Final Summary Overview

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Project Title: Chemical Imaging of Latent Fingerprint for Forensic Evidence

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Purpose

Chemical information of the fingerprints could provide a new avenue in individual identification. It may reveal the details of criminal activities or additional information about the suspect such as gender, age, or medical conditions. However, current gas-chromatography or liquid-chromatography based techniques have many limitations including the loss of fingerprint evidence due to extraction procedure, low sensitivity to detect low abundance compounds, and contamination form surface chemicals.

Mass spectrometry imaging (MSI) is a state-of-the-art technique for surface chemical imaging due to its extremely high sensitivity, label-free detection, and unbiased molecular characterization. There have not been much efforts to use this technique for forensic fingerprint analysis. The propose of this research is to adopt our expertise in MSI of small molecules and evaluate mass spectrometry imaging technique for forensic fingerprint analysis.

Research Design and Methods.

We have many years of expertise in matrix-assisted laser desorption ionization (MALDI)-MSI of small molecules[1-12]. The proposed research project is designed to best utilize our skills and know-hows, and to overcome the current four major bottlenecks in chemical fingerprinting: 1) limited sensitivity of low abundance small molecules, 2) ambiguity of chemical identifications, 3) lack of robust protocols compatible with traditional forensic investigations, and 4) demonstration of unique applications. Below is the excerpt of the proposed research plan.

Specific Aim 1: Nanoparticles to Assist Chemical Fingerprinting.

We hypothesize that nanoparticles or a mixed use of nanoparticles with traditional organic matrixes could be a good alternative matrix for small molecule analysis. As we have

shown in our recent study in nanoparticle screening as a matrix for MALDI-MS, some NPs show very unique analyte dependent specificity, which is consistent in both positive and negative ion mode. We will screen and test various NPs as well as a binary mixture of matrixes, and test their efficiency for MALDI-MS of fingerprint compounds.

Specific Aim 2: High mass resolution and high spatial resolution mass spectrometry imaging (HR^2MSI) for advanced chemical imaging of fingerprint.

Instrumentation in the Lee group (MALDI-ion trap-Orbitrap; Thermo Finnigan, San Jose, CA) has the capability of high-resolution MSI in both spatial and mass dimensions. High-mass resolution is possible with Orbitrap high-mass resolution mass spectrometer and high-spatial resolution is possible with a home-built laser optics that can reduce the laser spot size down to 5 microns[1]. Combining these, we can obtain high quality information in both chemical and spatial dimensions using high-resolution MSI in both the dimensions, or HR^2MSI.

Multiplex MSI strategy that we have previously developed is very useful to identify unknown compounds directly on the surface by obtaining MS/MS at the same time with MSI data acquisition[9]. This strategy will be adopted and optimized for chemical fingerprinting. Each imaging pixel will be split into four spiral steps. The first step will be used for Orbitrap MS scan in the low mass range (m/z 50-400) followed by data-dependent MS/MS scan on the second step. The third spiral step will be used for Orbitrap MS scan in the high mass range (m/z 400-1,000) followed by data-dependent MS/MS scan on the forth step. With dynamic exclusion, the data-dependent MS/MS scans will allow us to obtain tens of thousands of MS/MS spectra, which can be utilized to identify unknown compounds combined with accurate mass information from the Orbitrap scan. If MS/MS of unknown compounds are not present in our MS/MS library, an MS/MS search can be performed against a public MS/MS library.

Specific Aim 3: Expanding Utility of Mass Spectrometry Imaging for Fingerprinting.

The three sub-aims of the goal are to 1) aging study of chemical fingerprint, 2) surface modification of amino acids, and 3) compatibility with traditional fingerprint development techniques.

For aging of chemical fingerprints, we study the diffusion of fingerprint chemicals on surface as suggested by a group of researchers in NIST using fatty acid diffusion[13], however also to include triacylglycerols (TGs) that have three times higher mass and supposed to have slow diffusion. Amino acids have a good chance to be used as individual identification markers. But as discussed in the literature survey, it is challenging to reliably detect amino acids on fingerprints. In order to dramatically improve sensitivity and minimize local environment effects on the LDI efficiency of amino acids, we will adopt on-surface derivatization of amino acids previously developed by others[14, 15]. For sub-aim 3, we will test multiple development techniques for their compatibility with MALDI-MSI, cyanoacrylate fuming, forensic carbon powders, ninhydrin development, iodine fuming, and TiO_2 development. They will be compared with and without the development, to understand what are the chemicals affected by the development and whether we can overcome the limitation.

Specific Aim 4: Individual differentiation based on chemical fingerprint.

While exogeneous compounds can provide critical information about the suspect, it may not be always present or necessarily connected to individuals. It would be desirable if endogeneous compounds can provide additional information for individual differentiation. We will test this hypothesis with free fatty acids, TAGs and AAs that are commonly present in fingerprints as potential individual markers.

Findings and Scholarly Products

In total, we published seven peer-reviewed papers in scientific journals, and eight oral and nine poster presentations in scientific conferences. Here is the excerpt of the findings categorized to each specific aim along with full citations. It should be noted some of the outcome is done by Kelly O'Neill under her NIJ Graduate Fellowship as marked by #.

Specific Aim 1: Nanoparticles to Assist Chemical Fingerprinting: We found several nanoparticles are useful as a matrix for MALDI-MSI of fingerprints. Most notably, gold thin film sputter coating combined with sodium ion spray is very useful to improve the detection of TGs, and silver sputtering is useful for negative ion mode. These findings are not published separately but as a method part of other studies in application-oriented studies below.

Specific Aim 2: High mass resolution and high spatial resolution mass spectrometry imaging (HR^2MSI) for advanced chemical imaging of fingerprint: We have successfully adopted multiple MS imaging strategy combining MS/MS and high-mass resolution MS, to improve identification of unknown compounds directly from fingerprints. It has been demonstrated to characterize unknown exogeneous compounds from fingerprint that can be used to reveal individual lifestyle, as published in Scientific Reports. Demonstrated application includes the detection of marker compounds in bug spray, sun spray, food oils, citrus fruits, and wines.

1. "Revealing Individual Lifestyles through Mass Spectrometry Imaging of Chemical Compounds in Fingerprints", Paige Hinners, Kelly C. O'Neill, and **Young Jin Lee***, Scientific Reports, **2018,** 8:5149, DOI:10.1038/s41598-018-23544-7.

Specific Aim 3: Expanding Utility of Mass Spectrometry Imaging for Fingerprinting: In sub-aim 1) aging study of chemical fingerprint, we studied the diffusion of TGs and fatty acids