Research Article

SURFACE and INTERFACE ANALYSIS

SIMS fingerprint analysis on organic substrates†

Steven J. Hinder* and John F. Watts

ToF-SIMS has been used in the analysis of latent fingerprints (dactyloscopy) with a view to its use in forensic and biomedical applications. Szynkowska *et al*. have demonstrated that SIMS can be employed to produce images of whole fingerprints on inorganic surfaces such as steel, brass and glass.[1] We demonstrate the detection of a range of exogenous materials in fingerprints including industrial lubricants, personal care products and pharmaceuticals on organic surfaces. We demonstrate fingerprint image acquisition on model substrate materials such as Si wafer and on more 'difficult' organic substrates such as polymeric coatings, paper and printed card.

SIMS images, even when acquired at low resolution, clearly delineate those regions associated with the underlying substrate materials and those from the latent fingerprint. Fingerprint images acquired by SIMS imaging are capable of visualizing the minutiae associated with fingerprints with high resolution. Such minutiae are the key latent fingerprint features that must be visualized so that a forensic fingerprint examiner may make an identification. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: time-of-flight secondary ion mass spectrometry; fingerprint analysis; fingerprint minutiae; imaging SIMS

Introduction

The surface of human skin is covered with many natural substances secreted from the eccrine, apocrine and sebaceous glands. The major secretion from these glands is water; however, both inorganic and organic substances are also secreted. It is these secretions that form the basis of much of the material left in a latent fingerprint. Dactylocopy is the branch of Forensic Science dealing with the examination of skin ridge impressions, but mainly latent fingerprints, for the purpose of identifying individuals. Currently the majority of the techniques developed to analyze latent fingerprints, such as dusting with powders or fuming cyanoacrylates, requires that a chemical or adhesive reaction takes place between the substances present in the fingerprint and the applied reagent. Typically, these techniques allow the latent fingerprint to be visualized and an image captured for the purposes of analysis and identification. However, such techniques suffer from the inevitable drawback that much of the potential chemical data present in the fingerprint is lost or compromised. The use of static SIMS provides us with the opportunity to both visualize the latent fingerprint and to concomitantly acquire high-resolution mass spectra of the latent fingerprint from which chemical information may be extracted.

Here, ToF-SIMS has been employed in the analysis of latent fingerprints on organic substrates with a view to its use in forensic (and possibly biomedical) applications. Szynkowska *et al*. have demonstrated that SIMS can be employed to produce images of whole fingerprints on inorganic surfaces such as steel, brass and glass.[1] Here, we are interested in utilizing the mass spectra resulting from fingerprint image acquisition as a means to identify the chemistry involved in the fingerprint material. We demonstrate the detection of a range of exogenous materials in fingerprints including industrial lubricants, personal care products and inorganic compounds. Although latent fingerprints acquired on model substrate materials such as Si wafer and Al foil are demonstrated, latent fingerprint images were also acquired on more 'difficult' organic substrates such as a PVdF/acrylic coating, paper and cling-film.

Experimental

ToF-SIMS

ToF-SIMS analyses of latent fingerprints were carried out on an ION-TOF GmbH (Münster, Germany) TOF.SIMS 5 instrument. A 25 keV Bi_3^+ primary ion beam delivering 0.35 pA of current was employed. Images were acquired at 128 × 128 resolution in the MacroRaster mode of operation. The 128 resolution was selected as it provides good image resolution within an acceptable timeframe, i.e. 2+ h per image acquisition. Superior quality images can be acquired employing higher resolutions but these require significantly longer acquisition times. Image data was acquired using 256 cycles per pixel point with 1 scan per pixel. A cycle time of 100 µs was employed.

When producing doped fingerprints ~0.5 ml of dopant, i.e. PCP, was applied to the little finger and rubbed into the skin employing the thumb. The finger tip was then allowed to 'dry out' for at least 5 minutes before the finger was lightly pressed onto the substrate of choice.

* Correspondence to: Steven J. Hinder, The Surface Analysis Laboratory, Faculty of Engineering & Physical Sciences (A1), University of Surrey, Guildford, Surrey GU2 7XH, UK. E-mail: s.hinder@surrey.ac.uk

The Surface Analysis Laboratory, Faculty of Engineering & Physical Sciences (A1), University of Surrey, Guildford, Surrey GU2 7XH, UK
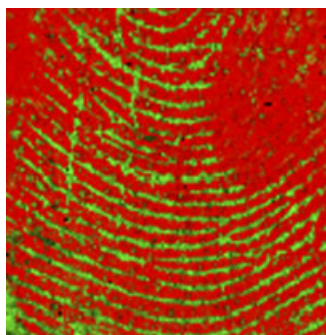
Figure 1. A 1 cm^2 mass selected ToF-SIMS image presented as a two-colour overlay image. The regions in red (low intensity) are from a latent fingerprint, while those in green (high intensity) are from the underlying substrate.

Results and Discussion

SIMS images, even when such images are acquired at low to moderate resolution, can clearly delineate those regions of the specimen associated with the underlying substrate material and those arising from a latent fingerprint. In Fig. 1 a SIMS image of a latent fingerprint (from a finger treated with a personal care product (PCP)) on an organic fluorocarbon-based coating is presented. The red (low intensity) regions observed in Fig. 1 contrast the intensity of the 181 u ion (tentatively assigned to $C_{13}H_9O^+$) over a 1 cm^2 region of the sample surface. Independent mass spectral analysis of the PCP, polymeric coating and 'clean' nondoped fingerprints (data not shown) indicates the 181 u ion is only observed in the PCP mass spectrum. It is clearly observed in Fig. 1 that the 181 u ion is confined to those regions of the sample surface associated with the latent fingerprint friction ridges. The green (high intensity) regions in Fig. 1 contrast the 133 u ion ($C_3H_2F_5^+$ fragment ion) originating from the poly(vinylidene difluoride) component of the polymeric coating employed as the substrate in this analysis. It is observed in Fig. 1 that the green (high intensity) regions are significantly narrower than the red (low intensity) friction ridge regions observed in Fig. 1. Typically, we find that individual fingerprint friction ridges are 200–400 µm in diameter, while friction ridge spacing is ∼100–200 µm. The ToF-SIMS image in Fig. 1 demonstrates that SIMS is clearly able to delineate between

the friction ridges features and substrate associated with a latent fingerprint.

SIMS mass spectra obtained from whole fingerprints, detailed fingerprint regions or even individual friction ridges often yield similar mass spectra. This is advantageous when chemical analysis of the fingerprint material is required, as 'real-world' samples are often not ideally flat and SIMS may only be able to analyze a limited number of friction ridge features. However, for an analysis or imaging technique to be of use for dactyloscopic purposes it must be capable of visualizing the minutiae (features associated with individual friction ridges) associated with latent fingerprints with good resolution. It is these minutiae that are the key latent fingerprint features required by a forensic fingerprint examiner to make an identification from a latent fingerprint. Minutiae such as bifurcations, terminals, dots, short ridges and enclosures are readily observed in the mass-selected ToF-SIMS images in Fig. 2. The SIMS images in Fig. 2 were acquired at 128 × 128 resolution over a 25 mm^2 region. Thus, the images are composed of 16,384 (each 39 × 39 um^2) pixels. Even at the moderately low pixel resolution and relatively large pixel size in Fig. 2, fingerprint minutiae are readily observed by employing ToF-SIMS imaging.

We have investigated fingerprints on both easy model substrates such as Al foil and Si wafer and more difficult substrates such as paper, cardboard and polymeric coatings (Fig. 1) with varying degrees of success (Table 1). Additionally, we have analyzed clean fingerprints and those treated with inorganic materials and organic compounds such as industrial lubricants and personal care products (Fig. 1). Clean fingerprints typically contain elements from perspiration, i.e. Na, K and Cl and fatty acid residues, one of the most common being squalene ($C_{30}H_{50}$, m.w. 410.39, see Schematic 1. Jickells and her colleagues have demonstrated that squalene oxidation can be used to track fingerprint aging.[2]

ToF-SIMS analysis of latent fingerprints bestows the added advantage that no processing of the fingerprint or substrate is required prior to analysis. The central image in Fig. 3 is that that would be expected if this sample was processed by a forensic scientist in a normal manner to visualize the fingerprint materials. In this sample, two fingerprints, one from a PCP and the other a fluorinated inorganic powder have been overlaid on a polyester-/polyurethane-based polymeric coating. Although the outer ridges of the individual fingerprints are observed in the central image of Fig. 3 the majority of the fingerprints are
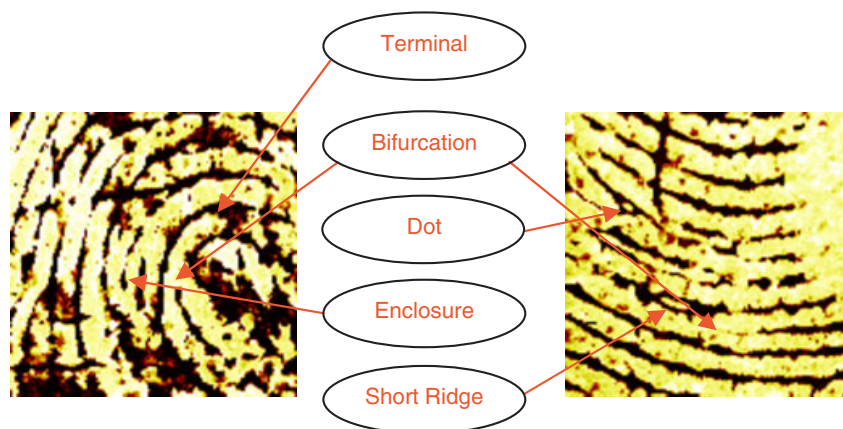

Figure 2. 25 mm^2 mass-selected ToF-SIMS images showing the minutiae associated with individual friction ridges in latent fingerprints.

Table 1. Author's comments on the effectiveness of SIMS imaging of latent fingerprints on the different substrates employed

Substrate	Comment on SIMS imaging effectiveness
PVdF coating	High quality fingerprint image obtained.
Si wafer	Very high quality fingerprint images are readily obtained.
Polyester coating	High quality fingerprint image obtained.
Carrier bag	Acceptable quality fingerprint image obtained, however, it is difficult to maintain the flatness of the substrate material.
Photocopier paper	Acceptable quality fingerprint image obtained, however, surface roughness and fingerprint material adsorption into the substrate is believed to lead to some loss of fingerprint image resolution.
Newspaper	Poor quality fingerprint image due to surface roughness and changes in the nature of the substrate material affecting fingerprint image resolution.
Cling-film	High-quality fingerprint image obtained once the substrate material is flattened.
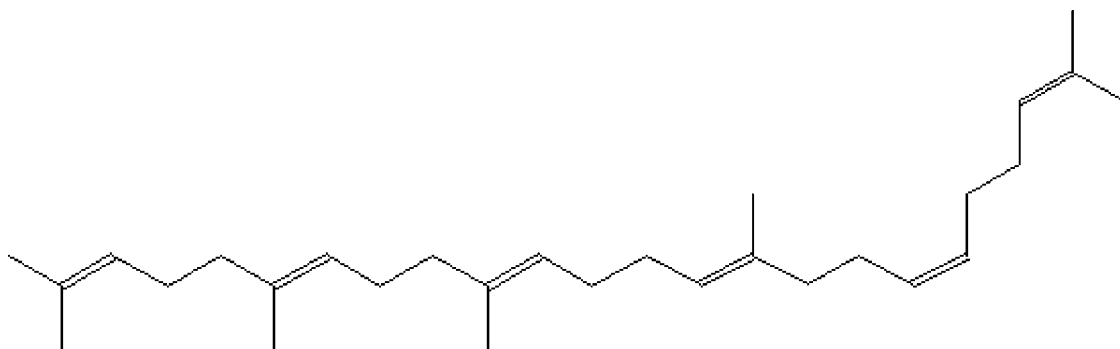
Scheme 1. The structure of squalene.

difficult to visualize due to their overlapping. However, using SIMS mass selected images for ions specific to each of the sample materials used to form the fingerprints, it is possible to extract latent fingerprint images of the individual fingerprints and thus eliminate the problems caused by the overlap. In Fig. 3, the image on the left is extracted from the ion at 97 u originating from the PCP while the image on the right is extracted from the F^- ion at 19 u which originates from the inorganic powder. The mass-selected images in Fig. 3 possess very good ridge detail even though the data was only acquired at a resolution of 128×128 pixels.

The ToF-SIMS mass-selected images presented in Figs 1 and 3 were acquired on what might be deemed idealized or model organic substrates in that the coatings employed were applied to sheet aluminium and their formulations contain components included to provide the coatings with flat, well defined surfaces, i.e. flow aids. In Fig. 4, a number of ToF-SIMS mass-selected images acquired on substrates known to be difficult, forensically speaking, are presented. In Fig. 4a, a two-colour overlay of a PCP fingerprint [in green (high intensity)] on a supermarket carrier bag [in red (low intensity)] is shown. The PCP fingerprint ridge detail is clearly observed, while the carrier bag substrate is clearly delineated. Indeed, the carrier bag region of the image in Fig. 4a clearly shows evidence of the substrates surface topography. In Fig. 4b, a more complete PCP containing latent fingerprint image on white photocopier paper is presented. Although the photocopier paper is fibrous in nature at the area (1.5 mm^2 $\times$ 1.5 mm^2) and pixel size ($\sim$120 µm^2 $\times$ 120 µm^2) employed the nature of the substrate does not affect greatly the quality of the latent fingerprint image. In Fig. 4c, a printed newspaper has had a PCP fingerprint applied to it such that the fingerprint sits astride both white typeset (right hand side) and coloured print (left hand side) regions of the newspaper. It is clearly observed in Fig. 4c that the clarity of the fingerprint detail may be influenced by the nature of the underlying substrate with, in this case, the white typeset region of the specimen providing superior and more intense fingerprint detail than the colour print region of the specimen. Employing

Figure 3. 15×15 mm^2, 128×128 resolution ToF-SIMS negative ion images of two overlaid finger prints on a polyester/polyurethane primer coating.
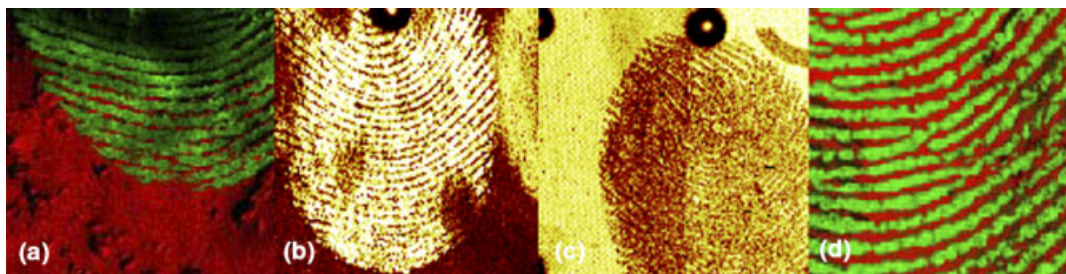
Figure 4. A montage of ToF-SIMS mass selected latent fingerprint images from a number of organic substrates: a. PCP on supermarket carrier bag; b. hand cream on white photocopier paper; c. PCP on printed newspaper; and d. industrial lubricant on cling-film.

ToF-SIMS imaging we were able to obtain excellent resolution mass selected images on a particularly difficult organic substrate, cling-film, as presented in Fig. 4d. A latent fingerprint containing traces of an industrial lubricant was applied to cling-film, and then the cling-film was teased out and stretched onto the SIMS instruments sample platen to make it as flat as possible. Indeed, the very nature of the material made it amenable to this procedure allowing a very flat specimen to be obtained. Figure 4d possesses very good fingerprint ridge [in green (high intensity)] definition and the delineation between latent fingerprint and cling-film substrate is excellent with fingerprint minutiae features being readily observed.

Conclusion

We have demonstrated that ToF-SIMS imaging of latent fingerprints can be performed on contrasting organic substrates. We have also demonstrated that SIMS imaging of fingerprints provides sufficient ridge and fingerprint minutiae detail to allow its use for forensic identification purposes. ToF-SIMS imaging of latent fingerprints also provides mass spectrometric data concerning the chemical composition of the fingerprint. These findings may allow fingerprint mass spectrometric data to be used in forensic applications.

References

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