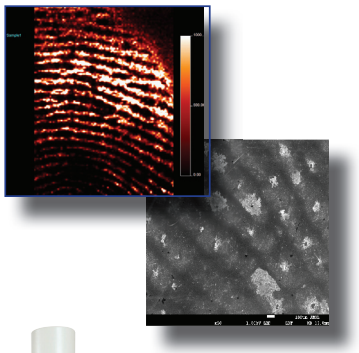
SpiralTOF™

Fingerprint Analyses Using MALDI Imaging and SEM Imaging



Introduction:

MALDI imaging is a state-of-art mass spectrometry technique that allows for the visualization of chemical distributions on the surfaces of biological and material samples. This analytical technique can provide the chemical distribution on the surface as an image that is mapped using the intensity of the observed ions. The image contains individual MALDI mass spectra at each pixel. Therefore, it is possible to simultaneously carry out high-mass-resolution qualitative analysis and chemical distribution analysis.

The JMS-S3000 SpiralTOF (Figure 1) has a unique 17m flight path that offers the highest mass resolution and mass accuracy MALDI-TOF MS system. In this work, we demonstrated the MALDI imaging measurement for the fingerprints of a smoker and a non-smoker by using the JEOL SpiralTOF system. Additionally, we looked at the smoker's fingerprint using the JEOL JSM-7800F thermal field emission scanning electron microscope (FE-SEM) shown in Figure 2.

Figure 1. JMS-S3000 SpiralTOF.

Experimental:

Sample information and preparation conditions are described below.

Samples

- A non-smoker's fingerprint
- A smoker's fingerprint

MALDI Imaging measurement

- Measurement mode: SpiralTOF positive mode
- Matrix: 2,5-Dihydroxybenzoic Acid (DHB), 2mL spray @ 30mg/mL
- Measurement region: Width 7.0 mm x Length 10.0 mm
- Analytics Software: Biomap 3.8 - Raw data was converted to imzML files

SEM Imaging measurement

- Sample preparation: Uncoated
- Acceleration voltage: 1 kV
- Magnification: 50x and 5,000x

Figure 2. JSM-7800F Thermal FE SEM.

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Sample Preparation and Measurement:

The fingerprint samples (Figure 3) were created by pressing the right index finger onto an electrically conductive ITO glass slide (HST inc., 0.7 mm thickness, Type II). The DHB MALDI matrix was dissolved in 70%-MeOH at a concentration of 30 mg/mL. Two milliliters of this DHB matrix solution was sprayed onto the fingerprint using an airbrush. PPG was used for the external calibration standard. After the samples were dried, they were measured using the JMS-S3000 SpiralTOF MS system. We also obtained SEM images for the smoker's fingerprints with the JSM-7800F.

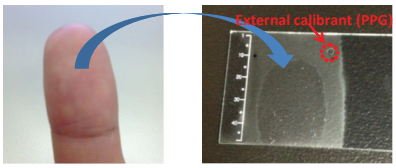

Figure 3. Fingerprint sample.

Results & Discussion:

Lipids analysis on the fingerprint

As a starting point, the MALDI images for three lipids (*m/z* 717.7, 827.8, 907.8) and a full-range mass spectrum averaged over a section of the fingerprint are shown in Figure 4. All MALDI images are set to the same intensity scale. The scale bar is displayed on the right side of each image with the white color indicating the highest intensities, the dark green color indicating the lower intensities, and the black color indicating the background (absence of ions). Figure 4a-c show the lipid distribution along the fingerprint. For these samples, the lipids appear to be most strongly present at the edge of the finger.

Nicotine analysis on the fingerprint

Next, we examined the nicotine distribution on both a smoker's and non-smoker's fingerprints. The MALDI mass spectra of nicotine and related chemicals are shown in Figure 5.

As might be expected, the smoker's fingerprint had several chemicals present around the expected mass for nicotine as shown in the top spectrum in Figure 5. First, we focused on determining the chemical composition of observed *m/z* 163 on the fingerprint by using the accurate mass values with internal calibration method. DHB matrix ions were used as internal calibrant for this accurate mass measurement. The mass error of the *m/z* 163 was just -0.6 mDa when compared to the protonated molecule of nicotine standard using internal calibration. However, the isotopic pattern was slightly different from the theoretical isotopic pattern of nicotine because more than one compound was present. On this fingerprint, both $C_{10}H_{15}N_2$ (Nicotine) and $C_{10}H_{17}N_2$ appear to be present.

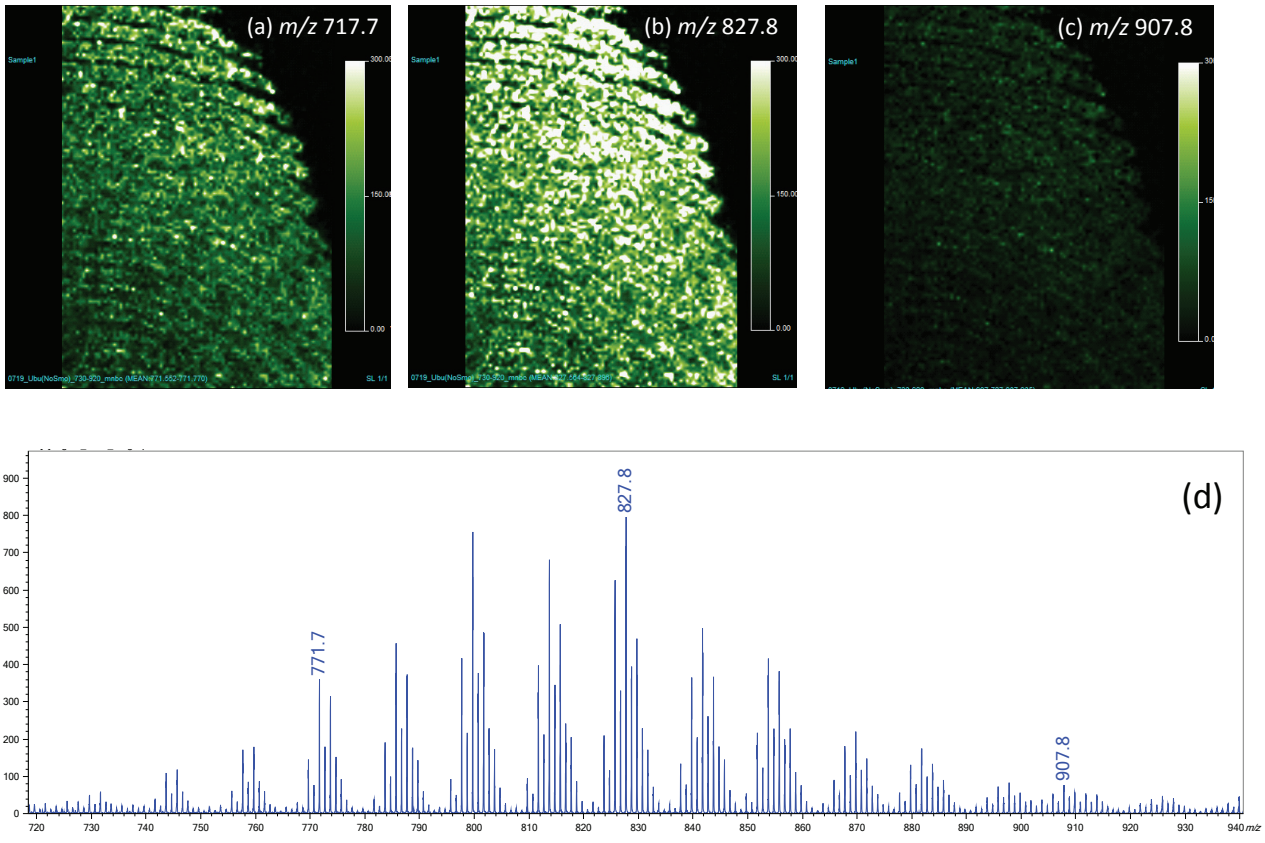

Figure 4. MALDI images: (a) *m/z* 717.7, (b) *m/z* 827.8, (c) *m/z* 907.7, and (d) full range mass spectrum.

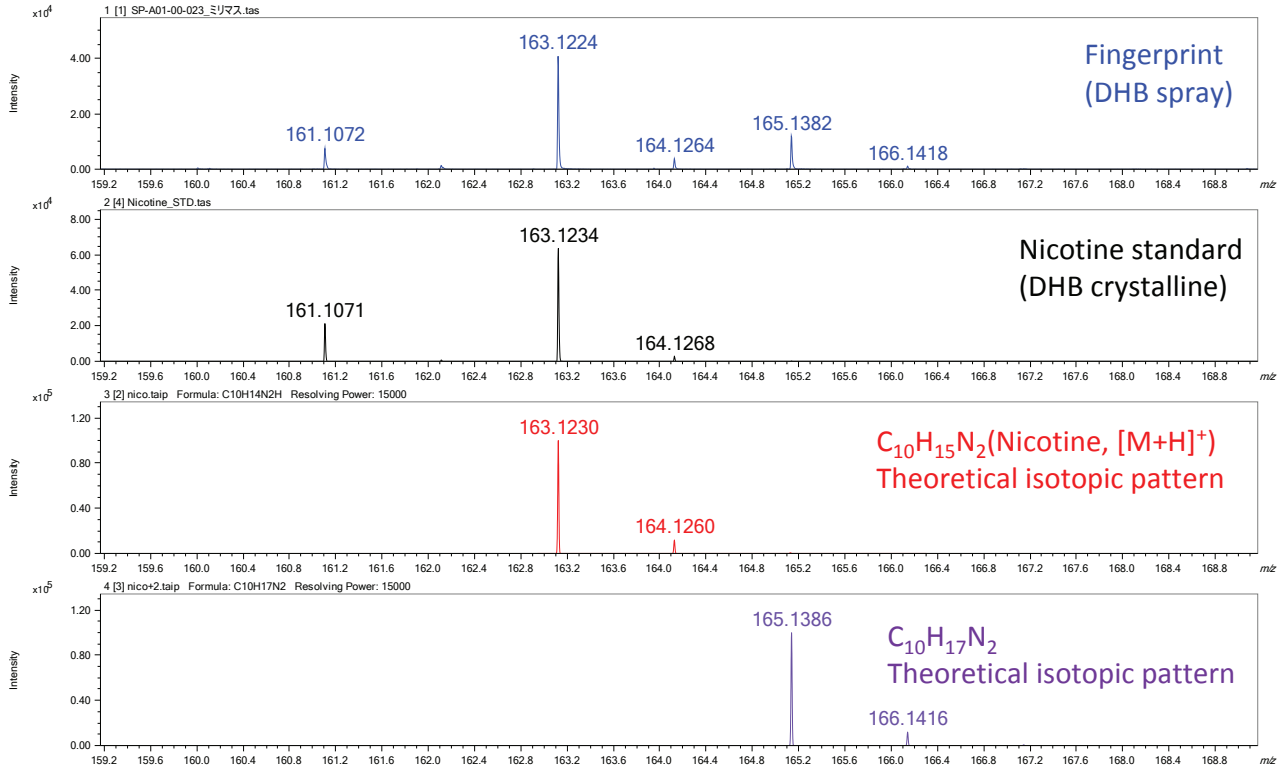

Figure 5. MALDI mass spectra of nicotine and other chemical.

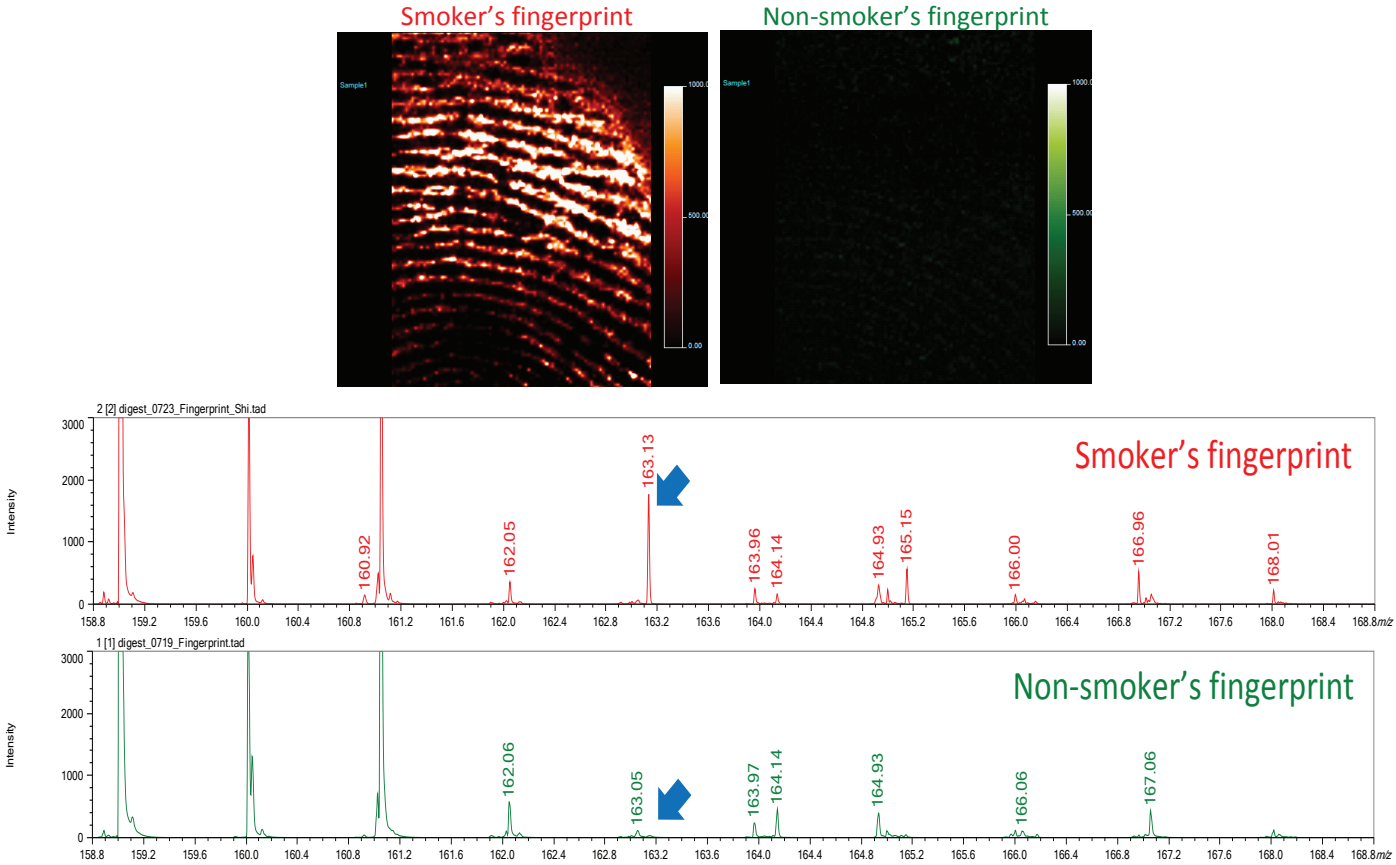

Figure 6. MALDI images: (left) smoker's, (right) non-smoker's, and enlarged digest mass spectrum.

The MALDI images for nicotine and a full range mass spectrum around *m/z* 163 are shown in Figure 6. Both MALDI images are normalized to the same intensity scale. The scale bar is displayed on the right side of each image with white indicating a higher intensity of protonated Nicotine molecule ion, dark red (green in nonsmoker fingerprint) indicating lower intensities, and black indicating background (absence of ions).

There was a strong nicotine distribution on the smoker's fingerprint that was not detected on the non-smoker's fingerprint. This is a very reasonable result considering the smoker is exposed to nicotine when smoking. The results show that SpiralTOF MALDI imaging can be a very useful analytical tool for visualizing the distribution of small molecules on surfaces.

SEM analysis of the fingerprint

Next, we examined a smoker's fingerprint with the JEOL JSM-7800F thermal field emission scanning electron microscope. The SEM images are shown Figures 7. There were a lot of sebum, particles and other contaminations observed in the fingerprint. The JSM-7800F provided clear imaging data for the organic matter by using a lower acceleration voltage.

Conclusions:

We were able to show MALDI images for Lipids and Nicotine on the fingerprint. The SpiralTOF MALDI imaging capabilities were shown to be:

1. High mass resolving power
2. Good for small molecule analysis
3. Good spatial resolution

Additionally, the JEOL JSM-7800F SEM provided clear images of the organic material present in the fingerprint.

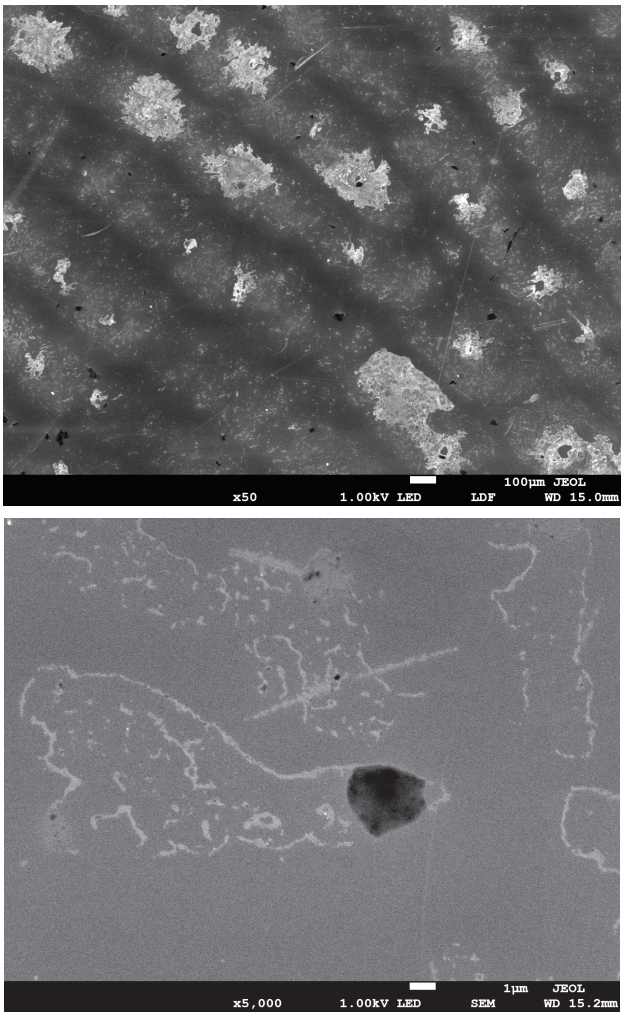

Figure 7. SEM images of a smoker's fingerprint: (top) 50X, (bottom) 5,000X.