

B168 Chemical Imaging of Cyanoacrylate-Fumed Fingerprints Using Mass Spectrometry Imaging

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After attending this presentation, attendees will understand how mass spectrometry imaging is compatible with some current forensic practices, such as cyanoacrylate fuming, and could therefore be a valuable technique in the forensic field.

This presentation will impact the forensic science community by drawing attention to compatibility issues that are inhibiting the adoption of new technologies. In addition, new insight into the polymerization mechanism of cyanoacrylate fuming is presented.

Introduction: Chemical analysis of fingerprints using mass spectrometry is a method for gaining valuable information about potential suspects. In order for the technique to be realistically integrated into an investigative procedure, it must be compatible with current forensic techniques. As much of current practices are focused on visualization of fingerprint ridges for a database match, procedures to enhance the quality of the fingerprint are common. Cyanoacrylate fuming is one such technique in which latent fingerprints are exposed to gaseous cyanoacrylate, forming a visible polymer on the surface of fingerprint ridges. In this work, the compatibility of cyanoacrylate fuming and Matrix-Assisted Laser Desorption/Ionization-Mass Spectrometry (MALDI-MS) is investigated as well as the cyanoacrylate polymerization mechanism.

Methods: Several fingerprint samples were prepared both with and without development by cyanoacrylate fuming and with different matrices for MALDI-MS. They were analyzed using a MALDI-linear ion trap-Orbitrap™ MS coupled to an Nd:YAG laser. Unique background peaks present in only the negative mode spectra of cyanoacrylate-fumed samples were further analyzed and structural information was obtained with Tandem Mass Spectrometry (MS/MS). Standard solutions of several common fingerprint compounds were used to study the polymerization reaction, including a triacylglycerol (glyceryl tripalmitate), several fatty acids (oleic, stearic, and palmitic acids), cholesterol, squalene, and an amino acid (isoleucine). The solutions were pipetted onto two slides, one of which was fumed with cyanoacrylate, while the other was not. The level of polymer formation was compared between different analytes.

Results: Dihydroxybenzoic Acid (DHB), α -Cyano-4-Hydroxycinnamic Acid (CHCA), iron oxide nanoparticles, and silver nanoparticles were tested as matrices, which are necessary to absorb the laser energy and desorb/ionize analytes. All endogenous compounds were still present at their expected masses with no significant change in their signals. The images of endogenous compounds in the fumed fingerprints were of equal quality to the images from the non-fumed fingerprints. Likewise, exogenous compounds appeared at their expected mass; however, one class of ionic compounds had suppressed signal in fumed fingerprints. Other groups have attempted similar analyses of fumed fingerprints on MALDI-Time Of Flight (TOF) without much success. It is proposed that the instrument used in this study, MALDI-linear ion trap-Orbitrap™, is superior to MALDI-TOF for MS imaging of cyanoacrylate-fumed fingerprints because there is minimal influence from electric field inhomogeneity on the MALDI plate surface.

Several peaks were observed in fumed fingerprints in negative mode that were not present in non-fumed fingerprints. These peaks were thought to be related to the cyanoacrylate polymer and were further analyzed by MS/MS. Based on the MS/MS as well as elemental composition from accurate mass, these peaks were determined to be cyanoacrylate dimer and trimer derivatives. A mechanism for their formation and polymerization is proposed based on their structure.

Varying amounts of polymer formed on the surface of different standard compounds. For example, some, such as triacylglycerols and squalene, had little-to-no polymer formation, while others, especially fatty acids, had significant polymer formation. This result indicates that fatty acids may play a more important role than other endogenous compounds in the polymerization process. In addition to the visual increase in cyanoacrylate polymer formation, signal intensities for the cyanoacrylate compounds also increased.

Conclusion: Cyanoacrylate fuming and MALDI-MSI of latent fingerprints are very compatible techniques. Important chemical information can be gained from fingerprints that have been cyanoacrylate fumed without sacrificing signal intensity. No compounds studied so far have been chemically modified by the fuming process, so data analysis is straight forward. In addition to the compatibility study, valuable insight into the mechanism for polymerization of cyanoacrylate on fingerprints was also achieved. Cyanoacrylate dimers and a trimer were identified in the mass spectra and the importance of fatty acids in the polymerization process was revealed.

Polymerization, Cyanoacrylate Fuming, Mass Spectrometry Imaging