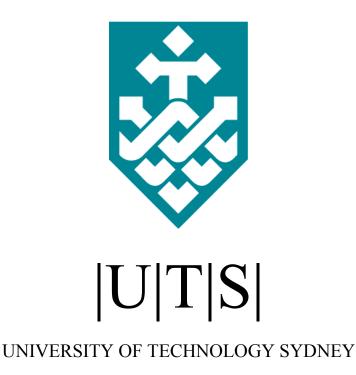
An investigation of latent fingermark residues and their development on porous substrates using physical developer and nile red

This thesis is submitted in fulfilment of the requirements for the degree of Doctor of Philosophy.



Mackenzie de la Hunty

Centre for Forensic Science

University of Technology, Sydney

March 2017

CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as part of the collaborative doctoral degree and/or fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of Student:

Date:

This research is supported by an Australian Government Research Training Program Scholarship.

Abstract

The detection of fingermarks on porous surfaces that have been wet is currently limited to only one routine technique, Physical Developer (PD). PD is a well-established fingermark development method that has a plethora of issues associated with its use, principally based around the preparation and relative instability of the working solution and lack of contrast on dark substrates as it is non-luminescent. While these issues have been mostly addressed at an operational level, in-depth chemical remedies for the PD process cannot be devised because the mechanisms and specific targets of PD remain largely unknown. This highlights the need to understand the fundamental chemistry of the technique to recognise what may be improved and what complementary detection methods could be applied to ensure that the maximum number of available fingermarks are developed in casework.

This research has also considered nile red (NR), a technique known to develop fingermarks on porous substrates that have been wet that remain undeveloped by treatment with PD. An investigation of the optimisation of the NR working solution was undertaken. An oil-in-water microemulsion containing NR was prepared using the solvent-diffusion method. The optimized NR solution was demonstrated to be effective in developing fresh latent fingermarks. The working solution is prepared with the slow addition of a NR in dichloromethane stock solution to a dual surfactant solution to create a lactescent dual organic-aqueous phase intermediate. Stirring promotes the evaporation of the solvent, resulting in a transparent NR microemulsion. The solution contains less hazardous solvents than the previously published formulation, with an extended shelf life and at a much lower cost. The optimized microemulsion was shown to outperform a previously reported aqueous nile blue working solution on both natural and groomed fingermarks, with shorter exposure times for image capture after development.

The storage, ageing and concentration of the components of a PD working solution was evaluated to determine the most effective formulation and protocol for the use of PD. A more thorough understanding of the working solution components of PD has allowed a refinement of the development method and the formulation itself, resulting in increased development success and a better understanding of when fingermarks will and will not be effectively developed by the technique. A revised PD working solution formulation and development protocol has been established that has been successfully utilised by undergraduate forensic science students.

Abstract

An investigation of the chemical targets of PD contained in latent fingermark deposits through reactivity assessments of various lipid, eccrine and lipid–eccrine mixtures in the residue was undertaken. Experimental results showed that silver deposition from the PD working solution occurs in the presence of an emulsion of both lipid and eccrine constituents. PD was interestingly shown to also be reactive towards emulsions of oleic acid and water, indicating that the silver deposition may occur as a result of nucleation sites at the emulsion phase boundary, or as a result of desorption of constituents from the substrate that promote silver reduction. These results explain the anomalies seen with the selective development by PD of a proportion of fingermarks on a substrate, and the development of other fingermarks by other techniques when used in sequence, such as Oil Red O (ORO) or NR. A consideration of the various processes that emulsions undergo also helps to rationalise the fluctuating developmental effectiveness of PD on ageing fingermarks.

A better understanding of the PD technique permits a more informed selection of alternative or complementary detection methods. This research provides further insight into not only the application of the PD technique but, more importantly, into the reasons behind the observed development. This increased understanding highlights the need to sequence PD with a lipid sensitive technique, such as NR, for the development of latent fingermarks on porous substrates that have been wet as the two techniques have discrete and complementary targets. It also emphasizes the need to develop a better understanding of latent fingermark residue–substrate interactions.

Acknowledgements

Words cannot express how grateful I am to have had this opportunity.

Claude, Chris and Xanthe,

Without you, this thesis, I couldn't have done,

I would have turned my back; I would have turned and run.

With all of your feedback, support and care,

You helped me imagine the finish line, and made sure I got there.

Conferences and presentations galore,

Thank you for your endless encouragement, and more.

Thank you for pretending I was onto something when I was not,

Thank you for being excited when the ideas turned from warm to hot,

Thank you for laughing with me when I thought I was funny,

(Because, in all honesty) my presentations tended to be overly-punny.

Sebastien,

Your insight and Lausanne style,

Made sure there were amazing ideas to compile.

Linda,

I never wanted for anything, especially not glassware,

You always stashed the best stuff, and always showed me where.

Bradley,

Your insight and help discussing the Tollen's reaction,

Showed me why there was a silver attraction.

Scott,

Your friendship inside and out of the laboratory,

Has helped me become who I am today, has helped me write my story.

Thank you for always lending an ear,

And helping me find the direction to take my career.

Dad,

Thank you for your endless support, love and validation,

Having you to throw ideas off has been a salvation.

Thank you for always being interested in this thesis,

Applauding my effort, and respecting the time taken to complete what feels like my own exegesis.

Thank you for helping me understand notions outside of my expertise,

Because my dad is the smartest; he explains everything with care, explains everything with ease.

Jess,

Thank you for your never ending support and motivation,

I'm so proud of everything you do, you are my inspiration.

Mum and Nana,

Thank you for always calling, to make sure I'm hanging in there,

For always telling me you love me and showing that you care.

Grandpop,

I wish you could have been here to see me cross the finish line,

But I know wherever you are, you're proud of me and doing just fine.

To everyone else who has supported me, and helped me get through,

It is because of you all that I've finally finished my thesis, and made my "Dr" debut.

Acronyms

Abbreviation	Word
	Dis(twins at hydright districtly a reason of the
BSTFA	Bis(trimethylsilyl)trifluoroacetamide
СА	Cyanoacrylate
CHCl₃	Chloroform
DCM	Dichloromethane
ECF	Ethyl chloroformate
EDTA	Ethylenediaminetetraacetic acid
EtOAc	Ethyl acetate
EtOH	Ethanol
FP	Whatman no. 41 ashless filter paper
GC-MS	Gas Chromatography Mass Spectrometry
Нех	Hexane
HLB	Hydrophilic-lipophilic balance
Ind-Zn	Indanedione + zinc chloride
IS	Internal standard
IsoP	Isopropanol
LPSP	Latent print standards pad
MeOH	Methanol
MMD	Multi-metal deposition
MSTFA	N-methyl-N-(trimethylsilyl)trifluoroacetamide
NB	Nile blue A
n-DAA	N-dodecylamine acetate

Nin	Ninhydrin
NP	Lined note paper
NR	Nile red
NR-OP	Optimised nile red working solution
NR-STD	Standard nile red working solution
o/w	oil in water (emulsion)
PD	Physical developer
PIT	Phase inversion temperature
RecP	100 % Recycled paper
RH	Relative humidity
RP	80 gsm Reflex Virgin Fibre UltraWhite copy paper
RT	Room temperature
SFR	Synthetic fingermark residue
SMD	Single-metal deposition
SynN	Synperonic N
ТВ	Toluidine blue
ТІС	Total ion chromatogram
TLC	Thin Layer Chromatography
TMCS	Trimethylcholorosilane
UV	Ultra-violet
w/o	water in oil (emulsion)

Table of Contents

AE	BSTRACT		III
A	CKNOWL	EDGEMENTS	v
A	CRONYN	IS	VII
LIS	ST OF TA	BLES	XII
LIS	ST OF FIG	GURES	xx
	Ρυβυζατ	FIONS	XX\/I
		NCES	
	PODCAST	s/ Exhibitions	. XXVI
1	THE	DEVELOPMENT OF FINGERMARKS ON POROUS SUBSTRATES	2
	1.1	LATENT FINGERMARK DEPOSITION	2
	1.1.1	Chemical Composition	2
	1.1.2	Factors affecting deposition	3
	1.2	LATENT FINGERMARK DEVELOPMENT ON POROUS SUBSTRATES THAT HAVE BEEN WET	6
	1.2.1	Physical Developer	7
	1.2.2	Oil Red O (ORO)	9
	1.2.3	Nile Red	10
	1.3	PROJECT AIMS AND OBJECTIVES	13
	2.1	ICAL DEVELOPER	19
	2.2	FINGERMARK QUALITY ASSESSMENTS FOR COMPARATIVE TESTING	
	2.2.1 2.2.2	,	
	2.2.2	DEPOSITION FACTORS	
	2.3		
	2.3.1		
	-	Composition of fingermark residue	
	2.4		
	2.4.1		
	2.4.2		
	2.4.5		
	2.4.4	Conclusion	
3	THE	APPLICATION OF NILE RED FOR LATENT FINGERMARK DEVELOPMENT	62
	3.1	INTRODUCTION	62
	3.2	NILE RED WORKING SOLUTION RE-EVALUATION	
	3.2.1		
	3.3	COMPARISON OF THE OPTIMISED SOLUTION WITH THE STANDARD SOLUTION	
	3.4	COMPARISON OF AQUEOUS NILE BLUE AND A NILE RED MICROEMULSION	
	3.4.1		
	3.4.2	-	
	3.4.3	Sample treatment	72

	3.4.4	Sample visualisation	73
	3.4.5	Results and Discussion	73
	3.5 N	R AND NB IN AQUEOUS AND ORGANIC MEDIA	76
	3.5.1	Thin layer chromatography	77
	3.6 C	ONCLUSIONS	85
4	PHYSIC	CAL DEVELOPER FORMULATION AND METHOD	87
	4.1 IN	ITRODUCTION	87
	4.2 D	ETERGENT SURFACTANT SOLUTION	89
	4.2.1	Storage and aging	91
	4.2.2	Concentration	92
	4.3 S	ILVER NITRATE	94
	4.3.1	Storage and aging	100
	4.4 R	EDOX SOLUTION	103
	4.4.1	Storage and aging	103
	4.4.2	Concentration	106
	4.5 P	D WORKING SOLUTION	106
	4.5.1	Storage and aging	106
	4.5.2	Control samples	110
	4.6 C	ONCLUSIONS	115
5	DETER	MINATION OF THE TARGETS OF PHYSICAL DEVELOPER PART I	.117
	5.1 IN	ITRODUCTION	117
	5.2 Is	PD DEVELOPMENT PROPAGATED BY LIGHT EXPOSURE?	119
	5.2.1	Experimental Method	119
	5.2.2	Results and Discussion	121
	5.3 D	OES PD TARGET LIPIDS IN FINGERMARK RESIDUE?	122
	5.3.1	Experimental Method	122
	5.3.2	Results and Discussion	126
	5.4 D	OES PD TARGET ECCRINE MATERIAL IN FINGERMARK RESIDUE?	
	5.4.1	Experimental method	
	5.4.2	Results and Discussion	
	5.5 C	ONCLUSIONS	151
6	DETER	MINATION OF THE TARGETS OF PHYSICAL DEVELOPER PART II	.154
	6.1 IN	ITRODUCTION	154
	6.2 S	YNTHETIC FINGERMARK RESIDUE	156
	6.2.1	Preparation of synthetic sebum	158
	6.2.2	Preparation of synthetic sweat	159
	6.2.3	Reactivity assessment of synthetic components	160
	6.3 Is	PD DEVELOPING A MIXTURE OF ECCRINE AND LIPID CONSTITUENTS?	
	6.3.1	Experimental method	161
	6.4 Is	PD DEVELOPING AN EMULSION OF ECCRINE AND LIPID CONSTITUENTS?	162
	6.4.1	Emulsion type	
	6.5 E	XPERIMENTAL METHOD	164
	6.6 R	ESULTS AND DISCUSSION	168
	6.7 Is	PD DEVELOPING AN EMULSION?	
	6.7.1	Experimental method Results and Discussion	

6.8	Conclusions	187
7 CO	NCLUSIONS AND FUTURE DIRECTIONS	190
7.1	Conclusions	190
7.1	1 The composition of fingermark residue	190
7.1.	2 The application of nile red to latent fingermark detection	191
7.1.	3 Modifications to the physical developer technique	192
7.1.	4 The determination of the targets of physical developer	193
7.2	FUTURE DIRECTIONS	194
	X I. DEVELOPMENT TECHNIQUE MATERIALS, FORMULATION, APPLICATION AND	100
	PHYSICAL DEVELOPER	
	NDANEDIONE-ZINC	
1.4 1	NINHYDRIN	201
APPEND	X II. FINGERMARK GRADING AND GC-MS DATA	203
II.1	FINGERMARK CONTRAST GRADING	203
11.2	GC-MS DATA	204
APPEND	X III. NILE RED EXPERIMENTAL DATA	211
III.1	PRELIMINARY OPTIMISATION TRIALS	213
111.2	THIN LAYER CHROMATOGRAPHY	231
APPEND	X IV. PHYSICAL DEVELOPER EXPERIMENTAL DATA	233
IV.1	UV-VIS Spectra	233
APPEND	X V. PHYSICAL DEVELOPER PROTOCOL AND TROUBLESHOOTING	237
V.1	GENERAL CONSIDERATIONS	237
V.2	PREPARATION OF SOLUTIONS USED IN DEVELOPMENT	238
V.3	DEVELOPMENT OF SAMPLES	239
V.4	TROUBLESHOOTING	240
REFEREN	CES	243

List of tables

Table 2-1: Grades assigned using the CAST and UNIL assessment schemes for four different NR
working solution formulations compared in Figure 2-4
Table 2-2: Comprehensive grading scheme used during the optimisation of the nile red working
solution formulation (continued on to page 28)25
Table 2-3: Grades assigned* to fingermark quarters in Figure 2-4 using the evaluation scheme
detailed in Table 2-2 27
Table 2-4: A series of three fingermark depletions that have been developed by nile red (left –
images have been inverted) and PD (right) 30
Table 2-5: Donor and deposition methodology used for the investigation of the effect of
deposition force on subsequent PD and Ind-Zn development
Table 2-6: Split natural fingermarks developed with PD (left half) and Ind-Zn (right half; images
have been inverted for comparison purposes) deposited by two donors using deposition forces
necessary to produce a reading of 100 g, 200 g, 500 g and 1000 g on a laboratory balance 39
Table 2-7: Donor and deposition methodology for fingermarks that were exposed to four
different (lipid extraction) solvents and subsequently developed using PD and then NR 46
Table 2-8: Split fingermark depositions developed with PD and NR after solvent exposure to
the left side of the marks. All NR images have been taken in the luminescence mode using 180
ms exposure times
Table 2-9: Development of fingermarks by PD followed by NR that had been washed with
EtOAc for varying lengths of time (left side). Exposure times for NR visualisation were 100-600
ms
Table 2-10: Donor and deposition methodology for the assessment of the effect of residue
derivatisation using two extraction solvents for subsequent GC-MS analysis
Table 2-11: Description of the GC-MS Parameters and temperature program used in this
research

Table 2-12: Spot tests of compounds where the lower half of each sample was extracted with
EtOAc for GC-MS analysis, and both halves developed with PD
Table 3-1: Donor and deposition methodology for nile red working solution evaluation
experiments
Table 3-2: Donor and deposition methodology used in the comparison of the NR-OP and NR-
STD solutions
Table 3-3: Donor and deposition methodology used in the comparison of the NR-OP and NB
solutions72
Table 3-4: Formulation and preparation of NR and NB solutions that were compared by TLC
analysis
Table 3-5: R _f values for samples spotted onto a TLC plate and developed with mobile phase 279
Table 3-6: Formulations of working solution made by Incorporating NB and TB into a NR
microemulsion
Table 2.7. Denon and deposition methodology for the accompany of four working
Table 3-7: Donor and deposition methodology for the assessment of four working
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets
solutions(NR-OP, NB, NR-OP/NB and NR-OP/TB) on natural and groomed quartered fingermark sets

in developing fingermarks when it is aged containing silver nitrate or not 101
Table 4-5: Redox solution formulations analysed by UV-Vis to observe degradation of a PD
working solution not containing a surfactant or silver nitrate
Table 4-6: Donor and deposition methodology used for experiments in for the analysis of the
storage and ageing effects of a PD working solution on subsequent fingermark development
Table 4-7: Age of PD working solutions made with the described surfactant formulations that
were used to investigate the effect of surfactant concentration on the aging of a PD working
solution inclusive of the reference formulation* [2] 108
Table 4-8: Donor and deposition methodology used to assess the effectiveness of different PD
working solutions on fingermarks and synthetic fingermark analogues
Table 4-9: Natural and groomed fingermark samples were compared to stamped deposits of a
Latent Print Standard Pad and SFR to assess the suitability of an SFR as a control for four
different PD working solutions inclusive of the reference formulation* [2] 113
Table 5-1: Donor and deposition methodology used in the assessment of a PD working solution
being propagated by light exposure 120
being propagated by light exposure
Table 5-2: Middle fingermarks from groomed and natural 3-finger depositions developed in PD
Table 5-2: Middle fingermarks from groomed and natural 3-finger depositions developed in PD in normal laboratory lighting conditions (left half of images) and in a photographic darkroom
Table 5-2: Middle fingermarks from groomed and natural 3-finger depositions developed in PD in normal laboratory lighting conditions (left half of images) and in a photographic darkroom (right half of images)
Table 5-2: Middle fingermarks from groomed and natural 3-finger depositions developed in PD in normal laboratory lighting conditions (left half of images) and in a photographic darkroom (right half of images)
Table 5-2: Middle fingermarks from groomed and natural 3-finger depositions developed in PD in normal laboratory lighting conditions (left half of images) and in a photographic darkroom (right half of images)
Table 5-2: Middle fingermarks from groomed and natural 3-finger depositions developed in PD in normal laboratory lighting conditions (left half of images) and in a photographic darkroom (right half of images)
Table 5-2: Middle fingermarks from groomed and natural 3-finger depositions developed in PD in normal laboratory lighting conditions (left half of images) and in a photographic darkroom (right half of images)
Table 5-2: Middle fingermarks from groomed and natural 3-finger depositions developed in PD in normal laboratory lighting conditions (left half of images) and in a photographic darkroom (right half of images) 121 Table 5-3: Donor and deposition methodology for the assessment of PD reactivity with the lipids in fingermark residue 122 Table 5-4: Properties of organic solvents used to wash the fingermark samples, including 124 the solvent [154] 124
Table 5-2: Middle fingermarks from groomed and natural 3-finger depositions developed in PDin normal laboratory lighting conditions (left half of images) and in a photographic darkroom(right half of images)121Table 5-3: Donor and deposition methodology for the assessment of PD reactivity with thelipids in fingermark residue122Table 5-4: Properties of organic solvents used to wash the fingermark samples, includingdipole moment, dielectric constant, solubility of the solvent in water and solubility of water inthe solvent [154]124Table 5-5: Images of spot tests of palmitic acid, cholesterol, stearic acid, squalene and oleic

Table 5-8: Typical amino acid volumes found in a deposited single wet thumb print and aclassification of their polarity [156]133

Table 6-5: Artificial ageing parameters for the top and bottom layers of the synthesised SFRprior to decanting167

Table 6-7: PD and Ind-Zn development on filter paper for the bottom, middle and top layers of emulsions made with varying ratios of synthetic sebum and sweat. PD-developed fingermarks were recorded using an Epson XP-200 A4 flatbed scanner using 2400 DPI resolution. Ind-Zn-developed fingermarks were visualised with a Polilight PL500 forensic light source coupled to a Rofin Poliview IV forensic imaging system (excitation 505 nm with a 555 nm band-pass barrier filter).

Table 6-10: Volumes and concentrations of oleic acid and NaCl used to make each emulsionand the number of layers visible after sonication182

Table 6-11: PD development of layered spot tests using oleic acid (OA) and sodium chloride (NaCl) solutions of varying concentration. Left columns have 5 μ L of NaCl solution pipetted

Table 6-12: Final NaCl concentration of 3 mL NaCl emulsified with 1 mL oleic acid in the emulsion. PD development on 15 μ L spots on RP of the top (left image) and bottom (right image) fractions of emulsions. PD treated samples were recorded using an Epson XP-200 A4 flatbed scanner using 2400 DPI resolution. 185

Table II-1: Description and colour examples for grading fingermarks developed using a
luminescent development technique 203
Table II-2: Gas chromatograms for cholesterol, oleic acid, stearic acid and palmitic acid
extracted from paper using ethyl acetate 209
Table II-3: Gas chromatogram for squalene, stigmasterol, vegetable oil and lanolin extracted
from paper using ethyl acetate 210
Table III-1: Donor and deposition methodology for nile red working solution evaluation
experiments

Table III-3: Grades assigned to developed fingermarks out of 5 for the development of naturalmarks using working solutions containing different organic solvents at four different pH in Trial1. Averages of the three replicates are reported.214

Table III-5: Grades assigned to developed fingermarks out of 5 for the development of natural marks using working solutions with pH 4 (made with HCl), pH 7 (deionised water), pH 9 (made

Table III-7: Grades assigned to developed fingermarks out of 5 for the development of natural marks using working solutions with pH 4 (made with HCl), pH 4 (buffer), pH 7 (deionised water) and pH 7 (buffer) aqueous components with EtOH and IsoP in Trial 3. Averages of the three replicates are reported.

Table III-8: Grades assigned to developed fingermarks out of 5 for the development of groomed marks using working solutions with EtOH compared to the NR-STD formulation, and IsoP compared to the STD formulation in Trial 4. Averages of the three replicates are reported.

Table III-9: Grades assigned to developed fingermarks out of 5 for the development of natural marks using working solutions with EtOH compared to the NR-STD formulation, and IsoP compared to the STD formulation in Trial 4. Averages of the three replicates are reported. 219

Table III-10: Grades assigned to developed fingermarks out of 5 for the development ofgroomed marks comparing EtOH and EtOAc working solution formulations in Trial 5. Averagesof the three replicates are reported.220

 Table III-13: Working solutions 7A–7G prepared using nile red stock solutions of different concentrations in EtOAc.
 222

Table III-14: Grades assigned to developed fingermarks out of 5 for the development ofgroomed marks comparing stock solution nile red concentrations of solutions 7A-7D in Trial 7-1. Averages of the three replicates are reported.223

Table III-15: Grades assigned to developed fingermarks out of 5 for the development of
groomed marks comparing stock solution nile red concentrations of solutions 7D-7G in Trial 7-
2. Averages of the three replicates are reported 223
Table III-16: Solutions compared for developmental effectiveness against the STD solution on
natural and groomed split fingermark samples 224
Table III-17: Solvents assessed for use in nile red stock solutions used to prepare nile red
microemulsions
Table III-18: Working solutions prepared using stock solutions of four different concentrations
of nile red in DCM
Table III-19: Nile red in DCM stock solution (0.01 mg/mL) and surfactant volumes in solutions
used to optimise their volume ratio in a nile red microemulsion containing 25 mL deionised
water 229
Table III-20: Comparison of nile red stock and surfactant ratios on split groomed fingermark
samples using solutions described in Table III-19. Developed fingermark halves were imaged
using the exposure best for each solution
Table III-21: Mobile phases used to separate components on TLC plates 231
Table III-22: TLC plates developed and visualised under various lighting conditions 232
Table V-1: Solution formulations [161], storage conditions and typical appearance for solutions
used in the PD development process

List of figures

Figure 1-1: Development method for physical developer. *This step is not recommended in the
literature [1, 2], however its inclusion stops the PD working solution from becoming too acidic
and destabilising after processing multiple items 8
Figure 1-2: Structure of ORO (Adapted from (Wood and James 2009); Chemsketch 2017) 9
Figure 1-3: ORO fingermark development procedure 10
Figure 1-4: Structure of nile red 11
Figure 2-1: CAST grading scheme for the evaluation of developed fingermarks [100] 21
Figure 2-2: UNIL grading scheme for the assessment of developed fingermarks [101] 22
Figure 2-3: UC grading scheme for the assessment of developed fingermarks [96] 22
Figure 2-4: Four different formulations of a nile red working solution compared using the
quartered fingermark method 24
Figure 2-5: Schematic representation of the deposition of a fingermark depletion series 29
Figure 2-6: Layout of deposited fingermarks when comparing techniques using the quartered
fingermark method 31
Figure 2-7: Split fingermarks developed by different formulations of the same technique. Single
(left) or three finger depositions (right) can be used
Figure 2-8: Fingermark developed by PD (left) followed by nile red (right) on natural and
groomed fingermarks 35
Figure 2-9: Nile red developed fingermarks deposited using deposition forces required to
produce a reading of 100 g (left), 200 g (centre) and 300 g (right) on a laboratory balance 40
Figure 2-10: Compounds in glass-extracted sebaceous fingermark residue detected using
different extraction solvents [113]

Figure 2-11: representative gas Chromatogram of natural fingermark halves (of the same deposition) extracted with DCM (black) and EtOAc (green) with an anthracene internal Figure 2-12: Representative gas chromatogram of groomed fingermark halves (of the same deposition) extracted with DCM (black) and EtOAc (green) with an anthracene internal Figure 3-1: Two synthesised water soluble NR derivatives [5]......63 Figure 3-2: Three NR derivatives synthesised and evaluated for the development of latent fingermarks [4]......63 Figure 3-4: Groomed fingermarks developed by the NR-OP solution (left half) and the NR-STD formulation (right half) at 382 ms (left image - optimal exposure for NR-OP solution) and 163 Figure 3-5: Natural fingermarks developed by the NR-OP formulation (left half) and the NR-STD formulation (right half) at 305 ms (left image – optimal exposure for the NR-STD formulation) Figure 3-6: Colour change observed after addition of the NR stock solution to the surfactant solution with stirring to then produce the NR microemulsion......71 Figure 3-7: Groomed fingermarks developed with NR-OP (left) and NB (right) at 126 ms exposure (optimal for NR-OP)......74 Figure 3-8: Groomed fingermarks developed with NR-OP (left) and NB (right) at 636 ms exposure (optimal for NB)74 Figure 3-9: Natural fingermarks developed with NB (left) and NR-OP (right) at 428 ms exposure (optimal for NR-OP)75 Figure 3-10: Natural fingermarks developed with NB (left) and NR-OP (right) at 1.87 s exposure Figure 3-11: Proposed mechanism for the spontaneous hydrolysis of NB A to NR in aqueous

Figure 3-12: TLC plates developed using mobile phase 2 and visualised at 490 nm excitation with 550 nm bandpass filter (left) and 490 nm excitation with 630 nm band-pass filter (right) 79

Figure 3-13: NB in equilibrium with NR 80

Figure 4-11: Groomed (left) and natural (right) quartered fingermark samples developed using PD-P (4 day old PD solution made with surfactant containing 3 g n-DDAA, 3 g Tween 20, 1 L DI H₂O) (top left), PD-Q (4 day old PD solution made with surfactant containing 1.5 g n-DDAA, 1.5 g Tween 20, 1 L DI H₂O) (top right), PD-R (4 day old PD solution made with surfactant containing 6 g n-DDAA, 6 g Tween 20, 1 L DI H₂O) (bottom left) and PD-S (4 month old PD solution made with surfactant containing 3 g n-DDAA, 3 g Tween 20, 1 L DI H₂O) (bottom right).

Figure II-5: Gas chromatogram of a natural 3-finger deposition (black) and a groomed 3-finger deposition (green) extracted with DCM containing an anthracene internal standard (peak at 14.03 min). Depositions were made from the same donor within 5 minutes of each other... 208

Figure III-1: Method of processing used for assessment of different nile red formulations.... 211

Figure III-2: Quartered fingermark layout to compare four different working solutions....... 212

Figure III-3: Split fingermark sample developed by solution 11-1 (left) and solution 11-2 (right)

Figure III-4: Split fingermark sample developed by solution 11-2 (left) and solution 11-3 (right)

Figure III-5: Split fingermark sample developed by solution 11-3 (left) and solution 11-4 (right)

Figure	IV-1:	UV-Vis	spectrum	of	redox	solution	2	overlaid	with	its	individual	solution
compo	nents						••••			•••••		233
Figure	IV-2:	UV-Vis	spectrum	of	redox	solution	3	overlaid	with	its	individual	solution
compo	nents									•••••		234
Figuro	N/ 2.		cip o otru ino	of	rodov	colution	Λ	overlaid	wi+b	ite	individual	colution
-											individual	
compo	nents			•••••			••••			•••••		234
Figure	\/ 1. т .		used for de	wol	onmon	mathada	. 1	and 2 for	חח			220
ingule	v-т. П	ays 1-5	useu IUI ue	ven	opmen	linethous	т	anu 2 101	г <i>D</i>	•••••	•••••	

Research communication

Publications

<u>de la Hunty, M</u>., Moret, S., Chadwick, S., Lennard, C., Spindler, X., and Roux, C., *Understanding physical developer (PD): Part I – Is PD targeting lipids?* Forensic Science International, 2015. 257: p. 481-487

<u>de la Hunty, M</u>., Moret, S., Chadwick, S., Lennard, C., Spindler, X., and Roux, C., Understanding *Physical Developer (PD): Part II – Is PD targeting eccrine constituents?* Forensic Science International, 2015. 257: p. 488-495.

<u>de la Hunty, M</u>., Spindler, X., Chadwick, S., Lennard, C., and Roux, C., *Synthesis and application of an aqueous nile red microemulsion for the development of fingermarks on porous surfaces.* Forensic Science International, 2014. 244: p. e48-e55.

Conferences

Oral presentation at the 23rd International Symposium on the Forensic Sciences held by the Australian and New Zealand Forensic Science Society (ANZFSS) in Auckland, New Zealand–September 2016

Oral presentation ANZFSS NSW Branch Meeting - Australian Museum – Sydney, Australia – August 2016

Oral presentation at the UTS Science Research Day 5MT competition – December 2015 (Awarded Best Presentation)

Oral presentation at 7th European Academy of Forensic Science Conference in Prague, Czech Republic – September 2015

Oral presentation at 22nd International Symposium on the Forensic Sciences held by the Australian and New Zealand Forensic Science Society (ANZFSS) in Adelaide, Australia–September 2014 (Awarded Best Oral Presentation in the Fingerprint Examination discipline)

Oral presentation at the University of Technology Sydney – University of Canberra Forensic Conference in Sydney, Australia– July 2014

Oral presentation at the University of Technology Sydney – University of Canberra Forensic Conference in Canberra, Australia– July 2013

Podcasts/ Exhibitions

Double Loop Podcast – Episode 140 (Interview with Glenn Langenburg and Eric Ray) - Released January 2017

Interactive installation and oral presentation of PhD research at the University of Technology Sydney Library – UTS Science Week – August 2016