Electronic Supplementary Material (ESI) for Analyst.
This journal is © The Royal Society of Chemistry 2018

# Detection of exogenous substances in latent fingermarks by silver-assisted LDI imaging MS: perspectives in forensic sciences.

Nidia Lauzon[1] and Pierre Chaurand[1]

[1] Dept. of Chemistry, Université de Montréal, Montreal, QC, Canada

## Supplemental Material

**Groomed latent fingermarks were prepared on ITO-coated slides, glass slides and porous surfaces according to published preparation methods (Ref.36).** The finger was rubbed on the forehead, nose and chin several times in order to produce a sebum-rich fingermark containing common exogenous substances.

**Blood revealing by either amido black, leuco crystal violet (LCV) or 1,2-Indanedione-Zinc treatments.** Amido Black staining requires 3 steps: 1) Proteins fixation is performed using pur methanol and allowed to dry for 5 minutes, 2) Staining with the working solution (amido black, acetic acid glacial and methanol), and 3) After 2 minutes, a washing solution (acetic acid glacial 5% v/v) is used to remove excess working solution. All solutions are directly deposited on the surface which is held at an incline to allow solutions to run off. The sample was then allowed to dry before metallic silver deposition. Leuco crystal violet treatment was performed in 1 step using the working solution (LCV, 5-sulfosalicylic acid, hydrogen peroxide). The solution is deposited on the slide surface which is held at an incline to allow the solutions to run off. The slide was then allowed to dry before metallic silver deposition. 1,2-Indanedione-Zinc solution was deposited on the paper containing the bloody fingermarks held at an incline. The paper was allowed to dry and was then heated on a hot plate at 125°C for 20 secondes.

**Metallic silver was sputtered on top of fingermarks using a Cressington 308R sputter coater (Ted Pella, Inc. Redding, CA, USA) as previously described (Ref.40).** The metallic silver depositions were time-controlled (30 s) with an argon partial pressure of 0.02 mbar and a current of 80 mA. The layer tickness was estimated at 14 ± 2 nm using a quartz crystal microbalance.

**Double-sided carbon conductive (DSCC) tape was first applied to ITO coated slides. All non-conductive surfaces containing the fingermarks were then mounted on the tape as previously described (Ref.41).** An aluminium sheet was used to flatten the surface onto the DSCC tape for better conductivity. For fingermarks retrieved using lifting tape, the DSCC tape can be mounted on the back of the forensic lifting tape for better conductivity.

# Supplemental Calculations

Heroin et Cocaine LOD's on an ITO-coated slide (diameter of droplets = 2mm)

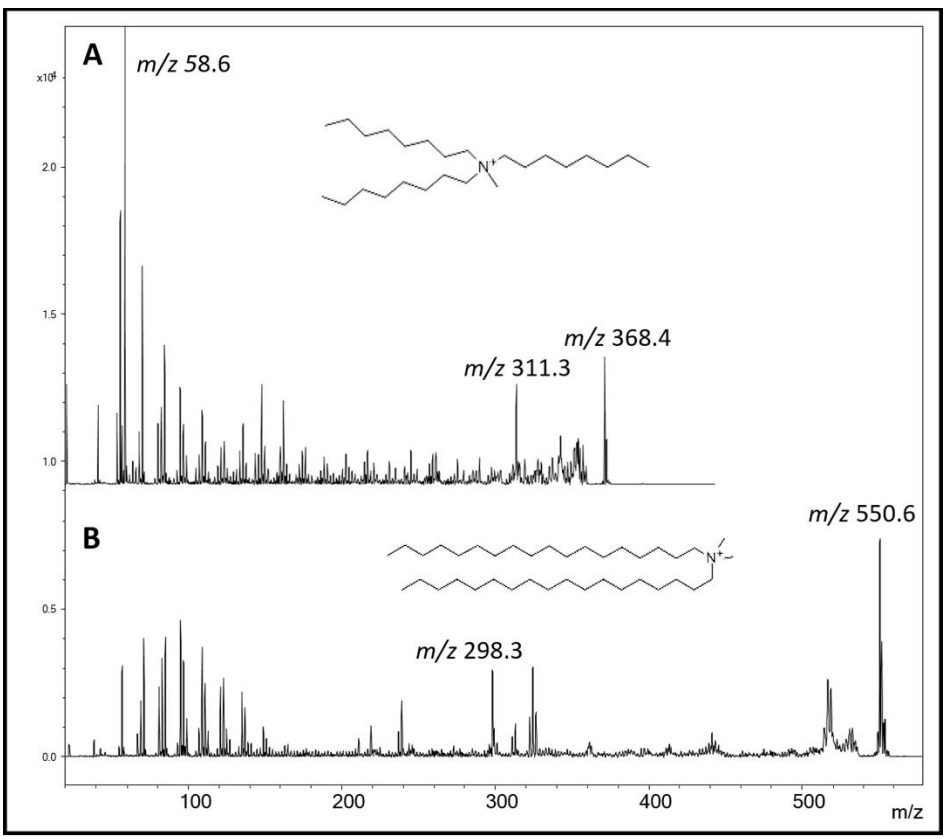
$$0.01\frac{\mu g}{mL} = 0.01\frac{ng}{\mu L}$$

$$0.01\frac{ng}{\mu L} \times 0.5\mu L = 0.005ng$$

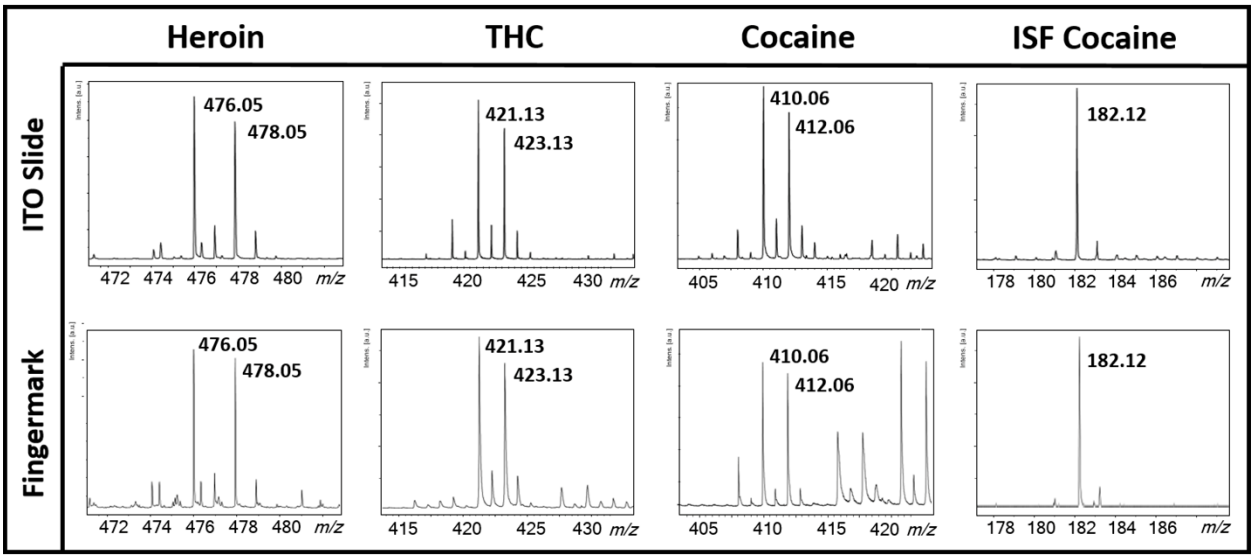
$$Droplet's\ Area = \pi r^2 = \pi(0.1cm)^2 = 0.031cm^2$$

$$LOD = \frac{0.005ng}{0.031cm^2} = 0.16\frac{ng}{cm^2}$$

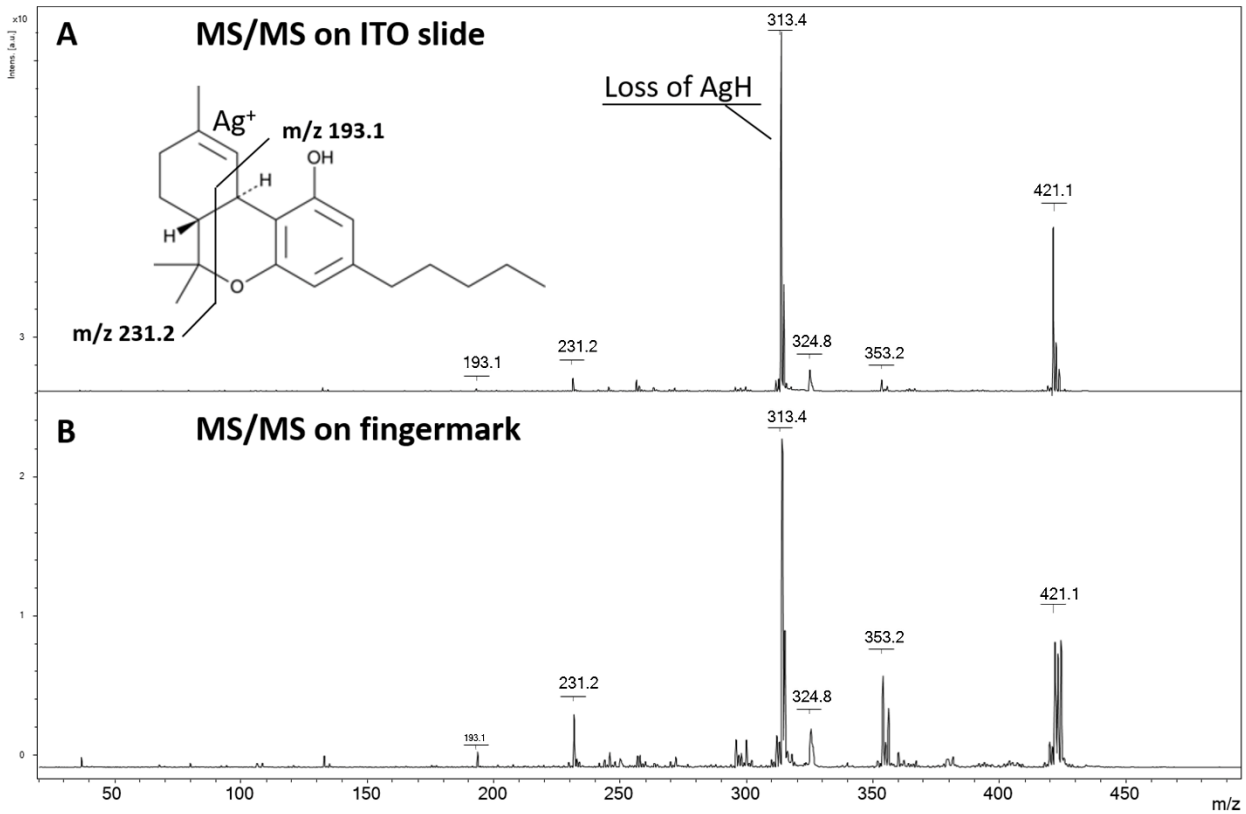
# Supplemental Figures



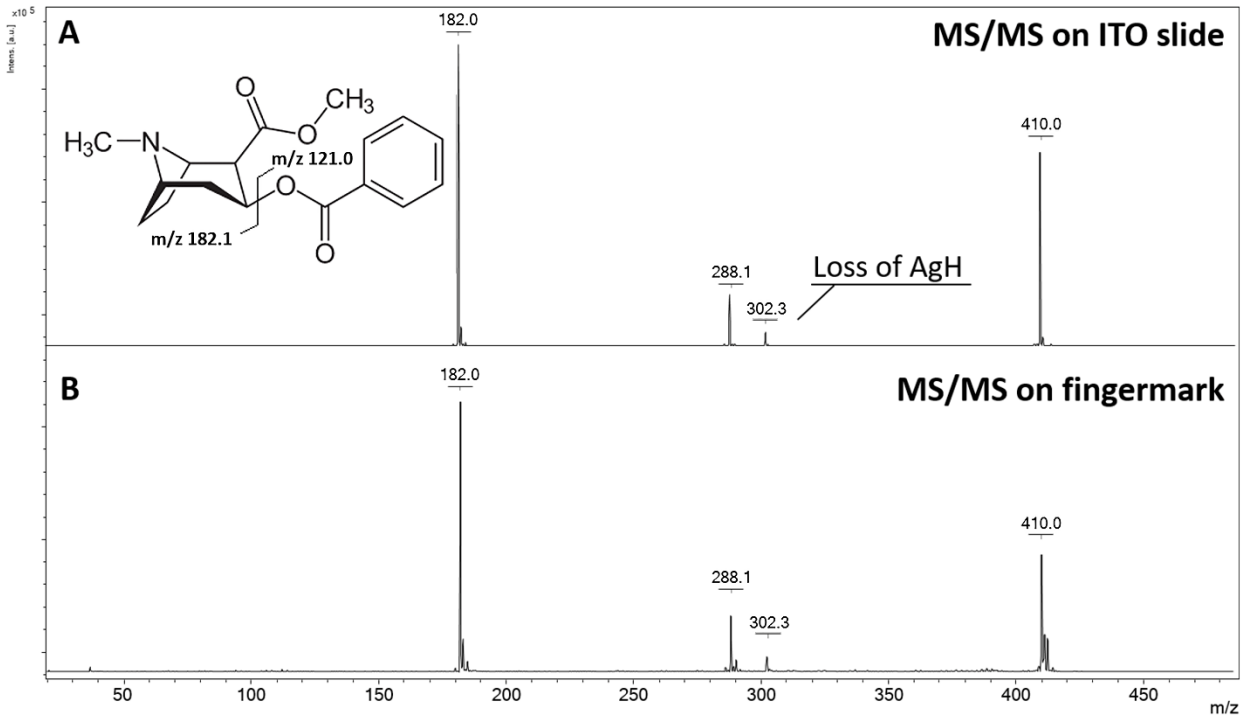

**Suppl. Figure 1. AgLDI MS/MS of contaminants in fingermarks.** A) *m/z* 368.4 and presumed structure, and B) *m/z* 550.6 corresponding to dimethyldioctadecylammonium (DTDMAC).



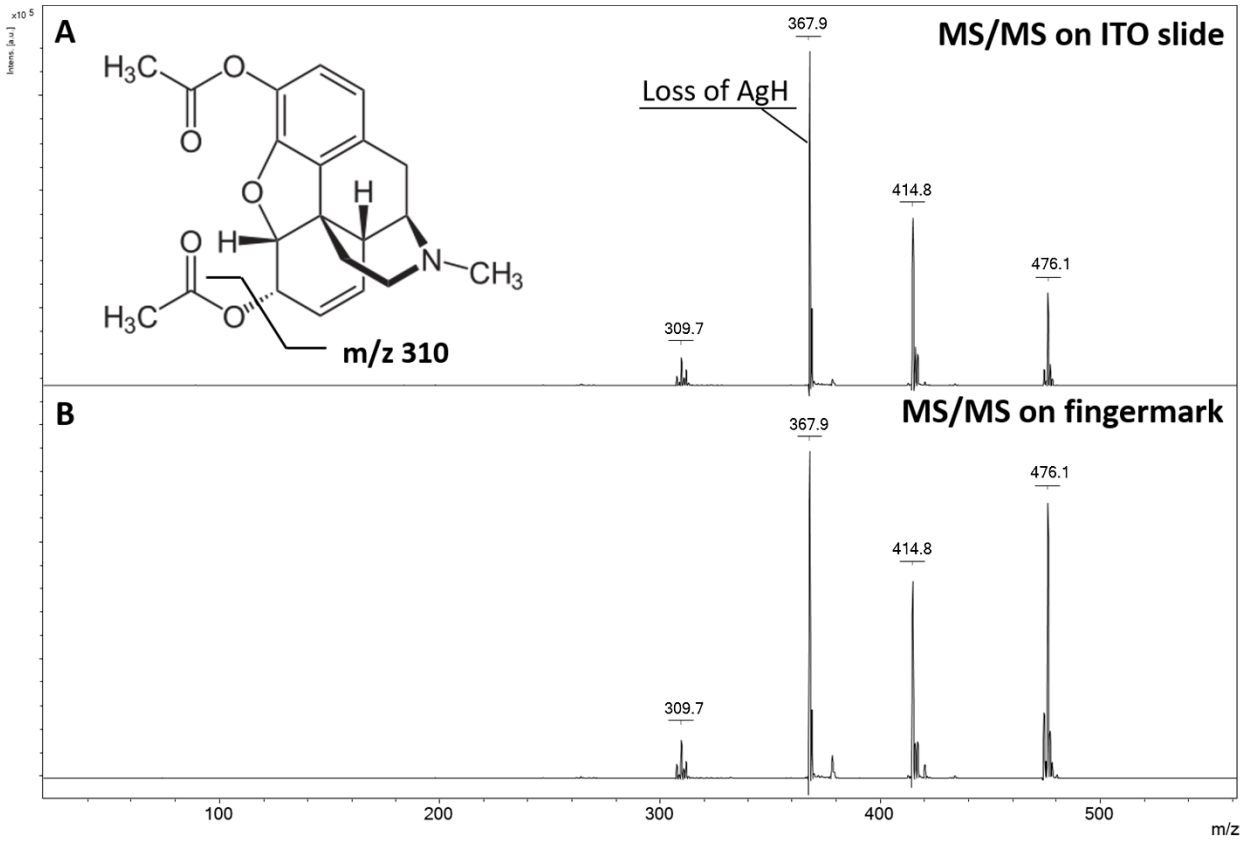

**Suppl. Figure 2. AgLDI MS of illicit drug standards**: Comparison of deposition on ITO-coated slides (top row) and on fingermarks (bottom row) of Heroin, THC and Cocaine and of its in-source fragment (ISF) ion.



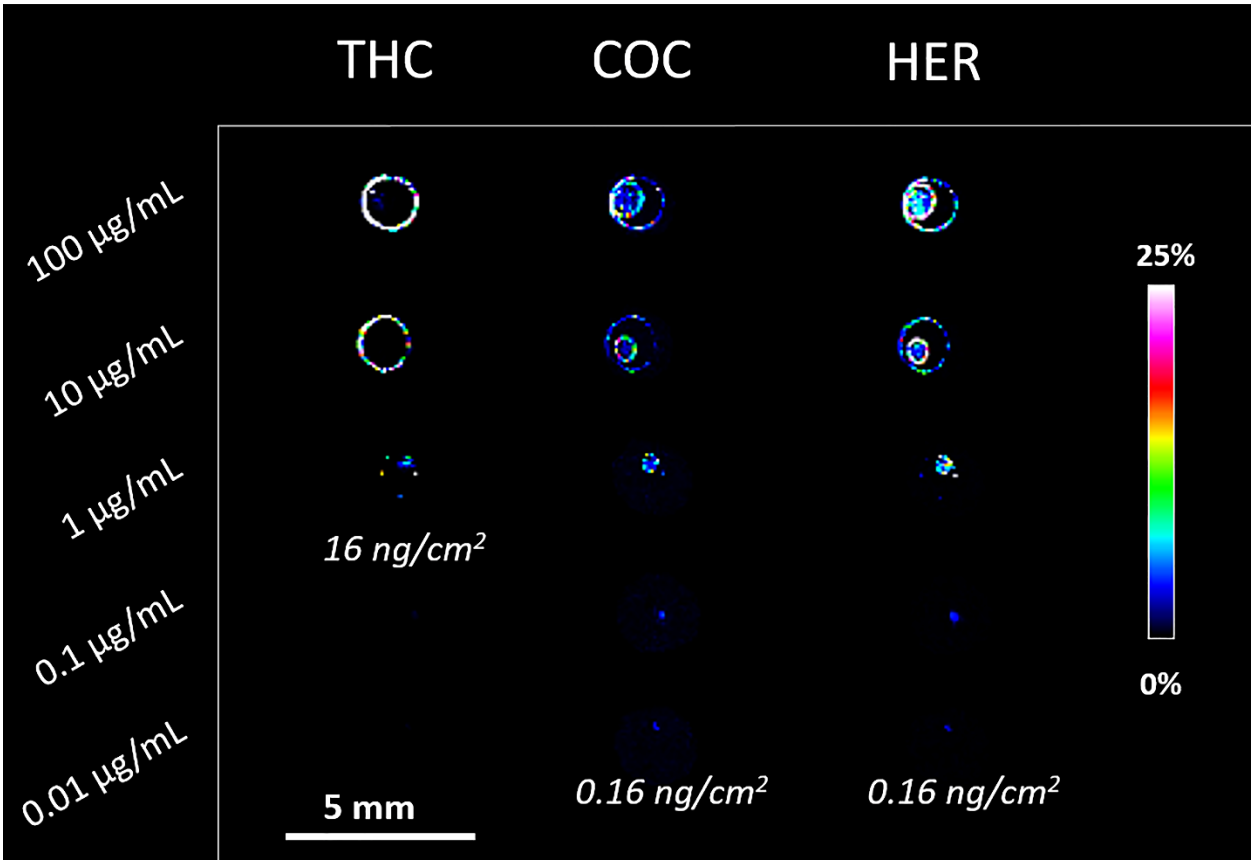

**Suppl. Figure 3. AgLDI MS/MS of a tetrahydrocannabinol standard.** THC deposited on A) a clean ITO-coated slide and B) on a fingermark.



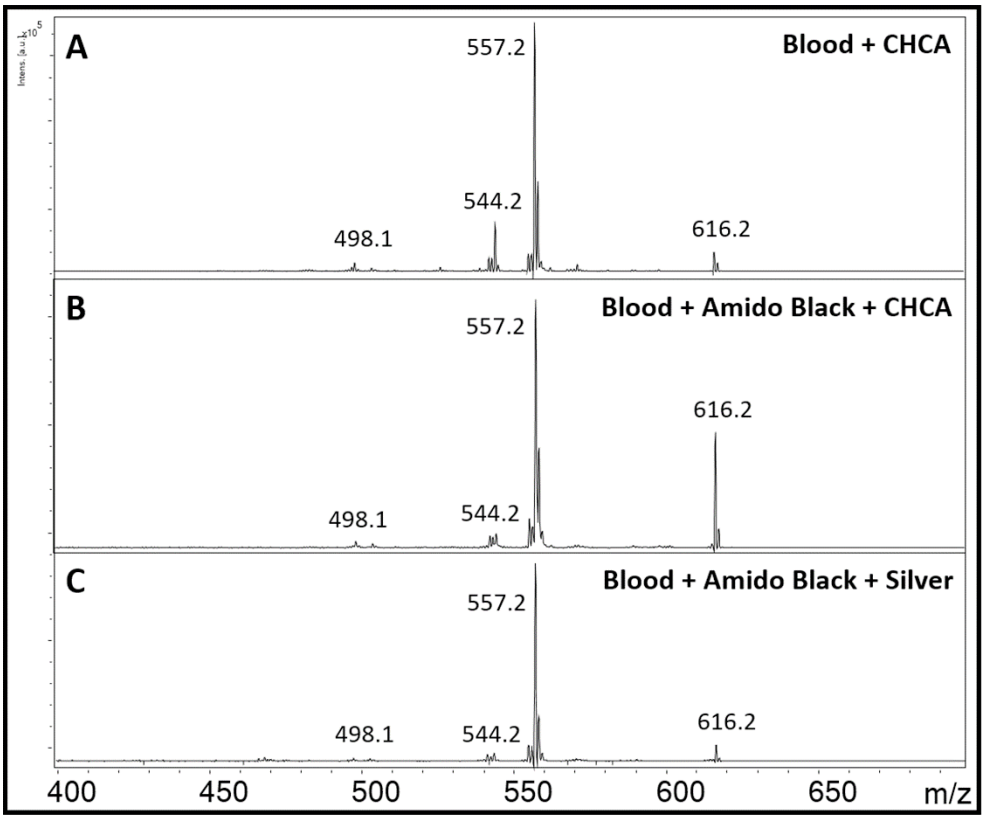

**Suppl. Figure 4. AgLDI MS/MS of a cocaine standard.** Cocaine deposited on A) a clean ITO-coated slide and B) on a fingermark.



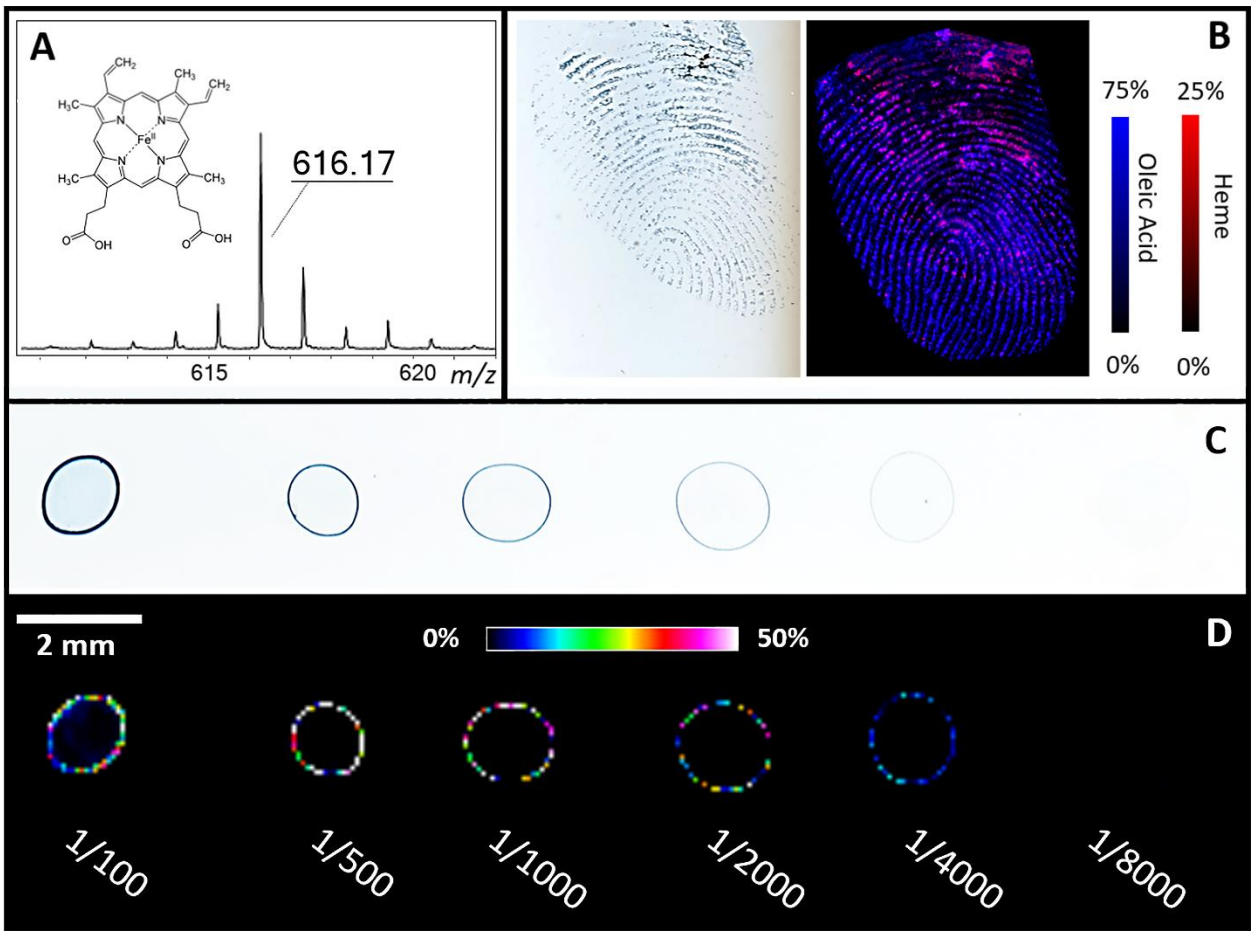

**Suppl. Figure 5. AgLDI MS/MS of a heroin standard.** Heroin deposited on A) a clean ITO-coated slide and B) on a fingermark.



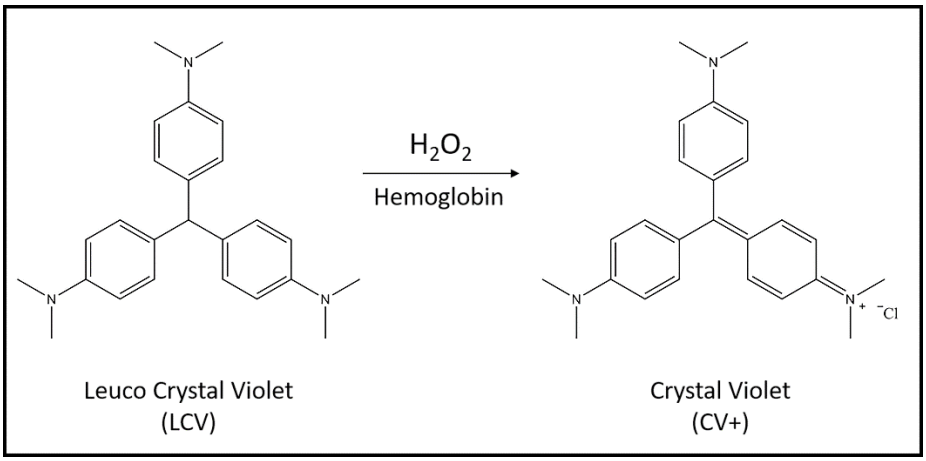

**Suppl. Figure 6. AgLDI IMS of serial illicit drug dilutions ranging from 100 to 0.01 µg/mL.** Tetrahydrocannabinol (THC) at *m/z* 421.13, Cocaine (COC) at *m/z* 410.06 and Heroin (HER) at *m/z* 476.05.



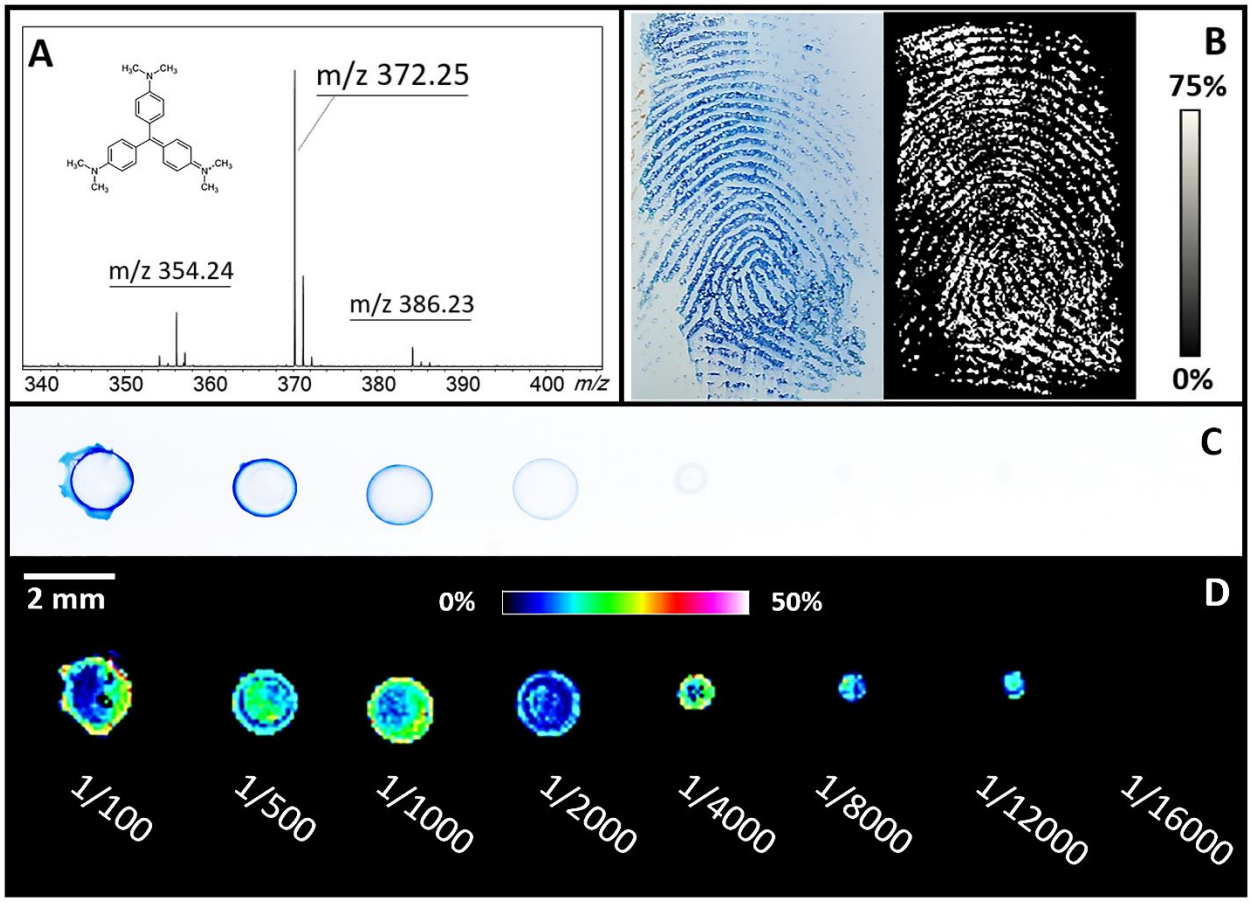

**Suppl. Figure 7. Comparison of AgLDI and MALDI MS/MS of the heme group in bovine blood after amido black staining.** A) MALDI MS/MS of heme using CHCA as matrix, B) MALDI MS/MS of heme after amido black staining using CHCA as matrix, and C) AgLDI MS/MS of heme after amido black staining.




**Suppl. Figure 8. AgLDI MS and IMS of the heme after amido black staining.** A) AgLDI MS of heme at *m/z* 616.17. B) Photomicrograph and AgLDI IMS of heme and acid oleic (*m/z* 389.16) of a human bloody fingermark deposited on an ITO-coated slide. C) Optical image and D) AgLDI IMS of serial blood dilutions ranging from 1/100 to 1/8000 after amido black staining.




**Suppl. Figure 9. Oxidation of Leuco Crystal Violet (LCV) in the presence of hydrogen peroxide and hemoglobin.** $CV^+$ is directly detectable by MS under LDI conditions.




**Suppl. Figure 10. AgLDI MS and IMS of blood after leuco crystal violet staining.** A) AgLDI MS of the crystal violet at *m/z* 372.25 $[C_{25}H_{30}N_3]^+$. B) Optical image and AgLDI IMS of the crystal violet after leuco crystal violet treatment of a human bloody fingermark deposited on an ITO-coated slide. C) Optical image and D) AgLDI IMS of serial blood dilutions ranging from 1/100 to 1/16000 after leuco crystal violet treatment.