Applications Note

SpiralTOF™

Ballpoint Ink Analyses Using LDI Imaging and SEM/EDS Techniques

Introduction

Recently, matrix assisted laser desorption/ionization (MALDI) imaging techniques have been developed for biological sciences to evaluate and understand the distribution of various chemicals on biological surfaces. In particular, this technique provides useful visual information about the locations of specific chemicals on surfaces. In this work, we explored the use of laser desorption/ionization (LDI) imaging for forensically applicable samples such as a handwriting sample with a ballpoint ink. These measurements were done using a spiral-trajectory ion optics time-of-flight mass spectrometer (SpiralTOF-MS). This TOF system has a 17m flight path that provides high resolution capabilities even down into the lower m/z region. Additionally, we looked at the SEM/EDS imaging using the JEOL JSM-6510LV scanning electron microscope.

Experimental

Sample information and measurement conditions are listed below.

Samples

- A ballpoint pen (black)
- A permanent marker (black)

LDI Imaging measurement

- Measurement mode: SpiralTOF positive mode
- No matrix
- Spatial resolution: 50 or 100 µm
- 5000 laser shots at 1kHz laser repetition rate for each position
- Analytics Software Biomap 3.8
  -Raw data was converted to imzML files

Results and Discussion

First, the ballpoint ink handwriting sample "JEOL" was analyzed using the SpiralTOF LDI imaging technique directly with no other sample preparation. The ink consisted of crystal violet as the main component and was easily detected directly on the surface of the handwriting sample. However, a portion of the letter "J" did not show the presence of this analyte (Figure 1). It was hypothesized that there was likely surface discharging and/or a conductivity problem with the paper. To address this situation, the surface was subjected to a gold vapor deposition in order to improve the conductivity of the paper. Afterwards, the sample was again tested and crystal violet was observed over the entire handwriting sample (Figure 2). These results confirm that the gold vapor deposition enhances the analyte signals from the surface of the paper.

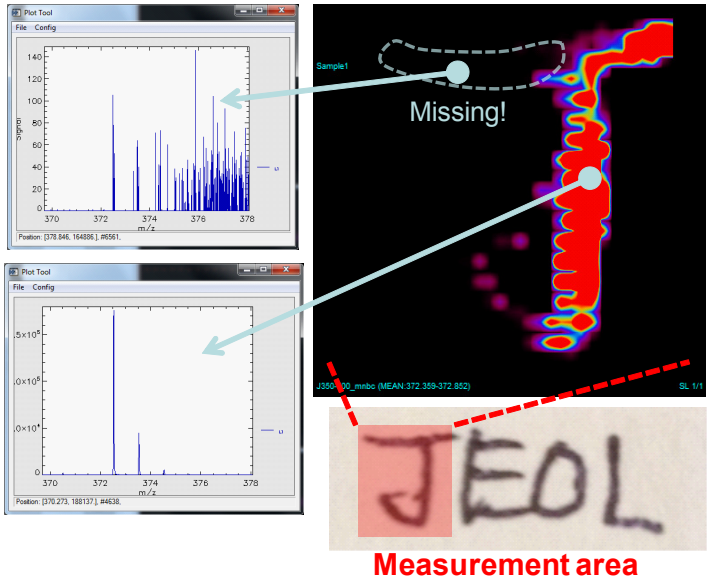

Figure 1. Crystal violet (m/z 372.2) LDI imaging of the handwriting letter "J" on a no-pretreatment paper.

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Next, a ballpoint ink sample "Spiral" was covered with black permanent marker and then analyzed using the LDI and a gold vapor desorption technique. The LDI imaging of the handwriting letter "Spiral" covered up with a permanent marker ink is shown in Figure 3. These results clearly show that "Spiral" was easily observed from the LDI imaging data even though it was covered up with another ink.

Afterwards, we then examined the "ral" in the "Spiral" handwriting by using the JEOL JSM-6510LA scanning electron microscope. EDS results showed that the areas containing the ballpoint ink were carbon rich while the areas containing the permanent marker ink were oxygen rich.

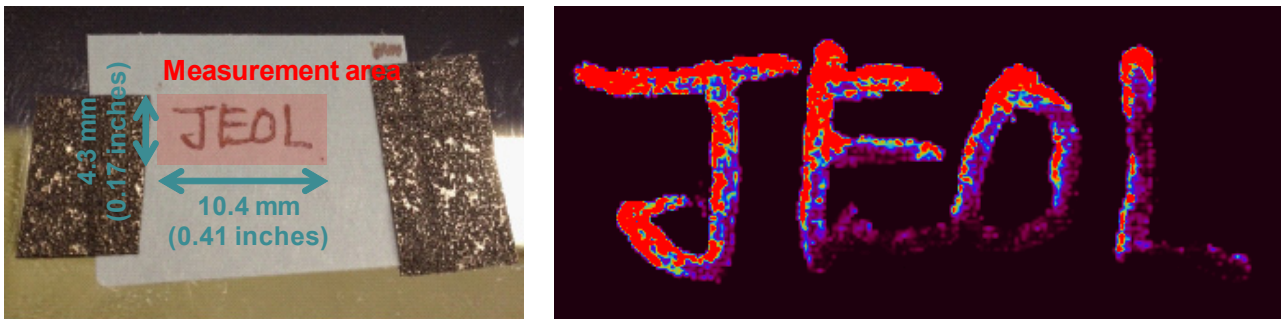

Figure 2. Crystal violet (m/z 372.2) LDI imaging of the handwriting letters "JEOL" with a gold vapor deposition.

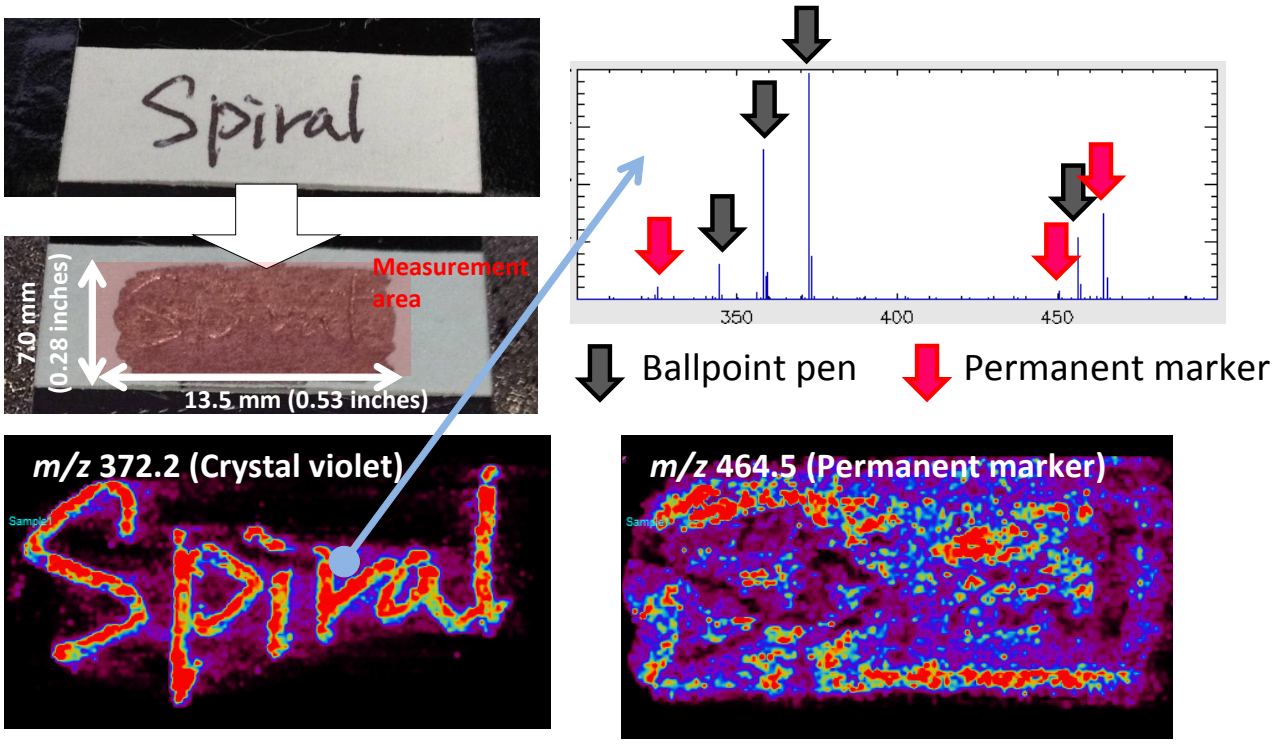

Figure 3. Crystal violet (m/z 372.2) LDI imaging of the handwriting letters "Spiral" covered up with a permanent marker ink.

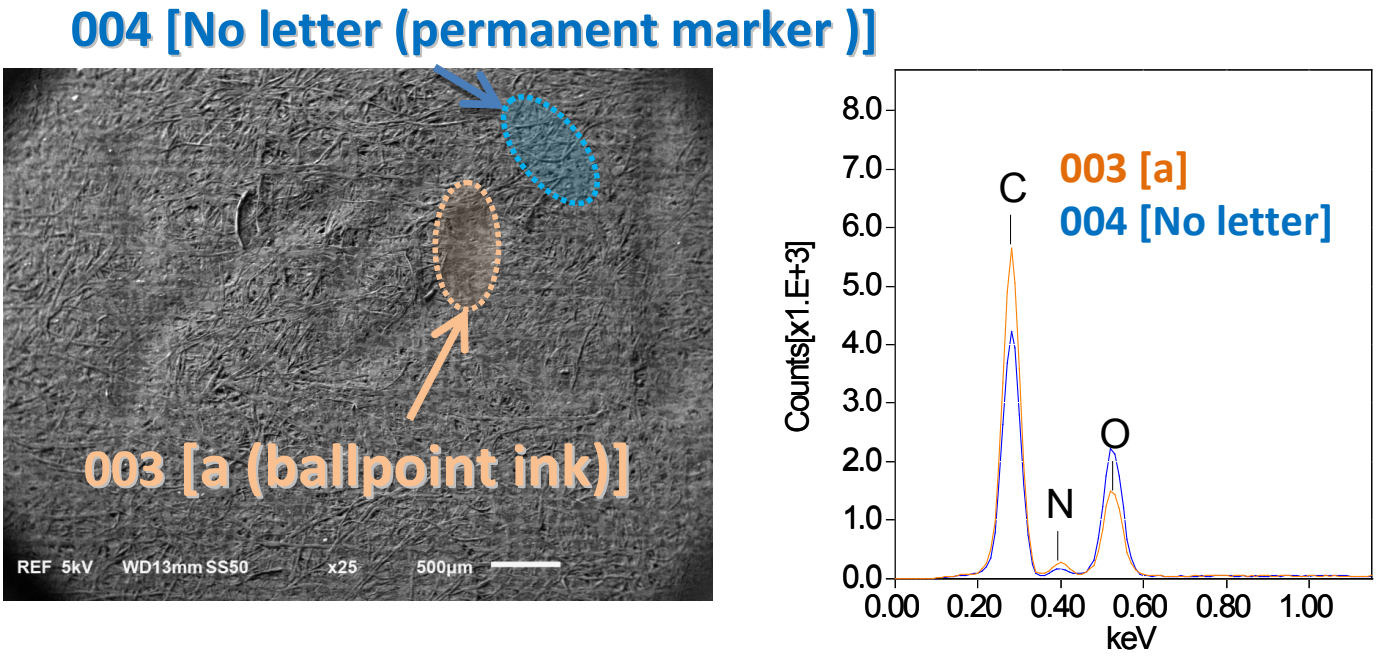

Figure 4. SEM image of the "ral" in "Spiral" handwriting on the paper (x25) and EDS spectrum.

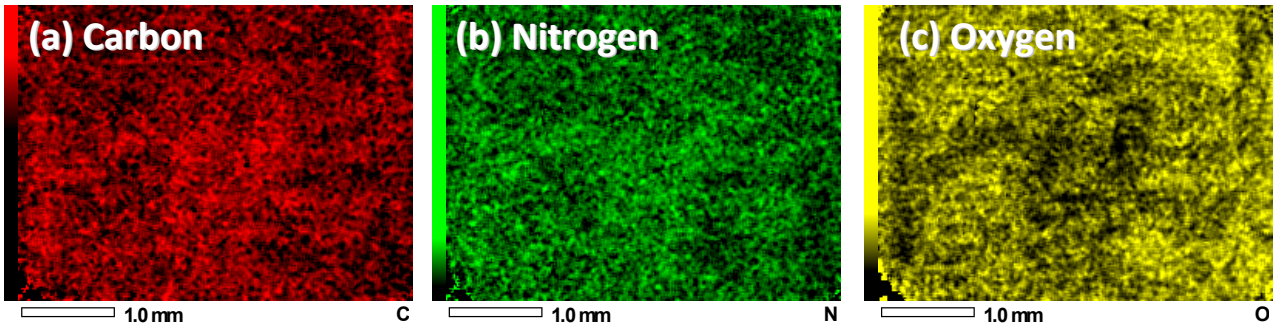

Figure 5. EDS images of the "ral" in "Spiral" handwriting on the paper and EDS spectrum, (a) Carbon, (b) Nitrogen and (c) Oxygen.

Conclusions

We were able to show LDI images and SEM/EDS images for the ink analysis of handwriting samples that have been obliterated by a marker. The LDI imaging provided the organic compound information and distributions for the ink across the surface. The scanning electron microscope rapidly provided the surface features (indentations and roughness) while also providing elemental differences observed for the two inks. Each instrument, the SpiralTOF and JSM-6510LA, provides complementary information for this kind of sample and could be useful for future forensic applications.