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MALDI-mass spectrometry imaging for touch chemistry biometric analysis: Establishment of exposure to nitroaromatic explosives through chemical imaging of latent fingermarks

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HIGHLIGHTS

- Fingerprints can be screened using ambient ionization mass spectrometry.
- Explosives are detected in fingerprints using mass spectrometry imaging.
- Spatial distribution of diagnostic ions maps to fingerprint ridge patterns.
- Mass spectrometry imaging reveals chemical and biometric information simultaneously.
- Tandem application of MS techniques enables high throughput and robust analysis.

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ABSTRACT

Fingerprint ridge patterns continue to be tremendously important in forensic science because of their power to identify individuals. However, the current emphasis on the patterns fails to take advantage of additional chemical information they contain that may have a bearing on an investigation. One way this information can be useful is through correlating the fingerprint pattern with the presence of compounds that suggest exposure to compounds of interest, such as energetic materials that can be used to create explosive devices. We report here how interrogation of fingermarks by MALDI-mass spectrometry imaging (MSI) can be used to expose the presence of the explosive compounds trinitrotoluene (TNT), tetryl and picric acid, while yielding the fingerprint pattern that is traditionally collected in crime scene investigation. Ion images derived from diagnostic $[M-H]^-$ ions at nominal *m/z* 226 and 228 for TNT and picric acid respectively, and the $[M\text{-}NO_2\text{-}H]^-$ ion at *m/z* 241 for tetryl were generated and revealed the fingerprint pattern. Direct analysis in real-time high-resolution mass spectrometry (DART-HRMS) analysis of fingerprints was found to be useful in enabling rapid detection of diagnostic ions, so that their presence could inform whether subsequent MALDI-MSI experiments should be performed. The approach illustrates how DART-HRMS and MALDI-MSI in tandem can be employed in touch chemistry biometrics for revealing a direct connection between an individual and materials of forensic interest to which they have been exposed, such as explosives.

1. Introduction

The use of fingerprints to identify individuals is an accepted practice that has been employed successfully for many years [1]. While the processes of revealing and collecting the physical pattern of a fingerprint are well-established, new techniques have begun to explore the chemical content of fingerprints to learn more about donor attributes. These can include information about biological traits, habits and lifestyles, and even recent activities [2–13]. In a forensics context, this type of information may reveal an individual's exposure to dangerous materials such as explosives through detection of diagnostic markers. In this regard, screening for the presence of explosives with the full knowledge and consent of the individual being screened is a routine occurrence in certain contexts (e.g., airports, concerts, and other large public venues), and it is typically conducted by swabbing an individual or their belongings and analyzing the swabs in real time and on-site by ion mobility mass spectrometry [14,15]. Nevertheless, there are numerous instances in which surreptitious detection of the content of

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latent fingermarks, in a fashion that also reveals the identity of the individual, would be highly desirable as a means of potentially providing probable cause for a search warrant (e.g., in counterterrorism investigations). As such, detection of explosive materials in latent fingerprint evidence recovered from surfaces could prove an effective tool in forensics and other detective work.

In order to perform this type of analysis, a variety of techniques can be utilized. Targeted approaches (e.g., antibody binding, enzymatic assays, etc.) are highly sensitive, though they typically require prior knowledge of the analytes present [2,16–18]. Spectroscopic techniques, including infrared and Raman, are advantageous in that they are non-destructive, which is especially important in forensics [19–23]. However, they often lack the specificity required to enable definitive compound identifications, particularly when complex sample matrices such as fingerprints are involved. To overcome these challenges, mass spectrometric techniques, which have long been a pillar of forensic laboratory analysis, and which offer high sensitivity and selectivity, can be employed [5,6,24]. An extension of typical mass spectrometry analysis that could prove especially rewarding is mass spectrometry imaging, which provides not only the chemical information necessary to identify compounds, but also furnishes a map of their distributions within the surveyed area. For analysis of fingerprints, this would mean that the detection of explosives could not only be accomplished, but the use of the ion's spatial distributions could also yield the fingerprint pattern which is typically collected by conventional latent print development techniques [13,25–27]. A major benefit of this approach would be the establishment of a direct link between the donor and the critical chemical information gathered, while at the same time revealing the print pattern. Thus, development of a sample analysis workflow that integrates mass spectrometry imaging could be of immense benefit in homeland security and counterterrorism investigations.

Matrix-assisted laser desorption ionization-mass spectrometry (MALDI-MS) is a well-established soft ionization technique that has proven to be a powerful tool for both targeted and untargeted analyses of molecules within a variety of complex matrix samples [28,29]. In fingerprint analysis, MALDI-MS imaging (MSI) enables chemical data to be rendered in a form that displays the distribution of the ions in 2D space. Thus, for compounds that are localized to the print ridges, the ion image reveals the fingerprint pattern [30,31]. The utility of MALDI-MS and -MSI in the analysis of latent fingerprints for the detection of endogenous and semi-endogenous compounds, including metabolites of some illicit drugs, has been demonstrated [8,9,32,33]. It has also been demonstrated that explosive materials applied to fingermarks *after* their deposition, and explosives contained within synthetic fingerprints can be detected by MSI [26,34]. However, the use of MSI to discover the prior exposure of the print donor to such compounds has not been reported. While MSI protocols for the routine analysis of latent fingermarks would need to be compatible with current fingerprint processing and lifting approaches in order to be optimally useful, a necessary first step for the development of such techniques is the demonstration that analytes of interest can be detected and imaged by MSI using real fingerprints that are imaged after the handling of energetic materials of interest.

While MALDI-MSI can yield an unprecedented amount of forensically relevant chemical information, a drawback to its use for routine interrogation of fingerprints is that depending on the instrumentation used, analysis times can be significant and extend upwards of ~20 h based on the size of the sample area being surveyed and the desired spatial resolution. Thus, in order for MSI-based analysis to be efficient in both time and cost, it is desirable to couple its use to a quick and facile triage method that can indicate whether ions diagnostic of the presence of energetic materials are present, so that a decision can be rapidly made regarding whether to subject a print to MALDI-MSI. A number of techniques can be used for this purpose with a common example being ion mobility spectrometry (IMS) which is often used in airport security. Another is direct analysis in real time-high resolution mass spectrometry (DART-HRMS), a soft, ambient ionization technique that is increasingly being used in forensics [35–37]. The DART ion source enables ambient ionization of analytes in their native form. Spectra can be produced in seconds, with little to no required pretreatment steps in most cases. In addition, DART-HRMS has been shown to be effective in detecting a wide range of compounds (e.g., flavoring additives, psychoactive biomolecules, food adulterants) while also being a suitable technique for analyses involving mixtures and complex matrices (e.g., condom residues, unprocessed plant products, foods and beverages) [38–40]. By comparison, ion mobility spectrometry (IMS) has more limited utility due to lower chemical specificity [14,15]. As such, DART-HRMS analysis, which was found to be rapid and simple, and to offer high specificity, was used as a screening technique for the detection of diagnostic ions for the energetic materials that were analyzed in this study.

Presented here is proof-of-principle for an approach to establish a direct connection between an individual, and explosives to which they have been exposed, using MALDI-MSI of fingerprints. As examples, the common energetic materials trinitrotoluene (TNT), tetryl, and picric acid were first rapidly detected in fingerprints by DART-HRMS as a presumptive screening method. Whole fingerprints deposited directly onto target substrates were then surveyed by MALDI-MSI to reveal contact with the explosive, as well as the fingerprint pattern of the donor.

2. Methods

2.1. Materials

Isopropanol and 9-aminoacridine were purchased from Sigma-Aldrich (Milwaukee, WI). Acetonitrile (reagent grade) was purchased from Fischer Scientific (Hampton, NH). Polyethylene glycol 600 sulfate was purchased from TCI America (Portland, OR). Methanol (HPLC grade) was purchased from Pharmco (Brookfield CT). Indium-tin-oxide (ITO)-coated glass slides (25 × 75 × 0.7 mm, R_s = 5–15 Ω) were purchased from Delta Technologies (Loveland, CO). Explosives were derived from certified reference material (CRM) solutions. These materials (tetryl, picric acid, and trinitrotoluene) were purchased as 1.0 mg/mL (0.1 mg/mL for picric acid) solutions in acetonitrile-methanol from AccuStandard (New Haven, CT).

2.2. Instrumentation

Direct analysis in real time-high resolution mass spectrometry (DART-HRMS) was performed using a DART-SVP ion source (IonSense, Saugus, MA) coupled to a JEOL AccuTOF high resolution time-of-flight mass spectrometer (JEOL USA, Peabody, MA). MALDI-MSI was performed using a JMS-S3000 SpiralTOF MALDI TOF/TOF mass spectrometer (JEOL USA, Peabody, MA). Matrix was applied to the target slides using a GREX GCK02 airbrush kit, comprised of an AC1810 compressor with a Tritium TS3 airbrush (GREX, Monterey Park, CA).

2.3. Fingerprint sample preparation and analysis by DART-HRMS

For all of the experiments involving human participants, the State University of New York at Albany Institutional Review Board deemed the project to be exempt. Nevertheless, informed consent was granted by participants for the collection and display of their fingermarks.

For the DART-MS studies, a single donor provided fingerprints, washing their hands thoroughly between handling each explosive. For each explosive tested, 80 μL of the CRM was deposited onto a watch glass and the solvent was allowed to evaporate, leaving behind a residue of the pure compound (80 μg for tetryl and TNT, 8 μg for picric acid). For experiments involving detection of explosives within the print residue, the donor pressed their forefinger, which had been

groomed through rubbing against the sebum-rich areas of the face (i.e. forehead and nose), into the explosive residue. Control fingerprints were derived from groomed fingertips that were not subsequently exposed to explosive material. Fingerprints were deposited onto a glass microscope slide, after which the closed end of a glass melting point capillary tube was used to swab a 1 mm by 2 mm area of the fingerprint. The capillary tube was stored in a GC vial until analysis. These samples were distinct from fingerprints that had been deposited for MALDI-MSI analysis.

For the DART ion source, the grid voltage and gas heater temperature were set to 250 V and 400 °C respectively. For the mass spectrometer, the ring lens, orifice 1, and orifice 2 voltages were set to −5 V, −20 V, and −5 V, respectively, and the RF ion guide voltage was set to −400 V. Spectra were acquired over the *m/z* range 80–800 at a rate of one spectrum per second. The flow rate for the helium gas to the ion source was 2.0 L/s. Fingerprint residues were analyzed directly by presenting the closed end of the glass capillary tube that had been used to swab the fingerprint, to the open-air interface between the ion source and the mass spectrometer inlet. PEG 600 was used as a mass calibrant at the end of each acquisition. Data processing of DART spectra, including averaging, calibration, background subtraction and peak centroiding, was performed using TSSPro3 software (Shrader Analytical Labs, Detroit, MI). Spectra were viewed and analyzed for analytes of interest using Mass Mountaineer (RBC Software, Portsmouth, NH). All analyses were performed in negative ion mode.

2.4. Explosive-laden fingerprint preparation and analysis by MALDI-MSI

For imaging studies, one donor provided fingerprints over the course of multiple days, handling only one explosive per day. For each explosive tested, and on separate occasions from DART-MS studies, 80 μL of the CRM was deposited onto a watch glass and allowed to dry to a residue of the purified compound into which a groomed forefinger was pressed (80 μg each for tetryl and TNT, 8 μg for picric acid). The donor then deposited the fingerprint onto an ITO glass slide, alongside a second fingerprint that was deposited prior to contact with the explosive (to serve as a control). These samples were separate from samples prepared for DART-MS analysis. Approximately 2 mL of a matrix solution comprised of 10 mg/mL 9-aminoacridine in 60:40 isopropanol-acetonitrile was applied to the slide with an airbrush from a distance of about eight inches, and the sample was allowed to dry in air. A calibrant solution (1:1 PEG 600 sulfate-matrix solution) was applied next to the fingerprints on the same ITO slide to serve as a mass calibrant. MALDI mass spectra were obtained in negative spiral mode. “Spiral mode” refers to the time-of-flight optics design that utilizes a figure-eight ion trajectory to allow a 17 m flight path that results in ultrahigh resolving power and sub-ppm mass accuracy. Spectra were acquired in the *m/z* 50–1000 range, at a sampling interval of 0.5 ns with a laser frequency of 1 kHz. Laser power, delay time, and detector voltage parameters were optimized for each sample individually. The pixel size for imaging experiments was between 70 and 80 μm for all samples. Once parameters were defined, the MALDI-MS was set to auto-acquisition mode, which acquired ~32,000 spectra from each fingerprint analyzed.

To confirm the identities of ions, MALDI-MS-MS experiments were performed on fingermark residues. Compound standards were comprised of ~5 μL of a 1:1 mixture of the CRM material (1.0 mg/mL TNT or tetryl, 0.1 mg/mL picric acid in acetonitrile-methanol) and the matrix solution (10 mg/mL 9-aminoacridine in 60:40 isopropanol-acetonitrile) which was applied to each ITO slide, adjacent to the fingerprint. MALDI mass spectra were first obtained from the spotted CRM in negative spiral mode. Spectra were acquired in the *m/z* 50–1000 range, at a sampling interval of 0.5 ns with a laser frequency of 1 kHz. Laser power, delay time, and detector voltage parameters were optimized for each sample individually. Using the collected spectra, ions of interest were selected using a 5 mmu window for further MS-MS analysis. MALDI mass spectra were then collected in negative TOF-TOF mode, subjecting the ion selected to further fragmentation. Spectra were collected in this way for both the CRM and the explosive material-laden fingerprint for comparison. Spectra were collected from the fingerprint by random sampling over a large area of the fingerprint. Parameters were again optimized per sample, with the lower bound of the mass range set to *m/z* 15, and the upper bound being defined by the ion selected for fragmentation.

Data processing was accomplished using the msTornado and msMicroImager suite of programs (JEOL Ltd, Akishima, Tokyo, Japan), including msMicroImager Extract for binning and compiling mass images; msTornado Analysis for centroiding, background subtraction, and peak picking; and msMicroImager View for smoothing, scaling, and exportation of mass spectral images.

3. Results and discussion

3.1. DART-HRMS screening of fingerprint residues

The use of a rapid screening method is essential to the successful integration of the chemical imaging of fingerprints into forensic science workflows. This is because while MALDI-MSI of fingerprint evidence is an extremely powerful source of information, its utility is offset by the time investment required to perform the analysis, which can take up to 20 h on some instruments and requires cumbersome sample preparation. As such, it is not feasible to apply this technique indiscriminately to all fingerprint evidence, and a method to presumptively assess samples for the presence of compounds of interest is desirable. DART-HRMS fulfills this need and can be used as a triage approach, although IMS can also be used.

To illustrate how DART-HRMS can be exploited for this purpose, the certified reference materials TNT, the military explosive tetryl, and picric acid (which can be used in improvised explosive devices (IEDs)) were analyzed (Table 1). Reference materials were first tested in both positive and negative ion modes to determine which was more suitable. It was determined in these experiments that negative ion mode produced easily distinguishable ions for each explosive tested. For tetryl, a major fragment at *m/z* 241, representative of loss of the *N*-positioned nitro group and a proton, was observed, while for picric acid and TNT, the precursor ions $[M-H]^-$ at nominal *m/z* 228 and 226 were observed. These ions have been previously described in the literature as diagnostic markers for each explosive, and they could all be readily detected in explosive-laden fingerprints which were swabbed and analyzed using DART-HRMS (Fig. 1) [41]. The area swabbed for each fingerprint, which was approximately 1 mm by 2 mm in dimension, was taken from the side of the fingerprint to minimally disturb the print. The representative spectra demonstrate the successful use of DART-HRMS as a screening method for the triage of fingerprint evidence,

Table 1
Explosive compounds tested, and the diagnostic ions of interest detected in fingerprint residues by DART-HRMS.

Compound	Amount of material handled	Ion detected	Molecular formula	Measured mass (Da)	Calculated mass (Da)
Trinitrotoluene (TNT)	80 μg	$[M-H]^-$	$C_7H_4N_3O_6$	226.0100	226.0095
Tetryl	80 μg	$[C_7H_6N_4O_6\text{-}H]^-$	$C_7H_5N_4O_6$	241.0209	241.0204
Picric acid	8 μg	$[M-H]^-$	$C_6H_2N_3O_7$	227.9893	227.9887

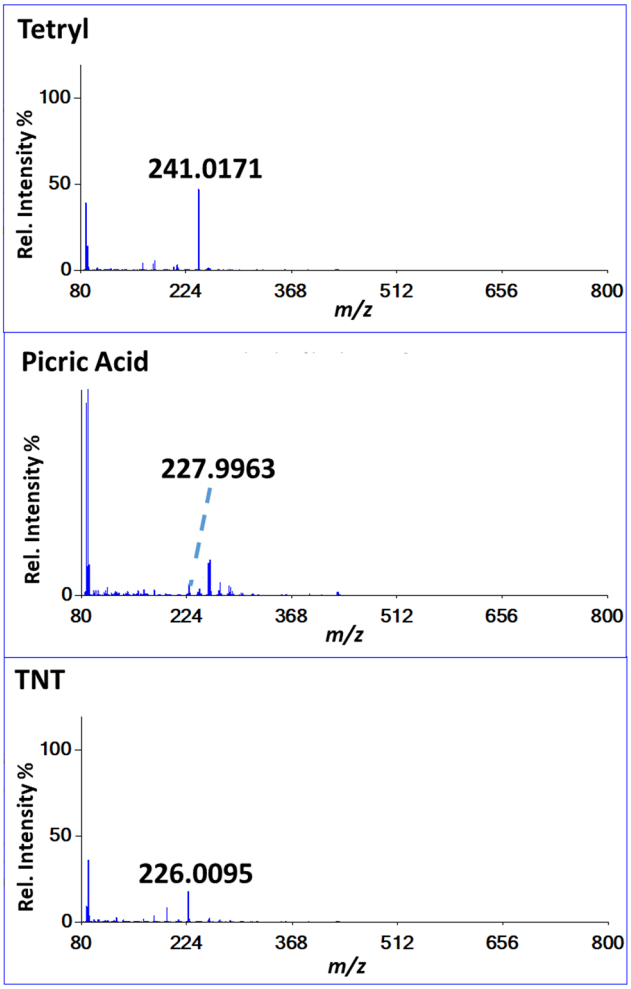

Fig. 1. DART high-resolution mass spectra of fingerprint residues collected after handling explosive materials. For each of the explosives listed, diagnostic markers in the form of either precursor ions or fragments previously documented in the literature were detected, enabling DART-HRMS to provide presumptive confirmation of an individual's exposure to the explosive. Each ion is indicated by its high-resolution mass.

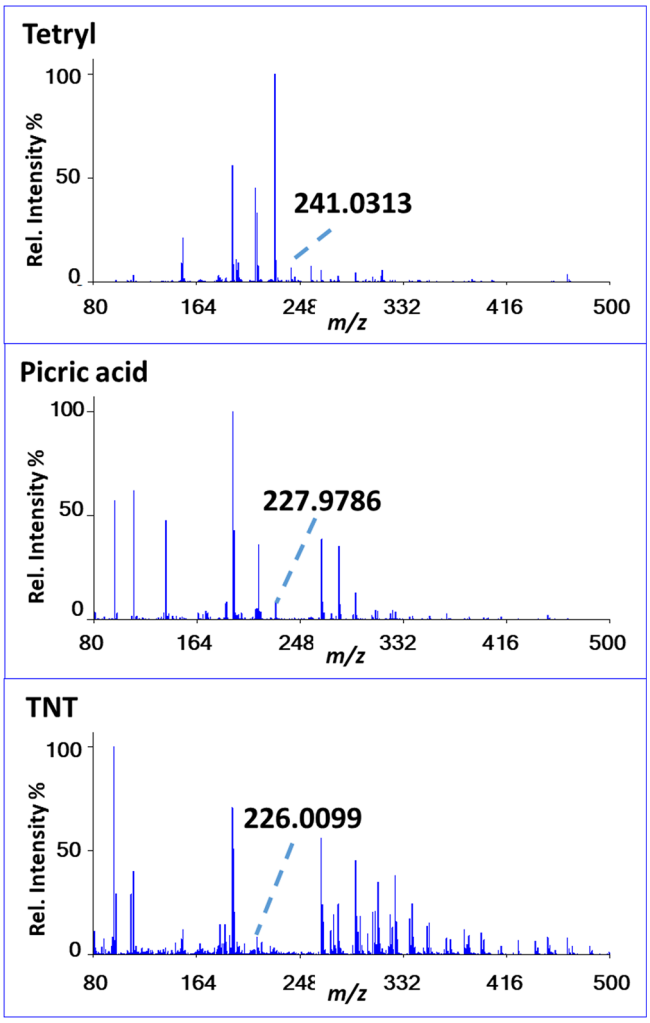

Fig. 2. Representative MALDI mass spectra from the imaging analysis of fingerprints laden with tetryl, picric acid, and TNT. In each spectrum, diagnostic ions are labeled.

which can expedite sample processing, and decrease overall costs associated with MSI analysis.

3.2. MALDI-MS imaging of explosive-laden fingerprints

While the detection of ions indicative of the presence of TNT, tetryl and picric acid can be rapidly accomplished using DART-HRMS, the ability to reveal the donor fingerprint from the spatial distributions of the relevant ions provides evidence of the donor's exposure to explosives. Thus, the explosives whose presence could be rapidly detected in print residues by DART-HRMS analysis, were then detected by MALDI-MSI. Representative MALDI mass spectra associated with these experiments for new fingermarks laden with tetryl, picric acid, and TNT are shown in Fig. 2 with the *m/z* values associated with the diagnostic ions indicated (i.e., 241.0313, 227.9786, and 226.0099 respectively).

Representative ion images are shown in Fig. 3 using a black and white color scale, where black represents the lowest abundance and white the highest. In all cases, fingerprint images based on *m/z* values associated with a range of endogenous molecules were readily observed. Examples of these appear beneath each of the ion images diagnostic of the energetic compounds. While mapping the distribution of these compounds in the fingerprint does not always provide a clear image with high enough levels of detail for identification, it should be noted that each MALDI-MSI experiment produces hundreds of ion images, many of which have higher levels of detail that can enable identification. For example, the ion image associated with *m/z* 226 from a fingerprint containing TNT may not be of sufficient quality to make a match to an exemplar print in a comparison database. However, the ion image derived from *m/z* 369 from the same fingerprint produces a pattern that much more clearly shows the ridge detail. Fig. 3 illustrates this concept; beneath the ion image of each explosive, is a second ion image derived from an alternative *m/z* value, and which more clearly shows the ridge details for each print. For fingerprints laden with tetryl or picric acid, nominal *m/z* 265 consistent with dehydroxylated stearic acid is rendered as an ion image, while for TNT, nominal *m/z* 369 which is consistent with dehydroxylated cholesterol is shown. In each of these cases, superior image quality is demonstrated. In this way, other endogenous markers can be used to make an identification.

In addition to the detection of precursor ions or other fragments, MS-MS experiments were performed to confirm the identities of the detected precursor ions. Fig. 4 shows several spectra comparing the fragmentation patterns of the diagnostic ions detected from analysis of the laden fingerprints, to those from analysis of the corresponding authentic standards. In each case, the fragmentation patterns match, and enable the identification of the ion selected that was associated with each explosive. Thus, the presence of each explosive tested can be confirmed in collected fingermarks that were analyzed in this way.

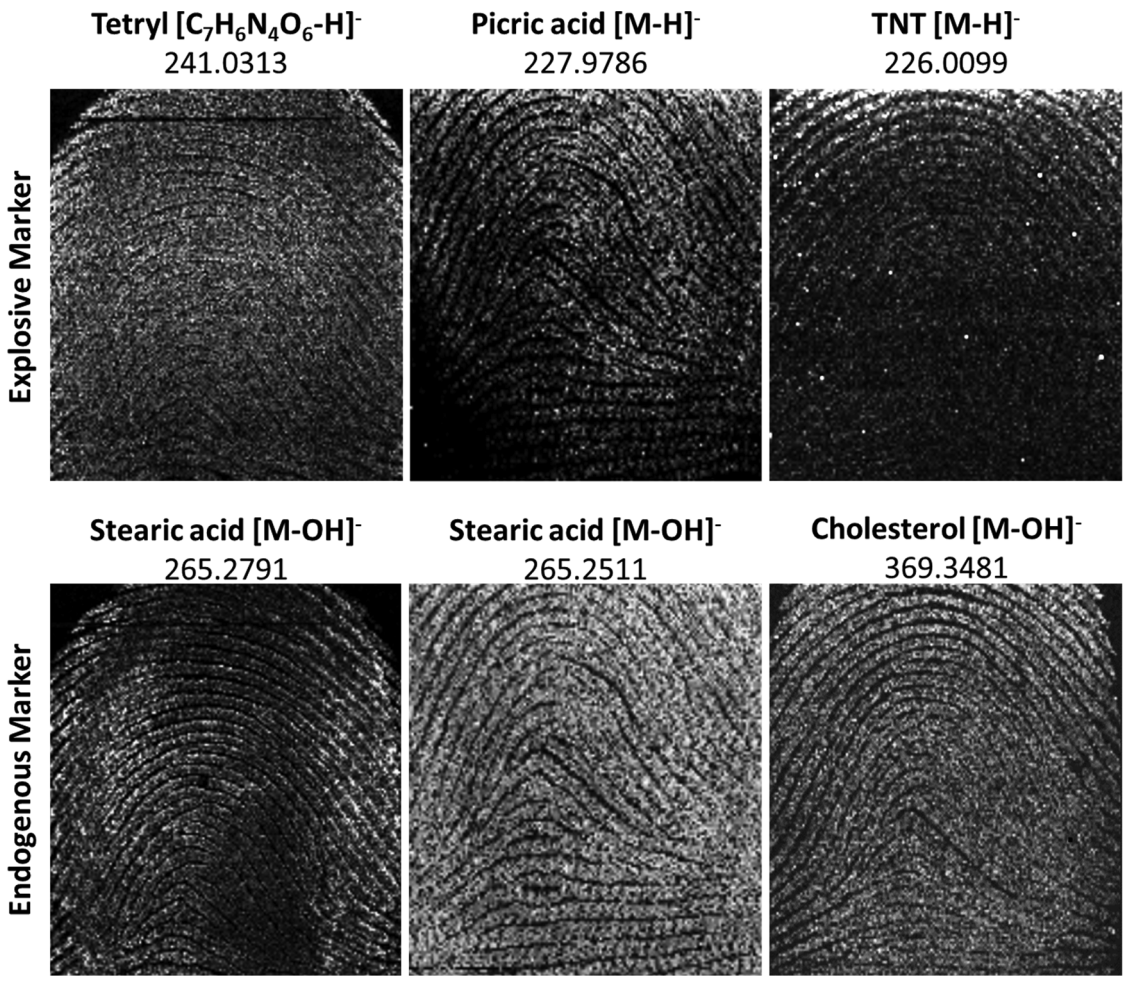

Fig. 3. Ion images from fingerprints laden with explosives. Diagnostic ions at nominal *m/z* 241, 228, and 226 are rendered as 2D ion images to reveal the donors' exposure to tetryl, picric acid, and TNT, respectively. In cases where the ion derived from the explosive does not produce a high clarity image of the fingerprint *minutiae*, other ion images generated from the same fingerprint can produce clearer images useful for identification. Accordingly, for each fingerprint a second ion image, generated from the endogenous compounds cholesterol or stearic acid and detected in the fingerprint, is presented below, with the corresponding *m/z* value indicated.

The observation of fingermark patterns derived from ion images of energetic materials permit several important inferences to be made. Most obviously, the unique fingerprint pattern generated in this manner can be used to identify the donor. In addition, even in cases where the ions diagnostic of contact with an explosive do not necessarily produce an image of high enough quality to identify an individual, the detection of the compound in and of itself indicates the individual's exposure. This is because the print pattern details can be acquired from the ion

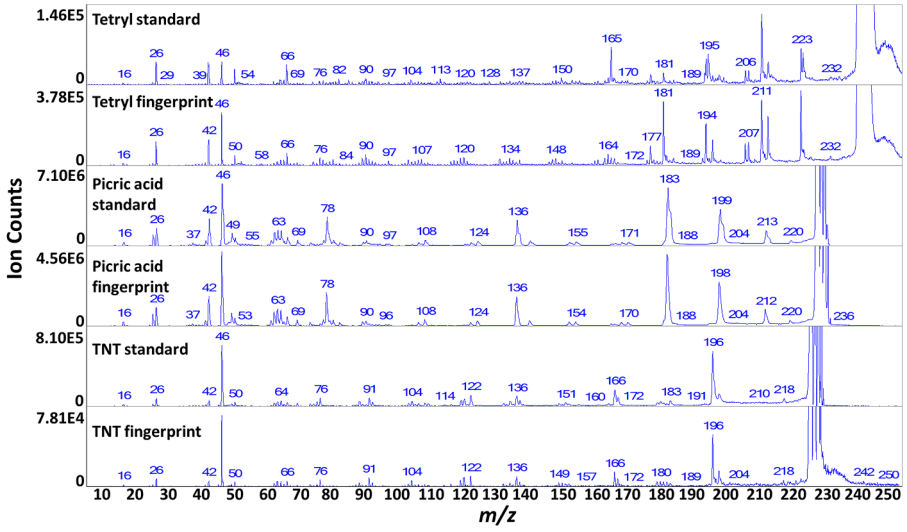

Fig. 4. Comparisons of MALDI mass spectra showing the fragmentation patterns of the diagnostic ions for the indicated energetic materials. Fragmentation of the ions diagnostic of exposure to each explosive was performed during analysis of both the energetic material-laden fingerprint residue and the CRM standard directly. For the explosives tested, fragmentation was performed for ions detected at nominal *m/z* 241, 228, and 226 corresponding to tetryl, picric acid, and TNT respectively. In each case, identical fragmentation patterns were observed, thereby confirming the identification.

images of m/z values representative of endogenous compounds such as lipids, that are detected in the MALDI-MSI analysis. If, through handling, the explosive was present on the finger pad when a fingerprint was deposited, it would be expected to be isolated to the ridges of the print. By contrast, an explosive that was present on a surface prior to or after the deposition of a fingerprint, would not be expected to be confined to the ridges. Rather, distinct isolated particles of explosive material may be detected. It should be noted however, that the method presented here does not necessarily enable distinctions to be made between purposeful immersive handling, in which the fingers are fully exposed to copious amounts of material as might be expected in the construction of an IED, versus secondary transfer, in which exposure is incidental. Systematic studies of the changes in the distribution of explosive substances across a fingerprint with time, and the extent to which their clarity is retained (and under what conditions), remain to be conducted. While the ability to detect diagnostic biomarkers of energetic materials may diminish over time and impact the extent to which they can be used to reveal an ion image in the form of the fingerprint pattern, the use of other ions present within the fingerprint can be used to generate print pattern ion images that can serve as the basis of identification. Even in this case, the ability to detect the explosive material may still be important information to have.

The results demonstrate proof-of-concept for touch chemistry biometric analysis for the detection of highly labile energetic materials using MALDI-MSI. The development of MALDI-MSI procedures that are optimized for the detection of a broad range of energetic materials, while at the same time being compatible with current procedures for the development and lifting of prints, are the subjects of continuing investigations.

4. Conclusion

Fingerprints, which contain a large variety of endogenous, semi-endogenous, and exogenous compounds, can reveal a tremendous amount of information about the donor, some of which may have relevance in counterterrorism or forensic investigations. Among the compounds of interest are energetic materials such as tetryl, TNT, and picric acid, the observation of which indicates exposure to bomb-making materials on the part of the donor. A MALDI-MSI approach to indicate the handling of these materials through analysis of latent fingermarks, while at the same time providing a fingermark image that can be used to identify the donor, was developed. The ridge pattern, which is revealed through the spatial distribution of an ion diagnostic of the energetic material itself, can be used to establish a direct link between the compound and the donor. DART-HRMS analysis of fingerprints was demonstrated to have utility as a screening method for rapid determination of the presence of energetic materials of interest, in order to assess whether samples should be further subjected to MALDI-MSI analysis. The approach illustrates how the use of DART-HRMS and MALDI-MSI in tandem can be employed in touch chemistry biometrics to detect explosives in fingerprints, which may provide grounds for further investigation of possible criminal intent.

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.

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