Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic Supplementary Information For:

Balancing the Utility and Legality of Implementing Portable Mass Spectrometers Coupled with Ambient Ionization in Routine Law Enforcement Activities

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The Effect of Surface Swabbing on Swab Deformation and Collected Spectra

A controlled experiment was conducted in order to preliminarily assess the effect of collection efficiency and possible swab deformation on PSI-MS spectra. Here, blank MQuant paper testing strips were used to swab a clean interior automobile door handle with no illicit drug residues present. Then, each utilized swab was spotted with a known mass of drug and subjected to PSI analysis. This experiment was conducted using both gentle and rough surface swabbing, and each scenario was examined with 250 ng of mephedrone as the deposited residue with five replicates. Spectral intensity stemming from PSI-MS was then used for comparison purposes in lieu of the total analytical efficiency metric, as there is no analyte deposition area in question.

Comparing with data collected via surface swabbing of mephedrone from the interior door handle (as seen in Table 1), a preliminary assessment of collection efficiency can be made from this surface type. Specifically, the PSI-MS spectral intensity resulting from gentle swabbing of a surface-bound mephedrone residue was 2706 ± 17%, whereas gentle swabbing followed by direct deposition of a similar mass of mephedrone to the used swab gave 3241 ± 19%. This yields a reduction in spectra intensity of ~ 20% stemming from surface collection event itself. However, spectral intensity for mephedrone analysis observed from a rough swabbing event (*i.e.* increased pressure applied, vigorous surface contact and movement) from the interior door handle was 1516 ± 18%, which represents a ~53% reduction compared to gentle swabbing.

The considerable decrease in spectral intensity observed from rough surface swabbing is anticipated to arise from swab deformation, particularly of the triangular egress of the paper substrate where an electrospray of charge droplets emanates during PSI analysis. For further investigation, the utilized swabs were examined via dissecting stereoscope and photographed to observe any potential deformation; here, a ZEISS Stemi 1000 dissecting stereoscope mounted with a Vernier Software and Technology ProScope SMP microscope camera was utilized. As seen in Figure S-1A, an unused paper substrate after manual cutting of the triangular egress is relatively unaltered. After gentle swabbing (Figure S-1B), only a minor raising of cellulose fiber at the tip is observed. However, rough swabbing (Figure S-1C) yields an extensive amount of fiber deformation, with an appreciable amount of fibers straying past the plastic backing of the strip. These stray fibers have the potential to effect the quality of Taylor cone produced during PSI analysis in several ways, such as introducing fringe electric fields and hindering the flow of spray solvent into the generated electrospray. The dramatic decrease in spectral intensity stemming from a rough swabbing event shows the importance of standard operating procedures and protocols if similar methodologies were to be employed in field-based enforcement scenarios. Further, this initial data highlights the importance of future work regarding the inter-user variability of PSI-MS.

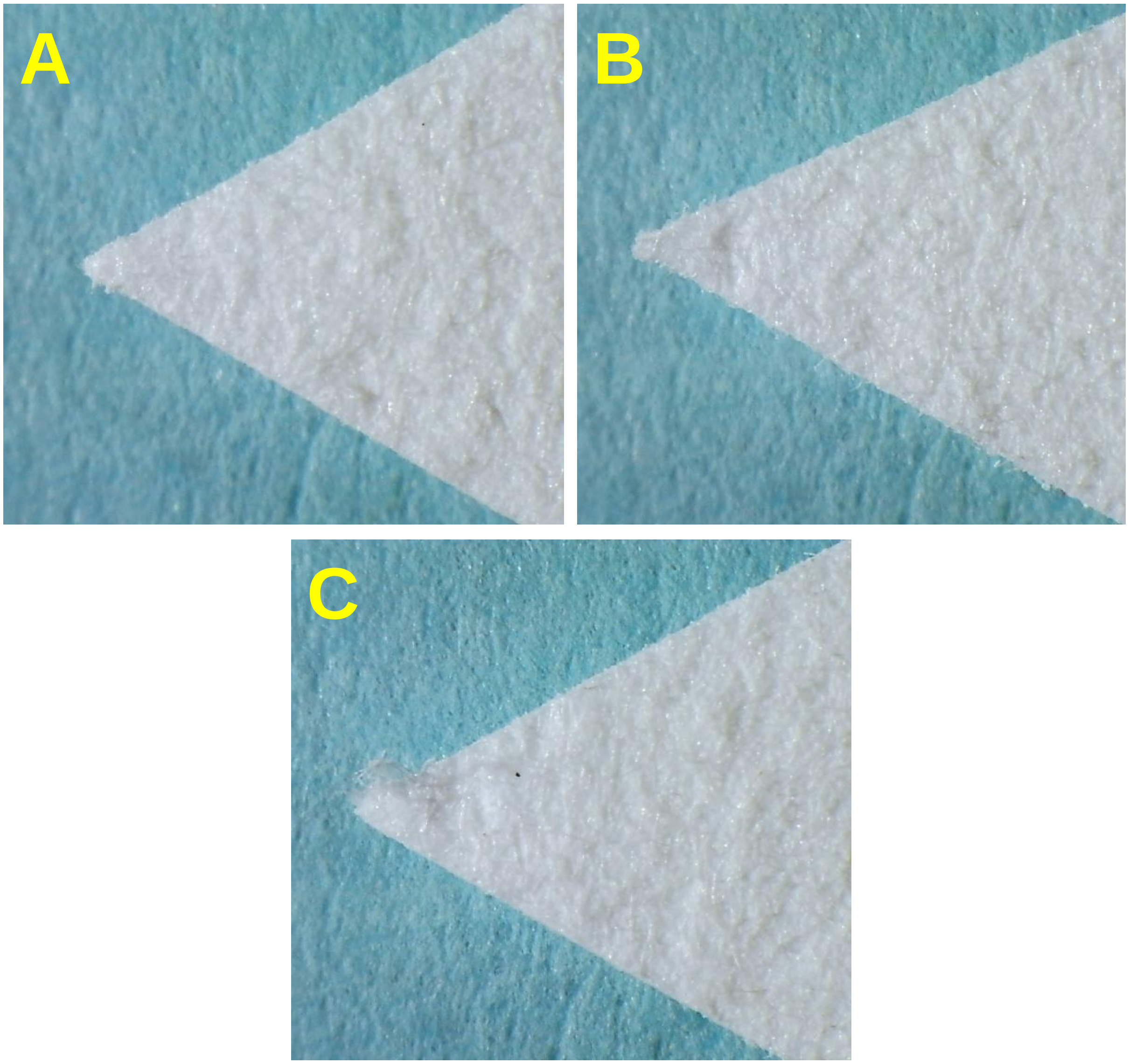

Figure S-1. Dissecting stereoscopic images stemming from the observation of triangularly-cut PSI paper substrates (A) prior to surface swabbing, (B) after gentle swabbing and (C) after rough swabbing of an interior automobile door handle. As seen, a harsh swabbing event can cause disturbance to the fibers at the swab egress, which can in turn affect the consistency and quality of the electrospray generated via PSI analysis.

Matrix Effects Stemming from Fouled Automotive Surfaces

In authentic enforcement scenarios, it is anticipated that surfaces of interest for swab-based screening will have highly variable levels of chemical complexity, which can in turn influence performance by reducing collection efficiency and introducing matrix effects into the ionization process. This could particularly effect the swab processing of external automotive glass, on which latent fingerprints, automotive cleaners, and dirt/debris would commonly reside.

A preliminary study involving fouled glass surfaces was undertaken to investigate the effect on total analytical efficiency (as defined in Eq. 1) stemming from surface swabbing events. Fouling of the glass slides utilized the following protocol: (1) deposition of a single, continuous layer of latent fingerprints, (2) a light tumble in loose soil, followed by (3) deposition of standard solution to produce a 250 ng surface-bound residue of cocaine. An example of the mock fouled glass surface produced for this study can be seen in Figure S-2A. A pre-wetted paper substrate was then used to probe the fouled surface and then subjected to PSI-MS investigation. Figure S-2B depicts the level of debris removal from the glass during the swabbing event.

Figure S-2. Photos of a glass slide coated with a layer of latent fingerprints and soil (A) prior to surface swabbing via PSI and (B) after swabbing for the purpose of screening illicit drug residues

When comparing the total analytical efficiencies collected for cocaine residues from fouled and clean glass (see Table 1) surfaces, a preliminary estimation of matrix effect can be made. For clean glass, a total analytical efficiency of 1936 ± 21% was observed, whereas fouled glass produced an efficiency of 776.4 ± 18%. The dramatic decrease of ~ 61% observed comes from a dual negative effect on the total analytical efficiency metric. That is, fouled glass yielded a reduced spectral intensity for cocaine, as anticipated from matrix effects stemming from soil transferred to the swab, but the hydrophobicity of the surface contaminants was also observed to lessen the amount of standard aliquot spreading. This, in turn, decreases the analyte deposition area factored into Eq. 1. Overall, this shows that the nature and state of the surface in question can have a substantial effect on the sensitivity of this field-based swabbing methodology.