Forensic Chemistry 15 (2019) 100173

Contents lists available at ScienceDirect

Forensic Chemistry

journal homepage: www.elsevier.com/locate/forc

Simultaneous imaging of latent fingermarks and detection of analytes of forensic relevance by laser ablation direct analysis in real time imaging-mass spectrometry (LADI-MS)

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HIGHLIGHTS

- Laser ablation direct analysis in real time Imaging-mass spectrometry was utilized.
- Spatial distributions of endogenous compounds revealed fingerprint ridge patterns.
- Detection of psychoactive materials within fingermarks was completed simultaneously.
- Micro-ablation of an explosive was completed without disturbing the fingermark.

ARTICLE INFO

Keywords:
Laser ablation direct analysis in real time
imaging-mass spectrometry
Latent fingermarks
Psychoactive biomarker detection
Explosives detection
TRL 2

ABSTRACT

Traditional analysis of latent fingermarks using dusting powders and cyanoacrylate fuming uncovers only the physical pattern of the fingerprint ridges, neglecting vast amounts of chemical information within the residue that could divulge more about the owner. Imaging mass spectrometry provides a means to retain the fingerprint ridge detail for identification while also revealing additional chemical information. The technique laser ablation direct analysis in real time imaging-mass spectrometry (LADI-MS) was applied to image the spatial distributions of small molecules of potential forensic relevance in latent fingermarks on non-conductive surfaces. By using this approach, no solvent, matrix, or high-vacuum conditions were required. An index finger was exposed to cocaine, psychoactive "legal high" plant material, pseudoephedrine, or the explosive RDX, and a fingermark was subsequently deposited on a glass slide for analysis. LADI-MS revealed the spatial distribution of endogenous cholesterol (localized to fingerprint ridges) and simultaneously detected the psychoactive small molecules cocaine, yangonin (derived from *Piper methysticum*), pseudoephedrine and the explosive RDX in latent fingermarks. The spatial distribution mapping of cholesterol in a lifted print on the non-conductive adhesive side of tape was also accomplished. The ion images of endogenous compounds and detection of exogenous molecules reveal details of chemical exposures, while connecting the exposure to the owner of the print.

1. Introduction

In a forensics context, fingermarks left behind by individuals can directly link them to a crime scene and are thus of high value to investigators. Historically, their visualization has been accomplished using a variety of techniques including dusting with powders, cyanoacrylate fuming, and the application of ninhydrin, among other approaches [1]. Fingerprint visualization by these methods exploits the presence of amino acids and endogenous molecules such as lipids in the latent fingermarks [1]. However, in principle, any chemical with which the fingers come into contact can be registered in the print, a fact that provides the opportunity to extract immense amounts of information about the owner. Chemical compounds found within latent fingermarks can include illicit drugs, psychoactive plant materials and explosive compounds. The observation of such substances can provide important information about exposures that may be directly relevant to a crime.

Recognition of the potential utility of knowing the chemical content of fingermarks has spurred development of various analysis methods. Swabbing followed by extraction of materials found in smudged fingerprints and analyzing their contents by gas chromatography (GC) or liquid chromatography (LC)-mass spectrometry (MS) techniques [2–6], as well as by direct analysis in real time–high-resolution (DART-HR)-

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https://doi.org/10.1016/j.forc.2019.100173
Received 7 May 2019; Received in revised form 18 June 2019; Accepted 18 July 2019
Available online 22 July 2019
2468-1709/

and desorption electrospray ionization (DESI) MS have been used [2,6–9]. These techniques are able to reveal the presence of both endogenous and exogenous molecules found in fingerprints, including fatty acids, drugs of abuse, drug metabolites, and explosive materials. However, in using these approaches, the fingerprint image that establishes a link between an individual and substances to which they have been exposed is destroyed.

In recent years, this challenge has been overcome through imaging spectroscopic and mass spectrometric techniques. For example, fingerprint imaging has been accomplished using IR and Raman spectroscopies [10–12]. However, these approaches have limited ability to provide definitive information on the identity of chemical constituents [13–15]. On the other hand, imaging mass spectrometry (IMS) techniques have proven to be well-suited to chemical imaging of latent fingermarks [6,13,14]. Their power lies in the ability to reveal fingermark patterns made from any one of a range of substances that are present, all from a single experiment. If the fingermark contains an illicit substance or other molecules of concern such as explosive materials, the MS ion images could provide a direct link to a specific individual. Additionally, if metabolites of illicit and psychoactive substances are detected within a latent fingermark, a distinction can be made between those individuals who have only handled the materials versus those who have ingested the product. Several MS techniques have been used to map the spatial distributions of endogenous and exogenous materials in latent fingermarks, with the most common being secondary ion mass spectrometry (SIMS), matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS), surface-assisted laser desorption/ionization mass spectrometry (SALDI-MS), and DESI-MS [6,13,14,16–29].

Laser ablation DART imaging-MS (LADI-MS) is a new technique that has potential to be applied to the imaging of a range of chemicals in latent fingermarks [30]. LADI-MS is comprised of a DART ion source and a high-resolution mass analyzer coupled to a 213 nm laser ablation system. While current IMS techniques enable spatial distributions of molecules to be obtained, there are several reasons why it would be advantageous if LADI-MS could be used. Experiments are performed in open-air and under ambient conditions, and do not require high-vacuum conditions. Other advantages of LADI-MS are its applicability to a range of sample types without the need for sample preparation steps, matrix deposition, or solvent for desorption and ionization. Its ease of set-up allows for the quick analysis of samples without the need for proper sample orientation in relation to the ion source. LADI-MS can be completed on non-conductive surfaces which permits analysis of samples on a variety of matrices, such as packing tape. As it utilizes a soft ionization source, LADI-MS does not cause extensive fragmentation of the molecules detected. The possible utility of the technique is demonstrated through the imaging of endogenous molecules within latent fingermarks and the detection of cocaine, yangonin and other kavalactones derived from a psychoactive plant, and pseudoephedrine. Micro-ablation and detection of RDX, an explosive, are also demonstrated.

2. Materials and methods

2.1. Chemicals

RDX, pseudoephedrine in methanol, and exempt preparations of cocaine in acetonitrile were purchased from Cerilliant (Round Rock, TX, USA). *Piper methysticum* powder was purchased from Bouncing Bear Botanicals (Lawrence, KS, USA). Methylene chloride (HPLC grade) was purchased from Fisher Scientific (Pittsburgh, PA, USA). High-purity helium and nitrogen gases were purchased from Matheson (Manchester, NH, USA) or Airgas (Albany, NY, USA).

2.2. Fingerprint residues

All of the handling and deposition of fingermark experiments were approved and conducted in accordance with the University at Albany's Institutional Review Board.

2.2.1. Cocaine-laden print

An aliquot (30 μL) of a solution of cocaine in acetonitrile (1 mg mL^{-1}) was deposited on a clean glass microscope slide (Thermo Fisher Scientific, Waltham, MA, USA) and allowed to dry. A finger was then rubbed on the dried residue and a fingermark was subsequently deposited onto a clean glass microscope slide for analysis.

2.2.2. Kava-laden print

A small amount (< 3 mg) of *P. methysticum* (Kava) powder was rubbed between the thumb and index finger. A fingermark was then deposited onto a clean glass microscope slide.

2.2.3. Pseudoephedrine-laden print

An aliquot (30 μL) of pseudoephedrine in methanol (1 mg mL^{-1}) was deposited onto a glass slide and allowed to dry. The residue was rubbed with the index finger and a fingermark was subsequently deposited onto a clean glass slide.

2.2.4. Lifted print

A human sebum-enriched fingermark was created by rubbing a clean index finger across the forehead and applying it to a clean glass microscope slide. The latent print was then dusted with black latent print powder (Sirchie, Youngsville, NC, USA). Clear single-sided adhesive packing tape (Staples, Albany, NY, USA) was then placed on the deposited and dusted fingermark to lift it. The tape was placed adhesive side up on the sample plate, and held in place on either side using additional packing tape for analysis.

2.2.5. RDX-laden print

RDX solution (1 mg mL^{-1}) was allowed to dry to a residue on a clean glass slide. A clean index finger was then swiped across the forehead and subsequently exposed to the RDX residue and a fingermark was deposited onto a clean glass microscope slide.

2.2.6. Blank print

A clean index finger was rubbed across the forehead to provide a human sebum-enriched fingermark that was then deposited on a glass microscope slide for LADI-MS analysis. A second fingerprint was deposited in the same manner and analyzed approximately 96 h later.

2.3. LADI-MS analysis

The LADI-MS system was set up as previously described [30]. Ion images were acquired through the coupling of an ESL NWR 213 laser ablation system (ESL, Bozeman, MT, USA) and a DART-HRMS instrument by way of a heated stainless-steel transfer line. A glass tee was used to direct the flow from the transfer line to the DART-HRMS interface. The high-resolution mass spectrometers used for the imaging and RDX experiments were a JEOL AccuTOF LC-plus JMS-T100LP HRMS and a JEOL AccuTOF-LP 4G HRMS (JEOL USA, Inc., Peabody, MA, USA) with resolving powers of 6,000 and 10,000 FWHM, respectively. The mass spectrometers were operated with an orifice 1 voltage of 20 V and orifice 2 and ring lens voltages of 5 V in positive and negative ion modes. The mass ranges collected for the experiments were m/z 100–700, with the exception of the RDX print which was collected with a mass range of m/z 150–700. The rate of the DART ion source helium flow was 2.0 L min^{-1}. Polyethylene glycol (PEG) was used as a reference standard for the calibration of the collected spectra. TssPro 3.0 (Shrader Analytical Software Solutions, Grosse Pointe, MI, USA) and the msAxel Data Processing software package (JEOL USA, Inc., Peabody, MA, USA) were used for peak calibration and peak centroiding. Reconstructed ion currents were created for each of the ions of interest and imported into Iolite imaging software (University of

Table 1
DART-HRMS parameters used for fingerprint analyses.*

Sample	Ion mode	Ion guide voltage**	MS acquisition rate
Cocaine	+	1000 V	0.5 s scan^{-1}
P. methysticum	+	1000 V	0.5 s scan^{-1}
Pseudoephedrine	+	1000 V	0.5 s scan^{-1}
Lifted (blank)	+	1000 V	0.5 s scan^{-1}
RDX	−	1500 V	0.3 s scan^{-1}

* All analyses were performed at a DART heater temperature of 500 °C, except RDX which was conducted at 350 °C.

** The ion guide voltage is also referred to as the "peaks voltage" of a JMS-T100LP instrument.

Table 2
Laser parameters used for fingerprint analyses.*

Sample	Fluence	Scan speed	Spot size	Spatial resolution
Cocaine	1.7 J cm^{-2}	55 μm s^{-1}	60 × 60 μm^2	126 × 60 μm^2
P. methysticum	1.7 J cm^{-2}	55 μm s^{-1}	60 × 60 μm^2	126 × 60 μm^2
Pseudoephedrine	1.7 J cm^{-2}	55 μm s^{-1}	60 × 60 μm^2	126 × 60 μm^2
Lifted (blank)	1.7 J cm^{-2}	55 μm s^{-1}	60 × 60 μm^2	126 × 60 μm^2
RDX	1.1 J cm^{-2}	–	80 × 80 μm^2	–

* The RDX detection experiment was not an imaging-based analysis, and thus does not have imaging-relevant parameters listed.

Melbourne, AUS). Mass spectral analysis, elemental composition determination and isotope analysis were performed using Mass Mountaineer software (Massmountaineer.com, Portsmouth, NH, USA).

The DART-HRMS and laser parameters used for the imaging experiments are listed in Tables 1 and 2, respectively. Each imaging experiment was completed within 3 hrs. The spatial resolutions attained in each experiment are shown in Table 2 and were calculated using Equation (1), where x is the spot size in the x-dimension (μm), a is the scan speed of the sample chamber (μm s^{-1}), b is the MS acquisition rate (s scan^{-1}), and y is the spot size in the y-direction (μm). In Eq. (1), 0.7 is representative of the sample cell washout time (s).

$$\text{Spatial Resolution} = (x + 0.7a + ab) \times y \quad (1)$$

In the case of the RDX detection experiment, the laser was used to ablate a single particle and the fingermark was not imaged. Methylene chloride was used as a dopant to assist in the detection of RDX. A syringe pump, operating at 0.03 mL h^{-1} was used to introduce methylene chloride to the glass tee junction at the DART-HRMS interface.

3. Results

The handling of a variety of materials was used to assess the utility of LADI-MS for detection of compounds of potential forensic interest in latent fingermarks. These included an illicit drug (cocaine), an unregulated psychoactive plant material (*P. methysticum*), the active ingredient in an over-the-counter medication (pseudoephedrine) that can also be used to synthesize illicit drugs, and an explosive material (RDX). Fig. 1 shows the representative results of a typical LADI-MS experiment that was performed on a fingermark that was deposited after the handling of cocaine. The mass spectrum in Fig. 1 (Panel A) shows a composite of all the detected ions, including protonated cocaine (m/z 304.1505). Also presented are the color-overlaid ion images of endogenous dehydroxylated cholesterol (m/z 369.3475) and exogenous protonated cocaine (m/z 304.1505) in Panels B and C respectively. The 1 mm scale bar applies to both ion images and the color intensity bars ranging from black to yellow are representative of a zero or low intensity to a high intensity of the indicated ion. The cholesterol and cocaine ion images (Panels B and C), both of which were acquired in the same experiment, reveal a characteristic fingerprint pattern which is identical to, and therefore can be superimposed over, the area that they represent in the optical image of the print (Panel D). The observation of an ion image for the endogenous compound representing the fingerprint image itself, and the detection of cocaine in the form of an ion image that aligns with the ridge pattern of the print (in the same experiment) indicate exposure to cocaine by the owner of the print.

To avoid prosecution for possession of illegal substances, many drug abusers are turning to plant materials that are not currently regulated but are psychoactive. The United Nations Office on Drugs and Crime (UNODC) has listed twenty of these as "plants of concern" [31]. As shown in Fig. 2 (Panel A), the mass associated with a psychoactive biomarker, yangonin, for one such plant of concern, *P. methysticum* (commonly known as Kava), was detected (m/z 259.0980). Other kavalactones that were also observed include methysticin (m/z 275.0960) and dihydromethysticin (m/z 277.1040). Fingerprint ridge details are displayed in the ion image for endogenous dehydroxylated cholesterol (m/z 369.3520) that was acquired from the same experiment (Panel B). Fig. 2 Panel C shows the magnified optical image of the same area represented by the cholesterol ion image, while Panel D shows the cholesterol ion image overlaid on the full latent fingerprint photograph.

Drug manufacturers also have a history of turning to over-the-counter sources of pseudoephedrine for use in the production of methamphetamine. Decongestants containing this compound are typically packaged and ingested in capsule form, thereby making direct exposure of the hands and fingers to pseudoephedrine highly unlikely. Therefore, the detection of pseudoephedrine in a latent fingermark may suggest that the drug was removed from the capsule for the purpose of being misused. Fig. 3 shows a mass spectrum and ion images of molecules detected in a print that was deposited after the handling of pseudoephedrine. Fingerprint ridge patterns for endogenous dehydroxylated cholesterol (m/z 369.3480) and exogenous protonated pseudoephedrine (m/z 166.1240) are presented in Panels B and C, respectively, and the mass spectrum in Fig. 3 (Panel A) shows the peak for protonated pseudoephedrine (m/z 166.1240), thus confirming the exposure of the individual's fingers to this material. Panel D shows an overlay of the ion image of dehydroxylated cholesterol on a photograph of the latent print prior to LADI-MS analysis to reveal that the ridge patterns in the ion image match those in the latent print.

While the aforementioned results demonstrate proof-of-principle that LADI-MS can be applied to latent print imaging under ideal conditions, the approach would be most useful if it could be applied to prints lifted from surfaces, including the tape used to lift developed fingerprints at a crime scene. To investigate if this could be accomplished, a fingerprint was deposited onto a glass slide and subsequently dusted with fingerprint dusting powder. The dusted print was lifted using clear packing tape. The tape was then deposited onto the sample plate (adhesive side up) for analysis. Fig. 4 shows the ion image of dehydroxylated cholesterol (m/z 369.3536) on the lifted tape. Some fingerprint ridge detail is revealed in the ion image. The loss of ridge detail in this ion image may be a result of the unpracticed hand used for the dusting of the fingermark prior to lifting, or the use of a fingermark development technique that is suboptimal for subsequent LADI-MS analysis.

Another way to link an individual to an illicit substance while retaining the fingermark image, is by completing an analysis without disturbing the print at all. As an example, the LADI-MS system's objective magnifying lens enabled visual detection in a fingermark of a particle of the explosive RDX post exposure of this substance to the fingers. This is illustrated in the Fig. 5 inset. The laser was used to ablate the RDX particle, thus preserving the full fingermark for further subsequent analysis by other forensic techniques. The mass spectrum in Fig. 5 clearly shows chlorinated RDX (m/z 257.0058) as the base peak.

Unlike many of the most widely used IMS techniques, LADI-MS experiments are conducted in open air without the need for high-vacuum. This is important, as the chemical composition of fingermarks has been shown to change within time frames as short as an hour on exposure to high-vacuum conditions [32]. Typical high spatial

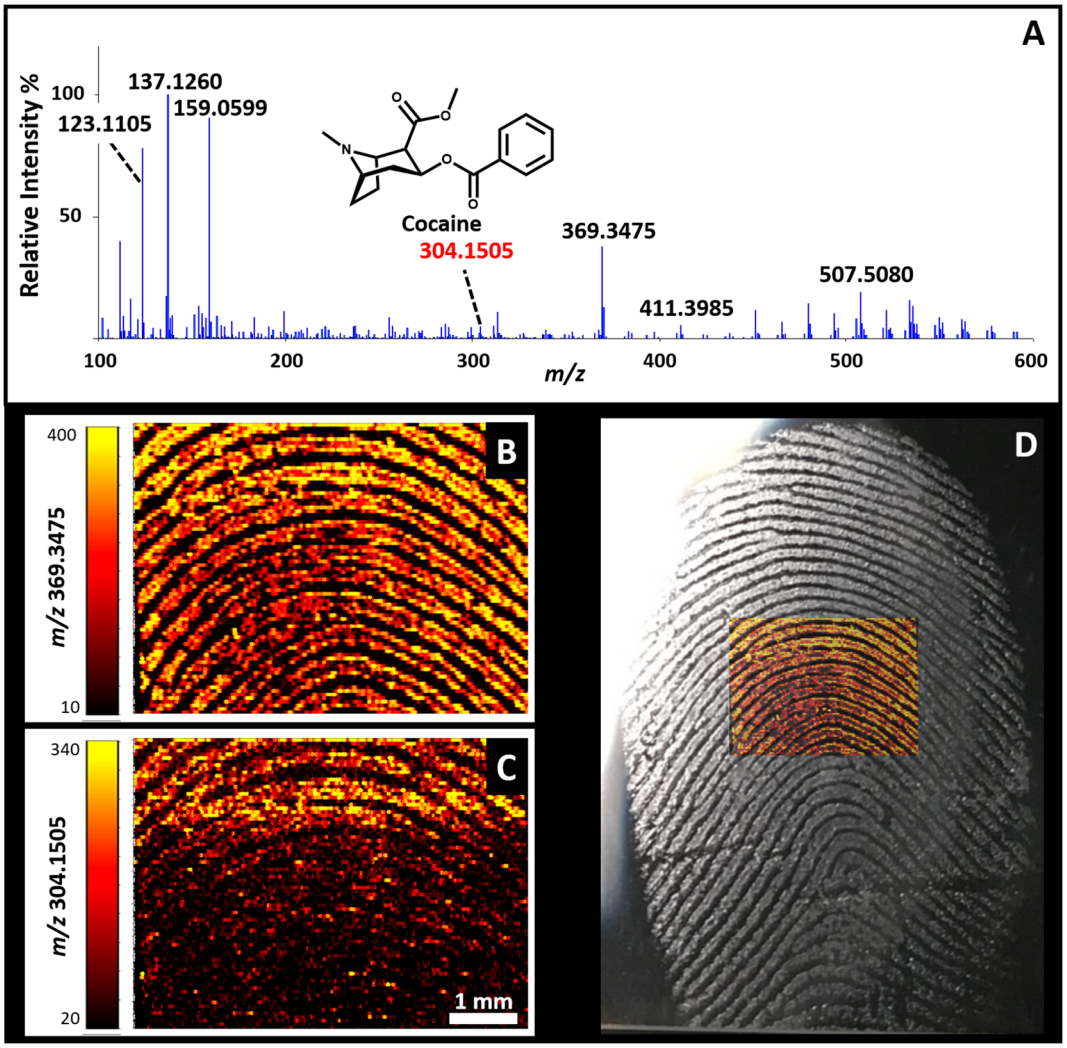

Fig. 1. A mass spectrum and LADI-MS ion images resulting from the analysis of a fingermark deposited after exposure to cocaine. Panel A shows a representative LADI-MS spectrum with the peak corresponding to protonated cocaine labeled in red (*m/z* 304.1505). The LADI-MS color-overlaid ion images of the masses consistent with dehydroxylated cholesterol (Panel B) and protonated cocaine (Panel C) in the same latent fingerprint are shown. The 1 mm scale bar applies to both ion images. The color scale bar ranging from black to yellow is representative of a zero or low intensity to high intensity of the indicated ions. The ion image of the mass consistent with dehydroxylated cholesterol is overlaid on a photograph of the latent print that was acquired prior to LADI-MS analysis (Panel D).

resolution IMS experiments require at least a few hours for analysis, during which the fingermark is exposed to high-vacuum conditions which change its composition over time. For example, squalene, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, and octadecanoic acid (with protonated masses of *m/z* 411.3991, *m/z* 229.2168, *m/z* 243.2324, *m/z* 285.2794, and *m/z* 257.2481, respectively) in fingerprints have been shown to be depleted after exposure to a high-vacuum environment [32]. In a LADI-MS spectrum (Fig. 6-top panel) acquired under ambient conditions, all five of the aforementioned molecules were detected within 6 mmu of their calculated protonated high-resolution masses (labelled in red). Additionally, to confirm that these molecules remained detectable in aged fingermarks, analysis of an aged print was performed. Fig. 6 shows a comparison of LADI-MS spectra of a fresh ~1 h print (top panel) versus a 96 h print (bottom panel). Although the mass spectrum of the aged print does not contain all of the molecules observed in the fresh print, the endogenous species tetradecanoic acid and squalene, in their protonated forms at *m/z* 229.2089 and *m/z* 411.3967 respectively, were detectable.

4. Discussion

While a variety of IMS techniques have been directed to latent fingermark detection, the method described here is distinguished from these in that there are no sample preparation steps necessitated by the MS approach, and the experiments are conducted under ambient and soft ionization conditions. The imaging experiments are also completed in a short time frame (not exceeding 3 h for a single analysis), which when combined with the limited sample preparation required is more rapid than most other IMS approaches. The absence of a vacuum circumvents the problem of outgassing and thus avoids instrument depressurization time [33] and the loss (evaporation) of analytes of interest [32]. As a soft ionization source, the DART does not cause extensive analyte fragmentation, which can occur in SIMS imaging experiments. However, SIMS is distinguished in providing high enough spatial resolution to reveal the locations of individual sweat glands in fingerprints [17].

In comparison to MALDI-MS, SALDI-MS and SIMS, DESI-MS and desorption electro-flow focusing ionization (DEFFI) MS are some of the only other ambient ionization IMS techniques (both utilizing a flow of solvent), that have been applied to latent fingerprints [22,34–36]. Although both approaches were successful in revealing fingermarks, the requirement for the application of solvent could potentially result in changes in the spatial distribution of analytes through molecule translocation caused by solvent [37]. Since LADI-MS does not require

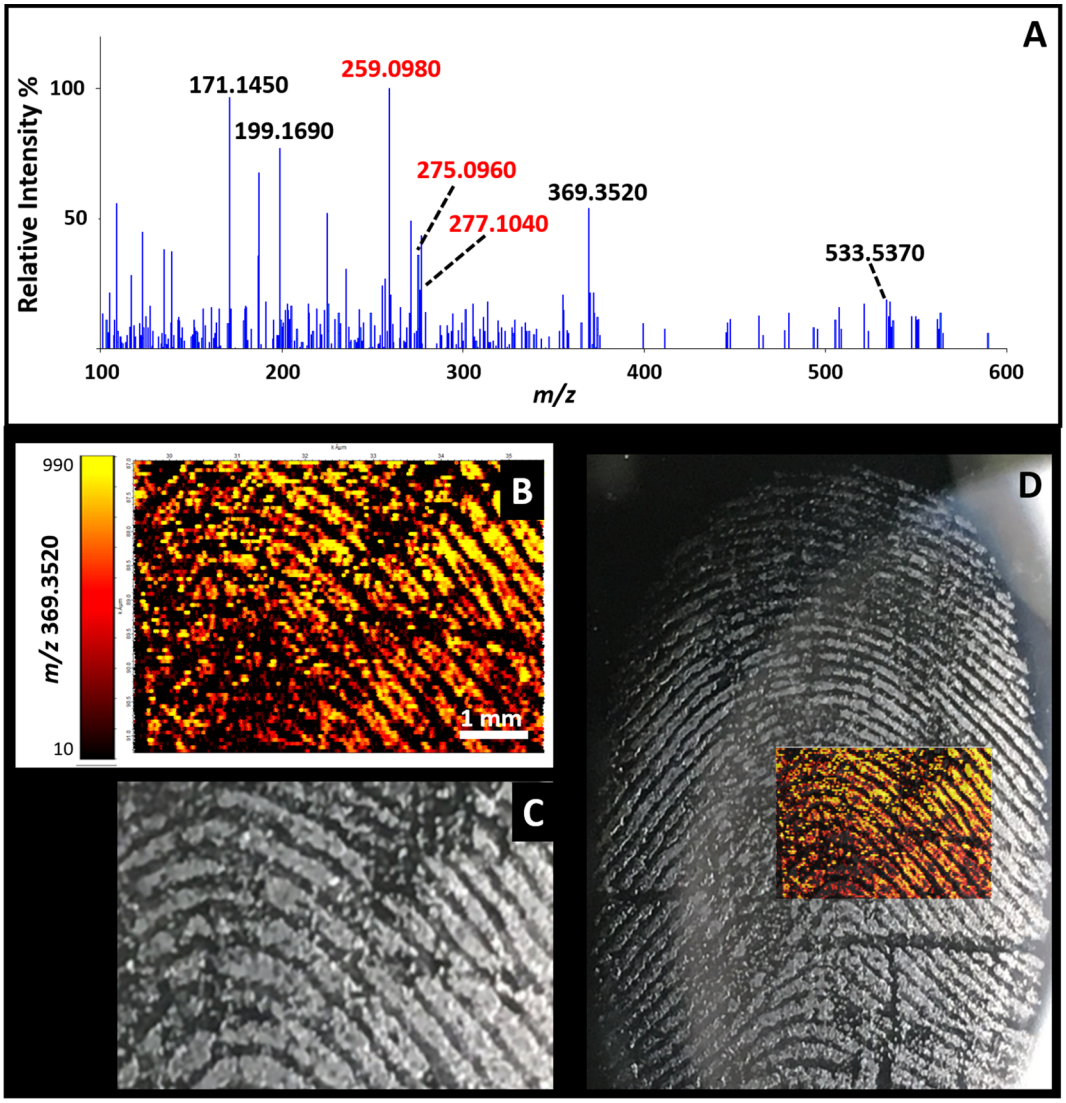

Fig. 2. A representative LADI-mass spectrum and LADI-MS-derived ion image obtained from the analysis of a fingermark deposited after the handling of *P. methysticum* plant material. The masses for several kavalactones detected in the mass spectrum are labelled (Panel A): *m/z* 259.0980-yangonin; *m/z* 275.0960-methysticin; and *m/z* 277.1040-dihydromethysticin. The LADI-MS ion image is shown of *m/z* 369.3520, a mass that is consistent with that of dehydroxylated cholesterol (Panel B). Panel C shows an optical image of the area of the fingermark that was ablated in the experiment. Panel D shows the cholesterol ion image overlaid on a photograph of the latent fingermark.

solvent, changes in small-molecule distributions are less likely. Also, because LADI-MS does not rely on solvent desorption, a broader range of molecules of varying polarities can be detected simultaneously in a single experiment. However, the ionization mechanism of the DART ion source relies heavily upon the proton affinity of the analytes. This can affect the sensitivity of the LADI-MS instrumentation for the detection of some analytes of forensic relevance. Additionally, it should be noted that for DEFFI- and DESI-MS experiments, the solvent selection could be optimized for the detection of specific molecules of interest, and both have been successfully used to detect cocaine and the explosive RDX [35,38–40]. In comparison to traditional DESI-MS imaging experiments, which typically have a spot size of ~200 μm [41], LADI-MS can achieve higher spatial resolution ion images. However, the development of *nano*-DESI-MS and DEFFI-MS has improved upon these spatial resolutions. Sensitivity experiments to explore analyte detection limits for the LADI-MS technique are the subject of ongoing investigations.

The micro-ablation application of LADI-MS described here is promising in its applicability to forensic fingerprint analysis. The latent fingermark is not destroyed and can be further analyzed using traditional development techniques with ninhydrin, cyanoacrylate fuming, or dusting with powders, all techniques that are broadly accepted in the courts. In addition, the sample can be micro-ablated to yield simplified spectra of materials of interest in a specific area of the print. This latter capability is similar to the approach reported by Clemons et al. [42] in which an area of a print was nanoextracted and the extract was subsequently analyzed by DART-MS to reveal the presence of explosives. However, the LADI-MS approach differs from this in that no solvent extraction step is required.

5. Conclusions

The LADI-MS technique was used to map the spatial distributions of endogenous fingerprint compounds and detect the psychoactive compounds cocaine and yangonin, and non-psychoactive pseudoephedrine, as well as the explosive RDX in latent fingermarks. The combination of the detection of psychoactive materials and the spatial distribution mappings of endogenous molecules in the same experiment can provide a direct link between an individual (through fingerprint identification) and substances with which they have come into contact. The laser was used to ablate a single particle of RDX in a latent fingermark without

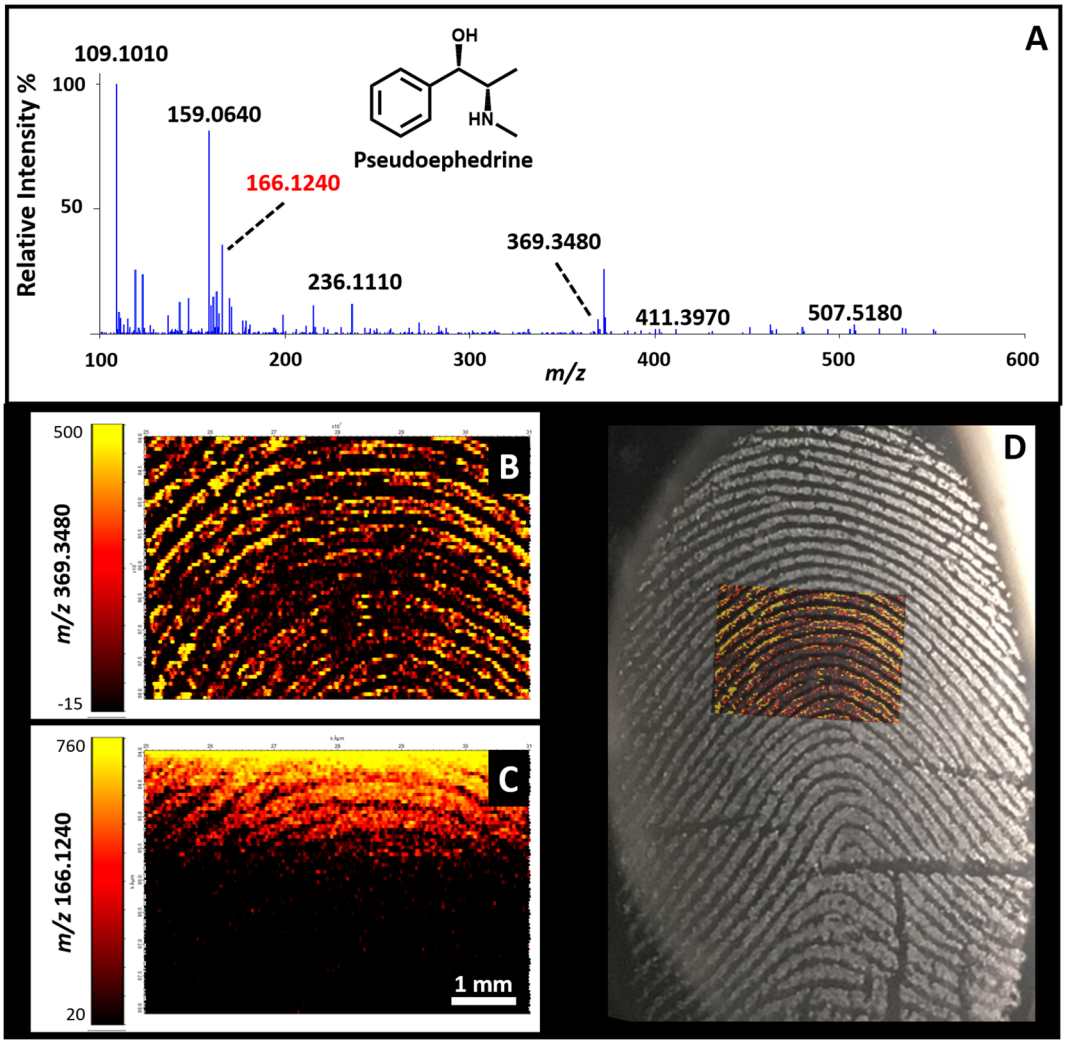

Fig. 3. A LADI-MS-derived mass spectrum and ion images showing the presence of endogenous and exogenous molecules in a pseudoephedrine-laden fingermark. Panel A shows the mass spectrum of a fingermark deposited after exposure to pseudoephedrine with the mass for protonated pseudoephedrine (*m/z* 166.1240) labelled in red. The color-overlaid LADI-MS ion images of endogenous cholesterol (Panel B) and exogenous pseudoephedrine (Panel C) in a latent fingerprint are shown. The 1 mm scale bar in the ion image applies to both images. The ion image of cholesterol is shown overlaid on a photograph of the latent print (Panel D).

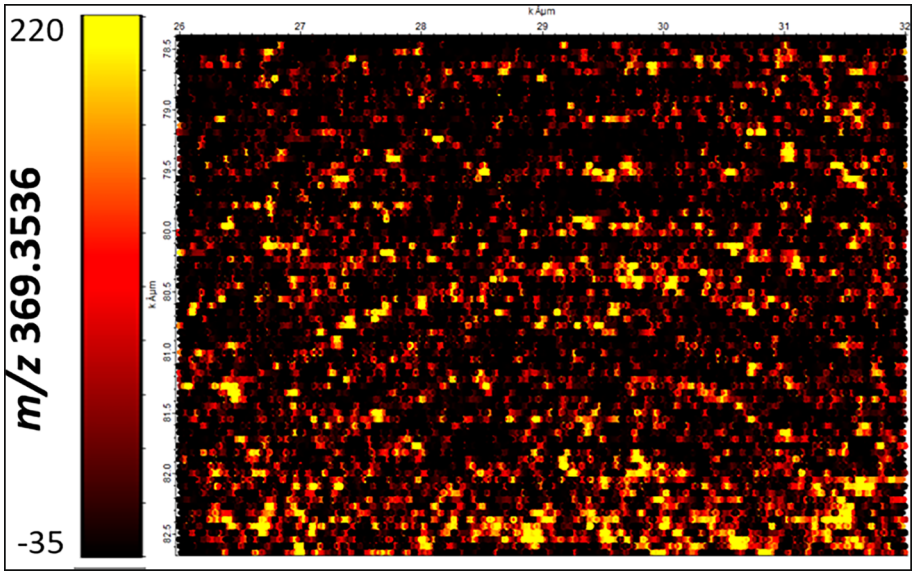

Fig. 4. Ion image of dehydroxylated cholesterol in a lifted latent fingermark, imaged on the adhesive side of packing tape by LADI-MS.

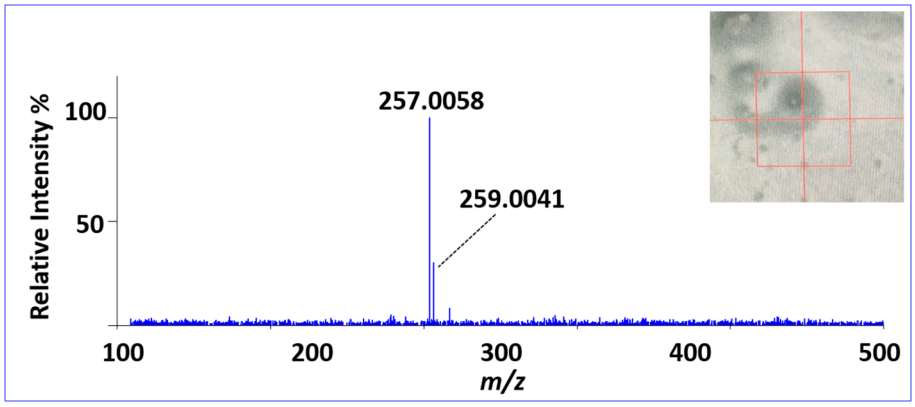

Fig. 5. Laser ablation DART-HRMS of an RDX particle located in a latent fingermark and detected using methylene chloride as a dopant. The *m/z* value 257.0058 is chlorinated RDX explosive. The inset shows a photograph of the magnified image of the RDX particle that appeared embedded within the print.

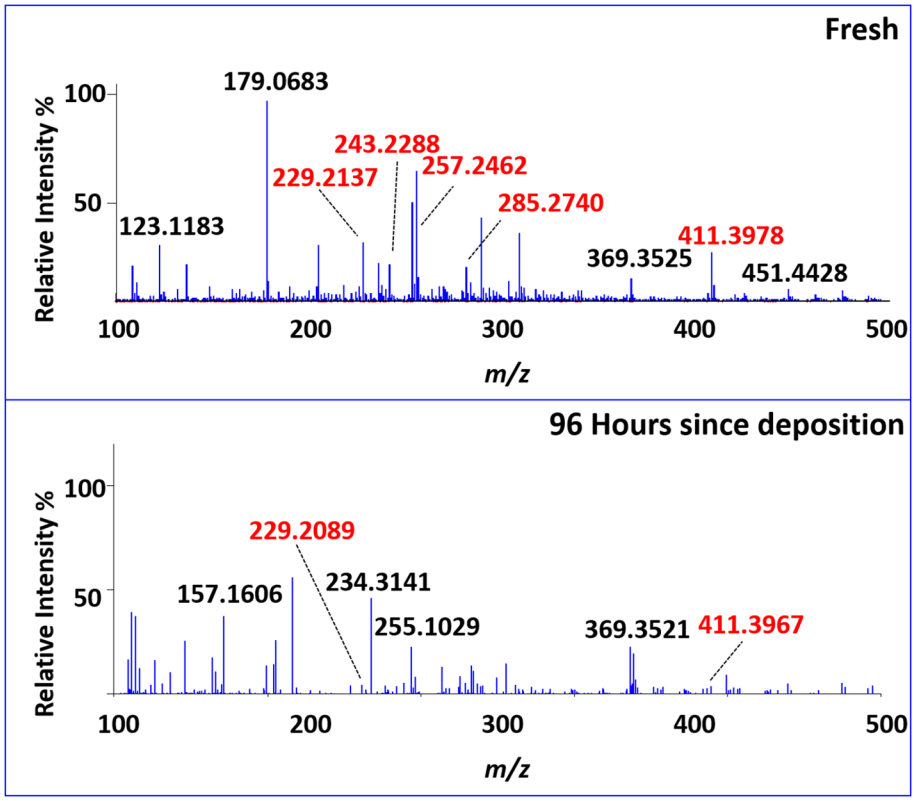

Fig. 6. Laser ablation DART mass spectra of a "fresh" blank fingermark (top) and a blank latent fingermark analyzed after 96 h (bottom). The masses indicated in red represent tetradecanoic acid (nominal *m/z* 229), pentadecanoic acid (nominal *m/z* 243), hexadecanoic acid (nominal *m/z* 257), octadecanoic acid (nominal *m/z* 285), and squalene (nominal *m/z* 411).

disturbing the rest of the print, thus allowing for further testing and photography by conventional methods. This technique could be applied to a range of psychoactive and explosive molecules in fingerprints and can be operated in positive or negative ion mode, permitting the detection of a variety of molecules. The ambient ionization conditions of the technique allow for the detection of molecules that would be lost under the high-vacuum conditions required by other methods and prevent extensive fragmentation of the analytes of interest. LADI-MS requires no sample pretreatment steps and can be performed on non-conductive surfaces. The application of LADI-MS to the detection in fingermarks of other small molecules such as endogenous/semi-endogenous drug metabolites are the subjects of ongoing investigations and could help distinguish between individuals who have handled the forensically relevant material versus those who have ingested it. Continued development of this approach in a forensics context opens up new vistas for the ever-increasing number of crime laboratories that are using DART-HRMS as a complementary tool in the analysis and detection of small molecules.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Thanks are extended to Elemental Scientific Lasers for the use of their NWR213 laser ablation system. This work was supported by the US National Institute of Justice [grant numbers 2017-R2-CX-0003 and 2015-DN-BX-K057] and US National Science Foundation [grant number 1429329], both of which are gratefully acknowledged.

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