Analysis of Fingerprints by Desorption Electrospray Ionization Mass Spectrometry Imaging

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GOAL
Here we demonstrate the ability of DESI-MSI to determine the gender of an individual from their fingerprint.

BACKGROUND
Over the past decade, mass spectrometry imaging (MSI) has been used increasingly by researchers to investigate the distribution of metabolites, drugs, peptides, and proteins at tissue surfaces. The chemical composition of fingerprints is dependent on glandular secretions, excretion of ingested substances, and exposure to environmental chemicals. Analysis of fingerprints may thus provide native and environmental information about a donor, which is of particular interest to forensic scientists.1,2

Matrix-assisted laser desorption ionization (MALDI) mass spectrometry has been widely applied to the analysis of fingerprints. Bradshaw et al. were able to assess the presence of blood by detecting the ions from haeme and haemoglobin.3 Gender was predicted with 85% accuracy by comparing protein and peptidic profiles.4 Caffeine, fatty acids, and amino acid detection has also been reported.1 MALDI used in imaging mode (MALDI-MSI) allowed investigation of spatial variations in the chemical composition of finger marks; additionally, localization of sweat pores has been achieved.1

To a lesser extent, desorption electrospray ionization mass spectrometry (DESI-MS) has been used, and lipidic endogenous compounds – as well as spiked exogenous drugs and explosives – have been detected in fingerprints.5

Recently, there has been a significant increase in the application of DESI because this soft ionization technique can be performed under ambient environmental conditions. Furthermore, it requires little to no sample preparation and is minimally invasive, which makes it suitable for direct tissue analysis. DESI-MSI is compatible with both the Waters™ SYNAPT™ G2-Si and Xevo™ G2-XS Mass Spectrometers.
THE SOLUTION

Two men and two women provided each six fingerprints. These were collected at the same time, from different fingers, on Polysine® glass slides (Thermo Fisher Scientific). DESI analyses were performed using methanol–water (95/5 v/v) at a flow rate of 0.7 µL/min, with 1 µg/mL raffinose as a lockmass compound and 4 bars of N₂ as nebulizing gas. The samples were analyzed in profiling mode, following a line drawn crossing the fingerprint (Figure 1), or in imaging mode, with a pixel definition of 100 µm. Combined spectra were lockmass-corrected, background subtracted, and aligned for multivariate statistical analysis.

Profiling experiments by DESI on multiple fingerprints were carried out in positive and negative ionization mode. Figure 2 shows the total ion count (TIC) of the line of acquisition across one of the fingerprints in positive mode. The corresponding MS spectrum is displayed in Figure 3 showing the presence of mono, di, and triglycerides, as well as phospholipids. In negative ionization mode, fatty acids, cholesterol sulfate, and phospholipids were detected (Figure 4).

Principal Component Analysis (PCA) allowed a good separation of male and female subjects, using only the two first principal components (Figure 5). The prediction of the donors’ gender taking 20% of the dataset out using a PCA-LDA (Linear Discriminant Analysis) model was 96% accurate in negative mode (Table 1) and 100% in positive mode (Table 2).
SUMMARY

DESI-MS using the Waters Xevo G2-XS QTof together with a Prosolia DESI 2D source allows the ambient, direct, and precise analysis of fingerprints. The detection of a great number of compounds belonging to various classes of lipid enables lipid-based investigations. Lipidomic profiles obtained here allowed the prediction of the donors' gender.

The advantages of this DESI-MSI include:

- Minimum sample preparation required prior to DESI-MSI analysis, with no need to apply matrix (as required in MALDI imaging, for example).
- Measurements can be performed under ambient environmental conditions.
- DESI-MSI is a non-destructive technique that allows additional analyses of the same sample.
- Good analytical sensitivity for a wide range of molecules.

References