

Latent Fingerprint Chemical Imaging by Mass Spectrometry

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Latent fingerprints (LFPs) are distributions of exogenous and endogenous chemicals in a particular pattern. They potentially contain more forensic information than the simple identification of the subject; they may contain evidence of contact with explosives or substances of abuse. Chemically specific surface analysis methods are required to reveal the full information contained in LFPs. Such techniques often require derivatization (1) or addition of fluorescent or other tags (2). Mass spectrometry (MS) imaging (3) provides spatially specific chemical composition information on surfaces. Unlike other MS imaging methods, desorption electrospray ionization (DESI) MS (4) offers chemical imaging capabilities through mass spectra recorded without sample preparation from ordinary samples in their native environment.

In DESI, a solvent is electrosprayed onto the surface. Secondary scattered droplets are generated and evaporated, and their constituents mass analyzed. A mass spectrum is recorded in turn at each point on the surface by rastering the stream of charged droplets across the surface (5). This method has a spatial resolution of 150 μm . Spectroscopic techniques such as Fourier transform infrared (FTIR) and Raman also provide ambient imaging analysis and have better spatial resolution but poorer chemical specificity than MS techniques (6). However, the use of these methods to reconstruct fingerprint images from ordinary surfaces based on exogenous compounds has not been demonstrated (6).

We report the application of imaging MS for the chemical analysis of LFPs. Small amounts (5 μg) [an amount selected for its forensic relevance; see supporting online material (SOM) text] of drugs of abuse such as cocaine and Δ^9 -tetrahydrocannabinol (Δ^9 -THC, psychoactive component from cannabis) and explosives such as trinitrohexahydro-1,3,5-triazine (RDX, high-energy explosive) were imaged

by DESI from LFPs produced after exposing the participant's fingers to solutions of these compounds (7) (see SOM text for further detail). In order to enhance the ionization of these compounds, additives such as ammonium hydroxide and sodium

chloride were used in the solvent spray. The prints were recorded from ordinary surfaces such as glass, paper, and plastic. Figure 1A shows the distribution of cocaine (monitored as mass-to-charge ratio, m/z , 304) in a LFP on glass. The level of detail of the image, acquired with a pixel size of 150 μm by 150 μm , allows clear distinction of the ridges and minutiae. Figure 1C shows an ink fingerprint of the same individual blotted onto paper and optically scanned at a resolution of 600 points per inch (ppi). These images were used as input in fingerprint recognition software. The output images with automatically detected minutiae (Fig. 1, B and D) matched with use of the usual fingerprint identification tools (7). This experiment demonstrates

that the mass spectrometry analysis allows physical identification of a subject. We recorded DESI images of LFPs for a wide range of chemicals and substrates, including tape-lifted fingerprints (fig. S1). Transfer of the original chemicals with retention of spatial relationships allowed the analytical mass spectrometer to be used to acquire chemical information on as well as the identification of a particular individual.

Endogenous components can also be imaged by using DESI. For instance, *cis*-hexadec-6-enoic acid, stearic acid, *cis*-octadec-8-enoic acid, palmitic acid, pentadecylic acid, myristic acid, and triacylglycerols were each used to record chemical fingerprints from sebum-rich LFPs.

The chemicals identified by their m/z ratios can be confirmed by their fragmentation patterns by using tandem mass spectrometry (MS/MS). For example, Δ^9 -THC and its non-psychoactive isomer, cannabidiol, can be distinguished readily within a single LFP by MS/MS (7) (fig. S1). Distinguishing between overlapping fingerprints left by different individuals is extremely difficult optically. Imaging by mass spectrometry can readily distinguish each individual print with a distinctive exposure history to chemicals, such as Δ^9 -THC (fig. S1).

References and Notes

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Supporting Online Material

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Materials and Methods

SOM Text
Fig. S1
References

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Fig. 1. (A) DESI image of distribution of cocaine on a LFP blotted on glass. (B) Computer-generated fingerprint from DESI image. (C) Ink fingerprint blotted on paper and optically scanned. (D) Computer-generated fingerprint from optical image. Some of the automatically detected points of interest (minutiae) are represented by dots in (B) and (D).

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