REVIEW



Recent progress on fingerprint visualization and analysis by imaging ridge residue components

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Abstract Fingerprints have long been and are still considered to be the gold standard for personal identification in forensic investigations. Developing or enhancing the visualization of invisible fingerprints, so-called latent fingerprints (LFPs), remains to be the core subject in forensic science. Moreover, the past few years have witnessed a renewal of research interest in the possibility that a fingerprint can provide additional information than just identification of individuals, such as personal traits, the presence of human metabolites with diagnostic values, and the evidence of contact with explosives or illicit drugs. Fingerprint analysis has manifested itself as a research area far beyond the scope of forensics, to which not only conventional fingerprint examiners but also researchers from chemistry, biochemistry, medical science, material science, and nanotechnology fields have made significant contributions in recent years. Beginning with a brief overview of the components present in LFP residue that essentially determines which method or reagent will give the best visualization result, this paper reviews the progress since 2007 on new reagents and methods developed for LFP visualization and simultaneous detection of specific chemicals present in the LFP residue, with an emphasis on the utilization of mass spectrometry, infrared spectroscopy, nanoparticles, and immunogenic and nucleic acid reagents.

Bin Su subin@zju.edu.cn **Keywords** Latent fingerprints · Forensic science · Visualization · Component recognition · Analytical chemistry

Introduction

The corrugated skin on the human fingertips contains a pattern of interleaved ridges and furrows, which has naturally developed to fulfill the evolutionary requirement for the exudation of perspiration, tactile facility, and provision of a friction surface. Such a pattern, as well as its impression left on the object surface, is termed fingerprint or fingermark. The ridge sequence of a fingerprint remains unchanged in a person's entire life, once fully formed at about 7 months of fetus development [1]. Superficial injuries, such as burns, abrasions, or cuts, will not generate permanent changes in the ridges because their formation roots in the underlying dermis layer. Secondly, the ridge characteristics/minutiae, classified as three levels of details, are absolutely unique. No two fingerprints ever have been found with identical characteristics, no matter whether they are from the same person or from different individuals. In addition, the fingerprint ridges are unclean, due to the deposition of perspiration through the pores of sweat glands and other contaminated substances occasionally picked up by the fingertip. Hence, whenever the fingertip touches an article, an exact impression of the ridges will be left on the surface, just like an inked rubber stamp leaves its impression on a piece of paper [2, 3]. Aforementioned unchanged, unique, and unclean ("3U") characteristics underlie the everyday use of fingerprints in personal identification and creditability.

The use of fingerprint ridges as a means for identification and individualization has a long history. It was used as a form of signature in old days on legal documents, scripts,

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and antiques to prevent imitation and counterfeit, although people at that time might not have been utterly aware of the individuality of fingerprints. Only after the systematic and scientific study and classification in the 19th century, fingerprint recognition has been formally accepted as a valid personal identification method, in particular in forensics. Since the first use of fingerprints for collecting a criminal conviction [4], latent fingerprint [(LFP) refers to the fingerprint invisible to naked eyes] development and comparison remain a standard routine in modern criminal investigations and law enforcement despite the rise of other methods such as DNA profiling [5]. The basic principle of LFP development is to generate a distinct contrast between the ridges and substrate surface by logically applying one or a sequence of physical, chemical, and instrumental techniques [6]. The selection of methods rests on the nature of the surface on which the LFP is deposited, the type of matrix of the LFP, and the condition of the LFP.

The fingerprint residue is a complex system composed of numerous compounds coming from different sources [7, 8]. Knowledge on the composition of the ridge residue helps in the detection and development of LFPs, and even determines which method will give the best results. For example, the well-known chemical development method using ninhydrin or 1,8-diazafluoren 9-ONE is based on the selective staining of amino acids in the LFP residue [9]. On the other hand, the past few years have witnessed a renewal of research interest in the possibility that a fingerprint can provide additional information about the donor than just identification [10], such as gender [11], age [12], personal diet and lifestyle [13], the presence of human metabolites with diagnostic values [14], and the evidence of contact with explosives or illicit drugs [15, 16]. This new trend has attracted not only conventional fingerprint examiners but also researchers from chemistry, biochemistry, medical, material, and nanotechnology fields. Fingerprint analysis has manifested itself a research area far beyond the scope of forensics. The intention of this review is to provide an overview of the recent advances in the development and visualization of LFP with an emphasis on the chemical and biochemical information obtained from the developed fingerprints.

Chemical composition of fingerprint residue

Determining the composition of fingerprint residue is an analytical challenge, although a large amount of research has been carried out. The ridge residue is a complex mixture of numerous compounds originating from different sources and processes, such as epidermal renewal, secretions by secretory glands in dermis, and exogenous contaminants (such as cosmetics, food residue and drugs).

Compounds from epidermis

The epidermis is the outermost layer of the skin [7]. Epidermal renewal refers to the regular desquamation process, in which epidermal cells migrate from the basal layer (the innermost layer of epidermis) to the horny layer (the outermost layer of the skin) and are converted to keratin. In this process, different proteins are expressed, two of which, keratins 1 and 10 (56 and 64 kDa) and cathepsin D (48 and 52 KDa), have been identified in the fingerprint residue [17]. Keratinocytes in the epidermis are known to produce a variety of antimicrobial peptides to the skin surface, including human β-defensin (HBD)-1, HBD-2, HBD-3, LL-37, adrenomedullin, and lysozyme. They are believed to display the antimicrobial activity by inhibiting the growth of, or killing directly bacteria [18], but the identification of these antimicrobial peptides in fingerprint residue has not been reported yet. In addition, the epidermis also physiologically functions as a barrier to protect the underlying tissue by the formation of a hydrolipidic layer consisting of lipid compounds, such as glycerides and fatty acids (65 %), cholesterol (20 %), and sterol esters (15 %) [8]. As discussed further below, these compounds also exist in the sebum secreted by the sebaceous glands.

Compounds from secretory glands

The underlying layer of the skin is the dermis, which contains a large number of secretory glands (mainly apocrine, eccrine, and sebaceous glands) responsible for the secretion of sweat. Sweat composition has been extensively analyzed in the medical community for many purposes [19–23], including attempts to diagnose certain diseases (such as cystic fibrosis) and studies of skin conditions (such as acne). The perfume and cosmetics industry also has an interest in determining the precise chemical composition of perspiration and its interaction with their personal hygiene products [24].

Apocrine glands are found primarily in the axillary, inguinal, and genital areas. They open to the hair shafts and secrete milky and odoriferous substances [25], in which proteins, carbohydrates, and cholesterol have been found. However, their contribution to the fingerprint residue has never been discussed because of the contamination from eccrine and sebaceous glands. Considering their restricted location, it can be assumed that the apocrine secretions play a minor role in the fingerprint residue.

Sebaceous glands are present on most skin surfaces with the greatest density on the scalp, forehead, and face. Most of sebaceous glands open to the hair follicular canals, through which a lipid-rich fluid known as sebum is secreted to the skin surface. The sebum protects the hair from drying out, keeps the moisture of skin surface and skin soft, and inhibits the growth of certain microbes. There are considerable varieties of compounds found in sebum, such as triglycerides, fatty acids, wax esters, squalene, and cholesterol, as well as a number of trace organic compounds (e.g., ketones, aldehydes, amide, tertiary amines, heterocyclic compounds, haloalkanes, and mercaptans) [7, 8]. Fingertips occasionally make contact with the face, forehead, or scalp to increase the sebum content of the perspiration on the fingerprint ridges.

Eccrine glands are present all over the body without exceptions, with a higher density on the forehead, the palms of the hands, the soles of the feet, and in the axillae [18]. Eccrine glands open directly to the skin surface via the sweat pores and secrete a hypotonic solution (sweat), which consists of 98-99 % water and numerous inorganic and organic constituents. Chloride salts occupy a significant percentage in the inorganic constituents, the levels of which are found to be isotonic to that in plasma and have been utilized to diagnose cystic fibrosis [26]. The presence of chloride in the fingerprint deposit also underlies the enhancement method using silver salts [27, 28]. Amino acids present in eccrine sweat and fingerprint residue have been extensively studied because they are target compounds for LFP development by ninhydrin, 1,8-diazafluoren-9one, and indanedione [9]. The total amount of amino acids in eccrine sweat has been estimated to be 0.3-2.59 mg/L, depending on the individual and the health, diet, gender, and age [7]. However, no quantitative data for respective amino acids has been achieved yet. The amount of amino acids in the fingerprint residue is usually represented by the relative abundance, with serine being the most abundant one [29-32].

Protein and polypeptide are the most abundant compounds in eccrine sweat with a total content of 15-25 mg/dL [7]. The presence of more than 400 proteins and polypeptides have been mentioned in human sweat, such as albumin, $Zn-\alpha_2$ -glycoprotein, α_1 -acid glycoprotein orosomucoid, α -lipoproteins, β -lipoproteins, γ -globulins, lysozyme, and transferrin [33–35]. Some of the proteins found, for examples IgA and IgG antibodies, are associated with the innate immune response [18]. A protein known as dermcidin has been found in human sweat (as shown in Table 1), which undergoes proteolytic cleavage to produce a 47-amino-acid peptide with antibacterial activity [18]. Epidermal growth factor (EGF) has also been detected but its biological function remains unexplored [36]. However, owing to their low concentration and high background interference, only a few proteins have been identified in the fingerprint residue, including albumin [37-39], keratins 1/10 [17, 39], cathepsin D [17],

dermcidin [17, 38-41], lysozyme [42-45], and EGF [44, 45], by using immunogenic or nucleic acid reagents, and psoriasin by matrix assisted desorption ionization (MALDI) mass spectrometry (MS) [11]. In addition, tryptophan-containing proteins have also been proposed to exist in the fresh fingerprint residue as the main origin of autofluorescence [46, 47].

Many other organic molecules have been identified in fingerprint residues, such as lactic acid, phenol, choline, urea, uric acid, and creatinine [7, 8, 48-51]. Riboflavin, a B-complex vitamin (likely responsible for the fluorescence of fingerprint residue under laser excitation in the 488-514.5 nm range) and choline (a hydrophilic nutrient grouped within the B-complex vitamins) also appear in fingerprint residue [7, 52]. Various drugs and their metabolites, such as nicotine and its metabolite (cotinine), heroin and its metabolite (morphine), Δ^9 -tetrahydrocannabinol, cocaine and its metabolite (benzoylecgonine), methadone and its metabolite (2-ethylidene-1,5-dimethyl-3,3diphenylpyrrolidene), have been detected in LFP residue [14, 15, 48, 53–57]. The detection of these compounds enables not only the visualization of LFPs but also the collection of the information on the donors' personal lifestyle. It also provides a potential approach for medical diagnosis as highlighted by Wolfbeis [58]. In fact, according to the exocrine physiology study, a large number of organic species found in the human sweat have potential values for this purpose. For example, the concentration of glucose in eccrine sweat is 0.2-0.5 mg/dL, which increases with the increase of the blood glucose level [36]. Ethanol as well as many other volatile organics are also present in the eccrine sweat [7]. However, whether these organic species also exist in fingerprint residue lacks sufficient investigation. If they do and their concentration is isotonic to that in blood or plasma, noninvasive detection methods can be developed for diagnosis (for certain diseases) and access/safety control (e.g., driving test and athlete screening).

Simultaneous LFP and component visualization—beyond forensic purpose

Fingerprints have long been used as the gold standard for personal identification in forensic investigations, and continue

Table 1 A summary of proteins/
polypeptides identified in
ingerprint residue

Proteins/peptides	Analytical techniques	References
Albumin	Immunogenic reagent	[37–39]
Keratine 1/10	Immunogenic reagent	[17, 39]
Cathepsin D	Immunogenic reagent	[17]
Psoriasin	MALDI MS	[11]
Dermcidin	Immunogenic/nucleic acid reagents	[17, 38–41]
Lysozyme	Immunogenic/nucleic acid reagents	[42-45]
Epidermal growth factor	Immunogenic reagent	[44, 45]
Tryptophan-containing proteins	Fluorescence spectroscopy	[46, 47]

to be the most reliable tool in crime cases and law enforcement. However, LFPs are invisible and thus require some means of development or enhancement for their visualization. So far, innumerable physical, chemical, and optical methods have been exploited, most of which rely on specific components in LFP residue, their potential reactions and interactions, as well as surface characteristics. Given the ineffectiveness of these conventional methods on some complicated surfaces and their drawbacks (e.g., inevitable destruction on the fingerprint details and health hazard to the examiners in the case of the powder dusting), there remains a strong need for new, more efficient, and user-friendly reagents/methods. Various novel reagents and methods, such as nanoparticles (NPs), fluorescent organic and polymer reagents, MS, infrared spectroscopy, and electrochemistry approaches, have been developed in the past few years for forensic LFP detection [59, 60]. Apart from the concern on the forensic purpose, recent research has also focused on the possibility that developed fingerprint can provide additional intelligence than just an image for suspect identification [10, 59]. For example, identification of endogenous and exogenous substances contained in LFPs is important to acquire evidence of criminal identities and contacts with specific chemicals. Additionally, these substances may reflect personal diet and lifestyle, and may be valuable for personal health diagnosis and safety/access control in public areas. This section will present an overview of simultaneous LFP and component imaging since 2007 using MS, infrared spectroscopy, and immunogenic and nucleic acid reagents.

Mass spectrometry (MS) imaging

As presented in the second section, various compounds that originate in eccrine and sebaceous glands have been quantitatively detected by various MS techniques in early studies [8]. Desorption electrospray ionization (DESI) MS is an ambient technique, which features the advantage for in situ analysis of ordinary samples in their native environment without treatment. Cooks et al. have pioneered the utilization of DESI MS for the chemical imaging of LFPs on the basis of spatial MS detection of different endogenous components, such as cis-hexadec-6-enoic acid, stearic acid, cis-octadec-8-enoic acid, palmitic acid, pentadecylic acid, myristic acid, and triacylglycerols, as well as small amounts of drugs of abuse such as cocaine and Δ 9-tetrahydrocannabinol, and contaminated explosives such as 1,3,5-trinitroperhydro-1,3,5-triazine [15]. In DESI, a solvent is electrosprayed onto the fingermark sample surface to generate the secondary scattered droplets, which carry the fingerprint components and are subsequently evaporated, ionized, and analyzed. By rastering the stream of charged droplets across the surface, mass spectra at each point on the surface are recorded. Eventually, the two-dimensional mapping MS signals of a certain fragment ion can retrieve spatial distribution of compounds investigated and can be simultaneously used to construct images of fingermark ridge details.

Since then, various other MS techniques, such as surface assisted laser desorption/ionization time-of-flight (SALDI TOF), MALDI, time-of-flight secondary ionization MS (ToF-SIMS), laser desorption ionization (LDI), and desorption electro-flow focusing ionization (DEFFI) have been introduced [61-66]. Various endogenous and exogenous substances have been identified and spatially mapped to construct LFP images. The chemical analysis of endogenous components is expected to provide information on personal traits, such as nutritional habits, drug use, hormonal level, and sexuality. Ferguson et al. demonstrated that the direct detection of peptides and proteins in fingermarks by MALDI MS profiling, along with the multivariate modeling of the spectra, enables the determination of sex with 85 % accuracy [11]. Very recently, Zhong et al. used an electron-directed soft ionization technique, termed laser activated electron tunneling, for MS imaging with improved spatial resolution and quantitative capability. Two estrogens, namely dienestrol and diethylstilbestrol, have been identified in female fingerprints with intensities comparatively higher than those in male fingerprints. Although the sex determination based on the hormonal level in LFPs is not that reliable because of its variation with physiological status, diet and ages, this technique offers the possibility of monitoring prohibited hormones abuses in cosmetic skin care products [67].

The detection and mapping of exogenous substances in LFPs would provide intelligence that is beneficial for police investigations, court cases, and safety/access control. For examples, recent studies have proven the versatility of the MS imaging technique to detect gunshot residues and explosive compounds in the fingerprint residue, and simultaneously by using their ion signals to construct ridge patterns for identification [15, 65, 68-70]. Another interesting work by MS imaging was the visualization of LFPs contaminated by compounds associated with sexual assaults, for instance condom lubricants (such as polyethylene glycol, polypropylene glycol, nonoxynol-9, and tween) [66, 71, 72]. In this scenario, the fingerprint image obtained simultaneously to the detection of lubricants enables forensic officers to link the assailant suspect (identification through fingermark ridge pattern) to the crime (detection of condom lubricant) in one analysis.

MS imaging approaches are advantageous in terms of their sensitivity and excellent specificity in identifying unknown and suspected molecules. Not only can different chemicals present in a single fingerprint be distinguished but also overlapped fingerprints left by different donors. However, conventional MS facilities are expensive and incompatible with detection and analysis at a scene of crime. They are unable to distinguish between optical and geometrical isomers and the positions of substituents. Recently, several reviews on the multi-informative analysis of LFPs by MS and MS imaging applications in forensic fields have been published [15, 73, 74]. In future, work should be devoted to identifying of proteins/polypeptides using advanced MS techniques, as they represent the most abundant group of compounds from eccrine origin in the fingerprint residues, and some of them might be useful in disease diagnosis [8, 11].

Vibrational spectroscopy imaging

Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy (RS) can provide the visual images of fingerprints by mapping the functional groups of the molecules. Ricci et al. have reported the potential of combining the tape-lift method with attenuated total reflection FTIR (ATR-FTIR) imaging approach for the collection of evidence at a crime scene and analysis of an individual's fingertip after handling drug abuse [75]. Later, they studied the distribution of lipids and amino acids in the fingerprint residues using this approach [48]. The absorbance between 2800 and 3000 cm⁻¹ due to the antisymmetric and symmetric stretching vibrations of the CH₂ groups arising from lipids present in fingerprint sebaceous residue was plotted to construct fingerprint images. Changes of lipids with temperature and time have also been detected, which are potentially important in understanding the aging process of LFPs. They subsequently demonstrated the practical application of this nondestructive technique for imaging fingerprints lifted from a variety of surfaces by gelatin tapes. Spatially resolved chemical images from different depths within the same sample were obtained with the possibility of avoiding spectroscopic interference from the lifting media [76]. Crane et al. have reported that FTIR chemical imaging allows the collection of images of unprocessed LFPs on various porous and nonporous substrates while preserving important trace evidence to be recovered and identified [77]. Tahtouh et al. demonstrated that FTIR chemical imaging allows the detection of LFPs on a wide range of difficult surfaces (including polymer banknotes, various types of paper, and aluminum drink cans) [78]. Bhargava et al. described the use of reflection-absorption mode for the distinction of overlapping fingerprints based on the difference of their chemical origins [79]. Recently, a preliminary study has demonstrated that LFPs across a range of highly patterned, colored nonporous and semiporous substrates can be developed and imaged in the near IR following a simple dusting with finely divided Spirulina platensis powders. Printed and multicolored backgrounds show less interference with the intrinsic fluorescence of this material [80]. More recently, a study using FTIR has shown that two spectral ranges, namely 1000 -1850 cm⁻¹ and 2700-3600 cm⁻¹, are most informative for dating fingerprints. In conjunction with using chemometric analyses, a precision of ± 3 d on the fingerprint age has been achieved [81]. Knowing the variation of fingerprint components is also useful in the estimation of the fingerprint age,

which can be used to distinguish fingermarks related and unrelated to the crime, to support or refute statements from witnesses, victims, and suspects. In addition to the endogenous components, FTIR imaging has been used to detect exogenous trace residues associated with forensic evidence, e.g., explosives [82–85], illicit substances [86], drugs [85, 87], and cosmetic and healthcare products [87, 88].

RS has been primarily used in the detection of explosives and drugs of abuse present in the fingerprints [89, 90]. The key advantage of RS is its nondestructive nature that allows the subsequent use of fingerprints in the identification of an individual and in further biometric analysis. Widjaja performed the study on using RS mapping to extract chemical information from LFPs that had been lifted by adhesive tapes. A sebum-rich fingerprint after touching the forehead, a drug model comprising ibuprofen, L-arginine, and sodium bicarbonate, and an additive model comprising sucrose and aspartame were investigated. In conjunction with using a powerful multivariate data analysis approach, namely band-target entropy minimization, all these test substances can be correctly identified using their unique pure Raman spectral signatures [91]. Emmons et al. performed the bright-field Raman imaging of contaminated fingerprints, in which explosives can be detected and identified using Pearson's cosine crosscorrelation analysis of the characteristic region (500 -1850 cm^{-1}) of the spectrum [92].

Compared with the conventional RS, surface-enhanced RS (SERS) holds an enhanced sensitivity of 10^{-4} - to 10^{-6} -fold [93]. For example, with SERS chemical imaging, the vibrational intensity of amino acids can be improved by the metaldielectric interface to create visual images of LFPs that are undetectable using conventional methods [50]. To further increase the chemical specificity, Song et al. have reported an indirect approach for the identification of specific proteins deposited within a LFP by employing an antibody/silver NPs/Raman probe conjugate [93]. This conjugate could indirectly provide the chemical information on the targeted proteins through the specific immune recognition, providing the possibility of detecting biomolecules in LFPs, such as those valuable for medical diagnostics or criminal investigations. In comparison with MS, vibrational spectroscopy is very sensitive to the molecular structure but not the molecular identity (such as molecular mass, isotopic composition of elements). But vibrational spectroscopy is less destructive, which causes no damage on the fingerprint residue, allowing further chemical analysis and identification by other methods. It is also safer to the examiners than other optical methods that require strong radiation illumination. However, vibrational spectroscopy imaging is still expensive and its compatibility with onsite fingerprint visualization also needs to be improved. In particular, Raman spectroscopy technique requires highstability laser sources and sensitive amplification equipment to detect the weak signal.

Immunogenic and nucleic acid reagents

The application of immunogenic and aptamer techniques in the selective detection of fingerprints can be referred to a recently published review [94]. The first use of immunoassay for the detection of forensic secretions within the sweat deposited in LFPs has been reported by Russell et al. [14]. As shown in their work, smokers' fingerprints can be visualized by incubating with gold NPs functionalized with antibody specific to cotinine and secondary antibody tagged by a dye. Fluorescence image of thus treated fingerprints can clearly reveal the second level details as well as third level details such as sweat pores, showing the capability of both identification of an individual and simultaneous determination of the chemical makeup of the sweat deposited in the fingerprint. As highlighted by Wolfbeis, this approach has a high potential in that it may not only serve to detect metabolites of nicotine but also chemical products of explosions, metabolic species that can act as diagnostic markers [58]. It also stimulates a wave of research on immunodetection of fingerprint components.

Based on their primary work, Russell et al. have later used magnetic particles functionalized with a range of antibodies for the detection of drug metabolites, such as methadone, cocaine, and heroin [53–57]. Importantly, a key advantage of the detection of drug metabolite is that it would prove the use of a drug, whereas detection of a drug in a fingerprint would only show the contact with a drug. In further studies, anti-cotinine/ magnetic particle conjugates were successfully applied for the development of fingerprints deposited on a highly reflective white porcelain surface [55] and those have been aged under different conditions [56]. To be mentioned is that multiple detection (one color or one fluorescence lifetime for each analyte) could be easily accomplished by using different antibodies and/or NPs [53].

Spindler et al. have shown that gold NPs conjugated with anti-L-amino acid antibodies are able to visualize LFPs, particularly effective for those aged and degraded on nonporous surfaces [13]. On the basis of sodium-dodecyl-sulfate polyacrylamide gel electrophoresis and silver staining techniques, Drapel et al. have identified three proteins, keratin 1 and 10, cathepsin-D, and dermcidin, in LFP residues. Using the corresponding antibodies of three proteins, they successfully developed LFPs left on polyvinylidene fluoride membrane, as well as on whitened and non-whitened paper [17]. Using dermcidin as the antigen of interest, Dam et al. have investigated the compatibility of immunolabeling with two commonly used fingerprint visualization techniques, magnetic powdering and ninhydrin staining. The results showed that the predeveloped LFPs with a variety of reagents/operations, such as magnetic powder, ninhydrin, indanedione-zinc, indanedionezinc followed by ninhydrin spraying, physical developer, cyanoacrylate fuming, cyanoacrylate followed by basic yellow staining, lumicyanoacrylate, and polycyanoacrylate fuming,

did not inhibit the specific detection of dermcidin [40, 41]. They also demonstrated multiple immunolabeling of fingermarks left on a porous nitrocellulose membrane and on a nonporous glass slide surface for simultaneous detection of specific components of interest [38]. Furthermore, it was found that immunolabeling could develop LFPs left on diverse surfaces, including nonporous (aluminum foil, stainless steel keys, plastic sheets, different colored garbage bags, sandwich bags, Ziploc bags), semiporous (tiles), and porous surfaces (thermal paper). Surprisingly, fingermarks left on thermal paper showed improved visibility when developed with the immunolabeling method [39].

My group has been working on new methods for the detection of various secretions within eccrine fingerprints by combining immunoassay with portable and efficient imaging techniques. Figure 1 illustrates the general principle of the enzyme immunoassay and the electrochemiluminescence (ECL) imaging for the detection of secretions in LFPs [44]. First, the primary antibodies specific for target analytes were incubated over the fingerprint. Then the fingerprint was sequentially processed by incubation with biotinylated secondary antibodies and horse radish peroxidase (HRP)-labeled streptavidin. The application of a sufficiently negative voltage to the electrode carrying the fingerprint leads to the electrochemical reduction of dissolved oxygen to H₂O₂. Then HRP can catalyze the ECL reaction of H₂O₂ with luminol, thus yielding an ECL image of the fingerprint. Specifically, we have detected epidermal growth factor (EGF), lysozyme, and dermdicin. The obtained ECL images not only reflect the unique ridge pattern of a fingerprint but also provide the chemical evidence of the presence of specific secretions. Since the light emission is triggered by electrochemical reaction, the ECL imaging approach allows the time of the light-emitting reaction to be controlled; also, it does involve a light source, hence eliminating the attendant problems of scattered light and luminescent impurities.

Multi-metal deposition (MMD) introduced to the forensic field by Saunders is a very sensitive method for visualizing LFPs on porous and nonporous surfaces, which involves the binding of gold NPs (AuNPs) to ridge details via the electrostatic and/or hydrophobic interaction and subsequently catalyzing the metallic silver deposition in a silver nitrate solution [95, 96]. Recently, we reported a modified MMD method termed immunological MMD (iMMD) by combining the conventional MMD and immunoassay [45]. As shown in Fig. 2a, iMMD uses antibody modified AuNPs (AuNPs/antibody conjugate), which bind with the corresponding antigens in the fingerprint residue via the specific immunoreaction. Then the AuNPs serve as the catalytic nucleation sites for the metallic deposition of silver particles from the silver staining solution, eventually enhancing a black fingerprint on a lighter background for visual detection. With this formulation, we successfully accomplished the visualization of LFPs via the



Fig. 1 Illustration of the detection of secretions deposited within a fingerprint using enzyme immunoassay (left) and ECL imaging and an ECL image of the as-treated eccrine fingerprints for the detection of dermcidin (right). Adapted from Ref. [44]

detection of two secreted polypeptides, EGF (Fig. 2b) and lysozyme (Fig. 2c). Different from the conventional MMD, AuNPs used in iMMD not only served as the nucleation sites for the deposition of silver particles but also as the carriers of recognition molecules, which could identify the existence of specific components. Moreover, a significant advantage of iMMD is that the developed fingerprints can be directly observed by naked eyes, without involving any sophisticated imaging equipment.

Aptamers are short, single-stranded nucleic acids that bind to a number of targets such as metal ions, proteins, and even whole organisms [97]. Over the past two decades, aptamers have shown a diverse range of applications in analytical chemistry. In 2012, Wood et al.

Fig. 2 Illustration of the iMMD process involving the binding of AuNPs/antibody conjugates with specific secretions and the silver staining enhancement (a), optical images of eccrine fingerprints via the detection of EGF (b), and lysozyme (c). Reproduced from Ref. [45] with permission by John Wiley and Sons)



reported the first work that utilized the unique recognition power of aptamers to detect lysozyme in LFPs [42, 98]. When being incubated with the fingerprint, the fluorescently labeled aptamers fold into specific threedimensional structures to bind to LFPs. Eventually, the light illumination revealed fingermarks with strongly fluorescent ridges and dark valleys. Recently, Li et al. have proposed a nanoplasmonic method by employing aptamer-bound AuNPs to visualize LFPs and detect the contact residues of cocaine [99]. Because the localized SPR of AuNPs is highly dependent on the interparticle distance, the cocaine-induced aggregation of aptamerbound AuNPs could result in a true green-to-red color change of the scattering in the dark-field image, thus providing the molecular recognition of cocaine loaded in LFPs. The minimally detectable cocaine loaded in LFPs was calculated as 90 ng. Yuan et al. have employed upconversion NPs (UCNPs) functionalized with aptamers for the detection of fingerprints through recognizing lysozyme [43]. The fingerprint treated with UCNPs/aptamer conjugates show much clearer luminescence image than those with fluorescein or CdTe QDs conjugates because of the ability of UCNPs to suppress background fluorescence.

Immunogenic and nucleic acid reagents are advantageous in terms of their strong specificity to a certain target molecule. They can also be applied in conjunction with various nanomaterials to achieve significant signal amplification, with a high potential in the detection of trace chemicals present in the fingerprint residue. The detection and visualization do not even rely on any instruments. In addition, immunolabeling has been shown to be compatible with pretreatments, such as magnetic powdering and ninhydrin staining, on the fingerprint residue [40]. However, sample treatment with immunogenic and nucleic acid reagents requires careful operation to inhibit the nonspecific adsorption, and the quality of eventual ridge development is also strongly dependent on the substrate surface where the fingerprint is deposited.

Summary and outlook

Fingerprint residue is a complex mixture of a large number of substances coming from different sources. Knowledge on the composition of the ridge residue is critical to understand how reagents used to visualize LFP work, to provide better guidance in improving existing reagents/ methods and developing new methods, and to find more potential usefulness of the residue than just identification of an individual. Therefore, future efforts should continue to focus on discovering new components, quantifying known comcponents, and determining how they interact with different surfaces. Taking advantage of the knowledge gained from these investigations and the recent advances in the fields of material science, synthetic chemistry, and analytical techniques, I can expect that various novel reagents/methods can be developed for forensic LFP imaging and identification. On the other hand, I also envisage that the fingerprint analysis is far beyond the forensic purpose, given the fact that the chemical formation extracted from the ridge residue can provide additional intelligence, e.g., the diet, lifestyle, medical condition, evidence of sexual assault, and the evidence of contact with explosives or illicit drugs of a donor. There remains enormous room for researchers to collect the guantitative information of specific components and evaluate their potential values in other applications, such as in vitro health monitoring, nondestructive diagnosis, security and access control, and athlete screening. There is also a strong need to develop efficient methods and portable devices suitable for on-site inspection. I believe that state-of-the-art analytical chemistry techniques, such as MS, vibrational spectroscopy, NPs, and immunogenic and nucleic acid methods, have huge potential in this area.

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Compliance with ethical standards

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