Imaging Mass Spectrometry of Fingermarks on Brass Bullet Casings using Sample Rotation

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Abstract

A rotation stage was developed to allow the surface of bullet casings to be imaged under ultra-high vacuum (UHV) conditions using time-of-flight secondary ion mass spectrometry (ToF - SIMS). Experiments were performed over a period of seven months to determine how fingermarks deposited on the surface of Webley MkII revolver rounds change over time. Stitching software written in Python was used to combine image strips that were collected by performing ToF-SIMS analysis along the length of the revolver rounds. The ToF-SIMS analysis was performed by analysing a thin strip along the length of the casings, before rotating them through a few degrees and analysing a new strip. This process was repeated until the entire casing had been imaged. The resulting secondary ion images of the fingermarks were compared to optical images obtained from the same and similar rounds that had been exposed to cyanoacrylate fumes and subsequently stained using Basic Yellow 40 (BY40) dye. ToF-SIMS images were shown to display evidence of ridge and sweat pore level detail on samples that displayed no evidence of fingermarks when developed with cyanoacrylate and BY40. The effects of the curvature of the round casings on the morphology of fingermarks were also assessed. ToF SIMS images were compared to marks that had been deposited onto flat paper surfaces using ink. The distortions caused by differences in surface curvature and the deposition methods were found to be within acceptable limits.

Introduction

Retrieval of fingermark evidence from bullet casings is an area of major difficulty for forensic scientists. While both fired and unfired casings can often be found at the scene of violent crimes, retrieving fingermark evidence and linking the person that loaded the gun to the crime has consistently proven to be difficult. There are a number of reasons why retrieving fingermarks from bullet casings is challenging. These are related to both the physical conditions that are experienced by the bullet casings during firing, as well as the techniques that are used to develop and image the fingermarks. When a bullet is fired, the casing experiences high temperatures, pressures and large friction forces inside the barrel of the gun [1]. They can also be coated by the residues of propellant and the powder that are used to generate the reaction that forces the bullet out of the chamber [2]. These combined effects often result in the removal, evaporation or degradation of the more volatile components of fingermark residue (such as water, amino acids and low molecular weight organics such as lipids), as well as potential smudging and/or otherwise obscuring the mark. Such factors can make it difficult for conventional methods of fingermark retrieval such as cyanoacrylate (superglue) fuming and fluorescent staining approaches to work [3]. Exposure to environmental conditions at the scene of a crime can also result in the modification of the surface of a bullet casing (fired or unfired) as a result of natural corrosion processes in the alloys that comprise them.

Many inorganic species, such as the simple salts that are found in eccrine fingermark secretions are expected to survive the harsh conditions that exist inside a gun barrel. Moreover, these salts are known to induce accelerated local corrosion of alloys such as brass and are expected to modify the physiochemical properties of the casing. These corrosion layers can leave a lasting imprint of any fingermarks on the casing [4]. While surface corrosion layers are very thin and not readily made visible using conventional fingermark recovery techniques, they could be detected using more sophisticated surface science techniques. For example, experiments using techniques such as scanning Kelvin microscopy have successfully detected corrosion layers [5]. Previous studies have also shown that the modified physiochemical properties of the casing surface can be useful when trying to develop fingermarks using electrostatic [6] and vapour deposition techniques [7]. Both of these approaches have resulted in the commercialisation of devices by Consolite Forensics Ltd. (CERA^{TM}) and Foster and Freeman (Recover) respectively. However, persuading policing and law enforcement agencies to use non-validated techniques before any of the conventional approaches are applied to try to retrieve fingermarks is extremely challenging and these techniques are seldom used on live forensic casework.

The physical properties of fired and unfired casings can also present additional problems when it comes to retrieving fingermarks [8]. Bullet casings tend to be made of high surface energy substrates such as metals and their alloys (e.g. brass) which are easily coated by cyanoacrylate, fluorescent dyes and other fingermark reagents (such as vapour deposits). This means that these surfaces can be quickly coated with a thin layer of these reagents making it difficult to isolate the fingermark from the casing itself. Moreover, the curvature and optical properties of the casings introduce additional difficulties when trying to obtain a suitable photographic image of a fingermark, even if it could be developed using conventional techniques.

One technique that has shown significant promise for the retrieval of fingermarks from metallic surfaces is time of flight secondary ion mass spectroscopy (ToF-SIMS) [3, 9]. This technique uses an ion beam to ablate small amounts of material from the surface of a sample and a time of flight mass analyser is used to sort any secondary ions that are emitted from the surface according to their mass-to-charge ratio. A mass spectrum can therefore be obtained at each point on the surface of the sample. If the incident ion beam is scanned across the surface, then spatial variations in the chemistry of the various species can be mapped out with sub-monolayer sensitivity by measuring variations in the intensity of peaks in the mass spectra. This approach can be used to determine where fingerprint components (such as simple salts) may be on that surface. The fact that so little material is removed means that this technique is essentially non-destructive and samples can be imaged numerous times without fear of destroying evidence.

Recent work by Thandauthapani et al. has shown that ToF-SIMS can be used to obtain images of fingermarks with exceptional ridge and pore level detail on metal alloy samples where conventional techniques such as cyanoacrylate and subsequent dye staining fail to show anything [3]. Moreover, the ToF-SIMS images that were obtained in this study had been collected under ultrahigh vacuum conditions (~10^{-10} mbar) and samples could be repeatedly removed from the vacuum conditions, replaced and re-imaged without degradation of image quality. The study by Thandauthapani et al. demonstrated that key fingermark components such as inorganic salts, food metabolites, lipids and simple surfactants (soap contamination) remain stable despite repeated exposure to these harsh conditions.

An additional advantage of using ToF-SIMS to image the surface of bullet casings is that it provides simultaneous detection and imaging of different chemical species without the need to contaminate the surface with any reagents or matrices. This means that there is the potential to retrieve other types of evidence after the ToF-SIMS imaging has been completed. The non-destructive nature of the technique is therefore very attractive and presents significant advantages when compared to conventional fingermark enhancement techniques such cyanoacrylate fuming [3], gun blueing [10], S_2N_2 vapour deposition [7] and palladium deposition techniques [11] which can all potentially result in the contamination of the bullet casing surface and prevent further analysis.

SIMS based techniques have already been used successfully to recover fingermarks from fragments of hand grenades [9]. Comparative studies of ToF-SIMS and conventional cyanoacrylate fuming and dye treatment of fingermarks have also shown that ToF-SIMS yields significantly superior results on metallic surfaces [3].

One potential drawback of ToF-SIMS is that it is restricted to the analysis of flat samples. This has meant that samples with more complicated or curved geometries have been difficult to analyse. In many cases, this often results in a small section of the surface being imaged and the properties of the rest of the surface being inferred from a few sampling points. However, this approach is often unsatisfactory in cases where a detailed knowledge of spatial variations in the chemical surface properties of the entire sample are required. This is particularly true in the case of fingermark enhancement, where recovery of as much of the pattern of ridges formed during the deposition of a mark as possible is required for identifying a person of interest. One way to circumvent the difficulties associated with curvature of the sample is to use a rotation stage for imaging small samples such as bullet casings. Such an approach would allow thin image strips to be collected along the length of the bullet casing (parallel to its axis), before it was rotated in small increments and imaged again. The resulting image strips could then be stitched together to form a composite image of spatial variations in any fingermark constituents that may or may not be present on the surface.

A recent study by Schneider and co-workers involved incorporating a rotation stage into the sample plate holder of a ToF-SIMS instrument to enable the imaging of bevelled focussed ion beam cuts in the surface of metallic multilayer samples [12]. This was a significant step forward in terms of enabling the imaging of samples with curved geometries and facilitating sample rotation. However, the use of a DC motor in the stage design meant that there was some uncertainty in positioning precision (+/-0.1^{o}), particularly when considering backlash in the motors.

In the present study we describe an improved design for a high precision UHV rotation stage that is capable of positioning samples with an angular precision of +/- 0.019^{o}. This rotation stage is used in a commercially available ToF SIMS instrument to image unfired bullet casings and to reconstruct images of fingermarks that have been deposited on their surfaces. We demonstrate for the first time that it is possible to image the entire curved surface of a cylindrical object (bullet casing) using ToF-SIMS and that images of fingermarks with pore level detail can be obtained from samples which reveal no evidence of fingermarks when developed using conventional techniques. In particular, the ToF-SIMS results are compared to fingermarks on the same and similar bullet casing surfaces that are developed using conventional superglue fuming and dye staining techniques.

Experimental

Deposition of fingermarks on bullet casing surfaces

Fingermarks were deposited on the surface of a replica MkII Webley round (D&B Militaria, Lingfield, Surrey). The round was cleaned by sonication in a dilute acetic acid solution for 15 minutes to remove any residues that may have been present on the surface. It was then rinsed with deionised water and dried using a stream of nitrogen gas. Care was taken to hold the casing with tweezers in such a way as to prevent contact with the cylindrical surface of the round. The round was then sonicated in a bath of methanol for 15 minutes and rinsed with deionised water, before being dried in a stream of nitrogen for a second time. Fingermarks were then deposited on the cleaned casings.

Two male donors were used to deposit the fingermarks studied in this work. Both donors cleaned their hands using ordinary hand soap and washed them for a minimum of two minutes. After cleaning, their hands were left to dry naturally in air. The donors then put on nitrile gloves and secretions were allowed to build up naturally on the fingertips over the course of two hours. All touching of face, hair, door handles, and other objects were avoided during these times to ensure that predominantly eccrine secretions were present on the fingertips.

After removal of the nitrile gloves, the donors deposited their marks on different regions of the bullet casing surface by aligning their thumb and index finger on their right hand with the axis of the bullet casing and pressing down. During deposition, the donors pressed each digit on to a different region of the surface of the casing for a total of three seconds while applying a peak force of 2 N (as measured using a balance, Ohaus CS5000E). The round was then stored in a sealed glass container at room temperature and at a relative humidity of 70% while being maintained in an upright position with its flat base in contact with the bottom of the container.

UHV bullet casing rotation stage

Figure 1 shows photographs of the bullet casing rotation stage that was developed for use in the experiments. A 19 mm diameter UHV stepper motor with a 200:1 planetary gearbox (Phytron GmbH, Grobenzell, Germany) was incorporated into the chassis of a ToF IV cryo sample holder from a ToF-SIMS IV (ION TOF GmbH) instrument. A friction mount with a slightly roughened end was placed on the shaft of the gearbox and the Webley MkII round was sandwiched between the mount and an end stop. The end stop contained a UHV compatible bearing that allowed the bullet to rotate freely around its long axis. The windings on the stepper motor were connected to a MCC-1 stepper motor controller (Phytron GmbH)

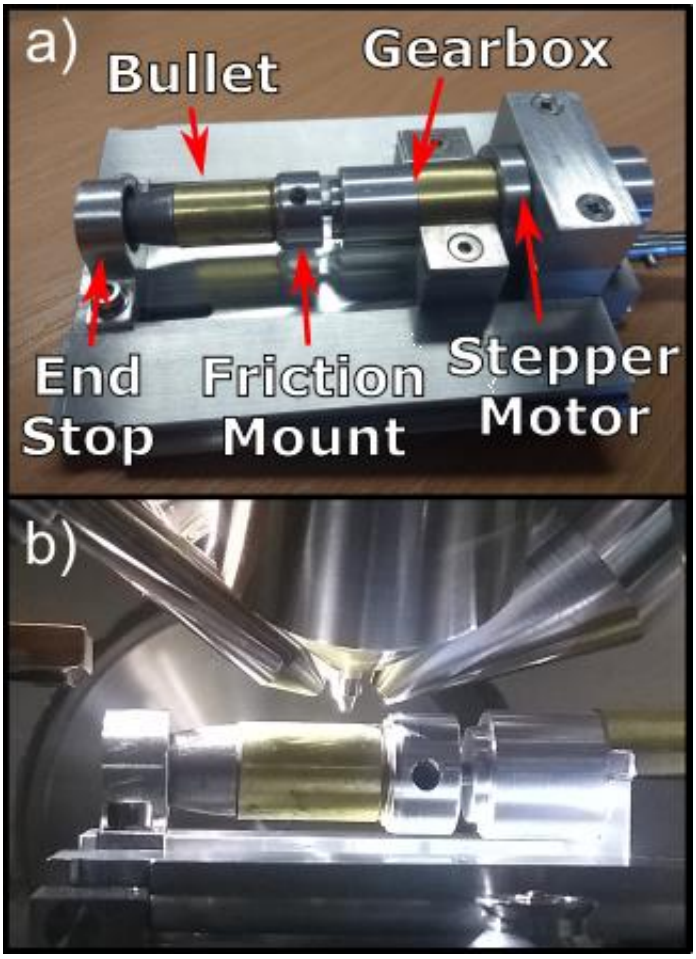

Figure 1. ToF-SIMS b*ullet casing rotation stage.* Panel a) shows a MkII Webley revolver round mounted on the stage. All components of the stage are labelled. Panel b) shows the stage and the bullet casing in the sample chamber of the ToF-SIMS IV instrument.

housed outside of the vacuum chamber using a suitable electrical feedthrough. The mount shown in Figure 1 was designed to hold MkII Webley revolver rounds (12mm diameter casing). However the stage is designed so that it can be easily adapted to take rounds of different calibres (fired and unfired).

ToF SIMS imaging

The sample holder with the UHV rotation stage was loaded into the chamber of the TOF-SIMS VI (IONTOF GmbH) instrument which was pumped down to a pressure of 5×10^{-7} mbar. During ToF-SIMS imaging, a 25 kV Bi_3^+ primary ion beam delivering a pulsed target current of approximately 0.3 pA was used. An electron flood gun was also used for charge compensation on the sample surfaces. The accelerating potential used in the mass spectrometer was 2 keV. Samples were rastered with the primary ion beam over an area of 0.5 mm ×14 mm at the uppermost surface and along the length of the casing. After each strip had been imaged, the stage was rotated through 2.86 +/- 0.01^{o} (equivalent to 0.3 mm along the circumference of the casing) and the casing reimaged. In this way, successive strips containing 0.2 x 14mm of overlap were obtained that would allow them to be stitched together to form a composite image of the distribution of material on the bullet casing surface. The variation in height of a 12 mm diameter bullet casing over a strip region 0.5 mm wide is approximately 5 microns as a result of its curvature. This is within the level of uncertainty caused by the roughness of the bullet casing surface and therefore each strip obtained during the raster scans could be locally approximated as if it were flat.

The bullet casing sample was imaged at a temperature of 23 °C and each strip took approximately 4 min to obtain. A spatial resolution of 100 pixels per mm was used during each scan. Data were acquired using an average of 20 incident primary ions for each region corresponding to a pixel in the ToF-SIMS images and data acquisition was performed using SurfaceLab 7 software (IONTOF GmbH). Images were obtained for a range of different emitted positive secondary ion species after periods of one day, seven days and seven months following deposition of the fingermarks.

Stitching of ToF SIMS images

Image stitching was performed using custom software written in Python. Briefly, the edges of the image strips obtained from the ToF SIMS scans were overlapped and compared in the software in order to find their optimum placement in the final composite image. The process began by scaling the intensity of each pixel in the image strips between zero and 255 in proportion to the detected ion intensities. The resulting grayscale images were then converted to binary images using a threshold value of 50 in each case. Values above this threshold were assigned a value of one and values below it were set to zero.

The edges of the binary image strips were then compared using a Boolean subtraction method. Neighbouring strips were overlapped by varying numbers of pixels (ranging from 1 to 30 pixels) and the regions of overlap were subtracted from one another. If the ridge patterns in the overlapped edge regions matched exactly, then only zeros were present in the resulting subtracted image. Conversely, areas of non-matching ridge patterns resulted in bright pixels (value of one) when the overlapped edge regions were subtracted. The total number of bright pixels remaining after subtraction of the overlap regions in the binary images was recorded and the process was repeated for varying amounts of overlap. The extent of overlap that gave the smallest number of bright pixels was designated the best match and used to construct the final images. This entire process was repeated for all the individual image strips to ensure that the overlap between successive strips was optimised. The pixel shifts obtained using the binary images were applied to the overlap of the original (non-binarised) image strips and used to construct the final composite image of the casing surface. In general, the extent of overlap of neighbouring strips was found to lie in the range of 15 to 25 pixels.

Optical imaging of fingermarks

Three replica Webley MkII rounds were sent to East Midlands Special Operations Unit (EMSOU) so that fingermarks could be developed using conventional techniques in an operational setting. The rounds that were sent included the sample that was used for the ToF SIMS imaging. This sample was sent only after the seven month data had been collected. The remaining two rounds were prepared in exactly the same way as ToF SIMS round, but were stored under the same conditions as the ToF-SIMS round for one day and seven days respectively. In this regard, these samples had been treated in the same way as the ToF SIMS sample when it was imaged at a similar stage in its aging.

All three casings were treated in a Foster and Freeman MVC 5000 superglue cabinet running on an automatic cycle. This includes a 15-minute humidity cycle (humidity reaches 75-90%), a 20-minute superglue/cyanoacrylate fuming cycle (the glue reaches ~120^{o}C on the hot plate before fuming) followed by a 40-minute purge cycle using contained carbon filters. A total of 4g of superglue was used in the fuming cabinet, as other (live casework) items were being treated at the same time. The cyanoacrylate treated rounds were immersed in a solution of Basic Yellow 40 dye (0.2wt% in ethanol) for 10 seconds, rinsed with cold running water and hung in a drying cabinet for eight hours.

A Basler ACA1300-30uc camera with a yellow filter (75 mm × 75 mm No.12, Kodak Wratten gelatin filter, excitation wavelength: 510–530 nm) was used to image the surface of the BY40 stained rounds. A purpose built stepper motor and driver assembly was constructed in which the round was mounted horizontally and illuminated using a 405 nm UV LED source (RS Components, 713-4891). To ensure that the light was normally incident on the surface, a beam splitter was used. A camera was placed directly above the rounds and used to image the surface as the rounds were rotated in increments of 1.9° around their long axis. Software written in LabView (National Instruments) was used to extract image strips from the top of the surface of the round. These were subsequently stitched together to form a complete image of the surface of the sample in a similar way to that used to construct the ToF-SIMS images. Bright field images were also collected using the same approach, but with white ambient light replacing the UV light source.

Fingermarks were also deposited on flat paper surfaces using ink. These marks were used to compare with the images collected from the curved surfaces in the ToF SIMS and cyanoacrylate/staining studies. Briefly, one of the donors pressed and rolled their thumb onto a black ink pad in order to sufficiently coat the surface of the thumb. A fingerprint was then applied to a sheet of white paper by rolling the thumb from left to right. The process of depositing prints onto paper was repeated a further four times without refreshing the ink on the surface of the thumb. This reduced the amount of ink that was deposited each time the thumb was pressed on to the paper, generating a depletion series of prints. The third print in the series was identified as being the clearest reproduction of the ridge marks on the thumb. This fingermark was imaged using white (natural) light illumination and with the same camera that was used to image to Webley rounds in the cyanoacrylate fuming studies.

Results and Discussion

Figure 2 shows sections of images of a thumb print on the surface of the Webley MkII round that were obtained from measurements of the cylindrical bullet casings using the ToF SIMS rotation stage after one day, seven days and seven months respectively. To the best of our knowledge these are the first examples of fingermarks that have been retrieved from curved bullet casing surfaces using ToF-SIMS – a technique that is usually only capable of imaging flat samples. Moreover, the quality of the fingermarks is such that pore level can be resolved in the images.

The images shown in figure 2 are sections taken from the same region of larger images of the whole bullet casing surface. Figure 2 also gives details of the secondary ions assigned to the peaks in the mass spectra that were used to create the image in each panel. Data were obtained for positively charged ion species only to speed up the process of data acquisition and analysis. Our previous work using ToF SIMS on flat metal surfaces [3] has shown that similar images are obtained when negative ionic species are used and that very little additional information about the morphology of fingermarks is obtained by using these ions.

The images in Figure 2 show evidence of secondary ion intensities for various fingermark components that are comparable to those detected on flat metal surfaces [3]. In a number of cases, there appears to be so much material deposited on the surface that the secondary ion intensities are close to saturation. Notably, there is very little variation in the intensities between the images collected after one day and those collected after seven months. This indicates that exposure to the UHV conditions in the ToF SIMS imaging chamber and repeated imaging does not significantly degrade the fingermarks on the surface. This is in agreement with the study of Thandauthapani et al which previously demonstrated the relatively non-

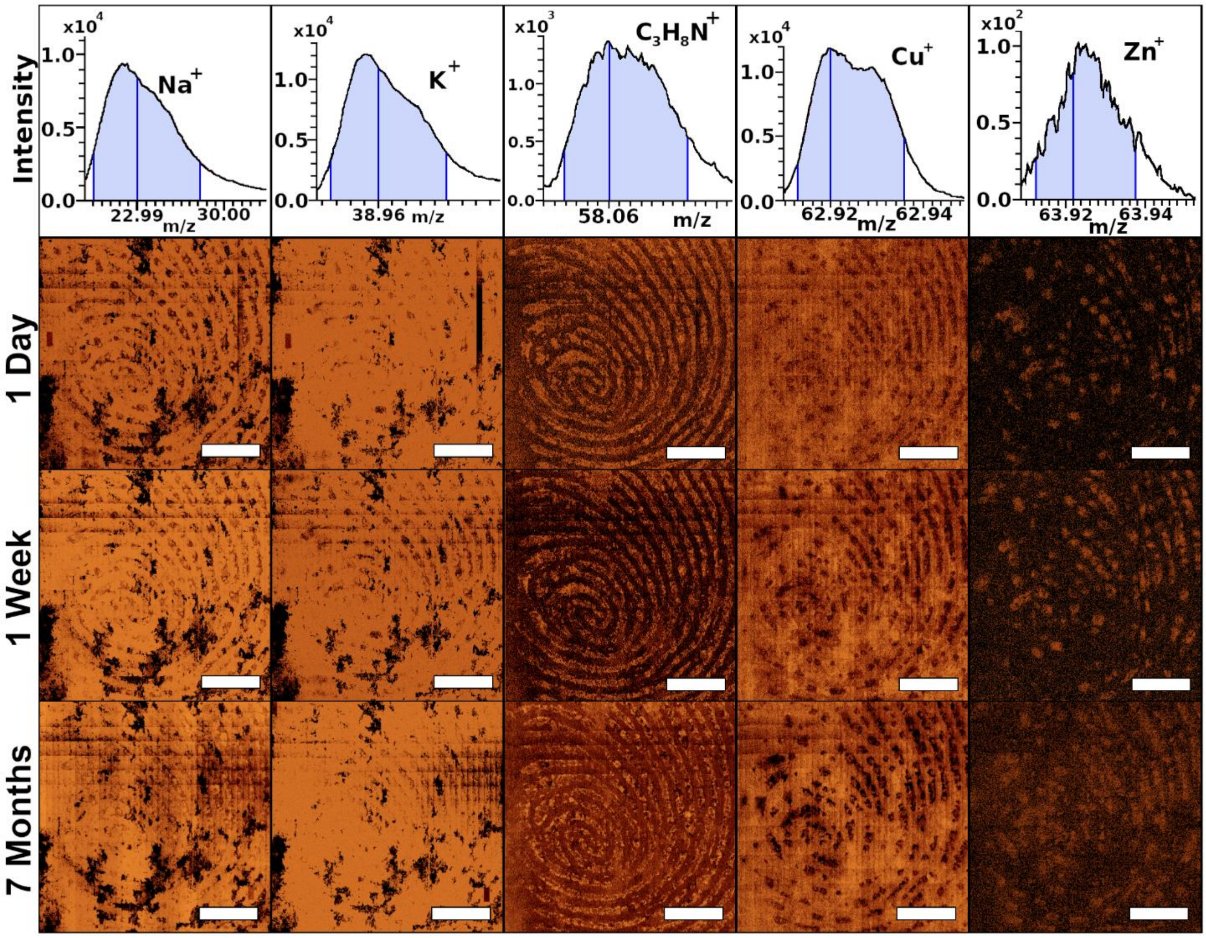

Figure 2. ToF-SIMS images showing the distributions of some of the positive secondary ions in a small region on the surface of a Webley MkII round in the region where a thumb print was deposited. Images were collected one day, seven days and seven months after deposition of the mark and acquired using the sample rotation stage. Secondary ion assignments (and their cumulative intensities) are shown above the images collected at each mass to charge ratio (m/z). Scale bars correspond to 2 mm in all cases. The intensity scale used in each image was normalised using the image intensity histogram in order to obtain the maximum contrast in each panel. An indication of the relative intensities of the ions can be obtained from the vertical axes of the cumulative secondary ion intensity plots.

destructive nature of the ToF-SIMS technique [3] when used to study fingermark samples on metal and alloy surfaces. In particular, Figure 2 shows that the intensities of ions such as Na^+ and K^+ that are present in the salts in sweat are very high. Similarly the signals from Copper and Zinc (the components of Brass casings) containing species are also quite intense. Additional species that were identified as being present on the surface include ions such as $C_2H_3N^+$, $C_3H_5^+$ (not shown) and $C_3H_8N^+$. Among these, $C_3H_8N^+$ has previously been attributed to the presence of the dimethyl (methylene) ammonium ion - a fragment from precursor amino acids such as serine or the betaines (choline or glycine betaine) [3,13]. The other species mentioned (not shown) are likely to be fragments of other hydrocarbon containing species such as lipids.

The images corresponding to the $C_3H_8N^+$ ion (amino acids fragments) show the most contrast with the background, demonstrating clear ridge detail and some evidence of the locations of sweat pores on the ridges in a manner that is consistent with that reported by Thandauthapani and co-workers [3].

Figure 3 shows the C_3H_8N+ secondary ion intensity distribution for the whole surface of the casing collected seven months after deposition of the mark. This image is the first example of an entire bullet casing surface that has been obtained using ToF SIMS and clearly shows that evidence of pore and ridge level detail are present in the images after such an extended period. To the best of our knowledge, images of fingermarks with this level of detail have not been retrieved from bullet casings (fired or unfired) before. Comparing the image in Figure 3 to the optical images of bullet casings that were treated with cyanoacrylate fumes and BY40 dye shown in Figure 4, it is clear that the quality of the marks that are retrieved by ToF-SIMS are far superior. It is worth recalling at this stage that the optical image in Figure 4 that was collected at seven months is from the same sample that was used to collect the ToF-SIMS image shown in Figure 3. In fact, comparing the data shown in Figures 2 and 3 with that in Figure 4, it is clear that ToF SIMS results in the recovery of fingermarks with significantly more detail than conventional superglue fuming and staining at all of the times studied. In the case of the optical images, there is perhaps some evidence of a fingermark after one day when the rounds are imaged using UV illumination. However, the quality of the mark is significantly

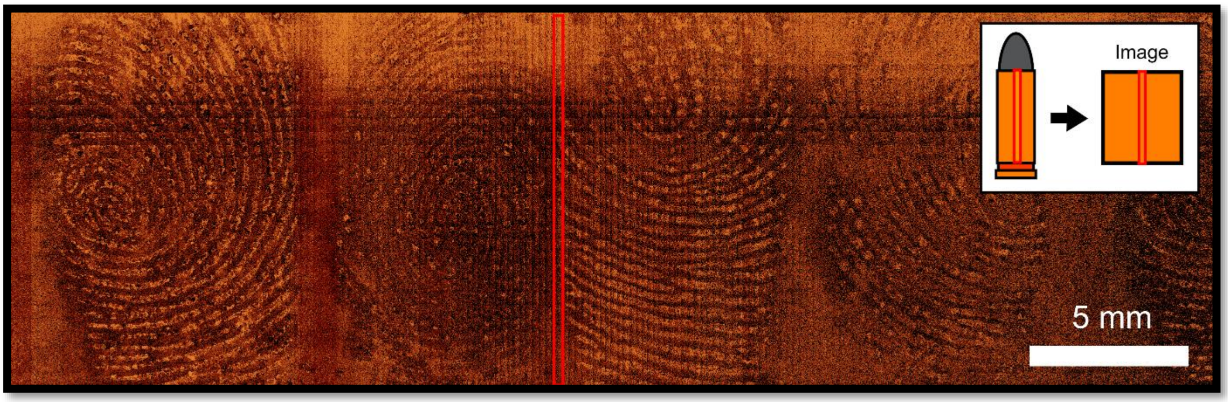

Figure 3. ToF SIMS image of the whole bullet casing surface showing all four fingermarks. This image was acquired using the rotation stage developed as part of this work and shows the distribution of the C_3H_8N+ secondary ion. The image was collected seven months after deposition of the fingermark. The intensity scale used in each image was normalised using the image intensity histogram in order to obtain the maximum amount of contrast. The inset shows a schematic of how the curved surface of the bullet casing is converted to a flat image by scanning thin strips (denoted by the red rectangles) along its length. A similar rectangle has been added to the main panel to indicate the location and orientation of an individual image strips in the composite image.

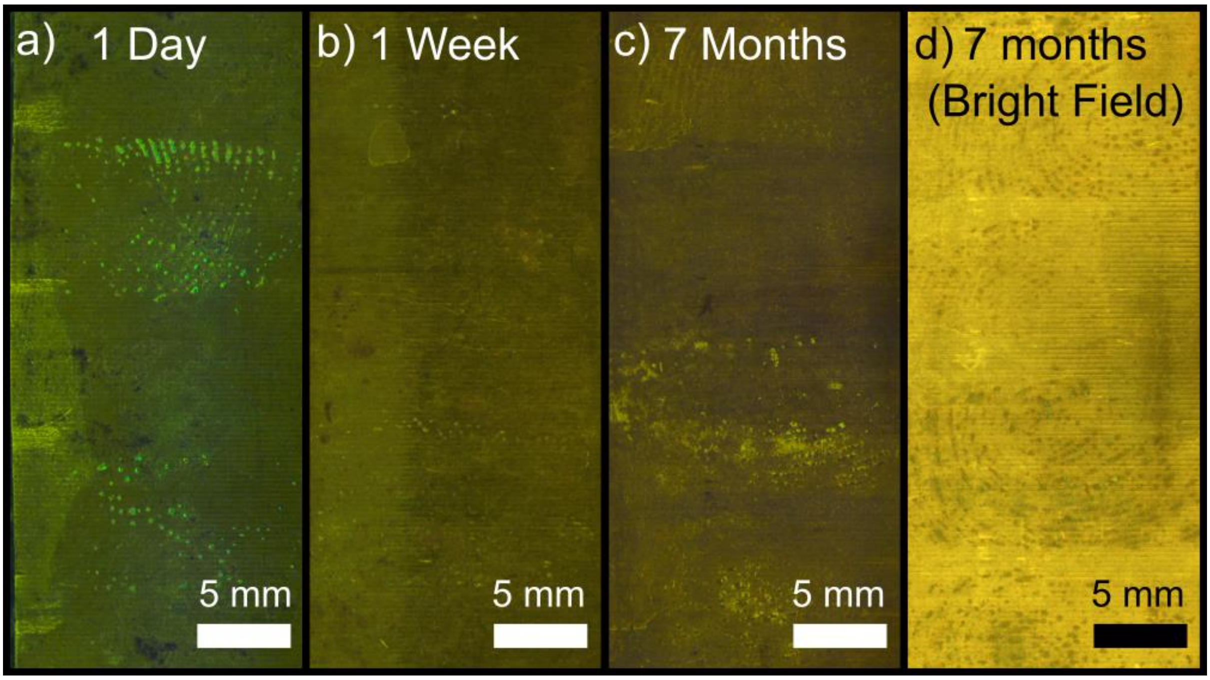

Figure 4. Optical (fluorescence) images of Webley MkII rounds after deposition of a fingermark and subsequent treatment with cyanoacrylate fuming and BY40 staining. Images are shown for rounds that were treated and imaged a) one day b) seven days/one week and c) seven months after deposition of the mark. Panel d) shows a bright field (white light illumination) of the same region shown in panel c). The images shown in panels c) and d) were collected from the round that was imaged using ToF-SIMS in figures 2 and 3. These images were collected after all the ToF SIMS images had been collected and the samples subsequently treated with cyanoacrylate and BY40.

degraded after one week and it is invisible after seven months when developed using conventional techniques.

Topography effects were not corrected for explicitly in the image stitching algorithm that was used to create the composite images shown in figures 2 and 3. Each image strip was treated as if the surface of the sample was locally flat within the region of the strip. While some decrease in the intensity was observed at the edges of the individual image strips due to the curvature of the bullet casings (this can be observed most clearly in figure 3) this was not significant enough to prevent the edges of the image strips being compared in the stitching algorithm used.

The assumption that the thin strips can be approximated as being flat is validated by the work of Lee *et al.* [14]. These authors discussed the effects of topography on ToF-SIMS images in a study of cylindrical gold wire surfaces using the same model of instrument used in the present study. The key result from Lee *et al.*'s work that is relevant to the current study is that the acceptance angle of the single reflectron analyser detector on the ION TOF IV instrument is ~4^{o}. This means that variations of the topography (angle of the sample surface) that create deviations in the secondary ion beam that are smaller than this acceptance angle should still be detected by the instrument. A consideration of the sample geometry used here (casing radius, r=6mm, image strip width d=0.5mm) shows that the maximum angular deviation, θ, of the surface of the sample within the strip region obeys the equation $\sin\theta = d/(2r)$. Inserting the values gives an angular deflection of $\theta \sim 2^{o}$ in the emitted secondary ion beam direction. This is within the range of the acceptance angle quoted by Lee *et al*. Secondary ions that are emitted from the thin strips should therefore be detected in a similar way to ions that are emitted from a perfectly flat sample. In fact, according to this simple analysis, the measured intensity of a given secondary ion species that is emitted from the regions corresponding to the edges of the image strips should be comparable to that obtained near the centre of the image strips. This lack of (or weak) variation of the intensity within strips allowed us to approximate the thin regions of the sample surface as being locally flat and greatly simplified the image stitching process.

At this stage, it is worth noting that fingermarks retrieved from bullet casing surfaces are likely to be distorted in different ways when compared to fingermarks that are deposited on flat surfaces simply because of the differences in contact geometry. In our particular case, there is also a possibility that the processes involved in acquiring the ToF-SIMS images and stitching them together may be introducing some additional distortion to the fingermarks.

Dealing with curvature of surfaces is largely unavoidable when examining everyday objects and this is something that fingermark examiners need to do on a regular basis. A simple test was performed in an attempt to quantify the total extent of the distortions caused by both the change in geometry (from curved surface to flat) and any potential distortions caused by image collection and processing. This test involved comparing the relative positions of *minutiae* (bifurcations and ridge endings) on two images; one obtained from a curved surface using ToF-SIMS and the other from a flat surface using a fingerprint deposited on paper using ink. Figure 5 shows two images of the same fingermark that were collected using these two methods. The ink print shows clear evidence of ridge detail and is similar to those that might be collected from a person of interest. The ink print also shows evidence of bifurcations and ridge endings that have a comparable level of clarity to those shown in the ToF SIMS image.

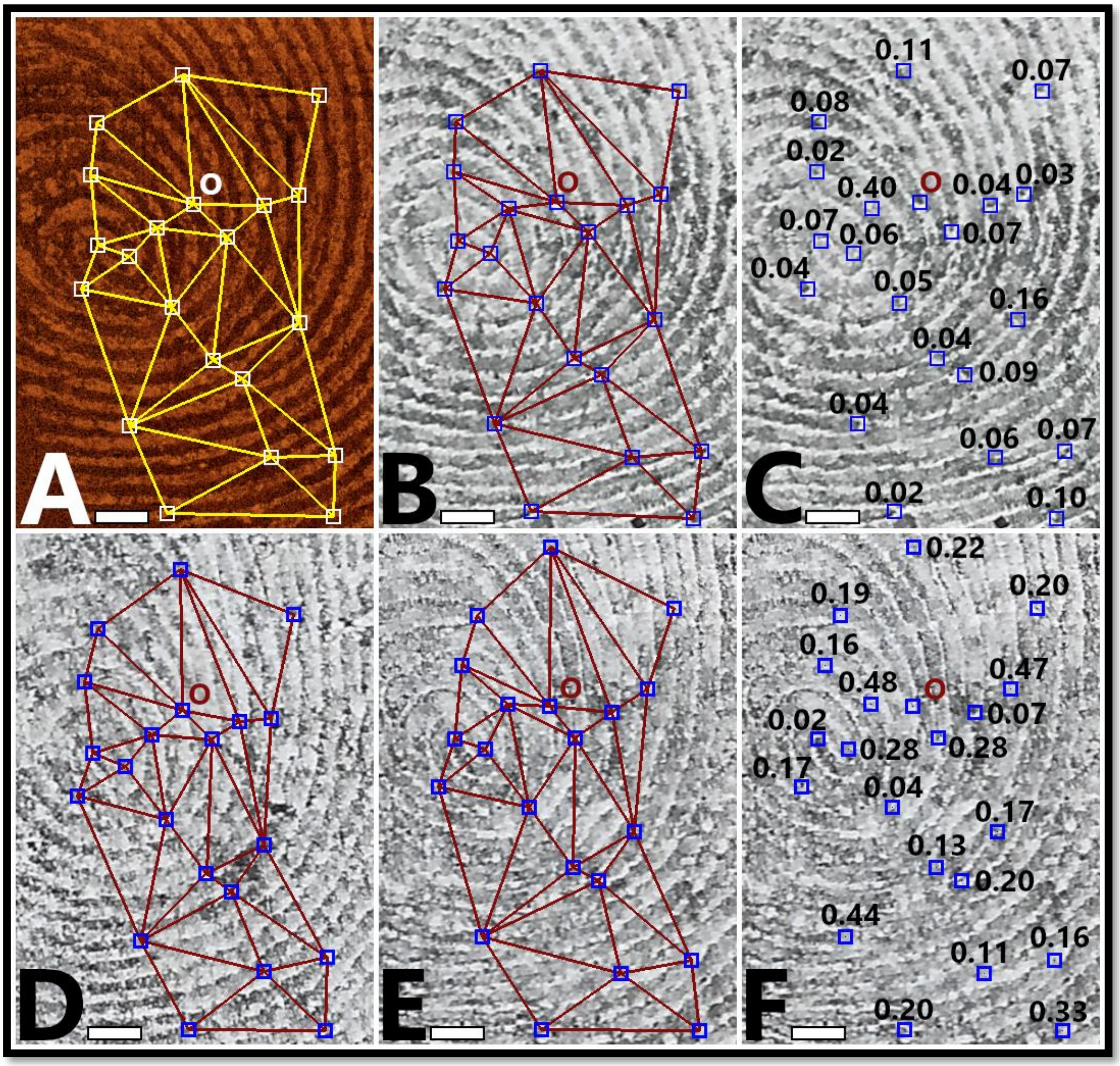

Figure 5. Comparison of fingermarks obtained using ToF-SIMS (panel A) and ink prints (panel B). The squares on each image show the positions of ridge endings and bifurcations and the lines drawn between the squares link neighbouring minutiae. Panel C shows the same grid structure that was constructed in panels A and B. The numbers at the nodes of the grid represent the difference in the measured distance (in millimetres) of each feature/minutae from a common origin (labelled O) as obtained from the two images. Panels D and E show two ink prints that were deposited on paper using the same digit on different days. Once again, the position of each minutiae feature is identified, marked with a square and an equivalent grid structure containing the differences in the measured distances from the origin is reproduced in panel F. Scale bars correspond to 1 mm in all cases.

For each of the images shown in Figure 5, the bifurcations and ridge endings were located and marked by placing a small square of a contrasting colour on the image. The centre of the square was placed directly over the feature of interest (bifurcation or ridge ending). Lines were then drawn to link the centres of two neighbouring squares and to act as a guide for the eye. An easily identifiable ridge ending with very definite edges was used as an origin in each image and the difference in distance of each minutiae from this origin was calculated. The origin for each image is clearly marked with an “O”. Each image was transformed so that it had the same scale, 50 pixels = 1 mm. To line up the images, the ink print was moved and rotated about its origin. After the rotation and translation of the ink print, the locations of the minutiae were compared. The numerical values given in Figure 5c show the differences in the distance from the origin obtained from the two images for each feature. The difference in the measured distances have values that range from of 0 mm (at the origin) up to 0.40 mm and give an average value of the differences in the distance between the same two minutiae obtained from the two images of 0.08 +/ 0.04 mm (error bars correspond to two standard errors of the mean). The same exercise was repeated for two fingermarks that had both been deposited using ink on paper. In this case, the same digit was used to deposit what should be identical marks on the same sheet of paper on different days. Figures 5D and 5E show these two prints with the minutiae marked in the same way as in panels 5A and 5B. The data showing the differences in the distance from the origin of each feature in the two images are shown in figure 5F. It was found that the variations in the positions of the same minutiae varied by 0.22 +/- 0.06 mm between the two ink prints in figure 5D and 5E.

A recent study by Sheets et al [15] demonstrated that the distortions in the pattern of minutiae from what should be identical fingermarks deposited on flat surfaces at different times varied by distances up to the width a single friction ridge when multiple marks were collected from the same individual under conditions of varying pressure and on different substrates. The width of the ridges in the fingermarks shown in figure 5 is 0.220 +/- 0.050 mm. Based upon the observations made by Sheets et al. and our simple test using ink deposited prints, the distortions between the ToF-SIMS and ink print images reported here are well within the limits of natural variation of fingermark morphology. This indicates that the techniques that were used to extract the fingermarks from the surface of the rounds and stitch together the resulting images does not cause unacceptable distortion of the fingermarks. Our comparisons between ink prints and ToF SIMS images and the study by Sheets et al. therefore give us a high level of confidence that the imaging and stitching techniques used here are perfectly capable of reliably reconstructing an “unknown fingermark” that has been deposited on a curved surface.

Although the results of the experiments presented above are extremely encouraging, there are clearly a number of limitations associated with the work. Firstly, the use of only two male donors represents a shortcoming of the present study; a greater number of donor types (sexes, ages and ethnicities) would be required to assess the validity of the techniques presented here. Moreover, while the use of unfired casings has allowed us to demonstrate the feasibility of using ToF-SIMS to image fingermarks on curved surfaces, the technique would need to be applied to fired casings in order to determine how distortions in shape during firing, the effects of heating and the contamination of the surface by gunpowder residues affects the quality of the images that can be obtained from these samples. These experiments will be the subject of future work.

An additional limitation relates to the effects of environmental factors. For example, exposure to the elements at the scene of a crime is likely to cause degradation of fingermarks. In the present work, the rounds were stored in carefully controlled conditions that are extremely unlikely to be replicated at a crime scene. Further work therefore needs to be undertaken to assess how exposure of samples to aqueous environments, high humidities and UV radiation affect the surface of the bullet casings and the deposited marks, as well as the ability to acquire images from them using ToF SIMS. The techniques described here should also be applied to “natural” fingermarks, where the composition of the fingermark secretions is not carefully controlled and where fewer inorganic salts are likely to be present.

A final limitation of the ToF SIMS technique is the relatively high costs associated with running the instrument when compared to conventional superglue fuming and other fingermark recovery techniques. Each sample/round also took ~12 hours to image including the time to set up the experiment and pump down the UHV chamber, which is a serious investment of time per casing. ToF-SIMS would therefore only be used to help solve major crimes or under conditions where other techniques are thought likely to fail, where the extra sensitivity was required and/or where a high chance of subsequently retrieving other types of evidence (such as DNA) would be desirable. There is a clear need for additional work to address all of these potential issues and also to determine whether a fingermark extracted from a bullet casing using ToF-SIMS can be successfully identified when compared to a fingerprint database.

While ToF-SIMS clearly has a number of limitations, we have demonstrated that it is a powerful tool for extracting fingermarks that would otherwise not be revealed by conventional development techniques. This is particularly true when it is combined with the bespoke rotation stage and image stitching algorithms that were developed as part of this study. While this work has concentrated specifically on the application of sample rotation to the study of fingermarks using ToF-SIMS, we anticipate that the same technique could be applied to a range of different curved sample geometries. This might include the study of the surface coatings on catheters used in medical applications or analysis of engine parts using ToF-SIMS, for example. The sample rotation technique applied here is also not restricted to a single instrument and we anticipate that similar rotation stages could be developed to image samples with curved geometries using other surface science techniques such as X-ray Photoelectron Spectroscopy and Raman Microscopy. These techniques are also often limited by their ability to image samples that are relatively flat and the development of similar rotation stages would significantly improve their range of application.

Conclusions

A bespoke ultra-high vacuum (UHV) rotation stage was developed for imaging latent fingermarks on the surface of cylindrical bullet casing (Webley MkII round) surfaces using Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The images obtained from unfired casings were found to display clear finger ridge detail and the locations of sweat pores on samples that showed no evidence of fingermarks when developed using cyanoacrylate fuming and subsequent staining with Basic Yellow 40. ToF-SIMS was used to identify the presence of a number of different components that are present in eccrine fingertip secretions. It was also shown to be a non-destructive technique with no evidence of image degradation observed over a period of seven months, even when samples were repeatedly exposed to UHV conditions. The lack of changes in the surface chemistry during imaging suggest that the casings could be used to extract other kinds of evidence (e.g. DNA) following the use of ToF SIMS. Moreover, the technique allows for different sized scans of the surface to be performed - ranging from small targeted regions that are only a few hundred microns across up to the entire curved surface of the bullet casings.

Conflicts of Interest

The authors do not have any conflicts of interest with regards to the work presented in this article.

Author Contributions

CJL was responsible for collecting the data, writing the programs used to drive the rotation stage and stitch the ToF-SIMS image strips together to form composite images. DJS and LJ helped with the data acquisition, modification of the ToF-SIMS instrument layout to accommodate the rotation stage and in writing the manuscript. AK was responsible for building the rotation stage. SRTB was involved in designing the project and writing the manuscript. JSS was responsible for project design as well as designing the rotation stage, coordinating all experimental activities and writing the manuscript.

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