Full length article

Silver-assisted development and imaging of fingermarks on non-porous and porous surfaces

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A B S T R A C T

In order to deal with the range of surfaces encountered in crime scenes and items associated with crimes, forensic fingermark examiners must have access to a range of latent mark enhancement techniques, each compatible with a particular type of surface. Consequently, the development of techniques with universal or even wide-ranging surface compatibility would be valuable to law enforcement.

Herein, we describe a one-step silver sputtering method for the enhancement of latent fingermarks on plastic, glass, paper and metal substrates. This method allows for the ridge pattern to be captured for human identification purposes and, more importantly, for the downstream mass spectrometric imaging of the fingermark in order to display the spatial distribution of common endogenous and exogenous substances such as illicit drugs

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1. Introduction

Fingermarks detected at crime scenes are often crucial to an investigation as they provide identifying information regarding the donor. Furthermore, with appropriate chemical analysis, compounds within fingermarks can be identified, which offers the potential to reveal circumstantial, non-biometric evidence in the form of substances that the donor has touched or ingested prior to deposition of the fingermark. Analytical techniques based on mass spectrometry (MS) are valuable in this application. These range from non-imaging approaches (e.g., swabbing the mark followed by gas chromatography-MS [1]) to techniques involving mass spectrometry imaging (MSI) with spatial resolution sufficient to demonstrate fingermark ridge pattern detail (e.g., time of flight-secondary ion MS [1], desorption electrospray ionization MS [2], matrix assisted desorption ionization MS [1,3,4] and laser desorption ionisation techniques [5]). Substances detected have ranged from environmental contaminants, such as quaternary ammonium compounds and siloxanes, to illicit drugs and their metabolites and many endogenous compounds [2–5].

Substrates onto which fingermarks are typically deposited vary in composition, and are divided into three categories – porous (e.g. paper), semi-porous (e.g. polymer banknotes) and non-porous (e.g. glass or metal). A range of particular protocols for enhancing or developing latent fingermarks (i.e., marks not visible to the naked eye) on each of these surfaces is available to the forensic fingermark examiner [6]. Unfortunately, there is no one universal technique that can be applied to visualize latent fingermarks on all surfaces.

Techniques for the detection of fingermarks by metal deposition are available to the fingermark examiner, such as multi metal deposition (MMD) [7] and vacuum metal deposition (VMD) [8]. These are relatively complex techniques or involve multiple preparation steps. For example, MMD requires the immersion of substrates in colloidal gold (Au) and subsequent enhancement using a physical

developer [7]. For this preparation the Au particle size, homogeneity and concentration as well as the pH and temperature of development are critical [7]. VMD requires the placement of a latent mark into a high vacuum chamber in which a metal (or metals) is vaporized at high temperature for condensation onto the fingermark [8].

We report here a variant of metal-assisted enhancement of latent fingermarks that involves simple sputter-coating of silver (Ag) onto the fingermark and its substrate. In metal sputter-coating, a metal target is bombarded with heavy gas ions, such as those in an argon (Ar) plasma. Sputtering occurs when the collisional energy transferred to the metal target exceeds surface binding energy and metal atoms are ejected from the target [9]. Traditionally, sputter-coating of substrates with Au, Ag and platinum (Pt) is used prevent sample charging and increase thermal conduction in electron microscopy, although there are reports of sputtered coatings of Au, copper, Pt and zinc being used to enhance latent fingermarks [10,11]. More recently, sputter coating of these metals has found application in MSI [12–14], where mass spectra are acquired in a rastered grid across samples that range from tissue sections to fingermarks. MSI is an emerging technique of interest for forensic applications as it allows the spatial mapping of chemicals trapped in fingermarks, including drugs, explosives, wax esters (WE), triacylglycerols (TAGs), and fatty acids (FAs) [12,13]. In addition to aiding molecular ionization, Ag-assisted MSI has several advantageous features, including the introduction of Ag clusters at regular mass intervals, allowing internal recalibration of MSI data, and the formation of Ag adducts with FAs, WEs and sterols [12–14]. During MSI experiments in our laboratories, it was observed that Ag sputter coatings create significant visible contrast between the substrate and deposited fingermark material. This was observed previously by Lauzon et al., specifically for the MSI analysis of paper and glass samples [12]; the present technical note is an exploratory extension of Lauzon's work. Here, we show that sputter coating with Ag coats the ridges (unlike VMD that coats the valleys) allowing for MSI analysis of ridge contents in fingermarks. Our method does not require the addition of matrix (which can degrade spatial resolution), uses Ag coatings for accurate mass identification and allows high fidelity optical imaging of ridge patterns.

We hypothesised that Ag sputter coating may i) be a viable addition to the range of metal deposition-based fingermark development protocols currently used in forensic science, ii) be amenable to a broad range of surfaces, and iii) facilitate the MS and MSI of endogenous and xenobiotic molecules in fingermarks.

The present work demonstrates that this one-step technique does potentially offer benefits, both as an alternative to the complex development procedures currently used to visualize fingermark ridge pattern and as a second tier of data that can be overlaid with fingermark morphology to provide mapping of small molecules of interest. We present the use of ≈15 nm sputter-coated Ag layers to develop and image fingermarks on porous (paper, cardboard and Parafilm^{TM}), semi-porous (polystyrene, PS and polypropylene, PP based plastic objects) and non-porous (glass, aluminium and silicon wafers) substrates. Subsequent interrogation of fingermarks on porous (card) and non-porous surfaces (silicon piece) by MSI was used to map fingermark-specific compounds and, for the first time, successfully detect flunitrazepam in latent fingermarks on glass.

2. Materials and methods

2.1. Fingermark deposition

Fingermarks from a female donor were deposited as a depletion series onto various substrates. The index finger was wiped once across the forehead and then consecutively deposited on various substrates (n = 8) in no particular order. Marks were sputter coated within 10 min of deposition. Prints were photographed after Ag deposition and then subjected to analysis by MSI.

2.2. Ag sputter coating

Substrates were coated with an approximately 15 nm thickness Ag layer using a Q300T-D sputter coater equipped with a quartz crystal microbalance (QCM, Quorum Technologies, United Kingdom). Ag of 99.9999% purity was used.

2.3. Flunitrazepam-spiked fingermark

The spiked fingermark was prepared by rubbing a male donor's finger across the back of the donor's neck and then rubbing the finger in a residue prepared by applying 50 μL of flunitrazepam solution in acetonitrile (200 μg/mL) to a microscope slide and then allowing it to dry. The fingermark was subsequently deposited on a glass slide and sputter-coated with Ag prior to MSI analysis.

2.4. Scanning fingermarks

After fingermark deposition and sputtering, substrates were scanned at 4800 dpi resolution using an Epson Perfection V600 flatbed scanner (Officeworks, Australia). After scanning, the substrates were attached to a pre-spotted anchor chip adaptor plate (Bruker Daltonics) with double sided carbon tape and MSI measurements were performed.

2.5. MSI analysis

Mass spectra were collected using an ultrafleXtreme MALDI-TOF/TOF mass spectrometer, equipped with a 2 kHz pulsed Nd:YAG laser, in reflectron positive mode in the mass range m/z 20–1500 (Bruker Daltonics, Bremen, Germany). Data acquisition used flexControl 3.4.78 software and data analyses were performed using flexImaging 3.4 and SCiLS Lab (SCiLS GmbH, Bremen, Germany), resolution of the MSI was 60 μm. Laser power was user-optimised, as required, for each Ag-coated substrate investigated. Ag isotopomers were used as internal calibrant points, as in Guinan et al. [13].

3. Results and discussion

Fig. 1 displays manually grey-scaled optical scans of fingermarks deposited onto example substrates and sputter-coated with Ag (≈15 nm). In each example, a clear contrast was observed between the substrate and the fingermark. On the semi-porous (PP plastic bottle cap, Fig. 1A) and non-porous (aluminium, Fig. 1B and polished silicon, 1D) substrates analysed in this sample set, clear ridge and pore detail was observed. For example, microscope images at both 0.75 and 2 x magnification, respectively, clearly showed visible pores and minutiae for Ag-coated semi-porous PS based coffee lids (Fig. S1A-B). In contrast, for porous materials such as paper (Fig. 1C), cardboard (Fig. 1E) and Parafilm (Fig. 1F), clear ridge detail is shown but the pores become less visible: these fingermarks were fresh (10 min old) and as such it is expected that older fingermarks may be more difficult to image in this way, due to continual absorption of the deposit into the paper matrix[15]. The absence of clear pore structure is further demonstrated by the Parafilm fingermarks where pores were not clearly visible (Fig. S2A-B). However, the ridge detail itself (yellow in colour) was evident with respect to minutiae. A Ag-coated PP bottle cap lid (Fig. S3A) and aluminium foil (Fig. S3B) are also shown. Fingermarks deposited onto aluminium foil (Fig. 1B and Fig. S3B) show clear contrast and the presence of both minutiae and pore patterns. Finally, contrast between the