Criminal profiling through MALDI MS based technologies – breaking barriers towards border-free forensic science

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Abstract

The theme of the 2018 ANZFSS symposium, "Forensic Science without borders" is probably the key to Forensic Science progress. Advocating the need for "no borders" acknowledges the existence of barriers to break and this can only be achieved through the delivery of research that is impactful. Certainly every researcher values their research but not every research generates impact; the first border to cross for research implementation is that of the laboratory in which the research takes place. This transition requires strategic planning through the design of the pathways to impact the beneficiaries of the research. The 2018 ANZFSS symposium theme offered a good opportunity for reflection on the several meanings of "forensic science without borders" and the barriers to break. This will be a reflection from a personal perspective in developing, alongside other researchers, a new discipline which the author has named "chemical criminal profiling" through fingermark analysis. Here, glimpses into the journey of developing this research area will be provided, highlighting the barriers needed to be broken in order to make the technology operational and available with no borders.

Keywords: MALDI MSI; fingermarks; offender; profiling; networking

Introduction

The very moment that the research described in this paper was born, a first barrier was broken: that of practice which had remained unchanged for a long time; for a century fingerprints have been the most powerful means of biometric identification and even with the advent of DNA, the largest Police force in UK reports that ¾ of the suspect identifications are still due to fingerprinting (personal statement, Neil Denison, Director of YHSS, UK). However, fingerprinting has remained at large unchanged and unchallenged in terms of workflow, scope and visualisation techniques. But despite successful, there is a number of scenarios, in which the process of matching a crime scene mark to a fingerprint record fails, for example because the mark is smudged, partial, empty, overlapped or beyond the "minimum" number of retrievable *minutiae*. The process would also fail if the offender has no fingerprint record. In all of these scenarios, it is desirable to have a technology or a range of technologies to help apprehending the offender based on what the chemical make-up of their fingermark can tell us. Already 1978[1] knowledge of what a fingermark is, aside a uniquely twisted pattern of lines, was available. This molecular knowledge probably informed existing visualisation techniques and the development of new methods but had not been exploited to contribute to additional physical information nor to obtain chemical intelligence from a fingermark until the first paper was published by Ifa and collaborators[2].

Always employed for direct biometric identification exploiting the ridge pattern characteristics, the chemical composition of a mark can indeed additionally reveal personal information about its owner which can be used to support an investigation; it may be particularly useful when the ridge detail is insufficient or the mark composition can be linked to a better physical quality mark of the same owner at the crime scene, thus helping with the crime scene dynamics reconstruction[3]. Through detecting substances that are normally produced by our body and present in sweat, and therefore in fingermarks, so called

endogenous, those that have entered the body and have been excreted through sweat (semi-endogenous), for example through medications, drugs etc., and those that come in contact with our fingertips (exogenous) we can potentially undertake a sort of criminal profiling[4]. Given that this profile reconstruction is not based on behavioural science, it has been named chemical criminal profiling[5]. The mission of the molecular fingerprinting research at Sheffield Hallam University is providing a range of personal information about the owner of the mark of interest such as state of mind of the individual and actions prior to or during committing the crime, sex, age, biogeographically provenance, on one analytical platform, whilst keeping the related protocols to a minimum number to allow panoramic investigation of the molecular intelligence contained within the mark. The analytical technique, the development of which the author has been pursuing for the specific application to fingermark analysis, is Matrix Assisted Laser Desorption Ionisation Mass Spectrometry[6,7] (MALDI MS). Initially conceived for the ionisation of large non volatile and labile molecules, MALDI MS capabilities have steadily developed to enable the ionisation of a vast range of molecular classes ranging from 100 Da to beyond 500 kDa in molecular weight thus enabling a wide range of molecular intelligence to be recovered from fingermarks. The technical description of the principles of MALDI MS have been recently summarised by Francese et al[8] but in brief, within this technique, ions are formed due to the transfer of energy of a laser firing in the UV region mediated by an UV absorbing chemical that has been co-crystallised with the analyte/s, called "matrix". The desorption and ionisation of the molecules produces at large singly charged ions, from the mass to charge of which, the molecular weight of the corresponding molecule can be easily inferred and this will be the first step to identify the molecule itself (and the type of intelligence inherently carried). The additional use of Tandem Mass Spectrometry in conjunction with Ion Mobility or using sophisticated techniques such as ICR FT MS will aid/confirm molecular identification.

In relation to fingermark analysis, MALDI MS can be used in Profiling or Imaging modes (MALDI MSP or MALDI MSI). In Profiling mode the laser can be directed on specific areas of the mark (for example on a ridge) with a routinely used spot diameter of 100 µm (approximately the width of a ridge) to gain molecular intelligence in a specific area of the mark. This can be repeated on a few more ridges and the overall acquisition time is of a few minutes. This analysis may be performed when the Police only requests molecular intelligence. The first peer reviewed publication on the imaging modality was brought to the analytical community in 1997 by Caprioli's group[9] ; since, MALDI MSI was extensively applied to solve biomedical or drug discovery problems whereas the research group at Sheffield Hallam University pioneered its application to latent fingermarks[10]. In Imaging mode, the laser is set to automatically fire in a raster fashion on pre-defined, known x,y coordinates points of the mark previously homogeneously coated with the MALDI matrix (in a non ridge destructive manner). Chemical information can be retrieved with very high spatial resolution (down to 10 µm) through an array of mass spectra each acquired at a precise location. The software can then allow visualisation of any ion detected, highlighting with a coloured pixel each x,y coordinate point at which it was detected. If the molecule is distributed throughout the ridge pattern, and given that thousands of molecules are detected in one analysis, potentially, thousand of images of the same fingermark ridge pattern can be reconstructed, as opposed to the one only generally obtained through conventional visualisation methods. Some images of the ridge pattern will be much clearer and stronger than others depending on ion distribution and ionisation efficiency.

What information can be obtained through the application of MALDI MSI to fingermarks?

The type of information retrievable is twofold: physical and chemical. From a physical point of view, the information allows the reconstruction of the ridge pattern through the

visualisation of the molecules present. It is possible two stitch images to increase the number of *minutiae* recoverable from a mark, or superimpose images to improve the continuity of the ridge pattern[4]. There might be understandable concerns around the introduction of artefacts in this process and dedicated software for stitching and superimposing images should be produced and validated. Exploiting the same principle (detection of thousands of molecules in one analysis), overlapped marks can also be separated[11]; this is possible by recalling, one at the time, images of ions uniquely present in one mark and the other.

From a chemical point of view, bearing in mind the personal information that this research is overall pursuing, the research group at Sheffield Hallam University has covered a number of applications and key applications will be briefly summarised here.

In terms of exogenous substances, and as an example of what they can tell us about the actions committed by the offender prior to or during the crime, an interesting application is the molecular mapping of condom lubricants (polymers) in fingermarks[12,13]. The detection and mapping of these traces is important because *potentially* connects a suspect to the crime scene and may corroborate the victim's testimony in rape cases in the scenario of the offender contaminating their fingertips with the condom lubricants and then leaving their fingermarks behind. The word *potentially* is important as much attention must be paid to activity level issues and to other scenario alternatives as to how the condom lubricants ended up being present in someone's fingermark. This caution should really apply to all the molecules detected (not just by this technique) as it is becoming evident that molecular transfers are entirely possible[14-15].

A range of condom brands could be detected and, within condom lubricants, polymers are persistent substances, well detectable even after months from the deposition of the contaminated marks, permitting ridge pattern reconstruction and thus strengthening the value of forensic information.

Since 2014, huge analytical efforts have been also put into the reliable detection of blood in both stains and fingermarks[16-19], since its detection is crucial for the crime scene dynamics reconstruction within violent crimes including murders (especially with no body). Additionally, being able to investigate multiple types of evidence (fingermarks and blood) on one platform, maximises its adoption and perhaps further justifies an investment into such technology by the end users.

Incidentally, this is also why, another application stream concerns the detection and mapping of drugs of abuse and metabolites in a single hair by MALDI MSI. This analysis exhibits numerous advantages over the gold standard in use and it is being developed by Sheffield Hallam University UK and M4I in the Netherlands[20-21].

The interest in blood detection moved from the observation that current crime scene techniques for visualisation of blood are presumptive – that is, false positives are indeed possible. The most representative example is the positive reaction of bleach to the Kastle Mayer test or luminol, belonging to the category of Haem reactive agents. However, amino-reactive compounds and protein dyes are not immune from false positives either; for example, as protein dyes are based on the detection of a large abundance of proteins such as that found in blood, semen and saliva would also be testing positive for blood due to the same reason (the presence of many proteins). A better method is one that carries a greater specificity, that is sensitive, that can provide additional information, for example on blood provenance, that is capable of working in a variety of conditions typical of crime scenes and that is compatible with the prior application of CSI or crime lab techniques for integration within the operational workflow. A specific test is not one that infers the presence of the biofluid through a color change or that generically responds to one of the classes of molecules present in blood. A specific test is one that detects blood-specific and individual molecules of interest, therefore, what better than the actual detection of haemoglobin and its heam group (the latter

being the actual oxygen carrier on Haemoglobin). MALDI MS can detect both of these molecules in one analysis[16]. Whilst no real quantification has been carried out yet, blood dilution experiments showed that it is possible to detect Haemoglobin and haem 1000 x and 250 million x lower than lower the physiological concentration in blood, respectively. The technique has been made compatible with the prior application of a number of protein dyes, haem reactive and amino-reactive compounds thus providing the opportunity for a quick *in situ* test (classic BET) and a remote confirmatory test. As an example, compatibility and sensitivity could be qualitatively appreciated through the application of ninhydryn-MALDI MSI sequence to a depletion series of three blood marks (Fig 1). Whilst ninhydrin failed to visualise the 3rd depleted blood mark, the consecutive application of MALDI MSI on this depleted mark enabled detection of haem and reconstruction of the ridge pattern through visualisation of the haem's distribution. In terms of additional information, human and animal source, can be differentiated through the detection of Haemoglobin which is detected at different *m/z* depending on provenance, due to a slightly different aminoacidic composition[16]. Although this method of detecting blood is more specific, specificity can be further increased to the application of a bottom up proteomic approach in combination with MALDI MS[17,18]. There are in fact additional blood specific proteins that could be targeted. However both sensitivity and mass accuracy, are generally much lower when performing intact protein analysis than those obtained by analysing much smaller species such as peptides. Using a bottom up proteomic approach it is possible to detect a greater number of proteins and with much better mass accuracy (in the order of parts per million) through the peptides that proteins generate via enzymatic hydrolysis. The *m/z* of the resulting peptide fragments can be measured and this *m/z* list acts as a "fingerprint" of the protein that has generated it; this is why this process of protein detection and identification is named "peptide mass fingerprinting". The provision of a bigger list of blood specific proteins with much greater

accuracy in support of the claim of the presence of blood makes the claim even more reliable. The Home Office CAST (UK) intellectually and financially supported this idea through a PhD programme. The major outcomes were the demonstration that it is possible to detect and visualise blood protein signatures in stains and in fingermarks[17-19] even from very old specimens (a 9 year old blood palm print[17] and a 37 year old blood mark on fabric (Fig. 2) which were previously enhanced by Acid Black 1 and ninhydrin respectively. This forensic opportunity paves the way to the investigation of cold cases involving blood evidence. Blood provenance determination was also demonstrated even with samples of mixed blood provenance[17]. Blood provenance is not a trivial question; the UK case of Susan May, accused of murdering her aunt, highlights how important is to have a method capable to ascertain whether the investigators are faced with blood and if so, whether of animal or human provenance. For implementation of such methods, robustness must be demonstrated; whilst the demonstration that the method works for very old and previously enhanced marks is a promising indicator towards the desirable robustness, a validation study is certainly needed to provide a comprehensive picture of the operational capabilities of the method. A first validation study using blind samples is well under way and a manuscript is in preparation (Heaton et al *in preparation*). This first study intends to prove the possibility to discriminate human blood from: animal blood, human biofluids and unrelated matrices which, either by colour or by false positive reaction to blood enhancement techniques "appear" to be blood. In addition, this study intends to prove the ability to provide animal species differentiation when in the presence of animal blood. Further, in the interests of a method that is quick and user friendly, this study intends to demonstrate the possibility to claim the presence of blood (human or animal) without tandem mass spectrometry confirmation. This last aspect quickly translated in a iterative study in which mass spectral interpretation was refined in stages by

disclosing the identity of a number of analysed samples following their complete spectral interpretation.

Semi-exogenous substances are also of great interest as they may provide information on the suspect lifestyle or again on their actions prior to committing the crime. The first proof of concept was obtained in 2012 showing that it is possible to detect caffeine in fingermarks, at different intervals within the hour from drinking coffee (knowledge later published in a different research question context[11]). This opportunity encouraged further studies into more forensically relevant molecules such as drugs of abuse metabolites enabling the indication that the suspect may have abused the drug rather than just handling it[22]. Subsequently, a second proof that substances that are metabolised and excreted through sweat, provided that they ionise, are detectable in fingermarks was published in 2015. Here through the use of MALDI Ion Mobility MS/MS profiling, benzoyilecognine along with THC and methadone where detected from the fingermark of a donor in a drug rehabilitation clinic. This detection was corroborated by that of the same drugs and additional metabolites in the corresponding bodily fluids[23]. The same type of analysis was successfully applied to the detection of propranonol's main metabolite (4-hydroxypropranolol) in fingermarks (unpublished data). Being able to infer the pathological/pharmacological state of an individual from a mark most certainly contributes to narrowing down the pool of suspects and/or strengthening evidence/testimony in a court of Law.

With respect to endogenous molecules, in 2012 there was the first publication highlighting the importance of this class of molecules detection of endogenous molecules and the role they may play in providing important intelligence around the owner of the mark[24]. In this paper it was demonstrated that it was possible to tell apart women from men through the peptide and protein composition of their fingermarks using a statistical model with an 85% accuracy of prediction. Since, the research group recruited a much bigger cohort of donors (200 donors)

without restriction criteria to their participation and using natural marks. Statistical modelling is in progress.

Research mission statement and barriers to break to cross borders

Since the very beginning of the fingerprint research, the vision was for this research to step out the laboratory and make an impact in the real world. What is research for if not for improving people's lives boosting health, safety, economy or protecting environment in a sustainable way?

In the case of fingerprinting research, a first statement of the above vision translated in the devise of a patented method to visualise fingermarks in a way that was compatible with MALDI MS based analysis[25]. MALDI mass spectrometers are not portable and the research becomes meaningless if the fingermarks are not located first and then transported to the lab for remote analysis. The "dry-method" addressed this issue by using the MALDI matrix to act as a CSI powder to visualise fingermark on surfaces. Visualisation is followed by mark tape lifting for transportation in the lab, minimal sample preparation and MALDI MS analysis. The recognition of practical and operational issues for future implementation caught the attention of the end users in particular of the Home Office who subsequently funded a PhD programme for the devise of protocols leading to implementation of the MALDI MS based methods within the conventional fingerprinting workflow. This was the first example of bridging the gap between academia and end users and of breaking the barrier of academic isolation. The work in collaboration with the end users led to the devise of protocols enabling compatibility between MALDI MS methods and CSI and crime lab techniques. Whilst the "dry-wet method" statement was important from a practical point of view and to establish a communication channel with the end users, realistically, crime scene marks will be primarily enhanced with currently used fingerprinting techniques and therefore it was paramount to

focus efforts on making MALDI MS method compatible with those techniques. Bradshaw et al demonstrated compatibility with a wide range of CSI and crime lab techniques[26] as well as with a sequence of four consecutive processes recommended by the Fingermark Visualisation Manual (FMV) edited by the Home Office[27] (Bradshaw et al in preparation); "the compatibility research theme" has been a constant focus of this research discussed and investigated in a number of other publications [5,11,13,16,17,22,25]. The number of applications and the attention to compatibility and implementable research had led the Home Office to include MALDI MS based methods as a category C technique ("processe at a development stage exhibiting potential as an effective fingermark recovery process") in their FVM. An update of the Manual is being planned and preliminary discussions instigated by the Editor have resulted in the invitation to promote MALDI MS based methods for fingermark analysis to Category B ("established processe likely to offer benefits but that have not been fully evaluated by the Home Office"). Although since 2008 the analytical community has worked tirelessly to provide chemical intelligence and/or additional fingermarks physical details, MALDI MS methods remain the most published as Fig 3. shows. Since literature data of the type reported in Fig. 3 were published in 2017[8], other analytical techniques have contributed to knowledge in this application area. However, the ratio between MALDI MS based outputs and other techniques' outputs applied to fingermarks has remained unchanged, if not improved in some cases.

The large number of outputs describing compatibility, feasibility of implementation and the range of applications enabling diverse intelligence to be gathered from a crime scene marks, provided the confidence to approach the regional police in the UK, West Yorkshire Police (WYP). This represented an additional effort to break barriers in order for the forensic research on molecular fingerprinting to cross the border of the labs and be implemented in the real world. The forward looking and open mind attitude of WYP led to the opportunity to co-

develop the technology through (i) direct intellectual input from an operational and practitioner point of view and (ii) observation of crime scene and crime lab officers during the search and visualisation of crime scene marks in real casework. Through this collaboration refined protocols were developed for the collection, storage and transport of the evidence and the compatible analysis by MALDI MS methods[28]. The new capabilities led to operational work in which MALDI MS based methods were applied in real police casework[5]. The technology and the protocols involved were not always successful but it is difficult to evaluate the reasons behind the outcome. The interplay of variables linked to fingermark composition, nature of the surface, environmental conditions to which the mark was exposed, and prior enhancement technique, superbly argued by Sears et al[29], make the elucidation of MALDI MS capabilities in operational work very difficult at this stage. Only the analysis of probably thousands of crime scene marks, which would encompass at large the range of variables to which a process is faced with, will yield some useful insights into the success rate of recovering physical and/or chemical information by applying MALDI MS methods to fingermarks. However, together with some missed opportunities, there have been instances in which MALDI MS based protocols were successfully applied either to provide physical details (case under investigation) or insights into the state of mind of the individual whilst committing the crime[5]. In both instances, MALDI MS has proven the ability to operate in full operational conditions whilst following the chain of custody.

It can be safely said that molecular fingerprinting has developed very quickly from an idea to operational implementation. However, it is important to highlight the barriers that this research has encountered, which the author believes are the same faced by any type of forensic research that intends to make an impact in the real world. The first barrier is probably institutional within an academic context. The severity of the barrier may vary in different academic institutions but there is generally a significant level of conflict between teaching

and research which are often managed by different departmental structures. Although the importance of research informed teaching is acknowledged, teaching commitments often dominate the time of an academic who wants to also engage in high profile research. Even more worrying is the accompanying amount of administration duties which seem to also take priority over research. At large, academic suffer from this conflict but there is not enough open discussions within the relevant Institution and across different Universities. This is not an easy issue to solve as whatever system is in place ,it is very much fuelled by a financial model for the running of the department. However, the author believes that it does help to keep in mind the bigger picture of delivering impactful research; in order to do this and to get around the time demands of teaching commitments, connecting and networking with other researchers in a multidisciplinary context and with the beneficiaries of the research are important activities to undertake to progress the research rapidly and meaningfully.

Nonetheless, networking and especially in a multidisciplinary context comes with another challenge which in many cases becomes a real barrier to research progress: communication. Often language barriers prevent meaningful interactions between scientists from different disciplines and this is even more problematic in the communication between academia, end users and industry. How is forensic science supposed to have no borders with innovations and best practice exploited and implemented if the above three key players do not or cannot communicate with each other? A synergy is most definitely needed; academia can still, on same levels, practice blue sky research typically leading to innovation and it does have advanced instrumentation; the end users have the knowledge of needs and requirements that research innovation must have in order to be practically applicable and withstand scrutiny in a court of law. An open and clear dialogue avoids academic intellectual and financial resource being wasted in addressing questions that do need addressing or by producing an underperforming technology in a real world. Conversely, this dialogue informs the end users

of the exciting developments in the research world and helps them re-evaluating the performances of the techniques that they have been using with a critical outlook. Most definitely, industry needs to partake the dialog with academia and the end users because they have the business vision and the know how to transform a research outcome into a viable product. If this three-way dialogue does not happen, then we assist to duplication of efforts, laboratory confined technologies and slow or no uptake by the end users leading to slow and confined forensic science progress. Conferences such as the ANZFSS symposium and the work of associated international societies are already a means to favour this dialogue, but it is important to seek further opportunities. Breaking barriers opportunities are currently offered by the EU Horizon 2020 programme through COST Actions scheme which does not fund research *per se* but does fund four years of networking opportunities through conferences, workshops, working group meetings, training schools and laboratory visit exchanges. A new forensic science Action has started in March 2017 entitled MULTI-modal imaging of FOREnsic SciEnce Evidence - tools for Forensic Science' (https://multiforesee.com/). This programme aims to promote innovative multi informative, operationally deployable and commercially viable imaging solutions for the analysis of forensic science evidence and already includes 28 EU countries, ENFSI and Australia. The three sectors, academia, industry and end users (LEAs, Police, and governmental agencies) are represented with interests spanning from digital to analytical forensics and under the constant understanding of having to adopt a controlled vocabulary. This type of funded initiative also helps break geographical and diversity barriers to improve inclusiveness and export innovation and good practice.

Political barriers are certainly much more difficult to break. Albeit not the only one, a prime and recent example is Brexit. The UK is already excluded from bidding for any of the European Network of Forensic Science Institute funding due to non adhesion to the Shengen treaty, perfected in 1999. The research in UK now faces severe and further funding

uncertainties because, as it stands, it will, at large, be excluded from very significant EU funding. At the time in which this article is being written, social media extensively report that research excellence is leaving the UK as a result of this political vote and UK scientists are already refraining from applying to EU funding due to post Brexit fears. Additionally, there is an estimate loss of half a billion pounds per year of EU funding due to Brexit. Certainly a political vote such as Brexit is not conducive to forensic research easily crossing borders from and to the UK. Again, there is no immediate cure that can be suggested but it is strongly felt that scientists should step out of the lab and make their research voce heard through the many research societies channels. The author of this paper has expressed her concerns on the ANZFSS 2018 platform, in other international conferences and through Universities UK[30]. She has also strengthened in parallel international collaborations both in Europe and in USA.

Another well known but unspoken issue which may prevent forensic research crossing borders is destructive competition in an age of diminished resources. There is a problem in the UK, where there is a concerning lack of bodies dedicated to funding forensic science. This discipline simply is not yet seen s a priority by the UK government, (although an inquiry has been launched in 2018 by the House of Lords Science and Technology Committee into forensic science in a bid to recapture forensic excellence in the UK). The combination of little funding and destructive competition can be especially brutal when bidding for peer-reviewed Government Funding. The implementation of molecular fingerprinting research into the real world would not have occurred without the research beneficiaries stepping in and financially supporting the research directly themselves. It is time that researchers took actively part in the relevant discussions to improve the current awarding system and counteract the combination of little funding and destructive competition.

Finally, with every bit knowledge comes responsibility, especially when disseminating to peers and to the public. The overall molecular fingerprinting research has attracted since 2011 a huge media interest and has been featured constantly by the BBC, European and American outlets. Most certainly, dissemination and especially through the Media is a way to cross borders especially in relation to establish new networks and collaborations. However, the interaction with the media is not an easy one. A huge amount of efforts have gone into avoiding both trivialisation of the molecular fingerprinting research and misleading claims, which in both cases are linked to the sensationalism aspect of the media communication. Though many reputable media have demonstrated an increased attention to these aspects, the academic does not always have "the last word" on the piece to be broadcast/disseminated and it is important to be aware of the potential risks (in addition to the benefits) of the media interaction, in order to pre-empt a misleading portrait of the research.

Conclusions

In the personal opinion of the author, for a forensic science research with no borders, scientists need to be more than researchers; they need to break the isolation barriers, network, debate, reach out to the beneficiaries of the research and engage in an active discussion to improve or theorise new mechanisms that enable financial support to their research and its dissemination. Let's be more than researchers, let's be research advocates.

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Figure Legends

Figure 1. Sequential ninhydrin-MALDI MSI workflow applied to depleted blood marks. This figure shows ninhydrin development of the first of blood marks (panel i) obtained as a depletion series of three. Ninhydrin failed to visualise blood and ridge detail on the 3rd mark of the depletion series (panel ii), whereas the same mark analysed by MALDI MSI offers reconstruction of the ridge pattern through visualisation of the ion at *m/z* 616.2 deriving from the presence of Haem.

Figure 2. Application of MALDI MS profiling and bottom up proteomics on a 37 year old blood mark on fabric previously developed by ninhydrin. The age of the sample did not permit the recovery of multiple blood signatures but the analysis did yield 3 ion signals indicating the presence of α and β Haemoglobin chains in addition to haem (data not shown for the latter).

Figure 3. Histogram showing the number of publications featuring the use of different analytical techniques for the analysis of fingermarks. The category “other techniques”. encompasses techniques reported for the analysis of latent fingermarks but that have not reached publication "critical mass". Figures in the histogram account for peer reviewed papers at large, with very few instances of on-line magazines, technical articles, application notes and patents. The histogram has been generated searching both Pubmed and Scopus databases using the keywords "fingerprints, fingermarks, GC MS, MALDI, ATR FTIR, Raman, DESI, DART, SIMS, SALDI and MALDI". The information constitutes an update from that published in reference 8.

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