THE EIGHT(Y) MILLION POUND QUESTION: USING DESI AMBIENT MS IMAGING FOR THE FORENSIC ANALYSIS OF CHEQUE FRAUD

THE SCIENCE OF WHAT'S POSSIBLE."

-180 -160 -140 -120 -100 -80 -60 -40 -20 0 20 40 60 80 100 120 140 160 180

Huiqin Zhong,¹ Zhengwei Jia,¹ Wei Rao,¹ <u>Anthony Midey</u>,² and Bindesh Shrestha²

¹Waters Technology (Shanghai) Limited, Shanghai, China

²Waters Corporation, Beverly, MA

INTRODUCTION

Cheque fraud is a major category of criminal activity that inflicts millions of pounds of economic damage every year. One commonly performed forgery is physical alteration of an existing cheque to inflate the payout amount or change the recipient. Traditional anti-fraud techniques such as handwriting analysis by a highly trained expert looking for mismatches can be labor intensive and do not work well for small scale alterations. A faster, more objective writing analysis method could greatly assist the investigation of difficult cheque fraud forgeries, potentially providing key evidence in solving such cases.

Desorption electrospray ionization (DESI) performs direct surface chemical analysis by desorption ionization. DESI operates under ambient conditions and requires no sample preparation. Mass Spectrometry Imaging (MSI) using DESI produces detailed spatially resolved patterns of compounds from a sample. The minimally destructive nature of DESI means that sample can be further analyzed using other methods afterwards.

A simulated cheque fraud case involving three individuals was conducted. DESI MS Imaging detected signature chemical markers of 3 different inks to reveal the location of forgeries that were almost impossible to discern with the naked eye. Difficult single character alterations were easily separated into their constituent parts directly from the cheque. The detailed spatial distributions of the ink chemicals identified the alterations made by specific individuals.

MASS SPECTROMETRY IMAGING

Mass Spectrometry Imaging (MSI) basic concept

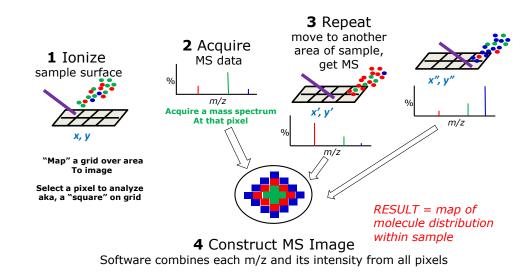


Figure 1. Illustration of how to do Mass Spectrometry Imaging (MSI).

DESORPTION ELECTROSPRAY IONIZATION MS IMAGING SOURCE

• A shower of charged ESI solvent droplets focuses into a beam by a

- high pressure gas flow (N_2) to washes the surface. (Fig. 3b) Desorbed analytes were then ionized and carried into an inlet
- capillary that transferred the ions to the MS for analysis.
- DESI is minimally destructive, allowing multiple analyses off of the same sample.

METHODS

DESI Mass Spectrometry Imaging

Source: 2D DESI stage (Waters Corp)

Mass Spectrometer: XEVO G2-XS QTof (Waters Corp) DESI conditions:

- 100% methanol at 1.5 μL/min
- Nebulizing gas pressure of 0.5 MPa nitrogen
- 4.5 kV sprayer voltage

Polarity: Positive

Mass range: 50 -1,200 m/z in sensitivity mode

MS Imaging Pixel size: 100 µm large area; 50 µm detailed area

Data management

MSI data were acquired using MassLynx 4.2. Experimental parameters were defined, raw files processed, and MS Imaging data visualized using High Definition Imaging (HDI) 1.4 software. Principal components analysis (PCA) performed on regions of interest (ROI) MS data exported from HDI to EZ Info 2.0.0.3.

SAMPLES

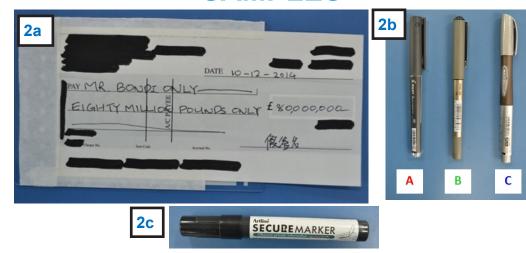


Figure 2. a) Standard bank cheque sample made out to "Mr. Bondi Only" for £80,000,000, dated, and signed; b) Pens used to create original amount (A) and fraudulent alterations (B) and (C); c) Marker used to obscure critical information.

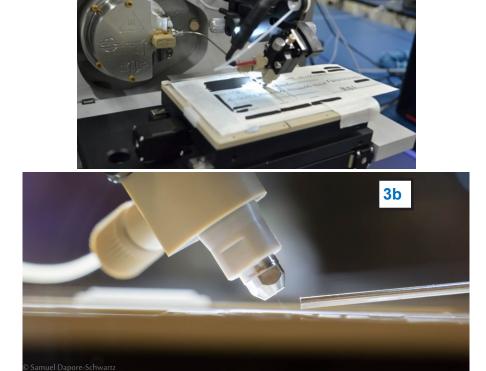
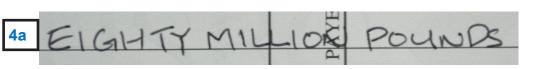


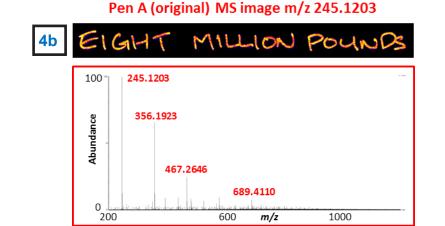
Figure 3. a) Direct DESI MS Imaging analysis of a cheque sample using Waters DESI source with SYNAPT G2-Si QTof MS.; b) DESI as an ion source for MS Imaging (Photo courtesy of Samuel Dapore-Schwartz, Waters Corp.)

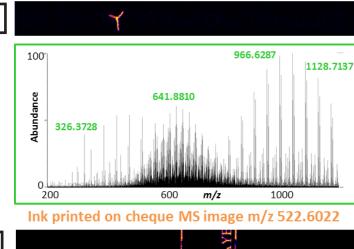
RESULTS

DESI MS Imaging of the monetary amount written in words

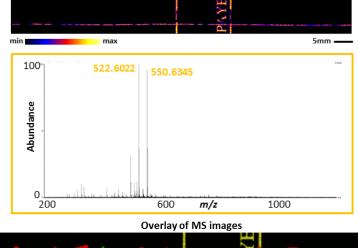
- DESI MS imaging of the words "EIGHTY MILLION POUNDS" on the cheque at 100µm pixel size (Fig. 4a).
- m/z 245.1203 corresponded to the writing "EIGHT MILLION POUNDS" using pen A (4b).
- m/z 996.6287 present only on the letter "Y" written with pen B (4c).
- m/z 522.6022 corresponded to a 3rd ink already present on the original cheque, shown with its corresponding chemical profile (4d).
- Regions of interest (ROI) corresponding to the different texts extracted to MassLynx from HDI showed different chemical profiles for the respective pens.
- Overlay of the MS images for the 3 signature m/z (4e) revealed the relative positions of the original text (pen A), the alteration (pen B),

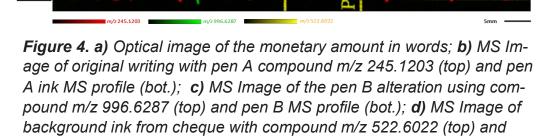






Pen B (1st alteration) MS image m/z 996.6287





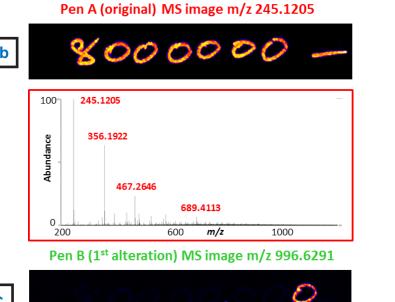
cheque ink MS profile (bot.); e) Single color MS Image overlay of 3 sig-

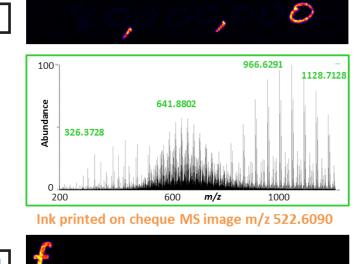
nature ink compounds.

DESI MS Imaging of the monetary amount written in numerals

- DESI MS imaging of the numerical amount at 100μm pixel size revealed alterations to "80,000,000-" (Fig. 5a).
- Original text written with pen A was "8000000-" (m/z 245.1205; 5b).
- Alteration increased the amount, placing extra commas and a 0 into the text to make the changes more authentic (m/z 996.6291; 5c).
- Extracted MS for each of the writing portions confirmed that the pens used were A and B, respectively.
- Pound sign printed using original check ink (m/z 522.6090, Fig. 5e).
- Fig. 5e shows an overlay MS Image of the signature m/z peaks.

80,000,000





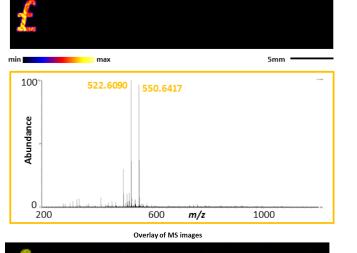
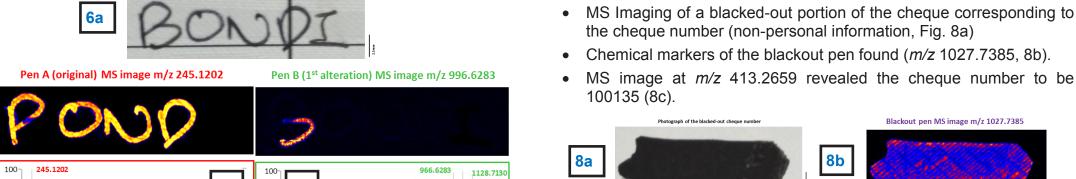
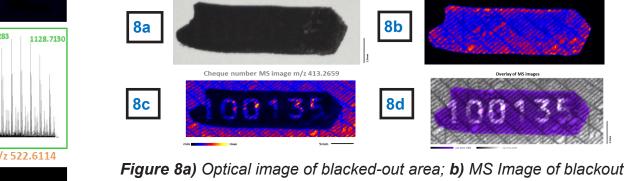


Figure 5 a) Optical image of the monetary amount in numbers; b) MS Image of original writing with pen A compound m/z 245.1203 (top) and pen A ink MS profile (bot.); c) MS Image of the pen B alteration using compound m/z 996.6287 (top) and pen B MS profile (bot.); d) MS Image of background ink from cheque with compound m/z 522.6022 (top) and cheque ink MS profile (bot.); e) single color MS Image overlay of 3 signature ink compounds.

DESI MS Imaging of the recipient's written name

- Recipient's name imaged at higher spatial resolution (50µm pixel) for greater visual clarity (Fig. 6a).
- originally made out to Mr. "POND" (6b).
- Further analysis revealed a second alteration created using pen C to
- MS extracted from letter "I" gave third separate ink profile different from pens A and B.
- m/z 522.6114 for the original cheque ink detected (5e).





pen compound m/z 102.7385; c) MS Image of the cheque number using compound m/z 413.2659; d) Single color MS Image overlays of 2 signature ink compounds.

Figure 7a) Regions of interest (ROI) to extract MS data from written

name MS images; b) Principal component analysis (PCA) of ROIs.

Revealing hidden information using MS Imaging specificity

DISCUSSION

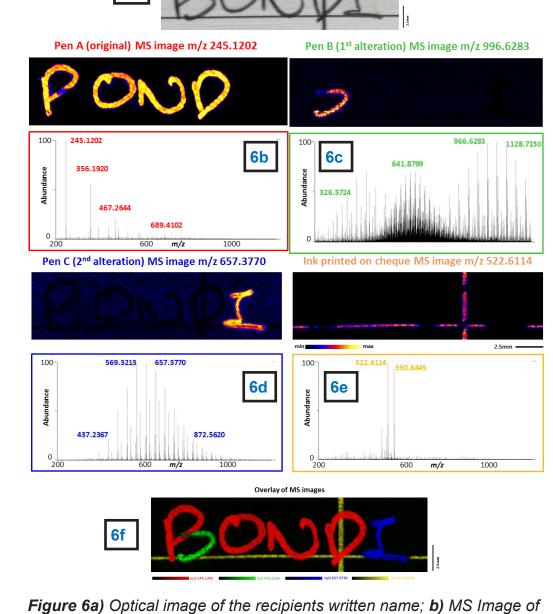
A complete picture of the various participants involved with the cheque fraud was constructed using DESI MS Imaging, with assignments of particular parts of the alterations clearly attributed to the responsible parties via signature ink m/z peaks. Direct analysis of the ink from the cheque itself without sample preparation showed the potential for determining the origin and authenticity of the specimen. The small scale, single character nature of the alterations performed made the fraud case more difficult to solve using traditional handwriting analyses. However, the ambient nature of DESI allowed true *in-situ* analysis of the sample with almost no discernible damage done to the specimen, providing other opportunities for downstream examinations. These tests could include additional MS Imaging with negative polarity, higher resolution MS Imaging of zoomed-in areas, or other forensic techniques.

CONCLUSIONS

- Direct detection of cheque fraud with ambient DESI MS Imaging was performed with minimal disruption to the specimen.
- High quality images with good visual clarity were obtained at 50 and 100 µm pixel sizes.
- Chemical profiles of three different pens were determined with exact spatial assignments, allowing even small scale single character alterations to be clearly identified within the text.
- Principle component analysis of mass spectra extracted from the MS images gave further confidence in the assignment of the different pens to their respective pen strokes.
- The findings of this analysis offered the potential to provide high quality evidence in similar cases of check fraud, allowing the generation of key insights that could lead to breakthroughs

- MS image for pen A at m/z 245.1202 showed that the cheque was
- Pen B altered the "P" to a "B" in a single stroke (m/z 996.6283, 6c).
- change the recipient to Mr. "BONDI" (m/z 657.3770, 6d).

- Overlay MS image of the signature m/z peaks from the different inks



original writing with pen A compound m/z 245.1203 (top) and pen A ink MS profile (bot.); c) MS Image of the pen B alteration using compound m/z 996.6287 (top) and pen B MS profile (bot.); d) MS Image of the pen C alteration using compound m/z 657.3770 (top) and pen C MS profile (bot.); e) MS Image of background ink from cheque with compound m/z 522.6022 (top) and cheque ink MS profile (bot.); f) single color MS Image overlay of 4 signature ink compounds.

Multivariate analysis (MVA) of ink MS Images for "fingerprinting"

- DESI imaging MS data of the name portion subjected to principal component analysis (PCA) to analyze the inks used for each part of
- 65 ROIs selected within the borders of the writing (Fig. 7a), which were exported via HDI to EZ Info • All but one of the ROIs segregated to three distinct regions of the
- PC1 and PC2 plot, corresponding to the 3 different pens used (7b). ROI 12 was the only one falling in-between the ROI clusters for pens A and B, consistent with its position at the point where the strokes for

those two pens overlapped.

in solving difficult cases.