Supplementary Information for "**Chemical Imaging of Artificial Fingerprints by Desorption Electro-Flow Focusing Ionization Mass Spectrometry**"

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Mass Spectrometry Imaging System Details

The overall MSI system was comprised of control software for the mass spectrometer and sample raster scanning, the ion source for sample desorption and ionization, the mass analyzer for data acquisition, and the imaging software for data analysis. The sampling stage consisted of two perpendicular linear motorized translational stages for 2-axis motion (Thor Labs, Newton, NJ). The motion control for sample scanning, including, raster type (i.e., uni-directional point-to-point/dwell, serpentine point-to-point/dwell, or constant velocity scan), step-size (i.e., pixel size), scan velocity, scan acceleration, overall scan dimensions, delay times, dwell/acquisition time, etc. was controlled by a custom LabVIEW code. The motion control code also included triggering of the mass analyzer data acquisition through a commercial software package. The MSI system was coupled to a 4000 QTrap® Triple-Quadrupole System (Applied Biosystems/MDS Sciex) controlled by the Analyst® software. The LabVIEW code triggered the Analyst software through a peripheral device analog synchronization by sending a TTL signal through the AUX I/O interface on the QTrap instrument. The synchronization was completed by developing the appropriate Acquisition Method and Acquisition Batch in the Analyst software, waiting for the necessary trigger signal to begin data acquisition at each pixel or constant-velocity row scan.

Materials and Methods

A 50/50 (volume fraction) solution of methanol and water (Sigma-Aldrich, St. Louis, MO) was delivered to the DEFFI source at a flow rate of 1.75 μL/min by a liquid infusion syringe pump (Legato 100, KD Scientific, Holliston, MA) and focused by a 140 kPa Zero Air assist gas. Methamphetamine hydrochloride and cocaine hydrochloride were obtained from Sigma-Aldrich (St. Louis, MO) at 1 mg/mL concentration, in methanol and acetonitrile, respectively; and 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) were obtained from AccuStandard (New Haven, CT) at 1 mg/mL in methanol. Gold Bond Ultimate Hand Sanitizer Sheer Moisture (Chattem Inc., Chattanooga, TN) was also used as a fingerprint material additive.

The artificial fingerprint material was comprised of a number of chemicals commonly found in eccrine and sebaceous secretions. Chemicals in this material include fatty acids, amino acids, cholesterol, squalene, urea, and ionic salts, at levels which mimic those of a typical fingerprint. An emulsion of the artificial fingerprint material in methanol was pipetted onto the mold and the solvent allowed to evaporate under ambient conditions for 5 minutes.

All fingerprints were imaged across a 23 mm × 18 mm area and continuously scanned in a unidirectional pattern at a constant 350 μm/s velocity. Each 100 μm × 100 μm pixel collected a single 0.2857 second mass spectrum in the *m/z* ranges of interest. Due to limitations in the maximum number of sample files per single batch file, defined by the mass spectrometer control software (Analyst®), final images were the stitched combination of two preliminary images. Potentials of ± 750 V and ± 500 V were applied to the spray solvent and MS inlet (Figure 1) for positive and negative mode MS, respectively.

Deposited, lifted, and imaged artificial fingerprints were developed using Omega-Print Cyanoacrylate Fuming Compound (Sirchie® Fingerprint Laboratories, Youngsville, NC) by placing the samples in a sealed plastic bag along with approximately 1 mL of the fuming compound and 1 mL of water.

Additional Images, Mass Spectra, and Figures

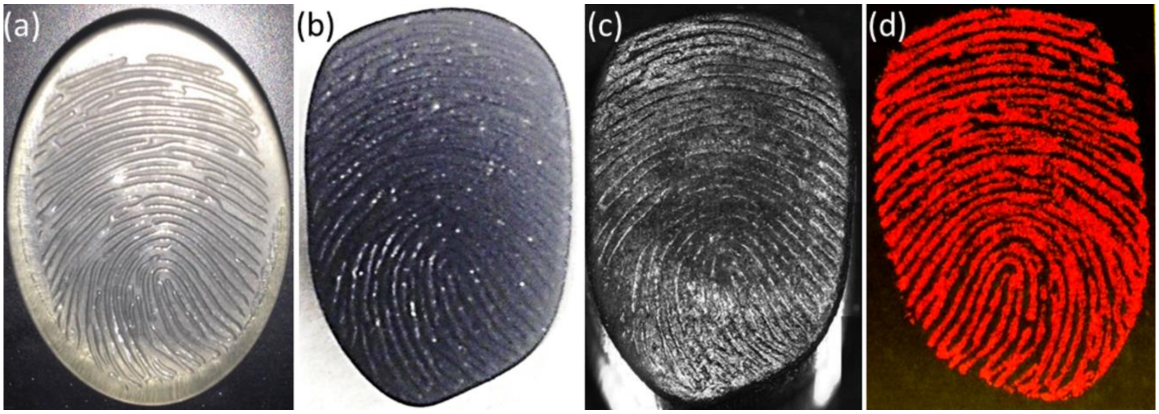


Figure S1. Optical images of the artificial fingerprint mold ridge detail, including (a) a plastic mold, (b) a rubber mold, (c) the mold covered with artificial fingerprint material, and (d) false color image of stamped ink (Exclusive Inks® Stamp Pad) on copy paper.

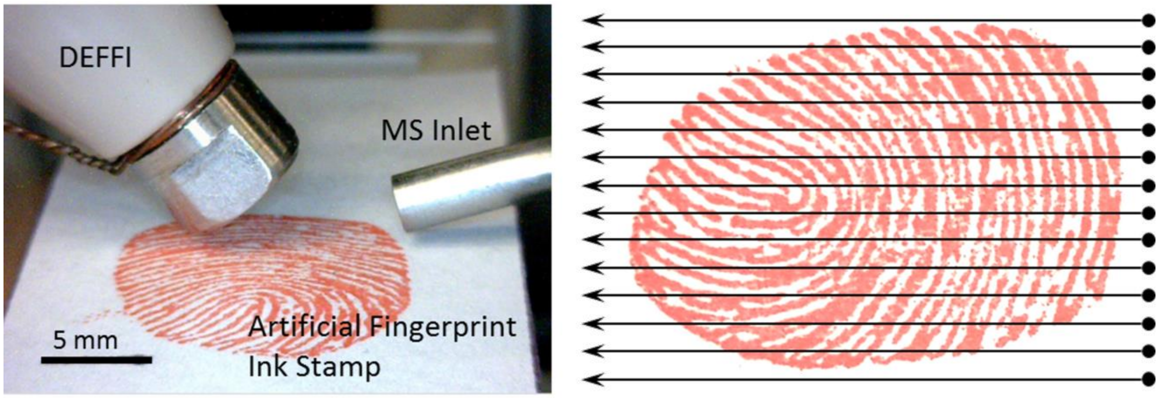
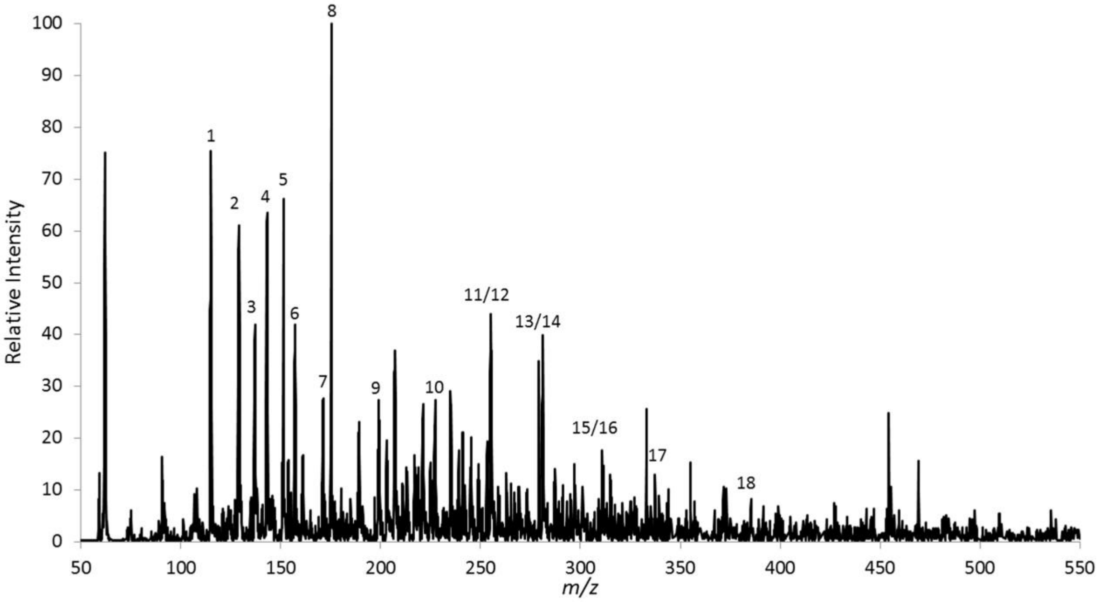
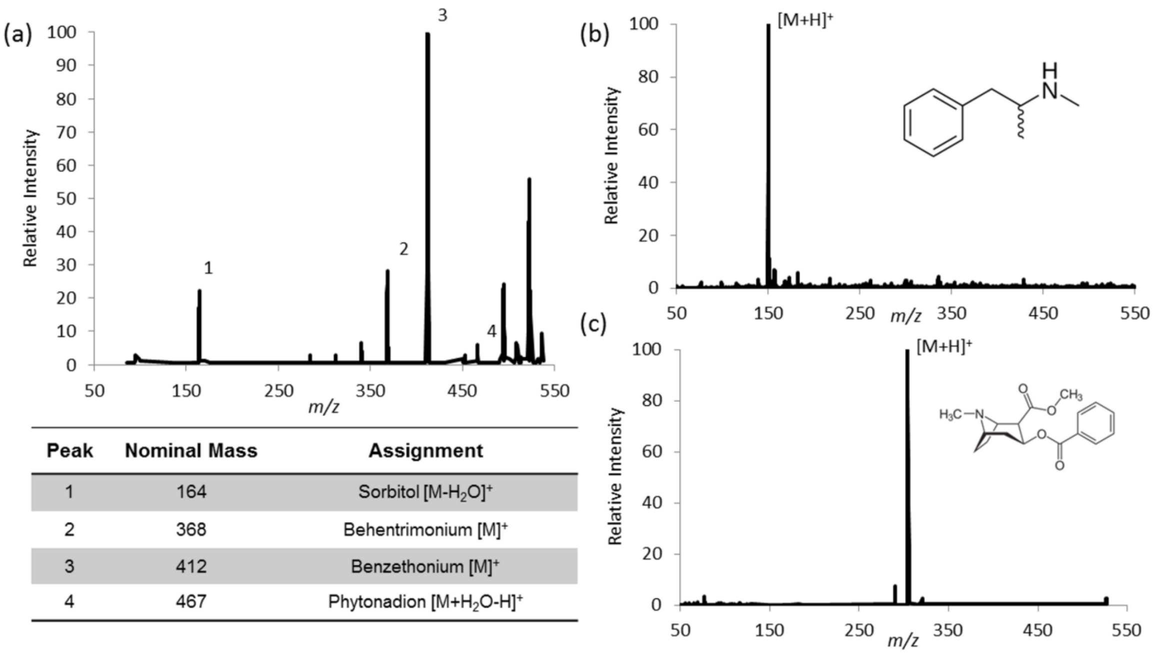


Figure S2. Optical photograph of the DEFFI-MSI experimental setup and schematic representation of the unidirectional constant velocity raster pattern (not to scale).



Peak	Nominal Mass	Assignment	Peak	Nomial Mass	Assignment
1	115	Hexanoic Acid $[M\text{-}H]^-$	10	227	Tetradecanoic Acid $[M\text{-}H]^-$
2	129	Heptanoic Acid $[M\text{-}H]^-$	11	253	Palmitoleic Acid $[M\text{-}H]^-$
3	137	Glycine $[M+NO_3]^-$	12	255	Hexadecanoic Acid $[M\text{-}H]^-$
4	143	Octanoic Acid $[M\text{-}H]^-$	13	281	Oleic Acid $[M\text{-}H]^-$
5	151	Alanine $[M+NO_3]^-$	14	283	Octadecanoic Acid [M-H]-
6	157	Nonanoic Acid $[M\text{-}H]^-$	15	311	Eicosanoic Acid $[M\text{-}H]^-$
7	171	Decanoic Acid $[M\text{-}H]^-$	16	316	Palmitoleic Acid $[M+NO_3]^-$
8	175	Pyruvic Acid $[2M\text{-}H]^-$	17	344	Oleic Acid $[M+NO_3]^-$
9	199	Dodecanoic Acid $[M\text{-}H]^-$	18	385	Cholesterol $[M\text{-}H]^-$

Figure S3. Representative DEFFI mass spectrum for the synthetic fingerprint material chemical composition in negative mode MS. The nominal position of a number of compounds are listed.



Peak	Nominal Mass	Assignment
1	164	Sorbitol $[M-H_2O]^+$
2	368	Behentrimonium $[M]^+$
3	412	Benzethonium $[M]^+$
4	467	Phytonadion $[M+H_2O-H]^+$

Figure S4. Background-subtracted, individual component, DEFFI mass spectra for (a) Gold Bond Lotion, (b) methamphetamine, and (c) cocaine in positive mode MS. Each analyte was sampled and spectra were summed for 30 s. Inset: chemical structure of methamphetamine. Nominal position for a few lotion components are listed.

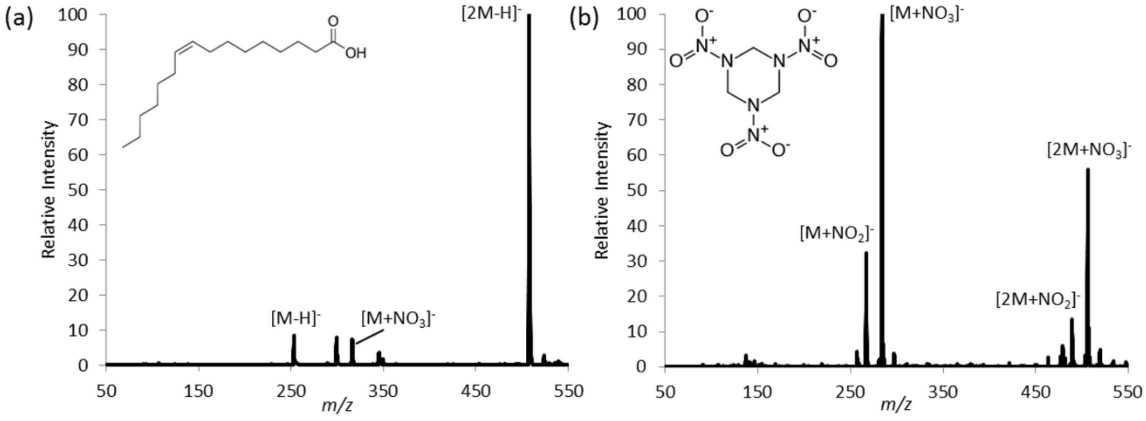


Figure S5. Representative, individual component, DEFFI mass spectra for (a) palmitoleic acid and (b) RDX, in negative mode MS. Each analyte was sampled and spectra were summed for 30 s. Insets: chemical structure of palmitoleic acid and RDX.

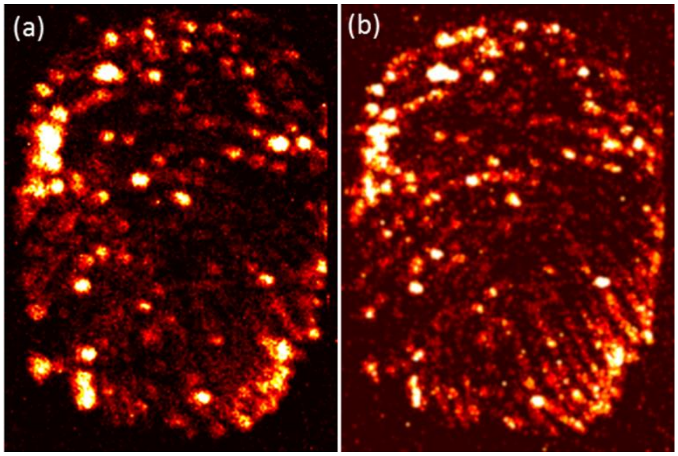


Figure S6. Desorption electro-flow focusing ionization mass spectrometry images of a RDX-laden artificial fingerprint deposited onto black painted, clear-coat finished, aluminum and pulled with forensic lift tape. Chemical images of (a) palmitoleic acid dimer, a component of the synthetic fingerprint material (*m/z* 507 $[2M\text{-}H]^-$) and (b) RDX dimer nitrate adduct (*m/z* 506 $[2M+NO_3]^-$).

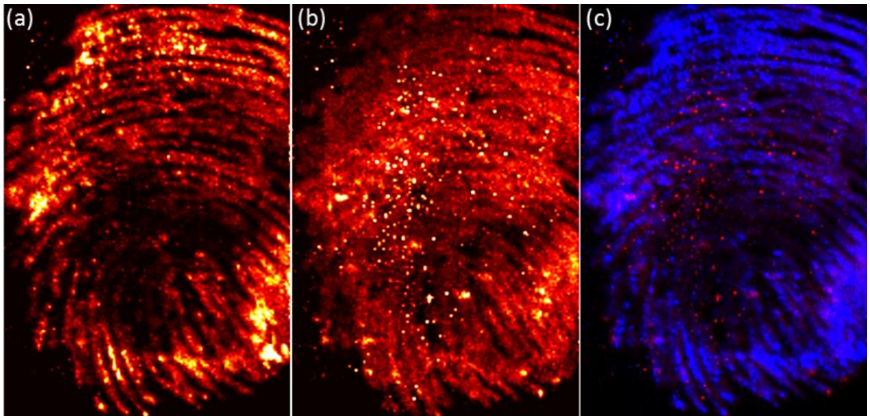


Figure S7. Desorption electro-flow focusing ionization mass spectrometry images of a cocaine-laden artificial fingerprint deposited onto black-painted, clear-coat finished, aluminum substrate and pulled with forensic lift tape. Chemical images of (a) benzethonium, a component of lotion spiked into the synthetic fingerprint material (*m/z* 412 $[M]^+$), and (b) cocaine (*m/z* 304 $[M+H]^+$). Lighter color indicates higher intensity. (c) A colocalization map of the fingerprint material indicator, benzethonium (blue) and the narcotic cocaine (red).

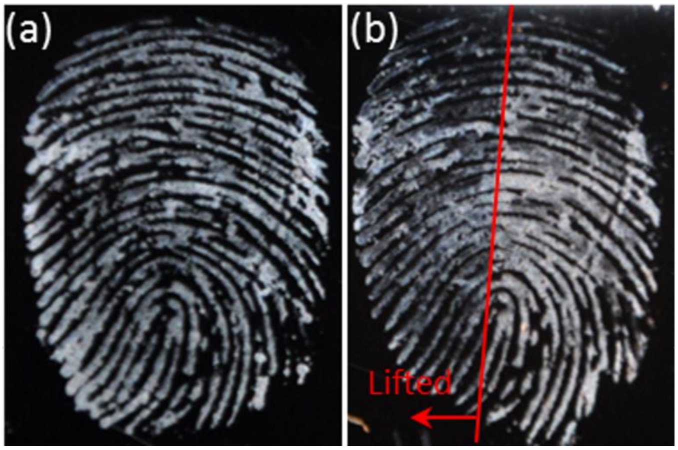


Figure S8. Optical images of fingerprints stamped onto a black-painted, clear-coat finished, aluminum substrate. (a) Image taken following the print being pulled with lift tape. (b) Fingerprint image with left half lifted and right half untouched.

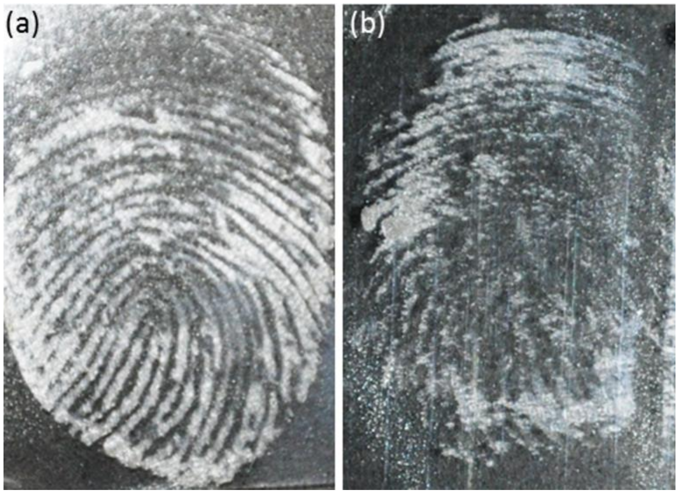


Figure S9. Optical images of artificial fingerprints developed using Omega-Print Cyanoacrylate Fuming Compound (Sirchie), (a) deposited directly onto forensic lift tape (not DEFFI imaged) and (b) lifted from a black painted, clear coat finished, aluminum substrate and scanned by DEFFI for imaging (lifted/imaged print from Figure S10).