

A multimodal mass spectrometry imaging workflow for ballpoint pen ink analysis and “forgery” detection †

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Table S1- DESI and MALDI parameters employed in the multimodal workflow.

DESI PARAMETERS		MALDI PARAMETERS	
SOLVENT COMPOSITION	95:5 MeOH:H2O spiked with 100 $\mu\text{g } \mu\text{L}^{-1}$ of Leu-enkephalin	MATRIX CONCENTRATION	CHCA 5 mg/mL
FLOW RATE	2 μLmin^{-1}	SOLVENT COMPOSITION	70:30 MeOH:0.5% TFAaq
LOCKMASS CORRECTION	Leu Enk at m/z 554.2615	NUMBER OF LAYERS	8
HTL TEMPERATURE	30 $^{\circ}\text{C}$	SPRAYING CONDITIONS	Nozzle temperature set to 60 $^{\circ}\text{C}$, solvent flow rate of 100 μLmin^{-1} and N2 pressure of 8 psi
IONISATION VOLTAGE	0.5 kV	LOCKMASS CORRECTION	CHCA at m/z 212.0324
CONE VOLTAGE	40 V	LASER TYPE	Nd:YAG
SOURCE TEMPERATURE	120 $^{\circ}\text{C}$	LASER RATE	1000

Figure S1 - Schematic representation of (A) Sample set 1 (2 pens used to prepare the number “1800”), (B) Sample set 2 (7 different ballpoint pens used to prepare the word “forgery”) and (C) Sample set 3 (2 different papers with fresh and aged samples spelling the word “Leo”)

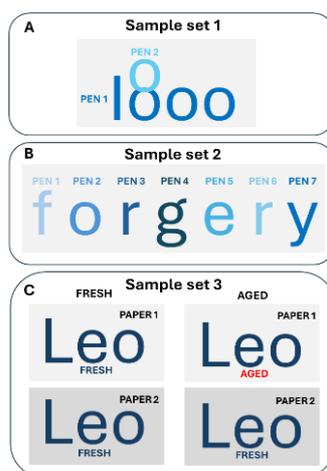


Figure S2 - A representative example of data extraction for statistical analysis of Sample set 1, including (A) the ROIs that were extracted (represented by different coloured squares) and (B) the list of ROIs showing that each contained the same number of pixels from the same sampling area.

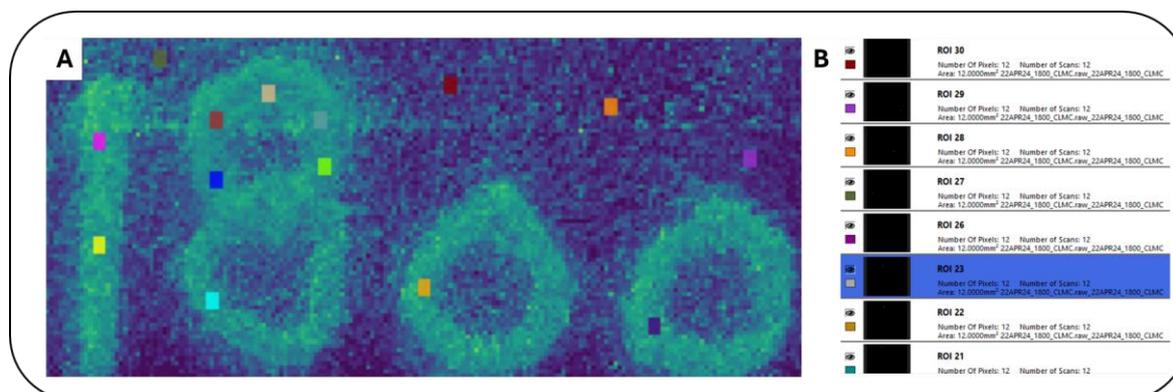


Figure S3 - (A) Ions of interest generated by PLS-DA analysis of the word “forgery” in 7 different pens following DESI-MSI analysis – the coloured boxes on the right indicate the relative peak intensities of the corresponding ions in each letter, (B-G) DESI MS images of m/z 281.2559, m/z 352.2946, m/z 279.2402, m/z 324.2626, m/z 321.2282 and m/z 350.2789 and (H) Tandem MS spectrum for m/z 279.2402, confirming the presence of linoleic acid.

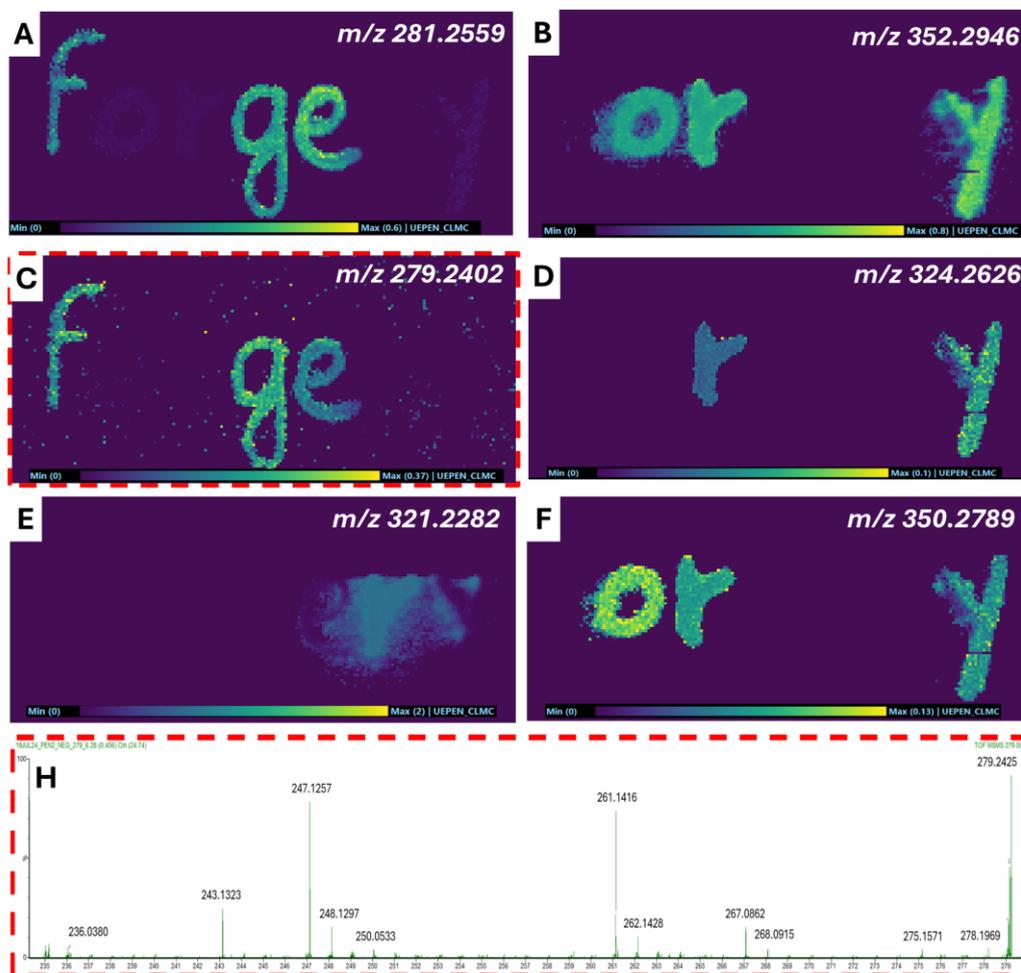


Figure S4 -MS/ MS of oleic acid, a common ink lubricant.

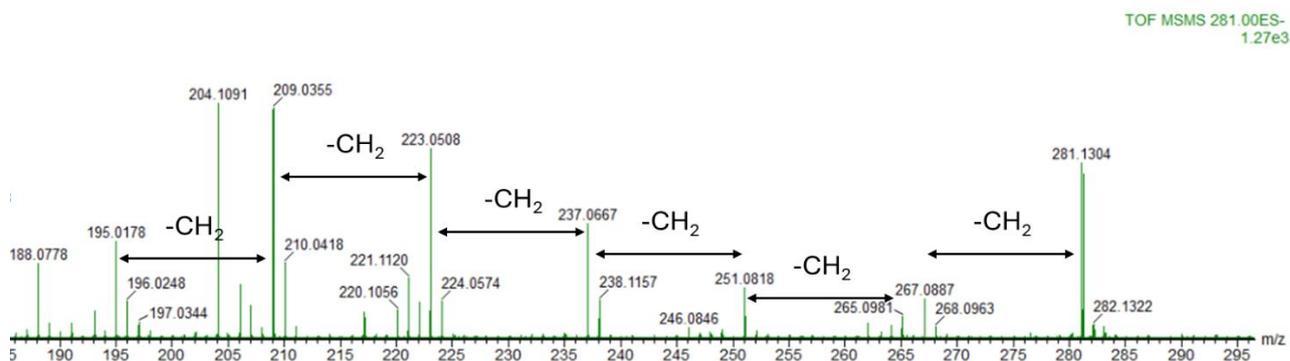


Table S2 - Theoretical and observed ions with calculated mass accuracy for triarylmethane compounds found by MALDI MSI.

Molecule	Theoretical m/z (+)	Observed m/z (+)	Mass Accuracy (ppm)
$(C_{25}H_{30}N_3)^+$	372.2434	372.2444	2.633
$(C_{24}H_{28}N_3)^+$	358.2278	358.2287	2.596
$(C_{23}H_{26}N_3)^+$	344.2121	344.213	2.557
$(C_{22}H_{24}N_3)^+$	330.1965	330.1973	2.514
$(C_{21}H_{22}N_3)^+$	316.1808	316.1817	2.783

Figure S5 -MS/MS analysis of the triarylmethane compounds and their expected fragmentation patterns.

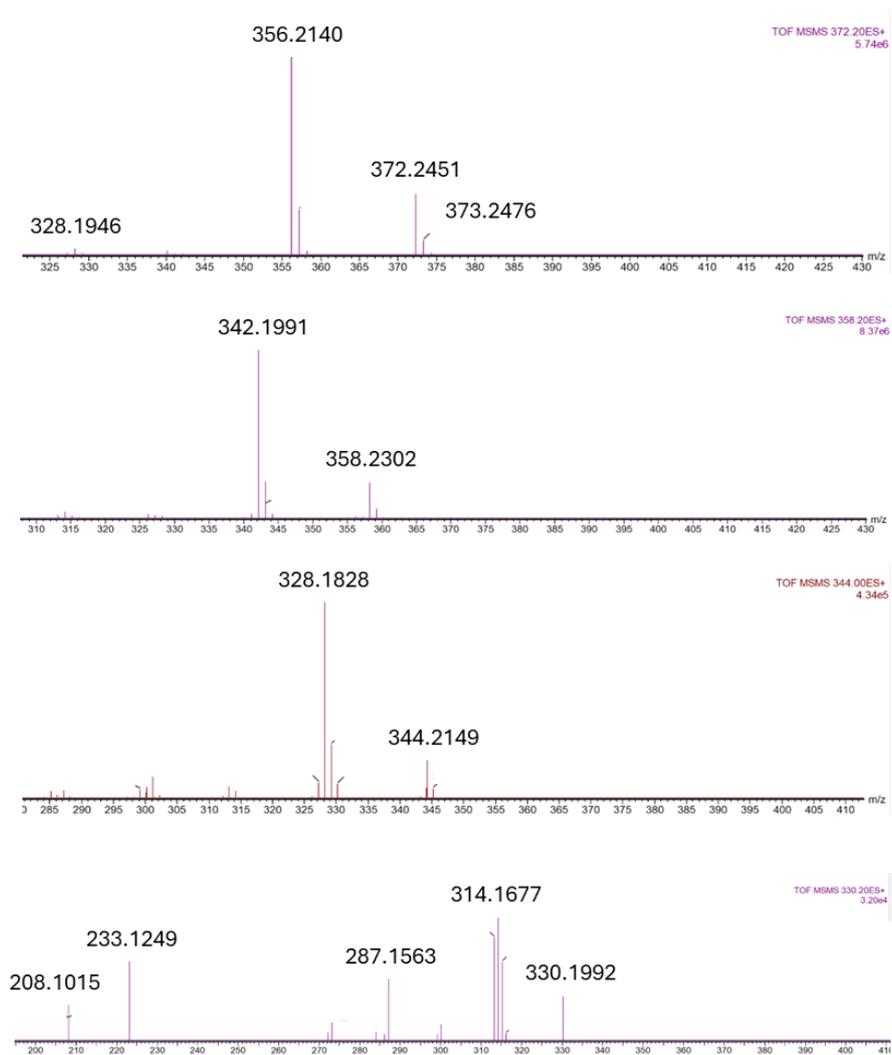


Figure S6 -Statistical analysis of ion intensity variations between ions in fresh vs aged inks observed with DESI (A and B) and MALDI MS (C and D).

