DRUGS ON FINGERPRINTS: A SHORT REVIEW

DETECCIÓN DE DROGAS EN HUELLAS DACTILARES: UNA BREVE REVISIÓN

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Abstract: The significance of fingerprints for either criminal or civil purposes, has been recognized since thousands of years ago. They are enormously valuable due to their uniqueness and persistent through life. At the beginning of the 20th century, they became a powerful tool for personal identification. The detection of latent fingermarks is actually a challenge, and this analytical problem has been investigated and improved significantly over the last 20 years due to the combined efforts from several research groups. Although usually they are employed on examination and comparison of the characteristic ridge skin patterns, it has been explained that the chemical composition of a fingermark can reveal very important information about the donor. This chemical composition provides generous assistance and new intelligence during an investigation, since it shows the endogenous or exogenous substances that one has been in contact with. For instance, it can expose if an individual has been in contact or consumed drugs during or prior the crime. To be able to gain this additional information from a fingermark, technology should be able to detect and reveal the chemical content. Here, a short review on the importance of fingermarks is presented together with the latest achievements and developments for the analysis of drugs on fingerprints.

Keywords: latent prints, fingerprints, drugs, exogenous, forensic.

Resumen: La importancia de las huellas dactilares para fines penales o civiles se reconoce desde hace miles de años. Son enormemente valiosos debido a su singularidad y persistencia a lo largo de la vida. A principios del siglo XX, se convirtieron en una poderosa herramienta para la identificación personal. La detección de marcas dactilares latentes es en realidad un desafío y este problema analítico se ha investigado y mejorado significativamente durante los últimos 20 años debido a los esfuerzos combinados de varios grupos de investigación. Aunque normalmente se emplean en el examen y la comparación de los patrones característicos de la piel de las crestas, se ha explicado que la composición química de una huella dactilar puede revelar información muy importante sobre el donante. Esta composición química proporciona una generosa ayuda y una nueva inteligencia durante el curso de una investigación, ya que muestra las sustancias endógenas o exógenas con las que se ha estado en contacto. Por ejemplo, puede exponer si una persona ha estado en contacto o consumido drogas durante o antes del delito. Para poder obtener esta información adicional a partir de una huella dactilar, la tecnología debería poder detectar y revelar el contenido químico. Aquí, se presenta una breve reseña sobre la importancia de las huellas dactilares junto con los últimos logros y desarrollos para el análisis de drogas en las huellas dactilares.

Palabras clave: huellas latentes, huellas dactilares, drogas, material exógeno, forense.

> When I was a youth, I knew an old Frenchman who had been a prison-keeper for thirty years, and he told me that there was one thing about a person which never changed, from the cradle to the grave – the lines in the ball of the thumb; and he said that these lines were never exactly alike.
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> Life on the Mississippi. Mark Twain

1- INTRODUCTION: HISTORY OF FINGERPRINTS

Unlocking our mobile phones or tablets, online payments, accessing the gates for international flights, opening our hotel room, or even entering our jobs nowadays often require the use of fingerprints. We do it mechanically, but its application is well settled in our lifes, and they slowly enhanced a key tool for personal identification worldwide. At the crime scene, fingerprints are essential on the course of an investigation, either to identify the possible suspects, the victims or any person present at the time of the crime. The social necessity of a proper human identification with a minimum error window had increased the research on the techniques over the past years. Although it seems someone pushed the fast forward button, that urgency is not new. Even thousands of years ago, friction ridge skin marks were used as proof of someone's identity back in the 300 B.C in China. So, it

seems is found in the chinese culture the first evidence of using fingermarks as means of identification [1]. Some studies suggest that in areas like India, his technique was reserved mainly for royalty. In Spain, also prehistoric handmarks are well preserved in the Altamira caves in Cantabria.

But let's make a jump through history to find the major discoveries and inventions that led us where we are now in terms of fingerprints. It is not until the 18th century that the uniqueness of fingerprints is recognized in Europe. Being Mayer, a german doctor and anatomist, the first one to notice it. In his book Anatomical Copper-Plates with Appropriate Explanations, he wrote for the first time how friction skin ridges are never duplicated for two individuals [2]. Later on the 19th century, the thesis of another german doctor published in 1823, Dr. Johannes Purkinje, shows the first classification of different fingerprint patterns, who serve now as the precursor of the Henry classification system (explained in the following). In Figure 1, those 9 patterns can be observed. Although he did not go further on the explanation, still it was very valuable information settling a starting point for the later developments [3].

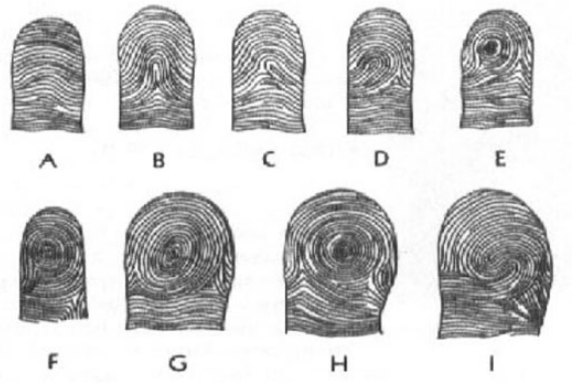

Figure 1: Purkinje's nine types of finger patterns. A: Transverse curves, B: Central longitudinal stria, C: Oblique stria, D: Oblique sinus, E: Almond, F: Spiral, G: Ellipse or elliptical whorl, H: Circle or circular whorl, and I: Double whorl.

Years later in 1853, a british man called Sir Williams James Herschel, moved from England to India to work as an administrator for the East India Company. During his years there, he had the idea of using a handprint as a signature in an official contract to pursue road materials (see Figure 2). That is the first time in history documented in which a friction ridge skin mark was used by a European and considered valid in official documents. This gesture urged him to continue documenting the fingermarks of colleagues, friends, family and of course, himself. He used this innovative method when years later oversaw criminal courts, prisons, official governmental registrations, and started to keep a fingerprint record while he suggested that this identification method should be spread to other countries as well. During his life he never ceased to study fingermarks and the relevance of their uniqueness and permanence, publishing years later a book that sets up the origins of fingerprinting [4].

Figure 2: Handprint that was impressed on the back of the contract. Bengal, India, July 28, 1858.

It is not until the last decades from the 19th century in which the major work on this topic and the consolidation of the ideas and techniques initiated. The Nature article written by Henry Faulds in 1880 is a good example of it [5]. Alerted by the observation of japanese pottery, he began thinking of fingerprints. *"In a Japanese man the lines on both thumbs form similar spiral whorls; those of the left forefinger form a peculiar oval whorl, while those of the right corresponding finger form an open loop having a direction quite to that of the right forefinger in the previous example. A similar whorl is found on both middle fingers instead of a symmetrically reversed whorl. [..] The lines at the ulna-palmar margin of this particular Japanese are of the parallel sort in both hands, and are quite symmetrical, thus differing from the Englishman's considerably"* [5]. He initiated the examination of fingerprints by making impressions on glass using different colours of ink. One of his last statements (i.e., nr. 5 in Ref. [5]) remarks for the first time: *"When bloody finger-marks or impressions on clay, glass, etc, exist, they may lead to the scientific identification of criminals"*. That is, pioneering the idea of using fingerprinting as means for criminal evidence.

During these years, Dr. Faulds decided to write a letter to Charles Darwin, explaining his system for classifying fingerprints and kindly asking for assistance. Darwin did not provide any help but agreed to forward the letter to his cousin, Sir Francis Galton. Although Faulds and Galton did not continue corresponding very much, they both arrived at a similar fingerprint classification. Speculation suggests that Galton did not acknowledge Faulds work but remembered that one of Herschel. Nevertheless, the book published by Dalton in 1892 *"Finger Prints"* addresses well the questions about the uniqueness of fingerprints and their consistency through life. Moved by his interest in understanding hereditary matters and anthropology, he studied cautiously the fingerprints, developing new techniques to record prints on paper in an accurate and reproducible way. He also stated that it does not exist a link between friction ridge patterns and the character of the individual [1].

It is a matter of debate to whom to credit the fingerprint classification system, Faulds or Galton. Considering the literature on this aspect, and leaving discrepancies aside, it seems fair to say that Henry Faulds represents, as stated in the paragraph above, the first European to publish the value of fingerprints as criminal evidence.

While Herschel and Faulds focused on fingerprints, there was a frenchman, Alphonse Bertillon, who created a system to identify humans by taking different body measurements. This anthropometric method studied from the height of the individual to the length/width of the head, passing through the length of the right/left ear, along with almost each body part. With this alternative method he wanted to standarized and recorded each person suspected of being a criminal [1]. Yet this method revealed to be often inaccurate.

Nevertheless, it was adopted by the British Indian Police in 1892. Not much after that, Sir Edward Henry, Inspector General of the Bengal Police in India, influenced by Galton's book (with whom he also corresponded), became interested in the use of fingerprints for criminal identification. After he studied Galton's method closely, he decided to include fingerprints marks from prisioners in addition to the anthropometric measurements that were already being taken. He refined Galton's method and created what we today call the Henry Classification System. Assisted by Qazi Azizul Haque, this new system outdated the previous *Bertillonage* as the standard method of criminal identification. Not only it was more accurate but also less time consuming and it did not need any special training as the previous one. In brief, consists in a logical characterization of ten fingerprints records into primary groupings based on fingerprint pattern types. It assigns each finger to a number, beginning with the thumb in the right hand as number 1 and ending with the pinky in the left hand as number 10 [6]. Considering the three main finger patterns described by Galton (loops, whorls, and arches). A graphical representation is shown in Figure 3.

The Henry Classification is giving different numbers depending on the presence or not of those patterns. If a whorl is present, then the assignment goes like that: fingers 1 and 2 each have a value of 16, fingers 3 and 4 have a value of 8, and so on, with the final two fingers having a value of 1. If, on the other hand, no whorl is present but a loop or an arch, then the numerical value is 0.

Figure 3: Three different fingerprint patters. Extracted from [6].

Thus, arriving to the numerical formula shown here:

Henry Classification System Formula:	1+ (Sum of whorled, EVEN finger value) 1+ (Sum of whorled, ODD finger value)	= Primary Grouping Ratio

The system allowed to identify and grouped fingerprints, excluding possible suspects. It was very succesful in India by the change of century, and it easily spread through Britain (exported by Henry himself) and other English-speaking countries as the standarized method. It represents the main influence that originated the IAFIS (Integrated Automated Fingerprint Identification System), used by the FBI since 1999.

Far away from Europe, in Argentina, there was an important fingerprint researcher at that time as well: Juan Vucetich. While working as a police officer in Buenos Aires, he read an article from Galton about the importance of fingerprinting. Soon thereafter, he started collecting fingerprints from arrested man, together with the Bertillon anthropometric measurements. He then devised a new fingerprint classification system called "dactyloscopy". To him we attribute the first use of fingerprint science by law enforcement personnel [1]. Also, it was used in personal identification cards as government control.

In 1892, Francisca Rojas will be known as the first criminal found guilty by evidence of fingerprints. The two children from Francisca (4 and 6 years old) were found brutally murdered in their home in Necochea, Buenos Aires, while the mother appeared with marks on her throat. At the beginning, the police had no suspects or leads for the investigation. Rojas denied having nothing to do with the murder of her two children and she immediately accused her neighbor, Pedro Velázquez. But Velázquez had a good alibi and was eventualy ruled out as a suspect. Turns out that the inspector in charge, Álvarez, had been trained by Vucetich himself. After some time, he found at the crime scene what it appeared to be a bloody fingerprint on the bedroom door. He collected it and then requested Rojas to be fingerprinted as well. After careful examination, it had been found that the fingerprint evidence matched that one of Francisca. She was confronted with the fact and confessed to the killings, together with the attempt to simulate an attack cutting her own throat. Later on, she was convicted of first-degree murder. As a consecuence of this, Vucetich realized the superiority of fingerprints versus the anthropometric measurements and Argentina became the first country in the world to abolish the later ones, considering them unnecessary and too complicated. It seems that Bertillon was bitter about that and spoke publicly very bad about Vucetich in Paris and even denied greeting him when Vucetich toured around the world presenting his book *Dactiloscopia Comparada* [7]. Until he passed away, he kept maintaining his anthropometric system as being superior, although many countries already pointed out their defects and granting the uniqueness of individuals to fingerprint measurements.

It was clear then that the 19th century and beginning of the 20th constituted the establishment and flourishing of fingerprinting as a reliable science. Nevertheless, the discipline had not remained static. Perhaps one of the most important and exciting facts that appeared in the past years is the application of computer technology to fingerprinting work. Nowadays it is incredibly fast to store new data and search for possible matches and of course, the developing of new techniques had speed up exponentially and continue to do so. The detection of fingerprints at the crime scene is one of the most effective tools in the investigation of a crime. At the moment, the work is not only done with visible fingerprints, but researchers can bring to light those that, in principle, remain hidden, the so-called latent fingerprints. A latent fingerprint can be defined as an invisible fingerprint left at the crime scene [8]. The application of different powders to make them *"visible"* has been an object of research since the early days of the fingerprint technology [8]. The effectiveness with which the powder adheres to the surface depends on the shape and size of the particules left, and a powder that does not interfere chemically or physically with the surface should be considered [9]. A good review article about the topic and the different techniques employed was written by Shodi and Kaur in 2000, see Ref. [9]. Indeed, it has been possible to prove that even under adverse conditions, it is feasible to develop marks, as shown by Castelló, *et al*. [10] in 2013. In their work is evaluated which reagents are more effective in developing marks produced under water to solve possible crimes that happened under these circumstances [10].

The focus of researchers and investigators is being able to find, reveal, store, compare fingermarks and based on the profile, matching them to a certain individual. Since two humans cannot have identical fingermarks, this technique is vital for the forensic or crime investigations. But one of the biggest turnouts on the field happened when in 1997 it was published that DNA can also be extracted and analyzed from fingerprints [11]. Showing that a DNA profile can be generated from swabs taken from objects touched by hands [11]. This so-called DNA fingerprinting provided the ultimate standard technique, plotting the unique pattern of one's DNA. Hence, settling what is considered one of the most essential tools for crime investigation. Furthermore, fingermarks have been proven to be a source to detect and analyze exogenous material which the donor of the print has been in contact with. That is, additionally to the physical evaluation, bring to light a chemical analysis of the substances that had been in contact with a person. That could be remains of explosives [12, 13], other substances [14–16], and surely drugs [17–23], which represent the topic of this review.

2- DRUGS ON FINGERPRINTS

Fingerprints, that *"crazy"* collection of ridge patterns, are unique for each indivilual. This fact makes them such a powerful identification tool. Not only that but, fingermarks are considered one of the most important types of evidence that can be encountered at a crime scene, being able to match those found with the ones stored into a database.

Now let's imagine a scenario in which a crime scene is dusted in search for fingermarks or latent fingerprints. Some are found, lifted, and compared into the database looking for a match. However, even if this procedure is well established and correctly followed by the crime scene investigators, could be that none of them result into a positive matching. Perhaps our perpetrator is not yet in the database, maybe the fingermark is smudged, distorted, or two fingermarks appear to be overlapping. Does the story end here? The short answer is no.

Even if the physical evidence provides no definite answer, fingermarks can tell a story above their ridge marks. There is a whole lot of information hiding under our fingerprints. Since they originated by contact

transfer from the tip of our finger to a surface and mainly consist in eccrine and sebaceous excretion [24], a chemical analysis is also possible. Finding a wide variety of chemical components that originate from endogenous and exogenous sources, may offer significant value in a forensic investigation. Here, this can be useful for lots of reasons: mainly enhancing the evidential value of fingerprints and providing new information about the donor. So now the door is open to know more about a potential suspect than just its identity. It is possible to gain information about the state of mind of a person prior or during the crime, as well as the age or gender, what type of medication is the person under or if it has been in touch with explosives or drugs. One of the most prolific research groups on this topic, have named that as "*chemical criminal profiling*" [25].

This exciting topic is relatively young, however, it was first published by A.M. Knowles in 1978 the relevance of chemical components of a fingerprint and envisioned what this could bring to the forensic field [8]. But it is not until 2008 that it is found the first work published in which chemical information is obtained additionally to the physical evidence. Ifa, *et al.*, reported the application of imaging mass spectrometry for the chemical analysis of latent fingerprints [26]. Since then, it has been exponentially researched over the past years. Although it appears to be not as accepted as testing with hair or/and oral fluid, it is starting to be widespread not only in the forensic field but also in other areas. Finding the chemistry behind our fingerprints is also very stimulating on the medical field, as it has been proven to be a valuable diagnostic tool since it is a rapid, non-invasive method with multiple benefits [27–30]. Although the topic is extense and expanding into different focus areas, here in this work it will be presented a state of the art regarding the detection of (mainly) ilicit drugs on fingerprints. But before progressing into it, let's review the complex chemical fingermark composition.

2.1- Fingermark composition

A developed fingermark chemical composition can be used to obtain tactical information about the donor. Each skin ridge is composed of pores, and through them is excreted the sweat which is then deposited on the surface of the skin. The so-called endogenous substances are those normally produced by our bodies. Nevertheless, the chemical composition can be as well contaminated by exogenous substances, which are the ones present when touching different sources, contact with cosmetics, food, as well as drugs, explosives, and many more. There is a very good review article from Girod, *et al.*, [24] that describes extensively the fingermark complex composition. Shortly, there are three parts of natural secretion glands in our bodies and each of them produces a different type of sweat. These are: eccrine, sebaceous and appocrine [31]. The most relevant are the eccrine sweat glands since are present in all our body. They are tiny but spread all over and thus, represent the major contributor of the chemical composition in fingermarks. Its main composition is water, but also several inorganic (ammonia, sodium, etc.) and organic compounds (lipids and/or proteins) can be present [32]. Sebaceous glands are also found in all our body (wherever we have hair follicles), except on the palms of the hands and soles of the feet. They excreted an oily material called sebum. This can be found in fingermarks when the person touches its face or hair. The composition of sebaceous glands is very complex and variates a lot between individuals. Mainly triglycerides (41%), wax esters, squalene and free fatty acids are found.

Next one, appocrine glands are found mainly on the axilary and genital regions. Studying them is usually complicated since contamination from the sebum or eccrine glands might take place. Their contribution to fingermark composition is lower because of its location. On the other hand, they might play a bigger role on sex crimes.

In addition to these natural endogenous contributions, the complexity of the analysis is increased when considering exogenous sources that an individual encountered. It is possible to include a countless number of substances that contribute to the fingermark composition. For instance, hair and cosmetic products, food, gunshot residue or any kind of drugs. Also, others that after ingestion will be excreted as metabolites and will influence the fingermark residue, i.e., medication or ilicit drug abuse, discerning between smokers and non-smokers, etc. Thus, all of this provides very good characteristics of a donor and significantly increases the forensic value of fingerprints during an investigation.

2.2- Methodology and Research Work

If a person is in contact with an opaque material, such as blood, their fingermarks will be clearly visible. However, often the situation is not as ideal. Most likely the residue left on a surface will be *"invisible"* to the naked eye. These invisible fingermarks are called latent, and before being able to analyze them, one needs to be able to detect them. That means, a major part of the work success on a crime scene relies in the ability to find them. Therefore, selecting the appropiate development techniques is essential. Choosing among the different methodology will strongly depend on the molecular target but also on the deposition surface. There is a very important manual written by T. Kent in 1998 [33] that describes in deep the techniques to be applied for a convenient enhancement of crime scene latent marks. This *Manual of Fingerprints Development Techniques* guide us through the appropiate method to follow depending on the surface and/or environmental conditions. Key is to generate a good contrast between the ridges of the fingerprint and the underlying substrate without disturbing the pattern formed. It is not the object of this review detailing all the development fingermarks existing techniques, however, here are a few examples.

- **Powder dust**: It is one of the first known techniques and its efficiency depends on the chemical and physical nature of the powder used, together with the experience of the investigator. Usually, fresh marks are easily visible using these powders, which can range from black dust (used on light surfaces) to aluminum flake powder (regarded as one of the most effective).

- **Amido Black:** It reacts with proteins present on blood and other biological fluids, generating a dark blue-black colour. Not recommended for porous surfaces and can easily be disolved in water or methanol.

- **Ninhydrin:** Reported in 1954 [34], it reacts with the amino acids present on the latent marks and it is very suitable for porous materials like papers. Ninhydrin is likely the most widely reagent used due to cost and strong initial colour.

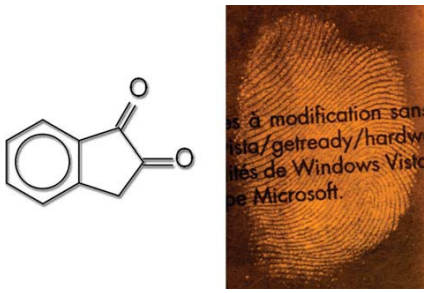

Figure 5: Left: molecular structure of 1,2-indanedione. Right: representative finger-mark detected using this technique with paper as substrate and observed using luminescence. Extracted from [35].

- **DFO:** 1,8-Diazafluoren-9-one introduced in 1989 [36], produces a highly fluorescent species with latent fingerprints on paper. DFO is regarded as more sensitive than ninhydrin.

- **1,2-indanedione:** Reagent very efficient for porous surfaces, it also reacts with amino acids, and it has replaced DFO [37, 38]. Also useful for blood marks. The addition of a small amount of zinc to the working solution seems to play a role in the reaction since zinc acts as a catalyst. It is necessary a fluorescence examination.

- **Cyanoacrylate fuming:** Involves the use of a colorless monomeric liquid, i.e., the cyanoacrylate ester (also known as Superglue) [39]. Cyanoacrylate shows a particular affinity for moisture, lipids, and some water-soluble components [35]. Through this method it is possible to reveal marks on non-porous surfaces, but a fluorescence reagent will be needed for enhancement afterwards.

- **Colloidal gold or Multimetal deposition (MMD):** Introduced by Saunde in 1989 [40]. It is a two-stage process: first, the object is immersed in a solution containing colloidal gold as the active component; second, a physical developer is needed for the enhancement of the detected fingermarks. This technique works well on both porous and non-porous surfaces. On the other hand, it is an arduous technique and often the obtained images are black. New research has been done by Becue, *et al*., showing that this technique could also be used to obtain luminescent fingerprints [41].

All those developing methods have been extensively studied and keep being updated through the years. There is a general desire of constantly looking for the most accurate, simple, economic and, of course, non-destructive method for a later visualization and analysis of the developed fingerprints. The choice for one technique over another, is driven mainly by the nature of the item or by the surface at the crime scene. Now the interest relies on the synthesis of developers with increased specificity to a constituent or contaminant of particular interest, and the use of analytical techniques to characterize and spatially map the substances present [42].

2.3- Drug analysis work

Now that it is established here that fingermarks can provide further information beyond a suspect's identification, let's put the focus on the detection of drugs residues on fingerprints. Although this research is a novel area, the attention to this topic has became intense lately. The use of ilicit drugs has increased worldwide on the latest years, as well as its production. Thus, there is a high forensic interest in gaining intelligence on drug distribution and drug abuse. By detecting drugs on a fingermark left at a crime, it is possible to gain *"activity level information"*, specifically knowing if a crime has been committed under the influence and correspondly its legal ramifications. Likewise, several studies have arised to explore the possibility of using a fingerprint to determine if a particular substance has been just in contact with the donor or it has been consumed based on the presence of drug compounds and their metabolites in fingerprints samples.

The drug testing industry is well established and used by many agencies since years ago and speaks for an economically high-profitable market. The growing interest on drug analysis from latent fingerprints explains itself since it represents a non-invasive technique, easy/quick to collect and provides relevant information for forensic applications, but additionally, could be potentially relevant for roadside and workplace drug testing. The idea is to try and combine the detection of specific drug metabolites with the visualization of the ridge details in fingermarks enhancing the profile information about the donor. To retrieve this information, the scientific community has put huge efforts towards investigating different techniques and methods. One of the major challenges is being able to discern between drug use and drug contact, especially if the later one can come from environmental contamination. Another important factor to consider for fingerprint testing is the detection time of drugs, which seems to be a topic not very much evaluated yet.

In 2008, Jacob, *et al.*, were able to detect methadone and its metabolite, EDDP, on patients from a maintenance methadone clinic by using ultra-high pressure liquid chromatography with tandem mass spectrometry (UPLC-MS/MS) [23]. Methadone is a syntetic opioid that is used on treatments/management of heroin abuse. They conclude that due to the detection of EDDP on those patients undergoing treatment, explains that excretion of drugs and metabolites can take place through sebaceous and/or sweat glands of the skin. Pioneering the idea that if the metabolite is present, methadone has been administered rather than being present due to external contamination. A year later in 2009, another group also used LC-MS methods to detect this time the presence of lorazepam and its metabolite [43]. This quantitative study from a prescription drug for anxiety, together with that of Jacob, *et al.*, represent the first reports in which a drug is detected on fingerprint deposits [23]. However, even if this method (LC-MS) provides good selectivity, the biggest limitation is the destructive nature of the technique and impossibility to access spatial information. Their works are impractical for use on the field since they rule out the repetition of the analysis.

The use of immunogenic techniques for drug detection on fingerprints has also been investigated by several groups. A good review on the topic is the one published by Woods, *et al.*, in 2013 [44], showing the recent advances and the potential of using these techniques to obtain additional chemical information. The group of David Rusell on the UK has focused on the target of different drugs and drug metabolites by immunolabelling [17, 18, 45–47]. For example, cotinine, the metabolite of nicotine, was dectected using antibody functionalized gold particles on the excreted sweat fingermarks of individuals who smoke tobacco [17]. They targeted others like methadone, morphin, benzoylecgonine (cocaine metabolite) and tetrahy-drocannabinol (THC, which is the main psychoactive component of cannabis) by combining antibody/magnetic particle conjugates. A very positive side of this technique is that they tried to combine it with the visualization of the ridge patterns. It is shown for the first time in Ref. [47] two drug metabolites (morphine and benzoylecgonine) detected simultaneously from a single fingermark. This is of particular interest for instance when the drug testing is performed over drug addicts that often consume a combination of substances. The conjugation of antibodies to magnetic particules resulted in a clear developed fingermark. Fig. 6 is a schematic representation of the followed method to detect these two metabolites from a single fingerprint by use of antibody-particle conjugates. Shortly, here the two antibody-magnetic particles were conjugated with antimorphine and antibenzoylecgonine antibodies to recombinant fusion Protein A/G coated magnetic particles, respectively. Next, the conjugates are applied to different sections of the fingermark at the same time. After incubation time and removing of excess particles, another antibody fragments are applied and imaged via fluorescence microscopy [47].

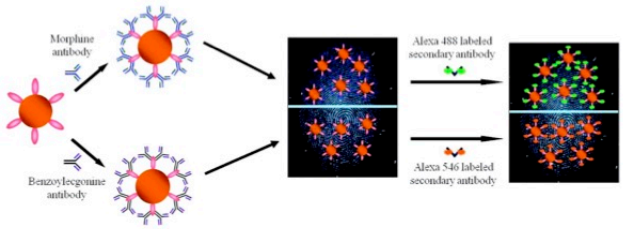

Figure 6: Extracted from Fig. 1 on Ref. [47]. Methodologic scheme of the latent print visualization using antibody-particle conjugates.

In these studies from Rusell's group, the fingerprints were usually collected on glass surfaces. A bit later, a Dutch group reviewed the compatibility of fingerprint visualization techniques with immunolabeling [48]; this time

examining the latent fingerprints left on porous and non-porous materials. A sensitive immunolabelling study was published in 2015 by Van der Heide, *et al.* [49]. Their quantitative enzyme immunoessay allows to detect cocaine in samples obtained from circulating banknotes and fingerprints from individuals who declare to be taking drugs.

Consequently, this method enables the desired situation for fingerprinting applications, i.e., enables both identification of an individual together with the determination of the chemical components of the sweat deposited in the fingerprint. However, it is still under development to make it feasible for case work due to the lack of a positive control and the inclusion of more negative controls.

Different spectroscopical techniques have also been studied and offer the possibility to identify drugs and simultaneously image the ridge patterns from fingerprints. For instance, Raman studies [50–52] and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) [53, 54] since they are less destructive and allow the interaction between the fingermark with light sources. The detection of drugs of abuse (codeine phosphate, cocaine hydrochloride, amphetamine sulphate, barbital and nitrazepam) in latent fingerprints using Raman was first reported by Day, *et al.* [50]. The main difficulty in the detection of these drugs of abuse was the visual location within the fingerprint. West, *et al.*, proved that after application of powders and lifting with adhesive tapes, spectroscopic detection of exogenous material, such as drugs, is still possible [55]. However, a potential complication arises due to the presence of interfering Raman bands from the adhesive tapes. Regarding the ATR-FTIR studies, Ricci, *et al.*, showed for the first time that this methodology allows chemical and spatial information to be obtained under controlled environmental conditions [54]. Later, they introduced the ability of a highly sensitive method combining ATR-FTIR to detect drug traces with the aid of lifting gel [53]. In 2009 appears a review called *"Detection of illicit substances in fingerprints by infrared spectral imaging"* [20] which provides a good overview of the work done so far. By testing spectral searching algorithms to find targeted substances deposited within fingerprints they try to improve one of the difficulties among this technique. Since spectroscopical techniques just provide information on the functional groups of the molecules analyzed, it could be complicated the identification of the present compounds without consulting a library or in case this does not appear in the present library. An advantage of this technique is that some are portable devices, making possible in-situ analysis [56]. In any case, it has been stated that to make them applicable extensively on the forensic field, further validation studies are necessary [57].

Moving forward now to mass spectrometry-based techniques, the most abundant body of research and publications is found here. The literature is filled with mass spectrometry techniques for fingermark analysis, especially on the last decade. This is because of their high selectivity since they measure the molecular weight of the species, and the compounds are detected and identify through structural elucidation/confirmation by tandem mass spectrometry [58]. While other techniques often need addition of fluorescent or other secondary treatments, Mass Spectrometry (MS) provides specific chemical composition information on surfaces. Amongst them, Gas Chromatograpy Mass Spectrometry (GC-MS) is one of the strategy techniques that, although it has been investigated [59–61], due to its destructive nature is not considered for operational casework. However, GC-MS has provided insights into changes occuring over time to different species, the so-called, fingermark aging. This, as stated in previous paragraphs, is an important factor not very much investigated. Therefore, the research on GC-MS techniques has helped to understand it better.

Ifa, *et al.*, reported desorption electrospray ionization (DESI) MS as the first suitable MS technique for fingermark imaging [26]. There is no need for sample preparation and offers spectra as well recorded on their native

environment. DESI is minimal invasive and can also be portable. Followed by Surface Assisted Laser Desorption Imaging (SALDI), Rowell, *et al*., applied a hydrophobic silica dusting agent as enhancement of latent fingermarks to generate a method for detecting a range of drugs using surface assisted laser desorption/ionization time-of-flight mass spectrometry (SALDI-ToF-MS) [22]. With this method they were able to analyze latent fingermarks for the detection of illicit drugs together with their metabolites and visualize their distribution over the lifted fingermark. For the last years, time-of-flight secondary ion mass spectrometry (ToF-SIMS) has become on of the most sensitive analytical techniques and has been widely use in forensic applications. Szynkowska, *et al.*, have demonstrated the application of this technique to the fingerprint evidence found at the crime scene [19]. In their study, they investigate fingerprints which have been contaminated with drug residues, such as amphetamine, metamphetamine and methylenedioxymethamphetamine (MDMA, also known as ectasy). Application of ToF-SIMS appears to be very effective not only for the identification of the trace residues of the drug but also its visualization and distribution over the fingerprint (see Fig.7). SIMS shows the highest spatial resolution amongst the MS techniques and provides extremely high-resolution molecular images. To the extent of being able to observe sweat pores in a ridge, as it was shown in the work published in 2017 by Cai, *et al*. [62].

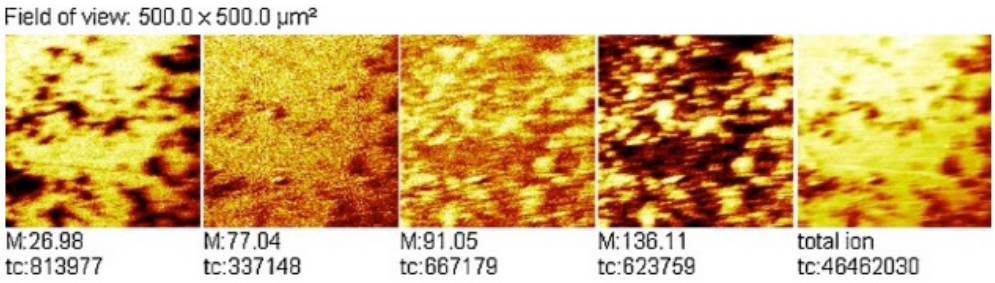

Figure 7: Extracted from Ref. [19]. This is a ToF-SIMS image of a fingerprint left after the finger was contaminated by amphetamine taken from an aluminium sheet surface.

Another recent tool in surface mass spectrometry that is commercially available and operates under ambient conditions is Liquid Extraction Surface Analysis (LESA). This technique is particularly suitable for the analysis of trace materials on surfaces and only consumes a small amount sample volume, making it minimally destructive. A limitation of the LESA method for fingerprint chemical analysis is the lack of spatial resolution.

Not casually, I left the most important and prolific technique reported for the analysis of fingermarks to the end. That will be Matrix Assisted Laser Desorption Ionization (MALDI), described as the most versatile analytical technology for gathering information from latent fingermarks by detecting and mapping their chemistry. It can be said that MALDI has been proven to be the most compatible with fingerprint enhancement techniques. MALDI-MS has been pioneered by the research group of Simona Francese at Sheffield Hallam University, UK, since 2008 (Francese's website). In a very short period of time, they have reached a state of maturity for this technique above any other mass spectrometry or spectroscopy techniques. Their first reported use of this technique for fingerprint analysis was published in 2009, already stating the potential that it could bring into the forensic field [64]. On a review paper published by Francese's group, it is found an extensive update on the MALDI MS based methods' achievements, limitations, and the current work on fingerprints analysis [65].

Before looking into their most relevant work, let's explain briefly the principles of MALDI MS. It is an ionization technique that uses a laser energy absorbing matrix to create ions from large molecules with minimal fragmentation. As described in Ref. [66], ions are formed due to the transfer of energy of a laser firing in the UV

region mediated by a UV absorbing chemical that has been co-crystallized with the analyte(s). The desorption and ionization of the molecules produces singly charged ions, from the mass-to-charge of which, the molecular weight of the corresponding molecule can be easily inferred; this will be the first step in identifying the molecule itself. The additional use of Tandem Mass Spectrometry in conjunction with Ion Mobility will aid/confirm molecular identification. For more technical specifications, go to Ref. [65].

Their work in 2012 [67] regarding the detection of caffeine in fingermarks after an hour of ingesting, has inspired later developments to obtain information about the suspect, particularly whether the person has been in contact or rather consumed illicit substances. That is how they arrive to their MALDI-MS study about the efficiency of detecting and mapping a large range of drugs of abuse and their metabolites in fingermarks for the first time reported [68]. The ability of mapping these substances directly onto the ridge fingerprint patterns allows for additional evidence about the suspect's lifestyle. Furthermore, following the idea from the earlier work of Day, *et al.* [50], they will show how the presence of the drug metabolite will indicate an *"abuse"* scenario rather than *"handling"*. Fig. 8 depicts graphically the previous fact.

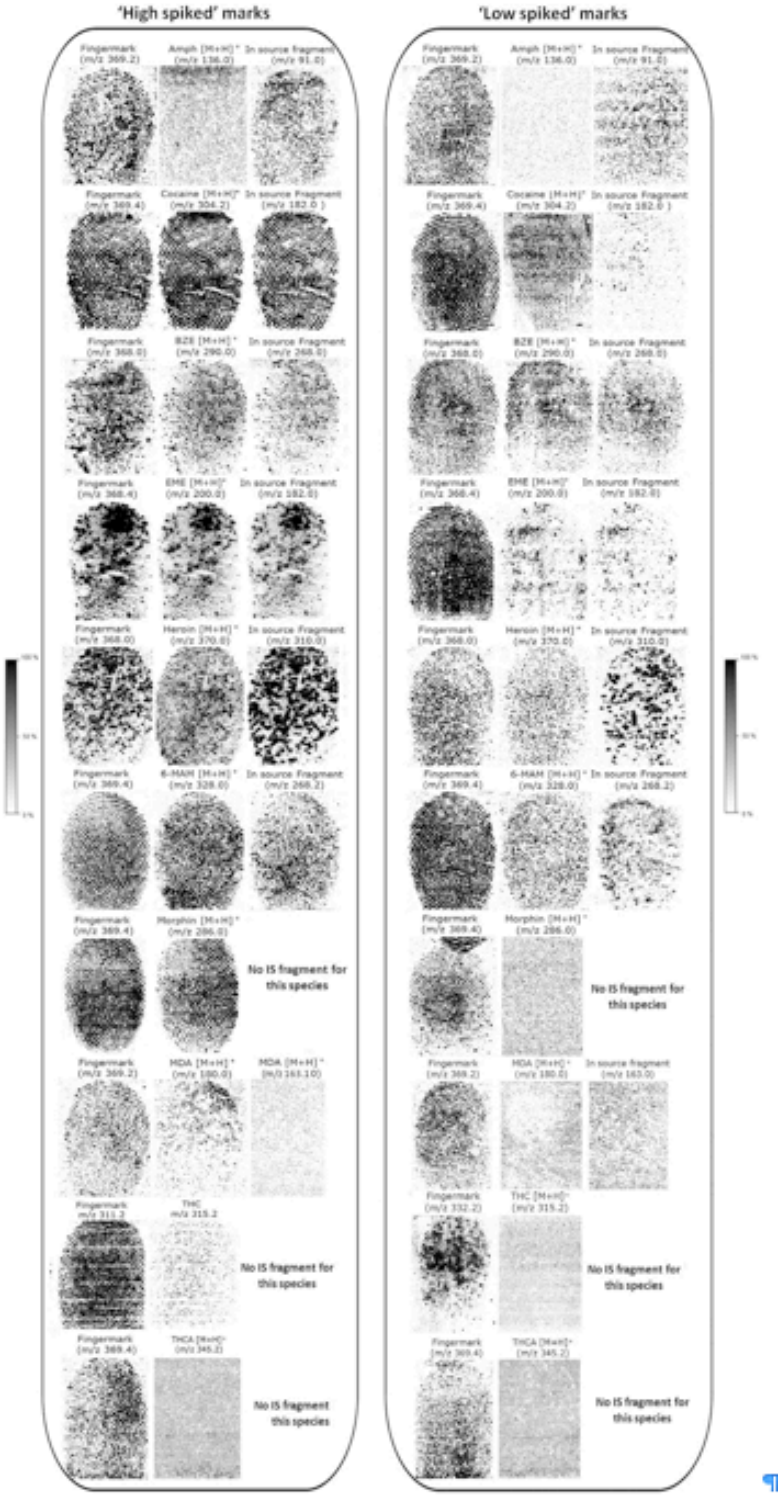

Figure 8: Extracted from Ref. [68]. MALDI MS images of 'high' ("handling" scenario) and 'low' ("abuse" scenario) spiked fingermarks contaminated with amphetamine, cocaine, BZE, EME, heroin, 6-MAM, morphine, MDA, THC and THCA.

Overall, within the *"handling"* scenario results in chemical images depicting the pattern of the mark, including second level detail or showing the distribution of the drug/metabolite within the mark. While at the "*abuse*" scenario, the MALDI drug/metabolite molecular images generally depict a speckled ridge pattern, except for cocaine, BZE, EME and heroin.

Furthermore, they have demonstrated that, MALDI-MSI (imaging) can be used for detecting fingermarks deposited on a range of surfaces by reporting a novel two-step matrix application method (dry wet), where the matrix is dusted onto the sample followed by solvent spray using a robotic device [69]. Hence, integrating in an easily manner the investigation of a crime scene with the later analysis. The dry-wet method was proven to be very reproducible, fast, and efficient.

By collaboration with police forces they have reported initial insight into the operational character of MALDI-MS based methods into real casework [25]. For the first time, crime scene marks from high-profile cases were analyzed with MALDI-MS methods. Although it just marks a preliminary work and seems very unpredictable the nature of the state of the fingermark, demonstrates robustness in the MALDI-MS methods.

In a real crime scene, it is presented often the case of recovering two overlapping fingerprints. That represents a major challenge, failing often to resolve the overlapping area and separate the two different impressions. Other groups have approached earlier this problem using other techniques. For instance, Ifa, *et al.* [26] were able to separate two overlapping fingerprints by employing DESI-MS methods using just one chemical species that was characteristic of one fingermark. On the other hand, the group of Chen, *et al.* [70], succesfully used a combination of Infrared Spectroscopy Imaging and multivariate analysis to separate overlapping fingermarks. A limitation to the use of both previous techniques (DESI and IR) is that knowledge of the presence of a fingermark is required to even start the analysis. A few years later, Francese's research group followed a different pathway by using their top technique: MALDI-MS [67]. They demonstrated once more the efficiency of this technique on separating by imaging both endogenous and exogenous species, including substances that have been ingested and secreted through sweat, as well as substances in fingermarks containing minute amounts of sebaceous material. If we imagine a real crime scene with two overlapping fingermarks, being able to separate them and discern the compounds present in one and the other, could likely guide us through who is the perpetrator and who is the victim. There is an interesting TED talk from S. Francese explaining a scenario in which this method is of high interest and present many advantages on a forensic investigation. See here.

As stated previously, one of the desired scenarios is being able to discern whether an illicit drug has been ingested by a donor or rather touched. Although there is the common belief that the detection of the metabolite of the drug of abuse on the fingerprint points out that the drug has been ingested, no confirmation was made until very recently. The study reported by Costa, *et al.*, displays the case in which contact and administration of heroin from a single fingerprint is feasible by High Resolution Mass Spectrometry [71]. Their study included samples from patients of a drug rehabilitation clinic who have ingested the drug compared with samples collected from non-drug users. Also, they explore the different scenarios when prior to the deposition of the sample, handwashing and wiping is occuring. They highlighted the importance of hand washing when differenciating between contact or administration of the drug, since the presence of the heroin metabolite after hand washing may be a clear indicative of heroin administration. Their results show that for non-drug users, non of the analytes of interest are present prior handwashing. A similar study published following a different technique (paper spray mass spectrometry) was just published last year in which for the first time the levels of cocaine and its primary metabolite, benzoylecgonine

(BZE), were explored on a fingerprint [72]. It is remarked here again the importance of handwashing prior analysis of fingerprints. Their study also compares samples collected from non-drug users and patients from a drug rehabilitation facility. They show that cocaine and BZE can be detected in fingerprints of non-drug users after contact with cocaine (no prior handwashing). It seems cocaine was persistent even after 48 hours of contact. So, the detection of cocaine and BZE in a fingerprint analysis should be taking prudently, since it does not indicate that the suspect/donor has ingested the substance. In contrast, if handwashing takes place prior donating the sample, it is then possible to distinguish between contact and ingestion of cocaine. That is, if hands were washed, BZE will only be detected if the person had ingested cocaine.

3- CONCLUSIONS

Fingermarks are an important tool in the investigation of a crime since they can be used to identify a particular individual and they have provided more criminal identifications worldwide than DNA. Although fingerprints have been used for more than 100 years now, the idea that a fingerprint could be used for more than its characteristic ridge details, really captured the attention of many different research groups on the past decade. It has been shown than together with the physical information obtained from a fingerprint, it is also possible to retrieve chemical information. In fact, fingermarks are the result of a molecular transfer from the fingerprint to a surface upon contact. Now here, this molecular content is potentially the carrier of important information that can be used for forensic applications but also for medical diagnostics or toxicology seeing that is a non-invasive method compared with hair or blood analysis. This forensic opportunity gives rise to a sort of criminal profiling (often called chemical profiling), no longer based on behavioural science but on the chemical content of the mark. For instance, it could indicate if a particular person has been in contact or consumed illicit drugs of abuse before or during a crime. In this respect, the scientific community has devoted huge efforts in understanding deeply the chemical composition of the marks and development of different analytical techniques to retrieve such information. These techniques can be mainly classified in two groups: spectroscopy techniques and mass spectrometry techniques. It is, however, the mass spectrometry techniques the ones showing superiority among others, since they are certainly more specific, non-destructive (or minimal destructive) and allow for detection and visualization of a compound with high resolution. Particularly MALDI-MS, with an abundant literature record, has allowed to resolve a major challenge by separating two overlapping fingerprints. On the past 5 years new studies have arised and show for the first time how MS of fingerprints can help distinguish between administration and contact with drugs (heroin or cocaine).

The idea of molecular fingerprinting has developed quickly from just an idea to applied methodologies. Even some techniques have been already succesfully applied on real crime investigations. However, it has not fully reached its total applicability and more test studies are needed. Nevertheless, this research is achieving major acomplishments in very short time and the impact in forensic investigations as well as other civilian activities will be promising in the future years.

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