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Rapid, Secure Drug Testing Using Fingerprint Development and Paper Spray Mass Spectrometry

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BACKGROUND: Paper spray mass spectrometry (PS-MS) is a technique that has recently emerged and has shown excellent analytical sensitivity to a number of drugs in blood. As an alternative to blood, fingerprints have been shown to provide a noninvasive and traceable sampling matrix. Our goal was to validate the use of fingerprint samples to detect cocaine use.

METHODS: Samples were collected on triangular pieces (168 mm^2) of washed Whatman Grade I chromatography paper. Following application of internal standard, spray solvent and a voltage were applied to the paper before mass spectrometry detection. A fingerprint visualization step was incorporated into the analysis procedure by addition of silver nitrate solution and exposing the sample to ultraviolet light.

RESULTS: Limits of detection for cocaine, benzoylecgonine, and methylecgonine were 1, 2, and 31 ng/mL respectively, with relative standard deviations $< 33\%$. No matrix effects were observed. Analysis of 239 fingerprint samples yielded a 99% true-positive rate and a 2.5% false-positive rate, based on the detection of cocaine, benzoylecgonine, or methylecgonine with use of a single fingerprint.

CONCLUSIONS: The method offers a qualitative and noninvasive screening test for cocaine use. The analysis method developed is rapid (4 min/sample) and requires no sample preparation.

Drug testing is carried out by an increasing number of entities, including courts, probation services, prisons, work places, and drug rehabilitation clinics *(1–3)*. To demonstrate use of an illicit substance, normally either a blood or urine sample is collected. Neither matrix is quick to collect, and the samples are biohazardous and must be stored and transported accordingly *(4)*. In contrast, a (latent) fingerprint is easy to collect and, most importantly, the ridge detail of the fingerprint assures traceability of the sample and chain of custody.

Recent publications have demonstrated the potential for detecting drugs and metabolites from fingertips. Approaches have included detection using spectroscopy *(5–8)*, antibodies *(9–12)*, and mass spectrometry *(13–18)*. Spectroscopic- and antibody-based detection of drugs in fingerprints offers limited analytical selectivity compared with mass spectrometry. Methadone *(15)* and lorazepam *(16)* can be detected in fingerprints by use of LC-MS. However, these methods require lengthy sample preparation, and therefore any commercialized test would be expensive to carry out due to the low throughput. These methods also do not offer the possibility for visualizing the fingerprint after collection, therefore missing a key advantage (i.e., traceability) of fingerprint-based drug detection.

Recently, desorption electrospray ionization *(14)* and MALDI *(19–21)* mass spectrometry techniques have been proposed for fingerprint chemical analysis. These techniques offer the advantages that the sample can be rapidly analyzed (approximately 2 min) and that the fingerprint ridge detail can be recorded before analysis to ensure traceability. However, limitations of these techniques include the cost of acquiring the ionization source and difficulty in obtaining quantitative data *(22)*.

Liquid extraction surface analysis *(13)* can also be used to detect cocaine and its metabolites in fingerprints. This technique has the drawbacks of a relatively expensive instrument cost and a slightly lower throughput than MALDI or desorption electrospray ionization.

Paper spray mass spectrometry (PS-MS)[6] is a technique that has recently emerged *(23, 24)* and is steadily gaining popularity, most likely due to the low setup cost (our home-built system cost approximately $50 to build) and the excellent analytical sensitivity. A commercial sys-

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[6] Nonstandard abbreviations: PS-MS, paper spray mass spectrometry; BZE, benzoylecgonine; EME, ecgonine methyl ester; ACN, acetonitrile; PS, paper spray; A/IS, analyte-to-internal standard ratio.

tem is now available, designed specifically for dried blood spot analysis *(25–27)*, and the technique has shown excellent analytical sensitivity for a number of drugs in blood *(25)*. The substrate used in commercial PS-MS systems is too small (typically dimensions of 8 mm^2 are used) to effectively sample a latent fingerprint. Here we report on an adaptation of the PS-MS technique, using triangles of 168 mm^2 area and applied as a rapid screening test for cocaine use by use of fingerprint samples. The method developed was applied to fingerprint samples collected from drug users as well as nondrug users to evaluate its efficacy. Finally, we tested the feasibility of using this method together with a development process to capture the ridge detail of the fingerprint before analysis.

Materials and Methods

MATERIALS

Drug standards [cocaine, benzoylegonine (BZE), ecgonine methyl ester (EME), cocaine-D_3, BZE-D_3, and EME-D_3] were prepared from certified reference materials (Cerilliant). LC-MS–grade solvents [methanol, acetonitrile (ACN), and water] were used to prepare all solutions and solvent mixtures (Fischer Scientific). Formic acid (Fischer Scientific) was added to every spray solvent at 0.1% v/v. Silver nitrate stock solution (0.1 mol/L) was bought from Sigma Aldrich and diluted with deionized water (18 mol/LΩ DI water) as required for the experiments. Artificial perspiration was purchased from Pickering Laboratories.

SAMPLE COLLECTION

Fingerprint and oral fluid samples were collected from 16 individuals seeking treatment at drug rehabilitation clinics. A favorable ethical opinion for collection and analysis of samples was received from the National Research Ethics Service (reference: 14/LO/0346). Oral fluid samples were collected using a Quantisal™ (Alere™) collection device. Analysis of the oral fluid samples was carried out at Claritest. Screening by Claritest used immunoassay testing followed by LC-MS/MS quantification if the screening result was positive. For fingerprint sample collection, the collection kit consisted of chromatography paper (Whatman Grade 1) cut into a "house-shape" that was comprised of a triangular area of dimensions 1.6 × 2.1 cm (base × height) and a rectangular extension that was used to tape the substrate to a glass slide (see Fig. 1 in the Data Supplement that accompanies the online version of this article at http://www.clinchem.org/content/vol63/issue11). The fingerprint sample was collected on the triangular area of the substrate, which was then removed for analysis. Fingerprint and oral fluid samples were collected from the 16 participants (10 fingerprints from each) using 3 different collection procedures. The first procedure—"wipes" (Participants 1–4)—comprised wiping the fingertips using alcohol-free wipes (Steroplast®) while wearing nitrile gloves for 10 min, touching the face (grooming), rubbing the fingertips together, and depositing the samples. For the second collection procedure—"soap" (Participants 5–7)—participants were asked to wash their hands with soap and follow the same procedure as above. Finally, the third collection procedure—"ungroomed wipe" (Participants 8–12)—was exactly the same as the wipe method, but participants did not touch the face before depositing the fingerprint sample (to avoid picking up analytes from the face and reduce the oil content in the sample). Samples were collected by use of kitchen scales (Sainsbury's Color) to measure the pressure applied during collection (800–1200 g for 10 s).

To observe the background concentrations of cocaine, BZE, and EME in the general population, fingerprint samples were collected from 40 participants not known to be drug users. Fingertips were wiped with alcohol-free wipes, and gloves were worn for 10 min to induce sweating. Samples were collected using the same collection kit described earlier (see Fig. 1 in the online Data Supplement) with 800–1200 g of pressure (measured with kitchen scales). Two samples—right index and right middle fingers—were collected from each participant (total of 80 samples). Therefore, a total of 240 fingerprint samples (80 from nondrug users; 120 and 40 from drug users with and without development, respectively) were collected. One sample failed to spray, giving a total of 239 samples successfully analyzed.

INVESTIGATION OF MATRIX EFFECTS

Artificial eccrine perspiration was used to optimize the paper spray (PS) source parameters because it was thought to represent the fingerprint matrix. To investigate the matrix effects of artificial perspiration vs fingerprints, standards of cocaine, BZE, and EME (50 ng/mL) were prepared in artificial perspiration or acetonitrile. To test the matrix effects of real fingerprints, 5 overlaid fingerprints (to provide an unrealistically high mass of matrix material) and 1 single fingerprint (to provide a more representative mass of matrix) from a single female participant were deposited on substrates before the addition of the analyte standard dissolved in acetonitrile.

PS ANALYSIS

The PS source was designed and built at the University of Surrey and was coupled with a Micromass QToF 2 mass spectrometer (Waters Alliance). Data processing of all spectra was performed by use of MassLynx 4.1 *(28)*. The cone voltage (25 V) and extraction voltage (5 V) were optimized by use of electrospray ionization by selecting the conditions that gave the highest yield of the protonated ions corresponding to the analytes—cocaine (*m/z* 304.15), BZE (*m/z* 290.14), and EME (*m/z* 200.13). The optimized collision energies for detection of frag-

ment ions corresponding to cocaine (*m/z* 304 > 182), BZE (*m/z* 290 > 168), and EME (*m/z* 200 > 182) were set at 21, 19, and 21 eV, respectively.

The PS analysis method was optimized as detailed below. The paper substrate consisted of Whatman Grade 1 chromatographic paper cut into a triangular shape (1.6 cm base, 2.1 cm height). Precut paper was submitted to a wash procedure consisting of 0.1% hydrochloric acid and 50:50 (% v/v) methanol:water and allowed to air dry before analysis.

The optimized PS-MS method, adopted in all following experiments (see Fig. 2 in the online Data Supplement), included the following steps. First, the sample (either a fingerprint or standard) was loaded onto the paper followed by deposition of the internal standard (20 μL of 50 ng/mL cocaine-D_3, BZE-D_3, and EME-D_3). The loaded paper was then allowed to air dry (5 min), before being placed in the source on top of a glass slide and below a folded piece of aluminum foil designed to minimize carryover effects (preventing direct contact between the high voltage clip and the sample). The tip of the paper was positioned perpendicular to the mass spectrometer inlet cone at a distance of 2 × 3 mm ($x \times y$) (see Fig. 3 in the online Data Supplement). A spray solvent [80:20 (%v/v) ACN:water] was then pipetted (100 μL) onto the paper and voltage applied (4.0 kV). Data was acquired for 2 min in full scan mode (*m/z* 50–500) for quantitative measurements, after which the voltage was turned off. Finally, another 100 μL of spray solvent was added to the paper and the voltage restarted for another 2 min for peak qualification using MS/MS.

SILVER NITRATE DEVELOPMENT

To demonstrate the efficacy of retaining fingerprint ridge detail while also providing chemical analysis, silver nitrate was used to develop fingerprints on chromatography paper. This was then applied to a selection of fingerprint samples collected from individuals at the drug rehabilitation center. Before sample collection, silver nitrate was pipetted onto the paper on the fingerprint collection kits: 40 μL of 25 mmol/L silver nitrate was pipetted onto 10 kits and 60 μL of 15 mmol/L silver nitrate were pipetted onto another 10 kits. Samples were allowed to dry before being placed in a storage box for transport to the clinic. Fingerprint samples were collected from 4 participants (Participants 13–16), in which fingerprints from one hand were collected on a substrate treated with silver nitrate and fingerprints from the other hand were collected on the untreated paper substrate (control samples). Fingerprint samples were collected with a pressure of 100–200 g. Samples were transported to the laboratory where they were exposed to ultraviolet light (254 nm) for 5 min.

Results and Discussion

INVESTIGATION OF MATRIX EFFECTS

Fig. 4 in the online Data Supplement shows the mean (n = 3) measured peak intensities for cocaine, BZE, and EME in the presence of artificial perspiration, acetonitrile only, and 5 or 1 fingerprint samples. The signal intensities for artificial perspiration were approximately 2-fold lower than with acetonitrile, implying ionization suppression. In contrast, with the exception of EME, which showed a small difference between acetonitrile and 5 or 1 fingerprints, no substantial difference in signal intensity was observed in the presence of either 5 or 1 fingerprints compared to acetonitrile only for cocaine or BZE. Therefore, no analytically important matrix effects of the fingerprints were observed. Furthermore, the results demonstrated that artificial perspiration was not a good representation of the fingerprint matrix.

METHOD PERFORMANCE

The PS method (Fig. 2 in the online Data Supplement) was applied to calibrators containing cocaine, BZE, and EME (20 μL, prepared in 100% ACN) in the 0–500 ng/mL range. Fig. 1 shows the calibration curves for, cocaine (Fig. 1A), BZE (Fig. 1B), and EME (Fig. 1C) plotted as the analyte-to-internal standard ratio (A/IS). The peak assignments in full scan mode were confirmed by the MS/MS measurements.

The method yielded relative standard deviations between 3%–33%, depending on the analyte and concentration (Table 1 in the online Data Supplement). The resulting correlation factors (R^2) were poorer than previously reported for PS-MS, which could be explained by the fact that for previous work on dried blood spot analysis the internal standard was mixed into the sample before being spotted on to the paper. In contrast, for fingerprint analysis, the fingerprint must first be applied to the paper before addition of the internal standard. For the calibration curves shown here, the calibrator was added separately from the internal standard to mimic real samples. This inevitably led to an unequal spatial distribution of fingerprint and internal standard on the paper and therefore increased variability.

The limits of detection (blank +3SD) and quantification (blank + 10SD) were calculated (Table 1 in the online Data Supplement). The calculated limits of detection (1, 2, and 31 ng/mL for cocaine, BZE, and EME, respectively) were inferior to the PS method for the detection of cocaine in dried blood spots *(25)* of 0.05 ng/mL. The difference in detection limits can be attributed partly to the difference in mass spectrometers used (quadruple-time-of-flight mass spectrometers generally exhibit inferior analytical sensitivity to a triple quadrupole in the multiple reaction monitoring mode) and also to the separate addition of analytes and internal standard,

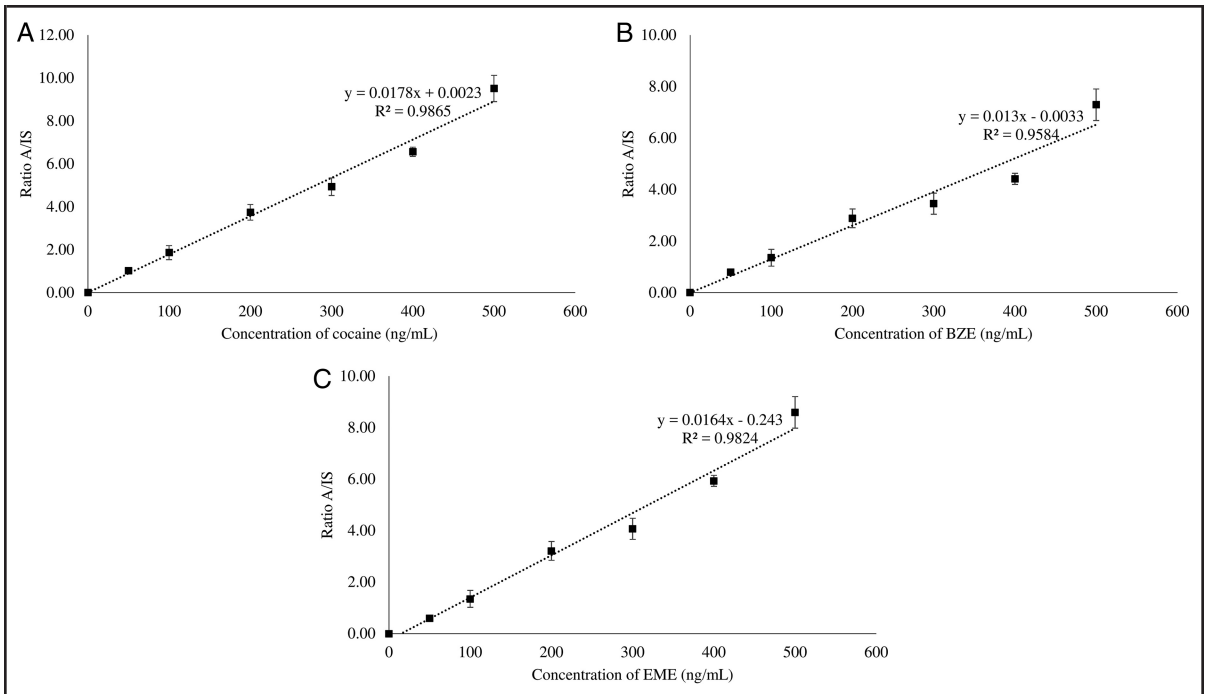

Fig. 1. Calibration curves for cocaine (A), BZE (B), and EME (C).

as mentioned above. Example cutoffs currently used for oral fluid testing (on the basis of BZE and cocaine) are approximately 8 ng/mL. Of course, a cutoff for fingerprint testing has not yet been established, but assuming an equal relationship between fingerprint and oral fluid concentration of drugs and metabolites, the method proposed here would be within industry cutoffs and likely better than previous publications on drugs in fingerprints.

ANALYSIS OF FINGERPRINT SAMPLES

The developed PS method was applied to fingerprint samples collected from individuals who reported taking cocaine in the last 24 h. Detection of EME, BZE, and cocaine was confirmed if the relevant fragment ion was detected above 3 counts above the background in the MS/MS scans, consistent with previous mass spectral interpretation *(29)*. Example MS/MS spectra are shown in Fig. 5 in the online Data Supplement.

Table 1 shows the detection rate for each analyte (10 fingerprints from 12 participants). The corresponding oral fluid confirmation results are also provided. Of the 120 fingerprints, 1 fingerprint (Participant 7) could not be analyzed due to a failed spray, resulting from the difficulty in consistently cutting a paper triangle with a sharp tip. Table 2 shows the detection rate for 4 further participants. The presence of at least one of the analytes—cocaine, BZE, or EME—was confirmed in 157 samples (98.7%) of the 159 fingerprint samples successfully analyzed.

There was a clear discrepancy for Participant 7 between oral fluid and fingerprint test results (Table 1). While the oral fluid tested negative for cocaine, the patient testified taking cocaine within the last 24 h, in agreement with the fingerprint results (9/9 positive). While the patient's testimony has not been verified, this observation implies a difference in detection window between fingerprints and oral fluid, which should be explored in further studies. Indeed, the United Nations Office on Drug and Crime has reported that the detection window for sweat is longer than for oral fluid, consistent with these observations *(30)*.

Fig. 2 shows the A/IS ratio of cocaine and BZE detected per fingerprint across the 10 fingerprint samples for Participants 2 and 3. A number of interesting observations resulted from these data. First, the variability in cocaine and BZE seen within a set of fingerprints was high, and this was expected because the contact area and positioning of fingers on the paper was not controlled. Other studies *(15)* have shown similar levels of variability for other substances even when fingerprint deposition was carefully controlled.

Second, different concentrations of cocaine were observed in the corresponding oral fluid samples for Participants 2 and 3 (>64 ng/mL and 8.2 ng/mL, respectively). In Fig. 2, the A/IS ratio for cocaine was

Table 1. Oral fluid results and fingerprint detection rate (number of fingerprints positive) for cocaine, BZE, and EME obtained for participants 1 to 12, analyzed by use of paper spray mass spectrometry.

	Oral fluid results		Cocaine, BZE, and EME (at least one of the three) detected in how many fingerprints?
	Cocaine, ng/mL	BZE, ng/mL	
Wipes			
Participant 1	>64.0	>64.0	10/10
Participant 2	>64.0	>64.0	10/10
Participant 3	8.2	>64.0	10/10
Participant 4	>64.0	>64.0	10/10
Soap			
Participant 5	>64.0	>64.0	9/10
Participant 6	12	30.0	10/10
Participant 7	Negative	Negative	9/9
Ungroomed wipes			
Participant 8	>64.0	>64.0	10/10
Participant 9	>64.0	>64.0	10/10
Participant 10	>64.0	>64.0	10/10
Participant 11	>64.0	>64.0	10/10
Participant 12	>64.0	>64.0	10/10

systematically higher in all 10 of Participant 2's fingerprint samples, in agreement with the oral fluid results. In contrast, the A/IS ratio for BZE did not systematically show the much higher concentrations in Participant 2 than in Participant 3, highlighting the potential difficulty in correlating oral fluid and fingerprint measurements in a quantitative manner.

Fig. 3 displays the mean ratios of A/IS ratio for cocaine measured from the thumb and index fingers (n = 4) samples collected from Participants 1–12 by use of the different collection procedures described previously. For the patients collected using the wipes method, a lower signal for cocaine was seen in the fingerprints from Participant 3 (with corresponding oral fluid of 8 ng/mL) than in those from Participants 1 and 2 (with oral fluid >64 ng/mL), showing the possibility for distinguishing between high and low cocaine concentrations. Comparing Participant 5 with Participants 1, 2, 4, and 8–12 (all with oral fluid > 64 ng/mL), showed that washing the hands with soap before deposition resulted in a lower signal for cocaine, possibly due to the removal of residue left on the hands after cocaine use, which the wiping method failed to completely remove. The results presented here show that cocaine and metabolites are readily detected in fingerprints after either washing hands with soap (soap method), wiping the fingertips (ungroomed wipes), or touching the face (wipes) to collect oily residues. Any quantitative difference arising from the fingerprint collection procedure could not be evaluated because no validated procedure exists for collecting replicate fingerprints.

To observe the background levels of cocaine, BZE, and EME in the general population, fingerprint samples were collected from 40 participants not known to be drug

Table 2. Oral fluid confirmatory results and fingerprint detection rate obtained for participants 13–16, analyzed with paper spray.

	Oral fluid results		Cocaine, BZE, and EME (at least one of the three) detected in how many fingerprints?
	Cocaine, ng/mL	BZE, ng/mL	
Participant 13	>64.0	>64.0	10/10
Participant 14	>64.0	>64.0	9/10
Participant 15	40.3	>64.0	10/10
Participant 16	Negative (5.77)	>64.0	10/10

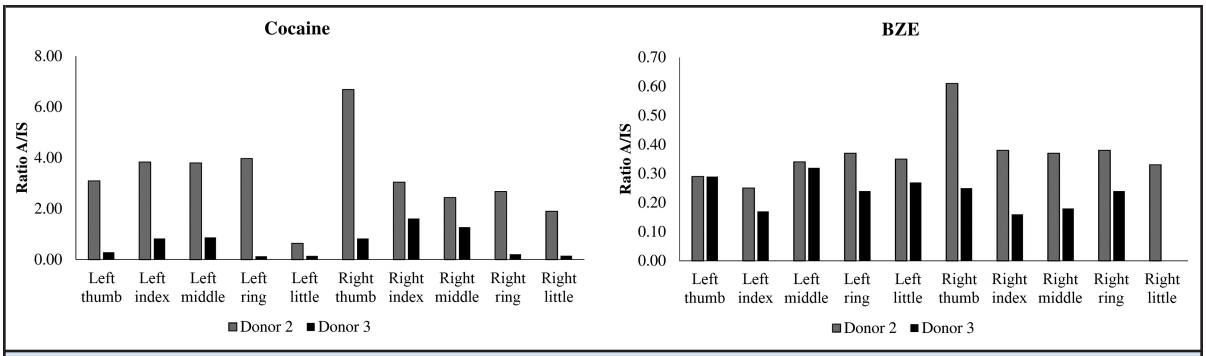

Fig. 2. Analyte-to-internal standard ratio (A/IS) measured for cocaine and BZE in fingerprint samples collected from individuals seeking treatment at a drug rehabilitation center (Participants 2 and 3).

users. Fragment ions relating to cocaine and EME were detected in MS/MS mode in 2 fingerprints (one each from 2 different participants) of the 80 samples analyzed. The origin of these 2 substances could not be confirmed as only one of the 2 samples collected from the 2 participants tested positive, and no oral fluid sample was collected from the participants. However, this could be the result of environmental exposure that could not be removed by the cleaning procedure. BZE was not detected in any of the samples.

A drug screening protocol that returns a positive result based on the detection of cocaine, BZE, or EME in a single fingerprint was applied to the data. Using this acceptance criterion, 98.7% of the patient fingerprint samples analyzed (n = 159) tested positive. Similarly, 2.5% of the background population samples (n = 80) gave a false-positive result (the 2 samples mentioned in the previous paragraph). By instead requesting 2 fingerprints—e.g., right thumb and index—and requiring both samples to be positive, a 94% true-positive and 0% false-positive rate would be obtained (on the basis of the right index and middle fingers only, using the data from 16 patients and 40 nondrug users). Therefore, despite the variability observed in the concentration of analytes present in the fingerprints, there is a clear discrimination between positive and negative participants.

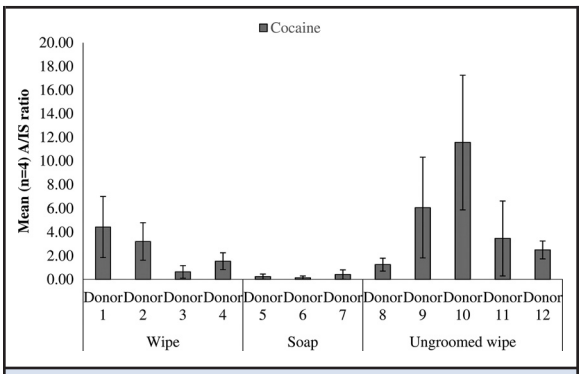

Fig. 3. Mean analyte-to-internal standard ratio (A/IS) for cocaine measured from the thumb and index fingers (n = 4) collected from Participants 1–12 and analyzed using paper spray mass spectrometry.

SILVER NITRATE DEVELOPMENT

One of the key advantages of using a latent fingerprint for drug detection is the ability to provide a traceable sample. Two different concentrations of silver nitrate (15 mmol/L and 25 mmol/L) were tested for their ability to detect fingerprints on the PS paper. An ultraviolet (254 nm) light source was used to develop fingerprints. Fig. 4 shows how application of silver nitrate to the paper enabled the visualization of fingerprint ridge detail. The higher concentration of silver nitrate resulted in the clearest ridge patterns (Fig. 4, A and B). The lower concentration of silver nitrate only allowed the visualization of fingerprints collected from Participant 16 (Fig. 4D). No ridge detail was visible for Participant 15 (Fig. 4C). In this case, the level of fingerprint ridge detail was not sufficient to be used for identification purposes, but it could be used to verify the presence of the sample on the collection kit.

Fig. 6 in the online Data Supplement shows the peak intensity of cocaine, BZE, and EME detected in standards of concentration 50 ng/mL (internal standards at 50 ng/mL) analyzed with PS-MS. The peak intensity for all 3 analytes was lower when silver nitrate was present, suggesting that the addition of silver nitrate to the PS work flow affects the analytical sensitivity of the method. Nonetheless, cocaine, BZE, and EME could be identified in fingerprints from patients through MS/MS scans (Table 2). Out of the 20 samples developed with silver nitrate, 20 tested positive for cocaine, demonstrating the viability of the procedure.

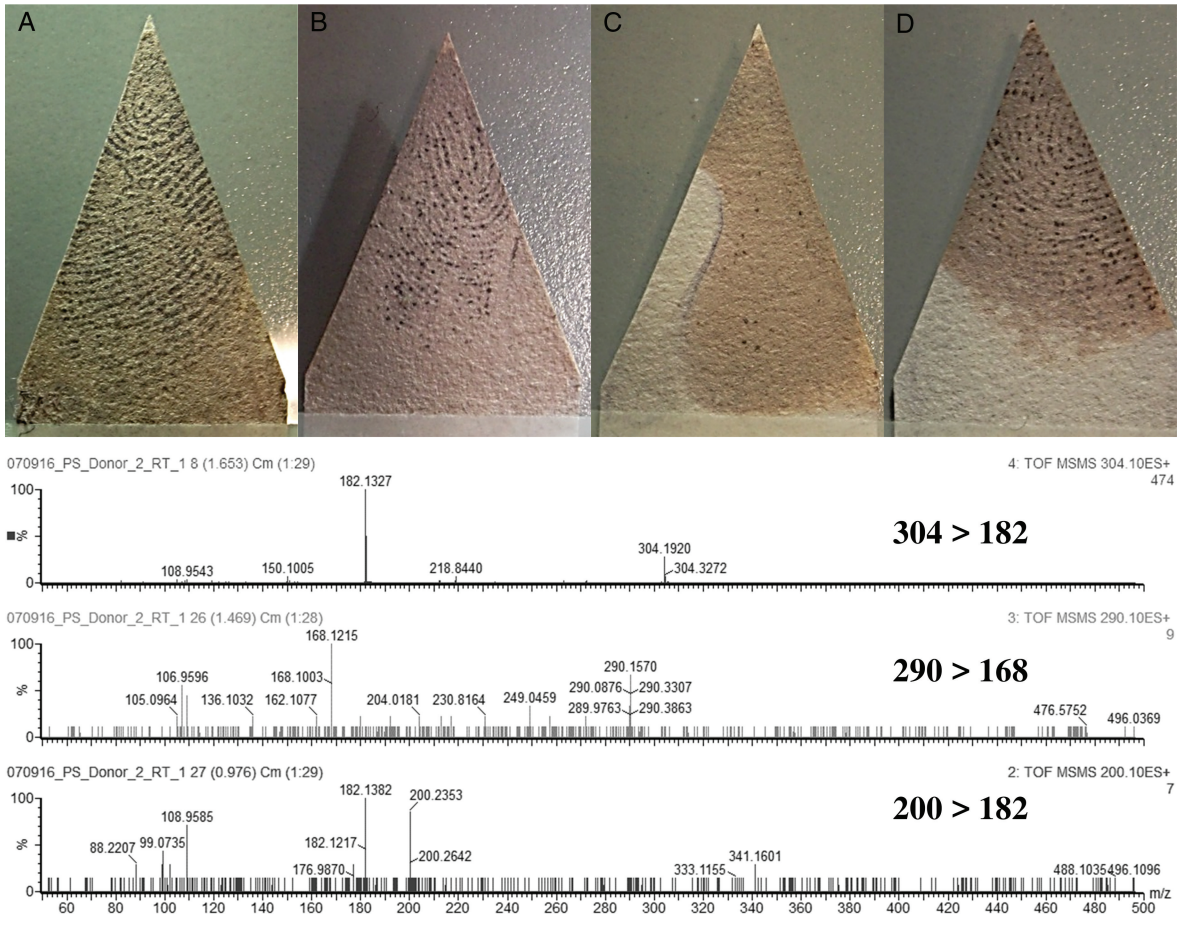

Fig. 4. Example of silver-nitrate-developed fingerprints collected from individuals seeking treatment at a drug rehabilitation clinic by use of 40 μL of 25 mmol/L (A, B) and 60 μL of 15 mmol/L, developed under ultraviolet light (254 nm) for 5 min.

Example MS/MS spectrum obtained from the analysis of a silver-nitrate-developed fingerprint sample (Participant 14, right thumb).

In summary, we have demonstrated the adaptation of PS-MS for the detection of cocaine, BZE, and EME in fingerprint samples. The method was applied to a total of 239 fingerprint samples, yielding a 98.7% detection rate and a 2.5% false-positive rate based on a single fingerprint. There was some capacity to discriminate quantitatively between the fingerprints of participants in the method presented here. We also showed the compatibility of the method with fingerprint development before analysis using silver nitrate, to allow a sample to be identified from its ridge characteristics.

Author Contributions: *All authors confirmed they have contributed to the intellectual content of this paper and have met the following 3 requirements: (a) significant contributions to the conception and design, acquisition of data, or analysis and interpretation of data; (b) drafting or revising the article for intellectual content; and (c) final approval of the published article.*

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