence of these factors on the enhancement of fingermarks using different techniques. As low enhancement quality was observed, it was concluded that the fingermark residue was adversely affected by the treatments.

The effect of **humidity** on fingermark composition was not directly studied but research on the enhancement quality of fingermarks depending on the humidity level was conducted [34,119]. In fact, Cuthbertson observed that the higher the humidity rate is, the worse the quality of enhanced fingermarks using the silver nitrate technique [34]. A more recent publication concerning the effect of humidity on the effectiveness of cyanoacrylate fuming for fingermark development highlighted the fact that at high humidity, eccrine fingermarks presented a higher enhancement quality than sebaceous ones [119]. It has thus been suggested that sodium chloride salt crystals (comprised in the eccrine secretions) absorb more water into fingermark ridges at higher humidity and that the water molecules are then responsible for initiating polymerization, thus resulting in a larger quantity of cyanoacrylate deposited on the ridges (i.e., higher enhancement quality). On the contrary, it is thought that some specific proteins (mucoproteins, the type of glycoproteins mainly found on the surface of the epidermis, in the horny layer) protect lipid secretions by forming a barrier against humidity, thus resulting in poorly enhanced sebaceous fingermarks at high humidity. It therefore appears that eccrine constituents of fingermarks are more affected by humidity changes than the sebaceous compounds [119].

These results therefore support the hypothesis that humidity influences the compounds available in fingermark residue. However, as enhancement quality is assessed in a subjective way and is largely dependent on the enhancement technique used, this parameter is probably not the best adapted to reliably determine the effect of humidity on the fingermark composition. Precise qualitative and quantitative data on fingermark composition after exposure to different humidity rates are thus missing.

The effects of **dust**, **friction** and **air circulation** on fingermark composition have not been precisely addressed in published studies, although these parameters are generally considered as

possible influence factors that should be controlled when preparing fingerprint samples for chemical analysis [106].

2.3.5. Enhancement techniques

Enhancement techniques will also influence the composition of fingerprint residue in operational cases. In fact, when a fingerprint is enhanced for visualization purposes, different solvents or compounds (e.g., powders) are applied to this fingerprint and hence influence its composition. This influence will depend on when the enhancement techniques are applied; right after deposition of the fingerprint or later. However, in practical cases, enhancement techniques will mainly be applied when the fingerprint is already a few hours or even days old, because crime scene technicians seldom encounter fingerprints immediately after they were deposited by a perpetrator.

Only one study observed the effects of enhancement techniques on fingerprint composition and focused only on the initial composition [46]. The fingerprint lipid residue was analyzed using GC/MS after the application of the following common enhancement techniques: indanedione, aluminium fingerprint powder (also called “argenteratum”; powder composed of flat aluminium particles and 3–5% (w/w) stearic acid) [120-122] and cyanoacrylate fuming. The results focused on three lipid compounds: squalene, cholesterol and myristyl myristate. It appeared that aluminium powder did not influence the qualitative analysis but contaminated the samples, thus affecting the resulting chromatograms. Contamination was also observed after treatment with indanedione. Furthermore, the solvent used in the indanedione formulation influenced the recovered amount of compounds. For example, when dichloromethane was used, significantly smaller amounts of squalene, cholesterol and myristyl myristate were found. This loss of quantity could be due to the capacity of the solvent to extract the lipid compounds during the enhancement protocol. Finally, cyanoacrylate fuming did not significantly influence the recovered amounts of the three targeted lipids and no contaminants were found in the analysis.

2.4. SYNTHETIC FINGERMARK COMPOSITION

In order to improve and develop enhancement techniques, numerous fingermarks are generally deposited on different surfaces before being developed with the tested techniques. The composition of the fingermark residue will influence the quality of the obtained results. Thus, the variability in naturally deposited fingermarks can impact on the assessment of the effectiveness of an enhancement method.

For this reason, attempts to produce synthetic fingermark secretions have been made [17]. In fact, sebaceous and eccrine synthetic secretions are now available on the market and aim to help fingermark examiners to standardize fingermark deposition. However, the composition of these synthetic secretions remains confidential and questionable results have sometimes been obtained using certain enhancement techniques focused principally on sebaceous compounds. For example, aged synthetic residue revealed with physical developer showed poorer quality in comparison to naturally aged fingermarks. This observation is contradictory to the fact that the physical developer usually yields good results on aged samples (up to 50 years) [63,123]. This difference in effectiveness between natural and synthetic fingermarks clearly indicates that the constituents of these synthetic fingermark secretions do not correspond to the natural sebaceous compounds found in fingermarks. The difficulty to reproduce natural fingermark secretions illustrates the lack of knowledge of fingermark composition and highlights the necessity of future research on the topic.

Thus, although studies to standardize fingermark deposition could indeed be useful, more precise knowledge about fingermark composition must still be obtained in order to create synthetic secretions corresponding to real fingermark specimens.

However, problems are still going to remain when using synthetic residue. For example, improper storage may lead to degradation of the compounds in solution, particularly for the sebaceous residue (lipids being very sensible to environmental factors such as light or temperature). Furthermore, the eccrine and sebaceous solutions should be mixed in order to obtain secretions corresponding to real fingermark residue. However, this mixture would require emulsification to become a truly homogeneous solution.

The behavior of synthetic solutions over time and exposure to different storage conditions should also be further studied. Given limited current knowledge, it is thus recommended that natural latent fingermarks continue to be used to confirm any results obtained using commercial synthetic solutions.

3. CONCLUSION & PERSPECTIVES

Fingerprint composition is a complex and variable system described by the *initial composition* (i.e., transferred fingerprint residue right after contact between a finger and a surface) and the *aged composition* (i.e., evolution of the initial composition over time). Moreover, five main types of influence factors were identified as affecting this system: the donor characteristics, the deposition conditions, the nature of the substrate, the environmental conditions and the enhancement techniques.

Numerous compounds of eccrine and sebaceous origin have been identified in fingerprint residue using many different analytical techniques. It would be unrealistic to obtain a comprehensive list of all compounds available in fingerprint residue, particularly if the fingerprint composition is highly variable and unique to an individual, as suggested in this paper. However, more precise information on **quantitative data**, **aging kinetics** and effects of **influence factors** could be obtained but remains generally unavailable. The lack of knowledge regarding these three topics seems to be due to two main causes:

- 1) *Lack of utility in operational work*: as the available enhancement techniques are working relatively well, there is no urgent operational interest to know precisely what happens to fingerprint residue over time or what the effects of influence factors are. While such information is important to improve our fundamental knowledge of fingerprint residue, it is not the focus of current operational research programs.
- 2) *Technical difficulties involved with such studies*: samples need to be prepared and stored under controlled conditions to conduct aging studies, taking into account influence factors. Numerous samples are necessary to obtain significant quantitative results and high performance analytical methods are often required. These aspects thus complicate and slow down research, resulting in a lack of data in this particular field.

However, a better in-depth fundamental knowledge on fingerprint composition would prove to be important for **advances in fingerprint enhancement and for the development of reliable fingerprint dating methods**.

In fact, it is necessary to possess qualitative and quantitative data concerning the compounds available in fingerprint residue to develop or improve enhancement techniques, particularly when focusing on target compounds that have received little attention to date. Moreover, information on aging kinetics and effects of influence factors on fingerprint composition is needed in order to understand the reaction pathways for existing enhancement techniques (e.g., physical developer).

Research concerning the dating of fingerprint residue could also take advantage of the information gained through research efforts focused on the initial and aged composition (including the effect of influence factors). In fact, the most promising dating approach relies on the use of aging curves built by quantifying intrinsic fingerprint compounds (or ratio of compounds) over time [37]. Thus, the initial fingerprint composition and its aging kinetics are of primary importance for this particular application.

Concerning the analytical techniques used to gain more information about fingerprint composition, it was not the aim of this review to give precise directives because all analytical techniques enumerated in this review could be used for this purpose. However, the following recommendations can be made:

- 1) As shown in this review, **GC/MS** has often been used to study eccrine and sebaceous fingerprint residue, probably because it is a relatively simple and inexpensive technique to implement. Thus, GC/MS could be employed to gain more quantitative information on the wide range of lipids and amino acids available in fingerprint residue.
- 2) In order to explore the protein content of fingerprints, more **advanced mass spectrometry techniques** should be tested, comprising modern ion sources (e.g. DESI, MALDI, SALDI) and mass analyzers (e.g., TOF, Quadrupole, Orbitrap). However, it has to be noted that such techniques are quite expensive. Furthermore, in order to obtain quantitative data concerning proteins, high performance analytical methods and well trained analysts are necessary because the task remains particularly challenging [93-94].
- 3) **Chemical imaging techniques** (FTIR, Raman, and mass spectrometry) should also be taken into consideration as exploratory techniques to study fingerprint composition. In fact, such techniques have garnered much interest in forensic science in general as well as in the field of fingerprints because of their ability to identify and map the compounds present in complex biological samples [35].

In conclusion, this review provides an update on the compounds that have been studied in fingerprint residue and their variability. Furthermore, it highlights the missing fundamental knowledge on fingerprint composition and the need to conduct future research on this topic to help to develop the fingerprint analysis field. Quantitative data should be collected on all compounds identified in fingerprint residue and aging kinetics should also be studied in detail, in order to gain more information on the reactions occurring over time and how these are affected by several types of influence factors.

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