Potential Applications of Scanning Probe Microscopy in Forensic Science

G S Watson¹ and J A Watson
Nanoscale Science and Technology Centre, School of Science, Griffith University, Kessels Rd, Nathan, QLD, 4111 Australia
E-mail: G.Watson@griffith.edu.au

Abstract. The forensic community utilises a myriad of techniques to investigate a wide range of materials, from paint flakes to DNA. The various microscopic techniques have provided some of the greatest contributions, e.g., FT-IR (Fourier-transform infrared) microspectroscopy utilised in copy toner discrimination, multi-layer automobile paint fragment examination, etc, SEM-EDA (scanning electron microscopy with energy dispersive analysis) used to investigate glass fragments, fibers, and explosives, and SEM in microsampling for elemental analysis, just to name a few.

This study demonstrates the ability of the Scanning Probe Microscope (SPM) to analyse human fingerprints on surfaces utilising a step-and-scan feature, enabling analysis of a larger field-of-view. We also extend a line crossings study by incorporating height analysis and surface roughness measurements. The study demonstrates the potential for SPM techniques to be utilised for forensic analysis which could complement the more traditional methodologies used in such investigations.

1. Introduction
Various techniques utilised by forensic scientists allow detailed studies of a multitude of materials. As science advances so do the tools of the trade. Any additions to these techniques may enhance the existing results building upon the evidence in order to convict or acquit a suspect in a crime. This study expands upon a relative newcomer to the Forensic field, Scanning Probe Microscopy (SPM), demonstrating its various modes of operation. The merits of SPM lie in its ability to characterise surfaces based on topographical features as well as chemical and physical properties.

2. Experimental details
2.1. Materials preparation
The fingerprints were deposited onto new, clean microscope slides, with no further alteration or manipulation. The surface lines were created on glossy photographic printer paper using a standard blue ink ball-point pen.

2.2. SPM instrumentation and probes
The probes utilised for this study consisted of a beam-shaped lever with an integral conical tip attached at its free end. Beam-shaped Si levers were supplied by Ultrasharp NT-MDT. The length (L), width (w), thickness (t), tip height (h), normal spring constant (kN) and tip radius of curvature (RTip) values were 350 μm, 35 μm, 1 μm, 15-20 μm, 0.01-0.08 Nm⁻¹ and 20-30 nm, respectively, as supplied by the manufacturer.

Forces acting between the tip and the sample will result in deflections of the cantilever. The lever bends vertically, i.e., in the ±z-direction (normal to the sample plane), in response to attractive and/or repulsive forces acting on the tip. When the tip is in contact with a sample, the deflection of the lever from

¹ To whom any correspondence should be addressed.
its equilibrium position is proportional to the normal load applied to the tip by the lever. As well as the measurement of normal forces, the simultaneous measurement of frictional forces is also possible as a result of a twisting motion of the lever from its equilibrium position [2]. Depending on the stiffness of the lever (i.e., \( k_N \) value), it may sense the tip/sample forces in the range from \( 10^{-6} \) to \( 10^{-12} \) N. As the instrument is capable of measuring such small forces with high spatial resolution, the study of local surface chemistry is possible [3].

During this study, the surface analyses were carried out in contact mode using the ThermoMicroscope Explorer and Discoverer instruments, with 130×130 and 70×70 \( \mu \)m\(^2\) tripod scanners, respectively, each with a z-range of ca. 9.7 \( \mu \)m. The experiments were carried out under air-ambient conditions with a relative humidity of 55% and a room temperature of 25ºC and under water (Milli-Q).

3. Results and discussion
3.1. Print analysis
3.1.1. Analysis in air. A freshly deposited fingerprint was imaged in the contact mode with a Si probe (nominal spring constant, \( k_N \), ca. 0.03 Nm\(^{-1}\)) in an air ambient environment. The resultant images (loading force, \( F_{Load} = 14 \) nN) are shown in figure 1. The force-calibration used to determine these values can be found in the literature [4, 5]. The transfer of material from the papillary ridges to glass is apparent. The deposits consist of a complex mixture of organic and inorganic components e.g., sodium, chloride, and amino and fatty acids, respectively, just to name a few [6, 7]. These contaminants adhere to most surfaces and analysis is generally carried out using the powder technique.

The Root-Mean-Square (RMS) surface roughness over a 40×40 \( \mu \)m\(^2\) area on the print and glass surface was found to be ca. 280 nm and 45 nm, respectively. By applying an artificial light source to the topographical image, the granular details are further enhanced (figure 1 (b)). Figure 1 (c) shows a lateral force image revealing the extent of frictional differentiation between the two interfaces. Lighter regions reveal higher frictional interactions. This has been verified utilising friction loop analysis (data not shown).

![Figure 1](image1.png)

Figure 1. (a) Topographical image revealing fingerprint residue deposited on a glass surface. Part (b) shows the surface features in greater by applying an artificial shadow, and (c) reveals a higher lateral contrast on the fingerprint. The surface was imaged in air.

3.1.2. Analysis in liquid. By submerging the sample under liquid, in this case (Milli-Q) H\( _2 \)O, any meniscus surface forces which may dominate (particularly where both the surface and probe are highly hydrophilic) are eliminated. There was no discernable difference in either the topographical or frictional data between analysis in air and liquid. The results illustrate the capability of the AFM for imaging such samples in an aqueous environment.

3.1.3. Force-vs-distance analysis. The strength of the adhesive interaction will depend on the degree of hydrophobicity/philicity on both the tip and surface. For example, hydrophilic surfaces in contact can form a meniscus bridge with adhesive forces greater than that when both surfaces are hydrophobic [8]. The adhesive forces in liquid environments are dependent on a number of factors such as pH of
the medium, electrostatic interactions, van der Waals interactions, and on steric/topographic effects [9].

Representative f-d curves illustrating and contrasting outcomes of analyses of the print and glass regions, in air and under water are shown in figure 2 (a) and (b), respectively. The difference in scale is a result of the meniscus layer dominating during experiments performed in air (a). The glass and Si tip exhibit higher hydrophilicity. The greater meniscus force dominates (e.g., snap-on features and adhesive interactions). The meniscus contributions are eliminated under water thus a small adhesive force is seen in (b) on the glass surface. The similar adhesive forces measured on the print in water and air arises from contact with the myriad of contaminants on the fingerprint (e.g., various residues, oils and waxes). The hysteresis observed in the f-d curves does not significantly affect the adhesion outcomes.

![Figure 2. Representative f-d curves obtained in (a) air and (b) under water (Milli-Q) on a fingerprint and on the glass slide.](image)

### 3.2. Print-on-print analysis

It is possible to investigate two fingerprints which overlap. A definite edge can be found revealing both prints and the underlying surface (glass). Figure 3 shows (a) topographical and (b) artificially shaded images of the two prints intersecting and the glass surface. The topographical images reveal the features; the shaded image and lateral force in (c) and 3-dimensional image in (d) clearly discern the interfaces. Again, the frictional signal is higher on the print (friction loop verified).

![Figure 3. Topographical image of two fingerprints crossing (a) and the same image artificially shaded in (b). A lateral force (c) and 3-dimensional (d) image.](image)

### 3.3. Step-and-scan analysis

Larger scan areas of the print deposits can be acquired using a step-and-scan function. Figure 4 illustrates this below with 40 images of 70 μm × 70 μm scan areas. Each sub image consists of 100×100 data points. The images were obtained at scan speeds of 1500 μms⁻¹.
3.4. Line crossing analysis

A pen will deposit a thin layer of ink. Figure 5 shows height profiles, topographical and lateral images of an intersection between two drawn lines, with the underlying paper also visible. The analysis was carried out under air ambient conditions. The line profile in (a) reveals the average height of the ink to be ca. 200 nm, with a similar result across the ink on ink profile shown in (b). Thus the height information can be used to determine the writing history of the sample. Figure 5 (c) shows an artificially shaded image where the ink deposits appear ‘smoother’. This was verified with the RMS surface roughness over a 20×20 μm² area on the paper to be ca. 65 nm, and the ink equalling ca. 45 nm.

The f-d curves shown in figure 6 demonstrate a lower adhesive interaction between the probe and paper. The results indicate that the tip-ink meniscus forces are higher than tip-paper interactions. The probe may also have a larger contact area with the ink at the same loading force. The snap-on feature (figure 6 (b)) also indicates a larger meniscus layer and/or deformation of the ink upon tip contact.
4. Conclusion

The SPM is now a crucial tool in many laboratories, however this technology/method has been utilised in only a handful of forensic applications, including an examination of line crossings on documents [10] and the characterization of residual hot-spot reaction sites [11, 12].

Potentially the SPM could be employed as a complementary technology for forensic studies offering non-destructive sample analysis with micro-to-nanometre resolution. Adhesive and lateral (frictional) contrast, 3-dimensional topographical information and analysis in air, fluid or gaseous environments facilitate this technique for a wide range of analyses.

Our study shows that the information output of the SPM technique, discriminating adhesive, topographical and frictional contrast can be used for qualitative and quantitative analysis of samples commonly used in forensic science investigations. One of the limiting constraints of the SPM method is the small scan size and data acquisition time. Incorporation of large size scanners, multi-arrayed lever systems and step and scan implementation would significantly reduce these constraints.

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