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Determining the order of deposition of natural latent fingerprints and laser printed ink using chemical mapping with secondary ion mass spectrometry

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Abstract

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) chemical mapping was used to investigate the order of deposition of natural latent fingerprints and laser printed ink on paper. This feasibility study shows that sodium, potassium and C_3H_5 positive ions were particularly abundant endogenous components of the natural fingerprints and also present in the paper examined, but were mostly absent in the laser printed ink. Mapping of these ions enables the observation of friction ridges from latent prints on the ink surface, only when a fingerprint was deposited above the layer of ink. As a demonstration of proof of concept, blind testing of 21 samples from three donors resulted in a 100% success rate. The sensitivity of this technique was investigated within this trial through the examination of up to fifth depletion fingerprints and ageing of up to 28 days. Migration of fingerprint and paper components to the ink surface, although observed with increased ageing time, was not found to compromise determination of the deposition sequence.

Keywords: Time-of-flight secondary ion mass spectrometry (ToF-SIMS); fingerprints; laser printing; paper; questioned documents; forensic science

1. Introduction

The development of a scientific understanding of fingerprint evidence is critical in ensuring continued confidence in forensics and validity of investigative methodologies [1-5]. Until recently, long-used forensic science techniques have been employed to provide evidence in criminal trials without the reliability being questioned, however, high profile cases and publicised errors have resulted in an increased scrutiny of the discipline [6, 7]. This is especially the case with latent fingerprint examination, where interpretation of fingerprint evidence is heavily dependent on the skill and expertise of latent print examiners [8]. Consequently, blind proficiency tests are now being recommended in favour of reference to experience or training [9]. Detection of fingerprints on absorbent materials such as paper is further complicated by the heterogeneous chemistry and morphology of this porous material, as well as by the rapid absorption of components from the surface into the paper, which occurs within seconds after deposition [10]. Penetration and lateral absorption of fingermarks also depends on the chemical components of a deposited print, which varies in relation to the person, their emotional state, food consumption and grooming regime. Studies have shown that depth of penetration of fingermarks varies with types of paper, with a good correlation between penetration depth and quality of chemically developed prints [11-15]. Establishing the depth of penetration of prints into surfaces, as well as order of layers in, for instance, overprinting with text or images, can provide considerable assistance to crime-scene investigations by providing an insight into the history of documents for forensic studies. In cases such as fraud or counterfeiting it can be imperative to know whether a fingerprint has been deposited before or after the paper is printed with compromising material, and therefore be able to assess whether a suspect is associated with the printed evidence. This is currently impossible to determine because existing, commonly implemented development techniques using ninhydrin or its analogues utilise a solution that permeates through an entire document and therefore cannot be used to information on the deposition sequence of the fingerprint and ink [10, 16].

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is one of the most sensitive of all laboratory surface analytical techniques, showing potential in the examination of

fingerprints for analysis of constituent metals and contaminants present [17-20]. ToF-SIMS provides detailed chemical and spatial information of the top few nanometres of a surface, and has shown its ability to capture images and extract chemical data in a minimally invasive manner, with only the first two monolayers being ablated off a surface [21-23]. This implies that the integrity of the print is not entirely compromised, and should potentially allow for additional extraction of information from the fingerprint; an important factor in forensic investigations. MeV-SIMS, a technique in development that utilises an MeV primary beam and operates in atmospheric conditions, has also demonstrated clear imaging of fingerprints and depth profiling capabilities. Exogenous components of moisturiser-doped fingerprints were mapped in sequenced fingermarks and pen ink marks on paper, giving depth information where other imaging techniques had provided limited results [24, 25].

This paper presents proof of concept and a systematic methodology for the use of ToF-SIMS chemical mapping as a reliable technique in establishing the order of sequencing of laser printed ink and natural, latent fingerprints on paper. As no grooming procedure was utilised to collect fingerprints; samples were not intentionally biased to eccrine or sebaceous deposits, nor doped with personal care products. This study therefore represents the first systematic examination wherein endogenous components of the fingermark are used as elemental and molecular markers. Variation of these markers with donor and presence or migration in depleted and aged fingermarks is also assessed in relation to discrimination of fingermarks deposited above or below a printed layer.

2. Experimental

2.1. SEM-EDX analysis and sample preparation

Analysis of 80gsm (Lyreco Premium) A4 printing paper and a 14 day-old sample of ink was conducted in a Zeiss Supra 35VP field emission scanning electron microscope (FEG-SEM), coupled with an Oxford Instruments Inca energy dispersive X-ray analyser (EDX). The black ink sample was printed using an HP LaserJet P2055 and a Longbow toner cartridge with factory default settings of fast resolution 1200 dpi. The SEM-EDX was operated under high vacuum conditions and samples were mounted on aluminium stubs using carbon-loaded pressure sensitive adhesive and coated with a thin layer of gold prior to analysis. Imaging

and elemental composition assessment was conducted at 20 kV under varying magnifications.

The component layers to be examined: paper, printed ink, and a set of natural fingerprints (the latter were deposited on silicon wafer) were analysed individually within ToF-SIMS for initial evaluative purposes. No grooming procedure was used to collect fingerprints; therefore samples were not doped with personal care products or intentionally loaded with eccrine or sebaceous secretions. Donors were, however, requested not to wash their hands for at least 30 minutes prior to deposition, and fingertips were lightly rubbed together to improve distribution of deposit prior to fingermark deposition from index, middle or ring fingers. This procedure has been utilised in previous studies in order to collect fingerprints approximating natural chemical composition [5, 26, 27].

2.2. SIMS analysis

Secondary ion mass spectra and images were obtained using a Kore Technology Ltd. SurfaceSeer ToF-SIMS spectrometer equipped with an $^{114}\text{In}^+$ primary ion source (FEI Liquid Metal Ion Gun). The spectrometer was operated in positive mode with 25kV-applied voltage and a 1 μA current. Secondary ions were analysed in a reflectron mass spectrometer and detected with a dual microchannel plate assembly. Flight times were recorded with a 0.5 ns time-to-digital converter. Mass spectra acquisition time was set at 40 seconds at a magnification of x100, and well-defined positive ion peaks on these spectra were used to select mapping regions. These are highlighted in Figure 2, and correspond to characteristic elemental (Na, K, Ca, Si) and molecular (CH_3 , C_2H_3 , C_2H_5 , C_3H_5 , C_4H_7 , $\text{C}_3\text{H}_5\text{N}$, SiOH) positive ions in the fingerprint, ink and paper. Relatively quick 40 minute 512 x 512 pixel chemical maps were obtained at 20 cycles per pixel for 4 frames, with multiple areas scanned per sample.

2.3. Blind trials of fingermark – ink deposition sequence discrimination

A series of natural, latent fingerprints for blind test studies were collected from one female and two male donors over a period of 10 days on the same batch of standard A4 printing paper. Some fingermarks were applied over a layer of laser printing (fingermark over ink:

FOI), while other marks were deposited on plain paper and subsequently printed over with laser ink (fingerprint under ink: FUI). The laser ink was deposited using the conditions outlined in section 2.1, and the time between fingerprint deposition and ink printing was varied, as detailed in Table 1. Samples were initially aged naturally together in a filing cabinet in a heated office, with no particular care taken to avoid contact with other surfaces, in an approximation of 'pseudo-case' scenarios. After ageing, the samples were stored separately in arbitrarily numbered polyethylene sample bags (packaging day) then transferred to the analyst, who was given the sample number information and no additional details of the fingerprinting process. Packaged samples were stored in a temperature-controlled laboratory at 20-25°C prior examination by ToF-SIMS (analysis day).

Table 1. An outline of the paper-fingerprint-ink samples produced for blind trials

3. Results and discussion

Figure 1 (a) shows an SEM image of paper and fused laser-printed ink on the paper surface. Paper fibres, voids and filler aggregates are visible at low magnification, with the crystalline structure of the filler and variation in surface texture of fibres becoming more discernable at increasing magnifications. EDX spectra (not presented) indicated the presence of calcium, consistent with filler aggregate composition of calcium carbonate, used during paper manufacture in both ground and precipitated forms [28, 29]. Varying quantities of sodium and chlorine were also observed, representing high sodium salt levels generally associated with the papermaking processes [30].

Figure 1 a, b. SEM images

Surface images of the ink additionally show irregularities and voids in the fused toner particles (Figure 1a). Elemental analysis showed lower sodium concentrations in the ink with respect to those in the paper, but high amounts of iron and silica. Calcium was also detected, and Figure 1(b) presents an example of crystalline calcium carbonate, a component of the underlying paper surface, which is visible through the voids in the ink.

Figure 2. Stacked SIMS mass spectra

While EDX analysis is limited to elemental identification, ToF-SIMS facilitates the examination of both elemental and molecular distributions, since characteristic secondary molecular ion fragments and elemental ions can be detected simultaneously. Chemical mapping of the paper, printed ink and fingerprints separately prior to the FOI/FUI blind trials therefore enabled an accurate determination of components in each that allowed for discrimination. Some characteristic species are highlighted in Figure 2, with the maps in Figure 3 showing the respective positive ions accrued on a paper-ink interface in S39. Although ion detection appeared to be limited towards the peripheries of the maps, abundance/sensitivity (relative to overall brightness of mapped ion) and ridge pattern identification was still possible.

Quaternary nitrogen ($\text{C}_3\text{H}_8\text{N}^+$) and calcium were both recognised as constituents of paper, which are used as additives during its manufacture [30]. Conversely, silicon and its associated molecular ion SiOH^+ were observed in the laser ink/toner. In contrast to EDX results, iron was not present in the laser printed sample, suggesting that the pigment was entirely embedded in fused silica. High counts were consistently observed for the sodium, potassium and C_3H_5 positive secondary ion maps in the fingerprint and paper samples, characteristic to the salts (Na^+ and K^+) and the long-chain hydrocarbon content [17, 30]. Complementary information was provided in the other hydrocarbon maps, but the level of detail of the friction ridges and paper fibres varied in direct proportion with peak heights, as shown in Figures 2, 3.

Figure 3, range of chemical maps from one sample

Fingerprint ridges were clearly visible in most maps; therefore ascertaining the sequencing order of the fingerprint and ink, with features better defined in Na^+ , K^+ and C_3H_5^+ maps. Sodium and potassium content in the fingerprint appeared to be higher than that in the paper; nevertheless it was consistently difficult to visualise the fingermark on the paper in these ion maps, unless accretions of Na ion deposits consistent with ridge pores were present. These results confirm that ToF-SIMS has limited applicability in the visualisation of a fingerprint on paper as has been previously observed [19]. However, they additionally

show that the differences in composition between the fingerprint and the ink allows for potential discrimination between these two components.

Interdependent variables potentially affecting the surface chemistry, lateral distribution and migration of components; and therefore SIMS maps, include the variation in composition between paper samples and printed ink; donor and depletion variation of fingerprint chemistry; as well as ageing of fingermark between and after layer depositions. This feasibility study utilized three donors, depositing depletion series of fingermarks on one paper type, with fixed printer, toner and device settings throughout. Deposition was carried out on different days by a range of donors (Table 1), and therefore validated the reliability of abundance of a particular elements or molecular species. Intermixing of fresh ink and freshly deposited fingerprints without allowing for discrete drying time was also taken into account in samples S4, S10, S24, S34, S46 and S48. SIMS sensitivity was assessed through depletion prints, with those analysed including fifth depletions (S12, S46). Lateral spreading and migration of components by diffusion through pores in the ink and paper with time, and other effects of ageing such as the evaporation of volatiles, were also examined in samples aged for up to 28 days after the initial printing or fingerprint deposition process (S35, S36).

Blind test results of the 21 samples that investigated friction ridge detail in the relatively quick positive ion chemical maps showed a success rate of 100%, with ToF-SIMS data indisputably enabling discrimination between a fingerprint overlying or underlying the ink. Examples are presented in Figure 4. The spectral maps for S15 display the ink-paper interface with a fingerprint deposited before the paper was printed (FUI). S5, S24 and S46 are examples of first, second and fifth depletion prints overlying a layer of ink (FOI). S5 and S24 show up to third level features, with distinctive pore shapes and relative pore positions observed [10]. S46 presents a paper-ink interface, and clearly demonstrates the poor visibility of a friction ridge mark on paper. Conversely, those fingerprints overlying a layer of ink, even in a fifth depletion, are very distinctive. Sodium migration was observed when analysis was executed after increased ageing periods. Migration from a fingerprint deposited below the ink up to the surface (FUI), however, was not consistent with a ridge pattern but depended on the surface ink porosity and therefore did not compromise

interpretation (For example S15, figure 4). Furthermore, the concentration of salts that migrated from the paper through to the fingerprint-ink surface in the FOI cases never did approach the abundance of those salts present in the fingerprint, even after 28 days, and with depleted prints, therefore the ridges remained easily identifiable. Determination of the fingermark – ink deposition order therefore necessitated observation of the fingerprint ridge pattern, which was only visible in the FOI, and was best observed in the sodium maps. Comparative evaluation of these maps with friction ridge patterns in potassium, C_3H_5 and other ion maps highlighted in figures 2 and 3 allowed for definite affirmation of a fingerprint deposited over the layer of ink.

This preliminary research presents proof of concept demonstrating the effective use of ToF-SIMS to discriminate between fingermarks deposited above or below a layer of printing. Although a 100% success rate was achieved in this study, further refinements to the technique, such as employing depth profiling, may be required in order to overcome potential limitations due to variations in printing method, including print density (dpi) and intermixing of components from different ink formulations. Complications may arise in studying previously developed fingermarks, or from the effects of the ToF-SIMS analysis on the fingermark chemistry, possibly affecting the efficacy of subsequent development.

Figure 4. Positive ion C_3H_5 , sodium and potassium maps

4. Conclusions

This paper demonstrates the potential of ToF-SIMS chemical mapping to be effective in providing chronological sequencing information of natural fingerprints on laser printed paper. The technique enables the identification of whether a fingerprint has been deposited before or after the paper has been printed. Here, mapping of selected endogenous elements and molecular species in the latent fingerprint, particularly the sodium, potassium and C_3H_5 positive ions, reveals the friction ridge pattern in fingerprints that deposited after printing. A 100% success rate in a 21 sample blind trial of fingermarks aged up to 28 days, and up to fifth depletion acts as initial indication of the reliability of the technique.

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Table:

Sample No.	Donor	Depletion	Ink (FOI) day	Fingerprint day	Ink (FUI) day	Packaging day	Analysis day
S3	A	2	-	0	4	5	7
S17	A	1	-	0	0	1	7
S19	B	1	-	0	0	1	7
S4	B	1	0	0	-	5	8
S5	B	1	0	4	-	5	8
S46	C	5	0	0	-	8	8
S8	A	4	0	1	-	9	9
S10	A	2	0	0	-	5	11
S15	B	2	-	0	4	5	11
S23	A	1	-	0	4	5	12
S24	B	2	0	0	-	5	12
S33	B	1	-	0	4	5	12
S34	A	1	0	0	-	5	13
S39	A	1	0	4	-	5	13
S30	A	1	-	0	9	21	22
S12	B	5	0	1	-	22	23
S48	C	3	0	0	-	21	23
S7	B	1	0	5	-	26	27
S14	B	1	-	0	4	26	27
S35	B	1	-	0	14	26	28
S36	B	2	0	4	-	26	28

Table 1. An outline of the paper-fingerprint-ink samples produced for blind trials to assess the effectiveness of ToF-SIMS to determine deposition chronology. Day zero is the day of deposition of the first layer (either ink or fingerprint) specific to each sample.

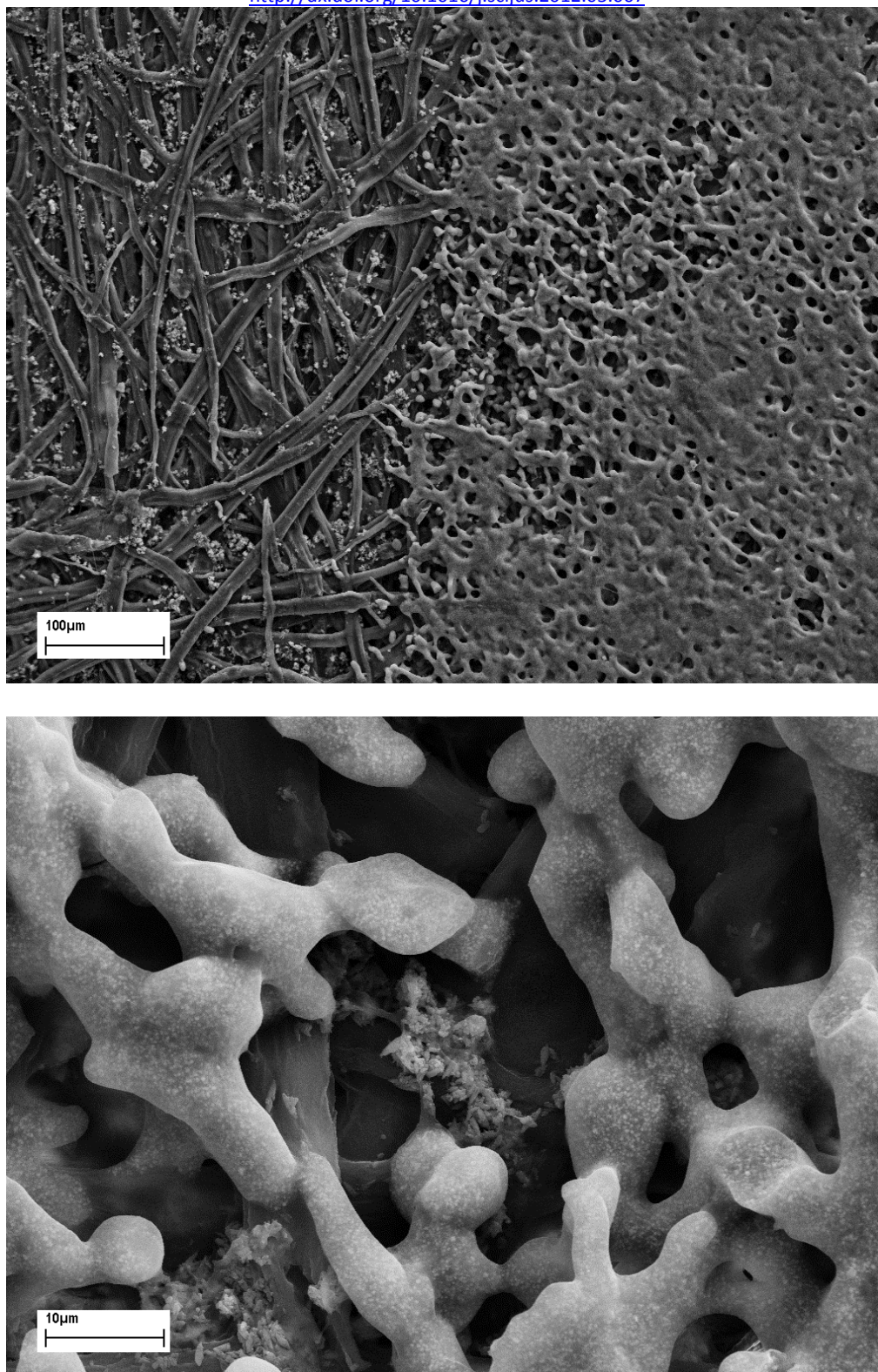


Figure 1. (a) SEM image of paper (*top*) and laser printed ink on paper interface, showing texture and components of paper substrate and pores in printed layer. (b) A higher magnification SEM image of the crystalline filler appearing through pores in the fused ink.

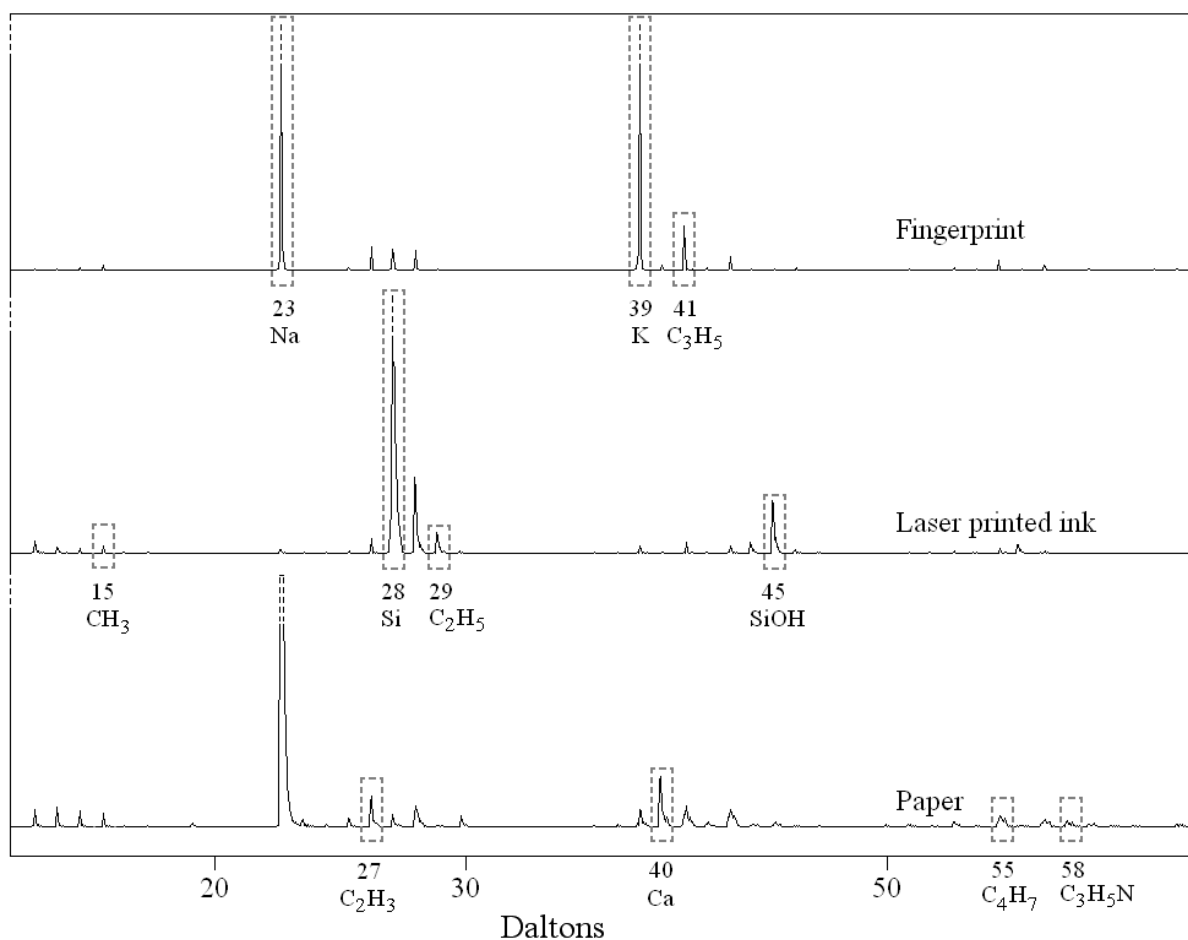


Figure 2. Stacked SIMS mass spectra of a natural fingerprint, laser printed ink and paper highlighting the positive ions and molecules mapped.

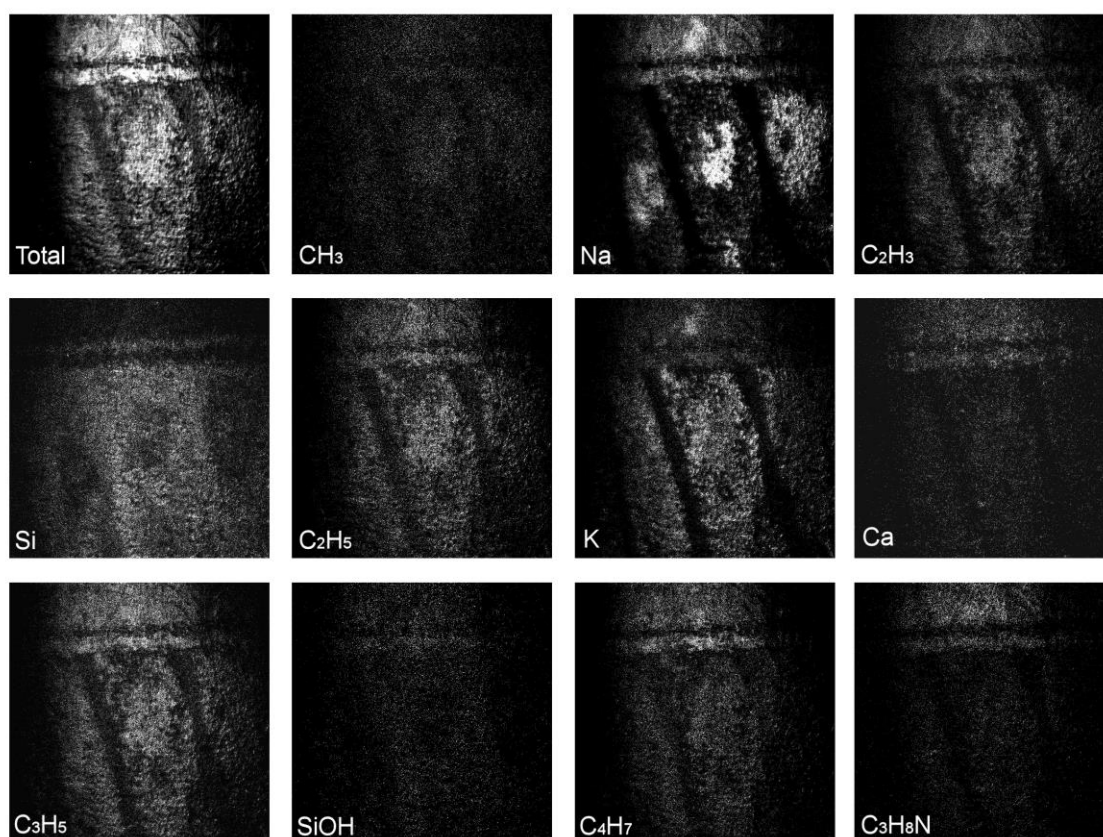


Figure 3. Chemical maps from ToF-SIMS analysis of a natural fingerprint S39, above ink, analysed 13 days from deposition (Image sizes approximately 750 x 750 μm)

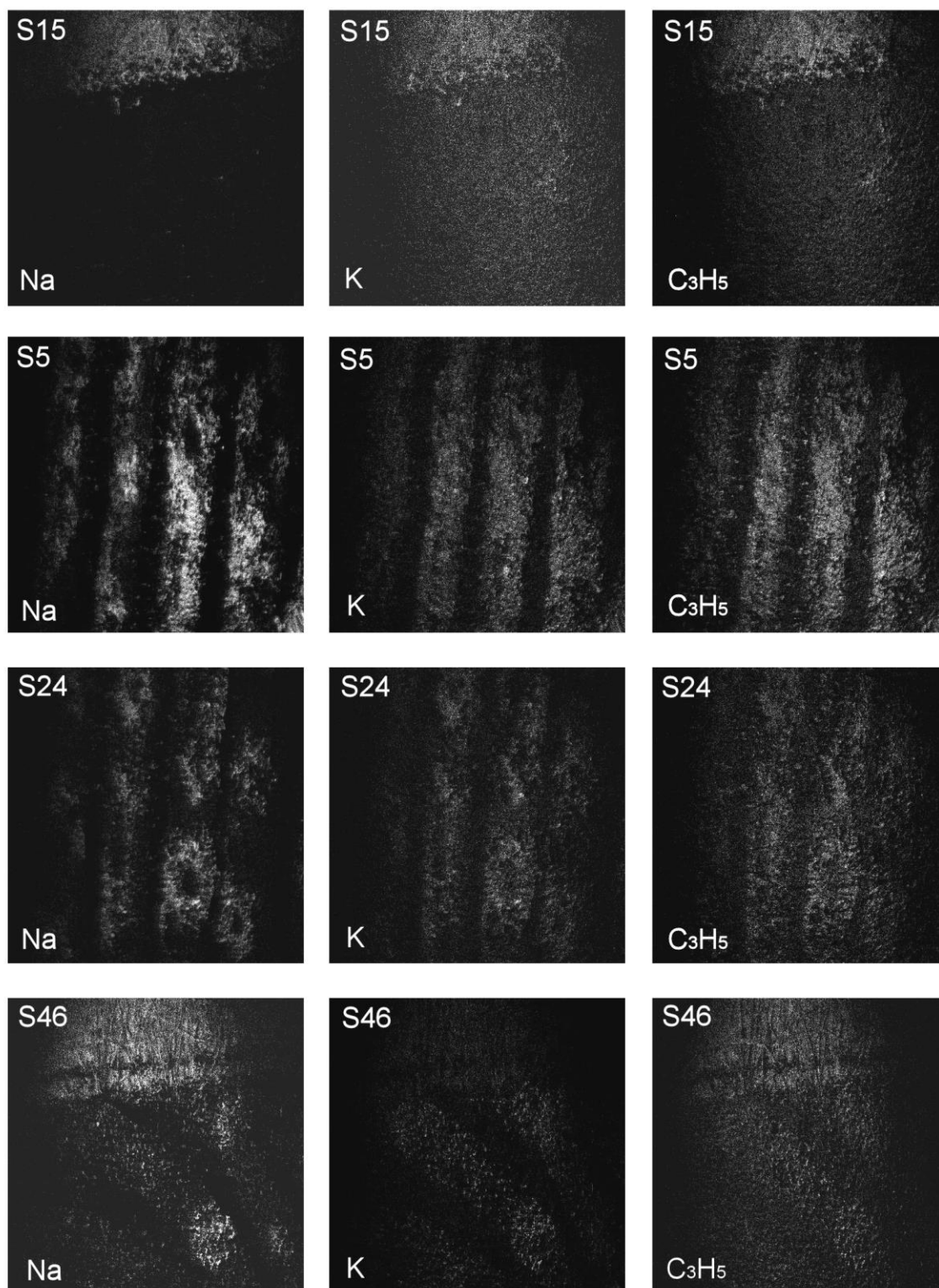


Figure 4. Examples of positive ion C_3H_5 , sodium and potassium maps of fingerprints deposited under and over a layer of laser printed ink. S15 is a second depletion FUI, aged for 11 days. S5, S24 and S46 are all FOI. S5 is a first depletion, analysed after 8 days; S24 is a second depletion print, aged for 12 days, whilst S46 is a fifth depletion left to age for 8 days. (Image sizes approximately 750 x 750 μm)