Science & Justice 63 (2023) 9–18

Contents lists available at ScienceDirect

Science & Justice

journal homepage: www.elsevier.com/locate/scijus

Short Communication

Improving the technological readiness of time of Flight-Secondary Ion Mass Spectrometry for enhancing fingermark recovery - towards operational deployment

Deborah Charlton [a,b], Catia Costa [c], Gustavo F. Trindade [d], Steve Hinder [e], John F. Watts [e], Melanie J. Bailey [a,*]

[a] Department of Chemistry, University of Surrey, Surrey, Guildford GU2 7XH, UK
[b] Fingerprint Development Laboratory, Thames Valley Police, Kidlington, Oxfordshire OX5 2NX, UK
[c] Surrey Ion Beam Centre, University of Surrey, Guildford, Surrey GU2 7XH, UK
[d] National Physical Laboratory, Teddington, London TW11 0LW, UK
[e] School of Mechanical Engineering Sciences, University of Surrey, Guildford, Surrey GU2 7XH, UK

A B S T R A C T

The processes routinely used by police forces to visualise fingermarks in casework may not provide sufficient ridge pattern quality to aid an investigation. Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS) has been proposed as a technique to enhance fingermark recovery. The technique is currently designated a Category C process in the Fingermark Visualisation Manual (FVM) as it shows potential for effective fingermark visualisation but has not yet been fully evaluated. Here the sensitivity of ToF-SIMS on three common exhibit-type surfaces - paper, polyethylene and stainless-steel was compared to standard processes. An adapted Home Office grading scale was used to evaluate the efficacy of fingerprint development by ToF-SIMS and to provide a framework for comparison with standard processes. ToF-SIMS was shown to visualise more fingerprints than the respective standard process, for all surfaces tested. In addition, ToF-SIMS was applied after the standard processes and successfully enhanced the fingerprint detail, even when the standard process failed to visualise ridge detail. This demonstrates the benefit for incorporating it into current operational fingermark development workflows. Multivariate analysis (MVA), using simsMVA, was additionally explored as a method to simplify the data analysis and image generation process.

1. Introduction

A fingermark is the trace evidence (residue) left behind, generally at a crime scene, as a result of the contact between the fingertip of an unknown donor and a surface. Fingermarks vary in quality and latent fingermarks are often not visible without specialised light sources or development. This will depend on many factors, including the surface upon which the fingermark is deposited and the initial composition of the fingermark residue [1]. Fingermark residue varies from donor to donor and even minute to minute. It consists of sweat components such as secretions from eccrine, sebaceous and apocrine glands as well contamination from external sources that the donor has touched [2].

Extensive research into physical and chemical techniques used for developing fingermarks has been compiled in the Fingermark Visualisation Manual (FVM) [2]. Despite the variety of physical and chemical techniques that are recommended by the FVM and employed within forensic laboratories, the quality of development of many fingermarks on crime scene exhibits is not sufficient for comparison at the fingerprint bureau. It may be that some fingermarks also go undeveloped [3].

Paper, stainless steel and plastic are representative of surfaces that are often encountered in the forensic laboratory. Ninhydrin, which reacts with amino acids in the fingermark, is a FVM recommended visualisation process for fingermarks on paper and produces a purple colour. On stainless steel and plastic, a FVM recommended process is cyanoacrylate (CA) fuming followed by Basic Yellow 40 (BY40) staining. The visualisation success of Category A processes such as ninhydrin and cyanoacrylate fuming are limited by their reaction with specific constituents in the residue. If the abundance of these constituents within a deposited fingermark is not high and/or homogenous enough for the detection limits of the visualisation process, there will only be partial or no development [3–6]. To improve evidence recovery, there is a real need to find more sensitive visualisation processes to improve existing fingermark visualisation workflows.

Category A techniques recommended by the FVM have undergone extensive evaluation and are recommended as effective. Lower categories include techniques that require further evaluation or have been

* Corresponding author.
E-mail address: m.bailey@surrey.ac.uk (M.J. Bailey).

https://doi.org/10.1016/j.scijus.2022.10.004
Received 18 May 2022; Received in revised form 16 August 2022; Accepted 23 October 2022
Available online 1 November 2022

deemed unsuitable for reasons such as providing no benefit to existing Category A techniques. Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS) is currently an FVM Category C process; it shows potential for effective fingermark recovery but has not yet been fully evaluated [2].

ToF-SIMS enables mapping of the molecules in the uppermost layers of the sample surface. Molecules in the fingerprint are identified by their mass to charge ratio (m/z), so mapping the distribution of different molecules across the surface can yield an image of fingerprint ridge detail due to the difference between the composition of the residue and the background surface [7–10]. This has been demonstrated previously by Szynkowska *et al.* and Bailey *et al.* [11,12]. However, it is not yet known whether the sensitivity of ToF-SIMS exceeds that of standard processes, i.e., whether ToF-SIMS can visualise fingerprints where standard processes visualised insufficient detail. Additionally, it is not known whether ToF-SIMS can be used in sequence with standard processes.

Matrix Assisted Laser Desorption Ionisation - Mass Spectrometry Imaging (MALDI-MSI) has also been explored as a fingermark visualisation process and has been used in sequence with Category A processes [13–15]. ToF-SIMS can complement MALDI-MSI in several ways. ToF-SIMS is suited to imaging small molecules, and inorganic species (such as sodium, potassium and chlorine which are common endogenous fingerprint residue constituents), which are unsuitable for analysis by MALDI-MSI. In addition, ToF-SIMS has superior spatial resolution compared to MALDI-MSI and therefore may yield more defined ridge detail. Finally, ToF-SIMS causes minimal destruction to the fingerprint and does not require a matrix to be applied prior to analysis [16]. This could be an advantage on exhibits that must be preserved and would only be subjected to high intensity light sources in the police laboratory.

This study aims to explore for the first time the sensitivity of ToF-SIMS compared with selected Category A processes, as well as its ability to develop fingerprints when Category A development has yielded no or low quality ridge detail. In contrast to previous work on mass spectrometry imaging of fingerprints, this study applies ToF-SIMS to three evidentially representative substrate types and demonstrates the added benefit to standard processes. ToF-SIMS imaging is used to map the constituents of fingerprint residue that remain but have not been visualised by the standard processes. Multivariate Analysis (MVA) statistical methods are used to reduce noise in ToF-SIMS images and facilitate the data analysis process [7,17].

2. Material and methods

All experiments were conducted with informed consent from the participants in accordance with the Declaration of Helsinki, and all donors consented to images of their developed fingermarks being used and published as part of this research. Experimental protocols were approved by Surrey Ion Beam Centre Management Board.

2.1. Fingerprint deposition

Naturally occurring “ungroomed” (without prescribed preparation such hand washing or loading with secretions) fingerprints were used to best represent fingermarks on crime scene exhibits. Ungroomed fingerprints from two donors (one male, one female) were deposited (using right index finger) on three substrates representative of common crime scene exhibits. Polyethylene was used to represent hard plastic packaging, stainless-steel to represent knives and white copier paper to represent documents. As recommended by Holder *et al.*, a depletion series was used to systematically reduce the amount of fingerprint residue left on the substrate surface and therefore test the sensitivity of the process [4,18]. Fingerprints were laid in a depletion series (using the same finger sequentially without reloading) up to n = 90. Fingerprints were aged for 12 (paper), 14 (polyethylene) and 16 (stainless-steel) days before being treated with the FVM recommended processes (sections 2.2 – 2.3) or analysed by ToF-SIMS (section 2.4). The residue loaded samples were stored in a cardboard box in the dark at room temperature.

2.2. Cyanoacrylate fuming and Basic Yellow 40 dye staining

Odd numbered fingerprint depositions on polyethylene and stainless-steel substrates were developed with cyanoacrylate (industrial grade with minimal additives, Scenesafe, UK) using a Foster & Freeman MVC 3000 cabinet (Foster and Freeman, UK). The cabinet is maintained within an ISO17025 accredited Police Laboratory and the process was conducted according to FVM guidelines and the Police Laboratory’s standard operating procedures (SOPs). The cyanoacrylate was heated to 120 °C and fuming was carried out at 80 % RH. Each processing run is set up with a piece of plastic planted with a fingerprint loaded with amino acids using an amino acid based latent print reference pad (Safariland, Jacksonville, Florida). This forms part of the quality control in the laboratory and development was monitored and halted when the reference fingerprint reached optimum development. The developed samples were then immersed in a working solution of ethanol (96 %, Acota, UK) and Basic Yellow 40 dye (>80 %, Scenesafe, UK), according to laboratory SOPs. Samples were gently rinsed in running tap water and dried at 30 °C with a drying cabinet. All samples were captured using a Nikon D300 camera with a 476 nm filter and crime-lite© 420–470 nm fluorescence illumination.

2.3. Ninhydrin

Odd numbered depositions on the paper substrate were developed using a ninhydrin working solution (Ninhydrin, HFE7100, Acetic Acid, Ethanol ≥ 99 %, Ethyl Acetate) in an oven (Sanyo Gallenkamp FDC185, Weiss Technik, UK). Following FVM guidelines and laboratory SOPS, samples were drawn through the ninhydrin working solution and dried in a fume hood. Once dry, the samples were placed in the oven for 4 mins at 80 °C and 65 % RH. The oven is maintained within an ISO17025 accredited Police Laboratory. All samples were captured using a Nikon D300 camera. Prior to processing the samples, a piece of paper planted with a fingerprint loaded with amino acids using an amino acid based latent print reference pad (Safariland, Jacksonville, Florida), was successfully processed as above. This control test forms part of the quality control in the laboratory.

2.4. ToF-SIMS Analyses

ToF-SIMS imaging was carried out without prior application of standard processes on the even numbered depositions. Additionally, ToF-SIMS imaging was used after standard processes on a selection of undeveloped or partially developed fingerprints. The imaging area was aimed at the centre of the substrate to maximise the ridge density.

Analyses were carried out on an IonToF GmbH (Münster, Germany) ToF.SIMS 5 instrument, using a 25 keV Bi_3^+ primary ion beam delivering 0.18 pA of current, operating in the high current bunched mode. Raw data sets of total ion images were acquired at 600 × 600 pixels resolution in the raster (sawtooth) mode of operation. From these mass selected images were constructed. These parameters were selected as they provide good image resolution within an acceptable time frame for 6 × 6 mm image size, i.e., 36 mins 48 secs per image acquisition. Superior quality images can be acquired employing higher resolutions; however, these require respectively longer acquisition times [12]. Run settings were 10 frames per patch, 0.25 mm patch side length, 5 shots per pixel, 100 pixel density/mm and 1 scan. These patches were then stitched together within the IonToF software to provide macro-images. Data analysis was performed using IonToF Surface Lab 6 software. After spectral calibration, all ToF-SIMS images were normalised to the Total Ion Current (TIC) to correct for fluctuations in ion beam current and differences in geometry as well as improve the quality of ridge detail. The exceptions were on the paper substrate where ToF-SIMS was

used after the ninhydrin process where ridge detail was better without normalisation.

2.5. Multivariate analysis

MVA of ToF-SIMS datasets was performed to enhance signal-to-noise ratio and facilitate finding the optimal contrast images of ridge detail on selected samples. Analyses for all imaging datasets were carried out using secondary ion masses as variables and mapping pixels as observations. For each dataset, Surface Lab *v6.5* was used to perform an automated peak search on the total spectra by restricting peak intensity and noise depending on the sample analysed. The data for peak areas only were then exported to BIF6 files for each measurement. A mapping dataset is arranged in a matrix containing mass spectra peak areas in columns and pixels in rows, which was processed by Principal Component Analysis (PCA) and non-negative matrix factorisation (NMF), using the simsMVA software[17].

Both methods seek to reduce the dimensionality of a dataset down to a few factors, which allows for the interpretation and visualisation of the surface chemistry. This provides data that can be directly assigned to groups of correlated secondary ions and their weight-averaged distribution maps, which will have improved signal-to-noise ratio. All datasets went through pre-processing steps including normalisation to TIC, peak range selection and pixel binning. Post-processing included normalisation by total factor intensity, brightness and contrast. The images giving the best ridge detail from one or more factors were selected for comparison with direct SurfaceLab *v6.5* output.

2.6. Image enhancement

After photo capture of fingerprint ridge detail developed by standard processes, images were enhanced using IRIS imager software (version 9.1.3), applying tools such as brightness, contrast, and gamma. ToF-SIMS images of ridge detail were adjusted using brightness and contrast tools in the Surface Lab software. MVA generated images were enhanced using brightness, contrast and gamma tools in the simsMVA software.

2.7. Scoring fingerprints

The Home Office grading scale [9], as shown in Supporting Information Table 1, is employed by Dstl and Thames Valley Police (TVP) for validation work to assess new fingermark visualisation methods. For the purpose of this work the Home Office grading scale was used, in combination with operational experience, to assess and quantify the quality of ToF-SIMS and standard process fingerprint images. The Home Office grading scale definitions were adapted to the smaller (6 × 6 mm) areas imaged by ToF-SIMS as these did not show the full fingerprint. Images were scored from 0 (no development of ridge detail) to 4 (full development with clear continuous ridges across the whole fingerprint or area imaged).

3. Results and discussion

3.1. Sensitivity

To compare the sensitivity of ToF-SIMS to Category A techniques, untreated (even numbered) depositions were imaged using ToF-SIMS and compared to sequentially adjacent odd numbered depositions treated with selected Category A processes. For example, sample “13” for Polyethylene, processed using CA and BY40, was compared with the sample “14” for Polyethylene, imaged using ToF-SIMS. Fingerprints were selected for ToF-SIMS imaging where the corresponding standard development started to fail to visualise ridge detail consistently (Home Office grading score of ≤ 2) or at the end of the deposition series. Sequential comparison of the fingerprints was used opposed to split fingerprints due to the risk of distortion of the stainless-steel and polyethylene surfaces when cut. Any distortion in the would have an adverse effect on ToF-SIMS imaging.

3.1.1. Sensitivity on stainless-steel

Table 1 (and Supporting Information Tables 2 and 3), supports research that with each contact in a depletion series less residue is left behind and so the sensitivity of the visualization process is tested [18]. This reduction of material leads to poorly developed fingerprints by the standard processes, CA and BY40. While operational experience is normally used to assess the level of fingerprint development, the Home Office grading scale [19] was used here to enable comparison of techniques. For the stainless-steel substrate, CA and BY40 development of the male donor fingerprints consistently failed to produce quality ridge detail (grading score of ≤ 2) at around deposition 47. ToF-SIMS was therefore used to image the fingerprints from depositions 48 to 64, as shown in Table 1 and Supporting Information Table 4. For the female donor, CA and BY40 did not develop ridge detail from deposition 1, so ToF-SIMS imaging was applied to even numbered depositions between 2 and 10, as shown in Table 1. The peak at m/z 39 (assigned to ^{39}K) was used to produce ion images as this showed the highest quality ridge detail. This is presumed to derive from the salts commonly found in eccrine secretions [2].

A reduction in the quality of ridge detail is shown in Table 1 (full deposition series shown in Supporting Information Tables 2 and 3). On stainless-steel the reduction in ridge quality across the depletion series occurred for most fingerprints after deposition 19 for the male donor, and all depositions from the female donor.

The quality of ridge detail developed from the male donor reduces from grade 4 (using the Home Office grading scale) to between grades 1 to 2 by the end of the depletion series.

For the female donor ridge development scored 1 for the first depletion and 0 from deposition 13 onwards. If these were fingermarks found on an exhibit processed in a police laboratory, based on operational experience, many of the higher depletions from the male donor and most of the female donor fingerprints would not show enough detail to be captured and sent for comparison by fingerprint experts at the fingerprint bureau.

For both male and female donors (Table 1, Supporting Information Tables 4 and 5), the quality of the ridge detail imaged by ToF-SIMS is very high and does not decline as the deposition number increases. All images show continuous ridge detail and even third level details such as sweat pores. These images were graded 4 on the Home Office grading scale. There was a higher level of ridge detail than the consecutive odd numbered fingerprint depositions developed using cyanoacrylate and BY40 (Table 1 and Supporting Information Tables 2 and 3). One caveat is that ToF-SIMS sampled only a 6 × 6 mm area, to increase throughput, so the comparison of ridge detail is only valid for the area imaged. Also, this comparison is on consecutive depositions and not on the same fingerprint. Nonetheless, ToF-SIMS was found to offer a greater level of sensitivity and consistency compared with the Category A process, in terms of the quality of ridge detail visualised.

3.1.2. Sensitivity on polyethylene

Table 2 summarises the images produced by CA with BY40 and ToF-SIMS for the polyethylene substrate. For the male donor, the quality of CA and BY40 developed fingerprints dropped off further down the depletion series than for the stainless-steel substrate. A Home Office grading score of grade 3 was still attained at depositions 81, 83 and 85, as shown in Supporting Information Table 6. The majority of these would be sufficient for comparison in an operational setting, however Table 2 highlights that some fingerprints from the series could be insufficient for use by a fingerprint bureau. Due to the success of CA and BY40 development, ToF-SIMS was used to image only the last deposition, depletion 90.

In contrast, for the female donor the CA and BY40 development did

Table 1
Optical images of fingerprints deposited by male and female donors on stainless-steel, developed with CA & BY40. *m/z* 39 Ion maps of central areas of fingerprints deposited by male and female donors on stainless- steel, imaged using ToF-SIMS.

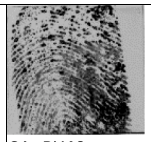
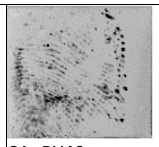
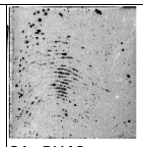
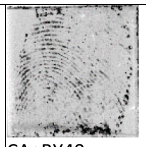
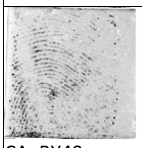
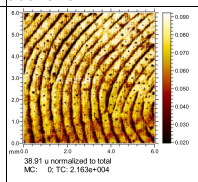
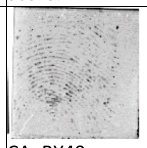
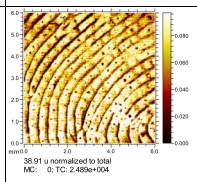
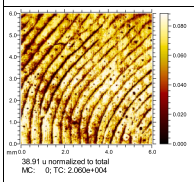
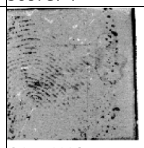
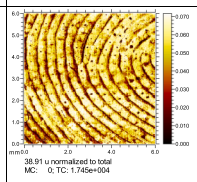
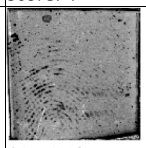
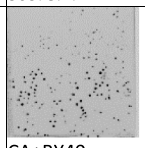
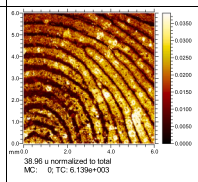
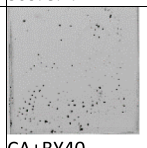
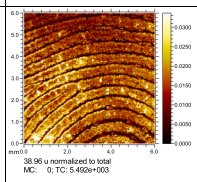
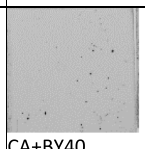
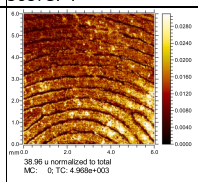
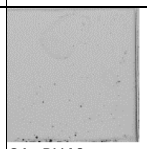
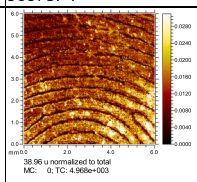
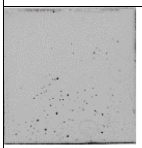
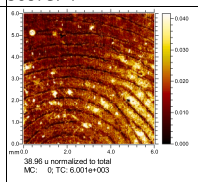
Male Donor	 CA+BY40 **Deposition: 1** Home Office grading Score: 4	 CA+BY40 **Deposition: 13** Home Office grading Score: 3	 CA+BY40 **Deposition: 25** Home Office grading Score: 1	 CA+BY40 **Deposition: 37** Home Office grading Score: 3
	 CA+BY40 **Deposition: 47** Home Office grading Score: 3	 ToF-SIMS **Deposition: 48** Home Office grading Score: 4	 CA+BY40 **Deposition: 49** Home Office grading Score: 3	 ToF-SIMS **Deposition: 50** Home Office grading Score: 4
	 ToF-SIMS **Deposition: 62** Home Office grading Score: 4	 CA+BY40 **Deposition: 63** Home Office grading Score: 2	 ToF-SIMS **Deposition: 64** Home Office grading Score: 4	 CA+BY40 **Deposition: 65** Home Office grading Score: 2
Female Donor	 CA+BY40 **Deposition: 1** Home Office grading Score: 1	 ToF-SIMS **Deposition: 2** Home Office grading Score: 4	 CA+BY40 **Deposition: 3** Home Office grading Score: 1	 ToF-SIMS **Deposition: 4** Home Office grading Score: 4
	 CA+BY40 **Deposition: 5** Home Office grading Score: 1	 ToF-SIMS **Deposition: 6** Home Office grading Score: 4	 CA+BY40 **Deposition: 7** Home Office grading Score: 1	 ToF-SIMS **Deposition: 8** Home Office grading Score: 4
	 CA+BY40 **Deposition: 9** Home Office grading Score: 1	 ToF-SIMS **Deposition: 10** Home Office grading Score: 4		

Table 2
Optical images of fingerprints deposited by male and female donors on polyethylene, developed with CA & BY40. Ion images taken from the central areas of fingerprints deposited by male and female donors on polyethylene and imaged using ToF-SIMS.

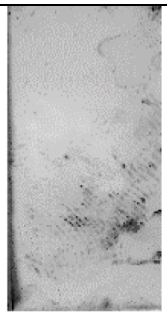
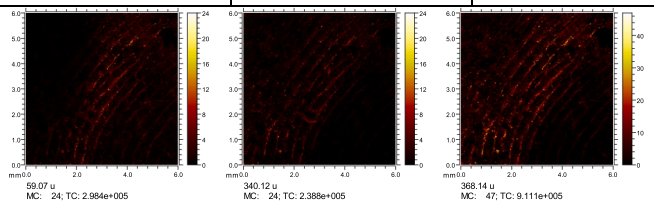
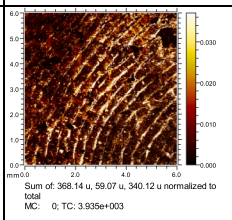
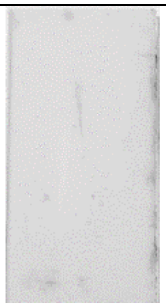
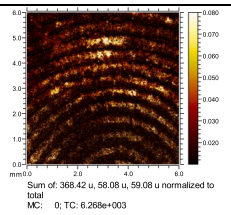
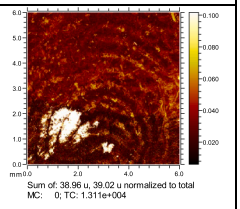
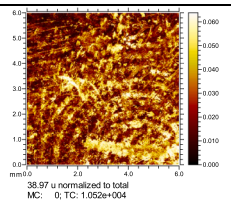
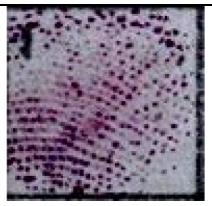
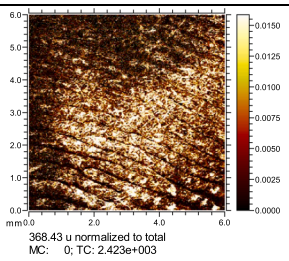
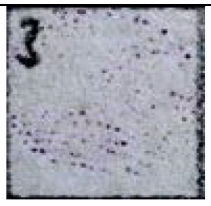
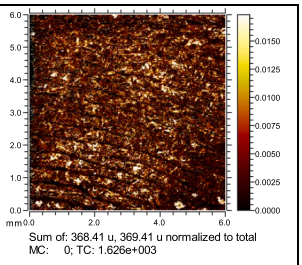
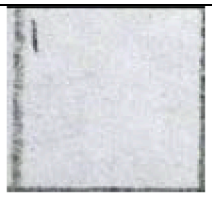
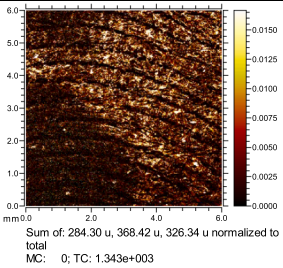
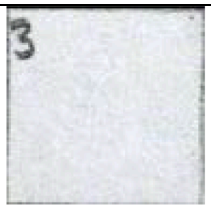
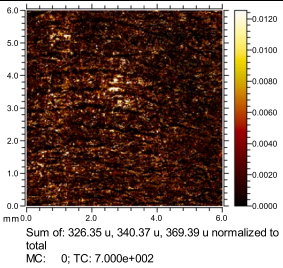
Male Donor	 CA+BY40 **Deposition: 1** Home Office grading Score: 4	 CA+BY40 **Deposition: 25** Home Office grading Score: 3	 CA+BY40 **Deposition: 45** Home Office grading Score: 1	 CA+BY40 **Deposition: 89** Home Office grading Score: 2
	 Breakdown of *m/z* values contributing the ToF-SIMS image at Deposition 90			 ToF-SIMS **Deposition: 90** Home Office grading Score: 4
Female Donor	 CA+BY40 **Deposition: 1** Home Office grading Score: 0	 ToF-SIMS **Deposition: 2** Home Office grading Score: 4	 CA+BY40 **Deposition: 9** Home Office grading Score: 0	 ToF-SIMS **Deposition: 10** Home Office grading Score: 3
	 CA+BY40 **Deposition: 13** Home Office grading Score: 0	 ToF-SIMS **Deposition: 14** Home Office grading Score: 2		

Table 3
Optical images of fingerprints deposited by male and female donors on paper, developed with ninhydrin. Ion images taken from the central areas of fingerprints deposited by male and female donors on paper and imaged using ToF-SIMS.

Male Donor	 Ninhydrin **Deposition:1** Home Office grading Score: 3	 ToF-SIMS **Deposition: 2**	 Ninhydrin **Deposition:3** Home Office grading Score: 1	 ToF-SIMS **Deposition: 4**
		Home Office grading Score: 3		Home Office grading Score: 2
Female Donor	 Ninhydrin **Deposition:1** Home Office grading Score: 0	 ToF-SIMS **Deposition: 2** Home Office grading Score: 3	 Ninhydrin **Deposition:3** Home Office grading Score: 0	 ToF-SIMS **Deposition: 4** Home Office grading Score: 2

not visualise ridge detail for any of the deposited fingerprints. This underlines the real need for a more sensitive visualisation process as this would mean that no comparison could take place in an operational setting. Imaging with ToF-SIMS was carried out on depletion 2, 10 and 14 to test its sensitivity at different points in the depletion series.

For the male donor, the peak at *m/z* 39 that was used to provide images of fingerprints on stainless steel gave no clear ridge detail. Different combinations of *m/z* values were chosen (those that yielded images of ridge detail) for imaging of each deposition and were then normalised to the TIC to provide the best images. From these combinations, continuous ridge detail was visualised across the entire area imaged. In Table 2, for deposition 90 the signal appears to be coming from the substrate, but this can still be used to generate an image of high-quality ridge detail.

Table 2 demonstrates that for the polyethylene substrate, there is a considerable improvement in sensitivity when using ToF-SIMS, compared with conventional development, particularly with the female donor. However, the contrast and clarity of the ToF-SIMS images on polyethylene were not as good as with stainless-steel. This may be due to charging (because the polyethylene is insulating), or the surface texture of polyethylene creating fluctuations in geometry (i.e., the distance from sample to detector causing flight time to vary). These are all phenomena that are known to cause a loss in peak resolution and sensitivity in ToF-SIMS [20].

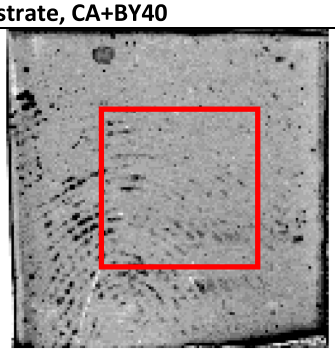
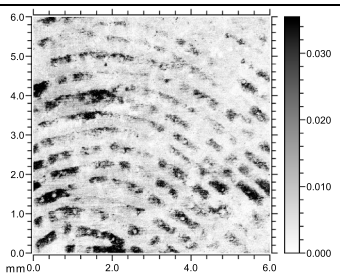
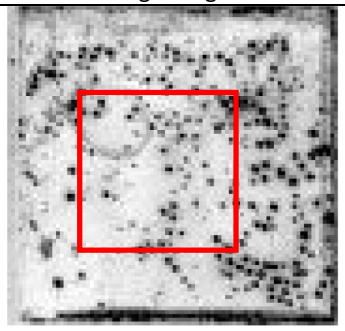
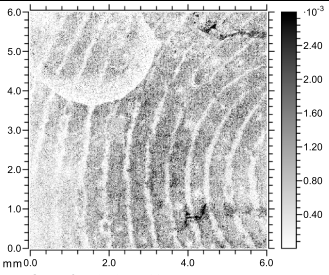
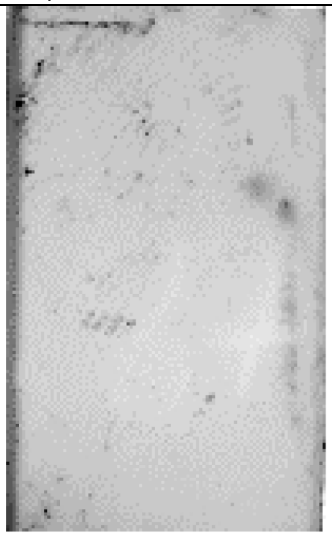
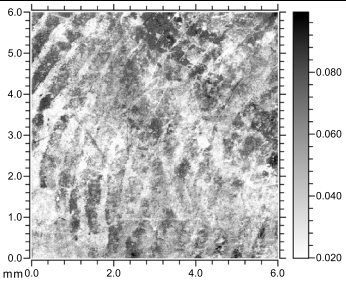
3.1.3. Sensitivity on paper

For the paper substrate, the ninhydrin process failed to visualise ridge detail that scored above a grade 1 after the first deposition from the male donor. Ninhydrin development of the female donor scored 0 on all depositions. A control test was successful showing the ninhydrin working solution was working correctly, suggesting that the lack of ridge detail was due to the limitations of Ninhydrin development. Therefore for both donors, ToF-SIMS imaging was started from the second deposition and the resulting ion images are shown in Table 3.

The paper substrate was found to have the poorest recovery of fingerprints using conventional development, especially for the female donor. This is consistent with previous studies, showing donor to donor variability and male/female donors depositing different amounts of amino acids [21,22]. Ninhydrin has been demonstrated to work on fingermarks that are several years old [23,24] so other variables, such as residue composition, are a more likely explanation for the poor recovery rate than fingerprint age [3]. This substrate-related challenge was also reflected in the ToF-SIMS images, where the Home Office grading scores were lower than with the non-porous substrates. Porous substrates can be problematic for fingerprint development due to the tendency for fingerprint residues to be absorbed into the porous surface. ToF-SIMS is a surface sensitive technique and this absorption into the substrate would explain the lower sensitivity of the technique for visualising fingerprints on paper. The surface roughness of the paper may also explain the lower quality ToF-SIMS images [25]. Despite this, Table 3 shows how ToF-SIMS can be used to generate images of fingerprints further into the depletion series than conventional processes, even on challenging surfaces like paper.

Occasionally, the development quality increases marginally down the depletion series, as seen in supporting Information Tables 2 and 6. This has been observed previously and is likely a consequence of not

Table 4
Sequential development using standard process (left) followed by ToF-SIMS imaging (right) on male and female donors' depositions on stainless steel, polyethylene, and paper.

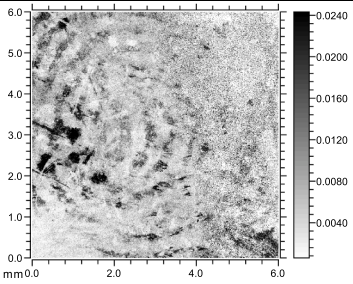
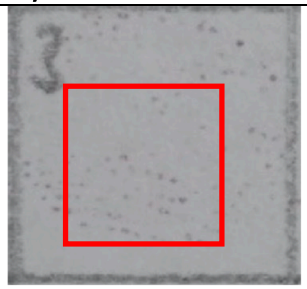
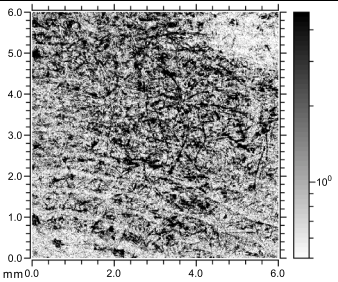
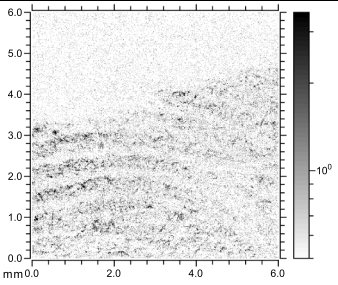
Deposition	Standard Process	ToF-SIMS
Stainless steel substrate, CA+BY40		
Deposition: 65 Donor: Male	 Home Office grading score: 2	 Sum of: 362.17 u, 154.10 u, 318.11 u normalized to total MC: 0; TC: 3.197e+003 Home Office grading score: 3
Deposition: 3 Donor: Female	 Home Office grading score: 1	 Sum of: 550.59 u, 522.55 u normalized to total MC: 0; TC: 2.719e+002 Home Office grading score: 4
Polyethylene substrate, CA + BY40		
Deposition: 87 Donor: Male	 Home Office grading score: 1	 Sum of: 362.16 u, 363.16 u, 98.03 u normalized to total MC: 0; TC: 1.756e+004 Home Office grading score: 4

controlling variables such as donor deposition pressure [26]. Despite this source of variability, Tables 1-3 and Supporting Information clearly show the limitations of currently deployed fingermark development processes, even if carried out under operational ISO 17,025 accredited procedures. These enhancement protocols have been developed to optimise sensitivity and reproducibility of the fingermark enhancement process and are representative of current practice in the field. The results clearly demonstrate the requirement for more sensitive methods so that less crime scene fingermarks are not left undetected.

3.2. ToF-SIMS in sequence after standard processes

Normally, sequential processing of exhibits means starting with the least destructive process. While ToF-SIMS is less destructive than the Category A processes used it is time consuming to image a small area. It would therefore be preferable to use it once a partial mark has been developed and can then be enhanced with targeted ToF-SIMS imaging. In police laboratories, while treatments can be used individually for lower priority cases, to maximise evidence recovery treatments can be performed in sequence. An added consideration is that ToF-SIMS is extremely time-consuming (taking 36 min 48 s to generate these images) and so it would be inefficient to use it without prior knowledge of the

Table 5
Comparison of images of fingerprints collected from a male and female donor on a stainless-steel, polyethylene and paper substrate as a direct Surface Lab output (middle) and simsMVA output (right).

Deposition: 1 Donor: Female	 Home Office grading score: 0	 Sum of: 318.06 u, 154.09 u, 98.03 u normalized to total MC: 0; TC: 2.515e+003 Home Office grading score: 2
Paper substrate, Ninhydrin		
Deposition: 3 Donor: Male	 Home Office grading score: 1	 368.40 u MC: 5; TC: 8.784e+005 Home Office grading score: 2
Deposition: 1 Donor: Female	 Home Office grading score: 0	 550.23 u MC: 4; TC: 9.092e+004 Home Office grading score: 2

location of the fingermark.

ToF-SIMS imaging was carried out after CA fuming and BY40 staining for both stainless-steel and polyethylene substrates, and post-ninhydrin treatment on paper. Samples where standard processes showed poor fingerprint ridge detail (Home Office grading score $\leq$ 2) were chosen for further ToF-SIMS imaging. The central 6 $\times$ 6 mm of each deposition was targeted. Due to the limited performance of standard processes, it was not always possible to precisely relocate the area imaged by ToF-SIMS; but where possible the imaged areas are highlighted in red. In some cases, the ridge detail produced by the standard process was not good enough to locate the area imaged by ToF-SIMS but could be tentatively located by using a feature on the surface (e.g., possible watermark used for deposition 3 of the female donor) from the standard process. All images were converted to grayscale for unbiased comparison of the different techniques. The ridges are shown in black, and the lighter areas show the substrate, representing the valleys between the ridges.

Table 4 shows how when ToF-SIMS is used in sequence with standard processes, the Home Office grading score increases, meaning enhanced fingerprint development for all donors and all substrates. For stainless steel, depletions 53 and 65 (male donor) and 1 and 3 (female donor) were chosen for further ToF-SIMS imaging. For both the male and female donors, sequential treatment on the selected depletions was successful, showing ToF-SIMS would be compatible for inclusion in the FVM charts for recommended treatment pathways. For the male donor, the ridge detail produced by ToF-SIMS (Table 4) is more defined than with the

standard process. Continuous ridge detail seen with ToF-SIMS shows more ridge characteristics that were difficult to determine with CA and BY40process. The added benefit was more evident from the female donor (Table 4) as high-definition continuous ridge was seen after sequential use of Tof-SIMS, whereas the CA and BY40 alone only produced "dotty" development and no ridge characteristics.

On polyethylene (Table 4) development by CA and BY40 of fingerprints from the male donor was seen on all samples so sequential treatment was done on deposition 87, where only partial development (score 1) was improved to score 4 after ToF-SIMS imaging. CA and BY40 failed to develop the fingerprint from the female donor on all samples so sequential treatment was carried out on deposition 1. This yielded ridge detail scoring 2 and visualised core characteristics not seen with the CA and BY40. It was observed that ToF-SIMS did not only improve on the quality of ridge detail developed but also reduced background interference. For example, the depletion number was written on the reverse of the substrate (the opposite side to where the fingerprint was deposited). As the substrate is translucent, the number is visible in the photograph captured after standard development for the male donor, but ToF-SIMS, which only samples from the top layers (the process and fingerprint residue in this case) is uninhibited by the writing. This could be useful on casework exhibits that have printed text or patterns that may interfere with ridge detail visualisation and capture. The ridge detail of the ToF-SIMS image in Table 4, for the female donor on polyethylene is poorly defined on the top right-hand side despite normalising to the TIC. It is possible it was the way the sample was mounted or an uneven surface.

For the fingerprint from the male donor on paper, development by ninhydrin was only sufficient (Home Office grading score 3) on deposition 1, so sequential ToF-SIMS imaging was done on deposition 3 (originally graded 1). The standard process failed to develop ridge detail from the female donor from deposition 1 so sequential ToF-SIMS imaging was carried out on deposition 1. Table 4 images clearly show that ToF-SIMS was able to visualise ridge detail where ninhydrin failed. As with untreated ToF-SIMS imaging, the definition of the ridge detail is reduced on paper, but the grading score still improved to 2 with both donors.

For untreated fingerprints deposited on the non-porous surfaces, *m/z* 39 (assigned to ^{39}K) gave some of the best contrast and detailed images. However, the same peak did not give the best ToF-SIMS images after the standard CA and BY40 developer process. This could be due to the step in the procedure where the samples were rinsed under tap water. This rinse step may lead to delocalisation of water-soluble ions from the fingerprint residue. It could also be that salts in the fingerprint residue are used in the initiation of polymerisation of the cyanoacrylate monomers and therefore could be obscured by layers of cyanoacrylate.

Similarly, on the porous surfaces, *m/z* 39 (assigned to ^{39}K) did not give the best images. This can be explained by ^{39}K being water-soluble and therefore being absorbed into the porous surface. This would result in fewer ^{39}K ions being available at the surface for detection by ToF-SIMS, which is surface sensitive. Post treatment it may also be that the constituents, including inorganic salts, are delocalised by the solvent in the ninhydrin working solution.

3.3. Spectral analysis

The images were explored for *m/z* values yielding ridge detail to explore whether a common constituent was present, for example as a target for future processes. After a peak search, filtering by signal to noise ratio and peak intensity to around 300 peaks, the images generated were manually examined. This was done across all samples imaged by ToF-SIMS after development by standard processes. Supporting Information Table 5 shows the *m/z* values that were detected in 3 or more samples.

Fingerprint residue can be highly variable day to day, donor to donor and surface to surface, but ToF-SIMS has shown some common *m/z* values associated with ridge detail post development (Supporting Information Table 5). Some were seen on all three surfaces, for example *m/z* 23 (assigned to ^{23}Na) and *m/z* 39 (assigned to ^{39}K), but even these markers did not consistently produce ridge detail from every fingerprint. Other peaks, such as *m/z* 98.0, were only noted on stainless-steel and polyethylene surfaces types which underwent CA-BY40 development but again these did not consistently provide ridge detail. These results show how the multiplexed detection of analytes in fingerprints afforded by mass spectrometry offers an advantage over any method that targets a specific fingerprint constituent.

3.4. Multivariate analysis (MVA)

Supporting Information Table 5 clearly shows how fingerprint images can be produced from multiple *m/z* values, and how those vary from fingerprint to fingerprint. The application of MVA to the ToF-SIMS data generated from imaging fingerprints could allow all the significant peaks to be automatically selected and the generation of a fingerprint image showing the contrast between the ridges and the substrate.

Additionally, in an operational scenario, where the aim of employing ToF-SIMS would be to visualise the ridges rather than to identify the substances present, it is not desirable to invest time in spectral calibration. Accurate mass calibration can be very challenging for novice ToF-SIMS users, especially when the substrate requires charge compensation or is not flat. In addition, Supporting Information Table 5 shows how fingerprint chemistry is extremely variable, and even more so after exposure to different environmental conditions. This means the calibration routine would have to be tailored to each fingerprint image. It may not always be possible to apply a previously made peak list or rely on peak identification without recalibration.

While a peak search can be used on the Surface Lab software to generate many ion images, this takes time to go through manually to combine and normalise. In this case the simsMVA software [17], was used to process the ToF-SIMS data. All data from Table 4 was run through PCA and NMF using simsMVA and Table 5 shows the best results from fingerprints deposited on stainless steel, polyethylene and paper treated with standard processes.

As shown in Table 5, 4 of the 6 images created using simsMVA contained ridge detail that was of the same quality (same Home Office grading score) as the corresponding ToF-SIMS generated images. In some instances (paper, male, deposition 3) the ridge contrast with the background is improved. This means that simsMVA could in some cases be used to streamline the image generation process and mitigate the need for mass calibration, particularly where surface imperfections cause spectral degradation. While training will be required to see the benefits of simsMVA, image generation would be unbiased with time saved from manual searches and enhancement of *m/z* values to yield images of optimum ridge detail.

3.5. Operational use

The use of ToF-SIMS in casework has some drawbacks such as the time taken to image a fingermark and the skill and knowledge required to operate the instrument and process the data. To generate the images in this publication takes just under 37 mins of instrument time and covers an area of 6 × 6 mm. A fingerprint approximately covers an area of 12 × 18 mm. This means that it would take ToF-SIMS 3 hrs 40 mins 13 secs to image a complete fingerprint under the same imaging conditions. This is lengthy and while the 6 × 6 mm area with high level detail would often be sufficient for comparison, ToF-SIMS would require the location of the fingermark to be known so the process could be applied to small areas of fingermarks where insufficient detail was developed. Further work should explore whether the analysis time could be improved without sacrificing good ridge detail. Alternatively, a larger area could be scanned faster at low resolution to indicate the location of a fingermark, and then targeted areasre-analysed at high resolution. Another

reason for targeted enhancement by ToF-SIMS is that there is a maximum exhibit size that can be mounted on the sample stage (10 × 7 cm) and into the vacuum chamber.

4. Conclusions

On all three surfaces, the ToF-SIMS imaging has shown greater sensitivity to fingerprints compared with standard processes. In particular, ToF-SIMS could image fingerprints further down the depletion series than the standard processes. Even when the standard process imaged sufficient ridge detail for operational comparisons, the ToF-SIMS image showed improved ridge quality with higher level detail such as ridge shape and sweat pores. This could mean in casework there is a greater chance of successfully visualising a mark sufficient for identification, that otherwise would have been lost.

Using ToF-SIMS after standard processes proved successful and provided a further enhancement in every tested case. While this needs investigation for more surfaces, donors, and standard processes, this shows promise that a potential fingermark could be located from as little as a few dots of the process and then successfully imaged using ToF-SIMS. ToF-SIMS would be suitable for targeted fingermark enhancement on flat and smooth surfaces. The higher quality ridge detail and added benefit of ToF-SIMS in a sequence observed in this study makes ToF-SIMS a strong candidate for specialised fingermark enhancement.

The MVA software looks for patterns in the peaks in terms of their distribution on the surface. This means images are less reliant on accurate calibration of the instrument and spectral/intensity changes due to topography. It can yield high quality fingermark images, and in this dataset, it mostly yielded equivalent images to SurfaceLab direct output and in some cases improved contrast. It may therefore be a promising approach for saving time and for surfaces where spectral calibration is challenging.

CRediT authorship contribution statement

Deborah Charlton: Conceptualization, Methodology, Investigation, Writing – original draft. **Catia Costa:** Writing – review & editing, Supervision. **Gustavo F. Trindade:** Software, Writing – review & editing. **Steve Hinder:** Resources, Writing – review & editing. **John F. Watts:** Resources, Writing – review & editing. **Melanie J. Bailey:** Conceptualization, Methodology, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to thank the Fingerprint Laboratory Supervisor and Thames Valley Police for the use of the accredited laboratory facilities. They would also like to thank Dstl for partial funding of this project, along with funding through EPSRC EP/R031118/1 and EP/P001440/1.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scijus.2022.10.004.

References

[1] Francese, S., *Emerging technologies for the analysis of forensic traces.* 2019.
[2] Great Britain. Home, O., *Fingermark visualisation manual.* 2014, [Place of publication not identified]: TSO.
[3] Bleay, S.M., et al., *Fingerprint source book.* 2012.
[4] Holder, E.H., et al., *The fingerprint sourcebook*. 2012.
[5] Bleay, S.M., Interpreting the results of fingermark enhancement, in Fingerprint Development Techniques. 2018. p. 469-488.
[6] G.S. Bumbrah, Cyanoacrylate fuming method for detection of latent fingermarks: a review, Egyptian journal of forensic sciences 7 (1) (2017) 4.
[7] R.N.S. Sodhi, Time-of-flight secondary ion mass spectrometry (TOF-SIMS): versatility in chemical and imaging surface analysis, Analyst 129 (6) (2004) 483–487.
[8] Croxton, R.S., S.M. Bleay, and M. de Puit, *Composition and properties of fingermarks*, in *Fingerprint Development Techniques*. 201p. 35-68.
[9] A.R. Buchberger, et al., Mass Spectrometry Imaging: A Review of Emerging Advancements and Future Insights, Anal. Chem. 90 (1) (2018) 240–265.
[10] S.J. Hinder, J.F. Watts, SIMS fingerprint analysis on organic substrates, Surf. Interface Anal. 42 (6–7) (2010) 826–829.
[11] M.I. Szynkowska, et al., Preliminary studies using imaging mass spectrometry TOF-SIMS in detection and analysis of fingerprints, The Imaging Science Journal 55 (3) (2007) 180–187.
[12] M.J. Bailey, et al., Enhanced imaging of developed fingerprints using mass spectrometry imaging, Analyst 138 (21) (2013) 6246–6250.
[13] R. Bradshaw, et al., Towards the integration of matrix assisted laser desorption ionisation mass spectrometry imaging into the current fingermark examination workflow, Forensic Sci. Int. 232 (1–3) (2013) 111–124.
[14] K.C. O'Neill, P. Hinners, Y.J. Lee, Chemical Imaging of Cyanoacrylate-Fumed Fingerprints by Matrix-assisted Laser Desorption/Ionization Mass Spectrometry Imaging, J. Forensic Sci. 63 (6) (2018) 1854–1857.
[15] R. Bradshaw, et al., Application of MALDI MS imaging after sequential processing of latent fingermarks, Forensic Sci. Int. 319 (2021), 110643.
[16] M.J. Bailey, et al., Chemical Characterization of Latent Fingerprints by Matrix-Assisted Laser Desorption Ionization, Time-of-Flight Secondary Ion Mass Spectrometry, Mega Electron Volt Secondary Mass Spectrometry, Gas Chromatography/Mass Spectrometry, X-ray Photoelectron Spectroscopy, and Attenuated Total Reflection Fourier Transform Infrared Spectroscopic Imaging: An Intercomparison, Anal. Chem. 84 (20) (2012) 8514–8523.
[17] G.F. Trindade, M.L. Abel, J.F. Watts, simsMVA: A tool for multivariate analysis of ToF-SIMS datasets, Chemometrics and Intelligent Laboratory Systems 182 (2018) 180–187.
[18] V.G. Sears, et al., A methodology for finger mark research, Sci. Justice 52 (3) (2012) 145–160.
[19] Bandey, H., *<Fingerprint_Update_Special_Edition_-_The_Powders_Process_54-04.pdf>*. 2004.
[20] C. Cushman, et al., Sample Charging in ToF-SIMS: How it Affects the Data that are Collected and How to Reduce it, Vacuum Technology & Coating (2018).
[21] R.S. Croxton, et al., Variation in amino acid and lipid composition of latent fingerprints, Forensic Science International (Online) 199 (1) (2010) 93–102.
[22] H. Chen, et al., Advances in fingermark age determination techniques, Analyst 146 (1) (2021) 33–47.
[23] C. Lennard, FORENSIC SCIENCES | Fingerprint Techniques, in: P. Worsfold, A. Townshend, C. Poole (Eds.), Encyclopedia of Analytical Science (Second Edition), Elsevier, Oxford, 2005, pp. 414–423.
[24] P.K. Yadav, Development of fingerprints on thermal papers—a review, Egyptian Journal of Forensic Sciences 9 (1) (2019) 47.
[25] J.L.S. Lee, et al., Topography and field effects in the quantitative analysis of conductive surfaces using ToF-SIMS, Appl. Surf. Sci. 255 (4) (2008) 1560–1563.
[26] I. Hefetz, et al., Touch DNA: The effect of the deposition pressure on the quality of latent fingermarks and STR profiles, Forensic Sci. Int. Genet. 38 (2019) 105–112.