RAMAN SPECTROSCOPY FOR THE FORENSIC EXAMINATION OF REACTIVELY DYED COTTON

by

Jane Thomas

A thesis

submitted as requirement for the

degree of Doctor of Philosophy (Science)

University of Technology, Sydney

Faculty of Science

October 2005

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:
Signature removed prior to publication.

Jane Thomas

31st October 2005

Acknowledgements

The completion of this thesis has been through the input and support of many people. First and foremost, I would like to thank my supervisor, Professor Claude Roux, your guidance and advice has been much appreciated. Thanks for all the fabulous opportunities you provided for making contacts in the field of Raman spectroscopy and the broader field of fibre examinations.

I would also like to thank: Adjunct Professor James Robertson, my external supervisor, who has provided much appreciated feedback at critical moments; Dr Brian Reedy for readily sharing his expertise in Raman spectroscopy; Dr Philip Doble for educating me in the ways of chemometrics; Dr Philip Maynard for his help in spectral interpretation and his time spent reviewing drafts, and; Dr Susan Bennet (nee Langdon) for sharing her data and experience in researching fibres.

I have been lucky enough to draw on the expertise of many and I would especially like to thank the members of the European Fibres Group (particularly Professor Genevieve Massonnet) for their interest, feedback and knowledge on all things fibre related. I would also like to thank Patrick Buzzini (and everyone at ESC) for making my research time in Switzerland informative AND fun.

To all my fellow PhD'ers - Karen, Bec, Tamsin, Daniel, Sonia, Katherine, Al, Matt, Tristan, Mark, Viv and Phil - thanks for all the sharing, caring and for making Uno time the best part of the day. To Sim and Dana, your support, cups of tea and time-out have saved my sanity.

Huge thanks to my family, your support and belief in me was sometimes the only things that kept me going. To my sister Meg, your time spent editing and formatting is appreciated in ways words cannot express.

Finally, to David. Your love, support and understanding are things that I have relied on and appreciated this whole journey. You are my rock.

Table of Contents

List of Figures

List of Tables

List of Equations

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
SWGMAT	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)
ΔE	energy change
μm	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