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Emerging fields in fingermark (meta)detection – A critical review

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Fingermarks represent an extremely valuable evidential element as it can link an individual with an item, a location, or an activity. To be used for identification purposes, fingermarks have first to be located and recorded, which generally requires the application of detection techniques. For more than a century, research efforts in the field aimed at optimizing the existing techniques or developing new detection mechanisms characterized by an increased efficiency, sensitivity, and selectivity towards secretion components. For a long time the primary (and sole) purpose of fingermark detection techniques remained the same: to establish a visual contrast between the (invisible) secretions and the items they are laying on. Research objectives were mostly driven by investigative outcomes and requirements, with techniques that would detect as many marks as possible (especially faint and/or aged ones) and would be compatible with the largest range of substrates (especially the problematic ones). Recently, the fingerprint community witnessed a shift in the research efforts, with a recrudescence of publications dealing with new high-end technologies. Besides the promise of capabilities going beyond the sole purpose of establishing a visible contrast, analytical prospects may unfortunately prevail over forensic and/or health and safety considerations. This review aims consequently at proposing a critical glance at three emerging technological trends: use of nanoparticles, chemical imaging, and immunodetection for fingermark detection. For each of these topics, a forensic perspective is opposed to the biological/chemical considerations. The covered period extends from 2000 to 2015, which represents more than 200 articles.

Before considering the latest advances in fingermark detection, it could be helpful for the readers not accustomed with the forensic field to briefly define what are fingermarks, as well as to present the related challenges (Note: the term "fingermark" may also be known as "(latent) fingerprint" in some countries, such as the United States). A fingermark is the result of an adventitious contact between the papillary ridges (present on the fingertips, palms and soles of an individual) and a surface.[1] During this contact, the secretions present at the surface of the skin are transferred towards the substrate, partly duplicating the original ridge pattern. From a chemical point of view, a fingermark is a complex emulsion: a mix of sweat (composed of water for 98% and of organic/inorganic endogenous components excreted through eccrine glands), of sebum (mostly organic and lipidic compounds excreted through sebaceous glands), and of various exogenous contaminants present at the surface of the skin (*e.g.*, blood, cosmetics, food grease). As a result, the secretion residue left on a surface contains hundreds of chemical species [2] which are most likely invisible to the naked eye given their nature and the minute quantities left (sub-microgram). In that case, fingermarks are said to be "latent" and require to be detected before being recorded. Taking this into consideration, fingermarks carry two extremely valuable information: (1) a partial reproduction of the ridge pattern they are issued from, which constitutes their main interest in an investigative context (depending on the substrate, the deposition circumstances, and the environmental conditions, the reproduced pattern will be of variable quality), and (2) a submicrogram sample of secretions originating from the donor, whose composition varies among individuals and contextual circumstances.

Given that the initial interest for fingermarks/fingerprints originates from their ridge pattern (allowing the identification of individuals, and historically the classification of ten-print cards to quickly retrieve recidivists), it is not surprising that most of the research efforts aim at developing detection techniques allowing the visualization of latent (invisible) marks on a crime scene or on related items. More specifically, it is awaited from an efficient technique to detect as many marks as possible by establishing an observable contrast between the secretion residue and the substrate bearing them. In this context, dozens of techniques are regularly used by practitioners.[3-5] Some have existed for more than a century (*e.g.*, powder dusting), while others appeared in the mid-50s (*e.g.*, ninhydrin [6]) or met a worldwide success recently (*e.g.*, 1,2-indanedione/zinc in 2007 [7, 8] or one-step fluorescent cyanoacrylate fuming in 2013 [9-12]). According to the location (crime scene or laboratory), the secretions to be targeted (*e.g.*, blood-contaminated, eccrine, sebaceous), or the item to be processed (*e.g.*, porous, non-porous, metallic, adhesive), practitioners usually refer to well-established detection sequences to make their choice among the existing techniques. The main role of these sequences is to optimize

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the likelihood of detection by combining existing techniques in a sequential order of application. A detection technique is consequently barely applied alone; if one reagent fails in detecting some of the marks in presence the next one in the sequence may be more successful. Such charts are regularly updated, as a result of extended validation works or due to the emergence of more efficient techniques. It also means that for a new technique to be accepted its efficiency must be thoroughly assessed and its compatibility with existing procedures carefully considered.

In regards with the latest reviews dealing with fingermark detection [13-18], the continuously growing number of publications reflects the scientific interest for this field (Figure 1). Although most studies have focused on the development - or optimization - of conventional detection techniques, new trends have emerged during the last decade (Figure 2), among which are (1) the use of (dye-doped/functionalized) nanoparticles, (2) chemical imaging applied to fingermarks (mostly related with scenarios such as explosive manipulation, illicit drug manipulation/consumption, and sexual aggression), and (3) immunodetection processes targeting secretion residue. Along with these emerging technologies, a new achievement arose among the scientific community: gathering additional information from the secretion residue, independently from the ridge pattern. The underlying principle is that sweat contains hundreds of components among which are amino acids, proteins and metabolites, linked to the individual and his/her daily habits. Consequently, it appears likely that extra information could be gained about the individual who has left the fingermark from his/her secretion residue (*e.g.*, gender, daily habits, health condition, or diet). The term "metadetection" is proposed in this review to characterize the ability to collect information other than the ridge pattern from a detected fingermark, emphasizing the fact that this additional information goes "beyond the detection". Metadetection purposes constitute a shift in the research linked to fingermarks, which still has to find its place among the conventional practices. Indeed, what may seem extremely challenging or valuable from an analytical point of view may be irrelevant or of limited use from an investigative point of view. The aim of this critical review is to try bringing a dual perspective (*i.e.*, analytical and forensic) on these emerging fields, as well as proposing perspectives of research to stay in tune with forensic needs.

< Figures 1 & 2 >

Tailoring the detection reagents – The rise of nanoparticles

The number of publications reporting the use of nanoparticles (NPs) for fingermark detection has dramatically increased during the last decade (Figure 2), which makes of NPs the most notable emerging technology in the field. This success can be explained by the versatility of structures and properties offered by NPs. For example, the range of external functionalization allows tailoring the interactions with the secretion residue as well as with the carrier solvent (*i.e.*, water or organic solvent). Additionally, the composition of the (dye-doped) core has a direct effect on the observation conditions (*e.g.*, UV-vis spectrum, near-IR domain, upconversion, or signal carrier for chemical imaging) but could also trigger additional properties (*e.g.*, magnetism). As shown in Table 1, there is a huge versatility of NP core compositions applied to fingermarks, with two prevalent ones: gold nanoparticles and cadmium-based quantum dots. For detailed information about the application of nanoparticles to fingermark detection, a book chapter specifically covers this topic [19], along with some reviews.[20-22]

Use of nanoparticles for detection purposes

When dealing with nanostructured materials to detect latent fingermarks, several researchers opt to consider NPs as new kinds of powders to be dusted on items (Table 1/Second column). This represents ca. 40% of the publications dealing with NPs applied to fingermarks. This mode of application is usually justified by the easiness of application combined with the commonly-accepted statement that small and fine particles adhere better on fingermark residue compared to large and coarse ones.[23] Moreover, detected marks are readily observed through naked eye or using an alternative light source for luminescent NPs. To promote the interactions with sebaceous secretion residue, hydrophobic alkyl chains were also added at the surface of the NPs.[24, 25] If NPs actually adhere to the fingermarks with more or less success compared to conventional micron-sized powders, serious health and safety issues may arise from airborne NPs dusted on a crime scene by an operator, especially those containing heavy-metals such as cadmium.[26-31] It should be stressed that the consequences of an operational use of such nanopowders are barely discussed in the literature.[32] This mode of application is consequently to be banned, unless explicitly justified.

A safer way to apply NPs is to put them in solution/suspension (ideally aqueous) in which the item to be processed is immersed (Table 1/Third column). In that case, the successful binding of NPs to the secretion residue is more challenging since it relies on physico-chemical parameters, varying immersion times (from a few minutes to hours), and complex molecular interactions. When trying to promote the affinity between the secretion residue and the NPs in solution, pH-driven protocols and immunodetection constitute the two most-frequently observed detection mechanisms (Figure 3). Formation of covalent bonds comes third (only ca. 12% of the publications), despite the fact that it could ensure a strong and specific binding between a NP and its molecular target. It should also be stressed that ca. 29% of the publications do not report the mode of interaction between the NPs and the secretions, which could mean that the underpinning mechanisms are unknown or barely understood. For example, when gold nanoparticles are applied in aqueous solution to detect fingermarks, the pH of the solution plays a crucial role in the success of the detection.[33] People generally rely on

commonly-accepted hypotheses based on empirical and theoretical considerations (*e.g.*, electrostatic attraction or steric hindrance), but those are disputed in recent studies.[34, 35] This constitutes therefore a field of research that still needs to be addressed.

<Table 1>

< Figure 3 >

Optical properties of the NPs

Most of the NPs applied to fingermark detection are characterized by a luminescent optical activity, explaining the success of quantum dots and dye-doped NPs. This is understandable by the fact that this mode of detection allows the observation of minute amount of material compared to colored materials. The conventional way of recording luminescent fingermarks is to excite them using a specific wavelength (generally from ultraviolet to blue-green range) and record the resulting image by using a camera equipped with an observation filter (generally from orange to red range). An emerging trend is the use of NPs possessing upconversion capabilities.[94-104] When excited with long-range wavelengths (generally in the near infrared range), upconverters emit in the visible range. This optical behavior is promising since it allows to get rid of the unwanted luminescence of the background which can be encountered with conventional photoluminescent particles. Upconverters could consequently mark their difference by drastically improving the contrast of the fingermarks detected on illustrated items (Figure 4).

<Figure 4>

Composition of the NPs

When applied as dried powders, silicon oxide NPs, upconverters, and cadmium-based quantum dots (QDs) represent the three kinds of NPs the most used; whereas in solution, gold NPs and cadmium-based QDs are preferentially considered (Figure 5):

- The interest for gold nanoparticles is historically due to the multimetal deposition (MMD), a technique proposed in the late eighties by the U.S. Secret Service [132, 133] and for which notable optimization studies followed.[66] Gold NPs also offer advantageous properties such as simple synthetic protocols, stability in solution, and easiness of modifications through strong binding of thiolated ligands;
- Silicon oxide NPs represent an ideal template for researchers given the extended functionalization and dye-doping capabilities. Silica NPs can be used to detect fingermarks [31, 108-114, 134], to try understanding the interaction mechanisms [34, 35], or as signal carriers/enhancers for the analytical characterization of secretion residues [118, 119, 121-123];
- The success of cadmium-based QDs is mainly due to their optical properties, characterized by an intense luminescence. Contrary to gold nanoparticles, QDs are more fragile and their application in aqueous solution usually consists in stabilizing them with thioglycolic acid, without additional functionalization. Their use as dried powders readily applied on items bearing fingermarks constitutes a surprising and unfortunate success. However, it should be noted that some authors reported the use of cadmium-free QDs applied in solution, which definitely represents a step toward to decrease the toxicity of such reagents [128-130];
- Upconversion NPs are mostly built around lanthanide-containing cores which are then applied as dried powders. Despite interesting optical properties, their preferential application mode should raise the same concerns as for QDs;
- Finally, the success of magnetic-core NPs in solution is mostly due to the development of immunodetection techniques applied to fingermarks.[89-93, 135] This topic is specifically discussed in the third section of this review.

< Figure 5 >

Use of nanoparticles for metadetection purposes

Most of the NPs aiming at gaining additional information about the secretion residue are used as signal carriers for chemical imaging.[118-123] For this reason, this use of NPs will be discussed in the second section of this review. Nevertheless, one article illustrates quite well the possibilities offered by NPs in terms of functionalization and optical properties dedicated to metadetection.[117] By combining a silica framework with two kinds of quantum dots and an optical trigger, Wu *et al.* have shown how NPs could be used as advanced sensors for specific compounds contained in fingermarks (in that case: explosive traces). Strictly speaking, this preliminary study aims rather at developing a live sensor than a fingermark detection technique. However, it illustrates that NPs could constitute suitable framework to carry advanced functionalities and thus answer specific questions related with forensic interests.

Pros/Cons of the technology

In regards of their nanoscale size combined with extended variability of structures and properties, the success of NPs applied to fingermark detection appears indisputable. People have shown that it was possible to target specific molecular components, to take advantage of the magnetic properties induced by magnetite-containing cores, or to offer a variety of optical properties among which upconversion to overcome optical disturbance originating from the item bearing the marks. All these characteristics have been successfully applied to detect latent fingermarks in controlled/ideal conditions and allow their recording in many ways. This success should however not mitigate some major drawbacks of the use of NPs: their reported use as dried powders, the labor-intensive protocols when applied in solution (partially understood detection mechanisms, multiple immersion baths, prolonged reaction times), the toxicity of some NPs, and the lack of studies reporting their integration in the existing detection workflow (in combination with existing conventional techniques). Consequently, and despite the huge number of publications in the field, only a couple of techniques based on

NPs went beyond academic research and are currently applied in casework.

Researchers or readers should also be particularly aware of erroneous detection cases which can be encountered in the literature. Indeed, it is possible that – contrary to what is claimed in an article – NPs did not successfully bind to the secretion ridges but did actually bind to the underlying substrates (inter-ridge valleys). It means that the proposed NPs have no affinity for the secretions or show a higher affinity for the substrate. A way to pinpoint this issue is to closely look at the illustrated ridge pattern. Indeed, in such cases, the observed ridge pattern is the negative image of the inked print (reference) or of other marks of the same finger processed with different reagents. In both cases illustrated in Figure 6, the authors did not raise this issue and failed in correctly recognizing the presence of pores (which are always set along the papillary ridges). Fundamental knowledge about fingermarks and close examination of the ridge pattern is the key to prevent researchers reaching erroneous conclusions and to promote further developments of the considered NPs.

< Figure 6 >

Expectations in terms of research

Nanoparticles used in the context of fingermark detection are promising but are still to be seen as a "young" discipline which needs to mature. Research should now focus primarily on their integration in existing workflow, as well as on the understanding of the intrinsic interactions between these reagents and the secretions. About the integration into detection sequences, it can indeed hardly be imagined that NPs would replace the conventional techniques (efficient, easy to use, relatively cheap, and well-established in forensic laboratories). However, most published studies – if not all – consider the use of NPs as sole technique and rarely consider their application in sequence with other (conventional) methods. As a consequence, it is currently difficult to assess the actual efficiency of nanocomposites in the context of fingermark detection. Finally, another interesting research route would be the development of nanostructured materials for forensic/security-oriented applications.[117] However, such aim deviates quickly from the detection of fingermarks, and has consequently not been covered extensively in this article.

The increasing use of chemical imaging

Chemical imaging (as part of hyperspectral imaging) constitutes the second most notable emerging trend in the field (Figure 2). In brief, hyperspectral imaging combines spectral information with digital imaging into a tridimensional datacube which is further processed to either highlight key information or enhance a visual contrast. In the context of fingermarks, two approaches can be distinguished. The first one is based on a set of pictures taken along the UV-VIS-NIR domain which are then combined to optimize the visual contrast of latent or chemically-processed fingermarks.[136-140] The second approach consists in digitally mapping ridge patterns on the basis of their molecular composition, obtained from spectrometric or spectroscopic data (*e.g.*, mass spectrometry or FTIR). The resulting image is an illustration of the chemical distribution along the scanned area. According to the nature of the emphasized component(s), it is consequently possible to use such data for detection purposes (*e.g.*, distribution of endogenous lipids) as well as for metadetection (*e.g.*, distribution of cocaine metabolites). In this review, the term "chemical imaging" will be associated with this second approach.

Numerous analytical techniques can be coupled with imaging capabilities and have consequently been applied to ridge pattern imaging (Table 2 and Figure 7). Four scopes can be identified in the literature: (1) imaging of latent fingermarks, (2) digital enhancement subsequent to a detection technique, (3) mapping/characterization of contaminated secretions (*e.g.*, through contact with drugs, explosives, cosmetics, condom lubricant, or artificial sweat), and (4) mapping/characterization of endogenous compounds (*e.g.*, metabolites excreted after ingestion of narcotics). Scenarios 1 and 2 are mostly dedicated to "detection" purposes, while scenarios 3 and 4 are rather associated with "metadetection". Due to the number of analytical methods involved, this review won't cover technical specificities, but will rather focus on the forensic considerations of chemical imaging. Mass spectrometry-related techniques (MS) and infrared spectroscopy (FTIR) will be extensively developed, for they are the two most prevalent ones with 56% and 22% of the published articles, respectively (Figure 7).

<Table 2>
< Figure 7 >

Chemical imaging for detection purposes

As explained in the Introduction, a digital camera combined with adequate light sources and observation filters represents the conventional equipment allowing the recording of a fingermark, being latent or detected by colored or luminescent reagents.[200] Nevertheless, there are some cases for which conventional photography reaches its limits (*e.g.*, luminescent background interfering with the reagent to be observed or pattern preventing the recording of an adequate contrast). This could be the case for the processing of a polymer banknote with cyanoacrylate fumes [158] (Figure 8A). In that case, FTIR imaging could greatly enhance the resulting contrast by selectively mapping the wavelengths corresponding to functional groups specific to the reagent – cyanoacrylate polymer in that case.[144, 158-161] Provided that the substrate and the reagent differ sufficiently regarding their chemical composition, this has for effect to mask the irrelevant information originating from the substrate and to optimize the resulting contrast (Figure 8A). FTIR imaging can also be applied on unprocessed fingermarks [141-143], and allow the study of the secretion composition by mapping the lipid distribution for

example.[142] Another reported application of chemical imaging for detection purposes is the digital separation of overlapped fingermarks, provided that the two marks differ sufficiently in their respective chemical composition [144, 146, 149, 168, 177, 196, 199] (Figure 8B). Several proof-of-concept studies were published on this topic, by carefully controlling the composition of the residue (artificially-enriched secretions). However, no successful operational case based on digitally separated marks (based on chemical imaging) has been reported yet, to the author's knowledge. Finally, chemical imaging could also bring information about the sequence of deposition of two elements of forensic interests, such as two fingermarks [168] or a fingermark and text writings [153-155] (Figure 8C).

< Figure 8 >

Chemical imaging for metadetection purposes

Combining chemical information with digital imaging could help mapping components homogenously present in the secretion residue as well as minute amount of substances whose presence is related to specific activities/scenarios. Most of the research dealing with metadetection applied to fingermarks aims at emphasizing the presence of explosives, drug powders and corresponding metabolites, as an indication of manipulation and/or ingestion of illicit substances by the fingermark donor.[118, 122, 183] Another example of metadetection is the imaging of lubricant-contaminated fingermarks in an effort to bring contextual information related with sexual assault cases.[193, 195, 196] In those cases, the analytical techniques are mostly based on mass spectrometry (*e.g.*, MALDI-, SALDI-, DESI-, DIOS-, DEFFI-, EASI-MSI). For each pixel of the scanned area, mass spectrometry is indeed able to provide accurate molecular information about the sample, which is required to confirm the presence of a specific molecule. Different protocols can be found in the literature: the contaminant is either proposed as a dried powder or in solution; the donor is then asked to touch it before leaving a mark or the contaminant is readily left on the finger tips prior to the mark deposition (see Table 2). This way of doing may result in highly enriched marks which can deviate from actual marks containing trace amounts of these elements. The only way of providing realistic contaminated marks would be to mimic an illegal activity requiring the manipulation of such substances (*e.g.*, synthesis, handling/transportation, selling).

Another trend that can be found in the literature is the obtaining of information about the donor from his/her fingermarks. The main leitmotiv of such studies is to find the value of (smudge) marks presenting no (apparent) use for identification purposes. Most of these studies however rely on the analysis of already located fingermarks without taking advantage of ridge pattern imaging. It is possible to cite the determination of the donor gender by MALDI-MS [201], GC/MS [202], or enzymatic assay.[203] Given that the role of chemical imaging is limited, these studies have voluntary not been covered in this review. Readers interested in "donor profiling" from fingermarks can refer to a recent review on this topic.[204]

It should be noted that all the researches claiming to gain additional information about fingermarks have to be carefully thought in an investigative context. Indeed, some information may be irrelevant/useless, could be obtained from existing/simpler processes (*e.g.*, criminological statistics or DNA profiling for gender determination), or may require the use of specific databases which does not exist (such as condom lubricants).

Integration into the forensic workflow

Among all the chemical imaging-related techniques, the use of MALDI-MSI has resulted in major developments having for focus its operational integration.[205] From a proof-of-concept status [148], the technique has been adapted to encompass some forensic constraints and be compatible with operational workflow.[167] The fact that MALDI requires the item to be covered with a matrix prior analysis was a major drawback that needed to be circumvented. First sprayed, which was detrimental for the fingermark and unrealistic for detection purposes, the matrix was adapted so that it could be dusted on items. By doing so, the powdered matrix could be used as a conventional detection technique (on crime scene mainly), the marks being located then lifted/captured and subsequently analyzed using MALDI-MSI, if required.[164-166] Metal sputtering combined with MALDI-MSI constitute a similar approach.[168, 169] Those examples illustrate how fingermark detection and chemical imaging are closely tangled. Recently, the Home Office has introduced MALDI-MSI as a Category C process in its Fingermark Visualisation Manual.[206] It means that this technique can be occasionally applied in operational use, mainly for mapping contaminants present in the secretion residues or enhancing partially-detected ridge pattern. However, as indicated in the manual, the size of the chamber may require to lift the fingermarks of interest from the item (meaning that the marks had to be detected beforehand) and that MALDI-MSI may be detrimental to subsequent processes.

Influence of fingermark detection techniques on chemical imaging

The compatibility of chemical imaging with conventional fingermark detection techniques is a major issue to be addressed. Indeed, in most cases, items bearing fingermarks would have already been processed using techniques available in forensic laboratories (*e.g.*, cyanoacrylate fumes or amino acid reagents) before chemical imaging is considered. It is consequently crucial to assess the compatibility of chemical imaging with fingermarks already exposed to other reagents/techniques. This question is progressively addressed for MALDI-MSI and SALDI-MSI techniques, as it can be seen from the recent publications in the field.[167, 183, 185-187, 190] For example, it appears quite logical that the powder specifically developed for detection and imaging purposes should be the reagent suiting the best MALDI-MSI. Successful imaging (with somewhat decreased efficiency) were obtained when MALDI-MSI was considered in sequence with conventional techniques, such as black powder, cyanoacrylate fuming combined with

black powder, or lifted marks.[186] A study assessing the impact of cyanoacrylate fuming on the MALDI efficiency led to the conclusion that "the thickness of the cyanoacrylate [left on the fingermark ridges] needs to be minimized to be compatible with MALDI" [187] or that marks should be exposed to organic solvents to be lifted for imaging (making them hardly available for any subsequent detection technique).[183] Such conclusions are extremely valuable since they bring forward the fact that – in addition to be closely tangled – fingermark detection and metadetection may also be detrimental to each other. In other words, processes optimized for one purpose may not suit the other.

Pros/Cons of the technology

By combining spectral data with analytical information, chemical imaging is undoubtedly a powerful tool. It can, for example, be used to emphasize poor contrast by mapping the distribution of a reaction product or attempt separating overlapped marks. Its major application field is however definitely related with the highlighting of exogenous components linked with illicit drug manipulation/consumption, explosive manipulation, or sexual aggression. In that context, most of the considered analytical techniques have proved that minute amounts of a compound can be identified and imaged along the ridge pattern of a scanned fingermark. From a technological point of view, chemical imaging does provide what it is aimed for: an additional layer of information for the operator. This enthusiastic perspective is however to be counterbalanced with two major considerations: technical requirements and forensic scopes.

One of the main limitations of chemical imaging applied to fingermarks is to be found in is technicity. First, the acquisition of high-end analytical devices is unlikely in conventional forensic laboratories without a massive industrial development combined with a proved efficiency over conventional procedures. Second, it is unfortunate that very limited information is found in the literature regarding the time and performance of the item processing. It is, for example, very unlikely to find the scanning times required for imaging a fingermark at a sufficient resolution (*i.e.*, minutes? hours?), the maximum area the equipment is able to scan (*i.e.*, a couple of square centimeters? an A4-size surface?) or if the technique is compatible with the versatility of shapes and textures encountered on commonly-processed items. Moreover, in most cases, the imaging process is applied on marks whose positions are already known. The fact that most of the fingermarks are latent and have to be located first on items is barely discussed, which may result in an underestimation of this crucial step for some readers or researchers. Surprisingly, these considerations were discussed in some early articles dealing with chemical imaging [157], but this tends not to be the case anymore. The actual contribution of chemical imaging for sole detection purposes has consequently still to be proved, and its operational applicability seriously hampered for technical considerations. Nevertheless, it has been shown that chemical imaging could be combined with existing detection techniques to improve an insufficient contrast in some "difficult" cases, or applied on marks that were detected beforehand (and subsequently lifted).

A second main limitation of chemical imaging is linked to forensic considerations. Indeed, forensic science encompasses many constraints: variability of substrates, uncertainties regarding the presence of latent fingermarks and their composition, needs for techniques which are quick, efficient and cheap, insertion in a complex investigative process, and interpretation of the results in terms of source (*i.e.*, individual) or activity (*i.e.*, comparative assessment of the different scenarios explaining the presence of a substance in a fingermark). Some information gained from chemical imaging may seem highly valuable from a chemical point of view, but are of no/little use for forensic considerations (or its use won't fit the investigative process). In this context, the evidential value of chemical imaging to gain additional information on fingermarks (such as gender, diet, contamination, and manipulation or consumption of illicit substances) is still disputable. Unfortunately, technical performances are often overstated to the detriment of forensic considerations, which are often ignored or hastily understated. Extensive work is consequently required to determine how such information could actually be relevant to investigators when placed in a forensic context. Finally, in some cases, chemical imaging may be facing legal constraints. Indeed, ridge patterns obtained by chemical imaging are digital reconstructions originating from chemical information and optimization algorithm. In some extreme cases (*e.g.*, separation of superimposed marks or situations for which conventional techniques wouldn't apply), there may be no possibility to verify that the digitally reconstructed pattern meets the actual ridge flow present on the surface of the item. This should not be overlooked in the context of chain custody.

Expectations in terms of research

When looking at the numerous publications reported in Table 2, it is quite clear that any analytical method supporting imaging capabilities can be virtually (and successfully) applied to fingermarks, especially when working on marks left under controlled conditions or on substrates specifically suiting the technique (*e.g.*, silicon wafer). Most of the proof-of-concept studies rely on unrealistic scenarios, such as unlikely contaminants (*e.g.*, fish oil, pure lipids), spiked-contamination using concentrated solutions left on the fingertips of donors before leaving a mark, or contact with powder readily followed by the deposition of a fingermark. If such methodology can suit a proof-of-concept stage, it also results in an overstatement of the capabilities of the technique. Unfortunately, except for some research groups, there is a lack of follow-up studies for most of the presented techniques. Research efforts should consequently be put on extensive assessment of the techniques, by considering authentic samples or larger scale experiments. It is, for example, awaited that comparative studies will also allow discriminating the promising techniques from unsuitable ones.[207] As it has been

observed by some authors, realistic scenarios may lead to insufficient quantities of transferred materials [186] or to a resolution lacking of ridge details.[122] Similarly to the use of nanoparticles to detect fingermarks, it appears unlikely that chemical imaging would be the sole technique applied on an item. In most scenarios, the considered fingermarks would have already been processed beforehand using a conventional technique and chemical imaging considered if requested. For this reason, it is crucial to pursue studies assessing the impact of conventional detection techniques on the subsequent recovery of analytes of interest, such as explosives, as it has been performed for conventional detection techniques.[208]

Starting from the fact that the relative effectiveness of chemical imaging techniques applied to fingermarks is difficult to assess, a group of researchers has recently developed an emulsion mimicking the natural secretion (*i.e.*, sweat + sebum).[182] Such initiative certainly goes in the right direction, as the whole fingerprint community may benefit from it. It should however not alter the fact that actual fingermarks should be used at some stage of the development of a new technique, especially if imaging of latent marks is aimed.

Similarly to the use of nanoparticles, a shift from detection purposes to security/drug testing has been observed for chemical imaging.[209-211] In that specific case, the aim is not to detect fingermarks or image ridge patterns, but rather to ask an individual to leave a mark on a specific sensor, so that his/her secretions are readily analyzed for the presence of specific components or metabolites. This application field may benefit from the development of substrates engineered for suiting the subsequent analytical techniques (*e.g.*, MALDI or SALDI) and on which fingermarks are voluntary left for further analysis.[150] This research deviates from strict detection purposes, and rather places itself in competition with conventional drug-testing procedures such as those based on oral fluids. People interested in this topic may refer to the following review of the use of MALDI-MS and SALDI-MS for security purposes.[212]

Finally, chemical imaging could be used for the fundamental study of secretion residue, as it would bring intrinsic information about the distribution of secretion components (Figure 9) and their evolution with time or environmental conditions. In that case, the analytical capabilities offered by chemical imaging could lead to a better understanding of the secretion residue, indirectly benefiting the overall detection field.

<Figure 9>

Specific targeting – Immunodetection applied to secretion residue

Immunodetection describes the specific recognition of molecular targets (*i.e.*, antigens) by antibodies through structural and physico-chemical interactions. Although this method is commonly used for biological purposes, early attempts to detect fingermarks with antibodies were conducted in the late 70s on blood type-related molecules [213] but didn't result in further extensive work. Recently, the interest for immunodetection has been renewed, as illustrated in Figure 2.

When considering the molecular composition of a fingermark combined with the variability between donors, several molecular components could be identified as potential antigens. Two main immunodetection strategies can be identified in the literature: "bulk targeting" of endogenous components and/or massively-present contaminants (such as blood or amino acids), or "specific targeting" of endogenous components and/or seldom-present contaminants. Targeting components commonly found in most individuals' fingermarks (*e.g.*, amino acids, proteins, lipids) aims at detecting the largest number of marks, independently from the donors, and is more akin to detection purposes. Targeting a narrow range of components contained in the sweat of some donors or contaminants linked to unusual activities (*e.g.*, handling of chemicals, explosives, or drugs) aims at restricting the number of marks detected to a limited number of donors. This approach is not common in the forensic context and is rather linked to metadetection purposes.

Immunodetection for detection

When considering the use of antibodies to detect fingermarks, it is necessary to choose endogenous molecular targets that are most likely to be found in secretion residue (Table 3). Dermcidin is currently the antigen the most considered since its presence in fingermarks is closely related with its natural antibacterial role.[214-218] Other antigens were also considered for detection purposes: amino acids [60], albumin [216, 219], lysozyme [218] or epidermal growth factor [218], all these molecules being present in conventional secretion residue. Aptamers were also proposed, as alternative to antibodies to target antigenic sites.[104, 213] Despite its success, dermcidin is far from being the perfect candidate for detection purposes. Indeed, this molecule is excreted by sweat through the pores (present along the ridges). A detection method based on the reaction with dermcidin only would consequently most likely result in dotty-patterns, highlighting the pore positions rather than a well-defined ridge pattern.[214] Antibodies can be applied free in solution, or bound to nanoparticles to increase the immunodetection signal.[60, 126] Finally, the possibility to introduce immunodetection in a detection sequence has also been explored by applying it subsequently to a selection of existing techniques.[215, 217] Successful results were obtained, but it would have been interesting to assess the (detrimental) impact of the conventional detection techniques on the subsequent immunodetection performance. The consideration of fingermarks cut in halves (*i.e.*, one half being processed following the "Conventional technique → Immunodetection" sequence, and the other half processed with "Immunodetection" only) could constitute a valuable way of getting information about that question.

Immunodetection for metadetection

Some antigens present in the secretion of individuals may reflect their life habits (*e.g.*, cotinine found in the sweat of smokers, or benzoylecgonine among cocaine consumers). Such antigenic targets are called "metabolites", and result from the modification of a molecule by the body upon ingestion or inhalation, followed by its excretion through sweat. The first report of such an approach is the publication of Leggett et al. [55] who targeted cotinine in fingermark residue through the use of anti-cotinine-functionalized gold nanoparticles. By doing so, fingermarks of smokers could be visualized whereas fingermarks containing no cotinine (non-smokers) remain latent. After this pioneering work, several publications followed [89-93] in an attempt to gain additional information about drug consumer-related fingermarks (Table 3). In this context, a commonly encountered protocol consists in grafting antibodies to the surface of (dye-doped) (magnetic) nanoparticles, allowing the specific binding to their targets. The magnetic core of nanoparticles is thought to be combined with the use of a magnetic bar to remove unbound nanoparticles. As a result, only the fingermarks containing a targeted component would "light up" on the item that has been processed. Recently, some researchers proposed an enzymatic immunoassay aiming at detecting minute amounts of cocaine contained in fingermark secretions.[220] However, their method requires the extraction of the fingermark in methanol before conducting the immunodetection process, which is rather in the perspective of developing a sensor than a detection technique.

<Table 3>

Pros/Cons of the technology

Immunodetection is the less mature emerging trend of this review. The recognition of antigenic targets by antibodies represents a powerful tool allowing a specific targeting of molecules of interest. This specificity should guarantee an efficient detection of secretion residue with limited risks of unwanted reaction of the substrate (background staining). Unfortunately, immunodetection suffers from its own limitations: cost and fragility of antibodies, storage conditions, limited volume of reagents, long and multiple immersion steps, which currently hamper its application as a fully operational detection technique. As an illustration of these limitations, most of published studies report the use of a hydrophobic pen to surround the fingermark of interest before applying few microliters of solution to perform the detection. Again, it is understandable from a proof-of-concept perspective, but it is then awaited to quickly upscale the volumes up to hundreds of milliliters to confirm the viability of the technique. In terms of metadetection (generally performed through the targeting of context-related antigens), the detection of a fraction of the fingermarks in presence is quite unusual in an investigative process. The aim would rather be to detect as many marks as possible, not only those of smokers or drug consumers. In that aspect, the immunodetection of fingermarks for metadetection purposes currently hardly fit forensic purposes, unless security scopes are considered (such as the development of sensors).

Expectations in terms of research

Immunodetection technology is worth being explored regarding its specific targeting abilities. If detection purposes are aimed, research efforts should quickly tackle the identified limitations of the technique, *e.g.*, dotty patterns and use of too small an amount of working solution. About the first limitation, the simultaneous detection of multiple antigenic targets currently appears as the best-so-far approach to circumvent this phenomenon. The targeted proteins have however to be carefully chosen so that they are stable over time and cover pore positions (*e.g.*, dermcidin) as well as the ridge pattern (*e.g.*, proteins involved in the desquamation process, such as keratin and cathepsin [214]). Addressing the second limitation requires to deal with hundreds of milliliters of active solution so that a proper processing of an item can be envisaged. Such on-going efforts can be witnessed in a recent publication assessing the application of antibody- and aptamer-based techniques to fingermark detection.[221] In this article, the authors reported a solution height of 0.75cm to process their samples by immersion in trays. Even if the total volume used per detection is not reported, it definitely constitutes a step forward. Additionally, a thorough review of the composition of secretion residue in terms of proteins and polypeptides is required. It is indeed necessary to clearly identify the potential antigenic targets in presence as it would drive the choice for specific and efficient antibodies. Proteomics or the use of aptamers could play a role here. Moreover, gaining knowledge about secretion residue composition (especially in terms of antigenic targets) combined with an appropriate detection approach could promote the emergence of metadetection purposes fitting forensic needs. Finally, and similarly to the two other emerging fields, it is awaited that the development of sensors for security purposes would prevail as they would get rid of some forensic constraints linked to an investigative process.

Conclusions

This critical review aimed at exploring three notable emerging trends in the field of fingermark detection/visualization: specifically-designed nanoparticles, chemical imaging, and immunodetection, each having an indisputable role to play. This review has been built so that the publications were classified along two main purposes: detection and metadetection. The first one encompasses all the techniques having for primary and sole aim to emphasize the fingermark ridge patterns (identification purposes); the second one encompasses all the techniques aiming at bringing additional information from the detected ridge patterns (*e.g.*, consumption habits, manipulation of explosives). Metadetection is quite recent and is closely related to

technological developments combined with an analytical trend in the researches linked to fingermarks, with sometimes opposing or conflicting interests regarding the investigative process and forensic requirements. Some of the reported techniques could constitute new efficient fingermark detection techniques, to be used in combination with existing ones; other could help studying the composition of secretion residue and its evolution with time or upon external influence; finally, those bringing additional information about the donor (*e.g.*, gender, life habits, or disease) appeared to rather find their place in the development of security-oriented sensors.

In the context of detection, the acceptance of a new technique by the forensic community is not solely relying on its efficiency to detect marks, but is also a matter of specific requirements to be met. Those are mainly dictated by operational work: as cheaper and simple as possible, ideally not requiring the purchase of additional equipment, not destructive regarding the item to be processed (or the least possible), and most importantly: more efficient than existing techniques and compatible with the operational workflow. In this regards, many publications do not go beyond the academic research level because researchers did not encompass these limitations in the early stages of the research. To sensitize the scientific community, the International Fingerprint Research Group has recently published guidelines for researchers willing to develop new fingermark detection techniques.[222] These guidelines are extremely valuable as they emphasize some specificities regarding fingermarks and recommendations about the design of an efficient research/evaluation protocol (*e.g.* number of donors, type of secretions, comparison with existing techniques using split marks). Also, contacts with operational forensic services (or at least awareness of their needs and resources) constitute a requisite to orientate the development of a detection technique in the right direction.

In the context of metadetection, the most-often emphasized argument is that there is much more information than a ridge pattern that could be extracted from secretion residue. This is true from a chemical point of view. However, contrary to what can be read, forensic investigators do not «forget that material transferred by the fingerprints may give additional opportunity for a more thorough analysis».[223] It is more a matter of pertinence (relevancy) of the information, of resources (*e.g.*, need for high-end equipment, specifically trained personnel, time available), and of workflow integration. If, from an analytical point of view, it appears valuable to obtain information regarding the gender, the age, or the diet of the person having left the mark from minute quantities of sweat left on a surface, it is not always the case from a forensic (investigative) point of view; additionally, other existing techniques may be more appropriate to obtain such information (*e.g.*, DNA to assuredly determine the gender from secretion residue, or criminological studies to establish reliable statistics).

Finally, scientists working on fingermark-related technologies should always ask themselves three questions: "What kind of information does my technique allow to obtain/retrieve?", "What question does this information allow to answer?", and finally "At which stage of the forensic workflow could my technique be implemented?" Too often it appears that authors do not have considered these questions soon enough. It should indeed be kept in mind that forensic science services are actually keen to modify their protocols if convincing elements are brought to them (encompassing betterment compared to existing protocols, maturity level of the technique, technological requirements and cost issues) or through feedback from academic partners. A new technique can spread worldwide very quickly, in a matter of a year or two in some cases. It has been observed in 2007 with an optimized formulation of 1,2-indanedione [7, 8] (an amino acid reagent) and more recently with one-step luminescent cyanoacrylate solutions.[9-12] In both cases, the key elements were the publication of efficiency/sensitivity assessment through pseudo-operational trials, blind comparisons, or integration into existing workflows. It is the aim of this review to bring people a matter of thoughts on this aspect of the forensic-oriented research, and to try reaching a stake level from all the research efforts carried out in the field of fingermark (meta)detection.

Disclosure statement

The author of this manuscript expressed his own view and has no conflict of interest with any cited author.

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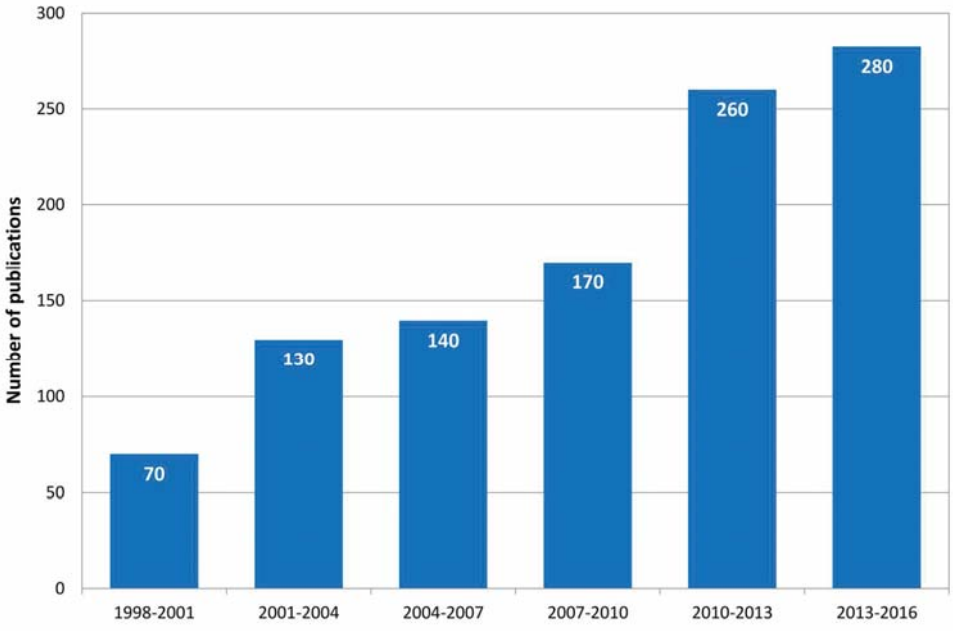
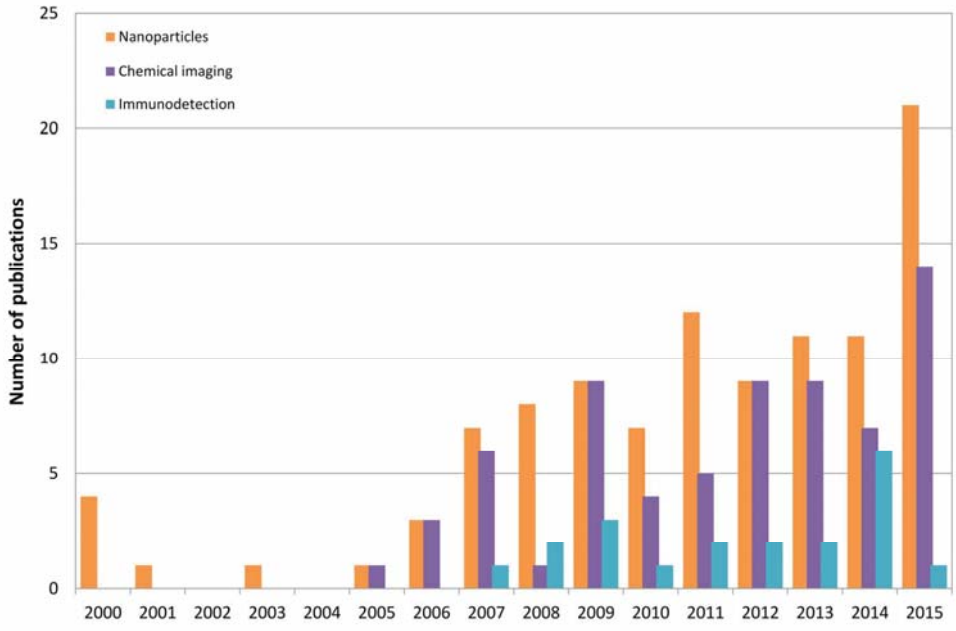
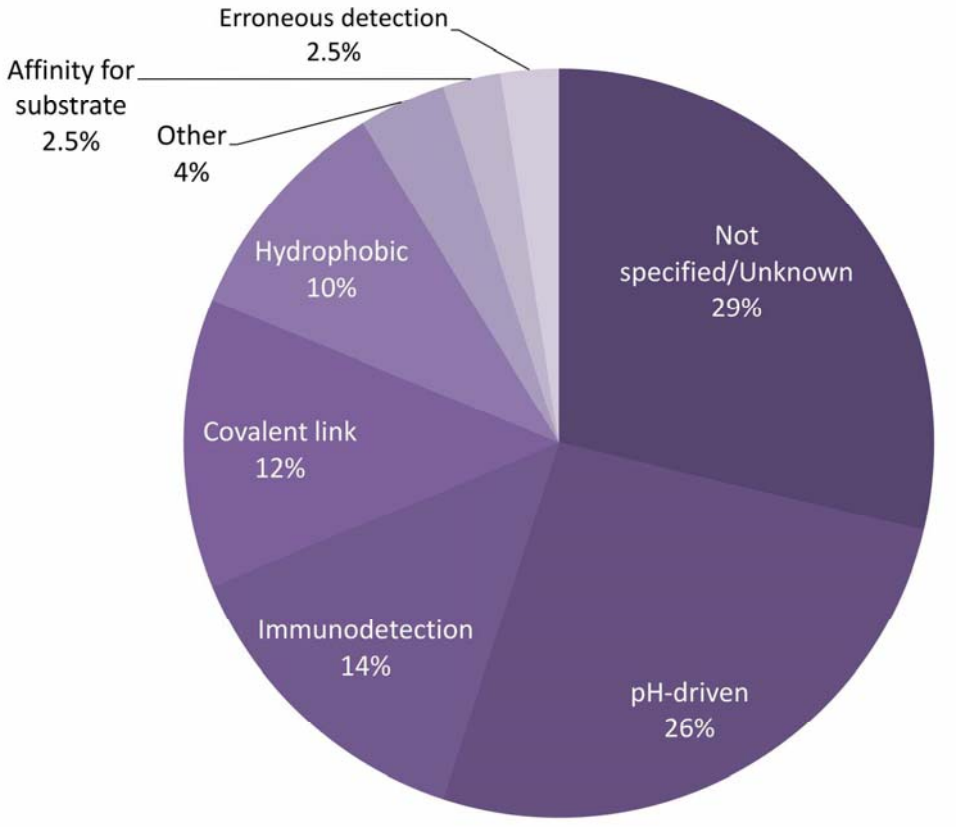


Number of articles related with the detection of fingermarks – or with the study of secretion residue – reported in the six last editions of the Interpol reports covering the field.[13-18] For information, Interpol reports are part of an exhaustive reviewing process among the forensic community and are published every three years. They constitute a valuable and exhaustive source of information on various topics, among which fingerprints and fingermark detection. Each 3-year period ends at July of a year to start again in August in the next report, avoiding any risk of overlap (explaining why some years appear twice in the legend). Latest documents can be obtained online (http://www.interpol.int/en/Internet/INTERPOL-expertise/Forensics/Forensic-Symposium).

Figure 1
168x110mm (300 x 300 DPI)



Total number of articles published per year linked to the use of nanoparticles to detect fingermarks (orange), chemical imaging of secretion residue (purple), and immunodetection applied to fingermarks (blue).
Figure 2
168x110mm (300 x 300 DPI)



Interaction modes reported in the literature in regards with the use of nanoparticles in solution are applied to fingermark detection. Please note that the articles referring to the use of dry powders - to be dusted - were not included in this chart.
Figure 3
168x144mm (300 x 300 DPI)

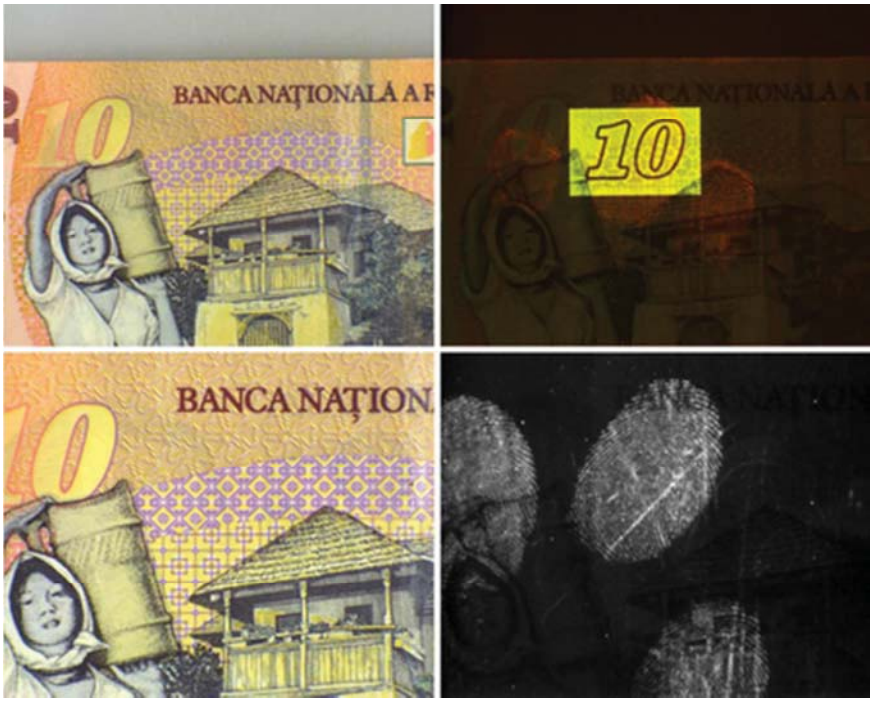
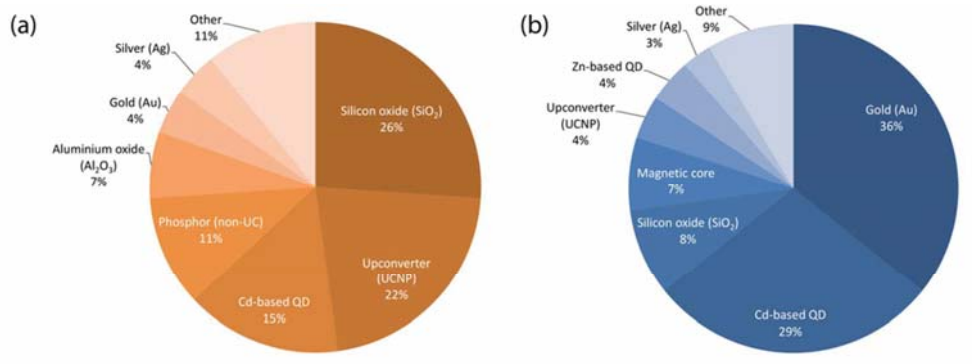


Illustration of the optical advantage offered by upconverter material (bottom) compared to conventional luminescent reagent (top) for the detection of fingermarks on complex substrate (a Nicaraguan banknote in that case). Under white light, no ridge details could be observed due to the illustrated substrate (left half). When excited in the UV range (conventional luminescent powder), the optical activity induced by the substrate prevents the observation of clear ridge details (top right). When excited in the near-infrared range (upconverter material), the substrate remains totally dark, offering a perfect background for the observation of fingermarks (bottom right). Please note that in this case, micron-size particles were dusted, not nanoparticles. [Image source: [224]]

Figure 4
37x30mm (300 x 300 DPI)



Core compositions reported in the literature in regards with the use of nanoparticles as dried powder (a) or in solution (b). [Abbreviation – QD: Quantum Dot]

Figure 5

85x31mm (300 x 300 DPI)

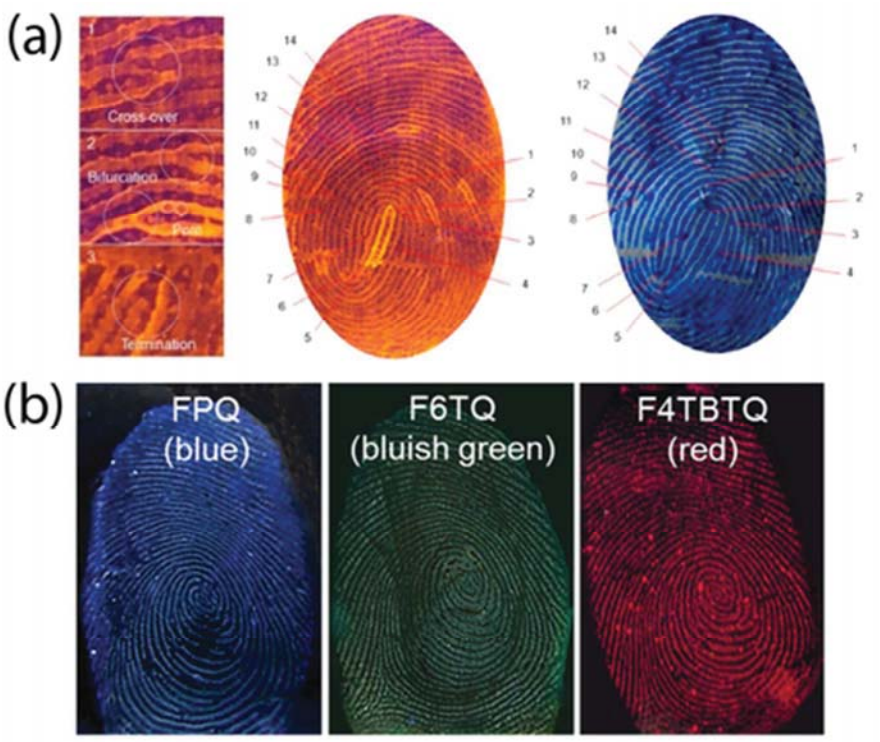
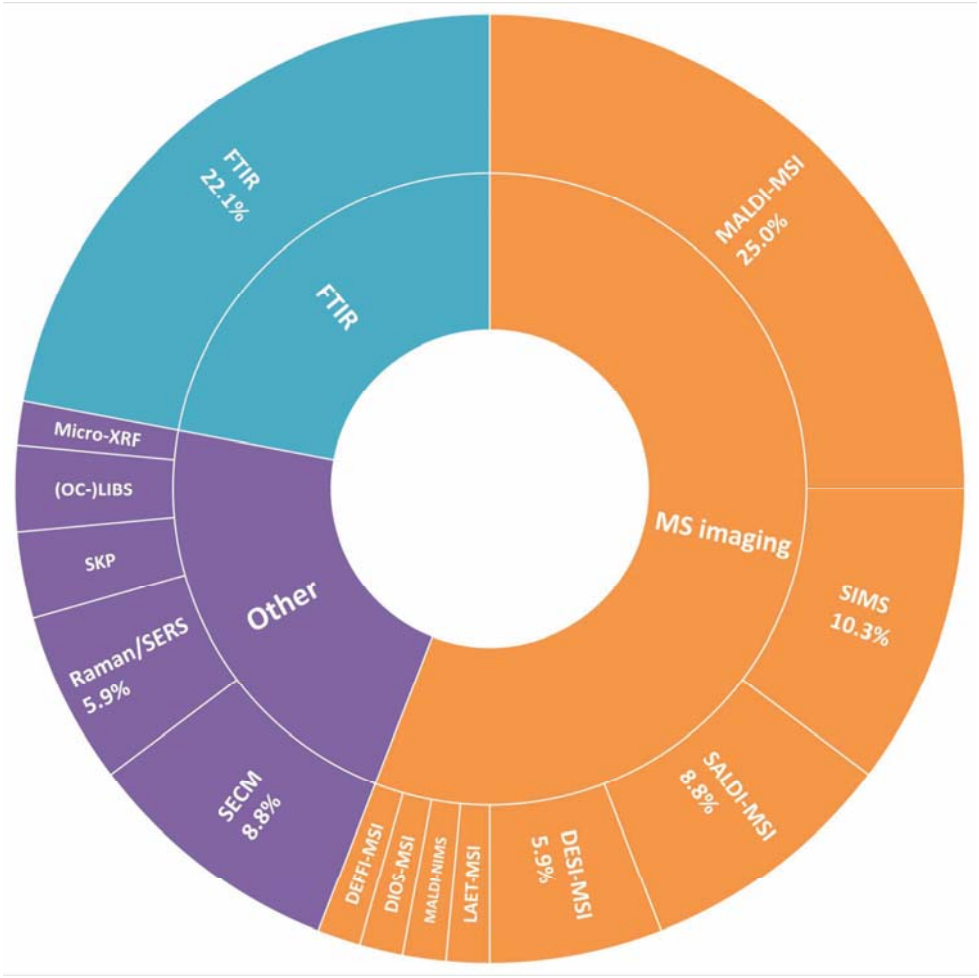
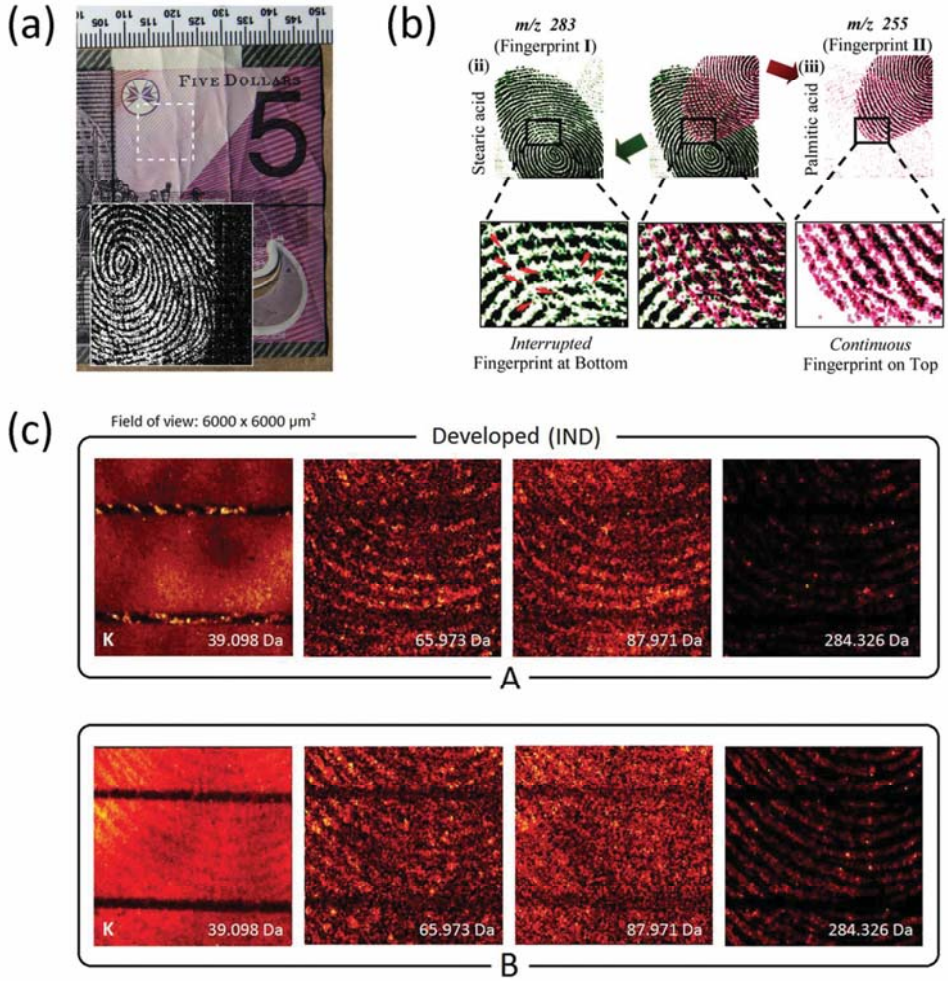


Illustration of two erroneous cases of ridge detection using nanoparticles: (a) on the left is the mark detected using luminescent nanoparticles, and on the right is the reference print (blue-inked). It can be seen that the luminescent ridge pattern on the left is the reverse pattern of the print (dark blue pattern), reflecting the fact that nanoparticles have actually interacted with the underlying substrate and the inter-ridge area, not with the ridges. This is also confirmed by the presence of pores all along the dark ridges on the mark, pores being present along ridges only. (b) three fingermarks left by the same finger; The mark processed with "FPQ" present a mirrored contrast compared to the two other marks, meaning that "FPQ" actually interacted with the inter-ridge area. [Image sources: [130] and [225]]

38x32mm (300 x 300 DPI)

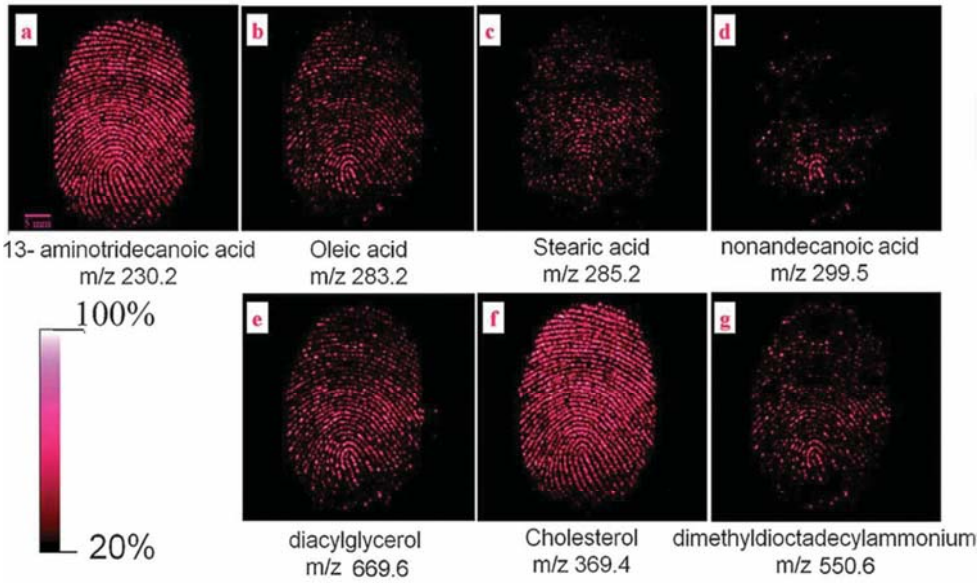


Sunburst representation of the different analytical methods applied to the chemical imaging of secretion residue. [Abbreviations – see Table 2]
Figure 7
168x168mm (300 x 300 DPI)



(a) FTIR chemical imaging of a cyanoacrylate-fumed polymer banknote (i.e., 5 AUD) [Image source: [160]]; (b) MALDI-MSI imaging allowing the separation of two overlapped fingermarks differing in their composition [Image source: [168]]; (c) ToF-SIMS imaging of two case scenarios: fingermark left after text writing (top) or before (bottom). [Image source: [155]]

Figure 8
108x112mm (300 x 300 DPI)



MALDI-MSI chemical imaging of a fingermark emphasizing the presence of fatty acids and of a drug contaminant (m/z 550.6). [Image source: [148]]
Figure 9
353x214mm (72 x 72 DPI)

Table 1

Core composition	Dry powder	In solution
(Dye-doped) Aluminium oxide	36-38	39
Calcium carbonate	40	/
Carbon-dot	41	42
Copper-based	40	43
Europium oxide	/	44
Gold	24	33, 45-68
Heavy metal-based QD [free or incorporated into a polymeric structure]	26-30, 69	29, 70-87
Iron oxide / gold nanocomposite [for SERS applications]	88	/
Iron oxide (magnetic) [for immunodetection]	/	89-93
Lanthanide-based phosphor/nanocomposite [with upconversion]	94-103	95, 96, 104
Lanthanide-based phosphor/nanocomposite [without upconversion]	105-107	/
(Dye- or QD-doped) Silicon oxide	31, 108-114	35, 113, 115-117
Silicon oxide [for chemical imaging or analytical purposes]	118-122	123
Silver*	24, 124	125, 126
Titanium dioxide	25	127
Zinc-based QD	/	128-130
Zinc oxide	131	131

Table 2

Analyzed material	Contamination (nature and deposition process)	Fingermark detection technique (prior to imaging)	Imaging technique	Remark	Reference(s)
Imaging of latent/unprocessed fingermarks	-	N/A	FTIR	-	141
			FTIR	Specific substrate; Study of the residue composition	142
			FTIR	Fingermarks lifted from substrate prior analysis/imaging	143
			FTIR	Separation of overlapped fingermarks; sebum-rich mark	144
			DIOS-MSI	Specific substrate	145
			LAET-MSI	Specific substrate; Separation of overlapped marks	146
			LIBS	-	147
			MALDI-MSI	Matrix required (sprayed)	148
			MALDI-MSI	Matrix required (silver clusters); Separation of overlapped marks	149
			MALDI-NIMS	Specific substrate; Study of the residue composition	150
			SKP	Limited to metallic substrates	151
			SIMS	-	152
			SIMS	Sequence between fingermark and text writing/printing	153-155
			SIMS	Age estimation of fingermarks	156
			Micro-XRF	Imaging of ions (Na, Mg, Al, Si, P, Cl, K, Ca, Fe)	157
Imaging subsequent to a detection technique	-	Cyanoacrylate fuming	FTIR	-	158-161
		Diacetylene copolymers	FTIR	-	162

		Pyrrole and EDOT copolymer	FTIR	-	163
		α-cyano-4-hydroxycinnamic acid (powder)	MALDI-MSI	Dual role of the □-CHCA (detection and imaging requisite)	164, 165
		Curcumin (powder)	MALDI-MSI	Dual role of the curcumin (detection and imaging requisite)	166
		Powder, powder suspension, cyanoacrylate fuming, dye staining, vacuum metal deposition, amino acid reagents	MALDI-MSI	Dual role of the powder as matrix (detection and imaging requisite)	167
		Gold sputtering	MALDI-MSI	Dual role of gold (detection and imaging requisite)	168
		Metal sputtering or 2-mercaptobenzothiazol (sublimation)	MALDI-MSI	Dual role of the metal/molecule (detection and imaging requisite)	169
		Diacetylene copolymers	Raman	-	170
		Multimetal deposition	SECM	-	171-173
		Metal sputtering	SECM	-	174
		Vacuum metal deposition (VMD)	SKP	Limited to metallic substrates	175
		Cyanoacrylate fuming (+stain)	SIMS	-	152

		Amino acid reagents; iodine fuming	SIMS	Sequence between fingermark and text writing/printing	155
Drug and/or explosive-contaminated fingermarks (by manipulation/contact)	Explosive /powder Protocol P1	-	FTIR	Particle imaging/identification	144
	Drug /powder See remark	-	FTIR	- Skin surface imaged after contact with powder - Particle imaging/identification	176
	Explosive /solution Protocol L2	-	FTIR	Separation of overlapped marks	177
	Drug and explosive /powders Protocol P2	-	FTIR	Particle imaging/identification	178
	Artificial sweat + mold – See remark	-	DEFFI-MSI	- Artificial sweat (including drug/explosive/cosmetics) - Mark lifted with an adhesive prior analysis	179
	Drug and explosive /solution Protocol L2	-	DESI-MSI	Sample to be sprayed before analysis	180
	Artificial sweat + mold – See remark	-	DESI-MSI	- Artificial sweat (including drug or explosive for one) - Sample to be sprayed before analysis	181, 182
	Drug /powder Protocol P1	-	DIOS-MSI	Specific substrate required for analysis	145
	Drug /powder Protocol P1	Cyanoacrylate fuming, followed by powdering (matrix)	MALDI-MSI	- Dual role of the powder (detection and imaging requisite) - Exposition to acetone vapors before adhesive-lifting and analyzing the detected mark - Particle imaging/identification	183
	Drug /powder	Gold sputtering	MALDI-MSI	Dual role of the gold (detection and	168

	Protocol P3			imaging requisite)	
	Drug /powder Protocol P1	-	MALDI-MSI	- Silver clusters as MALDI matrix - Particle imaging and identification	149
	Drug /powder Protocol P1	-	MALDI-MSI	MALDI matrix applied by sublimation	184
	Drug /solution Protocol L2	Curcumin (powder)	MALDI-MSI	Dual role of the curcumin (detection and imaging requisite)	166
	Drug /solution Protocol L1	Cyanoacrylate fuming, dye staining, vacuum metal deposition (VMD)	MALDI-MSI	- Sample to be sprayed before analysis - Influence of fingermark detection techniques on the chemical imaging	185
	Drug and explosive /powder and solution Protocols P1 and L1	Cyanoacrylate fuming, conventional powder	MALDI-MSI	- Sample to be sprayed before analysis - Influence of fingermark detection techniques on the chemical imaging	186, 187
	Artificial sweat + mold – See remark	-	MALDI-MSI	Artificial sweat (including Pb, Ba, Sb)	182
	Explosive /powder Protocol P3	-	OC-LIBS	-	188
	Drug /solution See remark + Drug /powder Protocol P1	Hydrophobic silica powder	SALDI-MSI	- Drug in solution applied on the fingermarks - Dual role of the silica-based powder (detection and imaging requisite) - Mark lifted by adhesive prior analysis	122
	Drug /solution Protocol L2	-	SALDI-MSI	Specific substrate; Mark lifted by adhesive then transferred before analysis	189
	Drug /powder Protocol P1	Cyanoacrylate, followed by powdering (matrix)	SALDI-MSI	- Dual role of the powder (detection and imaging requisite) - Exposition to acetone vapors before adhesive-lifting and analyzing the detected mark	183

				- Particle imaging/identification	
	Drug /powder and solution Protocols P2 and L2	Magnetic powder	SALDI-MSI	- Dual role of the powder (detection and imaging requisite) - Cross-contamination study	190
	Explosive /solution Protocol L2	Cyanoacrylate fuming	SECM	Combination with MALDI-MS for chemical identification	191
	Artificial sweat + mold – See remark	-	SIMS	- Artificial sweat (including drug) - Quantification attempts by using printed drug spots of known concentration	181
	Contamination protocols: P1 = the donor is asked to touch a surface contaminated with powder then to readily leave a mark P2 = same as P1 but the excess of powder is removed by brushing or contact with other fingers before leaving a mark P3 = the powder is left directly on the skin before the donor is asked to leave a mark L1 = a certain amount of solubilized contaminant is left on a surface and dried; the donor is then asked to touch the surface and readily leave a mark L2 = a certain amount of solubilized contaminant is left directly on the skin and dried; the donor is then asked to leave a mark				
Drug-contaminated marks (by ingestion)	Endogenous metabolites	-	DIOS-MSI	Specific substrate required for analysis	145
		Hydrophobic silica powder	SALDI-MSI	- Dual role of the silica-based powder (detection and imaging requisite) - Mark lifted by adhesive prior analysis	118
		Hydrophobic silica powder	SALDI-MSI	- Dual role of the silica-based powder (detection and imaging requisite) - Mark lifted by adhesive prior analysis	122
		Magnetic powder	SALDI-MSI	Dual role of the powder (detection and imaging requisite)	120
Other contaminants (by contact)	Cosmetics	-	FTIR	Fingermarks lifted from substrate prior analysis/imaging; Reference to drug-contaminated marks but no info regarding the protocol	192
	Lubricant (condom)	-	FTIR	-	193

	Lubricant (condom)	-	DESI-MSI	Sample to be sprayed before analysis	194
	Lubricant (condom)	-	MALDI-MSI	Sample to be sprayed before analysis ;	193, 195
	Lubricant (condom)	α-cyano-4-hydroxycinnamic acid (powder)	MALDI-MSI	Dual role of the α-CHCA (detection and imaging requisite); Separation of overlapped marks	196
	Fatty acids	Gold sputtering	MALDI-MSI	- Dual role of the gold (detection and imaging requisite) - Separation of overlapped marks	168
	Fish oil and β-carotene	-	Raman	-	197
	Artificial sweat	-	SECM	-	198
	Artificial sweat	-	SERS	-	125
	Protein (human IgG)	-	SERS	Antibody-functionalized nanoparticles	126
	Cosmetics	-	SIMS	Separation of overlapped marks	199
	Cosmetics, saliva, banana pulp	-	Micro-XRF	Imaging of ions (Na, Mg, Al, Si, P, Cl, K, Ca, Fe)	157

Table 3

Category	Antigen	Carrier	Observation	Reference
Common antigens	Dermcidin	/	Visual (colored or luminescent)	214-218
	Cathepsin D	/	Visual (colored or luminescent)	214
	Keratin (1 and 10)	/	Visual (colored or luminescent)	214, 216
	Albumin	/	Visual (colored or luminescent)	216, 219
	Lysozyme	/	Visual (chemiluminescent)	218
	EGF	/	Visual (chemiluminescent)	218
	L-amino acids	Functionalized gold NP	Visual (luminescent)	60
	Human IgG (artificially-enriched marks)	Functionalized silver NP	Chemical imaging (SERS)	126
	Lysozyme and EGF	Functionalized gold NP	Visual (colored)	63
	Lysozyme aptamer	Functionalized upconversion NP	Visual (luminescent)	104
Specific targets/metabolites	Benzoylecgonine (cocaine consumer)	Functionalized magnetic NP	Visual (luminescent)	91, 93
	Cocaine (handling)	Functionalized upconversion NP	Visual (luminescent)	104
	Cotinine (smoker)	Functionalized magnetic NP	Visual (luminescent)	89, 90, 92
	Cotinine (smoker)	Gold NP	Visual (luminescent)	55
	Morphine (heroin consumer)	Functionalized magnetic NP	Visual (luminescent)	93
	Methadone and its metabolite (EDDP)	Functionalized magnetic NP	Visual (luminescent)	91
	THC (cannabis smoker)	Functionalized magnetic NP	Visual (luminescent)	91