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ADVANCEMENT OF MASS SPECTROMETRY IN DETECTION OF COCAINE AND ITS METABOLITE IN LATENT FINGERPRINTS

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ABSTRACT

Since the late 19th century, latent fingerprinting has led to successful identification of the suspect in crime scene investigations (CSI). However, there had also been cases of wrongful convictions due to partial retrieval of the finger mark by classical fingerprinting techniques in CSI. Thereby, with intense research, mass spectrometry (MS) advanced to a point where a single fingerprint reveals whether a suspect is a cocaine abuser or a cocaine dealer. Likewise, since cocaine abusing is a growing public health issue, use of these advanced MS techniques and fingerprints enables rapid and sensitive detection of cocaine in suspected individuals. The types of MS techniques involved in the detection of cocaine and its metabolites include, matrix-assisted laser desorption ionisation (MALDI-MS), surface-assisted laser desorption ionisation (SALDI-MS), desorption electrospray ionisation (DESI-MS) and paper spray MS (PS-MS). MALDI-MS has a high specificity but based on the LOD values for cocaine (10ng/mL) and its metabolites (100ng/mL), it has a very low sensitivity. Comparatively, DESI-MS is more sensitive since it has a lower LOD for cocaine and its metabolites (5ng/mL). Nevertheless, the sensitivity of DESI-MS was not sufficient in situations where the suspect has washed or wiped hands after handling or ingesting cocaine. Thereby, PS-MS was found to be a more sensitive technique in such situations since it has a very high sensitivity based on a low LOD of 1ng/ml and it is the most rapid technique which performs LFP analysis of cocaine and its metabolites within 30 seconds. Key words: Public Health, Cocaine, Mass spectrometry, Latent Fingerprint

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INTRODUCTION

Fingerprints are unique patterns formed by the friction ridge skin of the fingers or palms, and they are commonly used in forensic investigations in the identification of a suspect (Croxton et al., 2010). The unique pattern in the friction ridge skin is not determined by genetics but are formed due to the differential pressure and growth experienced during embryo development. As a result, fingerprints of twins also differ (Kucken and Champod, 2013).

The earliest use of fingerprints dates back to 8th century where Chinese used fingerprints placed on clay tablets to seal important documents, which showed that they realized the uniqueness of a fingerprint (Trimm, 2005). These fingerprints are known as plastic fingerprints which is define as an impression of fingerprints formed on soft material. Later on, in 1880, Dr. Henry Faulds introduced the idea of using fingerprints as a means of personal identification by observing fingerprints in blood (visible fingerprint) (US Marshals Service, 2017). Then these blood fingerprints were used in forensic investigations. However, visible fingerprints left in blood are present only in murder cases. Therefore, in 1888, Wilhelm Eber proposed the use of invisible fingerprints called latent fingerprints (LFP) which could be present on any surface where the suspect has made contact via the friction ridge skin (Cole, 2009). A LFP is defined as an impression formed by the sweat which is excreted by the eccrine glands transferred to a surface by the friction ridge skin of fingers or palms of hands (Ulery et al., 2011; Dhir, 2009).

Since the late 19th century, the fingerprint pattern in LFPs are visualized from various conventional methods (Table 1). In general, these conventional techniques involve a chemical reaction with the components secreted by the eccrine glands, thereby producing a coloured fingerprint. Then the visualised fingerprints are analysed based on the friction ridge details that are described in a hierarchical order at three levels; level 1 (friction ridge flow), level 2 (minutiae) and level 3 (single ridge details). Based on these details, a fingerprint match is obtained from the National Fingerprint Database (NFD) by mean of Integrated Automated Fingerprint Identification System (IAFIS). Most AFIS requires only up to the second level details in order to find a match (Kellman et al., 2014).

Table 1: Various procedures involved in the common conventional methods used in latent fingerprinting (Bertino, 2008).

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Chemical	Uses	Application	Safety	Chemical Reaction	Latent Print
Ninhydrin	Paper	Object dipped or sprayed in Ninhydrin Wait 24 hours	Do not inhale or get on your skin	Reacts with amino acids (proteins) found in sweat	Purple-blue print
Cyanoacrylate Vapor	Household items: plastic, metal, glass, and skin	Heat sample in a vapor tent	Do not inhale or get on your skin: irritant to mucous membranes	Reacts with amino acids	White print
Silver Nitrate	Wood Styrofoam	Object dipped or sprayed in Silver Nitrate	Wear gloves to avoid contact with skin	Chloride from salt in perspiration on the print combines with silver nitrate to form silver chloride	Black or reddish brown print under UV light
Iodine Fuming	Paper Cardboard Unpainted surfaces	In a vapor tent, heat solid iodine crystals	Toxic to inhale or ingest	Iodine combines with carbohydrates in latent print	Brownish print (fades quickly) must be photographed or sprayed with a solution of starch

However, these conventional techniques had led to several wrongful convictions in the past. One such example is the high profile fingerprint misidentification case of Bradon Mayfield from United States in 2004, who was wrongly accused for bombing of four trains in Madrid, Spain. Followed by this event, the police had obtained digital images of partial LFPs taken from a plastic bag that contained detonator caps. Then this partial LFP was matched with that of Bradon Mayfield. However, he had not committed the crime nor even visited Spain. Later on, he was released from custody when the Spanish government stated that they had no record of Mayfield travelling to that country (Knoops, 2013; Spinney, 2010). Thereby, it shows that these methods fail in identifying the correct suspect in situations where the fingerprint is smudged, partial or distorted. In addition, they have other disadvantages; sample destruction, low specificity and low sensitivity (Bradshaw et al., 2013).

Henceforth, with intense research and dedication, forensic science grew into an era where the chemicals excreted by the sweat glands on the friction ridge skin and any environmental contaminants or ingested substances are identified to determine a chemical profile unique to each individual. Based on this chemical profile, the forensic investigators could determine the lifestyle and activities of a suspect prior to committing a crime (Figure 1) (Michalski, Shaler and Dorman, 2013; Szynkowska et al., 2009).

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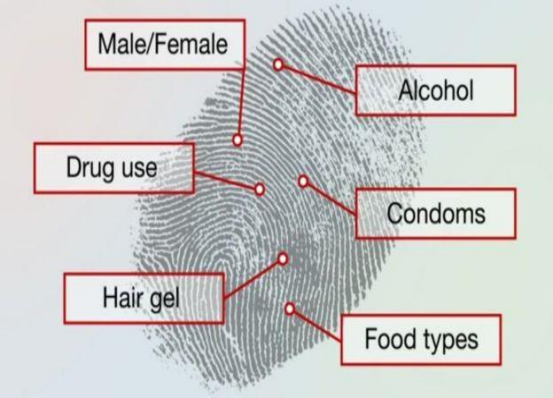

Figure 1: Clues obtained about the lifestyle and activities of the suspect before committing the crime (NaturPhilosophie, 2017).

Many criminals are under the influence of drugs when committing a crime. This is due to psychological instability in drug abusers and they commit crime in order to pay for their drugs. Therefore, there is a strong association between drug abuse and crime (Rafaiee et al., 2013). For instance, statistics demonstrated a high homicide rate in countries which are on the main cocaine route (Figure 2). Thereby, it implies that homicide rate increases with drug trafficking due to competition between different drug markets and also it increases with drug abusing (United Nations on Drug and Crime, 2016).

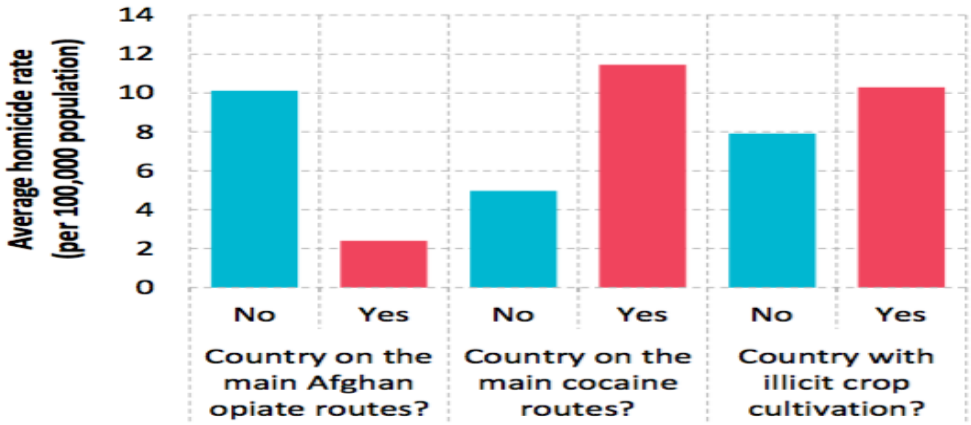

Figure 2: A high homicide rate in countries which are on the main cocaine route (United Nations Office on Drugs and Crime (UNODC), 2016).

Furthermore, over the past few years the prevalence of cocaine and illicit drug abusing have continually risen. For instance, in Sri Lanka in 2016, it was reported that 1500kg of cocaine was seized by the police as shown in Figure 3 and the majority of it was found to be trafficked from India, Pakistan and Maldives. Thus, it shows that cocaine abusing has become a major public issue in Sri Lanka, thereby posing a threat to both public health and peace (Jayawardana,

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2017). In addition, the worldwide prevalence of illicit drug abusing was statically found to increase from 208 million in 2006 to 255 million in 2015 (Figure 4). It was further reported that among the population of illicit drug abusers, 225 thousand have died of hepatitis C while 65 thousand have died of HIV (Figure 5) (UNODC, 2016). Moreover, apart from these serious health complications associated with cocaine abusing, cocaine itself has several side effects such as myocardial infarction, headaches, strokes, seizures, coma and nausea (National Institute on Drug Abuse, 2016).

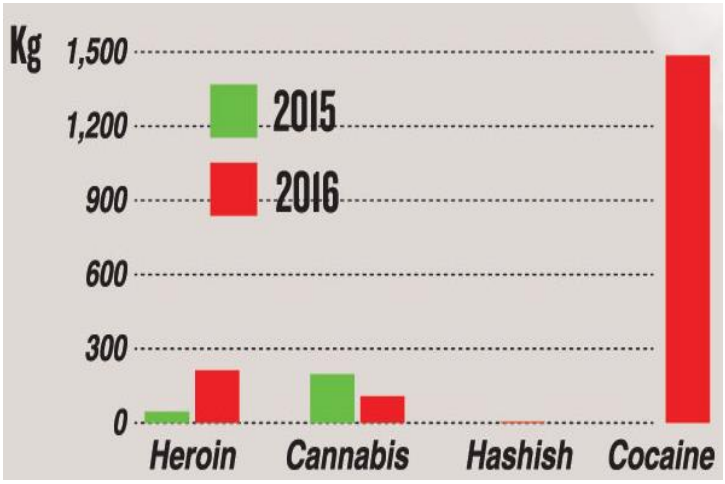

Figure 3: Quantity of illicit drugs seized by the Police Narcotics Bureau in Sri Lanka (Jayawardana, 2017)

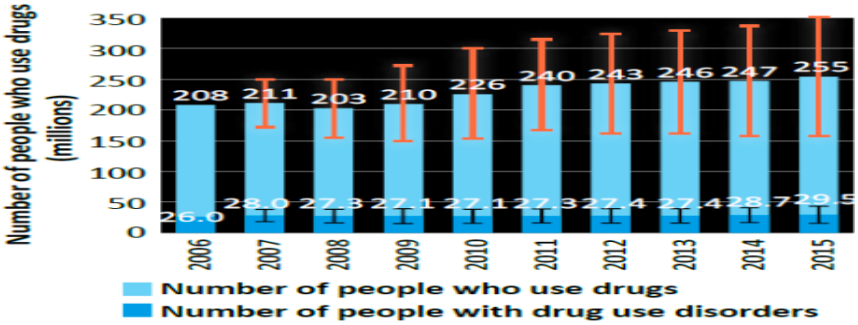

Figure 4: Worldwide prevalence of drug and drug use disorders, 2006-2015 (United Nations Office on Drugs and Crime, 2017)

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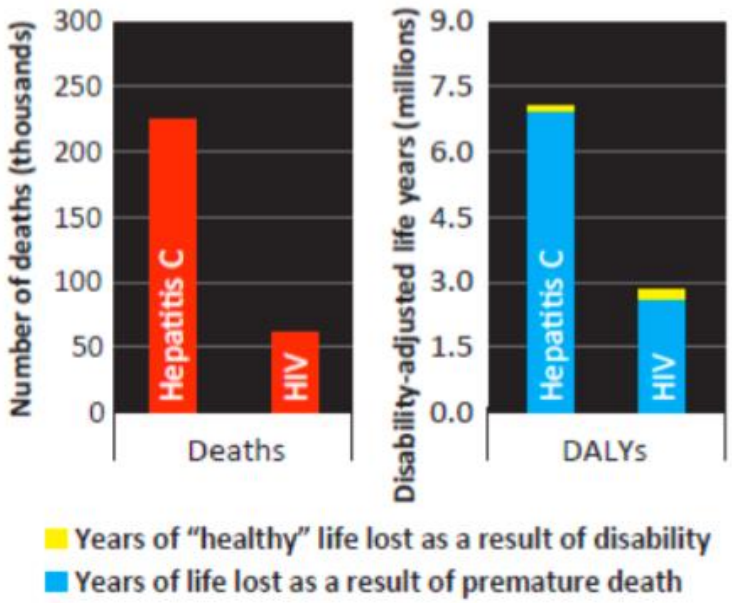

Figure 5: Burden of disease from hepatitis C and HIV from injecting drug use, 2013 (UNODC, 2017)

Overall, it shows that cocaine abusing has become a major public health issue due to ingestion of cocaine causing several health complications and it is also associated with an increased rate of crime. Thereby, scientists were stimulated to carry out research in detecting cocaine in LFPs which would be beneficial in both drug testing and crime scene investigations. Hence, latent fingerprinting revolutionized to a point where scientists can detect cocaine and its metabolites (Figure 6) that enable them to determine whether the suspect is a cocaine abuser (detection of its metabolites) or a cocaine dealer (detection of the parent drug). Thereby, it facilitates the identification of the suspect by reducing the pool of suspects. This would be advantageous for both police investigations and court cases. Likewise, it would also prevent wrongful accusation of possessing drugs by analysing the fingerprints. In addition, it would also benefit drug testing performed in probation services, prisons, work places and drug rehabilitation clinics (Costa et al., 2017; Francese et al., 2013).

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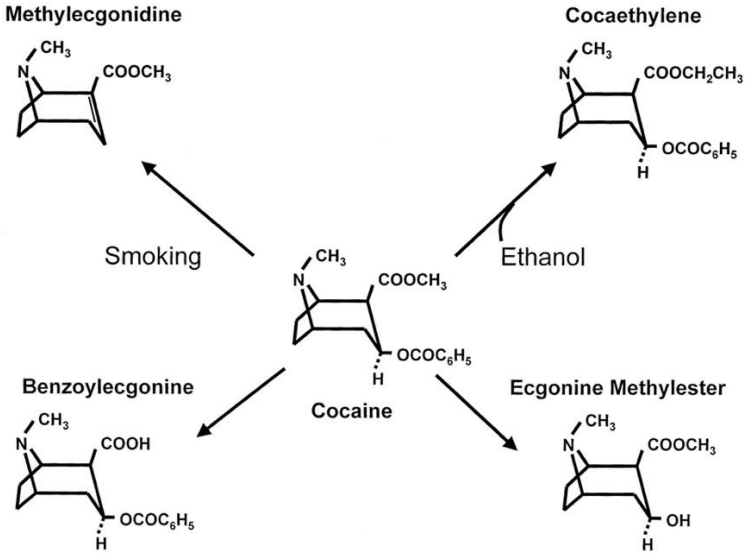

Figure 6: Types of metabolites formed from cocaine metabolism (Ferreira et al., 2001).

The types of techniques involved in detecting cocaine and its metabolites in LFPs are mass spectrometry (MS), vibrational spectroscopy and nanoparticles. However, MS offers higher analytical selectivity in comparison to vibrational spectroscopy and nanoparticle-based detection. Therefore, more research was carried out in MS with different types (Table 2) (Costa, 2017). This review focuses on the advancement of MS techniques according to their sensitivity and selectivity on LFPs.

Table 2: Development of mass spectrometry in the detection of cocaine and its metabolites in latent fingerprints

Year	Type	References
2008	Desorption electrospray MS (DESI-MS)	Ifa *et al*., 2008
2009	Surface-assisted laser desorption ionization MS (SALDI-MS)	Rowell, Hudson and Seviour, 2009
2015	Matrix- assisted laser desorption ionization MS (MALDI-TOF MS)	Groeneveld *et al*., 2015
2017	Paper spray MS (PS-MS)	Costa *et al*., 2017

Matrix-assisted laser desorption ionization-time of flight MS (MALDI-TOF-MS)

MALDI-MS is a soft ionization technique involving the use of a matrix. In here, the sample is initially mixed/coated with an organic matrix in MALDI target plate (Figure 7). The organic matrix comprises of small, organic and ultra violet (UV)-absorbing molecules. The matrix is dried to crystallize with the analyte (Singhal et al., 2015). Then an automated UV laser pulse strikes causing the matrix molecules to absorb the UV energy in the laser pulse and become excited resulting in desorption of the matrix molecules along with the analyte molecules into gaseous phase followed by ionization (Manz, et al., 2004). Then the charged analytes are separated depending on their mass to charge (m/z) ratio by accelerating at a constant potential difference. The time of flight (TOF) detector identifies the individual m/z ratio by the time taken for the charged analytes to travel

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through a known distance. Thereby, a mass spectrum called peptide mass fingerprint (PMF) is generated and is normalized against the matrix peak (Singhal et al., 2015; Deininger et al., 2011).

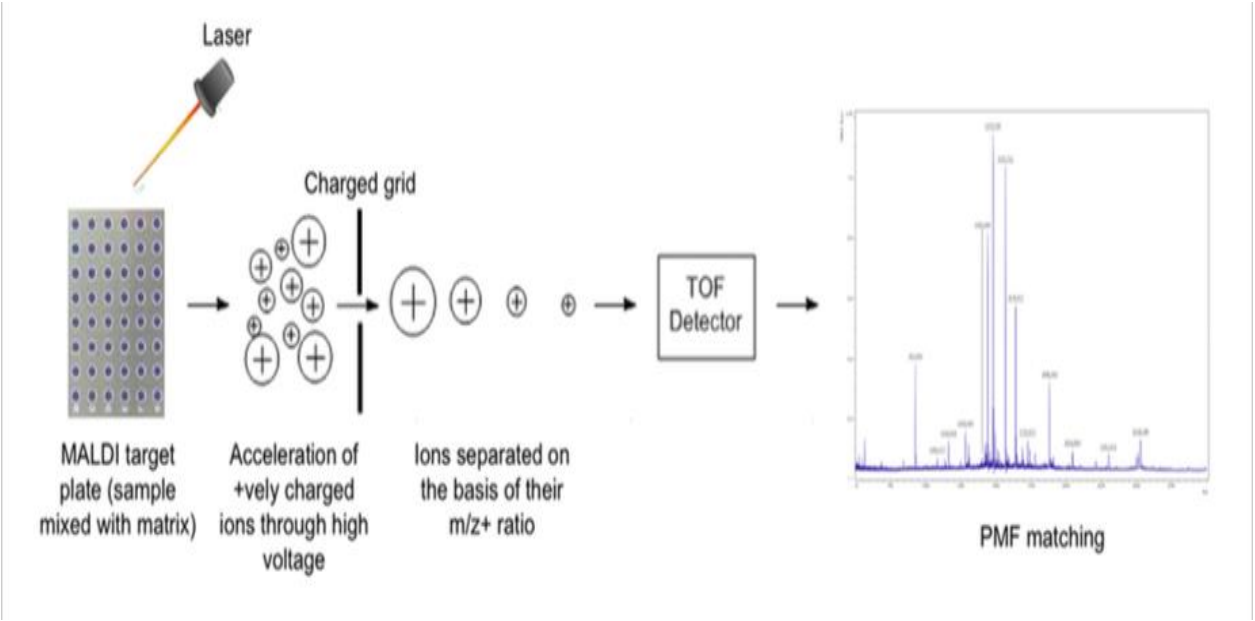

Figure 7: Schematic diagram of MALDI-TOF MS (Singhal et al., 2015).

MALDI-MS is operated in either profiling mode or imaging mode (Figure 8). MALDI-MS profiling (MALDI-MSP) provides the chemical information of the analyte fingerprint around 5-10 minutes while MALDI-MS imaging (MALDI-MSI) enables physical development of the mark through chemical imaging with a spatial resolution ranging from 10-150 microns. However, MALDI-MSI takes a long time (above 1 hour on average) depending on the laser frequency, fingermark area, acquisition mode and rastering speed (Francese et al., 2013).

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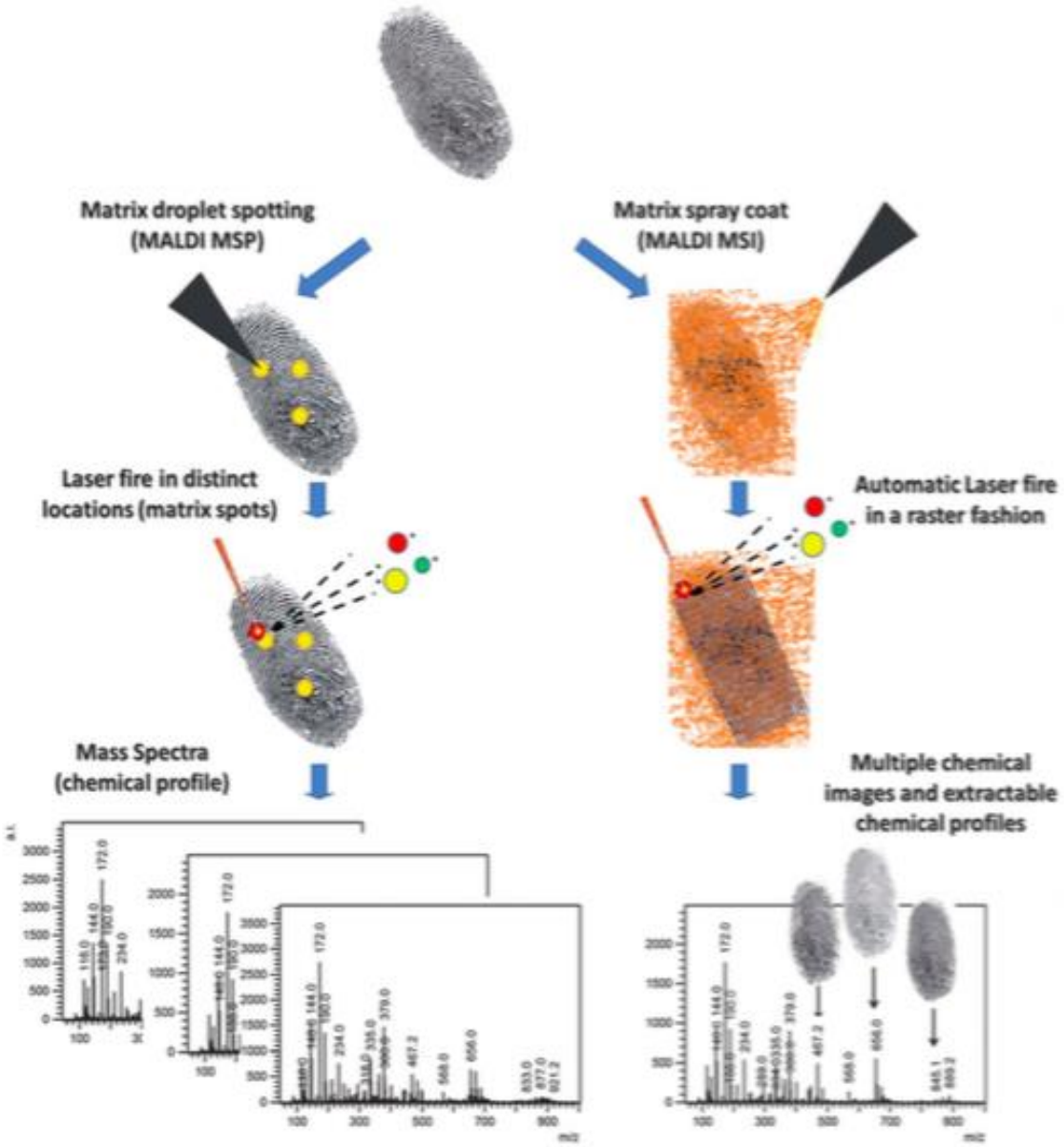

Figure 8: Schematics of MALDI-MS profiling (MALDI-MSP) and MALDI-MS imaging (MALDI-MSI) for fingerprint analysis. In MALDI-MSP, the MALDI matrix is spotted on the fingerprint followed by firing of a laser beam in distinct locations in the spots. In MALDI-MSI, the matrix is spray coated and the spectra are obtained at each x y location in a raster fashion (Francese et al., 2013).

In 2015, researchers demonstrated the ability of MALDI coupled with Quadrupole TOF (QTOF) mode in the detection of 10 illicit drugs. Each was diluted to a concentration of 10μg/mL using MeOH and mixed with 10μg/mL α-cyano-4-hydroxycinnamic acid (α-CHCA). All ten drugs were detected without any ion suppression, thereby proving a high specificity and the ability to detect individual drugs in the LFPs of multiple-drug abusers (Figure 9).

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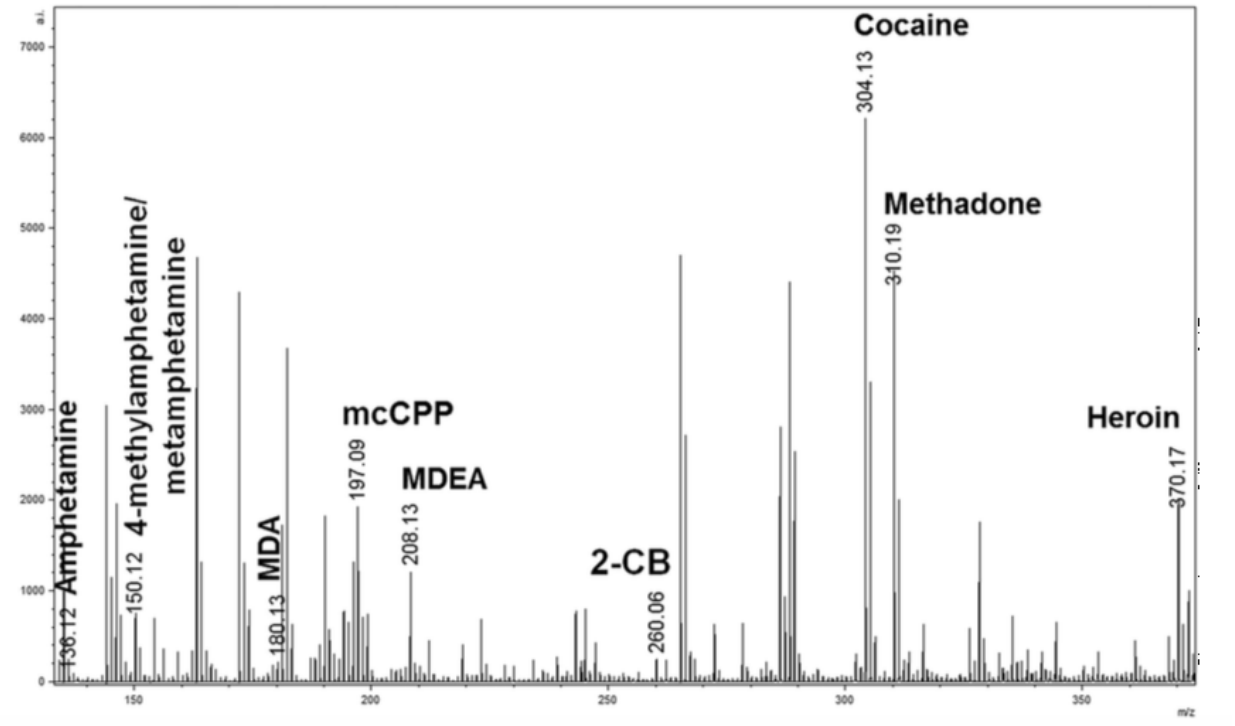

Figure 9: MALDI-QTOF MS spectrum obtained in the detection of 10 illicit drugs at a concentration of 10μg/mL mixed with an equal volume of matrix solution (Groeneveld et al., 2015).

Meanwhile, MALDI-MSI was performed to obtain the ridge pattern. Fingertips were spiked with 5 μg of cocaine, 0.5 μg of Benzoylecgonine (BZE) and 0.5μg of Ecgonine Methyl Ester (EME) at a ratio of 5:1:1. Then LFPs were obtained and imaged via MALDI-MSI (Figure 10). MALDI-MSI of cocaine shows a better continuity of the ridges in comparison to BZE, however EME does not show the ridge pattern but only a dot-like distribution which may be due to low sensitivity of this technique for EME (Groeneveld et al., 2015).

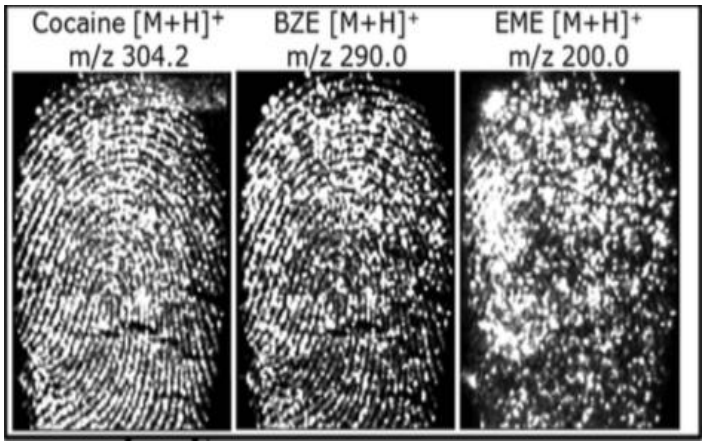

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Figure 10: MALDI-MS images of LFPs simultaneously spiked with cocaine and its metabolites at a define ratio of 5:1:1 for cocaine, BZE and EME (Groeneveld et al., 2015).

Currently, crime scene investigators (CSIs) are using conventional fingerprinting methods also known as fingerprint enhancement techniques (FET). The most commonly used FET is dusted and lifted fingerprints for suspect identification. In spite of advancement in MS techniques in LFP, FETs would still be used in order to localize the fingerprint. Therefore, in order to investigate the compatibility of powder dusting and cyanoacrylate fuming of LFP with MALDI-MS, scientists performed MALDI-TOF MS analysis of dusted, cyanoacrylate (CNA) developed and lifted fingerprints spiked with cocaine. However, no peaks were observed in the spectrum since the fingermark was only partially lifted onto the adhesive tape. Nevertheless, with acetone pre-treatment, most of the fingerprint was transferred to the adhesive tape due to partial dissolution of the CNA polymer in the LFP, thereby enabling the detection of cocaine in the lifted fingermark (Sundar and Rowell, 2014).

Due to compatibility of MALDI-MS with FETs demonstrated by the above study, MALDI-MS had been used in crime scene LFP from a high profile case of harassment. In one CSI case, police had dusted the LFPs with Carbon black powder followed by optical observation. However, the ridge details could not be observed (Figure 11 A). Thereby, scientists obtained the lifted LFPs from CSIs and subjected it to MALDI-MS, but yet the ridges were not visible (Figure 11 B and 11 C). However, the molecular ion signals at m/z 304.1 and 182.1 were of intact cocaine and fragmented cocaine. Thereby, demonstrating the applicability of MALDI-MS in detecting cocaine in natural LFPs in CSI (Bradshaw et al., 2017).

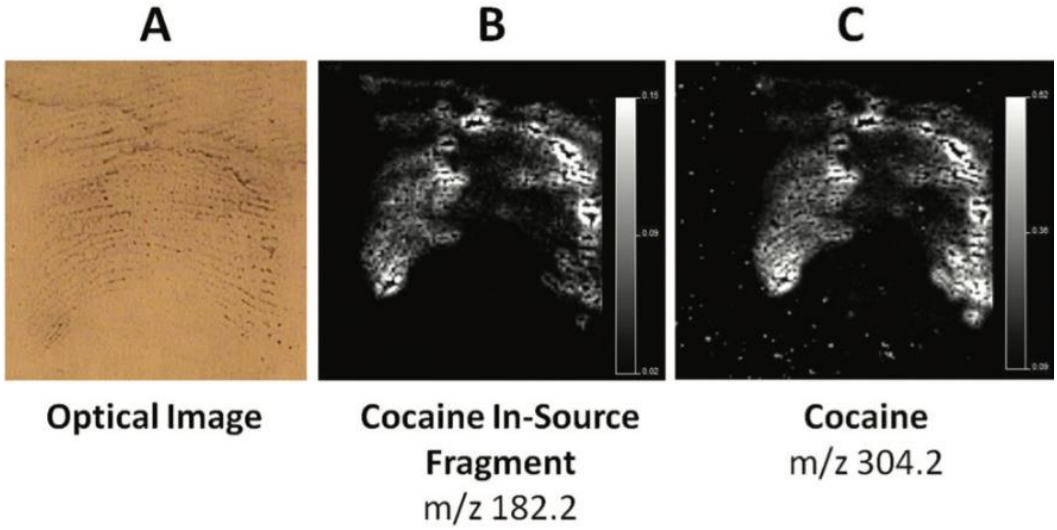

Figure 11: MALDI-MS analysis of a LFP recovered from the interior of a window frame following enhancement with carbon black powder and lifting onto a forensic lifting tape (A) Optical image of the LFP (B) MALDI-MS ion signals (m/z 182.2 and m/z 304.2) for intact and fragmented cocaine, normalized against matrix peak at m/z 190.0 (Bradshaw et al., 2017).

Scientists utilized MALDI-MS technique for visual determination of the limit of

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detection (LOD) of cocaine and BZE. Initially, they obtained ungroomed fingerprints by washing hands with alcohol wipes and performing normal activities for 15 minutes prior to depositing the fingerprints on pre-coated aluminum sheets (Groeneveld et al., 2015; Wolstenholme et al., 2009). Cocaine and BZE were prepared in a range of dilutions: 10, 1, 0.1, 0.01 and 0.001 μg/mL and then spotted on the deposited fingerprint from top to bottom. Upon drying, it was spray coated with 5mg/mL α-CHCA. Thereby, MALDI-MS was obtained for diluents (Figure 12). Based on this image, it can be concluded that the LOD of cocaine is 10ng/mL while for BZE it is 100ng/mL. For EME, the LOD is 100ng/mL (Table 3). Thereby, this technique is more sensitive in the detection of cocaine rather than its metabolites. However, in order to confirm the LOD values for cocaine and BZE, concentration values in between 1ng/mL and 10ng/mL for cocaine, and 100ng/mL and 10ng/mL for BZE requires further research (Groeneveld et al., 2015).

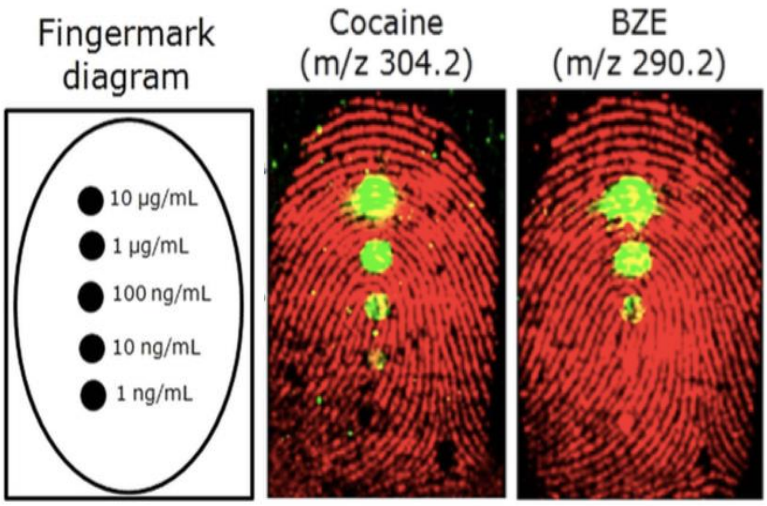

Figure 12: MALDI MS imaging of cocaine and benzoylecgonine spotted on top of a fingermark and subsequently spray-coated. The ion signals of the compounds are displayed in green (overlay) while red depicts the ion signals of an endogenous species (Groeneveld et al., 2015).

Table 3: LOD values of cocaine and its metabolites obtained from MALDI-MS (Groeneveld et al., 2015).

Drug	LOD (ng/mL)
Cocaine $C_{17}H_{21}NO_4$	10
BZE $C_{16}H_{19}NO_4$	100
EME $C_{10}H_{17}NO_3$	100

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Since MALDI-MS has a low sensitivity in detecting BZE and EME which is reflected by its high LOD values, it was used with liquid extraction surface analysis (LESA) which uses only a small volume of sample. This was demonstrated by a study conducted in 2016, where scientists obtained fingerprints, two oral fluid samples and a urine sample from an individual attending drug and alcohol treatment service. The first oral fluid sample was subjected to standard immunoassay drug screening procedure to screen for cocaine along with other illicit drugs. The fingerprint samples were deposited onto a glass slide. Meanwhile, 0.2 μL drops of the second oral fluid sample and the urine sample which were spotted onto separate glass slides, were subjected to LESA-MS analysis. Collision induced dissociation (CID) spectra of the sample subjected to LESA exhibited peaks for cocaine, BZE and EME (Figure 13) which was corroborating with the results obtained from the immunoassay (Table 4). The study states that the sensitivity could be increased by repeatedly spotting and evaporating to increase the volume of the sample. However, LESA method has a low spatial resolution. Thereby, it was used in tandem with MALDI-MSI (Figure 14) to obtain both quantification and imaging of cocaine and its metabolites in fingerprints (Bailey et al., 2016).

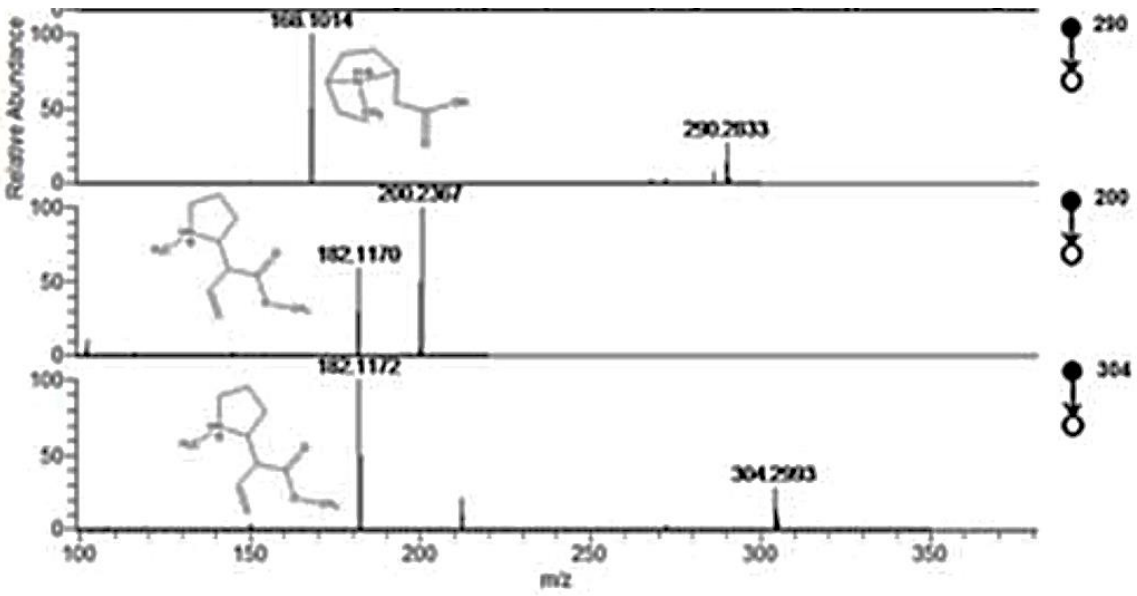

Figure 13: Collision induced dissociation (CID) spectra produced from liquid extraction surface analysis (LESA) of a fingerprint obtained from a donor attending a drug rehabilitation centre, showing peaks for (from top to bottom) (a) cocaine (b) benzoylecgonine and (c) methylecgonine (Bailey et al., 2016).

Table 4: Cocaine and its metabolites detected in fingerprints, oral fluid and urine samples obtained from the same donor. Four spots were selected randomly from the fingerprint and analysed using LESI-MS while three 0.2μL spots of oral fluid and urine were analysed. Y= Detected (Bailey et al., 2016).

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Drug and associated metabolites	Parent ion m/z detected $(M+H)^+$	Δ ppm from accurate mass	CID transition precursor →product ion	Oral fluid immune assay screen	Fingerprint (LESA)	Oral Fluid (LESA)	Urine (LESA)
Cocaine	304.1538	35	304→272, 182, 150, 82	Y	Y	Y	Y
EME	200.1272	53	200→182, 82		Y	Y	Y
BZE	290.1377	73	290→272, 168, 150		Y	Y	Y

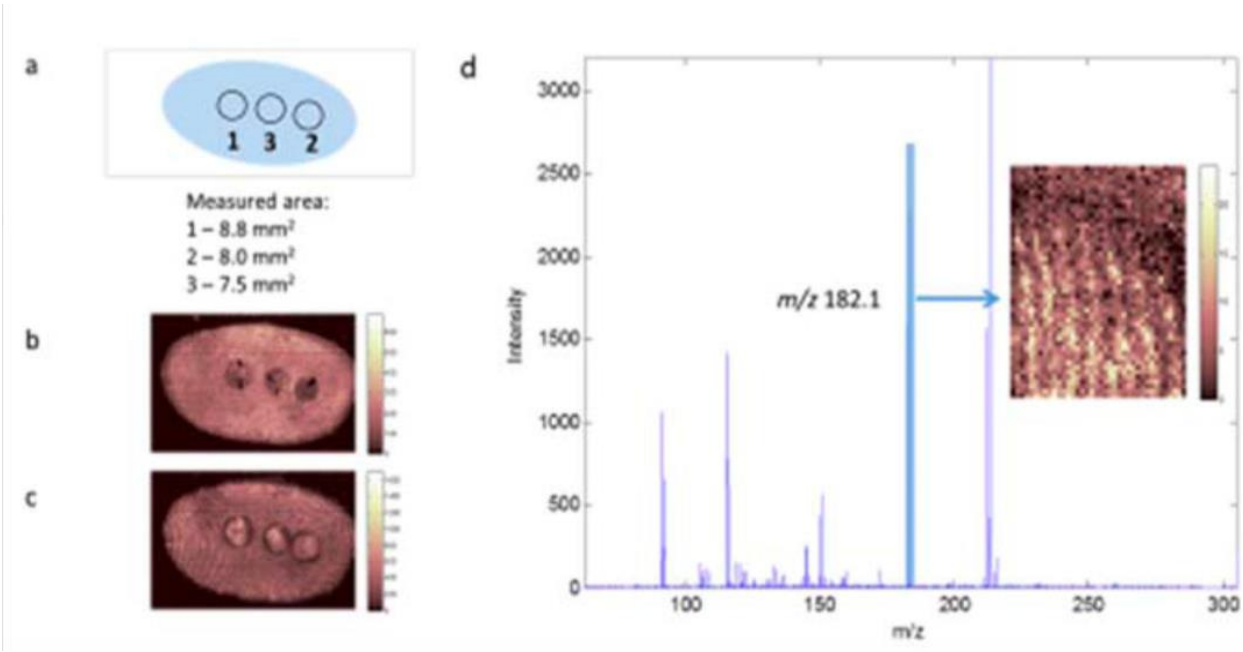

Figure 14: MALD-MSI of fingerprints previously analysed by LESI. (a) Representation of the areas analysed by LESI; images of (b) m/z 638.6 and (c) m/z 550.6 (d) MS/MS spectrum obtained during CID of m/z 304 (cocaine) for the area of the fingerprint shown in the inset, exhibiting the peak for the fragment ion for cocaine at m/z 182 (Bailey et al., 2016).

However, using two techniques in order to overcome low sensitivity of MALDI-MS would be time-consuming and labour-

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intensive. Therefore, scientists further improved MALDI-MS by eliminating the need for an organic matrix which causes ion suppression and background noise (Wen, Dagan and Wysocki, 2007).

Surface-assisted laser desorption ionization (SALDI-MS)

Surface-assisted laser desorption ionization (SALDI-MS) is an alternative to MALDI-MS and it enables detection of smaller molecular weight substances in the absence of a matrix (Brown et al., 2015). It is similar to MALDI-MS but it uses other inorganic substrates such as nanomaterials coating the analyte molecules instead of an organic matrix. Coating of the analyte molecules by these substrates increases the surface area exposed to ionization/desorption (Figure 15) (Watanabe et al., 2008).

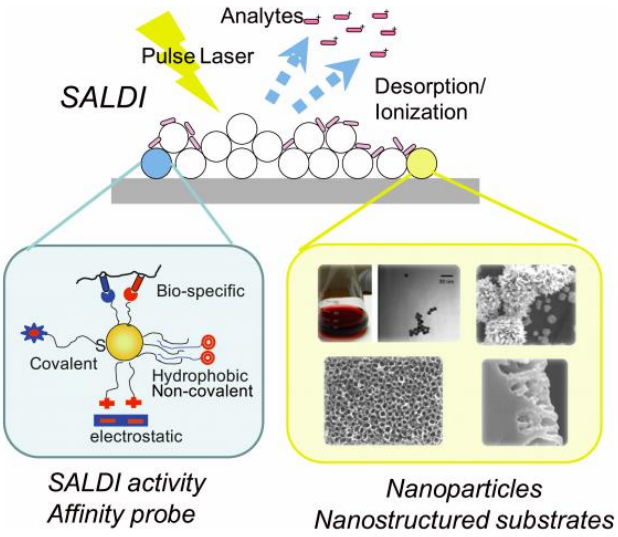

Figure 15: Schematics of SALDI-MS using different types of nanoparticles and nanostructure substrates, and an affinity probes (Arakawa and Kawasaki, 2010).

In 2009, Rowell and his co-workers used chemically engineered silica particles embedded with carbon black as a dusting agent in LFPs obtained from a drug user attending a rehabilitation centre prior to SALDI-MS (Rowell et al., 2009). These silica particles with fluorescent dyes interact with the hydrophobic components in the fingerprint (sebum), thereby enabling its visualization (Theaker et al., 2008). Presence of an intense peak for cocaine at 304.4 m/z (Figure 16a) demonstrated enhancement of the ionization of cocaine by these silica particles. Furthermore, imaging data obtained from the peak intensities of cocaine from a small area of the fingerprint (Figure 16b) exhibited hot spots arising from contact residues. Thereby, it shows that these silica particles not only aid in locating the fingerprints but also act as a SALDI-TOF-MS enhancer (Sundar and Rowell, 2015; Rowell et al., 2009).

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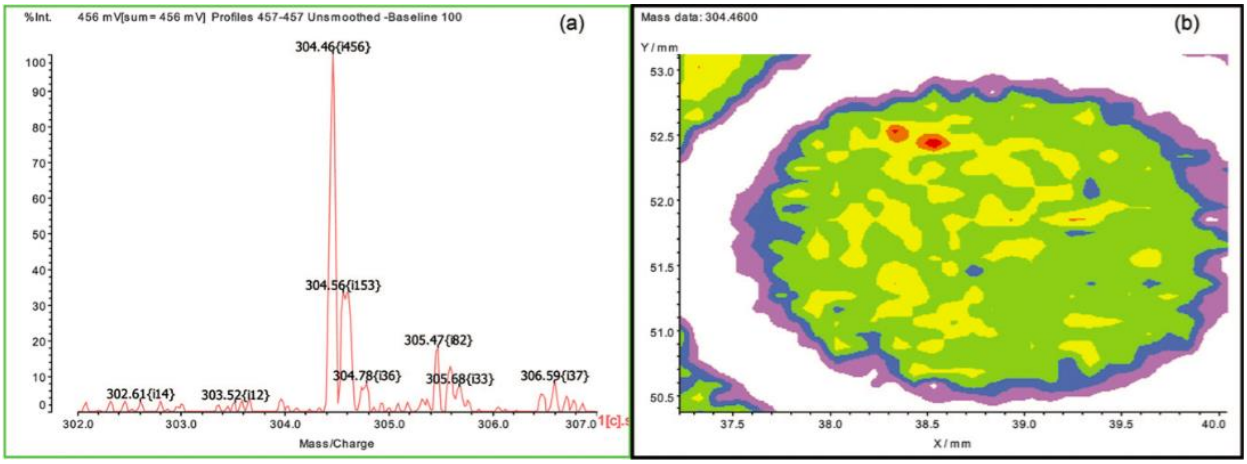

Figure 16: (a) SALDI-TOF mass spectrum of a hydrophobic silica dusted fingerprint obtained from a drug user attending a rehabilitation centre showing peak for cocaine at 304.4 m/z (b) Image of the peak intensity of cocaine in a small area of the fingerprint obtained from the software (Rowell, et al., 2009).

In order to assess the compatibility of SALDI-MS with a typical FET which is magnetic black powder, scientists obtained SALDI-MS of LFPs dusted with magnetic black powder followed by spiking with 100ng, 10µg and 1µg of cocaine. Presence of an intense peak (Figure 17) demonstrated its compatibility with magnetic black powder (Sundar and Rowell, 2015).

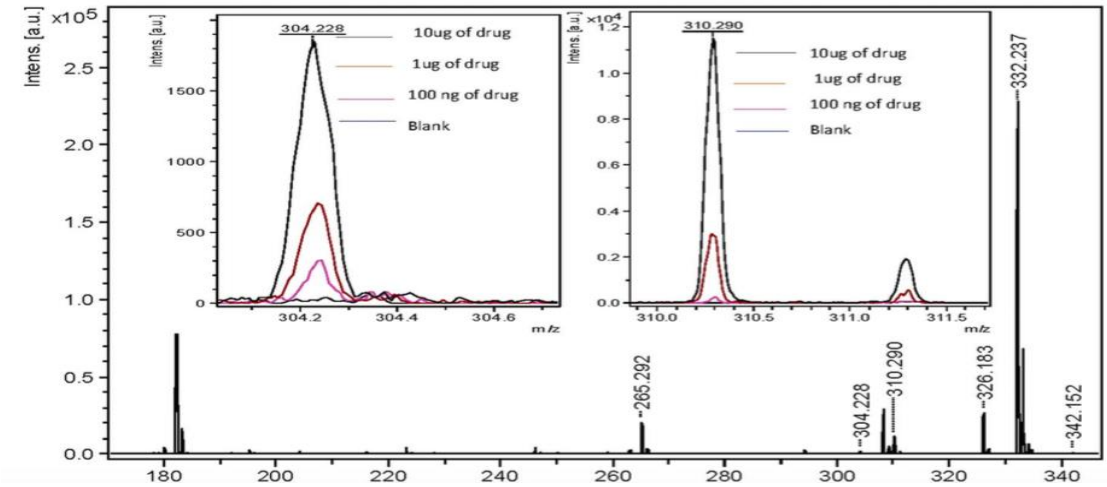

Figure 17: SALDI-MS of LFPs spiked with cocaine and dusted with black magnetic powder displaying peaks for cocaine at [M+H] + at m/z 304.08 (Sundar and Rowell, 2015).

In 2017, in order to enhance the sensitivity of SALDI-MS, scientists used silicone nanowire as the substrate. This was commercialized as nanostructure-assisted laser desorption ionization MS (NALDI-MS). In this study, LFPs were obtained

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from two volunteers A and B who previously had their fingers pressed onto a cocaine contaminated (100μM) ceramic tile. Then these fingerprints were subjected to MALDI-MS and NALDI-MS (Figure 18). Intensity of cocaine is higher in NALDI-MS image in comparison to MALDI-MS image (especially in volunteer B) which is due to absence of matrix effect in NALDI-MS (Skriba and Havlicek, 2017).

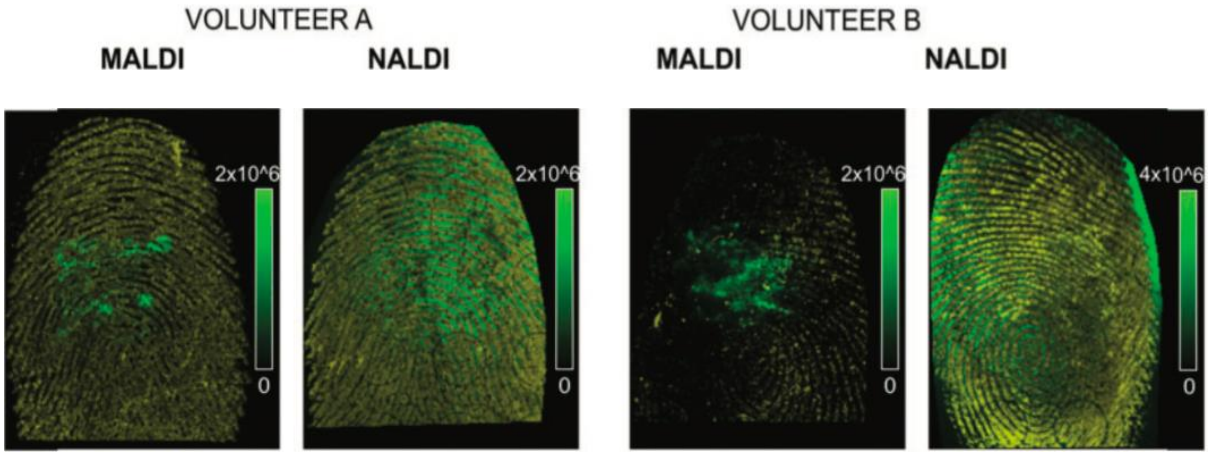

Figure 18: Visualization of oleic acid in fingerprints contaminated with cocaine obtained from two volunteers and the images generated from MALDI-MS and NALDI-MS. The images are constructed from oleic acid (yellow) in conjunction with cocaine (green) (Skriba and Havlicek, 2017).

Ambient mass spectrometer

MALDI-MS and SALDI-MS are generally time consuming since there is sample pre-treatment which is not ideal in CSI and drug testing. Therefore, scientists moved to ambient MS which enables in situ analysis of samples in the absence of sample pre-treatment, thereby short analysis time, high salt tolerance and low matrix effect (Shelley and Hieftje, 2009; Jackson et al., 2007).

Desorption electrospray ionization MS (DESI-MS)

DESI-MS was first developed by Cooks and his co-workers in 2004. However, it was first used in 2008 by Ifa and his co-workers in the detection of cocaine and its metabolites in LFPs (Ifa et al., 2008; Takáts et al., 2004). In DESI, an electrospray source emits charged ion droplets to the targeted surface (Figure 19). Thereby, the charged primary droplets from the electrospray forms a thin liquid layer where dissolution of the analyte molecules takes place. Due to continuous spraying of the charged particles, the surface particles undergo desorption and ionization, and the desorbed particles enter into the MS (Venter et al., 2006). The efficiency of DESI depends on several geometrical parameters such as the incidence angle (α), collection angle (β), tip to surface distance (mm), MS inlet to surface distance (mm) and the tip to MS inlet distance (mm) (Figure 20). These should be changed depending on the type of sample used (Przybylski et al., 2012).

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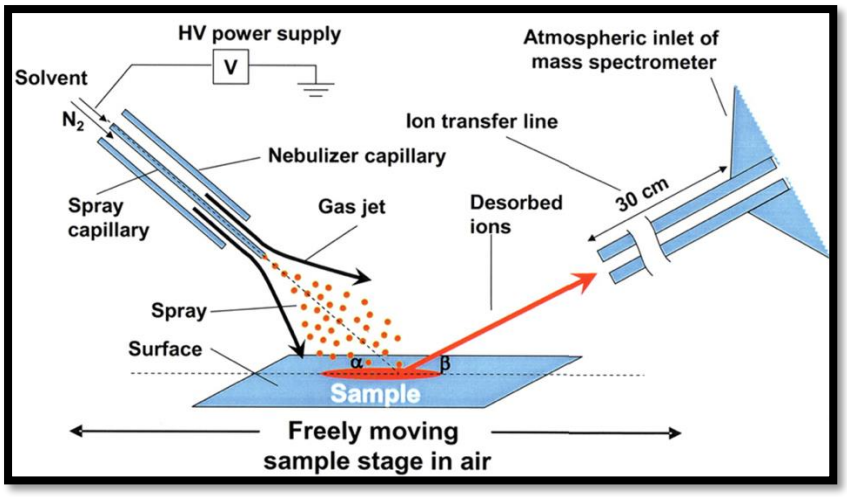

Figure 19: Schematic showing how DESI works (Takáts et al., 2004).

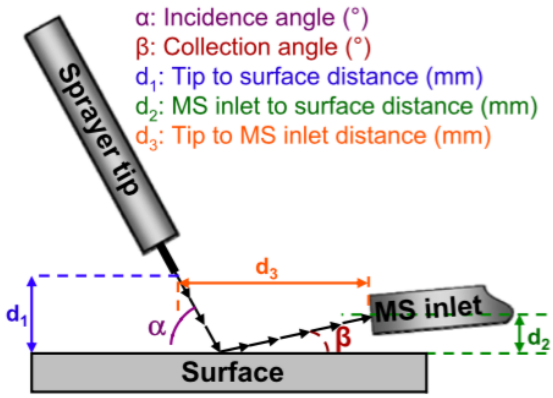

Figure 20: Geometrical parameters of DESI-MS. The efficiency of DESI depends on several parameters such as incidence angle, collection angle, tip to surface distance, MS inlet to surface distance and tip to MS inlet distance. (Przybylski et al., 2012).

In 2015, a group of scientists obtained a concentration map for cocaine using DESI-MS (Figure 21). Initially they obtained inject printed arrays of cocaine on paper with cocaine masses varying from 10pg to 50ng. Then calibration curves were generated for each spot with a diameter of 500µm. Then these calibration curves were used to quantify and construct the concentration map of cocaine in simulated fingerprints with 2µL of cocaine along with 20µL of artificial sebum. According to Figure 21, the second level details (ridges) are visible however, the details are not clear due to uneven distribution of cocaine which may be due to spraying of the charged particles onto the surface. Furthermore, the tertiary level details cannot be obtained from DESI-MS as it has a low spatial

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resolution (>100μm) due to minimal spray head diameter and flow rate (Muramoto et al., 2015).

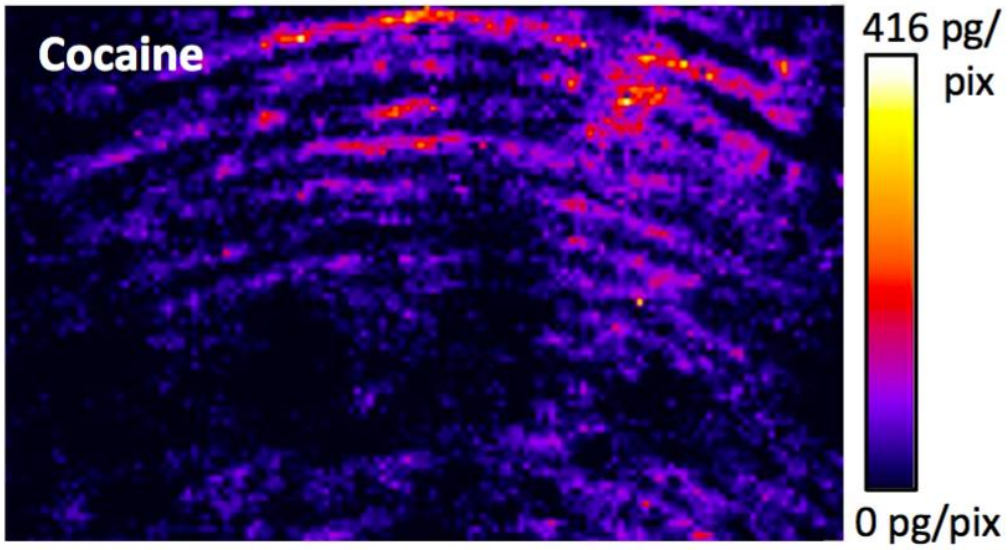

Figure 21: DESI-MS concentration map of 14mm to 9mm area of fingerprint spiked with cocaine deposited on paper. LOD is 1ng/spot for cocaine (Muramoto et al., 2015).

In another study, in order to assess the compatibility of DESI-MS with FETs, scientists obtained DESI-MS image of groomed and lifted fingerprints (from metal and plastic surfaces) and unlifted fingerprints on glass spiked with 10μL cocaine. According to Figure 22, ridge pattern details are visible in all images. However, the LFP lifted from plastic surface exhibited a less clear ridge pattern (50% signal intensity) comparatively. This could have been due to partial transfer of fingermark to the tape or due to effect of surface (plastic) on fingermark deposition (Ifa et al., 2008).

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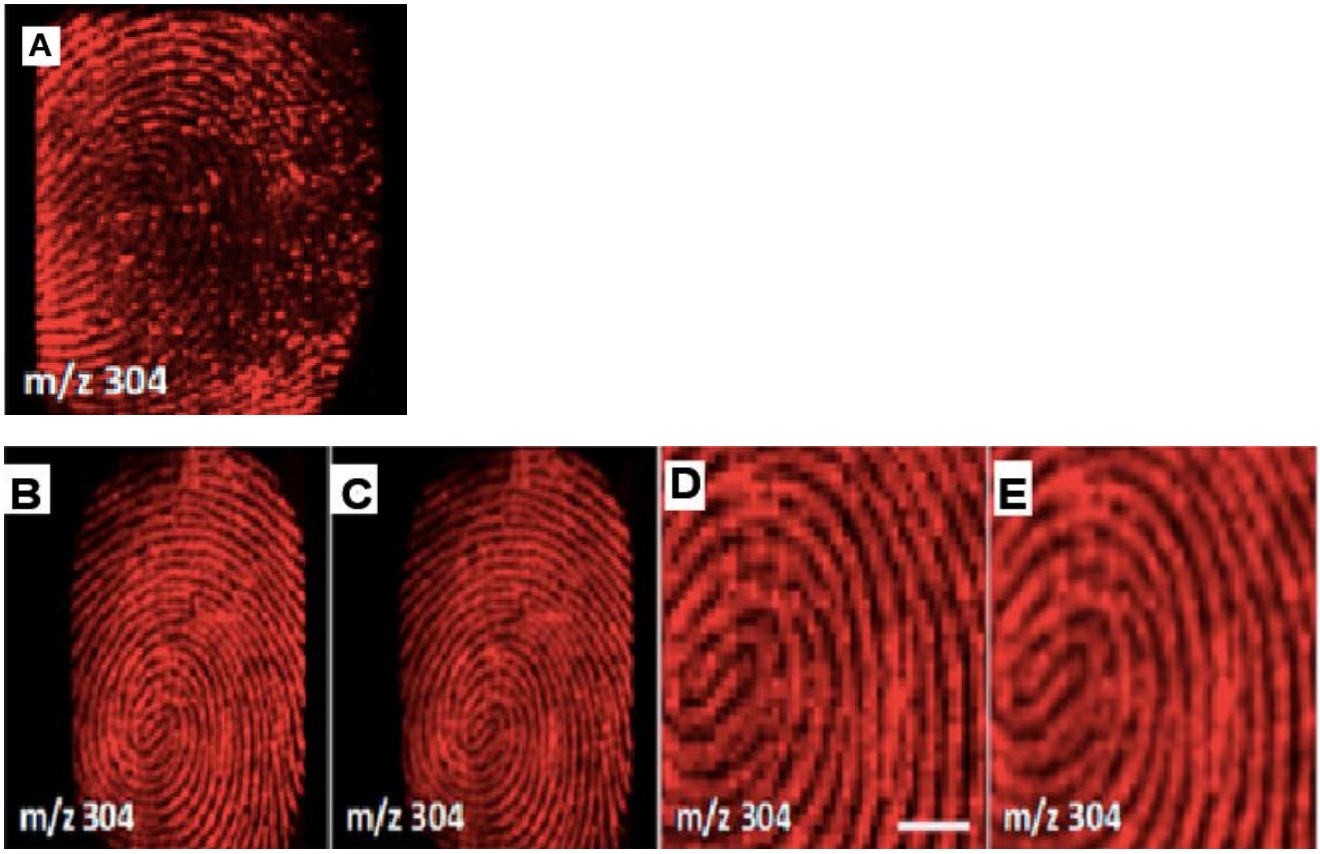

Figure 22: DESI-MSI of (A) LFP spiked with cocaine lifted on to adhesive tape from a plastic surface (B & D) LFP spiked with cocaine on glass in pixel mode (C & E) interpolated mode. LFP images of cocaine (protonated molecules) are obtained in positive mode (Ifa et al., 2008).

Another group of scientists assessed the ability of DESI-MS in the detection of cocaine/metabolites in a real drug testing scenario. In this study, they obtained fingerprints and oral fluid samples from six drug users attending a rehabilitation centre. Oral fluid samples were subjected to Gas Chromatography coupled with MS and the corresponding LFPs were subjected to DESI-MS (Figure 23). Thereby, cocaine and BZE were detected. Table 5 compares the results of DESI-MS with the oral screening results. According to this Table, similar results were obtained from DESI-MS and GC-MS for 5 donors (1, 2, 3, 5 and 6) thereby validating DESI-MS results. However, a discrepancy was observed with donor 4 implying an insufficiency in the sensitivity of DESI-MS in the detection of BZE. Meanwhile, in standards of concentrations of cocaine, BZE and EME, signals were detected above 5ng/mL for cocaine and BZE. Thereby, LOD of cocaine and BZE is 5ng/mL while for EME, it is 50ng/mL, all of which are greater than that in MALDI-MS (Bailey et al., 2015).

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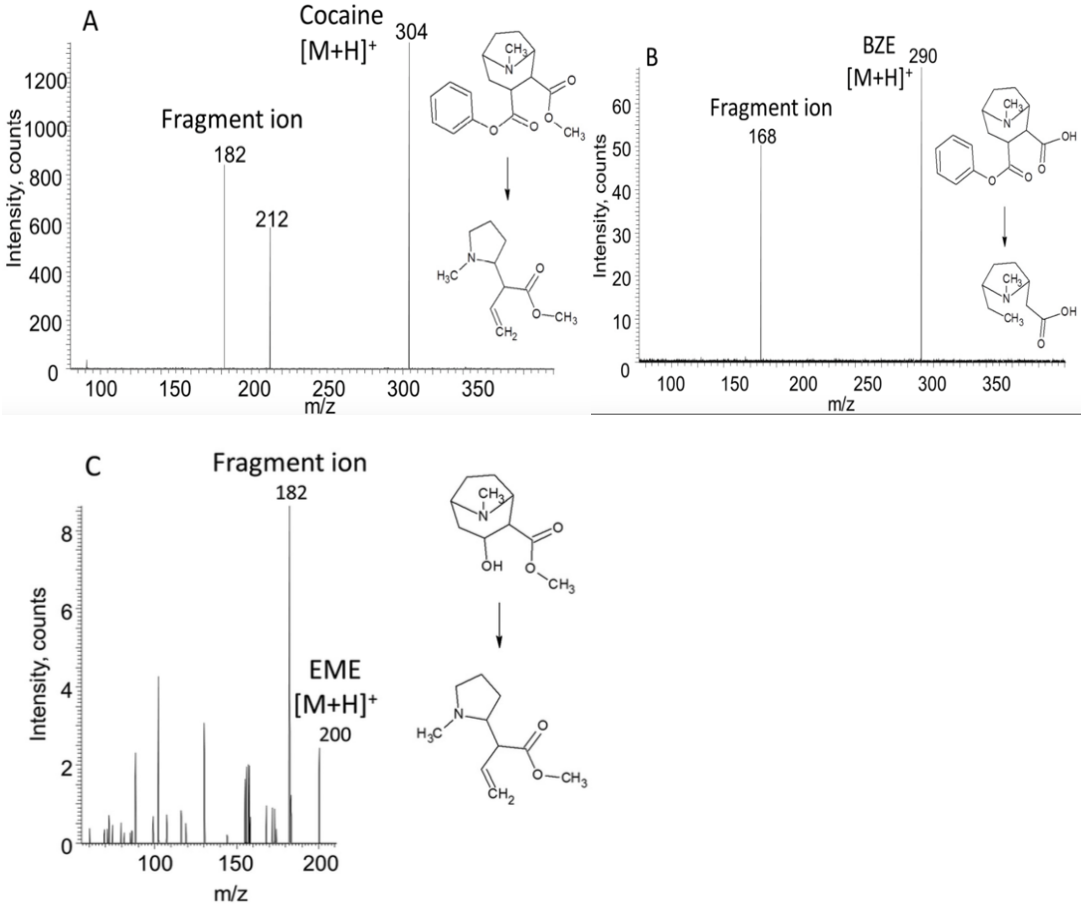

Figure 23: Detection of cocaine, BZE and EME in a fingerprint from a drug user attending a rehabilitation centre using DESI MS. Spectra from a fingerprint with ions of

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m/z (A) 304 (cocaine) (B) 290 (BZE) and (C) 182 (EME) (Bailey et al., 2015).

Table 5: Oral fluid test results and corresponding DESI results in the fingerprints of six donors (Bailey et al., 2015).

	Oral fluid Screening Result	DESI fingerprint analysis	
Donor		Cocaine	BZE
1	Positive	y	y
2	Negative	n	n
3	Positive	y	y
4	Positive	y	n
5	Positive	y	y
6	Positive	y	y

However, all drug dealers and abusers began washing their hands in order to get rid of cocaine deposited in their fingers. Thus, the sensitivity of DESI-MS was not sufficient enough to detect cocaine in such situations.

Paper spray mass spectrometry (PS-MS)

Paper spray MS (PS-MS) is a recently emerged technique (Figure 24). It is a very rapid technique in which fingerprint analysis of cocaine takes place within 30 seconds and it has a low set up cost.

In paper spray mass spectrometry (PS-MS), a paper triangle wetted by a solvent mixture (methanol, acetonitrile and water) with the analyte is held by a copper clip followed by the application of a high voltage to the paper. Thereby, an electric field is generated between the apex of the paper triangle and the MS inlet which results in a dissolution process to generate dry ions. Then these generated ions are captured by the mass spectrometer through the MS inlet (Costa *et al*., 2017; de Paula *et al*., 2015; Liu *et al*., 2010).

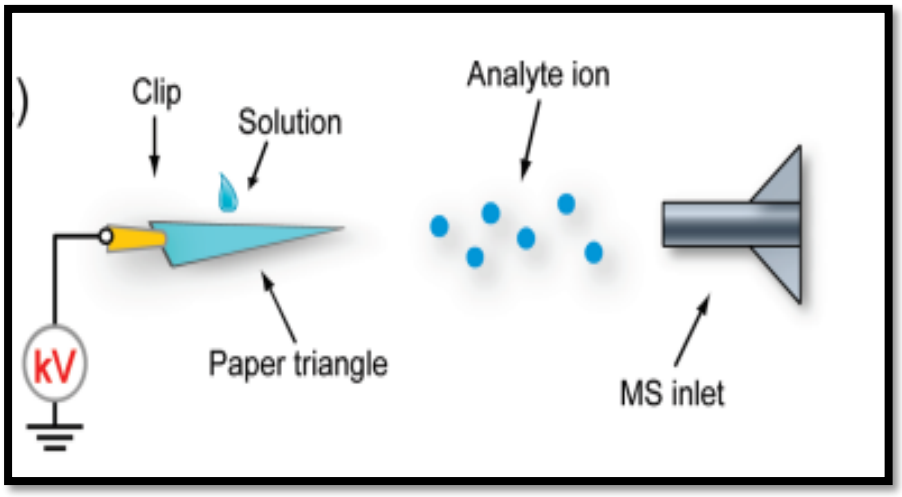

Figure 24: Schematic diagram of PS-MS (Liu et al., 2010)

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In September 2017, a group of scientists from UK, came up with a highly sensitive and a rapid technique called PS-MS. In this study, initially, they obtained 12 donors and divided them into twelve groups. The first wiped their hands, second group washed their hands with soup and in both groups the fingertips were groomed prior to deposition while the third maintained ungroomed fingertips and wiped their hands. Grooming was done to investigate the effect of sebum in detection of cocaine. Then these fingerprints were subjected to PS-MS and the analyte signal to internal standard signal was calculated to construct the bar chart shown in Figure 25. According to this figure, cocaine and BZE were detected even after wiping or washing hands with soap. LOD values for cocaine, BZE and EME were found to be 1,2 and 31 ng/mL which demonstrates a very high sensitivity in comparison to DESI-MS and MALDI-MS (Costa *et al.*, 2017).

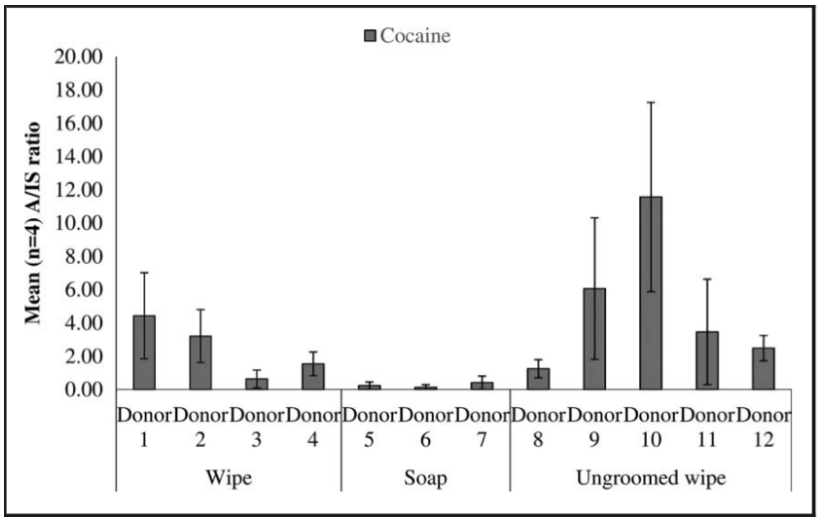

Figure 25: Mean analyte-to-internal ratio obtained from the detection of cocaine in the LFPs taken from the thumb and index fingers (n=4) of donors 1-12 using paper spray mass spectrometry. (Costa et al., 2017).

SUMMARY AND FUTURE SCOPES

Mass spectrometry techniques such as MALDI-MS, SALDI-MS, DESI-MS and PS-MS have been used in the detection of cocaine and its metabolites in LFP. Comparatively, PS-MS seems to be the most rapid, sensitive and economical technique. However, PS-MS is only applicable in drug testing scenarios since the fingerprint samples were collected onto the chromatography paper prior to analysis. Therefore, future research is essential for a methodology involved in extraction of the sample from the surface of deposition to the chromatography paper with minimal sample destruction. Thereby, PS-MS could be used in both drug testing and crime scene investigations.

Nanoplasmic technique involving rationally engineered cocaine-specific aptamers bound to AuNPs is an emerging technique that enable targeted identification and imaging of cocaine in LFPs up to the tertiary level details which was not possible with the existing MS techniques. Thereby, this high resolution technique could be used in tandem with a

highly sensitive technique such as PS-MS in order to obtain both detailed chemical information and physical development of the fingerprint (Li *et al*., 2013). Yet, combination of two techniques could be labour-intensive and time-consuming. Henceforth, DESI-MS could be used, which acquires the potential for improvement of its sensitivity and spatial resolution via further optimisation of the physical parameters such as the flow rate and the spray head diameter. For instance, a higher spray head diameter would improve the spatial resolution. Another potential MS technique involved in detection of cocaine/metabolites is time of flight secondary ion MS (TOF-SIMS) which was only used in one study showing a clearer ridge pattern in simulated LFPs containing cocaine in comparison to DESI-MS. Therefore, in future, extensive research needs to be performed with TOF-SIMS and requires further comparisons with the existing MS techniques (Muramoto *et al.*, 2015). Henceforth, future research should aim at a simple, rapid, user-friendly, economical and cost-effective technique with no sample destruction. Thereby, contributing to successful mitigation of health and crime issues associated with cocaine abusing.

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