E87 The Forensically Relevant Applications of Laser Ablation Direct Analysis in Real Time Imaging-Mass Spectrometry (LADI-MS)

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Learning Overview: The goals of this presentation are to introduce attendees to: (1) the basics of the new imaging mass spectrometry technique known as LADI-MS; (2) its wide applicability to small molecule spatial distribution mapping in forensic sample types, including psychoactive compounds in latent fingermarks and inks on paper; and (3) its non-imaging capabilities, including derivatization of the psychoactive component of psilocybin mushrooms (i.e., psilocybin).

Impact on the Forensic Science Community: This presentation will impact the forensic science community by presenting a new technique that is being developed for potential integration into crime laboratories and research institutions. The wide applicability of the technique means that a single instrument could tackle a number of forensic sample analyses, thus reducing the cost and training that would be required for multiple instruments.

Imaging mass spectrometry provides a means to obtain chemical composition information while retaining the spatial distribution of the detected analytes in the sample of interest, thus providing two types of information that would typically require multiple instruments. Most current imaging techniques require the use of solvent, high vacuum, and/or the application of a matrix. However, these steps can complicate the ability to routinely detect and map the spatial distribution of small molecules and can also be time-consuming and contribute to casework backlogs. It is demonstrated that using an approach that integrates a Direct Analysis In Real Time (DART®) ionization source, an ultraviolet neodymium-doped yttrium aluminum garnet (Nd:YAG) laser ablation system and a Time-Of-Flight (TOF) mass spectrometer, small-molecule spatial distribution maps can be acquired for a broad range of sample types, with no sample pretreatment requirements.

The ability of the technique to detect small molecules within latent fingerprints was demonstrated using prints that were deposited after exposure of hands to psychoactive plant material (*Piper methysticum*), cocaine, or pseudoephedrine. LADI-MS revealed spatial distributions of endogenous cholesterol, localized to fingerprint ridges, while providing confirmation of exposure to the psychoactive small-molecule cocaine, kavain (derived from *P. methysticum*), and pseudoephedrine. The spatial distribution mapping of cholesterol in a lifted print on the non-conductive adhesive side of tape was also accomplished. The ion images obtained of the endogenous compounds revealed the fingerprint ridge pattern necessary for identification of an individual.

The approach was also applied to the detection of differently sourced inks on paper. A peace sign image was drawn using two different brands of black markers (one used to draw the outer circle and the other, the inner lines). LADI-MS small-molecule spatial distribution maps allowed the two inks to be distinguished based on the chemical composition. This technique was also applied to numbers that were subsequently altered with a second pen to form a different number (i.e., number 1 changed to 7). This technique would be useful in determining alterations made to a document using differently formulated inks.

The robust LADI-MS system can also be utilized for non-imaging experiments. Typically, the psychoactive compound psilocybin undergoes dephosphorylation to psilocin during traditional chromatographic-mass spectrometric analysis. To confirm its presence in a sample, derivatization is required, thus prohibiting the ability to detect the intact molecule in imaging experiments of psychoactive mushrooms. Here, the laser was used for the instantaneous derivatization of psilocybin directly on the sample by firing at a drop of psilocybin solution and the derivatizing agent (*N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide) on the surface of a piece of cloth. Both psilocybin+2TMS and psilocybin+3TMS were detected by LADI-MS. This could lead to the potential imaging of psilocybin spatial distributions in intact mushroom material by spraying the derivatizing agent on the surface of mushroom samples prior to imaging experiments.

The newly developed LADI-MS technique can be applied to a number of forensic sample types, including latent fingermarks, inks on paper, and derivatization of psilocybin. It is shown to be a powerful tool for the detection and mapping of a range of small molecules in a variety of sample types with no sample preparation steps.

Imaging Mass Spectrometry, Latent Fingerprints, Inks on Paper