Supporting Online Material for

Latent Fingerprint Chemical Imaging by Mass Spectrometry

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1. Materials and Methods

a. Chemicals, Solvents and Substrates
   i. Cocaine, Δ9-THC, Cannabidiol and RDX were purchased from Cerilliant Corporation (Round Rock, TX) and diluted in water to a final concentration of 500µg/mL. Methanol was purchased from Mallinckrodt (Phillipsburg, NJ) and the water purified (18MΩ-cm) using a PureLab ultra System by Elga LabWater (High Wycombe, UK). Ammonium hydroxide and sodium chloride were from Sigma-Aldrich. The surfaces employed were glass (Electron Microscopy Sciences, Hatfield, PA), printer paper (Xerox business 4200, 75 g/m², Xerox Corp., Rochester, NY), plastic (CD storage jewel cases from OfficeMax, Naperville, IL) and metal (a stainless steel structure in our lab, Bindley Bioscience Center, Purdue University, IN). A Teflon sheet (McMaster-Carr Supply Co.) with a square cut-out of 19.2 x 14.8 mm² or 29.6 x 19.2 mm² was used as a mask in order to delimit the scanning area. Invisible tape (OfficeMax, Naperville, IL) was used for tape-lifting experiments.

b. Latent fingerprint (LFP) blots
   i. Blank latent fingerprints: Sebum rich fingerprints were produced by touching the fingertips on the forehead and then blotting on glass, paper, plastic or metal through a Teflon mask. These fingerprints were visible under oblique lighting, except on paper.
   ii. Spiked latent fingerprints: Ten microliters (10µL) of a solution of an individual compound (500µg/mL) was deposited on the fingertips of volunteers using a micropipette. The solution was spread on the fingertip surface using the micropipette tip. After a drying time of approximately 3 minutes, the fingers were blotted on glass, paper and plastic using a Teflon mask. These fingerprints were visible under oblique lighting, except on paper. Note: Experiments were conducted on volunteers under a human subject protocol approved by the Institutional Review Board of Purdue University. The volunteers were never exposed to the same compound more than once. For tandem mass spectrometry experiments, 10 µL of Cannabidiol was deposited on the finger, and after drying, 5 µL of Δ9-THC was deposited on the edge of the same fingertip, Fig S1.
   iii. Overlapping Fingerprints: Ten microliters (10µL) of Δ9-THC solution (500µg/mL) was deposited on the fingertips of volunteers using a micropipette. The solution was spread on the fingertip surface using the micropipette tip. After a drying time of approximately 3 minutes the fingers were blotted on paper using a Teflon mask (29.6 x 19.2 mm²). After drying, a second blank fingerprint was blotted on top of the one containing Δ9-THC, Fig S1 (E-F).
   iv. Tape-lifting was performed manually on plastic and metal surfaces by using an ordinary office tape. The tapes were analyzed by DESI without any pretreatment.
c. DESI Imaging
   i. The DESI instrumentation was essentially the same as that presented in ref 5. Briefly, all DESI imaging data were acquired using a Thermo Fisher LTQ (San Jose, CA, USA) linear ion trap mass spectrometer, equipped with a custom-built automated DESI ion source. The LTQ operating parameters were as follows: spray voltage, 5 kV; automatic gain control, off; MS injection time, 203 ms; 2 microscans were summed; spectra were collected in full-scan (m/z 100-600) profile mode. For the tandem MS experiments, fingerprints, fingerprints bearing both Δ9-THC and cannabidiol were examined by MS/MS while monitoring the fragmentation of the precursor ions of m/z 313. The DESI source conditions were: nitrogen sheath gas pressure, 7 bar; incident angle, 50-58° to surface; tip-to-surface, 1-2 mm; and tip-to-inlet, 3 mm; scattering angle, ca. 10° to surface. A mixture of methanol:water (9:1, v/v) was sprayed at a constant volumetric flow rate of 1.5µL/min delivered by the instrument’s syringe pump. Solutions of NH₄OH (for Δ9-THC experiments) and NaCl (for RDX experiments) were added to the spray solution at final concentrations of 0.1% and 1mM, respectively.

d. Image acquisition
   i. The sample surface (19.2 x 14.8 mm²) was imaged using 99 lines. The lines were scanned at a constant velocity of 300 µm/s while collecting one mass spectrum each 0.5 seconds. This procedure resulted in arrays of 128 x 99 pixels, each pixel covering an area of 150 x 150 µm² (∼169 points-per-inch, ppi). The same conditions were applied to overlapping fingerprint experiments, where the larger surface area (29.6 x 19.2 mm²) resulted in arrays of 198 x 128.
   ii. Lab-written software was used to convert the XCalibur mass spectral files (.raw) into a format compatible with BioMap (.img).

e. BioMap (freeware, www.maldi-msi.org) was used for visualization and basic enhancement of the images. The images were rotated 90 degrees clockwise and the selection of different color templates and their maximum and minimum intensity values in the color bar was performed in order to increase the contrast of the images. All images were processed in the voxel mode (pixilated) and exported (in the voxel mode) in TIFF format. Note that exporting the data (a feature available in BioMap) increases its resolution. The images have the same appearance before and after, however, the number of pixels in the exported picture is 443 x 343 pixels or 584 ppi.

f. Fingerprint recognition software and image resolution
   i. To assess the value of DESI images for fingerprint analysis, an ink fingerprint blotted on paper was scanned at a resolution of 600 ppi (Fig. 1C) and inserted into a databank with 300 other fingerprints (scanned at 500 ppi resolution). When the DESI image (Fig. 1A) exported as a TIFF file and extracted as 584 ppi was challenged against the databank, (Verifinger 5.0 by Neurotechnologija, Lithuania) only the original ink blotted picture (Fig. 1C) was returned as a positive match (G=123, Result=Identified, Similarity=779). Resolution could be further increased by interpolation. In most cases the software mathematically averages adjacent pixel densities and places a pixel of that density between the two. This process, available in BioMap, was found to improve the images (Fig S1, panels I-L); however for full latent fingerprint visualization and for computer-based fingerprint recognition, this method was not needed.
2. Text

Further considerations

Five micrograms represents an upper limit to the total amount transferred to the surfaces employed in this study. After handling the plastic explosive composition Semtex-H (~ 50% RDX + 50% PETN), the amount of RDX on fingerprints detected on 10 consecutive blots was reported as 4.59; 1.17; 1.24; 0.83; 0.28; 0.24; 0.22; 0.23; 0.37; and 0.13 micrograms, respectively (Ref. S1). This material can be transferred to the surface after dissolution in perspiration or even as particulates. Our group reported detection (but not imaging) of RDX by DESI on a fingerprint after touching the plastic explosive Composition C-4 (Ref. S2). It is known that European bills contain traces of cocaine; one in twenty typically has 10 micrograms, while the rest usually have one hundredth of that (Ref. S3). All these data suggest that amounts on the order of less than 5 μg, as examined here, are forensically significant.

Solutions of the chemical of interest were used in these experiments because these low concentration solutions could be purchased under an exemption from the regulations of the U.S. Drug Enforcement Administration (DEA). Detection of chemicals after exposure to powdered material seems possible but was not directly investigated.

Compared to original blots, similar signal intensities were found from fingerprints lifted from metal (e.g. fatty acids) and around 50% of the signal intensity was observed for fingerprints lifted from plastic surfaces (e.g. cocaine). These values, as expected, are highly dependent on the kind of surface and the chemicals on the surface. In no case do the contaminants coming from the surface represent a problem since imaging mass spectrometry can readily discriminate the locations of the chemicals, viz. on the latent fingerprint or in the surrounding area.

Endogenous compounds can compete for ionization but they do not compete well with many drugs and explosives. Ion suppression affects all ionization processes in mass spectrometry (MALDI, ESI, SIMS, DESI, etc). However, in DESI the use of an appropriate solvent can minimize this effect. For instance, the use of polar spray solvent favors desorption of polar compounds. In the experiment presented, given the solvent system and amounts of material involved, there was no evidence for any ion suppression from sebum-rich fingerprints nor was it expected.

The evaluation of the best algorithm for fingerprint extraction or identification or the best mathematical procedure to increase the resolution of images was not attempted here. More information about these interesting topics can be found in Refs. S4, S5, S6 and S7.

In summary, we can distinguish individuals and their exposure history to chemicals such as drugs of abuse, explosives or personal grooming products. We are commencing a large scale project to discriminate between individuals by MS using endogenous compounds such as fatty acids, amino acids and squalene present in their fingertips. Experiments are also underway to couple DESI to a miniature mass spectrometer, as well as to increase the spatial resolution of this technique.
3. Figures

**Figure S1** – (A) Virtual DESI image of the fatty acid cis-hexadec-6-enoic acid from a LFP blotted on glass; (B) $^{37}$Cl-RDX on plastic (C); cocaine on adhesive tape; (D) fatty acid on adhesive tape; (E) chemical m/z 235 present in both overlapping fingerprints on paper; (F) Δ9-THC present in first (lower) fingerprint on paper; (G) Δ9-THC and/or cannabidiol on paper as identified by the MS/MS transition m/z 313 → m/z 245; (H) Δ9-THC distinguished from cannabidiol by the unique MS/MS transition m/z 313 → m/z 191; (I and K) cocaine on glass in pixel mode and (J and L) interpolated mode. Fingerprints images of fatty acids (deprotonated molecules), $^{37}$Cl-RDX (adducts), Δ9-THC, and cannabidiol (deprotonated molecules) were acquired in the negative ion mode. Fingerprint images of cocaine (protonated molecules) were acquired in the positive ion mode. Scale bar shown in panel A (2mm) also applies to panels B-D, G and H; that in panel E (4mm) also applies to panel F; that in panel K (1.5 mm) also applies to panel L. For more information, see Materials and Methods.
4. References


