A215 MALDI/TOF-MS for Chemical Analysis of Fingerprint Residues Using Conventional Fingerprint Development Methods

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After attending this presentation, attendees will understand the benefit of measuring chemical information from fingerprint residue, and how image chemical information is obtained from latent fingerprint residue using conventional latent fingerprint development techniques coupled with Matrix-Assisted Laser Desorption Ionization/Time-Of-Flight Mass Spectrometry (MALDI/TOF-MS).

This presentation will impact the forensic science community by demonstrating the ability to extract measurable identifiable chemical markers detected in fingerprint residue with the potential to assist in forensic investigation.

Chemical information gained from analysis of latent fingerprints, "touch chemistry," at a crime scene might provide investigative or other forensically relevant information. Studies reported in the literature demonstrate the ability to gain intelligence information (smoker/nonsmoker, drug exposure, and ingested drugs of abuse) from chemicals recovered within fingerprint residue using MALDI/TOF-MS. One of the main challenges with fingerprint imaging is the ability to integrate MALDI/TOF-MS with current protocols used by latent fingerprint examiners. For this presentation, two experimental approaches are described for imaging latent fingerprint residue. For the first design, conventional methods used by latent fingerprint examiners will be evaluated as a way of visualizing a print and acting as the matrix for MALDI in order to ascertain chemical information that can be measured in fingerprint residue. For the second experimental design, a new method incorporating a MALDI matrix will be used to compare with conventional approaches.

For the experimental design, fingerprint residues were developed with powder, cyanoacrylate fumed or lifted. Control fingerprints included grooming the fingers by rubbing across the nose or neck to include sebaceous secretions. A second groomed print was deposited next to the control print after handling powder from either an over-the-counter pharmaceutical or explosive. The prints were developed with black powder, black magnetic powder, black magnetic nanoparticle powder, black nanomagnetic powder, or cyanoacrylate fuming. The lift experiments followed the same procedure for depositing and developing latent prints on metal surfaces. An alternative method included using a MALDI matrix sprayer to deposit alpha-Cyano-4-Hydroxycinnaminic Acid (CHCA) on dusted, cyanoacrylate fumed, and lifted fingerprints.

Fingerprint images from direct deposition and lifts gave distinct differences between the control fingerprint and the fingerprint after handling the drug or explosive. Powders of trinitrotoluene (TNT) along with three pharmaceutical products (containing aspirin, acetaminophen, and ibuprofen) were used for the handling experiments and both positive and negative ionization mode was used to collect fingerprint images. The pharmaceuticals all formed $[M+Na]^+$ and $[M+K]^+$ adducts in positive ionization mode. TNT formed an $[M]^-$ for negative ionization mode. From the MALDI image of the handled powders, the detail of the fingerprint ridges were not observed but the distribution of the powders across the finger was shown. In order to view the ridge details of the fingerprint, target ions from the groomed fingerprints were extracted. For all fingerprints analyzed, some ridge detail was observed after development by either powder or cyanoacrylate prior to MALDI analysis. Fingerprints developed with powders used less laser power and provided less chemical interferences than cyanoacrylate fuming. The cyanoacrylate method worked well for detecting the handled compounds, but the remaining spectral chemical information from the fingerprint was from the cyanoacrylate polymer. Initial experiments using nanoparticle powder visually demonstrated greater detail of the fingerprint compared to conventional black magnetic powder. However, all powders demonstrated the ability to work as MALDI matrix in the handled experiments.

With the addition of the MALDI matrix, compounds of interest were more efficiently ionized at a lower laser power and enhanced signal to noise response for the handled pharmaceuticals and explosive. By incorporating CHCA into the fingerprint method, protonated or deprotonated ions were observed for acetaminophen, aspirin, ibuprofen, and TNT. Less sodium and potassium adducts were also observed, potentially allowing for structural MS/MS information to be obtained. The conventional and new methods both demonstrated the ability to obtain chemical information from fingerprint residues using MALDI/TOF-MS.

MALDI/TOF-MS, Fingerprint Residue, MALDI/TOF-MS Imaging

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