

# SpiralTOF™

## Gunshot Residues (GSR) Analysis by Using MALDI Imaging

### Introduction

Recently, matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS) 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 MALDI-MS imaging for the forensically applicable sample of gunshot residues (GSR). These measurements were done using a spiral-trajectory ion optics time-of-flight mass spectrometer (SpiralTOF-MS) which has a 17m flight path that provides high resolution capabilities, even down into the lower  $m/z$  region. Additionally, the  $m/z$  axis remains very stable over the long time period required for MALDI-MS imaging.

### Experimental

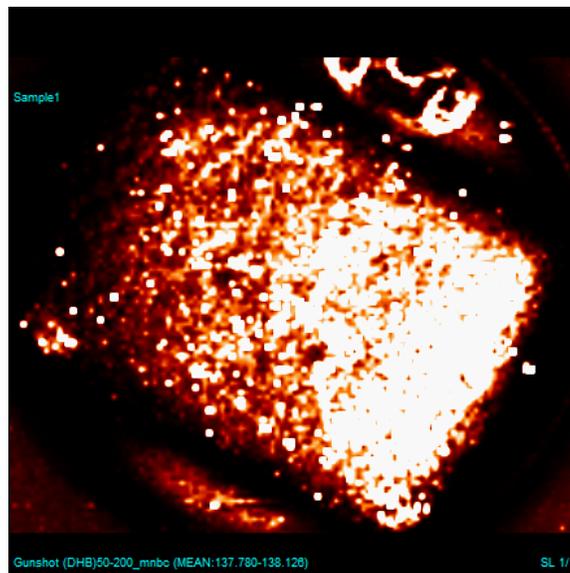
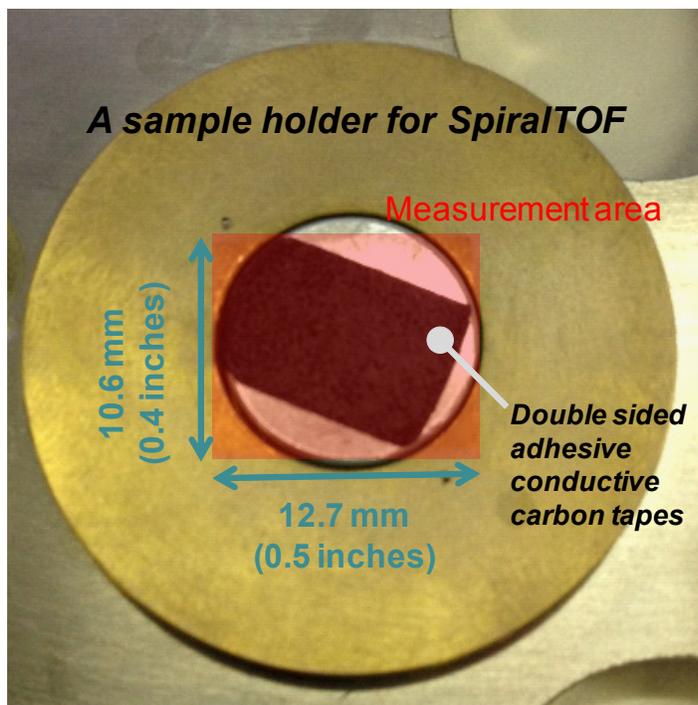
#### Sample Preparation and Measurement

The GSR samples were obtained on an electrically conductive adhesive that was adhered to the back of a shooter's

hand while a handgun was discharged. 2, 5-Dihydroxybenzoic acid (DHB) was dissolved in MeOH at a concentration of 30 mg/mL. Two milliliters of this DHB matrix solution was sprayed onto the GSR using an air-brush. Polypropylene glycol (PPG) was used for the external calibration standard. After the samples were dried, they were measured using the JMS-S3000 SpiralTOF MS system.

#### MALDI-MS Imaging measurement

- Measurement mode: SpiralTOF positive mode
- Matrix: DHB, 2mL spray @ 30mg/mL (MeOH)
- Spatial resolution: 100  $\mu$ m
- Measurement region: Width 12.7 mm x Length 10.6 mm
- Number of spectra: 13,462
- 5000 laser shots at 1kHz laser repetition rate for each position
- Analytics Software Biomap 3.8 - Raw data was converted to imzML files



MALDI imaging  
(Matrix ion distribution)

Figure 1. Sample pictures.

## Results & Discussion

As a starting point, we evaluated the mass accuracy of the SpiralTOF-MS with external calibration using two different DHB ions,  $C_7H_5O_3$  and  $C_7H_6O_4Na$ , in the measured digest spectrum. Because their monoisotopic ions were saturated, the  $[M+1]$  isotope ions were used, and the calculated mass error for each was +6.4 mDa and -5.1 mDa, respectively. As a result, an internal calibration was not required for the

qualitative MALDI imaging measurements done on the SpiralTOF-MS.

Next, the GSR sample surface was analyzed for inorganic specie distributions. Figure 2 shows a zoomed in portion of the measured digest mass spectrum and theoretical isotopic distribution for barium. Additionally, this figure shows the MALDI images for the  $^{138}Ba$   $m/z$  137.9016 and the DHB  $[M+1]^+$  isotopic ion  $m/z$  138.02671 ( $C_7H_5O_3$ ).

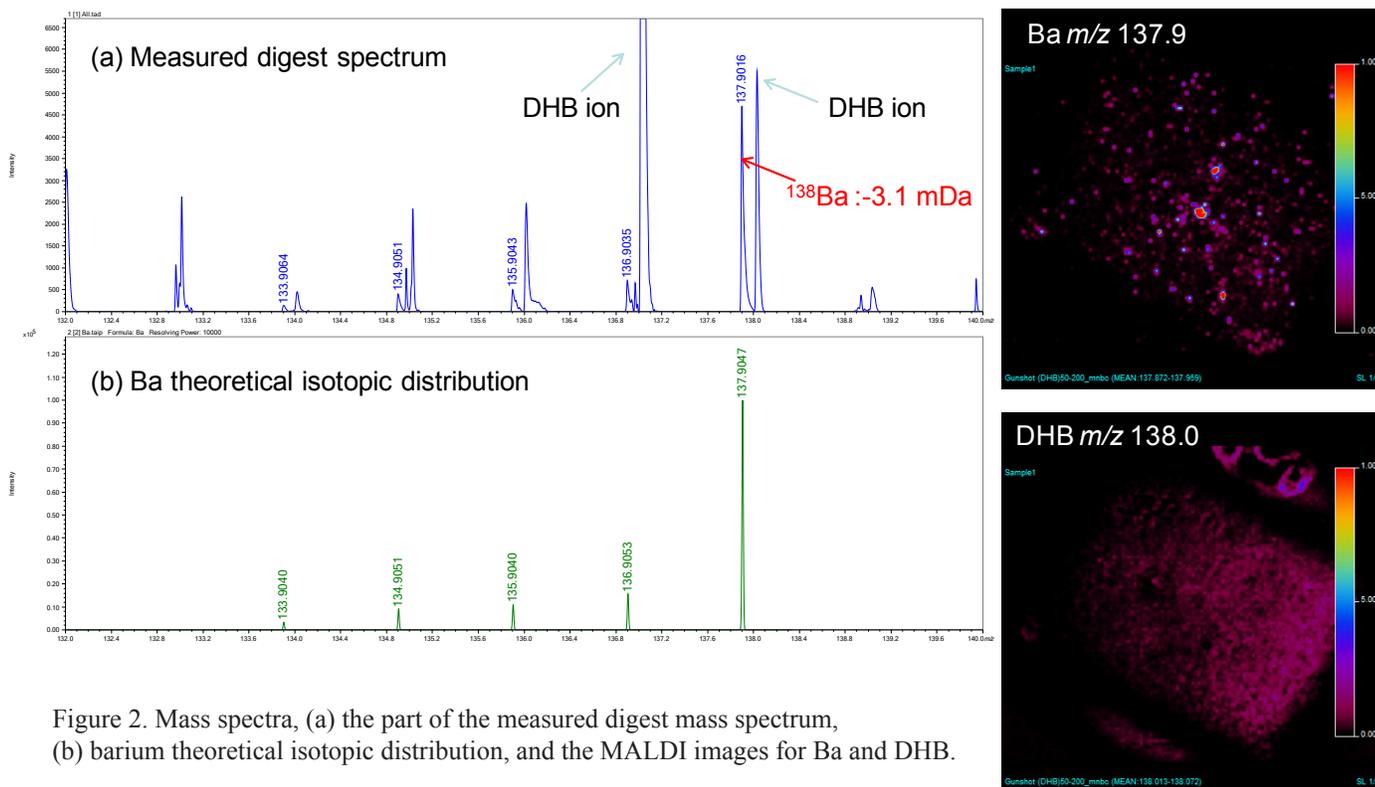


Figure 2. Mass spectra, (a) the part of the measured digest mass spectrum, (b) barium theoretical isotopic distribution, and the MALDI images for Ba and DHB.

Although the difference between each  $m/z$  is only 0.125Da, the SpiralTOF-MS provided full separation for both ion peaks which in turn produced strikingly different images for each analyte on the surface. The distribution of the  $^{138}Ba$   $m/z$  137.9016 was randomly distributed across the surface while the DHB  $m/z$  138.02671 was homogeneously present across the matrix surface.

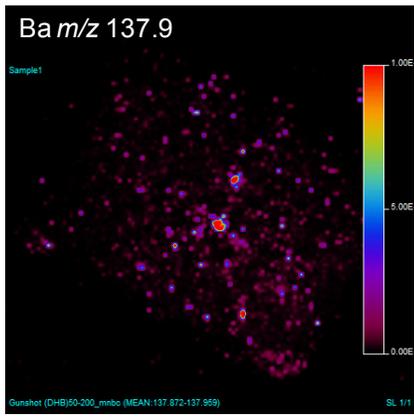
Figure 3 shows the barium and barium oxide particle distributions while Figure 4 shows the particle distributions for lead (Pb), bismuth (Bi), and calcium oxide (CaO). Each of these images was distinctive for their corresponding metals and metal oxides.

## Conclusions

The MALDI-MS images were useful for visualizing the presence of inorganic particle found in the GSR samples. The SpiralTOF MALDI imaging showed:

1. High mass resolving power.
2. High mass accuracy using the external calibration. An internal calibration is not necessary.
3. Good for small molecules.
4. Good spatial resolution.

Therefore, SpiralTOF MALDI imaging is a useful tool for the visualization of forensically significant molecules found in GSR samples.



Measured mass spectrum of a Barium particle (not digest mass spectrum)

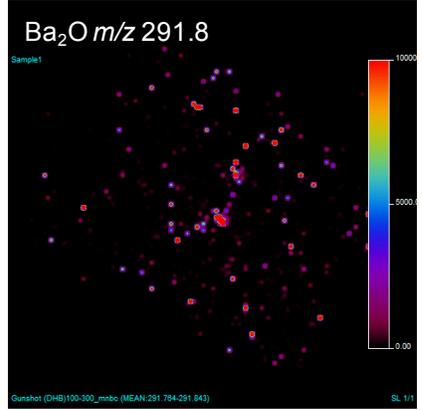
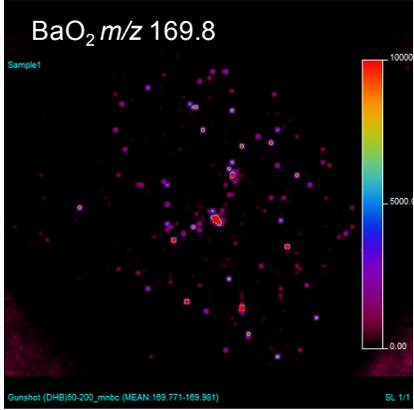
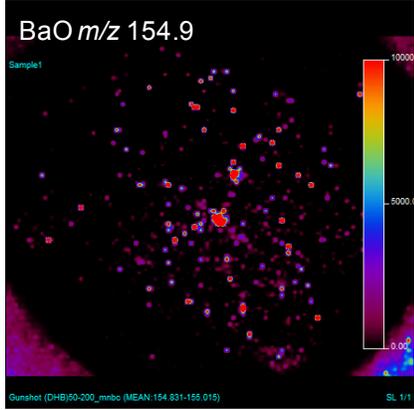
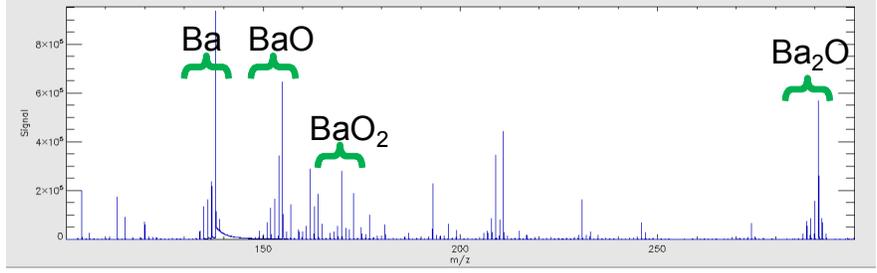


Figure 3. Barium and barium oxide particle distributions.

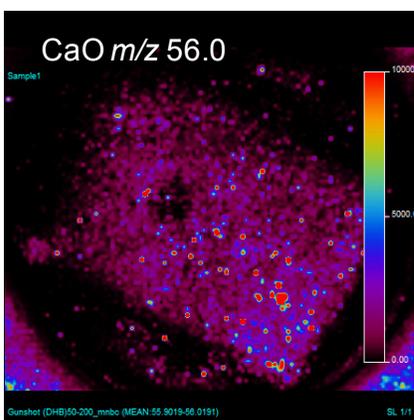
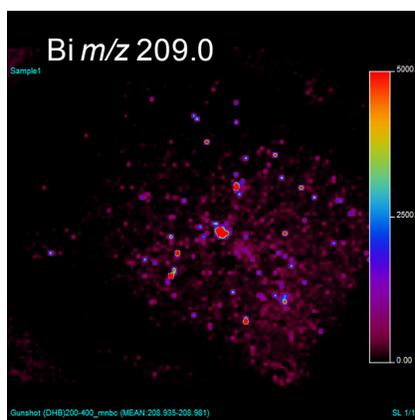
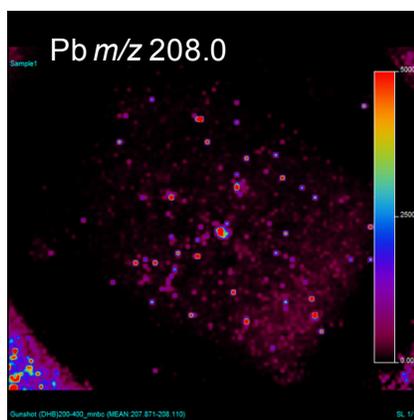


Figure 4. Lead, bismuth and calcium oxide particle distributions.