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Fingerprinting

Advances in Fingerprint Analysis

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***F**ingerprints have been used in forensic investigations for the identification of individuals since the late 19th century. However, it is now clear that fingerprints can provide significantly more information about an individual. Here, we highlight the considerable advances in fingerprinting technology that can simultaneously provide chemical information regarding the drugs ingested and the explosives and drugs handled by a person as well as the identity of that individual.*

1. Introduction

The pattern of friction ridge skin on the palms of the hands and soles of the feet are unique to each individual.[1] The development of this friction ridge skin occurs in the womb between the 9th and 24th week of embryo development.[2] As each embryo experiences differential growth and pressure within the womb, the final pattern of the friction ridge skin is different for each individual, even for identical twins.[3] Fingerprints are the contact impression of the raised portion of the friction ridge skin.[1] This unique pattern has been used in forensic investigations to establish the identity of an individual since the late 19th century.[4] Friction skin contains a series of lines corresponding to ridges and grooves. It is the pattern of these ridges and grooves that impart individuality to a fingerprint and remains unchanged throughout a person's lifetime.[1] Each skin ridge is populated by a single row of pores, through which sweat is excreted and deposited on the surface of the skin. There are three types of natural secretion glands in the body. Each gland produces a different type of sweat, namely, eccrine, sebaceous, and appocrine.[5] The composition of these three secretions is of particular interest for forensic investigations. Eccrine sweat glands are found all over the body, but are in higher density in palmar and plantar surfaces.[6] Eccrine sweat consists of 98–99% water, various inorganic salts (such as chloride, bromide, iodide, fluoride, and phosphate), and organic materials (such as amino acids, fatty acids, and urea).[7] Sebaceous glands are found all over the body, except on the friction ridge surfaces of the hands and the feet. Sebaceous glands excrete sebum, which mainly consists of saturated fats, waxes, and squalene.[8] Appocrine glands are found primarily in axillae and anogenital areas of humans, and these glands excrete a viscous milky fluid.[6]

When a finger touches a surface, eccrine sweat, together with oily substances such as sebum picked up by the finger, forms an impression of the finger's ridge pattern. Such an impression is known as a latent fingerprint because of its invisibility to the naked eye. Chemical or physical treatments are required to visualize latent fingerprints.[9] The earliest detection techniques for developing latent fingerprints on porous surfaces include ninhydrin solution[9] and iodine/benzoflavone spray.[10,11] These two techniques are still used by scene of crime officers. Fuming with cyanoacrylate esters ("superglue") is an effective technique for developing fingerprints on nonporous surfaces.[12,13] Since contrast is often a problem with fingerprints developed by cyanoacrylate fuming, some form of post enhancement is also generally required.[14,15] Another important technique for fingerprint detection on nonporous surfaces is vacuum metal deposition.[16,17] However, the most widely used fingerprint detection method at a scene of a crime is that of fingerprint powdering.[18] A range of different powders, for example, aluminum flake powder, magnetic powder, iron flake powder, and luminescent powder, are commercially available.[19] The choice of which particular powder to use depends on a number of factors, including the nature of the surface to be treated and personal preference of the forensic officer.

Although the current methods for chemically and physically developing latent fingerprints are all used successfully in forensic investigations, there is still a need for simple, accurate, cost-effective, and nondestructive universal methods for the detection of fingerprints. Additionally, the possibility that a fingerprint can provide more information about a person than just identity is particularly exciting. For example, information about whether a person has taken narcotic drugs[20–23] or has been in contact with explosive materials[24–27] has recently been reported by using methods to

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develop latent fingerprints. Various spectroscopic and microscopic techniques have also been employed successfully for fingerprinting.[28,29] The main challenge lies in finding a suitable portable method that can be used at the scene of a crime for forensic investigation. The method must be able to deliver accurate results within a short time period as well as produce and maintain high-quality evidence. Here we review the recent advances in the development and visualization of latent fingerprints and show the potential of these techniques for obtaining additional chemical information from the developed fingerprints.

2. Metal and Semiconductor Nanoparticles in Fingerprint Detection

Over the last decade, metal and semiconductor nanoparticles have been used extensively for the detection and analysis of latent fingerprints.[30] In this section, the use of such nanoparticles for the development of fingerprints and to obtain chemical information from the sweat deposited within a fingerprint is discussed.

2.1. Gold Nanoparticles

Gold nanoparticles are the most stable, and probably the most frequently studied, nanoparticles.[31] Many research groups have used gold nanoparticles for the detection of fingerprints. Multimetal deposition (MMD) is a well-known technique used for the enhancement of fingerprints. It is based on the deposition of colloidal (nanoparticle) gold on the finger secretions followed by signal amplification by silver reduction on the gold surface.[32,33] MMD works on both porous and nonporous surfaces, dry and wet surfaces, as well as fresh and aged fingerprints. Although it has many advantages, MMD does have some major drawbacks. For example, it is quite labor intensive and the technique only produces fingerprint images that are dark gray or black. Becue et al. have developed a modified version of the MMD technique for the detection of fingerprints.[34,35] This research group have functionalized gold nanoparticles with cyclodextrins, which could trap dyes or other luminescent tags within the cyclodextrin cavities, to detect fingerprints in a single step. They showed that the MMD technique could also be used to obtain luminescent fingerprints.[35] Luminescent ZnO nanoparticles were prepared by the in situ deposition of zinc oxide onto the gold nanoparticles. These nanoparticles were used for the detection of fingerprints, as they show visible luminescence at approximately 580 nm when excited with UV light. Stauffer et al. proposed a modified MMD technique, known as single-metal deposition (SMD), for latent fingerprint detection, which replaces the silver enhancement of the gold colloids with a gold enhancement procedure.[36] The SMD technique was reported to be less labor intensive and less expensive, thus making it an attractive alternative to the MMD system. Gao and coworkers have used glucose-stabilized gold nanoparticles for the detection of latent fingerprints on nonporous surfaces by using the SMD technique.[37] In a further report based on gold nanoparticles, Sametband et al. used gold colloids stabilized with *n*-alkanethiols for the enhancement of latent fingerprints.[38]

The first report on the detection of forensic analytes that had been secreted within the sweat deposited with latent fingerprints was published by Leggett et al.[20] In this study it was shown that gold nanoparticles functionalized with an antibody specific to cotinine,[39] the major metabolite of nicotine, could be used to detect the presence of cotinine in the fingerprints of smokers and simultaneously obtain an image of the fingerprint. This method was used to detect a drug or drug metabolite in a latent fingerprint and simultaneously used to identify an individual. In this study, protein A was self-assembled on the gold nanoparticles. The anti-cotinine antibody was then bound to the nanoparticles functionalized with protein A. These antibody/gold nanoparticle conjugates were incubated on a fingerprint collected on a glass microscope slide (Figure 1 a). A secondary antibody fragment, tagged with a fluorescent dye, was used to fluorescently label the fingerprint. When the fingerprint was imaged using a fluorescence stereomicroscope, a high-resolution image was obtained when the fingerprint was deposited by an individual who smoked cigarettes (Figure 1 A4 and Figure 2). The images clearly showed the typical fingerprint ridge pattern in sufficient detail that would enable identification of an individual. At higher magnifications (Figure 2), second level details such as ridge ending, bifurcations as well as third level detail such as pores are clearly visible.

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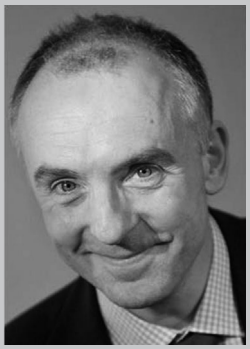

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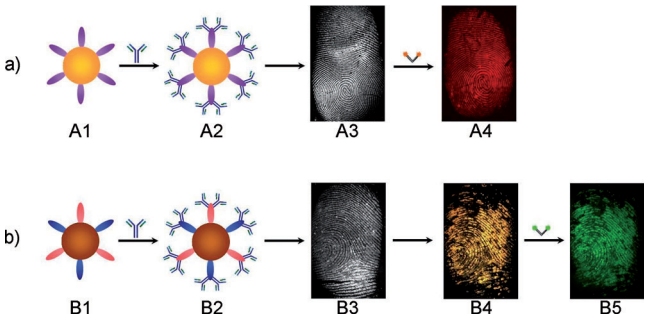

Figure 1. Schematic representation of the detection of drugs and/or drug metabolites in latent fingerprints using a) gold nanoparticles and b) magnetic particles. Either gold nanoparticles coated with protein A (A1) or magnetic particles coated with recombinant protein A/G (B1) are used to bind a primary antibody to form antibody conjugates of the particles (A2 and B2, respectively). The conjugates are then incubated on a latent fingerprint deposited on a glass microscope slide (A3, B3). Finally a secondary antibody fragment tagged with a fluorescent dye that produces a fluorescent image when bound to the fingerprint is incubated on the fingerprint (A4, B5). A fluorescence stereomicroscope is used to image the fingerprint. In the case of magnetic particles, the successful binding of the particles to the fingerprint can be observed by a change in the color of the fingerprint from colorless to yellowish-brown under white light illumination (B4). The different color of the fluorescent images of the fingerprints (A4, B5) is obtained by varying the dye used for labeling the secondary antibody fragments.

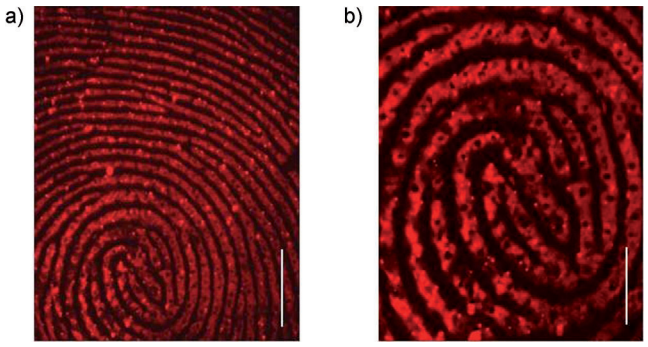

Figure 2. Detection of cotinine in a fingerprint using anti-cotinine/gold nanoparticle conjugates and a secondary antibody fragment tagged with Alexa546 dye.[20] The fluorescence images shown in (a) and (b) are of the same fingerprint section, but at two magnifications. The black dots visible along the ridge pattern (readily seen in b) are the pores from which the sweat is secreted. The scale bars in (a) and (b) correspond to 2 mm and 1 mm, respectively.

Importantly, no fluorescence image was obtained of the fingerprint when the volunteer was a nonsmoker. This result shows that the antibody/nanoparticle conjugates were specifically binding to the cotinine antigen present in the fingerprint. When the experiment was performed using anti-cotinine antibodies alone, that is, without conjugation to the gold nanoparticles, the quality of the images was poor.[20] The research showed the importance of the nanoparticles in obtaining high-resolution fingerprint images that could be used for identification purposes and importantly could establish drug use.

Recently, Spindler et al. have extended the use of antibody-functionalized gold nanoparticles for the enhancement of latent fingerprints.[40] This research group has used L-amino acid antibodies to functionalize the gold nanoparticles to facilitate the detection of amino acids in the sweat of a latent fingerprint. This research group found that the anti-amino acid nanoparticles were particularly effective for the enhancement of aged and dried fingerprints.[40]

2.2. Magnetic Particles

Magnetic powder has been used in forensic investigations for the development of latent fingerprints since the 1960s.[41–44] Recently, we reported a combined approach based on antibody/magnetic particle conjugates, in which the advantages of both magnetic powders and the recognition properties of antibodies were used.[21–23,45] The conjugates were fabricated (Figure 1b) using commercially available iron oxide particles (1 μm total diameter) which were functionalized with recombinant protein A/G. The iron oxide particles are superparamagnetic, due to the individual size of the particles, thus the particles are only magnetic when a magnetic field is applied. The combination of protein A and G on the surface of the iron oxide particles enables the conjugation of a wide range of subclasses of mouse IgG antibodies, and so provides the possibility of detecting a broad range of antigens. These antibody/magnetic particle conjugates were used for the detection of drugs and drug metabolites present in the eccrine sweat deposited within latent fingerprints. The magnetic particles were functionalized with a range of primary antibodies for the detection of Δ^9-tetrahydrocannabinol (THC; the main psychoactive component of cannabis),[46,47] methadone (a synthetic opioid, generally prescribed as a substitute pharmacotherapy to heroin-dependent patients),[48,49] 2-ethylidene-1,5-dimethyl-3,3,-diphenylpyrrolidine (EDDP; the major metabolite of methadone),[50,51] benzoylecgonine (the major metabolite of cocaine),[52] and cotinine (the major metabolite of nicotine).[39] The approach involved the conjugation of primary antibodies to the magnetic particles coated with recombinant protein A/G to produce antibody/magnetic particle conjugates. The conjugates were incubated on a fingerprint and then a secondary antibody fragment, tagged with a fluorescent dye, was used to fluorescently label the bound magnetic particle conjugates (Figure 1b). The fingerprints were then examined using a fluorescence stereomicroscope. The successful detection of a drug or a drug metabolite was evident by the change of color of the fingerprint from gray (Figure 1B3) to yellowish-brown (Figure 1B4) after application of the antibody/magnetic particle conjugates. The presence of the fluorescently tagged secondary antibody fragment produced a fluorescent image when visualized under fluorescent light. This method has been successfully used to detect THC (Figure 3), methadone, EDDP, benzoylecgonine, and cotinine in latent fingerprints deposited on glass slides by using brightfield and/or fluorescence microscopy.[21,22] The antibody/magnetic particle conjugate approach produces images of high evidential quality. In the case where the fingerprint is deposited by a nondrug user,

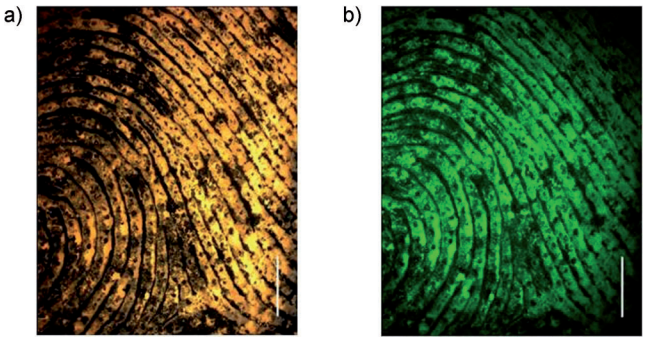

Figure 3. Detection of THC in a fingerprint using anti-THC/magnetic particle conjugates and a secondary antibody fragment tagged with Alexa488 dye. a) Brightfield and b) fluorescence image of a fingerprint section showing the successful detection of THC using brightfield and fluorescence microscopy. The pores are visible as black dots along the ridges of the fingerprint. The scale bars correspond to 2 mm.

the color of the fingerprint does not change (from the original gray color) following application of the antibody-functionalized magnetic particles. Additionally, no fluorescence image of the fingerprint is observed, thus confirming the specificity of this approach. By using the antibody/magnetic particle conjugates, it has also been demonstrated that multiple drug metabolites can be detected simultaneously from a single latent fingerprint. In this case, the fingerprint is partitioned into two parts and then different antibody/magnetic particle conjugates are applied to the separate parts of the fingerprint. This method was successfully used to simultaneously detect the metabolites of heroin and cocaine, that is, morphine and benzoylecgonine, respectively, in a single fingerprint.[23] In a further recent development, the antibody/magnetic particle conjugates have been successfully applied for the development of latent fingerprints and the detection of cotinine on a highly reflective, nonporous white porcelain surface.[53]

2.3. Semiconductor Quantum Dots

Quantum dots (QDs) are semiconductor nanocrystals with unique optical and electronic properties that are size-dependent.[54] Quantum dots can luminesce with a greater intensity than commercially available organic fluorescence dyes, and so potentially are ideal reagents for the enhancement of latent fingerprints. As a consequence of their high luminescence, QDs bound to fingerprints can be visualized directly using UV illumination without the need for further chemical treatment. Sametband et al. have shown that CdSe/ZnS QDs stabilized with *n*-alkaneamines in organic solution can be used for the direct visualization of latent fingerprints on wet nonporous surfaces such as silicon.[38] CdS/dendrimer nanocomposites in organic solvents have also been used for the detection of cyanoacrylate ester fumed fingerprints on nonporous surfaces.[55–57] To avoid the use of organic solvents, QDs can be solubilized in aqueous solvents through variation of the outer-surface coating. Water-dispersible CdSe nanocrystals have been applied for the development of latent fingerprints that were deposited on adhesives.[58] In addition, CdTe QDs in aqueous solution have been used to detect fingerprints that were deposited by a volunteer who had covered their finger in blood.[59] The fingerprints were deposited on four different nonporous surfaces. The water-soluble QDs were found to have a strong affinity for haemoglobin, thereby enabling the visualization of the bloody fingerprints, even when the prints were faint.[59] Multicolored CdTe QDs in aqueous solution have been used for the development of fingerprints on objects with various background colors.[60] The production of a freeze-dried quantum dot surfactant (QDS) powder made of CdS/chitosan nanocomposites shows promise in developing unfumed cyanoacrylate latent fingerprints on aluminum foil.[61] However, further development of this area is needed to realize the full potential of QDs as a reagent for the detection and development of latent fingerprints.

3. Mass Spectrometry in the Detection of Fingerprints

The ability to selectively detect a particular molecular ion which can uniquely identify an illicit drug or an explosive residue from a fingerprint is potentially extremely useful for forensic work. Consequently, a number of research groups are developing techniques based on either mass spectrometry (MS) alone or chromatography coupled with MS detection.

3.1. Chromatography with MS Detection

Chromatography coupled with detection using mass spectrometry has been used to obtain information regarding the natural components of sweat deposited in fingerprints and the breakdown products of these components as a function of fingerprint aging. For example, by using GC-MS and subsequently LC-MS, Jickells and co-workers have shown that squalene, a major component of the sebaceous fraction of freshly deposited latent fingerprints, is readily oxidized and is not detectable nine days after deposition.[62,63] The same research group have used LC-MS/MS to detect and quantify methadone and EDDP found in fingerprints deposited by volunteers receiving treatment for heroin dependence.[64] Typical values for the methadone and EDDP were in the range 0.90–9.20 and 0.07–0.08 ng per fingerprint, respectively. The concentration of the drug detected was dependent upon the dose of methadone that each volunteer was prescribed. Recently, lorazepam, a drug which is associated with drug-facilitated sexual assault, has been detected in the fingerprints of healthy volunteers by using LC-MS/MS.[65] In this study, a single 2 mg oral dose of lorazepam was given to each of the volunteers. The parent lorazepam drug and its glucuronide metabolite were both quantitatively detected (11 and 210 pg, respectively), but only when ten fingerprints from a single individual were combined. Improvements in the sensitivity of the developed technique would be required to detect the parent lorazepam or its metabolite from a single fingerprint, although it should be noted that the original dose (2 mg) of the drug was low. Although the ability to separate, identify,

and quantify all of the species present in a fingerprint is undoubtedly a significant development in forensic fingerprint science, the disadvantage of using such techniques is that the fingerprint, that is, the evidence, is ultimately destroyed during the analysis. Clearly, the destruction of the original forensic evidence is not desirable and indeed may not be acceptable for the legal processes in some countries or jurisdictions.

3.2. Imaging of Fingerprints through the Combination of Particles and MS

Surface-assisted laser desorption/ionization (SALDI) has been used with mass spectrometry to detect illicit drugs and their metabolites in exogenously doped fingerprints and those obtained from known drug users.[66] In SALDI, particles are mixed with a surface-bound sample to enhance the desorption and ionization of the analyte from the surface upon laser irradiation. Rowell et al. have used SALDI in combination with a hydrophobic silica powder that incorporates carbon black. The silica powder interacts with hydrophobic components within a fingerprint, especially sebum-rich fingerprints, and so acts as a dusting powder to locate and visualize fingerprints.[66,67] The presence of the powder also acts as a SALDI enhancer and, therefore, enables the detection of analytes by mass spectrometry. Rowell et al. have used these silica particles in combination with SALDI-MS to detect contact residues of codeine, diacetylmorphine (heroin), cocaine, and products related to opium resin in fingerprints.[66] This technique has also been used to detect methadone and EDDP[66] as well as nicotine and cotinine[68] in sebum-rich fingerprints from volunteers. It is not clear whether this technique can achieve similar results from fingerprints which do not contain sebum, that is, fingerprints containing only eccrine (aqueous) sweat. In a further development, Tang et al. have shown that gold nanoparticles, in combination with laser desorption/ionisation MS, can be used to molecularly image endogenous and exogenous compounds deposited within latent fingerprints.[69]

3.3. Imaging with DESI

A particularly exciting development has been reported by the Cooks research group.[24] Desorption electrospray ionization (DESI) mass spectrometry has been used to image fingerprints through the detection of a molecular ion associated with both endogenous and exogenous species.[24,28] In the DESI technique, charged solvent droplets are sprayed onto the fingerprint, thereby creating a thin liquid film. Analyte species from the fingerprint then dissolve in this liquid film. Additional solvent droplets impact with the liquid film and cause dissolved analyte to be released from the surface. These secondary droplets are then heated under a vacuum to remove the solvent, and the ionized analyte is detected using the mass spectrometer.[28] The Cooks research group, who originally developed this MS technique, have shown that DESI can be used to image endogenous compounds such as *cis*-hexadec-6-enoic acid, steric acid, *cis*-octadec-8-enoic acid, palmitic acid, pentadecylic acid, myristic acid, and triacylglycerols in sebum-rich fingerprints.[24] However, this research group were also able to image fingerprints that had been exogenously doped with the narcotics cocaine and THC, as well as explosive materials such as trinitrohexahydro-1,3,5-triazine (RDX).[24] An example of the DESI image obtained from a fingerprint artificially doped with cocaine is shown in Figure 4.[24]

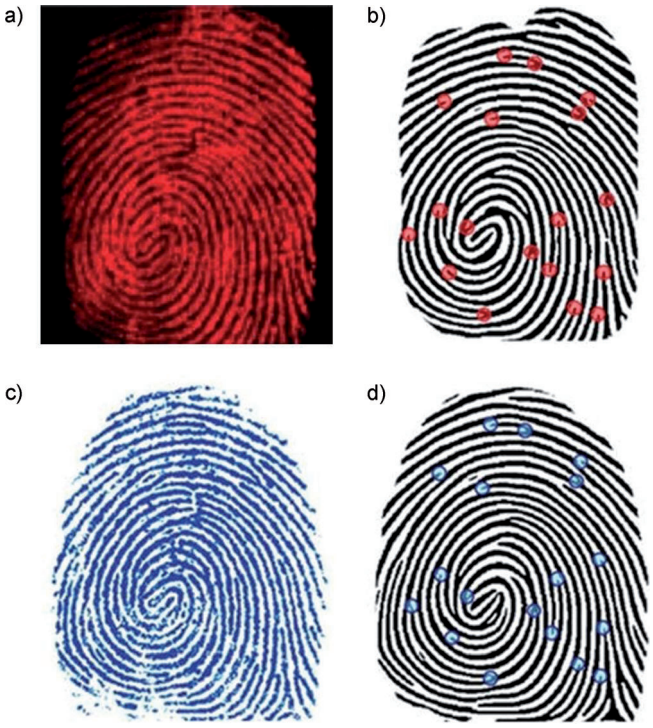

Figure 4. a) DESI image of the distribution of cocaine on a latent fingerprint on glass. b) A computer-generated fingerprint from the DESI image. c) Ink fingerprint blotted on paper and optically scanned. d) Computer-generated fingerprint from the optical image. Some of the automatically detected points of interest (minutiae) are represented by dots in (b) and (d). Figure reproduced from *Science*, with kind permission.[24]

3.4. Imaging with Matrix-Assisted Laser Desorption/Ionization (MALDI) MS

The use of techniques such as DESI ensures that an image of the fingerprint is obtained which may then be used as forensic evidence. However, the use of MS is generally destructive and so the original evidence would still be destroyed. Recently, a MALDI-MS method was devised in which oleic acid, an endogenous component deposited within a fingerprint, was imaged.[70] Importantly, this research group has shown that the MALDI matrix can be applied to the surface of a fingerprint, then removed with a simple washing procedure, thus allowing the underlying fingerprint to be enhanced and imaged with standard magnetic powder.

4. Vibrational Spectroscopic Imaging of Fingerprints

Vibrational spectroscopy offers the combined advantages of non-invasive imaging of fingerprints together with spectroscopic characterization of the prints or residues deposited within the prints. Both infrared and Raman imaging have been used to obtain such spectroscopic information from fingerprints.

4.1. Infrared Spectroscopy

Kazarian and co-workers[71] have used attenuated total reflection (ATR) infrared spectroscopic imaging to obtain chemical images of fingerprints under controlled environmental conditions. The combination of Fourier transform (FT) infrared spectra with an imaging capability provided information regarding the characterization, distribution, and total concentration of the compounds present across the fingerprint. Fingerprints were deposited onto a ZnSe crystal for ATR infrared imaging to study the distribution of lipid and amino acid components as a function of time. The ATR infrared imaging technique enabled chemical images of latent fingerprints to be obtained. The images were obtained by plotting the integrated absorbance of the antisymmetric and symmetric stretching vibrations of the CH_2 group between 2800–3000 cm^{-1} which arose from lipids present in sebaceous material deposited in the fingerprints. The authors also found evidence of amino acids and protein material in fingerprints, as indicated by absorption bands at 1654 cm^{-1} (C=O), 1551 cm^{-1} (N–H in-plane bend), and the weak N–H stretching vibration (3080–3100 cm^{-1}) corresponding to amide B. In addition, by using a combination of the ATR spectra of the chemical species together with univariate and multivariate analyses, the authors showed that temporal changes of the spectra obtained from the lipid portion of the fingerprint occurred as the fingerprint aged. The study clearly showed that infrared imaging techniques can be readily applied to fingerprint examination. The same research group subsequently showed the practical application of the ATR infrared imaging technique by chemically imaging fingerprints that had been lifted, from a variety of surfaces, using gelatine tapes.[72]

Clearly the use of an ATR crystal is not always practicable in forensic analysis. Infrared imaging of fingerprints has been achieved by using the reflection-absorption mode for spectroscopic imaging.[25] This infrared imaging mode enabled overlapping fingerprints to be distinguished on the basis of their chemical origins.[25] When the two fingerprints were imaged using the CH stretching vibration at 2940 cm^{-1}, the overlapping prints were observed. However, one fingerprint had a different chemical composition as it contained oil-rich sebaceous components arising from the individual rubbing their finger across their forehead or side of the nose prior to depositing the print. As the two fingerprints had different chemical compositions, the print with the high sebaceous content was isolated by imaging the carbonyl stretching band. The second underlying print was imaged on the basis of the ratio of the carbonyl band near 1730 cm^{-1} and the amide band near 1640 cm^{-1}. The imaging of the fingerprints by using various absorption bands resulted in two separate fingerprints being obtained that could be used for identification purposes.

In addition to the imaging of fingerprints on the basis of the chemical composition of endogenous components, infrared imaging has the potential to be used to identify exogenous trace residues for forensic evidence. For example, it has been shown that trace residues of explosive materials such as RDX can be identified from the background fingerprint and protein material.[25,73] Figure 5 shows a false color image of a fingerprint constructed from the 2920 cm^{-1} C–H stretching absorption band from the sebum-rich print (blue), the 3240 cm^{-1} absorption band of the N–H stretch from the proteins found in skin flakes (green), and the 3072 cm^{-1} absorption band indicative of particulates of the plastic explosive RDX (red) lodged between the ridges of the fingerprint. The authors suggested that the presence of explosive particulates between the ridges of the fingerprint enhanced the probability that the individual had handled the explosive as opposed to random contamination of the print.[25] In addition to plastic explosives, particulates of other materials used for the manufacture of explosive devices, such as ammonium nitrate, have been detected in fingerprints by using ATR infrared microscopy.[26]

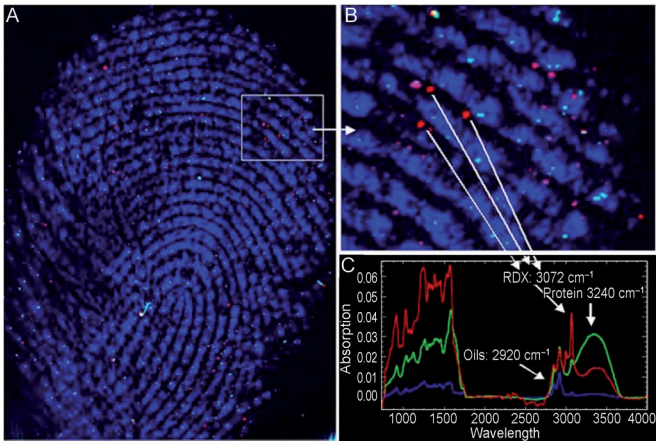

Figure 5. A) Image of a fingerprint obtained using specific absorbance modes for oil, protein, and particulate matter. B) Expanded view of the box in (A). C) Spectra of the components, showing the absorption bands indicative of the specific components. Figure reproduced with kind permission.[25]

The ability to image fingerprints and to detect particulates of explosive residues within a fingerprint will undoubtedly mean that infrared imaging will find utility in forensic practice. A potential drawback of infrared imaging is the inherent sensitivity of the technique. For example, with the detection of the RDX explosive residues, Bhargava et al. reported that about 1.0 ng of material was necessary to ensure accurate identification.[25] As the authors suggest, this sensitivity is not as good as that expected from techniques such as GC-MS, although, as noted earlier, the latter technique is destructive, which is not ideal when dealing with forensic evidence.

4.2. Raman Spectroscopy

Day and co-workers[74] have used Raman spectroscopy for the detection of drugs of abuse and other exogenous substances present in doped latent fingerprints. This research group reported the successful detection of various drugs of abuse (codeine phosphate, cocaine hydrochloride, amphetamine sulphate, barbital, and nitrazepam) and similar non-controlled substances (caffeine, aspirin, paracetamol, starch, talc) in both sweat- and sebum-rich fingerprints. Raman spectra of all the exogenous substances could be distinguished from each other and the spectra obtained from the doped fingerprints were analogous to the reference spectra of the substances collected beforehand. The main problem faced in this study was to visually locate the particles of dopant in the latent fingerprints before collecting a Raman spectrum. Day et al. have also reported that the detection of such exogenous substances in latent fingerprints by Raman spectroscopy can be enhanced by cyanoacrylate fuming.[75] They have successfully used Raman spectroscopy to detect exogenous substances in fingerprints beneath a layer of cyanoacrylate polymer. Similarly, West and Went used Raman spectroscopy to study the detection of exogenous substances[76] and drugs of abuse[77] in contaminated fingerprints that had been treated with powders and then lifted with adhesive tapes. The application of aluminum- or iron-based powders to develop contaminated fingerprints did not interfere with the detection of the contaminants in powdered and lifted fingerprints.[76,77] A combination of three techniques, that is, Raman spectral mapping, tape-lift, and multivariate data analysis, has also been used to analyze latent fingerprints.[78] Widjaja used these techniques to extract chemical information from latent fingerprints and to analyze trace amounts of materials deposited in fingerprints by studying sebum-rich fingerprints, a drug model comprising ibuprofen, L-arginine, and sodium bicarbonate, and an additive model comprised of sucrose and aspartame.[78] The tape-lift method was used to lift any material present in the fingerprint. The lifted materials were then studied by Raman spectroscopy and the collected Raman spectra were analyzed by using the multivariate technique 'band-target entropy minimization' (BTEM). The spectra of the pure components recovered using BTEM were identified by comparison with known spectral libraries.

Although Raman spectroscopy is useful in detecting materials in fingerprints, other Raman-based techniques such as surface-enhanced Raman spectroscopy (SERS), with its enhanced sensitivity, has greater potential. SERS has been used to detect latent fingerprints, as well as print contaminants, by sensitive chemical imaging of fingerprints, thus recreating a visual image of fingerprint topography by mapping the vibrational band intensities.[79]

5. Summary and Outlook

In this Minireview we have highlighted various methods and techniques that have been developed for the detection and analysis of fingerprints. Gold nanoparticles as well as magnetic particles have shown huge potential as reagents for fingerprint analysis, especially for the detection of drugs and drug metabolites that have been excreted and deposited within a fingerprint. Another important area of nanoparticle technology that has significant potential for fingerprint analysis is the use of quantum dots. Chromatographic techniques have shown that ingested drugs can be isolated and identified from fingerprints. Mass spectrometric methods have similarly been used to identify fingerprint components and more recently to image the fingerprint using the individual constituents. Finally, vibrational spectroscopic techniques have also been shown to enable the simultaneous detection and imaging of latent fingerprints on the basis of the constituents of the prints itself. With these significant developments in fingerprinting technology, there is now a need to find a portable, efficient method that can be taken to scenes of crime for forensic investigations. The ultimate goal is to develop a nondestructive, miniature, cost-effective, and rapid system that can detect latent fingerprints and the chemical constituents within. With such a system, not only will forensic investigations benefit, but other applications such as the screening of athletes as well as in vitro diagnostics for patient care will be advanced.

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