

Catia Costa

Mahado
Ismail

Shelley
Watkinson



Fingerprints – beyond identity

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chemical analysis
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We all know that fingerprints can be used for the identification of people involved in crimes; but what if you could learn more than just a person's identity from their fingerprint? In this article, three postgraduate students from the University of Surrey describe what can be achieved today and what may be possible in the future.

When a person touches a surface, they leave behind a fingerprint. This fingerprint is a result of sweat excreted from the skin. The material from sweat that is left behind can be referred to as fingerprint residue. Fingerprint residue contains materials from substances ingested (foods or drinks), illegal substances taken (for example cocaine or heroin), nicotine from smoking, and natural components such as amino acids and fatty acids, just to name a few. Due to the numerous compounds found in fingerprint residues, it is possible to determine personal habits (drug use) and maybe even

determine the age, gender or diet of an individual. This can be useful to police because a fingerprint gives no useful information if it is smudged or if the offender is not on the fingerprint database. Also, it is thought that fingerprints can be used to assess the medical condition of an individual and this may one day be useful in medical diagnostics.

In our research at the University of Surrey we are exploring the use of fingerprints for more than just identity. By surveying the surface chemistry of a fingerprint, it is possible to gain a wealth of new information.

Drug testing using fingerprints

The chemical analysis of fingerprints is a new and interesting field in the areas of analytical and forensic science. One of the key areas being investigated is the possibility of using fingerprint residues for drug testing purposes. Fingerprints can offer advantages over other biological fluids (e.g. blood, urine and saliva) as they are easy to collect. Furthermore, because a fingerprint can be used to identify an individual, the test is difficult to falsify and there is a lower chance of mixing up samples.

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Rapid detection of cocaine, benzoylcegonine and methylecgonine in fingerprints using surface mass spectrometry

Melanie J. Bailey,^{1*} Robert Bradshaw,^{1†} Simona Franceschi,^{2*} Tara L. Sallier,³ Cátia Costa,⁴ Mahado Ismail,^{5*} Roger P. Webb,⁶ Ingrid Bosman,⁷ Kim Wolff⁸ and Marcel de Pui⁹

Latent fingerprints provide a potential route to the secure, high throughput and non-invasive detection of drugs of abuse. In this study we show for the first time that the secreted metabolites of drugs of abuse can be detected in fingerprints using ambient mass spectrometry. Fingerprints and oral fluid were taken from patients attending a drug and alcohol treatment service. Gas chromatography mass spectrometry (GC-MS) was used to test the oral fluid of patients for the presence of cocaine and benzoylcegonine. The corresponding fingerprints were analysed using Desorption Electrospray Ionisation (DESI) which operates under ambient conditions and Ion Mobility Tandem Mass Spectrometry Matrix Assisted Laser Desorption Ionisation (MALDI-IMS-MS/MS) and Secondary Ion Mass Spectrometry (SIMS). The detection of cocaine, benzoylcegonine (BEZ) and methylecgonine (ME) in latent fingerprints using both DESI and MALDI showed good correlation with oral fluid testing. The sensitivity of SIMS was found to be insufficient for this application. These results provide exciting opportunities for the use of fingerprints as a new sampling medium for secure, non-invasive drug detection. The mass spectrometry techniques used here offer a high level of selectivity and consume only a small area of a single fingerprint, allowing repeat and high throughput analyses of a single sample.

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Introduction

The drug testing industry is worth several billion dollars worldwide, and is routinely used by probation services, prisons, courts and other law enforcement agencies. Recently there has been a push towards workplace drug testing, as well as new initiatives to test motorists for drug driving.¹ Drug testing is usually carried out by taking a sample of urine or saliva from a suspect and using either an antibody assay or chromatographic analysis to detect the relevant drug and its metabolites. However, these methods of sampling have limitations – blood testing can require trained staff, urine testing has associated privacy concerns and in both cases the samples must be treated as a biological hazard, which increases the complexity of sample handling in terms of storage and disposal. Oral fluid and sweat have been proposed as alternative non-invasive collection matrices. These matrices, as well as oral fluid and sweat, frequently require extraction steps from the collection devices or precipitation from the biological fluids prior to analysis and this contributes to the cost of analysis.²

In contrast, a latent fingerprint can be deposited quickly and transported easily. The identity of the donor is encephalated within the fingerprint ridge detail, making the test impossible to falsify. It has recently been shown that drugs and their metabolites can be detected in latent fingerprints using antibody reagents.³ Whilst antibody reagents provide a rapid screening test, non-specific binding can lead to false positive results. Mass spectrometry techniques provide a higher level of specificity, providing confirmation of the identity of the substance detected.

Recent work by Gombacher *et al.*⁴ has shown that liquid chromatography mass spectrometry (LC-MS) can be used to detect lorazepam, methadone and their metabolites in latent fingerprints. However, a positive detection was only achieved when ten fingerprints were used (and consumed) in combination, making it impractical for use in the field as this

*University of Surrey, Department of Chemistry, Surrey, GU2 7XH, UK
E-mail: m.j.bailey@surrey.ac.uk
†Academic Research Centre, Anglia Ruskin University, Merrist Drive, IP14 3SQ, UK. E-mail: r.p.webb@anglia.ac.uk
National Physical Laboratory, Teddington, Middlesex TW11 0LX, UK
University of Surrey, School of Chemistry, Surrey, GU2 7XH, UK
Netherlands Forensic Institute, The Hague, Netherlands
Fritz-Haber Center for Forensic Science, Berlin, Germany
*Equally contributing to the authors.

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Figure 1 This scientific paper, published by the Royal Society of Chemistry in its journal *Analyst*, describes how cocaine and two of its metabolites can be detected in a fingerprint. It has 10 authors from 6 collaborating scientific institutions.

A recent article published by our supervisor, Dr Melanie Bailey and her colleagues (**Figure 1**), describes how desorption electrospray ionisation – mass spectrometry (DESI-MS, **Figure 2**) enabled the detection of cocaine and its metabolites in fingerprints of individuals attending a drug treatment service for their drug dependency. DESI-MS uses a beam of charged solvent (a mixture of water and methanol to which a voltage is applied) to strike a small area of the sample, thus causing molecules from the sample to desorb (lift off). It also causes ionisation of the target molecules. The ionised molecules (positively charged, in this case) are then sucked into an instrument called a mass spectrometer, which measures their mass. DESI-MS allows a fingerprint to be analysed in air and can be carried out in under two minutes.

Although the detection of the parent drug (cocaine, in this case) in a fingerprint is important, it does not prove that the person took the drug, as it could be present by contact with a contaminated surface (e.g. a bank note). The detection of the metabolites (molecules resulting from the breakdown of the drugs by the body) will give a better indication of whether the person ingested the drug. The results obtained using this method were corroborated by analysis of saliva collected from the same individuals, which showed a very good correlation. A positive result for cocaine in saliva was matched by a positive result in fingerprint.

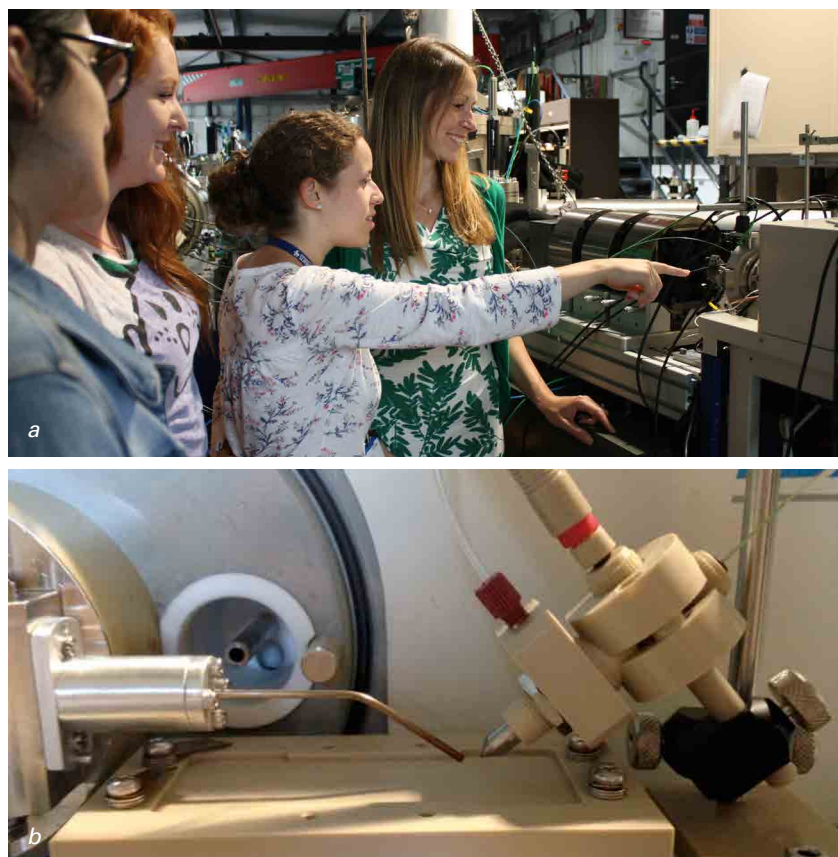


Figure 2 a) The desorption electrospray ionisation – mass spectrometry (DESI-MS) instrument available at the University of Surrey; b) The DESI spray head (right) produces a beam of charged solvent which is directed at the sample, causing desorption and ionisation of molecules. The stainless steel capillary (left) extracts the ionised molecules onto the mass spectrometer for mass measurement.

Overlapping fingerprints and inks on documents

Using available technology, forensic investigators are not able to distinguish whether a fingerprint is above or below a layer of ink on a document. This can have implications in cases where a suspect claims to have handled the document before any text was written. If, however, forensic investigators could determine the chronology of deposition of fingerprints and inks on a document, the evidential value of the questioned document would be increased.

Research carried out at the University of Surrey explored the potential use of secondary ion mass spectrometry (SIMS) for determining the deposition sequence of overlapping fingerprints and inks on paper. Secondary ion mass spectrometry (SIMS) is a technique that is used for surface analysis (**Figure 3**). It only looks at the first few monolayers of the sample surface and therefore does not visibly change the sample making it suitable for document analysis. SIMS is a very sensitive technique and is used for its imaging capabilities as it produces high resolution chemical images. These images show the distribution of molecules on a surface and therefore can determine where the molecules originate from.

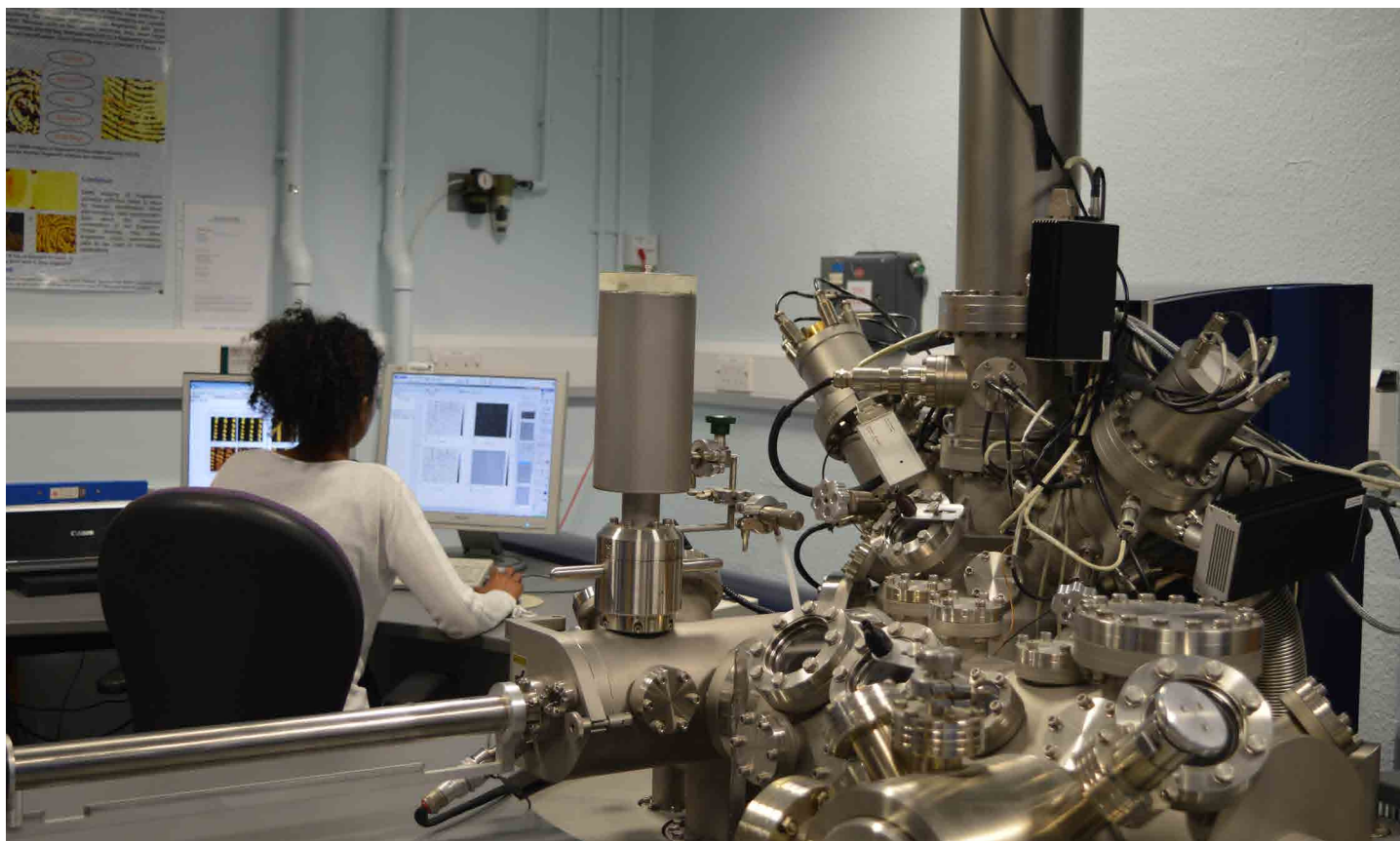


Figure 3 Surface Analysis Laboratory at the University of Surrey.

SIMS uses a primary ion beam that is directed onto the sample surface for surface ionisation. This causes a process called sputtering, whereby secondary ions are generated from the sample surface due to the impact of the pulsed primary ion beam. These secondary ions can then be detected using a mass spectrometer.

SIMS has demonstrated that when a fingerprint is deposited over a layer of ink, chemical images from compounds present in fingerprints will allow the observation of fingerprint ridges on top of the ink line (Figure 4). When the fingerprint is placed below a layer of ink, the fingerprint signals are masked by the overlapping ink.

Forensic investigators normally use chemical development reagents to visualise fingerprints on surfaces. A popular chemical developer is ninhydrin, which reacts with amino acids present in fingerprints to produce a purple colour. The SIMS method has also been applied to overlapping fingerprints and laser printed ink on documents after development with either ninhydrin and 1,2-indandione. Similar to images in Figure 4, the chemically developed fingerprints on documents also gave indication of the deposition order. Therefore, this method has shown real-life applicability.

A look forward

Fingerprints can offer more to an investigator than just the identity of an individual. As explained above the analysis of fingerprint residues can be used to detect drugs and metabolites in fingerprints and differentiate between overlapping fingerprints and inks on paper, the use of which is valuable in real world forensic science. Whilst the DESI technique shows great promise for drug testing, it cannot provide any information on how much drug or metabolite is present, and this is currently being investigated. The work on overlapping fingerprints and inks on documents is at a more advanced stage of research and we are working with the Netherlands Forensic Institute on a validation study, which is the final hurdle before it can be adapted in casework.

Catia Costa, Mahado Ismail and Shelley Watkinson are postgraduate students in Dr Melanie Bailey's lab in the Chemistry Department, University of Surrey, UK.

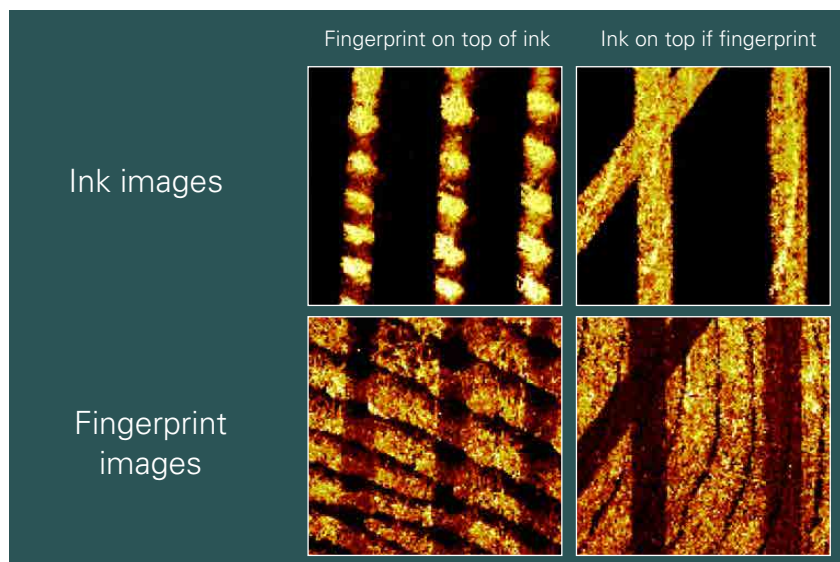


Figure 4 SIMS ion images of overlapping fingerprints and inks on paper.