

**RAMAN SPECTROSCOPY**  
**FOR THE FORENSIC EXAMINATION**  
**OF REACTIVELY DYED**  
**COTTON**

by

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A thesis

submitted as requirement for the  
degree of Doctor of Philosophy (Science)

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Faculty of Science

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## Certificate of Authorship and Originality

I certify that the work in this thesis has not been previously submitted for a degree nor has been submitted as part of the requirements for a degree except as fully acknowledged in 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 the information sources and literature used are indicated in the thesis.

**Production Note:**

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Jane Thomas

31<sup>st</sup> October 2005

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# Table of Contents

|                                                        |              |
|--------------------------------------------------------|--------------|
| <b>LIST OF FIGURES.....</b>                            | <b>V</b>     |
| <b>LIST OF TABLES.....</b>                             | <b>XII</b>   |
| <b>LIST OF EQUATIONS.....</b>                          | <b>XVI</b>   |
| <b>LIST OF ABBREVIATIONS .....</b>                     | <b>XVII</b>  |
| <b>ABSTRACT .....</b>                                  | <b>XVIII</b> |
| <b>CHAPTER 1: INTRODUCTION.....</b>                    | <b>1</b>     |
| 1.0 SUMMARY .....                                      | 1            |
| 1.1 TEXTILES.....                                      | 1            |
| 1.1.1 <i>History and Classification</i> .....          | 2            |
| 1.1.2 <i>World Fibre Production</i> .....              | 4            |
| 1.1.3 <i>Cotton Fibres and Forensic Science</i> .....  | 6            |
| 1.2 DYES .....                                         | 7            |
| 1.2.1 <i>History of Dyes</i> .....                     | 8            |
| 1.2.3 <i>Production Statistics</i> .....               | 15           |
| 1.3 TEXTILES AS FORENSIC EVIDENCE .....                | 16           |
| 1.3.1 <i>How Fibres Come to be Evidence</i> .....      | 19           |
| 1.3.2 <i>Prevalence and Importance of Fibres</i> ..... | 21           |
| 1.3.3 <i>History of Fibre Examinations</i> .....       | 22           |
| 1.4 COLLECTION OF FIBRES.....                          | 23           |
| 1.5 ANALYSIS OF FIBRES .....                           | 24           |
| 1.5.1 <i>Identification</i> .....                      | 25           |
| 1.5.2 <i>Comparison</i> .....                          | 28           |
| 1.6 INTERPRETATION OF FIBRE EVIDENCE.....              | 31           |
| 1.6.1 <i>Fibre Frequency and Trends</i> .....          | 33           |
| 1.6.2 <i>Bayesian Analysis/Inference</i> .....         | 37           |
| 1.7 RESEARCH AND FIBRE EXAMINATIONS .....              | 39           |
| 1.7.1 <i>Research into in-situ Dye Analysis</i> .....  | 40           |
| <b>CHAPTER 2: RAMAN SPECTROSCOPY .....</b>             | <b>42</b>    |
| 2.0 SUMMARY .....                                      | 42           |
| 2.1 THEORY.....                                        | 42           |
| 2.2 HISTORY AND DEVELOPMENTS .....                     | 46           |
| 2.3 RAMAN SIGNAL ENHANCEMENT .....                     | 52           |
| 2.3.1 <i>Resonance Raman Scattering (RR)</i> .....     | 52           |

|                                                     |                                                                     |           |
|-----------------------------------------------------|---------------------------------------------------------------------|-----------|
| 2.3.2                                               | <i>Surface Enhanced Raman Scattering (SERS)</i> .....               | 52        |
| 2.3.3                                               | <i>Surface Enhance Resonance Raman Scattering (SERRS)</i> .....     | 52        |
| 2.4                                                 | RAMAN SPECTROSCOPY RESEARCH .....                                   | 53        |
| 2.4.1                                               | <i>Raman and Forensic Samples</i> .....                             | 53        |
| 2.4.2                                               | <i>Raman and Dyes/Pigments</i> .....                                | 54        |
| 2.4.3                                               | <i>Raman and Fibres</i> .....                                       | 55        |
| 2.4.4                                               | <i>Raman Spectroscopy and the European Fibres Group (EFG)</i> ..... | 56        |
| <b>CHAPTER 3: DIRECTION AND AIMS</b> .....          |                                                                     | <b>58</b> |
| 3.0                                                 | SUMMARY .....                                                       | 58        |
| 3.1                                                 | SAMPLE SELECTION.....                                               | 60        |
| 3.1.1                                               | <i>Fibre Type and Colour</i> .....                                  | 60        |
| 3.1.2                                               | <i>Dye Type</i> .....                                               | 61        |
| 3.2                                                 | OPTIMISATION OF METHODOLOGY .....                                   | 64        |
| 3.3                                                 | COMPARISON OF RAMAN SPECTROSCOPY AND MICROSPECTROPHOTOMETRY .....   | 65        |
| 3.4                                                 | USE OF CHEMOMETRICS FOR RAMAN SPECTRAL DATA.....                    | 65        |
| 3.5                                                 | LIBRARY OF COMMON REACTIVE DYES .....                               | 66        |
| <b>CHAPTER 4: OPTIMISATION OF METHODOLOGY</b> ..... |                                                                     | <b>67</b> |
| 4.0                                                 | SUMMARY .....                                                       | 67        |
| 4.1                                                 | INTRODUCTION.....                                                   | 67        |
| 4.1.1                                               | <i>Fluorescence</i> .....                                           | 68        |
| 4.1.2                                               | <i>Changing Laser Wavelength to Overcome Fluorescence</i> .....     | 71        |
| 4.1.3                                               | <i>Effect of Mounting Conditions</i> .....                          | 74        |
| 4.2                                                 | AIMS .....                                                          | 76        |
| 4.3                                                 | MATERIALS AND METHODS.....                                          | 76        |
| 4.3.1                                               | <i>General</i> .....                                                | 76        |
| 4.3.2                                               | <i>Samples</i> .....                                                | 77        |
| 4.3.3                                               | <i>Raman Microprobe Conditions</i> .....                            | 77        |
| 4.3.4                                               | <i>Microspectrophotometer Conditions</i> .....                      | 78        |
| 4.3.5                                               | <i>Experiments</i> .....                                            | 79        |
| 4.3.6                                               | <i>Data Treatment</i> .....                                         | 81        |
| 4.4                                                 | RESULTS AND DISCUSSION .....                                        | 84        |
| 4.4.1                                               | <i>Mounting Variations</i> .....                                    | 84        |
| 4.4.2                                               | <i>Dye Analysis</i> .....                                           | 88        |
| 4.4.3                                               | <i>Sample Degradation</i> .....                                     | 90        |
| 4.4.4                                               | <i>Fluorescence</i> .....                                           | 92        |
| 4.4.5                                               | <i>Microspectrophotometry</i> .....                                 | 95        |
| 4.4.6                                               | <i>Varying the Laser Wavelength</i> .....                           | 97        |

|                                                            |                                                              |            |
|------------------------------------------------------------|--------------------------------------------------------------|------------|
| 4.5                                                        | CONCLUSIONS .....                                            | 106        |
| <b>CHAPTER 5: COMPARISON OF RAMAN SPECTROSCOPY AND</b>     |                                                              |            |
| <b>MICROSPECTROPHOTOMETRY .....</b>                        |                                                              | <b>109</b> |
| 5.0                                                        | SUMMARY .....                                                | 109        |
| 5.1                                                        | INTRODUCTION .....                                           | 110        |
| 5.1.1                                                      | <i>Raman Spectroscopy for Pigments</i> .....                 | 112        |
| 5.1.2                                                      | <i>Raman Spectroscopy for Undyed Fibres</i> .....            | 113        |
| 5.1.3                                                      | <i>Raman Spectroscopy and Coloured Man-made Fibres</i> ..... | 113        |
| 5.1.4                                                      | <i>Raman Spectroscopy and Dyed Natural Fibres</i> .....      | 114        |
| 5.2                                                        | AIMS .....                                                   | 115        |
| 5.3                                                        | MATERIALS AND METHODS.....                                   | 116        |
| 5.3.1                                                      | <i>General</i> .....                                         | 116        |
| 5.3.2                                                      | <i>Samples</i> .....                                         | 116        |
| 5.3.3                                                      | <i>Raman Microprobe Conditions</i> .....                     | 120        |
| 5.3.4                                                      | <i>Microspectrophotometer Conditions</i> .....               | 120        |
| 5.3.5                                                      | <i>Experiments</i> .....                                     | 121        |
| 5.3.6                                                      | <i>Data Treatment</i> .....                                  | 123        |
| 5.4                                                        | RESULTS AND DISCUSSION .....                                 | 124        |
| 5.4.1                                                      | <i>Known Sample Set</i> .....                                | 124        |
| 5.4.2                                                      | <i>Unknown Sample Set</i> .....                              | 144        |
| 5.5                                                        | CONCLUSIONS .....                                            | 162        |
| <b>CHAPTER 6: CHEMOMETRICS OF RAMAN SPECTRAL DATA.....</b> |                                                              | <b>163</b> |
| 6.0                                                        | SUMMARY .....                                                | 163        |
| 6.1                                                        | INTRODUCTION .....                                           | 163        |
| 6.1.1                                                      | <i>Principal Components Analysis (PCA)</i> .....             | 165        |
| 6.1.2                                                      | <i>Linear Discriminant Analysis (LDA)</i> .....              | 167        |
| 6.2                                                        | AIMS .....                                                   | 169        |
| 6.3                                                        | MATERIALS AND METHODS.....                                   | 170        |
| 6.3.1                                                      | <i>General</i> .....                                         | 170        |
| 6.3.2                                                      | <i>Samples</i> .....                                         | 170        |
| 6.3.3                                                      | <i>Raman Microprobe Conditions</i> .....                     | 171        |
| 6.3.4                                                      | <i>Experiments</i> .....                                     | 171        |
| 6.3.5                                                      | <i>Data Treatment</i> .....                                  | 172        |
| 6.4                                                        | RESULTS AND DISCUSSION .....                                 | 175        |
| 6.4.1                                                      | <i>Known Sample Set</i> .....                                | 175        |
| 6.4.2                                                      | <i>Unknown Sample Set</i> .....                              | 190        |
| 6.5                                                        | CONCLUSIONS .....                                            | 194        |

|                                                                      |            |
|----------------------------------------------------------------------|------------|
| <b>CHAPTER 7: RAMAN SPECTROSCOPY FOR FORENSIC FIBRE EXAMINATIONS</b> |            |
| <b>– DISCUSSION, CONCLUSIONS AND FUTURE DIRECTIONS.....</b>          | <b>195</b> |
| 7.1 DISCUSSION.....                                                  | 195        |
| 7.2 FUTURE DIRECTIONS.....                                           | 199        |
| 7.3 CONCLUSIONS .....                                                | 200        |
| <b>APPENDIX 1: LIBRARY OF REACTIVE DYES .....</b>                    | <b>203</b> |
| <b>CHAPTER 8: REFERENCES .....</b>                                   | <b>228</b> |

## List of Figures

|                                                                                                                               |    |
|-------------------------------------------------------------------------------------------------------------------------------|----|
| FIGURE 1-1 CLASSIFICATION AND SUB-CLASSIFICATION OF FIBRES [15] .....                                                         | 3  |
| FIGURE 1-2 CONVERSION OF FIBRES TO FINISHED PRODUCT (GARMENT) .....                                                           | 4  |
| FIGURE 1-3 WORLD PRODUCTION OF FIBRES IN 2002 [19] .....                                                                      | 5  |
| FIGURE 1-4 ELECTROMAGNETIC SPECTRUM WITH VISIBLE LIGHT DETAIL [26] .....                                                      | 7  |
| FIGURE 1-5 STRUCTURE OF TYRIAN PURPLE .....                                                                                   | 8  |
| FIGURE 1-6 AN AZO DYE - CI ACID ORANGE 7 .....                                                                                | 10 |
| FIGURE 1-7 EXAMPLES OF RED REACTIVE DYES [29, 30] .....                                                                       | 13 |
| FIGURE 1-8 RED DYE CREATED DURING FIRST STEP OF REACTIVE BLACK 5 MANUFACTURE .....                                            | 14 |
| FIGURE 1-9 BISAZO CI REACTIVE BLACK 5 IN ITS PURE FORM .....                                                                  | 15 |
| FIGURE 1-10 T-SHIRT SHOWING VARIATIONS DUE TO NORMAL WEAR AND TEAR (UV LIGHT<br>DAMAGE INDICATED BY AREAS CIRCLED) [33] ..... | 17 |
| FIGURE 1-11 EXAMPLES OF (LEFT) FIBRE PLASTIC FUSION, AND (RIGHT) PLASTIC COATING MARK<br>(REPRINTED FROM [34]) .....          | 18 |
| FIGURE 1-12 PROCEDURE FOR THE COLLECTION AND EXAMINATION OF HAIRS AND FIBRES [61] ..                                          | 25 |
| FIGURE 1-13 FLOW CHART SHOWING SCHEME OF FIBRE IDENTIFICATION [62] .....                                                      | 26 |
| FIGURE 1-14 FLOW CHART SHOWING SCHEME OF FIBRE ANALYSIS/COMPARISON [62] .....                                                 | 29 |
| FIGURE 1-15 FACTORS AFFECTING THE EVIDENTIAL VALUE OF FIBRES [16] .....                                                       | 32 |
| FIGURE 1-16 DATA CONSIDERED FOR INTERPRETATION OF FIBRE EVIDENCE [52] .....                                                   | 33 |
| FIGURE 2-1 SCHEMATIC OF THE RAMAN EFFECT SHOWING RAMAN AND RAYLEIGH SCATTERING<br>(ADAPTED FROM [114]) .....                  | 43 |
| FIGURE 2-2 ORIGIN OF RAYLEIGH AND RAMAN SCATTERING, ADAPTED FROM [113] .....                                                  | 45 |
| FIGURE 2-3 RAMAN SPECTRUM FOR CCL <sub>4</sub> , FROM [113] .....                                                             | 46 |
| FIGURE 2-4 TIMELINE OF ADVANCES IN RAMAN INSTRUMENTATION AND THEORY [118, 119] .....                                          | 47 |
| FIGURE 2-5 THE 'RENISHAW' RAMAN SPECTROSCOPY SYSTEM 2000, EXTERNAL VIEW [130] .....                                           | 50 |
| FIGURE 2-6 SCHEMATIC OF RENISHAW 2000 SYSTEM [128] .....                                                                      | 51 |
| FIGURE 3-1 SCHEMATIC REPRESENTATION OF THE COMPONENTS OF A TYPICAL BI-FUNCTIONAL DYE<br>WITH REACTIVE GROUPS .....            | 63 |
| FIGURE 3-2 PRINCIPLE OF COTTON DYING WITH TRIAZYL REACTIVE DYE .....                                                          | 63 |
| FIGURE 4-1 ORIGIN OF RAYLEIGH AND RAMAN SCATTERING, ADAPTED FROM [113] .....                                                  | 69 |
| FIGURE 4-2 SIMPLIFIED <i>JABLONSKI DIAGRAM</i> SHOWING FLUORESCENCE .....                                                     | 69 |
| FIGURE 4-3 SPECIALLY CONSTRUCTED CELL USED BY BOURGEOIS AND CHURCH [168] .....                                                | 75 |
| FIGURE 4-4 FIBRE MOUNTED ON DOUBLE SIDED TAPE .....                                                                           | 79 |
| FIGURE 4-5 FIBRE MOUNTED IN XAM BENEATH A GLASS COVERSIP .....                                                                | 79 |

|                                                                                                                                                                                                   |     |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| FIGURE 4-6 EXAMPLE OF: 1-NO SPECTRA DUE TO FLUORESCENCE.....                                                                                                                                      | 82  |
| FIGURE 4-7 EXAMPLE OF: 2- SOME SPECTRAL DETAILS WITH LARGE AMOUNTS OF FLUORESCENCE<br>.....                                                                                                       | 82  |
| FIGURE 4-8 EXAMPLE OF: 3- GOOD SPECTRAL DETAILS WITH SOME FLUORESCENCE .....                                                                                                                      | 83  |
| FIGURE 4-9 EXAMPLE OF: 4- EXCELLENT SPECTRAL DETAILS WITH LITTLE TO NO FLUORESCENCE                                                                                                               | 83  |
| FIGURE 4-10 RAMAN SPECTRUM OF DYED FIBRE WITH NO COVERING (METHOD (I)) .....                                                                                                                      | 84  |
| FIGURE 4-11 RAMAN SPECTRA OF: (TOP) XAM THROUGH GLASS COVERSIP, (MIDDLE) XAM, AND<br>(BOTTOM) GLASS COVERSIP.....                                                                                 | 85  |
| FIGURE 4-12 RAMAN SPECTRA OF: (TOP) BLACK COTTON THROUGH GLASS COVERSIP (MOUNTED<br>IN XAM), AND (BOTTOM) BLACK COTTON SAMPLE (NO COVERING).....                                                  | 86  |
| FIGURE 4-13 RAMAN SPECTRA OF (TOP) BLACK COTTON MOUNTED (GLASS AND MOUNTANT<br>SUBTRACTION), AND (BOTTOM) BLACK COTTON NO COVERING OR MOUNTANT .....                                              | 87  |
| FIGURE 4-14 SPECTRAL SUBTRACTION FROM MILLER AND BARTICK [111] - ARROWS IN SPECTRUM<br>C INDICATE ARTEFACT PEAKS .....                                                                            | 88  |
| FIGURE 4-15 SAMPLE MOUNTING VARIATIONS (632.8NM LASER). TOP SPECTRUM: SYNAZOL GOLD -<br>YELLOW DILUTED AND DRIED ON ALUMINIUM SLIDE. BOTTOM SPECTRUM: SYNAZOL GOLD -<br>YELLOW DYE PARTICLE ..... | 89  |
| FIGURE 4-16 RAMAN SPECTRUM OF CARBON (FROM CARBON NANOTUBES) [179].....                                                                                                                           | 90  |
| FIGURE 4-17 IMAGES (USING RENISHAW INSTRUMENT IMAGING) OF SAMPLE A1 AT (TOP) TIME = 0<br>AND (BOTTOM) LASER =100%, 20 X ACCUMULATIONS OF 20 SECONDS.....                                          | 91  |
| FIGURE 4-18 RAMAN SPECTRA OF (TOP) A1 SAMPLE 100% LASER AND 1 ACCUMULATION OF 20<br>SECONDS (BOTTOM) A1 SAMPLE 100% LASER AND 25 ACCUMULATION OF 20 SECONDS .....                                 | 92  |
| FIGURE 4-19 RAMAN SPECTRUM OF FIBRE - UNDYED COTTON AT 514.5NM SHOWING SIGNAL<br>SWAMPING DUE TO FLUORESCENCE.....                                                                                | 93  |
| FIGURE 4-20 RAMAN SPECTRUM AT 514.5NM OF MOROCCAN BLUE FIBRE. SOME SAMPLE SIGNAL<br>ABOVE THE FLUORESCENCE (BOXED AREA) .....                                                                     | 94  |
| FIGURE 4-21 RAMAN SPECTRUM OF FIBRE MOROCCAN BLUE AT 514.5NM, BASELINE CORRECTED                                                                                                                  | 94  |
| FIGURE 4-22 VIS-MICROSPECTROPHOTOMETRY (SEE 2100) RESULTS FOR (FROM LEFT) SYNAZOL<br>GOLD-YELLOW, SYNAZOL RED, SUMIFIX NAVY AND DYED FIBRE MOROCCAN BLUE.....                                     | 96  |
| FIGURE 4-23 ANALYSIS OF SUMIFIX NAVY DYE WITH (FROM TOP) 514.5NM, 632.8NM, 785NM AND<br>830NM LASER SOURCES.....                                                                                  | 98  |
| FIGURE 4-24 ANALYSIS OF SYNAZOL GOLD-YELLOW DYE WITH (FROM TOP) 514.5NM, 632.8NM,<br>785NM AND 830NM LASER SOURCES .....                                                                          | 99  |
| FIGURE 4-25 RAMAN SPECTRA AT 514.5NM ANALYSIS OF (FROM TOP) DYED FIBRE - MOROCCAN<br>BLUE, SUMIFIX NAVY DYE, SYNAZOL GOLD-YELLOW DYE AND SYNAZOL RED DYE .....                                    | 100 |
| FIGURE 4-26 RAMAN SPECTRA AT 632.8NM ANALYSIS OF (FROM TOP) DYED FIBRE - MOROCCAN<br>BLUE, SUMIFIX NAVY DYE, SYNAZOL GOLD-YELLOW DYE AND SYNAZOL RED DYE .....                                    | 101 |

|                                                                                                                                                                                                                   |     |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| FIGURE 4-27 RAMAN SPECTRA 685NM ANALYSIS OF (FROM TOP) DYED FIBRE - MOROCCAN BLUE, SYNAZOL GOLD-YELLOW DYE, SYNAZOL RED DYE AND SUMIFIX NAVY DYE.....                                                             | 102 |
| FIGURE 4-28 RAMAN SPECTRA FROM 785NM ANALYSIS OF (FROM TOP) DYED FIBRE - MOROCCAN BLUE, SUMIFIX NAVY DYE, SYNAZOL GOLD-YELLOW DYE AND SYNAZOL RED DYE .....                                                       | 103 |
| FIGURE 4-29 RAMAN SPECTRA FROM 830NM ANALYSIS OF (FROM TOP) DYED FIBRE - MOROCCAN BLUE, SUMIFIX NAVY DYE, SYNAZOL GOLD-YELLOW DYE AND SYNAZOL RED DYE .....                                                       | 104 |
| FIGURE 4-30 RAMAN SPECTRA FROM 785NM ANALYSIS OF (FROM TOP) DYED FIBRE – MOROCCAN BLUE, BLUE DYE - SUMIFIX NAVY BLUE AND COTTON .....                                                                             | 104 |
| FIGURE 5-1 COMPARISON OF A PIGMENTED FIBRE BY (TOP) RAMAN SPECTROSCOPY - SPECTRA INVERTED AND (BOTTOM) IR SPECTROSCOPY [171] .....                                                                                | 114 |
| FIGURE 5-2 RAMAN SPECTRA (785NM LASER) OF (TOP) SAMPLE 31 AND ITS THREE COMPONENT DYES SYNAZOL BLACK B (2 <sup>ND</sup> ), SYNAZOL GOLD-YELLOW HF 2GR (3 <sup>RD</sup> ), AND SYNAZOL RED HF 6BN (BOTTOM) .....   | 124 |
| FIGURE 5-3 RAMAN SPECTRA (632.8NM LASER) OF SAMPLE 31 (TOP) AND ITS THREE COMPONENT DYES SYNAZOL BLACK B (2 <sup>ND</sup> ), SYNAZOL GOLD-YELLOW HF 2GR (3 <sup>RD</sup> ), AND SYNAZOL RED HF 6BN (BOTTOM) ..... | 125 |
| FIGURE 5-4 RAMAN SPECTRA (785NM LASER) OF (TOP) SAMPLE 14, (MIDDLE) SAMPLE 25 AND (BOTTOM) SAMPLE 40 - EACH CONTAINING DYE SYNAZOL BLACK B .....                                                                  | 126 |
| FIGURE 5-5 RAMAN SPECTRA (632.8NM LASER) OF (TOP) SAMPLE 14, (MIDDLE) SAMPLE 25 AND (BOTTOM) SAMPLE 40 - EACH CONTAINING DYE: SYNAZOL BLACK B .....                                                               | 126 |
| FIGURE 5-6 RAMAN SPECTRA (785NM LASER) OF CIBACRON NAVY LSN (TOP), AND CIBACRON BLACK LSN (BOTTOM) .....                                                                                                          | 127 |
| FIGURE 5-7 RAMAN SPECTRA (632.8NM LASER) OF CIBACRON NAVY LSN (TOP), AND CIBACRON BLACK LSN (BOTTOM) .....                                                                                                        | 128 |
| FIGURE 5-8 RAMAN SPECTRA (785NM LASER) OF (TOP) SAMPLE 32, (2 <sup>ND</sup> ) CIBACRON BLUE LSBR, (3 <sup>RD</sup> ) CIBACRON RED LSB, AND (BOTTOM) CIBACRON ORANGE LSBR .....                                    | 129 |
| FIGURE 5-9 RAMAN SPECTRA (785NM LASER) OF (TOP) SAMPLE 35 (2 <sup>ND</sup> ) CIBACRON BLUE LSBR (3 <sup>RD</sup> ) CIBACRON RED LSB, AND (BOTTOM) CIBACRON ORANGE LSBR .....                                      | 130 |
| FIGURE 5-10 RAMAN SPECTRA (785NM LASER) OF (TOP) SAMPLE 35, (MIDDLE) COTTON, AND (BOTTOM) SAMPLE 32 .....                                                                                                         | 131 |
| FIGURE 5-11 RAMAN SPECTRA (632.8NM LASER) OF (TOP) SAMPLE 32, (2 <sup>ND</sup> ) CIBACRON BLUE LSBR, (3 <sup>RD</sup> ) CIBACRON RED LSB, AND (BOTTOM) CIBACRON ORANGE LSBR .....                                 | 132 |
| FIGURE 5-12 RAMAN SPECTRA (632.8NM LASER) OF (TOP) SAMPLE 35, (2 <sup>ND</sup> ) CIBACRON BLUE LSBR, (3 <sup>RD</sup> ) CIBACRON RED LSB, AND (BOTTOM) CIBACRON ORANGE LSBR .....                                 | 132 |
| FIGURE 5-13 RAMAN SPECTRA (785NM LASER) OF (RED) SAMPLE 39, AND (BLUE) SAMPLE 38....                                                                                                                              | 133 |
| FIGURE 5-14 RAMAN SPECTRA (RED) SAMPLE 14 (LIGHT BLUE) SAMPLE 31 (PURPLE) SAMPLE 25, AND (BLUE) SAMPLE 40 - 785NM .....                                                                                           | 134 |
| FIGURE 5-15 RAMAN SPECTRUM OF SAMPLE 1 - 785NM .....                                                                                                                                                              | 134 |

|                                                                                                                              |     |
|------------------------------------------------------------------------------------------------------------------------------|-----|
| FIGURE 5-16 RAMAN SPECTRUM OF SAMPLE 35 - 785NM .....                                                                        | 135 |
| FIGURE 5-17 RAMAN SPECTRUM OF SAMPLE 32 - 785NM .....                                                                        | 135 |
| FIGURE 5-18 RAMAN SPECTRA OF (RED) SAMPLE 39, AND (BLUE) SAMPLE 38 - 632.8NM .....                                           | 136 |
| FIGURE 5-19 RAMAN SPECTRA (RED) SAMPLE 14 (LIGHT BLUE) SAMPLE 31 (PURPLE) SAMPLE 25,<br>AND (BLUE) SAMPLE 40 - 632.8NM ..... | 137 |
| FIGURE 5-20 RAMAN SPECTRUM OF SAMPLE 1 - 632.8NM .....                                                                       | 137 |
| FIGURE 5-21 RAMAN SPECTRA OF SAMPLE 32 (GREEN) AND SAMPLE 35 (RED) - 632.8NM .....                                           | 138 |
| FIGURE 5-22 VIS-MSP SPECTRUM OF SAMPLE 39 .....                                                                              | 139 |
| FIGURE 5-23 VIS-MSP SPECTRUM OF SAMPLE 25 .....                                                                              | 139 |
| FIGURE 5-24 VIS-MSP SPECTRUM OF SAMPLE 14 .....                                                                              | 140 |
| FIGURE 5-25 VIS-MSP SPECTRA OF SAMPLES 32, 35 AND 38 .....                                                                   | 140 |
| FIGURE 5-26 VIS-MSP SPECTRUM OF SAMPLE 1 .....                                                                               | 141 |
| FIGURE 5-27 VIS-MSP SPECTRUM OF SAMPLE 18 .....                                                                              | 141 |
| FIGURE 5-28 VIS-MSP SPECTRUM OF SAMPLE 20 .....                                                                              | 142 |
| FIGURE 5-29 FLOWCHART OF SAMPLE DISCRIMINATION USING RAMAN SPECTROSCOPY THEN VIS-<br>MSP .....                               | 143 |
| FIGURE 5-30 FLOWCHART OF SAMPLE DISCRIMINATION USING VIS-MSP THEN RAMAN<br>SPECTROSCOPY .....                                | 143 |
| FIGURE 5-31 FREQUENCIES OF THE SEVEN DIFFERENT SPECTRAL CATEGORIES (RAMAN) .....                                             | 144 |
| FIGURE 5-32 EXAMPLE RAMAN SPECTRUM FROM GROUP I .....                                                                        | 145 |
| FIGURE 5-33 EXAMPLE RAMAN SPECTRUM FROM GROUP II .....                                                                       | 146 |
| FIGURE 5-34 EXAMPLE RAMAN SPECTRUM FROM GROUP IV .....                                                                       | 147 |
| FIGURE 5-35 EXAMPLE RAMAN SPECTRUM FROM GROUP V .....                                                                        | 148 |
| FIGURE 5-36 EXAMPLE RAMAN SPECTRUM FROM GROUP VI .....                                                                       | 149 |
| FIGURE 5-37 FREQUENCIES OF THE EIGHT DIFFERENT SPECTRAL CATEGORIES (MSP) .....                                               | 150 |
| FIGURE 5-38 EXAMPLE UV/VIS-MSP SPECTRUM FROM GROUP A .....                                                                   | 151 |
| FIGURE 5-39 EXAMPLE UV/VIS-MSP SPECTRUM FROM GROUP B .....                                                                   | 151 |
| FIGURE 5-40 EXAMPLE UV/VIS-MSP SPECTRUM FROM GROUP C .....                                                                   | 152 |
| FIGURE 5-41 EXAMPLE UV/VIS-MSP SPECTRUM FROM GROUP D .....                                                                   | 152 |
| FIGURE 5-42 EXAMPLE UV/VIS-MSP SPECTRUM FROM GROUP E .....                                                                   | 153 |
| FIGURE 5-43 EXAMPLE UV/VIS-MSP SPECTRUM FROM GROUP F .....                                                                   | 153 |
| FIGURE 5-44 EXAMPLE UV/VIS-MSP SPECTRUM FROM GROUP G .....                                                                   | 154 |
| FIGURE 5-45 RAMAN SPECTRAL SUB-CLASSES IN MSP GROUP A .....                                                                  | 156 |
| FIGURE 5-46 RAMAN SPECTRAL SUB-CLASSES IN MSP GROUP B .....                                                                  | 156 |
| FIGURE 5-47 RAMAN SPECTRAL SUB-CLASSES IN MSP GROUP C .....                                                                  | 157 |
| FIGURE 5-48 RAMAN SPECTRAL SUB-CLASSES IN MSP GROUP D .....                                                                  | 158 |
| FIGURE 5-49 RAMAN SPECTRAL SUB-CLASSES IN MSP GROUP E .....                                                                  | 158 |
| FIGURE 5-50 RAMAN SPECTRAL SUB-CLASSES IN MSP GROUP F .....                                                                  | 159 |

|                                                                                                                                                                                                                                          |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| FIGURE 5-51 RAMAN SPECTRAL SUB-CLASSES IN MSP GROUP G.....                                                                                                                                                                               | 159 |
| FIGURE 5-52 RAMAN SPECTRAL SUB-CLASSES IN MSP GROUP H.....                                                                                                                                                                               | 160 |
| FIGURE 5-53 SUGGESTED ANALYSIS SEQUENCE OF KNOWN AND EXTRANEIOUS FIBRES;<br>INCORPORATING RAMAN SPECTROSCOPY .....                                                                                                                       | 161 |
| FIGURE 6-1 ILLUSTRATION OF A DATA VECTOR, $R_i$ [184] .....                                                                                                                                                                              | 165 |
| FIGURE 6-2 RAMAN SPECTRA OF 785NM ANALYSIS OF (FROM TOP) DYED FIBRE - MOROCCAN BLUE,<br>SUMIFIX NAVY DYE, SYNAZOL GOLD-YELLOW DYE AND SYNAZOL RED DYE. RED BOX<br>INDICATES APPROXIMATE AREA OF INTEREST AFTER SPECTRAL TRUNCATION ..... | 173 |
| FIGURE 6-3 RAMAN SPECTRA (FIVE REPEATS) OF SAMPLE 14 SHOWING MULTIPLICATIVE AND<br>BASELINE EFFECTS .....                                                                                                                                | 174 |
| FIGURE 6-4 RAMAN SPECTRA FROM SAMPLE 14 AFTER SPECTRAL TRUNCATION .....                                                                                                                                                                  | 174 |
| FIGURE 6-5 SPECTRA OF (TOP) SAMPLE 35 AND (BOTTOM) SAMPLE 32, FROM CHAPTER 5. RED BOX<br>INDICATES TRUNCATED AREA USED FOR PCA ANALYSIS. ....                                                                                            | 176 |
| FIGURE 6-6 SCREE PLOT OF PRINCIPAL COMPONENTS FOR SAMPLES 32 AND 35 SHOWING MAJORITY<br>OF VARIATION IS ACCOUNTED FOR IN THE FIRST FOUR PRINCIPAL COMPONENTS (PC1-PC4)<br>.....                                                          | 177 |
| FIGURE 6-7 SCREE PLOT SHOWING THE KAISER CRITERION CUT-OFF (AT THE <i>EIGENVALUE</i> OF 1,<br>THEREBY USING 4 FACTORS) AND THE CATTELL'S SCREE TEST (CUT-OFF AT 2.5 <i>EIGENVALUE</i> ,<br>THEREBY USING 2 FACTORS) .....                | 178 |
| FIGURE 6-8 COMPARISON OF PRINCIPAL COMPONENT 1-3 (PC1 – PC3) FOR SAMPLES 32 AND 35<br>.....                                                                                                                                              | 179 |
| FIGURE 6-9 PRINCIPAL COMPONENT 2 AGAINST PRINCIPAL COMPONENT 3 .....                                                                                                                                                                     | 180 |
| FIGURE 6-10 PRINCIPAL COMPONENT 3 LOADING PLOT FOR SAMPLES 32 AND 35 .....                                                                                                                                                               | 181 |
| FIGURE 6-11 SPECTRA OF (TOP) SAMPLE 35 AND (BOTTOM) SAMPLE 32, FROM CHAPTER 5. RED<br>BOXES INDICATE AREAS OF INTEREST FROM THE PC3 LOADING PLOT .....                                                                                   | 181 |
| FIGURE 6-12 SCREE PLOT OF PRINCIPAL COMPONENTS FOR SAMPLES 14, 25, 31 AND 40 SHOWING<br>MAJORITY OF VARIATION IS ACCOUNTED FOR IN THE FIRST THREE PRINCIPAL COMPONENTS<br>(PC1-PC3).....                                                 | 183 |
| FIGURE 6-13 COMPARISON OF PRINCIPAL COMPONENT 1-3 (PC1 – PC3) FOR 14, 25, 31 AND 40                                                                                                                                                      | 184 |
| FIGURE 6-14 SCREE PLOT OF PRINCIPAL COMPONENTS FOR SAMPLES 38 AND 39 SHOWING<br>MAJORITY OF VARIATION IS ACCOUNTED FOR IN THE FIRST THREE PRINCIPAL COMPONENTS<br>(PC1-PC3).....                                                         | 187 |
| FIGURE 6-15 COMPARISON OF PRINCIPAL COMPONENT 1-3 (PC1 – PC3).....                                                                                                                                                                       | 188 |
| FIGURE 6-16 SCREE PLOT OF PRINCIPAL COMPONENTS FOR SAMPLES 5, 9, 10, 41, 43 AND 47 (FROM<br>UNKNOWN SAMPLE SET) SHOWING MAJORITY OF VARIATION IS ACCOUNTED FOR IN THE FIRST<br>THREE PRINCIPAL COMPONENTS (PC1-PC3) .....                | 190 |
| FIGURE 6-17 COMPARISON OF PRINCIPAL COMPONENT 1-3 (PC1 – PC3).....                                                                                                                                                                       | 192 |

|                                                                                                                   |     |
|-------------------------------------------------------------------------------------------------------------------|-----|
| FIGURE 7-1 SUGGESTED ANALYSIS SEQUENCE OF KNOWN AND EXTRANEIOUS FIBRES;<br>INCORPORATING RAMAN SPECTROSCOPY ..... | 201 |
| FIGURE A-2 RAMAN SPECTRUM OF CIBACRON BLACK C-NN HC (RAW) .....                                                   | 206 |
| FIGURE A-3 RAMAN SPECTRUM OF CIBACRON BLACK C-NN HC (BASELINE ADJUSTED) .....                                     | 206 |
| FIGURE A-4 RAMAN SPECTRUM OF CIBACRON BLACK LSN (RAW).....                                                        | 207 |
| FIGURE A-5 RAMAN SPECTRUM OF CIBACRON BLACK LSN (BASELINE ADJUSTED).....                                          | 207 |
| FIGURE A-6 RAMAN SPECTRUM OF CIBACRON BLACK LS-N HC (RAW) .....                                                   | 208 |
| FIGURE A-7 RAMAN SPECTRUM OF CIBACRON BLACK LS-N HC (BASELINE ADJUSTED) .....                                     | 208 |
| FIGURE A-8 RAMAN SPECTRUM OF ORTHOCRON BLACK WNN (RAW).....                                                       | 209 |
| FIGURE A-9 RAMAN SPECTRUM OF ORTHOCRON BLACK WNN (BASELINE ADJUSTED).....                                         | 209 |
| FIGURE A-10 RAMAN SPECTRUM OF REMAZOL BLACK B (RAW).....                                                          | 210 |
| FIGURE A-11 RAMAN SPECTRUM OF REMAZOL BLACK B (BASELINE ADJUSTED).....                                            | 210 |
| FIGURE A-12 RAMAN SPECTRUM OF SYNAZOL BLACK B (RAW) .....                                                         | 211 |
| FIGURE A-13 RAMAN SPECTRUM OF SYNAZOL BLACK B (BASELINE ADJUSTED) .....                                           | 211 |
| FIGURE A-14 RAMAN SPECTRUM OF SYNAZOL BLACK HF-GRP (RAW).....                                                     | 212 |
| FIGURE A-15 RAMAN SPECTRUM OF SYNAZOL BLACK HF-GRP (BASELINE ADJUSTED).....                                       | 212 |
| FIGURE A-16 RAMAN SPECTRUM OF CIBACRON BLUE C-R.....                                                              | 213 |
| FIGURE A-17 RAMAN SPECTRUM OF CIBACRON BLUE LS-3R HC.....                                                         | 213 |
| FIGURE A-18 RAMAN SPECTRUM OF CIBACRON BLUE LSBR.....                                                             | 214 |
| FIGURE A-19 RAMAN SPECTRUM OF CIBACRON BRILLIANT BLUE LSBR.....                                                   | 214 |
| FIGURE A-20 RAMAN SPECTRUM OF CIBACRON NAVY LS-G HC (RAW).....                                                    | 215 |
| FIGURE A-21 RAMAN SPECTRUM OF CIBACRON NAVY LS-G HC (BASELINE ADJUSTED).....                                      | 215 |
| FIGURE A-22 RAMAN SPECTRUM OF EVERCION BLUE (HERD) .....                                                          | 216 |
| FIGURE A-23 RAMAN SPECTRUM OF LANASOL NAVY CE (RAW) .....                                                         | 217 |
| FIGURE A-24 RAMAN SPECTRUM OF LANASOL NAVY CE (BASELINE ADJUSTED).....                                            | 217 |
| FIGURE A-25 RAMAN SPECTRUM OF LEVAFIX NAVY BLUE E-BNA (RAW).....                                                  | 218 |
| FIGURE A-26 RAMAN SPECTRUM OF LEVAFIX NAVY BLUE E-BNA (BASELINE ADJUSTED).....                                    | 218 |
| FIGURE A-27 RAMAN SPECTRUM OF ORTHOCRON BLUE HEGN (RAW) .....                                                     | 219 |
| FIGURE A-28 RAMAN SPECTRUM OF REMAZOL TURQUOISE BLUE G (FLUORESCED).....                                          | 219 |
| FIGURE A-29 RAMAN SPECTRUM OF SUMIFIX SUPRA BLUE BRF .....                                                        | 220 |
| FIGURE A-30 RAMAN SPECTRUM OF SUMIFIX SUPRA NAVY BLUE BF .....                                                    | 220 |
| FIGURE A-31 RAMAN SPECTRUM OF CIBACRON RED LSB .....                                                              | 221 |
| FIGURE A-32 RAMAN SPECTRUM OF LANASOL RED CE (RAW) .....                                                          | 222 |
| FIGURE A-33 RAMAN SPECTRUM OF LANASOL RED CE (BASELINE ADJUSTED) .....                                            | 222 |
| FIGURE A-34 RAMAN SPECTRUM OF PROCION RED HEXL .....                                                              | 223 |
| FIGURE A-35 RAMAN SPECTRUM OF PROCION BR RED HEGXL .....                                                          | 223 |
| FIGURE A-36 RAMAN SPECTRUM OF SUMIFIX SCARLET 2GF (RAW) .....                                                     | 224 |
| FIGURE A-37 RAMAN SPECTRUM OF SUMIFIX SCARLET 2GF (BASELINE ADJUSTED).....                                        | 224 |

|                                                               |     |
|---------------------------------------------------------------|-----|
| FIGURE A-38 RAMAN SPECTRUM OF SYNAZOL RED HF 6BN.....         | 225 |
| FIGURE A-39 RAMAN SPECTRUM OF CIBACRON ORANGE LSBR.....       | 225 |
| FIGURE A-40 RAMAN SPECTRUM OF LANASOL YELLOW CE.....          | 226 |
| FIGURE A-41 RAMAN SPECTRUM OF PROCION YELLOW HEXL .....       | 226 |
| FIGURE A-42 RAMAN SPECTRUM OF SYNAZOL GOLD-YELLOW HF 2GR..... | 227 |

## List of Tables

|                                                                                                                                  |     |
|----------------------------------------------------------------------------------------------------------------------------------|-----|
| TABLE 1-1 WORLD PRODUCTION FIGURES FOR FIBRES (1980 AND 2002) [19] .....                                                         | 6   |
| TABLE 1-2 COLOUR AFTER ABSORPTION/REFLECTANCE (ADAPTED FROM) [26] .....                                                          | 8   |
| TABLE 1-3 DYE CLASS AND RELATED FIBRE AFFINITY [26] .....                                                                        | 9   |
| TABLE 1-4 DYES CLASSES BASED ON CHEMICAL STRUCTURE [28].....                                                                     | 10  |
| TABLE 1-5 TOTAL SALE OF DYES (WITH THE EXCLUSION OF SOLVENT AND PIGMENT DYES) IN 1991<br>[31].....                               | 15  |
| TABLE 1-6 COMPARISON OF FINDINGS FROM THREE TEXTILE DATABASES .....                                                              | 35  |
| TABLE 1-7 COMPARISON OF THE FINDINGS FROM THREE DIFFERENT POPULATION STUDIES .....                                               | 36  |
| TABLE 3-1 TOP FIVE FIBRE/COLOUR COMBINATIONS IN THE AUSTRALIAN DATABASE [25].....                                                | 61  |
| TABLE 3-2 ESTIMATED ANNUAL CONSUMPTION OF DYES FOR CELLULOSIC FIBRES [173] .....                                                 | 62  |
| TABLE 4-1 FIBRE TYPE, COLOUR AND WAVELENGTHS THAT HAVE BEEN INVESTIGATED .....                                                   | 71  |
| TABLE 4-2 MOUNTING METHODS USED IN VARIOUS STUDIES .....                                                                         | 74  |
| TABLE 4-3 VISIBLE-MICROSPECTROPHOTOMETRY PEAK MAXIMA, MINIMA AND SHOULDER.....                                                   | 96  |
| TABLE 4-4 SUMMARY OF RESULTS FROM THE VARIOUS RAMAN LASER WAVELENGTHS.....                                                       | 106 |
| TABLE 5-1 REFERENCES WITH FIBRE TYPE AND COLOUR AS WELL AS THE TECHNIQUES USED.....                                              | 111 |
| TABLE 5-2 COMPARISON OF RAMAN SPECTROSCOPY WITH OTHER TECHNIQUES FOR THE ANALYSIS<br>OF PIGMENTS [140] .....                     | 112 |
| TABLE 5-3 ABILITY TO USE IR VS. RAMAN ANALYSIS IN FIBRE CLASS AND SUBCLASS<br>IDENTIFICATION OF SOME NON-DYED FIBRES [111].....  | 113 |
| TABLE 5-4 SAMPLE NUMBERS AND SHADE (ASSIGNED BY MANUFACTURER).....                                                               | 117 |
| TABLE 5-5 SAMPLE NUMBERS AND THEIR DYE COMPONENTS .....                                                                          | 118 |
| TABLE 5-6 PEAK POSITIONS AND RELATIVE INTENSITIES FOR RAMAN SPECTRAL GROUP I .....                                               | 145 |
| TABLE 5-7 PEAK POSITIONS AND RELATIVE INTENSITIES FOR RAMAN SPECTRAL GROUP II .....                                              | 146 |
| TABLE 5-8 PEAK POSITIONS AND RELATIVE INTENSITIES FOR RAMAN SPECTRAL GROUP IV.....                                               | 147 |
| TABLE 5-9 PEAK POSITIONS AND RELATIVE INTENSITIES FOR RAMAN SPECTRAL GROUP V .....                                               | 148 |
| TABLE 5-10 PEAK POSITIONS AND RELATIVE INTENSITIES FOR RAMAN SPECTRAL GROUP VI.....                                              | 149 |
| TABLE 5-11 GROUPINGS CREATED WHEN ANALYSING WITH THE TWO TECHNIQUES: RAMAN<br>SPECTROSCOPY AND UV-VIS MSP .....                  | 155 |
| TABLE 6-1 SAMPLE TYPES, PRE-PROCESSING AND CHEMOMETRIC METHODS THAT HAVE BEEN<br>INVESTIGATED FOR RAMAN SPECTROSCOPY .....       | 167 |
| TABLE 6-2 FACTOR NUMBER AND CORRESPONDING <i>EIGENVALUES</i> (PLUS PROPORTION) FOR SAMPLES<br>32 AND 35 .....                    | 179 |
| TABLE 6-3 LINEAR DISCRIMINANT ANALYSIS RESULTS FOR SAMPLES 32 AND 35 – USING FIRST<br>THREE PRINCIPAL COMPONENTS (PC1-PC3) ..... | 182 |

|                                                                                                                                                                                                      |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| TABLE 6-4 FACTOR NUMBER AND CORRESPONDING <i>EIGENVALUES</i> (PLUS PROPORTION) FOR SAMPLES 14, 25, 31 AND 40.....                                                                                    | 184 |
| TABLE 6-5 LINEAR DISCRIMINANT ANALYSIS RESULTS FOR SAMPLES 14, 25, 31 AND 40 – USING FIRST THREE PRINCIPAL COMPONENTS (PC1-PC3) – NOTE INCORRECT CLASSIFICATION OF SAMPLES (HIGHLIGHTED IN RED)..... | 185 |
| TABLE 6-6 LINEAR DISCRIMINANT ANALYSIS RESULTS FOR SAMPLES 14, 25, 31 AND 40 – USING FIRST FOUR PRINCIPAL COMPONENTS (PC1-PC6) – NOTE INCORRECT CLASSIFICATION NO LONGER OCCURRING .....             | 186 |
| TABLE 6-7 FACTOR NUMBER AND CORRESPONDING <i>EIGENVALUES</i> (PLUS PROPORTION) FOR SAMPLES 38 AND 39 .....                                                                                           | 188 |
| TABLE 6-8 QUADRATIC DISCRIMINANT ANALYSIS RESULTS FOR SAMPLES 38 AND 39 – USING FIRST THREE PRINCIPAL COMPONENTS (PC1-PC3) .....                                                                     | 189 |
| TABLE 6-9 FACTOR NUMBER AND CORRESPONDING <i>EIGENVALUES</i> (PLUS PROPORTION) FOR UNKNOWN SAMPLE SET MSP GROUP A/RAMAN GROUP I.....                                                                 | 191 |
| TABLE 6-10 QUADRATIC DISCRIMINANT ANALYSIS RESULTS FOR UNKNOWN SAMPLE SET MSP GROUP A/RAMAN GROUP I – USING FIRST FIVE PRINCIPAL COMPONENTS (PC1-PC5) .....                                          | 193 |
| TABLE A-1 BLACK DYES ANALYSED BY 785 NM SHOWING MANUFACTURER’S NAME AND CI NUMBER (IF KNOWN).....                                                                                                    | 203 |
| TABLE A-2 BLUE DYES ANALYSED BY 785 NM SHOWING MANUFACTURER’S NAME AND CI NUMBER (IF KNOWN). .....                                                                                                   | 204 |
| TABLE A-3 RED DYES ANALYSED BY 785 NM SHOWING MANUFACTURER’S NAME AND CI NUMBER (IF KNOWN). .....                                                                                                    | 205 |
| TABLE A-4 YELLOW AND ORANGE DYES ANALYSED BY 785 NM SHOWING MANUFACTURER’S NAME AND CI NUMBER (IF KNOWN). .....                                                                                      | 205 |
|                                                                                                                                                                                                      |     |
| TABLE 1-1 WORLD PRODUCTION FIGURES FOR FIBRES (1980 AND 2002) [19] .....                                                                                                                             | 6   |
| TABLE 1-2 COLOUR AFTER ABSORPTION/REFLECTANCE (ADAPTED FROM) [26] .....                                                                                                                              | 8   |
| TABLE 1-3 DYE CLASS AND RELATED FIBRE AFFINITY [26] .....                                                                                                                                            | 9   |
| TABLE 1-4 DYES CLASSES BASED ON CHEMICAL STRUCTURE [28].....                                                                                                                                         | 10  |
| TABLE 1-5 TOTAL SALE OF DYES (WITH THE EXCLUSION OF SOLVENT AND PIGMENT DYES) IN 1991 [31].....                                                                                                      | 15  |
| TABLE 1-6 COMPARISON OF FINDINGS FROM THREE TEXTILE DATABASES .....                                                                                                                                  | 35  |
| TABLE 1-7 COMPARISON OF THE FINDINGS FROM THREE DIFFERENT POPULATION STUDIES .....                                                                                                                   | 36  |
| TABLE 3-1 TOP FIVE FIBRE/COLOUR COMBINATIONS IN THE AUSTRALIAN DATABASE [25].....                                                                                                                    | 61  |
| TABLE 3-2 ESTIMATED ANNUAL CONSUMPTION OF DYES FOR CELLULOSIC FIBRES [173].....                                                                                                                      | 62  |
| TABLE 4-1 FIBRE TYPE, COLOUR AND WAVELENGTHS THAT HAVE BEEN INVESTIGATED .....                                                                                                                       | 71  |
| TABLE 4-2 MOUNTING METHODS USED IN VARIOUS STUDIES .....                                                                                                                                             | 74  |
| TABLE 4-3 VISIBLE-MICROSPECTROPHOTOMETRY PEAK MAXIMA, MINIMA AND SHOULDER.....                                                                                                                       | 96  |

|                                                                                                                                                                                                            |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| TABLE 4-4 SUMMARY OF RESULTS FROM THE VARIOUS RAMAN LASER WAVELENGTHS.....                                                                                                                                 | 106 |
| TABLE 5-1 REFERENCES WITH FIBRE TYPE AND COLOUR AS WELL AS THE TECHNIQUES USED.....                                                                                                                        | 111 |
| TABLE 5-2 COMPARISON OF RAMAN SPECTROSCOPY WITH OTHER TECHNIQUES FOR THE ANALYSIS<br>OF PIGMENTS [140] .....                                                                                               | 112 |
| TABLE 5-3 ABILITY TO USE IR VS. RAMAN ANALYSIS IN FIBRE CLASS AND SUBCLASS<br>IDENTIFICATION OF SOME NON-DYED FIBRES [111] .....                                                                           | 113 |
| TABLE 5-4 SAMPLE NUMBERS AND SHADE (ASSIGNED BY MANUFACTURER).....                                                                                                                                         | 117 |
| TABLE 5-5 SAMPLE NUMBERS AND THEIR DYE COMPONENTS.....                                                                                                                                                     | 118 |
| TABLE 5-6 PEAK POSITIONS AND RELATIVE INTENSITIES FOR RAMAN SPECTRAL GROUP I .....                                                                                                                         | 145 |
| TABLE 5-7 PEAK POSITIONS AND RELATIVE INTENSITIES FOR RAMAN SPECTRAL GROUP II .....                                                                                                                        | 146 |
| TABLE 5-8 PEAK POSITIONS AND RELATIVE INTENSITIES FOR RAMAN SPECTRAL GROUP IV.....                                                                                                                         | 147 |
| TABLE 5-9 PEAK POSITIONS AND RELATIVE INTENSITIES FOR RAMAN SPECTRAL GROUP V .....                                                                                                                         | 148 |
| TABLE 5-10 PEAK POSITIONS AND RELATIVE INTENSITIES FOR RAMAN SPECTRAL GROUP VI.....                                                                                                                        | 149 |
| TABLE 5-11 GROUPINGS CREATED WHEN ANALYSING WITH THE TWO TECHNIQUES: RAMAN<br>SPECTROSCOPY AND UV-Vis MSP .....                                                                                            | 155 |
| TABLE 6-1 SAMPLE TYPES, PRE-PROCESSING AND CHEMOMETRIC METHODS THAT HAVE BEEN<br>INVESTIGATED FOR RAMAN SPECTROSCOPY .....                                                                                 | 167 |
| TABLE 6-2 FACTOR NUMBER AND CORRESPONDING <i>EIGENVALUES</i> (PLUS PROPORTION) FOR SAMPLES<br>32 AND 35 .....                                                                                              | 179 |
| TABLE 6-3 LINEAR DISCRIMINANT ANALYSIS RESULTS FOR SAMPLES 32 AND 35 – USING FIRST<br>THREE PRINCIPAL COMPONENTS (PC1-PC3) .....                                                                           | 182 |
| TABLE 6-4 FACTOR NUMBER AND CORRESPONDING <i>EIGENVALUES</i> (PLUS PROPORTION) FOR SAMPLES<br>14, 25, 31 AND 40.....                                                                                       | 184 |
| TABLE 6-5 LINEAR DISCRIMINANT ANALYSIS RESULTS FOR SAMPLES 14, 25, 31 AND 40 – USING<br>FIRST THREE PRINCIPAL COMPONENTS (PC1-PC3) – NOTE INCORRECT CLASSIFICATION OF<br>SAMPLES (HIGHLIGHTED IN RED)..... | 185 |
| TABLE 6-6 LINEAR DISCRIMINANT ANALYSIS RESULTS FOR SAMPLES 14, 25, 31 AND 40 – USING<br>FIRST FOUR PRINCIPAL COMPONENTS (PC1-PC6) – NOTE INCORRECT CLASSIFICATION NO<br>LONGER OCCURRING .....             | 186 |
| TABLE 6-7 FACTOR NUMBER AND CORRESPONDING <i>EIGENVALUES</i> (PLUS PROPORTION) FOR SAMPLES<br>38 AND 39 .....                                                                                              | 188 |
| TABLE 6-8 QUADRATIC DISCRIMINANT ANALYSIS RESULTS FOR SAMPLES 38 AND 39 – USING FIRST<br>THREE PRINCIPAL COMPONENTS (PC1-PC3) .....                                                                        | 189 |
| TABLE 6-9 FACTOR NUMBER AND CORRESPONDING <i>EIGENVALUES</i> (PLUS PROPORTION) FOR<br>UNKNOWN SAMPLE SET MSP GROUP A/RAMAN GROUP I.....                                                                    | 191 |
| TABLE 6-10 QUADRATIC DISCRIMINANT ANALYSIS RESULTS FOR UNKNOWN SAMPLE SET MSP<br>GROUP A/RAMAN GROUP I – USING FIRST FIVE PRINCIPAL COMPONENTS (PC1-PC5) .....                                             | 193 |

|                                                                                                                   |     |
|-------------------------------------------------------------------------------------------------------------------|-----|
| TABLE A-1 BLACK DYES ANALYSED BY 785 NM SHOWING MANUFACTURER'S NAME AND CI<br>NUMBER (IF KNOWN).....              | 203 |
| TABLE A-2 BLUE DYES ANALYSED BY 785 NM SHOWING MANUFACTURER'S NAME AND CI NUMBER<br>(IF KNOWN). ....              | 204 |
| TABLE A-3 RED DYES ANALYSED BY 785 NM SHOWING MANUFACTURER'S NAME AND CI NUMBER<br>(IF KNOWN). ....               | 205 |
| TABLE A-4 YELLOW AND ORANGE DYES ANALYSED BY 785 NM SHOWING MANUFACTURER'S<br>NAME AND CI NUMBER (IF KNOWN). .... | 205 |

## **List of Equations**

|                                                       |     |
|-------------------------------------------------------|-----|
| EQUATION 1 BAYESIAN POSTERIOR ODDS EQUATION .....     | 37  |
| EQUATION 2 BAYESIAN LIKELIHOOD RATIO .....            | 38  |
| EQUATION 3 RAYLEIGH SCATTERING .....                  | 43  |
| EQUATION 4 STOKES RADIATION .....                     | 44  |
| EQUATION 5 ANTI-STOKES RADIATION .....                | 44  |
| EQUATION 6 CALCULATION FOR DISCRIMINATION POWER ..... | 123 |

## **List of Abbreviations**

|               |                                                            |
|---------------|------------------------------------------------------------|
| AFP           | Australian Federal Police                                  |
| CI            | Colour Index                                               |
| CCD           | Charged Coupled Device                                     |
| CCTV          | Closed Circuit Television                                  |
| DP            | Discriminatory Power                                       |
| DNA           | Deoxyribose Nucleic Acid                                   |
| EFG           | European Fibres Group                                      |
| ENFSI         | European Network of Forensic Science Institutes            |
| ESI-MS        | Electrospray Ionisation – Mass Spectrometry                |
| ESI-MS/MS     | Electrospray Ionisation – tandem Mass Spectrometry         |
| FBI           | Federal Bureau of Investigation                            |
| FPF           | Fibre Plastic Fusion                                       |
| FSS           | Forensic Science Service                                   |
| FTIR          | Fourier Transform Infrared                                 |
| GSR           | Gun Shot Residue                                           |
| IR            | Infrared                                                   |
| MPFSL         | Metropolitan Police Forensic Service Laboratory            |
| MSP           | Microspectrophotometry                                     |
| mW            | milli-watt                                                 |
| NIR           | Near Infrared                                              |
| nm            | nano-meter                                                 |
| PCA           | Principal Components Analysis                              |
| PCM           | Plastic Coating Mark                                       |
| Py-GC         | Pyrolysis Gas Chromatography                               |
| SERRS         | Surface Enhanced Resonance Raman Spectroscopy              |
| SERS          | Surface Enhanced Raman Spectroscopy                        |
| SWGMAF        | Scientific Working Group for Materials                     |
| TLC           | Thin Layer Chromatography                                  |
| TWGFIBE       | Technical Working Group for Fiber Examinations             |
| UV            | Ultraviolet                                                |
| Vis-MSP       | Visible Microspectrophotometry                             |
| XAM           | Neutral medium improved white Gurr (Xylene based mountant) |
| $\Delta E$    | energy change                                              |
| $\mu\text{m}$ | micro-meter                                                |

## **Abstract**

In the 21st Century, fibre examiners are faced with the constraints of time and money. Rapid advances in DNA technology has seen fibre evidence undervalued due to it being time consuming, costly and (when competing with DNA) perceived to be less discriminatory. However, DNA is not present in all cases and when present may require other evidence to interpret the circumstance/s. The only way forward for fibre examinations is through research that will address issues of time and money whilst increasing their evidentiary value by demonstrating reliability through improved statistical information.

Raman spectroscopy was investigated as it is a technique that is growing in popularity for the analysis of materials. It is quick, discriminatory, non-destructive and requires minimal sample preparation. The ability of Raman spectroscopy to discriminate black/grey and blue cotton fibres was investigated to determine how effective the technique would be for analysing this often undervalued fibre evidence.

Various parameters of Raman spectroscopy were investigated to determine the optimal conditions for the analysis of the samples selected. The major variable investigated was laser wavelength with the 785nm and 632.8nm lasers providing the best results. Results indicated that, at least, the major dye component could be identified using Raman spectroscopy.

The discriminatory power of the technique was then investigated for a sample set of 11 black/grey and blue cotton samples as well as a set of 91 black and blue cotton fibres of unknown dye types. This was then compared to the discriminatory power of microspectrophotometry (MSP) for the same sample sets as well as the discriminatory power of the combined techniques.

In analysis of both sample sets, Raman spectroscopy showed a lower discriminatory power than microspectrophotometry. However, combining the two techniques significantly increased the discriminatory power. Using

chemometrics increased the discrimination provided by Raman spectroscopy indicating that chemometrics may be used as an aid for interpreting data.

Whilst the advantages of Raman spectroscopy were evident during these studies one major limitation of the technique was also highlighted. The problem of fluorescence has long been regarded as the major drawback to using Raman spectroscopy for fibre examinations. The problem was overcome in some instances by changing the laser wavelength but not all.

Even with the occurrence of fluorescence, it was shown that, for the sample sets investigated, Raman spectroscopy (when combined with microspectrophotometry) provided a level of discrimination not able to be achieved with microspectrophotometry as a single technique. Therefore, Raman spectroscopy should be considered when undertaking analysis of these sample types.

Keywords: Fibre evidence, Reactive Dyes, Raman Spectroscopy, Microspectrophotometry, Chemometrics