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Chemical analysis of pharmaceuticals and explosives in fingermarks using matrix-assisted laser desorption ionization/time-of-flight mass spectrometry

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ABSTRACT

Chemical analysis of latent fingermarks, "touch chemistry," has the potential of providing intelligence or forensically relevant information. Matrix-assisted laser desorption ionization/time-of-flight mass spectrometry (MALDI/TOF MS) was used as an analytical platform for obtaining mass spectra and chemical images of target drugs and explosives in fingermark residues following conventional fingerprint development methods and MALDI matrix processing. There were two main purposes of this research: (1) develop effective laboratory methods for detecting drugs and explosives in fingermark residues and (2) determine the feasibility of detecting drugs and explosives after casual contact with pills, powders, and residues. Further, synthetic latent print reference pads were evaluated as mimics of natural fingermark residue to determine if the pads could be used for method development and quality control.

The results suggest that artificial amino acid and sebaceous oil residue pads are not suitable to adequately simulate natural fingermark chemistry for MALDI/TOF MS analysis. However, the pads were useful for designing experiments and setting instrumental parameters. Based on the natural fingermark residue experiments, handling whole or broken pills did not transfer sufficient quantities of drugs to allow for definitive detection. Transferring drugs or explosives in the form of powders and residues was successful for preparing analytes for detection after contact with fingers and deposition of fingermark residue. One downfall to handling powders was that the analyte particles were easily spread beyond the original fingermark during development. Analyte particles were confined in the original fingermark when using transfer residues.

The MALDI/TOF MS was able to detect procaine, pseudoephedrine, TNT, and RDX from contact residue under laboratory conditions with the integration of conventional fingerprint development methods and MALDI matrix. MALDI/TOF MS is a nondestructive technique which provides chemical information in both the mass spectra and chemical images.

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1. Introduction

"Touch chemistry" is a forensic technique that could provide investigative leads by analyzing chemical data from fingermark residue. Chemical intelligence gained from the analysis of latent fingermarks has the potential to provide information about the suspect even if the fingermarks are smudged or the patterns cannot be matched through an automated fingerprint search. In order to collect latent fingermarks at a crime scene, the prints must first be made visible using development techniques such as fingerprint powder or cyanoacrylate fuming [1]. Once fingermarks are located, chemical information to be gained about the individual could include exposure to illicit substances/explosives, drug-use history, gender, and approximate age [2–8].

Past approaches for fingermark residue characterization include Fourier transform-infrared spectroscopy (FTIR) [9], gas chromatography mass spectrometry (GC/MS) [10], fluorescence microscopy [11], desorption electrospray ionization mass spectrometry (DESI/MS) [12], and secondary ion mass spectrometry (SIMS) [13,14]. An alternative approach that has recently

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demonstrated high potential for characterizing a broad array of endogenous chemicals and exogenous components is matrix-assisted laser desorption/time-of-flight mass spectrometry (MALDI/TOF MS) [2–4,14–17]. The combination of spectral and imaging information may help determine whether a detected chemical in a fingermark was from contact or excretion. The chemical imaging from MALDI/TOF MS allows for a more definitive answer than spectra alone because the analyte ion patterns should be uniformly visible in the print if deposition is through excretion. If the residue is simply left from the contact points after touching drugs or explosives, the chemical image will be unevenly dispersed on the print, reflecting the limited regions of contact [3]. Studies of limited sample sizes have demonstrated the ability to use "touch chemistry" to indicate if an individual smokes [4,11,17], has been exposed to or ingested illegal drugs of abuse [3,12], or has contacted explosives [2,18]. Many of these studies were simulations, and further efforts are needed to demonstrate applications in authentic samples and larger sample populations.

In order to integrate touch chemistry with conventional fingerprint development methods, the requirements of the analytical technique must be considered. For example, MALDI requires an appropriate matrix for efficient ionization. Incorporating conventional fingerprint powders as the MALDI matrix has been shown to be effective in previous studies [4]. Alternative approaches from the literature include alpha-cyano-4-hydroxycinnamic acid (CHCA), a MALDI-specific matrix, as the fingerprint powder developer [15,16] or functionalized nanoparticle fingerprint powders specific for MALDI/TOF MS [2–4]. Investigating additional fingerprint developers that are compatible with MALDI is necessary for incorporating chemical analysis with current latent print identification processes.

MALDI/TOF MS was used for this study to detect compounds in fingermark residue. A select group of drugs and explosives with different chemical properties was handled and analyzed. There were two main purposes of this research: (1) develop effective laboratory methods for detecting drugs and explosives in fingermark residues and (2) determine the feasibility of detecting drugs and explosives after casual contact with tablets, powders, and residues. As part of the laboratory study, we investigated synthetic latent print reference pads as mimics of natural fingermark residue to determine if the pads could be used for method development and quality control.

2. Materials and methods

2.1. Chemicals and materials

Advil® (200 mg ibuprofen tablets, Wyeth Consumer Healthcare, Madison, NJ), Tylenol® Extra Strength (500 mg acetaminophen tablets, McNeil Healthcare LLC, Las Piedras, Puerto Rico), Bayer® (81 mg aspirin tablets, Bayer Healthcare LLC, Morristown, NJ), and non-drowsy Sudafed® 24 h (240 mg pseudoephedrine hydrochloride tablets, McNeil Consumer Healthcare, Fort Washington, PA) were purchased from CVS® Pharmacy. The weight percent based on label information (weight of drug/total weight of tablet × 100) for each pill was 76% acetaminophen in Tylenol®, 64% pseudoephedrine hydrochloride in Sudafed®, 79% aspirin in Bayer®, and 42% ibuprofen in Advil®. Pseudoephedrine (1 mg/mL in methanol standard) was purchased from Cerilliant (Round Rock, TX). Angiotensin II human (>93% powder), α-cyano-4-hydroxycinnamic acid (CHCA) (≥99% HPLC), procaine hydrochloride, and reserpine were purchased from Sigma–Aldrich (St. Louis, MO). TNT and RDX (1 mg/mL in 1:1 methanol:acetonitrile) were purchased from AccuStandard (New Haven, CT). TNT powder was obtained from our reference collection. Water (Optima grade), acetonitrile (Optima grade), acetic acid (certified ACS Plus), and precleaned glass microscope slides were purchased from Fisher Scientific (Fair Lawn, NJ). Glass microscope slides (1 in. × 3 in.) coated with approximately 100 nm aluminum were purchased from Deposition Research Lab, Inc (St. Charles, MO). Latent print reference pads for amino acid and sebaceous oil were purchased from Forensics Source (Jacksonville, FL). XYZ-Axis electrically conductive 3M™ double-sided tape (25 mm (*W*) × 32.9 m (*L*)) was purchased from Electron Microscopy Sciences (Hatfield, PA). Ethyl cyanoacrylate adhesive INSTAbond® S-100 was purchased from ACCRAbond, Inc (Olive Branch, MS). Conventional black latent fingerprint powder and white marabou feather brush were purchased from Arrowhead Scientific Inc. (Lenexa, KS).

2.2. Handling powders with artificial amino acid and sebaceous pad residue

2.2.1. Artificial fingermark residue

All of the handling and residue experiments involving human subjects were approved and conducted in accordance to our Institutional Review Board. Artificial pads were used to create samples for initial development of MALDI/TOF MS methods. The pads were used to simulate fingermark residue in a controlled manner. Hands were washed with soap and water followed by an alcohol wipe prior to touching the artificial residue pads. For negative controls, artificial fingermark residues were directly deposited on aluminum-coated slides after rubbing the fingertips on the individual pads. With artificial residue still present on the fingertips, drug powders (aspirin, ibuprofen, and acetaminophen ground tablets) were handled before a second print was deposited next to the control print on the aluminum slide. Fingermarks were aged for approximately 30 min and developed using four separate processes: (1) dusted directly with black fingerprint development powder, (2) cyanoacrylate fumed followed by dusting with black fingerprint development powder, (3) dusted with black fingerprint development powder and lifted using tape, and (4) sprayed with MALDI matrix to apply a thin layer of CHCA. An improvised cyanoacrylate chamber was used for these initial experiments.

2.3. Handling tablets, powders, and transfer residues with natural fingermark residue

2.3.1. Analyte powder residue

Hands were first washed with soap and water followed by an alcohol wipe to clean off external contaminants. "Groomed" control fingermarks were created by rubbing the fingers across the nose or neck to coat them with sebaceous gland secretions. Likewise, groomed fingertips were prepared for handling whole and broken aspirin, ibuprofen, and acetaminophen tablets. The whole tablets were placed between two fingers and held briefly to mimic the process of ingesting tablets. Tablets were then broken in half and the exposed drug/excipient side was dabbed once on the finger to imitate handling broken pills. Groomed fingertips were also used to touch ibuprofen, aspirin, acetaminophen, and pseudoephedrine hydrochloride powders from ground tablets. Likewise, ground analytical standards of procaine hydrochloride and TNT were touched with groomed fingertips to generate samples. Deposited fingermark residues were aged for approximately 30 min and developed with black fingerprint development powder, cyanoacrylate fuming followed by black fingerprint development powder, black fingerprint development powder and hinge lifting tape, and matrix sprayer with CHCA.

2.3.2. Analyte transfer residue

An alternative to handling analyte powder was to establish a protocol for transferring residue to generate fingermark samples. First, calibration spots were generated with images to estimate the