J Forensic Sci, March 2007, Vol. 52, No. 2
doi:10.1111/j.1556-4029.2007.00384.x
Available online at: www.blackwell-synergy.com

TECHNICAL NOTE

Amy Richmond-Aylor,[1] *B.S.; Suzanne Bell,*[1] *Ph.D.; Patrick Callery,*[1] *Ph.D.; and Keith Morris,*[1] *Ph.D.*

Thermal Degradation Analysis of Amino Acids in Fingerprint Residue by Pyrolysis GC–MS to Develop New Latent Fingerprint Developing Reagents*

ABSTRACT: Conventional development of latent fingerprints is compromised when the prints are decomposed by extreme temperatures, such as those encountered when a weapon cartridge is fired, an improvised explosive device is detonated, and/or in arson cases. Understanding how these extreme temperatures alter the chemical and physical properties of latent fingerprint residue could aid in the discovery of a reagent that could effectively develop these decomposed fingerprints. To mimic scenarios where fingerprints may be exposed to high heat conditions, standards of the five most abundant amino acids in fingerprint residue as well as extracted fingerprint residue were pyrolized under controlled conditions. Compounds identified as pyrolytic decomposition products were 3,6-dimethylpiperazine-2,5-dione (from alanine), maleimide, and 2,5-furandione (from aspartic acid). The pyrograms and selected ion traces show these products to hold promise as indicators of decomposed fingerprint residues and, therefore, may serve as good candidate substrates for a developing reagent.

KEYWORDS: forensic science, criminalistics, pyrolysis, gas chromatography/mass spectrometry, amino acids, fingerprint residue, latent fingerprints

Fingerprints can be seen, developed, and lifted from many different surfaces such as paper, drywall, glass, metal, cartridge cases, and firearms. However, if these surfaces are exposed to extreme temperatures, the latent print may no longer be visible. Previous work shows treatment of metal cartridge cases with acidified hydrogen peroxide as an effective method to visualize latent prints, but only when these prints were placed on the cartridge postfiring (1). There is evidence that thermal decomposition, such as may occur during combustion or the firing of a weapon, affects the results of fingerprint development techniques (both quality and intensity) on thermally decomposed latent prints. A study performed by the United States Secret Service illustrated that not only was the developing reagent reaction chemistry affected by the extreme heats but also the chemical and physical properties of the substrate (latent print residue) (2). Fortunately, a study performed by the United Kingdom's Home Office Scientific Development Branch concludes that, under certain circumstances, fingerprint residues can also survive conditions experienced in fire scenes (3). However, high-heat conditions are not the only source of print decomposition. For example, ridge detail is lost on spent cartridge cases. Previous work suggests that high-temperature effects do not significantly contribute to this loss, indicating that blowback during firing and/or damage occurring while loading the round is a contributor (4). Vacuum cyanoacrylate (with BY40 staining) and selenious acid are shown to be sensitive current methods for developing prints on weapons cartridges (4). An understanding of thermal degradation of fingerprint residues could lead to the development of new reagents targeting thermally degraded residues.

The goals of this work were to pyrolyze fingerprint residue, identify the pyrolytic products, and their sources, determine whether the sources and resulting pyrolytic products were suitable indicators of fingerprint residue, and evaluate the potential of these sources to be used as the basis for developing a decomposed fingerprint developing reagent.

This study was performed in three phases. First, a list of fingerprint residue components was compiled. The main components of fingerprint residue (mostly eccrine sweat and sebaceous fluid, which is present only as a product of contamination) are amino acids (such as serine, alanine, and lysine), cations (barium, sodium, and calcium), anions (such as phosphate and sulfate), biochemicals (such as pyruvate and uric acid), vitamins, and proteins (7). The scope of this work was limited to the analysis of amino acid components of fingerprint residue that are likely to be present at analytically suitable concentrations and are known substrates for fingerprint developing reagents such as ninhydrin and diazafluoren-9-one (DFO). While pyrolysis studies of amino acids have been performed before (5,6), none included the amino acids studied here.

Based on previously published data, the six most prevalent amino acids in fingerprint residue are serine, glycine, ornithine, lysine, alanine, and aspartic acid (6). Once the scope and target analytes of the study were identified, the next phase involved the collection of fingerprint residue for analysis via the extraction of

[1]C. Eugene Bennett Department of Chemistry, West Virginia University, 217 Clark Hall, Morgantown, WV 26506-6045.

*This work has been previously presented at the American Academy of Forensic Sciences 58th Annual Meeting, Seattle, WA, February 25, 2006.

Received 7 May 2006; and in revised form 30 Sept. 2006; accepted 8 Oct. 2006; published 6 Feb. 2007.

Copyright © 2007 by American Academy of Forensic Sciences

TABLE 1—*Pyrolysis conditions.*

Ramp Rate	Temperature (°C)	Hold Time
Pyroprobe accessory temperature program		
30°C/min	50	1.00 min
	310	1.00 min
Pyroprobe temperature program		
10°C/sec	50	1.00 sec
	500	10.00 sec
Valve oven temperature: 350°C		
Transfer line temperature: 350°C		

cotton gloves in a Soxhlet extractor (Soxhlet, Vineland, NJ). The final phase of the study concentrated on pyrolyzing the five amino acids and the extracted fingerprint residue and analyzing the pyrolytic products with gas chromatography and mass spectrometry (GC–MS). Three characteristic compounds of the pyrolyzed amino acids in fingerprint residue were identified based on the results of this work.

Materials and Methods

Fingerprint residue was extracted from 100% cotton gloves (VWR International, Westchester, PA) via extraction with HPLC-grade methylene chloride (purchased from Fisher Chemical Company, Fair Lawn, NJ). Ten cotton gloves were worn by five individuals. No sample preparation was performed on the gloves before extraction. All 10 gloves were placed in a Soxhlet extraction apparatus and extracted continuously with 500 mL of methylene chloride for 5 days. The recovered solution was dried, filtered, and the solvent was removed using a Buchi Rotovapor (Flawil, Switzerland) (model R-114) and Waterbath (Flawil, Switzerland) (model B-480). The flask containing the remaining fingerprint residue was dried under vacuum overnight to remove any residual solvent. A blank sample of 10 cotton gloves was also run using the same method as a negative control.

The fingerprint residue was then analyzed via pyrolysis GC–MS. The pyrolysis was performed using a CDS Analytical Pyroprobe (Oxford, PA) 5150 under the conditions listed in Table 1. Pyrolysis temperatures were selected based on estimated surface fire and gun chamber temperatures of 500°C and 400–500°C, respectively. The separation by GC–MS was carried out on a Perkin-Elmer Elite 5MS column (Wellesley, MA) (30 m × 0.25 mm inner diameter × 0.25 μm film thickness) using a Perkin-Elmer-Clarus 500 GC/MS instrument under the conditions listed in Table 2.

Standard grade L-amino acids (purchased from Sigma Aldrich, St. Louis, MO) were analyzed via pyrolysis GC–MS under the same conditions listed above. The five amino acids studied were serine, lysine, alanine, glycine, and aspartic acid.

Results

The blank analysis did not yield any signal from target analytes. The fingerprint residue extracted from the cotton gloves had an oily gray appearance and a greasy texture. Figure 1 shows the pyrogram of the extracted fingerprint residue that exhibited an elevated baseline profile consistent with a lipophilic hydrocarbon material. Lipid compounds identified included isopropyl palmitate, eicosanol, and benzoic acid in the residue. These organic components could originate from the fingers and/or from environmental factors such as moisturizers or food. This variability provides additional support directed toward the amino acid components of the latent print residue.

TABLE 2—*Gas chromatography and mass spectrometry (GC–MS) conditions.*

Ramp Rate	Temperature (°C)	Hold Time (min)
GC temperature program		
10°C/min	50	1.00
	320	5.00
Carrier gas: helium at 1 mL/min.		
MS: EI mode, no solvent delay, mass range scanned from 50 to 600 m/z.		

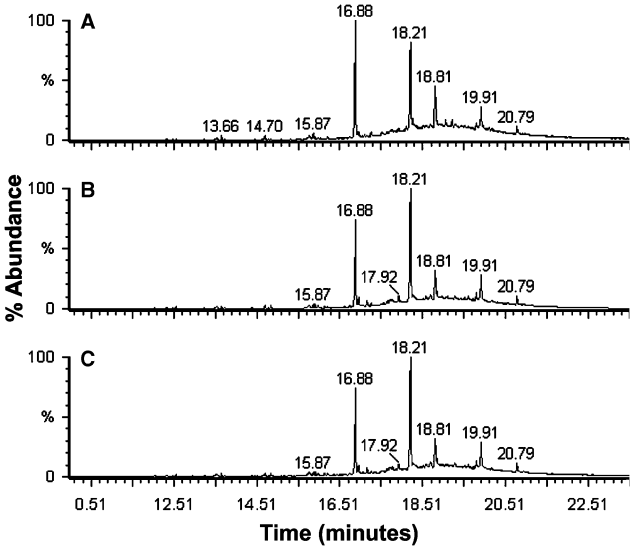

FIG. 1—*Areas of interest from the pyrograms of: (A) fingerprint residue (m/z of 142, 98, and 97 extracted), (B) fingerprint residue with background subtraction, and (C) fingerprint residue. Note the characteristic hydrocarbon pattern.*

TABLE 3—*Pyrolytic products of alanine and aspartic acid.*

Amino Acid	Pyrolytic Product	Molecular Weight (g/mol)	Retention Time (min)
Alanine	3,6-dimethylpiperazine-2,5-dione	142	13.70
Aspartic acid	2,5-furandione	98	3.02
	Maleimide	97	5.83

Interpretations of the resulting amino acid pyrogram mass spectra confirm the presence of the pyrolytic products listed in Table 3. These products are formed from a condensation reaction (Fig. 2) and high heat decomposition (Fig. 3). Figure 4 shows the mass spectrum from the aspartic acid signal at 5.83 min. The ions at *m/z* 97, 69, and 43 result from maleimide (M), M minus carbon monoxide, and M minus imino-methanone radical ion, respectively. Alanine and aspartic acid yielded the most promising amino acid pyrolytic markers with 3,6-dimethylpiperazine-2,5-dione and maleimide and 2,5-furandione, respectively. No pyrolytic products, and therefore no markers, were identified in the cases of serine, glycine, and lysine.

Extracted ion pyrograms show the presence of masses 142, 97, and 98 (3,6-dimethylpiperazine-2,5-dione, maleimide, and 2,5-furandione, respectively) in the pyrolized fingerprint residue. This suggests that these pyrolytic products are potential markers for the presence of alanine and aspartic acid in thermally decomposed fingerprint residue.

Discussion

The method developed in this study yielded qualitatively reproducible results from the pyrolysis of amino acids and

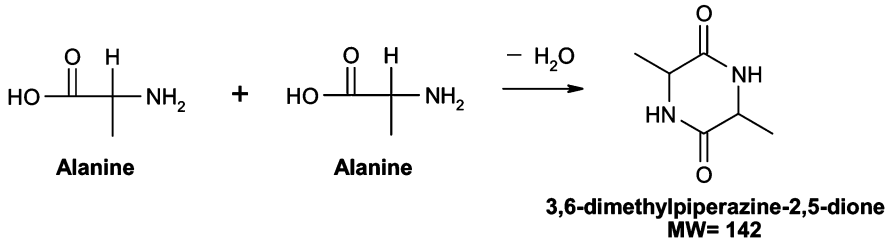

FIG. 2—*Condensation of alanine.*

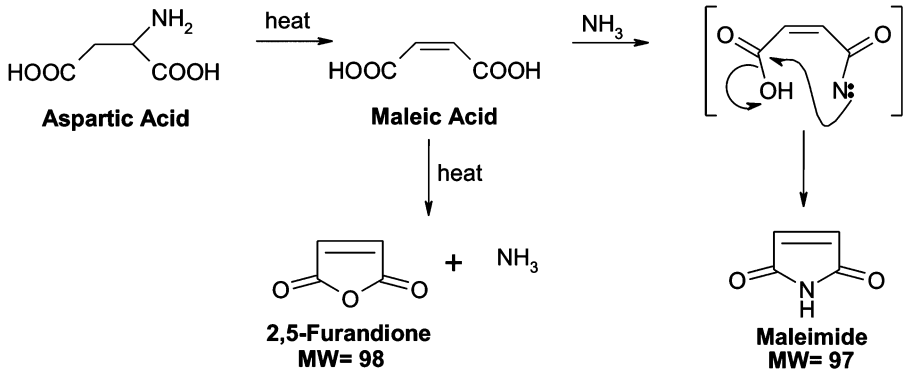

FIG. 3—*Thermal decomposition of aspartic acid.*

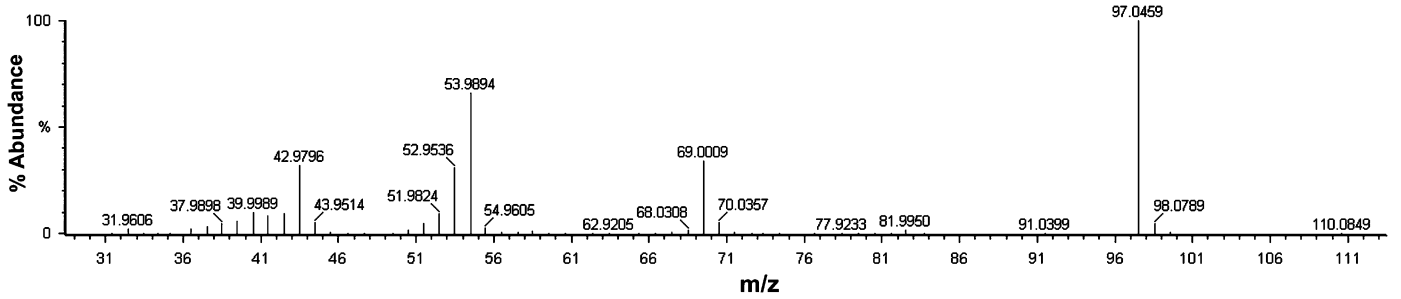

FIG. 4—*Mass spectrum of aspartic acid at 5.83 min.*

fingerprint residue. Dimethylpiperazine-2,5-dione, maleimide, and 2,5-furandione were identified as pyrolytic markers from two of the amino acids in fingerprint residue. Despite the fatty appearance and texture, the pyrolyzed fingerprint residue did not yield any previously reported animal or human tissue combustion products (8). The chromatographic presence of organics, such as isopropyl palmitate, suggests that environmental factors may coelute with the pyrolitic amino acid markers in fingerprint residue. However, there is currently no evidence to suggest these organics interfere with the markers or will inhibit a reaction between the markers and a target-specific reagent. The results from this study support amino acids as a viable candidate for such a substrate when latent fingerprints are found or suspected to be present on evidence that has been exposed to specific heat.

Acknowledgment

This work was funded by the National Institute of Justice, #2001-RC-CX-K003, West Virginia University.

References

1. Cantu AA, Leben DA, Ramotowski R, Kopera J, Simms JR. Use of acidified hydrogen peroxide to remove excess gun blue from gun blue-treated cartridge cases and to develop latent prints on untreated cartridge cases. J Forensic Sci 1998;43(2):294–8.
2. Ramotowski RS, Regen EM. The effect of electron beam irradiation on forensic evidence. 1. Latent print recovery on porous and non-porous surfaces. J Forensic Sci 2005;50(2):298–306.
3. Bleay SM, Bradshaw G, Moore JE. Fingerprint update-arson. Home Office Scientific Development Branch: Crime Investigation and Officer Safety Sector Fingerprint Development and Imaging Newsletter; 2006 Apr. Publication No.: 26/06.
4. Bentsen R, Brown JK, Dinsmore A, Harvey KK, Kee TG. Post firing visualisation of fingerprints on spent cartridge cases. Sci Justice 1996; 36(1):3–8.
5. Ratcliff MA, Medley EE, Simmonds PG. Pyrolysis of amino acids: mechanistic considerations. J Org Chem 1974;39(11):1481–90.
6. Chiavari G, Galletti G. Pyrolysis-gas chromatography/mass spectrometry of amino acids. J Anal Appl Pyrolysis 1992;24:123–37.
7. Lee HC, Gaensslen RE. Advances in fingerprint technology. 2nd ed. Boca Raton, FL: CRC Press, 2001.
8. DeHaan J, Brien DJ, Large R. Volatile organic compounds from the combustion of human and animal tissue. Sci Justice 2004;44(2): 223–36.

Additional information and reprint requests:
Amy Richmond-Aylor, B.S.
C. Eugene Bennett
Department of Chemistry
West Virginia University
217 Clark Hall
Morgantown, WV 26506-6045
E-mail: amyaylor@gmail.com