The Recoverability of Fingerprints on Paper Exposed to Elevated Temperatures – Part 2: Natural Fluorescence

***Ainsley J. Dominick*[1]**

***Niamh Nic Daéid*[1]**

***Stephen M. Bleay*[2]**

***Vaughn G. Sears*[2]**

[1]Centre for Forensic Science, University of Strathclyde, Glasgow, UK

[2]Home Office Scientific Development Branch, Sandridge, UK

For further information, please contact:

Ainsley J. Dominick

Centre for Forensic Science

University of Strathclyde

Royal College 204 George Street

Glasgow G1 1XW

United Kingdom

ainsley.dominick@strath.ac.uk

Abstract

Previous work by the authors [1] investigated the recoverability of fingerprints on paper which had been exposed to elevated temperatures by comparing various chemical enhancement techniques (ninhydrin, 1,8-diazafluoren-9-one (DFO), and physical developer (PD)). During that study, it became apparent, as a consequence of

observations made in operational work [2], that fingerprints on paper subjected to 150 C fluoresced under examination with green light of waveband 473-548nm with a 549nm viewing filter.

This work examined the three types of prints (eccrine, sebaceous, and ungroomed) after 20 min exposure to the temperature range 110 C to 190 C (in 10 C increments) and found that the eccrine fingerprints fluoresced more brightly. This indicated that it was a component of the eccrine deposit which was causing the fluorescence. Luminance measurements found that the maximum fluorescence was experienced at 170 C on both types of paper.

As a consequence, eccrine heat-treated fingerprints were viewed under violet-blue (350-469nm), blue (352-509nm), and green light (473-548nm) which indicated that the greatest luminance intensities were obtained under blue light and the smallest under green light. In order to determine what component of the eccrine fingerprint was causing this fluorescence, five of the most prevalent amino acids (alanine, aspartic acid, glycine, lysine, and serine) [3-4] were exposed to this temperature range. The luminance measurements were taken under exposure to the green light in order for the minimum fluorescence to be observed, with an assumption that blue-violet or blue illumination will provide brighter fluorescence in practice. The results indicated that four of the amino acids are behaving similarly across the temperature range, but with slightly different luminance measurements, but all are exhibiting some level of fluorescence. Thermal degradation products of alanine and aspartic acid have been suggested by Richmond-Aylor et al. [5]. The structure of these thermal degradation products is cyclic in nature, and as such, there is a possibility that two of these products would fluorescence. Sodium chloride and urea were also exposed to the temperature range and they also fluoresced to some extent.

This work shows that eccrine fingerprints that have been exposed to temperatures of between 130 C to 180 C will fluoresce under violet-blue, blue, and green light. This level of fluorescence for ungroomed fingerprints is much less but this will be dependent on the individual, the more eccrine the deposit, the stronger the fluorescence. This work shows that the amino acids, sodium chloride, and urea

present in fingerprint deposits are all contributing to the fluorescence of the print, but may not be the sole contributor as other eccrine components have not yet been tested.

Introduction

The term latent literally means "present and capable of becoming though not now visible, obvious, or active". The latent fingerprint is the most common form of fingerprint evidence and also the one that poses the most problems: it is present but invisible [6]. There are three major glands on the body but in most instances, only the eccrine and sebaceous glands contribute significantly to the latent print deposit [7]. Eccrine sweat consists of a complex mixture of organic (amino acids, proteins, and lactates) and inorganic material (Na^+, K^+, Cl^-, and trace metal ions). Sebaceous sweat consists of fatty acids, glycerides, cholesterol, squalene, and a variety of lipid esters [6-8].

Fluorescence is a form of luminescence which is mostly observed as an optical phenomenon in cold bodies. This occurs through the absorption of light of one colour (a photon) that results in the emission of light of a different colour (a different photon). This involves a change in energy and this energy difference is normally converted to heat or molecular vibrations. The energy in a single photon determines its wavelength (colour).When a molecule absorbs a photon its energy is transferred to electrons that become excited. Electrons in this excited state are very unstable and rapidly lose this excess energy, emitting a photon with less energy, longer wavelength, and as a consequence a different colour [9].

Lasers and other light sources have, since the late 1970s, been proposed for the detection of untreated fingerprints on non-luminescent surfaces [10-11]. According to Menzel [12-13], positive results have been obtained on many surfaces but these reported high success rates could not be achieved in practice, and good results have mostly been obtained with fingermarks contaminated by luminescent products [14] or marks that consist solely of sweat [15]. Despite the low success rate of the technique, a search for luminescent prints should always proceed the application of any further detection methods [6, 15]. Although previous research has shown that riboflaxin and pyridoxin will fluoresce [16], no comprehensive work to

date has been performed to identify the components of fingerprints residue that are responsible for the observed fingerprint luminescence [13].

Materials and Method

Eccrine, Sebaceous and Ungroomed Fingerprints on Recycled Paper

The paper used was taken from an unopened packet of white 80g/m^2 A4 recycled paper manufactured by Niceday (Andover, Hampshire, UK) and handled only whilst wearing gloves.

As the fingerprints fluoresced at 150 C, and not at 100 C and 200 C [1], heating experiments were conducted between 110 C and 190 C. A deliberately eccrine deposit was donated (achieved by washing hands then wearing nitrile gloves for half an hour), a deliberately sebaceous deposit (achieved by rubbing the nose before donation), and an ungroomed deposit (achieved by rubbing hands together to evenly distribute the sweat but only after a minimum of half an hour after hand washing) were donated. These fingerprints were placed on the same piece of paper and heated to temperatures in the range of 110 C to 190 C in 10 C increments. The exposure time for each sample was 20 minutes.

Eccrine Fingerprints on Filter Paper

The eccrine fingerprint placed on paper at 150 C was placed into a Shimadzu RF-5301 spectrofluorophotometer (Milton Keynes, Buckinghamshire, UK) in order for the optimal excitation and emission wavelengths to be determined [17].

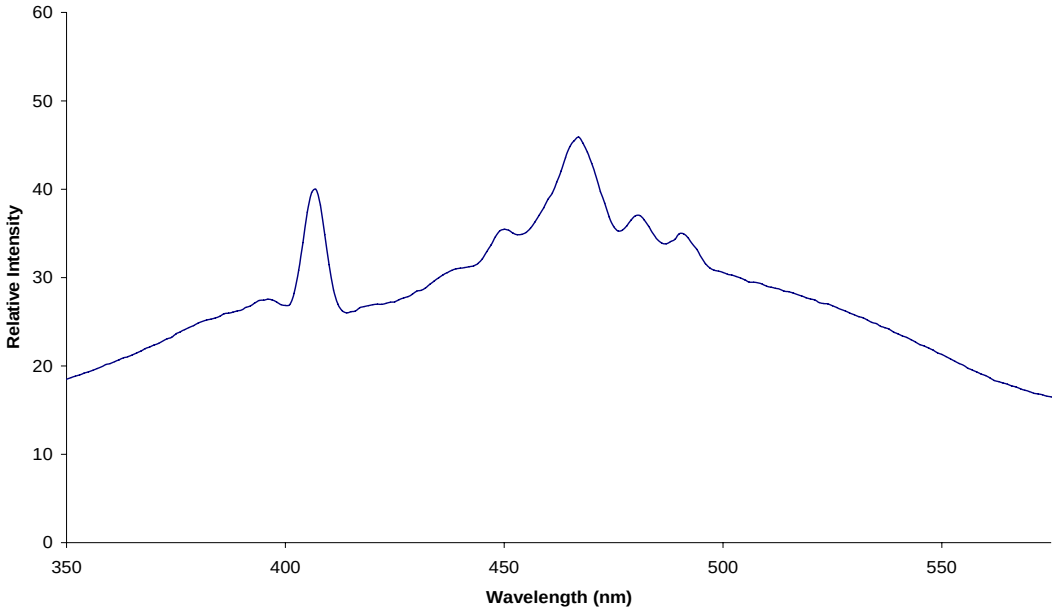

Figure 1: Excitation Spectrum of an Eccrine Fingerprint on Paper heated at 150 C

Figure 1 shows the excitation spectrum generated by the spectrofluorophotometer for the eccrine fingerprint at 600nm emission.

As the principal excitation peaks were detected at approximately 405nm and 475nm, the fingerprint was excited at these wavelengths and the resultant emission spectra are shown in figure 2. The actual excitation spectrum observed for the eccrine fingerprint is very broad.

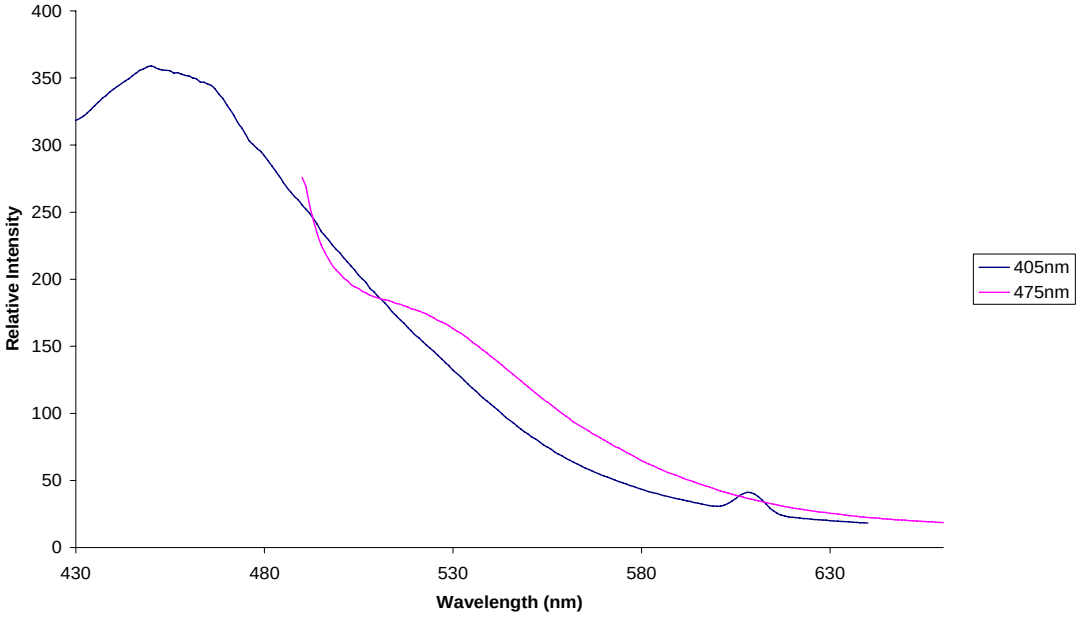

Figure 2: Emission Spectrum of an Eccrine Fingerprint on Paper Heated at 150 C

Eccrine fingerprints were then deposited onto filter paper which was 110mm in diameter, in hardened, ashless circles (Whatman Ltd, Maidstone, Kent, UK) and only handled whilst wearing gloves. These fingerprints were exposed to the temperatures in the same range of 110 C to 190 C and examined under violet-blue light between 350-469nm with a 476nm viewing filter, blue light between 352-509nm with a 510nm viewing filter, and green light between 473-548nm and a 549nm viewing filter provided by a Quaser 40 (Foster + Freeman, Evesham, UK), as the spectrofluorophotometer results show that fluorescence would be observed within these three bandwidths.

The luminance of the prints was measured using a Konica Minolta LS-100 luminance meter, with the Quaser 180mm away from the paper and the luminance meter 400mm away from the paper (shown in figure 3). These were fixed in position for all the luminance measurements. These results indicated that blue light will provide the brightest fluorescence, followed by violet-blue, and finally green.

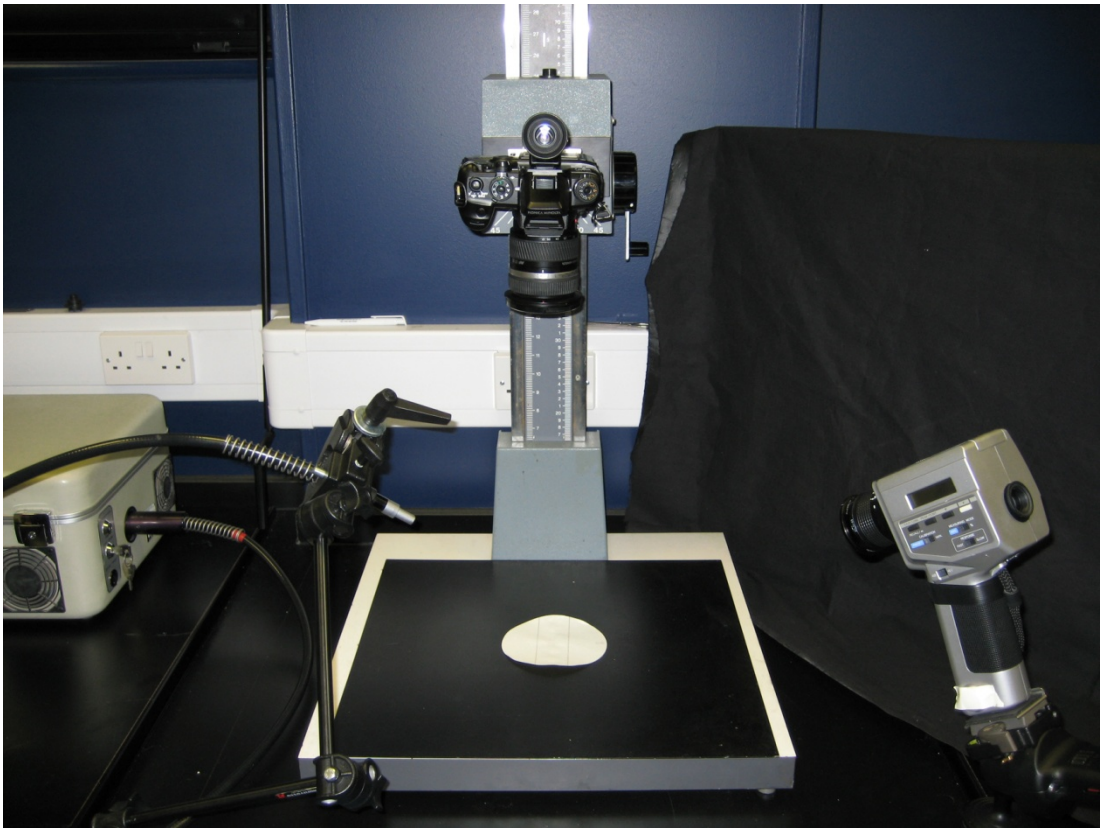

Figure 3: Setup of Quaser, Digital Camera and Luminance Meter

Exposure of Eccrine Sweat Constituents to Elevated Temperatures

Five of the most prevalent amino acids present in fingerprint deposits [4] were subjected to the same temperature conditions as before. 10μL of 1mg/mL of L-alanine, L-aspartic acid, L-lysine hydrochloride, glycine, and L-serine (Fluka BioChemika, Sigma-Aldrich, Gillingham, Dorset, UK) was deposited onto filter paper, as was 10μL of 1mg/mL of sodium chloride and urea (Sigma-Aldrich, Gillingham, Dorset, UK). These were examined under green light as this was first bandwidth found to fluoresce these heated prints. Also, the green NdYAG 532nm laser is a common search laser used for examining crime scenes in the UK and as such, is appropriate for speculatively searching large areas for this type of fluorescent prints.

Results and Discussion

Eccrine, Sebaceous and Ungroomed Fingerprints on Recycled Paper

A preliminary study was conducted to investigate whether the type of fingerprint deposit influenced the resulting natural fluorescence. This was achieved by comparing an eccrine, a sebaceous, and an ungroomed fingerprint over a temperature range of 110 C to 190 C in 10 C increments. These fingerprints were then examined under green light between 473-548nm with a 549nm viewing filter in order to determine which of the three deposits provided the greater fluorescence intensity. The following figure shows the photographs taken of the eccrine, sebaceous, and ungroomed deposits across the temperature ranges. The photographs were taken at various exposure times in order for the photographs produced to be to the best of the camera's ability and are shown in figure 4.

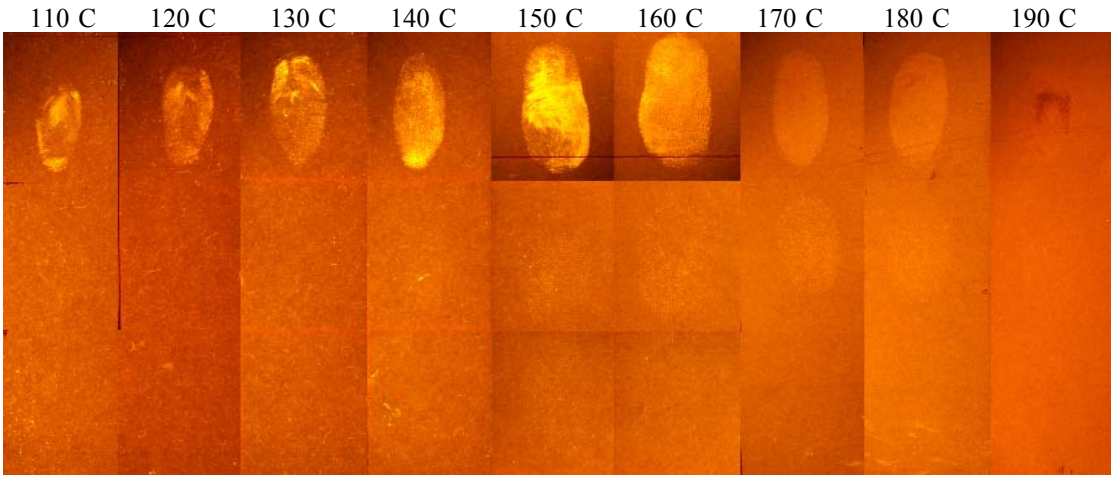

Figure 4: Photographs of fingerprints exposed to various temperatures for 20min
(Top to bottom: eccrine, sebaceous, and ungroomed)

By visualisation alone, the eccrine fingerprints are producing the brightest fluorescence. These brightness levels were measured using a luminance meter (with a 549nm filter over the lens) and the results are displayed in figure 5 (a scatterplot outputted using Minitab v.15).

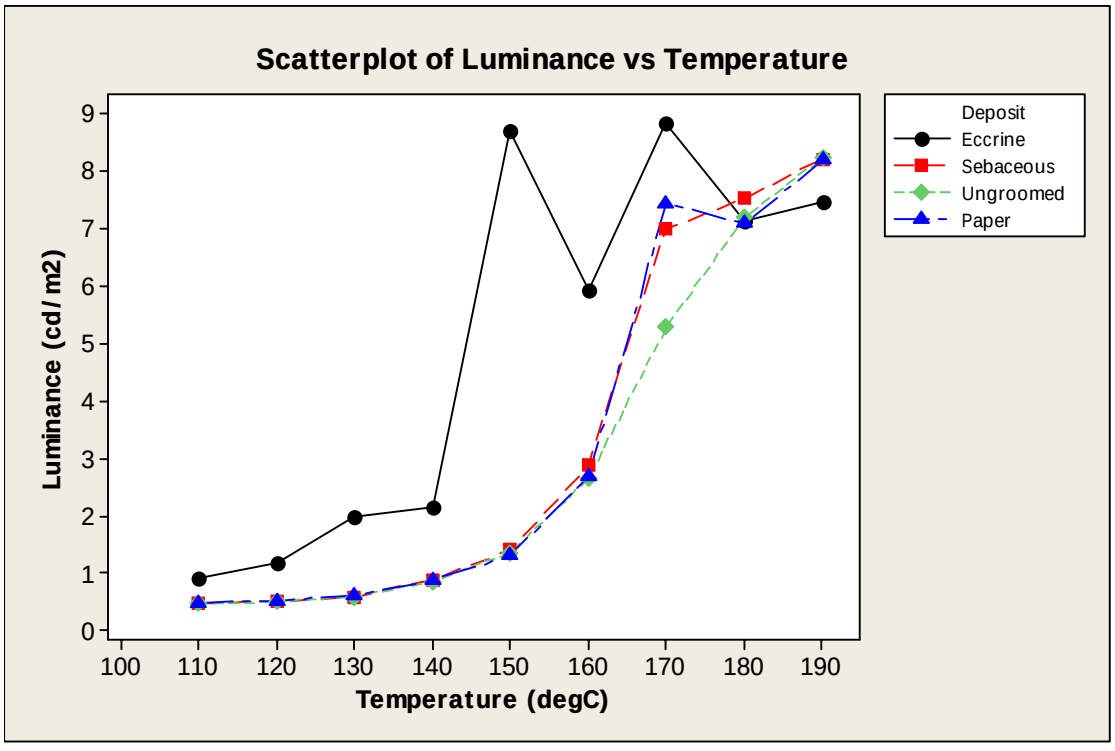

Figure 5: Scatterplot of different fingerprint deposits on white 80g/m^2 A4 recycled paper

The graph shows that the eccrine fingerprints' luminance is greater than that of the other two deposits and that of the background paper (upto 170 C). An anomalous result was also observed at 160 C for the eccrine deposit. The luminance measurements of the sebaceous and ungroomed marks are very similar to the paper fluorescence until 170 C. These results coincide with the visual interpretation of the fingerprints, indicating it is one or more components of the eccrine fingerprint deposit which are thermally degrading to produce this fluorescence.

3.2 Eccrine Fingerprints on Filter Paper

Eccrine fingerprints were deposited onto filter paper to examine the effects of different wavebands of light on the resultant fluorescence. Filter paper was used for this part of the experiment because it contains fewer additives that may degrade and add to background fluorescence. These eccrine fingerprints were excited by violet-blue light between 350-469nm with a 476nm viewing filter, blue light between 352-509nm with a 510nm viewing filter, and green light between 473-548nm and a 549nm viewing filter provided by a Quaser 40. This fluorescence was photographed at various exposure times and shown in figure 6.

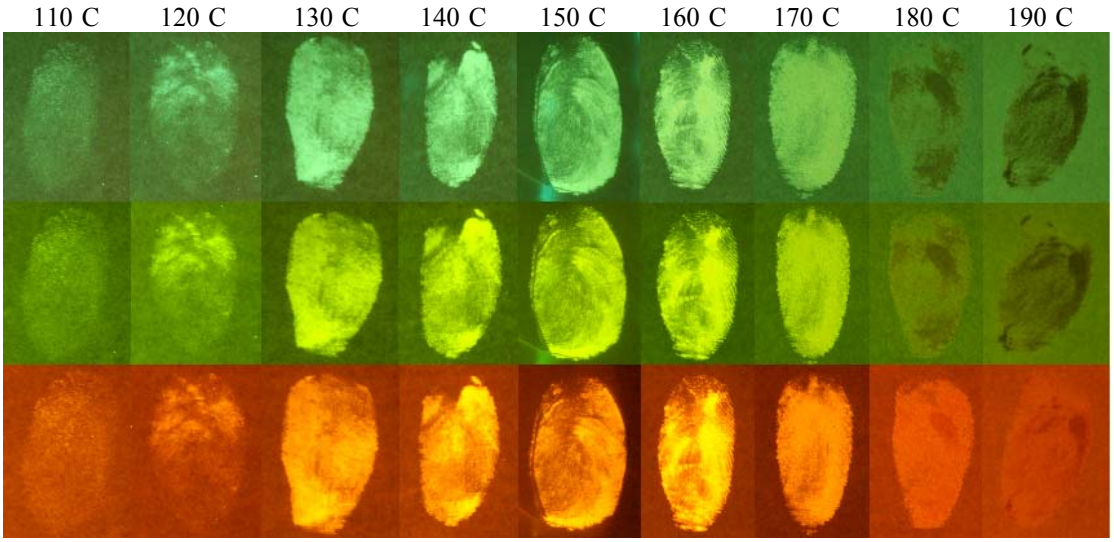

Figure 6: Photographs of the eccrine fingerprint exposed to various temperatures for 20min
(Top to Bottom: illumination bands of violet-blue, blue, and green)

The fluorescence for each bandwidth of light was measured using the luminance meter and compared in figure 7.

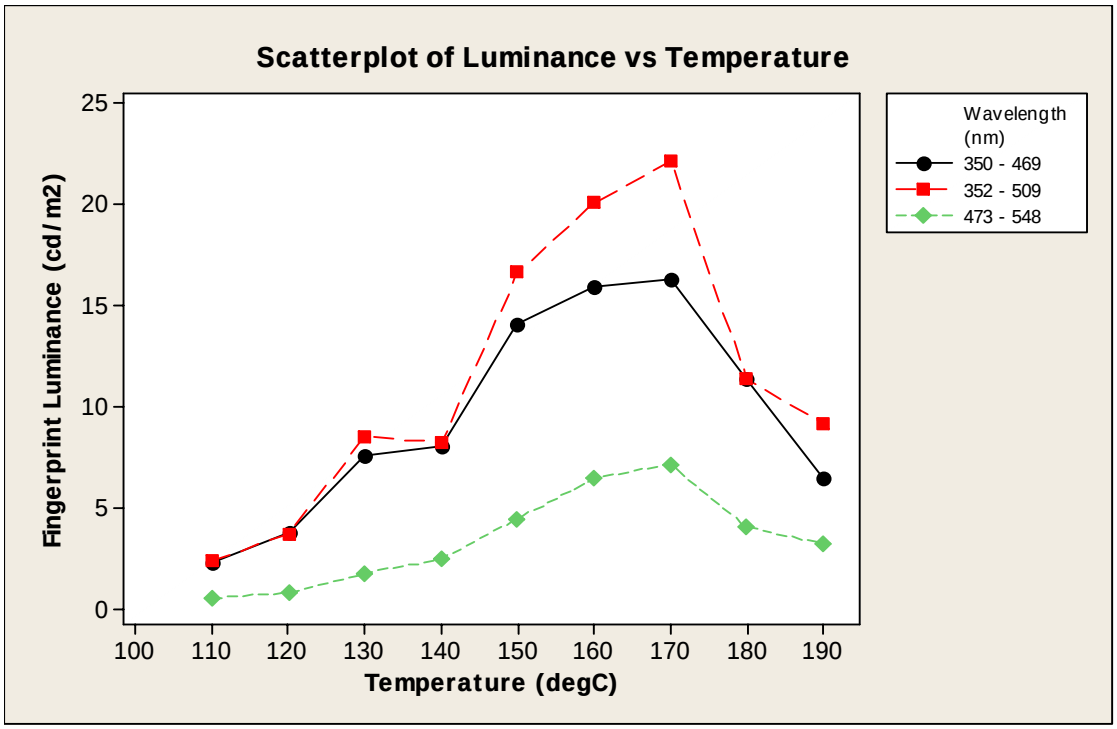

Figure 7: Scatterplot of eccrine fingerprint deposits excited by different bandwidths of light on 110mm diameter, hardened, ashless filter paper

The photographs and the graph indicate that blue light is producing a brighter fluorescence, followed by violet-blue, and finally green. The photographs were taken at various exposure times automatically selected by the camera. As green light is producing the dullest luminance measurements, it was selected for examination of the amino acids, sodium chloride, and urea as if luminance is found with green light, then violet-blue and blue would have to be brighter. Also 532nm (within the green waveband) is a common search laser which scene of crime officers in the UK would regularly take to scenes.

3.3 Exposure of Eccrine Sweat Constituents to Elevated Temperatures

Eccrine fingerprints consist of a very high percentage of water. The remainder is a complex mixture of organic (amino acids, proteins, and lactate) and inorganic material (Na^+, K^+, Cl^-, and trace metal ions) [7]. This work concentrates on investigating the effects of the elevated temperatures on the amino acids, sodium chloride, and urea of which the total amounts present in a print is reported to be between 0.3-2.59mg/L, 0.52-7mg/mL, and 10-15mM respectively [3].

Filter paper was used again for this part of the experiment due to its fewer additives and also due to its absorbency in allowing the solutions to dry faster on this substrate than the white 80g/m^2 A4 recycled paper. Therefore 10μL of each of the solutions was deposited onto the filter paper and subjected to the same temperatures range.

Figure 8 shows the photographs taken under fluorescent lighting conditions for each amino acid, sodium chloride and urea.

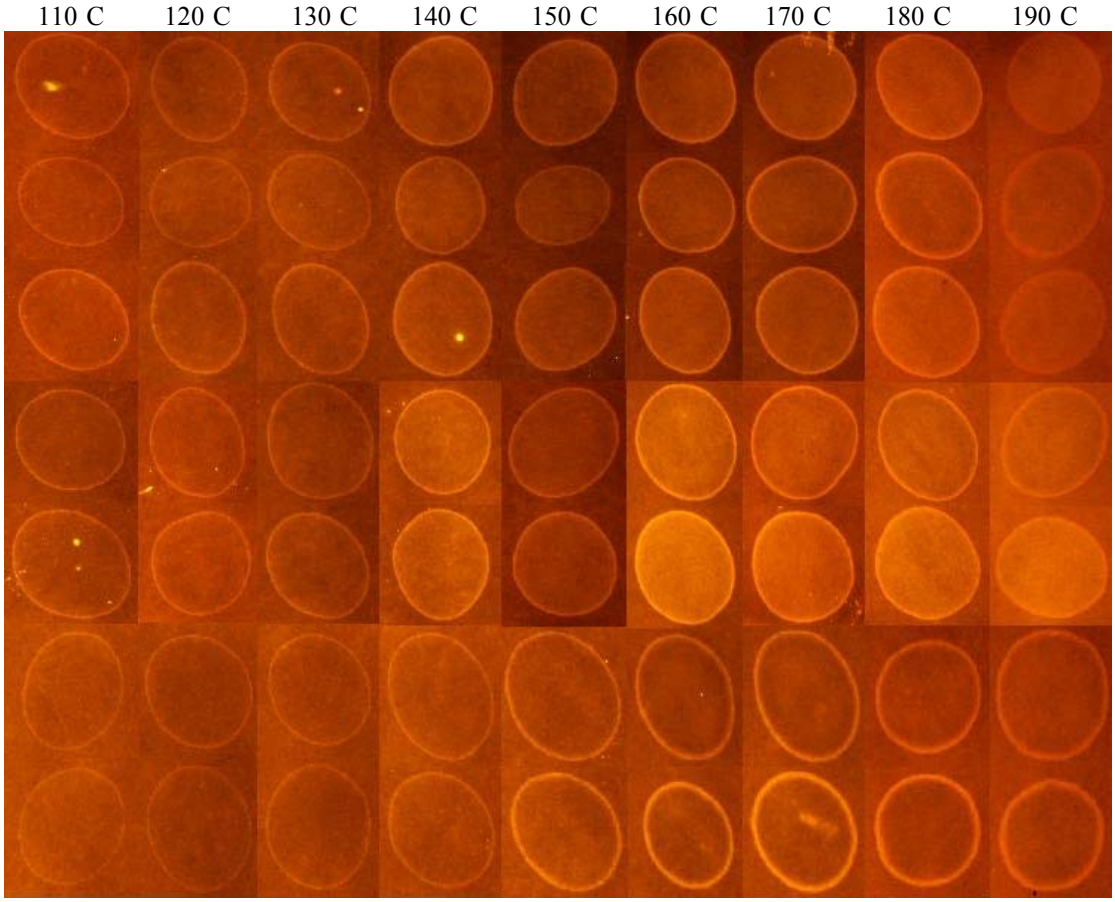

Figure 8: Photographs of the solutions exposed to various temperatures for 20min
(Top to Bottom: alanine, aspartic acid, glycine, lysine, serine, sodium chloride, and urea)

Figure 9 shows the luminance measurements for the eccrine fingerprint, each amino acid, and the filter paper.

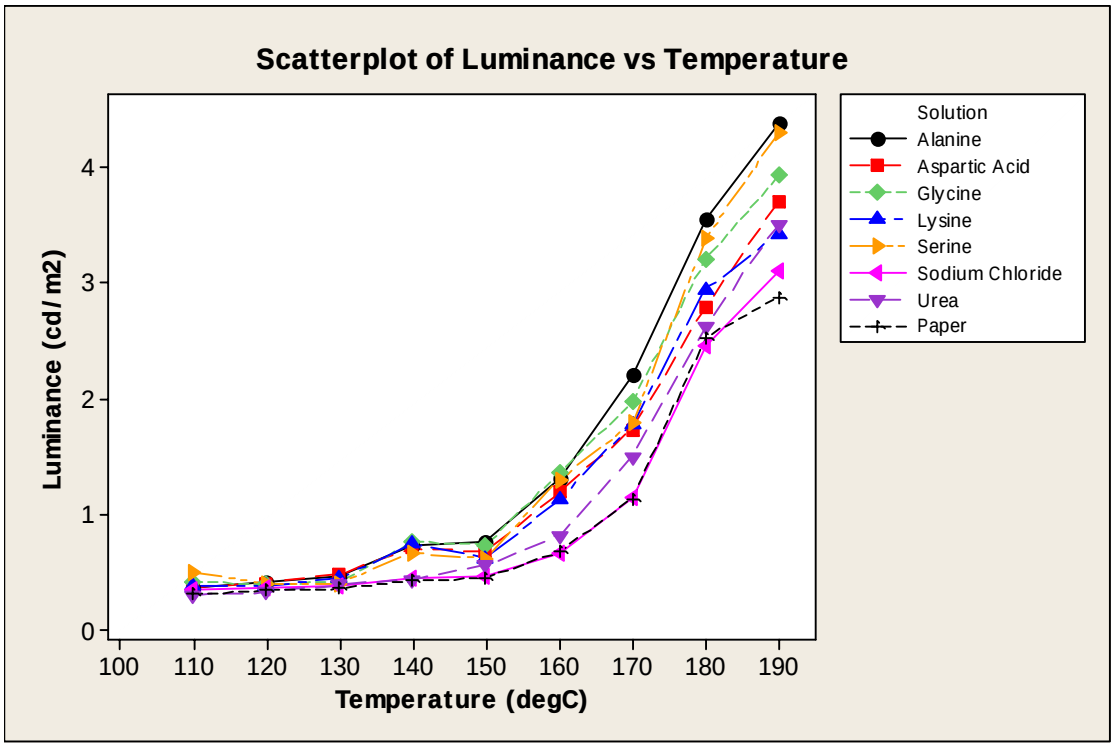

Figure 9: Scatterplot of each solution on 110mm diameter, hardened, ashless filter paper

All five amino acids appear to be behaving in a similar manner to each other until 160 C. They deviate away from the background fluorescence of the paper at 140 C, where a slight shoulder on the graph is observed before the larger increase observed at 160 C. Alanine shows the greatest fluorescence, followed by the other four. Urea is also showing a slight fluorescence but the shoulder at 140 C is not shown, indicating that this is a feature of the amino acid degradation only. Sodium chloride does show a slight fluorescence visually but it isn't detected by the luminance meter until 190 C. The level of fluorescence is not recorded as high as the measurements for the eccrine fingerprints but this may be due to the concentrations of the solutions, as amino acid concentrations in fingerprints can vary as much as 2 to 20 times depending on collection methods [18].

Richmond-Aylor et al. [5] have undertaken work into identifying the thermal decomposition products of several amino acids using pyrolysis gas chromatography/mass spectrometry. This work indicated that the decompositions in figure 10 were taking place.

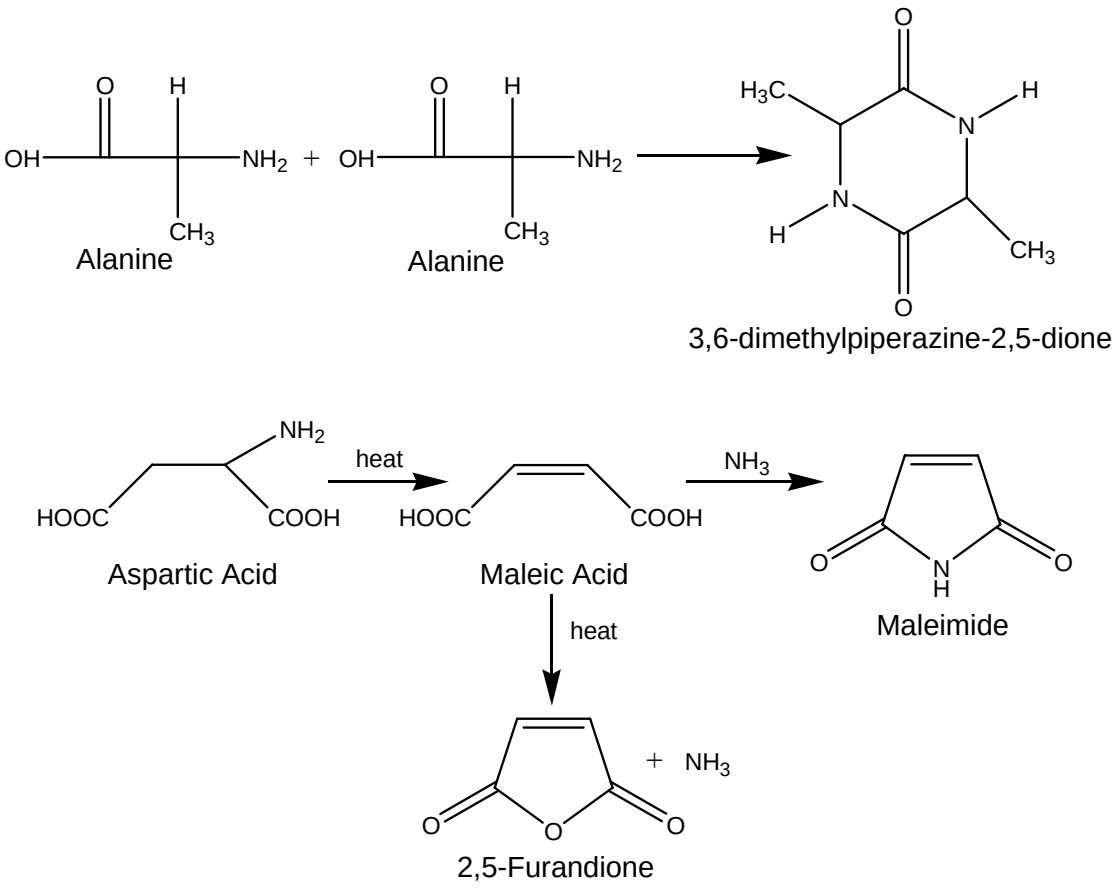

Figure 10: Decomposition of amino acids

From the above structures, it is unlikely 3,6-dimethylpiperazine-2,5-dione would fluoresce. Although it is cyclic in nature, it is not planar and also is not completely conjugated [19]. Alternatively, there is a possibility that 2,5-furandione and maleimide could fluoresce. Richmond-Aylor et al.'s study involved pyrolysis parameters of 50 C to 500 C, which is 2.5 times greater than the temperatures in this work. Therefore as the 3,6-dimethylpiperazine-2,5-dione structure does not represent an aromatic molecule, the molecule which is fluorescing may be an intermediate and not the resultant product suggested by Richmond-Aylor et al. [5]. Thermal decomposition products of urea could not be found in the literature.

Brown et al. [20] have recently published work that also discusses the fluorescence of fingerprints exposed to elevated temperatures. The authors did not observe fluorescence at exposed temperatures below 220°C, but the exposure times used in this study were shorter than those reported here. Brown et al. also report that fluorescence of the fingerprints is independent of the type of secretion, and also propose that the reason for the observed contrast is that the presence of the fingerprint

constituents causes the paper to heat more rapidly than it otherwise would, accelerating charring in these regions. The studies reported here suggest that composition may actually play a more important role in fluorescence, with the brightest fluorescence being observed for eccrine fingerprints and amino acid samples.

Conclusions

It has been shown that fingerprints will fluorescence under excitation from violet-blue light between 350-469nm with a 476nm viewing filter, blue light between 352-509nm with a 510nm viewing filter, and green light between 473-548nm and a 549nm viewing filter. The study showed that it is the eccrine component of the latent fingerprint which is causing the fluorescence of the marks after exposure to temperatures in excess of 100 C, with the maximum luminance observed for marks heated in the range of 160-180 C. Thermal decomposition of amino acids has been investigated by Richmond-Aylor et al. [5] and has suggested three decomposition reaction products, of which two have the molecular structure which could account for this fluorescence, although this has not be directly investigated in this work. Sodium chloride and urea are also accountable for the fluorescence in the mark but other eccrine sweat constituents could also be contributing to the fluorescence.

References

1. Dominick, A.J., S.M. Bleay, and N. Nic Daéid, *The Recoverability of Fingerprints on Paper Exposed to Elevated Temperatures – Part 1: Enhancement Technique Comparison* submitted to Journal of Forensic Identification, 2008.
2. Personal Communication, *Andrew Townley, Fingerprint Development Technician, Thames Valley Police.* 2005.
3. Bayford, F., *Sweat.* Fingerprint Whorld, 1976. **1**: p. 42-43.
4. Chiavari, G. and G. Galletti, *Pyrolysis-Gas Chromatography/Mass Spectrometry of Amino Acids.* Journal of Analytical and Applied Pyrolysis, 1992. **24**(2): p. 123-137.

5. Richmond-Aylor, A., et al., *Thermal Degradation Analysis of Amino Acids in Fingerprint Residue by Pyrolysis GC-MS to Develop New Latent Fingerprint Developing Reagent.* Journal of Forensic Sciences, 2007. **52**(2): p. 380-382.
6. Champod, C., et al., *Fingerprints and Other Ridge Impressions*. 2004: CRC Press LLC.
7. Lee, H.C. and R.E. Gaensslen, *Advances in Fingerprint Technology*. 2nd ed. 2001: CRC Press LLC.
8. Cuthbertson, F., *The Composition of Fingerprints: AWRE Report.* SSCD Memorandum SAC/2/65, 1965.
9. Menzel, E.R. and K.E. Fox, *Laser Detection of Latent Fingerprints: Preparation of Fluorescent Dusting Powders and the Feasibility of a Portable System.* Journal of Forensic Sciences, 1980. **25**(1): p. 150-153.
10. Menzel, E.R. and J.M. Duff, *Laser Detection of Latent Fingerprints - Treatment with Fluorescers.* Journal of Forensic Sciences, 1979. **24**(1): p. 96-100.
11. Dalrymple, B.E., J.M. Duff, and E.R. Menzel, *Inherent Fingerprint Luminescence - Detection by Laser.* Journal of Forensic Sciences, 1977. **22**(1): p. 106-115.
12. Menzel, E.R., *Fingerprint Detection with Lasers*. 1st ed. 1980: Marcel Dekker Inc.
13. Menzel, E.R., *Fingerprint Detection with Lasers*. 2nd ed. 1999: Marcel Dekker Inc.
14. Salares, V.R., C.R. Eves, and P.R. Carey, *On the Detection of Fingerprints by Laser Excited Luminescence.* Forensic Science International, 1979. **14**: p. 229-237.
15. Home Office Police Scientific Development Branch, *Fingerprint Detection by Fluorescence Examination - A Guide to Operational Implementation*. 2nd ed. 1992: Heanor Gate Printing Ltd.
16. Guilbault, G.G., *Practical Fluorescence, Theory, Methods, and Techniques*. 1973: Marcel Dekker Inc.
17. Shimadzu, *RF-5301 Spectrofluorophotometer Manual*.
18. Hadorn, B., et al., *Free Amino Acids in Human Sweat from Different Parts of the Body.* Nature, 1967. **215**: p. 416-417.

19. McMurry, J., *Organic Chemistry*. 4th ed. 1996: Brooks/Cole Publishing Company.
20. Brown, A.G., et al., *Revisiting the Thermal Development of Latent Fingerprints on Porous Surfaces: New Aspects and Refinements.* Journal of Forensic Sciences, 2009. **54**(1): p. 114-121.