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University of Southampton

Faculty of Humanities

School of History

Nineteenth Century Synthetic Textile Dyes.  
Their History and Identification on Fabric.

by

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Thesis for the degree of Doctor of Philosophy

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ABSTRACT  
FACULTY OF HUMANITIES  
SCHOOL OF HISTORY  
Doctor of Philosophy  
NINETEENTH CENTURY SYNTHETIC TEXTILE DYES.  
THEIR HISTORY AND IDENTIFICATION ON FABRIC.  
by Rosemary Molly Baker

Textile dyes have been the subject of many studies from the varied perspectives of historians, conservators and scientists. Most of these have focused on natural compounds but nineteenth century synthetic dyes form the basis of this thesis. The dual areas of interest have been the social history of those dyes developed between the introduction of Mauveine in 1856 and the end of the century and the investigation of novel spectroscopic methods for their identification *in situ* on textiles.

Although the first synthetic dye was manufactured in England, the centre of the industry soon moved to Germany and Switzerland. Education and contacts in Switzerland or Germany were important in advancement in the field as can be seen in the previously unresearched biography of J.J. Hummel who, through his Swiss step-father, was able to travel to Zurich to study and subsequently progressed from working as a cotton printer to become the first professor of textile dyeing at the Yorkshire College, later Leeds University.

Evidence was found in newspapers and popular periodicals for three other factors which had an important influence on the attitude to synthetic dyes in England. One was English reluctance to invest in speculative ventures rather than the established textile industries. The second was the possession of colonial holdings and overseas trade networks which encouraged continued research into imported natural products. Thirdly the particular form of the Arts and Crafts movement in England emphasised the craft means of production in a way which the equivalent aesthetic in Germany did not. Nineteenth century dye manuals show that there was no exclusive use of either natural or synthetic dyes in the trade despite the fashion in artistic circles for 'natural' colours.

The identification of synthetic dyes on textiles is important in textile history and conservation especially in the context supplied by the investigations described above into the usage of the dyes. It is highly desirable in the field of cultural heritage to devise analytical techniques which are non-destructive and non-sampling. Dyed wool and silk samples were prepared using 12 dye compounds. Different techniques were tested and Fourier transform Raman spectroscopy was able to provide diagnostic spectra for a variety of synthetic dyes. Clear features in the spectra could be used to identify the dye class and to distinguish between dyes of the same class. This technique allowed the detection of dyes on the textile for the first time and it was applied successfully to original samples from dye manuals. One unknown mauve sample was also analysed and a combination of infrared and Raman spectroscopy allowed a definite identification of the dye as a triphenylmethane and tentatively as Methyl violet.

This study combines investigations into material culture and social history and demonstrates the use of science together with historical research to reveal new insights into the history of textile dyes.

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Last but not least I would like to thank John for all his encouragement and for taking an interest in textile dyes.

## Chapter 1 Introduction

The period covered by this study was a time of great change in Europe in many diverse areas. There was an accelerating move of population from the country to the cities, swelling the size of many provincial towns particularly in areas near rich coal deposits such as Leeds.<sup>1</sup> The population was also becoming increasingly affluent with more disposable income and the retail trade expanded to cater to their needs. This new middle class section of society<sup>2</sup> had increasing leisure to study new subjects and large numbers of general periodicals were produced and read widely.<sup>3</sup> Education became universal<sup>4</sup> and universities all over Europe were expanding and changing in nature from purely vocational institutions for the upper classes to include a wider range of subjects relevant to the new industries and attracting the middle classes.<sup>5</sup>

The synthetic dye industry was a very small part of this change but it incorporates many of the main themes of the time.<sup>6</sup> Unlike the textile industries which changed in this period by applying mechanisation to existing products and production methods,<sup>7</sup> this was a new industry for which novel apparatus and methods had to be devised. It was, however, very quickly entirely factory based and these factories grew in size to rival the textile mills themselves. The industry produced dyes which were more uniform from batch to batch and

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<sup>1</sup> FRASER, D. (Ed.) (1980) *A History of Modern Leeds*, Manchester, Manchester University Press.

<sup>2</sup> DAVIDOFF, L. & HALL, C. (1987) *Family Fortunes. Men and women of the English middle class 1780-1850*, London, Routledge.. Although this study ends in 1850 just as the time period covered by this thesis starts, the social changes described continue into the second half of the century.

<sup>3</sup> Wach examines the ways in which popular culture was enjoyed in Manchester WACH, H. M. (1988) Culture and the Middle Classes: Popular Knowledge in Industrial Manchester. *The Journal of British Studies*, 27, 375-404.

Topham summarises popular publishing of science TOPHAM, J. R. (2000) Scientific Publishing and the Reading of Science in Nineteenth-Century Britain: A Historiographical Survey and Guide to Sources. *Studies in the History and Philosophy of Science*, 31, 559-612.

<sup>4</sup> STEPHENS, W. B. (1980) Elementary education and literacy, 1770-1870. IN FRASER, D. (Ed.) *A History of Modern Leeds*. Manchester, Manchester University Press.

<sup>5</sup> SANDERSON, M. (1975) *The universities in the nineteenth century*, London and Boston, Routledge & Kegan Paul.

<sup>6</sup> Indeed Mokyr suggests that it was the paradigmatic industry of the second industrial revolution MOKYR, J. (2001) The Industrial Revolution and the economic history of technology: Lessons from the British experience, 1760-1850. *The Quarterly Review of Economics and Finance*, 41, 295-311.

<sup>7</sup> BIERNACKI, R. (2002) Culture and Know-how in the 'Satanic Mills': An Anglo-German comparison. *Textile History*, 33.

easier to apply than the previous natural dyes and therefore assisted the expansion of the textile industry to cater for the new consumer demand.

This study of the synthetic dye industry contributes to the history of fashion or costume which is a relatively new academic field.<sup>8</sup> Cumming (2004)<sup>9</sup> in her discussion of its development prefers to use the term ‘dress’ and considers the diversity of origins of the subject which has helped to produce parallel terminologies. She suggests that the application of academic theory, invaluable as a tool, has moved the emphasis of enquiry away from the analysis of the object itself. Taylor (2002) in her book *The Study of Dress History* surveys the multi-disciplinary nature of the field and suggests that the object based approach (represented largely by curators) and the academic approach have been partially but not yet entirely reconciled. She points out that the ‘overall picture becomes flawed’ unless evidence from both types of study are included.<sup>10</sup> Many of the pioneers in the field of dress study were firmly object based such as Janet Arnold who produced detailed studies of the construction of costume through the ages.<sup>11</sup>

The area of textile conservation, where the present study was initiated, requires in-depth study of the object to inform sensitive intervention. This research took as its starting point the application of scientific methods to the identification of Victorian textile dyes, then broadened to include the study of the development of the dye industry in Britain in the second half of the nineteenth century and the reactions to these fashion changes in the wider culture. Therefore this interdisciplinary study includes both object analysis and archival study. The investigator in this study has a strong background in dress history and was previously trained in biochemistry and subsequently in textile conservation taking options concentrating on conservation science. This gave a unique opportunity to combine insights from both areas and therefore draw out conclusions which could not necessarily have been reached on the basis of one area of study alone. This combined approach has rarely been attempted before with a few notable exceptions. One is de Graaff who

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<sup>8</sup> TAYLOR, L. (2004) *Establishing Dress History*, Manchester, Manchester University Press, pages 315-316

<sup>9</sup> CUMMING, V. (2004) *Understanding Fashion History*, BT Batsford, London, pages 130-131

<sup>10</sup> TAYLOR, L. (2002) *The Study of Dress History*, Manchester, Manchester University Press pages 272-274

<sup>11</sup> See for example, ARNOLD, J. (1972) *Patterns Of Fashion 2. Englishwomen's dresses and their construction c.1860-1940* new edition 1977 London, Macmillan London Ltd



combines a survey of the chemistry and identification of natural dyes with case studies of dye identification on historic examples to answer questions of textile history.<sup>12</sup> Also Tímár-Balázs and Eastop cover the chemistry relevant to textile conservation and again include case studies.<sup>13</sup> The conferences and publications of *Dyes in History and Archaeology* also combine the two strands of science and textile history although in this case authors tend to concentrate on one aspect or the other or two authors address separate aspects in one paper.<sup>14</sup>

This work aims to address questions which have arisen in the field of dress history relating to fashionable colours and how they were created on textiles. The textile industry in the nineteenth century was very much influenced by increasing industrialisation including the development of the synthetic dyes. The rise of the factory system and the increasing use of mechanization are known but it is not clear to what extent the new dyes were used and how quickly and widely they were adopted. Some contemporary commentators were against them but to what extent were these views spread through the industry as a whole? The investigation of this requires a rapid, non-destructive analytical method for the synthetic dyes to allow surveys of collections. Chapters 2 and 3 research further into the attitudes to the new dyes after 1856 and the later chapters describe the application of chemistry and conservation techniques to the analytical method. One of the main challenges of this thesis has been to present it so that it is accessible to all the different constituencies who will have an interest in it.

The growth of the dye industry has been well researched<sup>15</sup> and the dominance of Germany by the last quarter of the nineteenth century has been unequivocally demonstrated.<sup>16</sup> The

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<sup>12</sup> GRAAFF, J.H.H.D. (2004) *The Colourful Past: The origins, Chemistry and Identification of Natural Dyestuffs*. London, Archetype Press

<sup>13</sup> TIMAR-BALAZSY, A. & EASTOP, D. (1998) *Chemical Principles of Textile Conservation*. Oxford, Butterworth Heinemann. See, for example p. 412, scientific analysis informs the treatment of the Hungarian Coronation Mantle

<sup>14</sup> See for example QUYE, A., CHEAPE, H., BURNETT, J. FERREIRA, E.S.B., HULME, A.N. & MCNAB, H. An Historical and Analytical Study of Red, Pink, Green and Yellow colours in Quality 18<sup>th</sup>- and Early 19<sup>th</sup>-Century Scottish Tartans. *Dyes in History and Archaeology*. 19, 1-12

<sup>15</sup> The rise of gas lighting provided the abundant raw material which gave rise to the synthetic dye industry. It is noteworthy that this was adopted domestically most enthusiastically by the middle classes DILLON, M. (2002) *Artificial Sunshine. A social history of domestic lighting*, London, National Trust Enterprises Ltd. page 145

nature of the industry was very technical and required well-educated chemists (a new specialism in itself) to provide staff not only to develop new products but also to run the factories successfully and give technical support to the manufacturers. Germany and Switzerland proved the most adept at this and the industry expanded in these countries at the expense of the textile powerhouses of England and Italy. The USA followed Germany but rather later. Germany was the pioneer of effective university chemical courses and many early dye chemists traveled to England where they had a ready market for their products in the thriving textile factories. Unfortunately, once investment in their home countries reached a point where they could pursue successful careers there, they returned home leaving a lack of trained chemists in England which heavily contributed to the decline of the English dye industry. The reasons for this failure to develop the industry in England have been discussed since the end of the nineteenth century and the relative lack of chemistry education has been cited as a major cause.<sup>17</sup> The range of reasons for this failure of the English industries are discussed here and additional factors suggested.

Since the state of education in chemistry in England is often quoted as a pivotal factor it is considered in this study.<sup>18</sup> Newspaper reports concerning the establishment of the Yorkshire College in Leeds were consulted to provide a fresh approach to this topic. This was the first college to teach textile dyeing and developed into the University of Leeds.<sup>19</sup> The inaugural instructor of textile dyeing was John James Hummel (1850-1902) and his biography was researched using a range of archival sources. Periodicals, as well as newspapers, are used to explore the reactions of the public to the synthetic dyes.<sup>20</sup> The articles range from the scientific to fashion comments. There is not a large current literature

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<sup>16</sup> Travis has published extensively on this topic. His most comprehensive work is TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses.

<sup>17</sup> GARDNER, W. M. (Ed.) (1915) *The British Coal Tar Industry:- Its Origin, Development and Decline*, London, Williams and Norgate.

<sup>18</sup> Ibid. Gardner provides a perspective from the start of the twentieth century Travis offers a more modern analysis TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses.

<sup>19</sup> GOSDEN, P. H. J. H. & TAYLOR, A. J. (Eds.) (1975) *Studies in the History of a University 1874-1974. To Commemorate the Centenary of the University of Leeds.*, Leeds, E.J. Arnold & Son Limited.

<sup>20</sup> Topham is a key reference here with a comprehensive survey of publishing about science in the nineteenth century TOPHAM, J. R. (2000) Scientific Publishing and the Reading of Science in Nineteenth-Century Britain: A Historiographical Survey and Guide to Sources. *Studies in the History and Philosophy of Science*, 31, 559-612.

on the synthetic dyes in fashion and costume and a proportion of the studies which have been published refer to the synthetics as foils for the naturals rather than as the main object of the work.<sup>21</sup>

This study seeks to add to the debate concerning the level to which the public embraced the new colours or alternatively espoused the Arts and Crafts philosophy of returning to the natural hues.<sup>22</sup> Two nineteenth century dye manuals are used to further explore how much use the professional dyers were making of the synthetic dyes, where they were buying them and how much distinction they made between the synthetic and natural compounds.

The second type of source used in this study is dyed textiles themselves. The increase of the use of the synthetic dyes is of much interest to historians, especially those with an interest in textiles. Much research has been carried out into the identification of natural dyes on fabrics as this can address such issues as the status or origins of garments.<sup>23</sup> Less emphasis has been placed on synthetic dyes, perhaps because there are a greater range of these. However, their identification in collections is now of interest and can be used both to aid conservation and, since their dates of introduction are known, provide *post quem* dating for objects.<sup>24</sup> Non-sampling and non-destructive methods for these analyses are preferred of course and interest has centered on spectroscopy for this reason. Many such studies for dyes and other chemicals are included in the section on non-destructive testing from the

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<sup>21</sup> Nicklas has used fashion plates and other sources for a study of the dyes NICKLAS, C. All the world laid by art and science at her feet: Colour, Dyes, Popular Science, and Women's Fashion in Great Britain and the United States, 1840-1880. *Design History and Material Culture Research Group*. Brighton, University of Brighton. NICKLAS, C. All the world laid by art and science at her feet: Colour, Dyes, Popular Science, and Women's Fashion in Great Britain and the United States, 1840-1880. *Design History and Material Culture Research Group*. Brighton, University of Brighton..

Buruma uses the Liberty & co archive BURUMA, A. (2007) 'A Clinging Liberty Tea-Gown Instead of a Magenta Satin': The Colour Red in Artistic Dress by Liberty & Co. *Costume*, 41.

Murphy discusses colour at the fashionable seaside MURPHY, D. (2006) 'The Girls in Green': Women's Seaside Dress in England, 1850-1900. *Costume*, 40.

<sup>22</sup> NAYLOR, G. (1980) *The Arts and Crafts Movement: a study of its sources, ideals and influence on design theory*, London, Studio Vista.

<sup>23</sup> GRAAFF, J. H. H. D. (2004) *The Colourful Past: The Origins, Chemistry and Identification of Natural Dyestuffs*, London, Archetype Press.

QUYE, A. & CHEAPE, H. (2008) Recovering the Arisaid. *Costume*, 42, 1-20. Quye and Cheape use the results from dye analysis to draw conclusions about the status of textiles.

<sup>24</sup> BAKER, R. M. (2007) Patents as a source of information about synthetic textile dyes. IN HAYWARD, M. & KRAMER, E. (Eds.) *Textiles and Text. Re-establishing the Links between Archival and Object-based Research*. AHRC Research Centre for Textile Conservation and Textile Studies, Archetype Publications.

Conservation Science Conference held in Edinburgh in 2002.<sup>25</sup> At a slightly later conference a paper presented the use of Raman spectroscopy to identify pigments on intact painted textiles.<sup>26</sup> In this type of method the object can be illuminated and information on its chemical structure deduced from changes in the light reflected or scattered. Thus there is no need to dismantle an object and perhaps even no need to bring it into a laboratory.<sup>27</sup> This study will therefore seek to identify a suitable method of this type for the analysis of synthetic dyes on textiles.

This study is therefore truly interdisciplinary combining the use of archives to investigate the development of the synthetic dye industry, the public responses to the industry itself and the use of the dyes on textiles with the development of a non-destructive method for analysis of the dyes applied to textiles. Finally this method is applied to samples of nineteenth century dyed textiles found in contemporary dye manuals.

Thus the scope of the study ranges over history, dress and textile history, history of science and conservation science. Within these, history requires a critical analysis of primary sources such as written and visual sources and objects. This study makes particular use of written sources in this area to address questions about synthetic and natural dyes and construct a narrative about their use exclusively or together. Dress and textile history use similar approaches but text and objects in this area have often been approached separately whereas here both types of source are used equally. Conservation science is also a major strand of this research using analytical chemistry to answer questions about date, provenance and preservation all of which can be related to issues important for textile

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<sup>25</sup> TOWNSEND, J.H., EREMIN, K. & ADRIAENS, A. (Eds.) (2003) *Conservation Science 2002*. London, Archetype Publications.

<sup>26</sup> MACDONALD, A.M., ROGERSON, C., VAUGHAN, A.S. & WYETH, P. (2005) Raman microspectroscopy interrogating 19<sup>th</sup>- and 20<sup>th</sup>-century painted trades union banners. In JANAWAY, R. & WYETH, P. (eds.) *Scientific Analysis of Ancient and Historic Textiles*. AHRC Research Centre for Textile Conservation and Textile Studies, Archetype Publications.

<sup>27</sup> CASTRIOTA, M., MEDURI, E., BARONE, T., DE SANTO, G. & CAZZANELLI, E. (2008) Micro-Raman investigations on the fresco 'Trapasso della Vergine' in the Church of 'S. Giovanni Battista' of Paterno Calabro in southern Italy. *Journal of Raman Spectroscopy*, 39, 284-288.

conservation. The definition of the term ‘synthetic dye’ is technically problematic.<sup>28</sup> In one sense all dyes are ‘synthetic’ since they are processed in some way. The term is used here to encompass those compounds prepared from chemical rather than naturally sourced starting materials. In the nineteenth century they were never referred to as ‘synthetic’ but had a variety of popular names including ‘aniline’ or ‘coal tar’ dyes. In the nineteenth century dye manuals studied here they are classed as ‘artificial’ as opposed to ‘natural’ dyes.

## Outline of the thesis

The period covered by this study has a natural starting point at the celebrated date of the discovery of ‘mauveine’ by William Henry Perkin (1838-1907) in 1856. There had been a few manufactured dyes before this date but from this point the production of synthetic dyes from coal tar developed dramatically. The chosen end-point for investigation here is 1897 with the development of synthetic indigo at the Badische Anilin und Soda Fabrik (BASF). Although the initial method for the production of indigo was expensive, cheaper methods were soon developed and the market for synthetic indigo grew dramatically.<sup>29</sup> After this date new synthetic dyes continued to be produced but most flowed from the discovery of new types of compounds chemically different from the earlier dyes. Thus the time period of the thesis is situated entirely in the long reign of Queen Victoria (reigned 1837-1901). During this time the Industrial Revolution, begun in the latter part of the eighteenth century, continued to develop and establish new ways of working in the textile industry.<sup>30</sup> This period also saw rapid changes in fashion including the crinoline and the bustle.<sup>31</sup> Running counter to this was the rise of the Arts and Crafts movement as a reaction to increasing mechanisation and, associated with it, aesthetic dress.<sup>32</sup>

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<sup>28</sup> BARNETT, J. C. (2007) Synthetic organic dyes, 1856-1901: an introductory review of their use and related issues in textile conservation. *Reviews in Conservation*, 8, 67-77. Barnett suggests ESOD (early synthetic organic dye) but even this is not necessarily definitive.

<sup>29</sup> TRAVIS, A.S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*. London & Toronto, Associated University Presses. Page 223

<sup>30</sup> WILSON, E. & TAYLOR, L. (1989) *Through the Looking Glass. A history of dress from 1860 to the present day*. London, BBC Books. Page 33

<sup>31</sup> Ibid. Pages 20- 27 outline the changes in fashion in this period.

<sup>32</sup> Ibid., Pages 30-32

Chapter 2 introduces the background to the chemical industry and, more specifically, the dye industry in the second half of the nineteenth century. Dye manufacture was particularly dependent on skilled labour both to work in the factory and to research and develop new products. Key early players were either German or had taken research degrees in Germany or Switzerland and the lack of suitably academic teaching in chemistry is reviewed. The earliest course specifically devoted to textile dyeing was introduced at the Yorkshire College which went on to develop into Leeds University. The early foundation of the College and establishment of this course is charted through reports in the local press which introduces a dimension of freshness and brings the voices of the protagonists into focus. John James Hummel (1850-1902) was the first instructor, and later professor, of textile dyeing and his biography has been researched for the first time. The development of the dye firms is reviewed and data from dye manuals is introduced to assess the dominance of Germany in the trade.

This part of the study used newly introduced digital resources, principally the Gale online database of 19<sup>th</sup> century newspapers accessed via the British Library website.<sup>33</sup> This provided much of the information about the development of the Yorkshire College and the career of Hummel. Online access to census records via Ancestry.co.uk provided information about Hummel's private life. The advantage of these databases to the researcher lies in their easy searchability which allowed articles relating to the Yorkshire College to be sourced over multiple years and publications. Also the ProQuest LLC online database<sup>34</sup> of British Periodicals provided much contextual information about the public attitude to dyes and the dye industry and was heavily drawn on for Chapter 3. The use of search words is key in the use of these databases. Searching contemporary sources requires the use of contemporary terms. For example, 'synthetic dye' was not used at the time, whereas the words 'aniline dye' or 'coal tar colours' were common. The Yorkshire College was first identified by a search looking for references to dyes and was followed up with further searching. Inevitably many references found are not of interest but each needs to be

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<sup>33</sup> Accessed via University of Southampton.

<http://find.galegroup.com/bncn/start.do?prodId=BNCN&userGroupName=unisoton>

<sup>34</sup> <http://britishperiodicals.chadwyck.co.uk>

accessed and evaluated for relevance. As the search progresses it can be refined by adjusting the search terms and limits on dates of references can also be set (before 1900 for example).

Chapter 3 examines the dye industry from a different perspective, that of the consumer. The 1862 International Exhibition in London was important in introducing the new dyes to the public and was extensively reported at the time. Again newspaper and periodical archives are used to explore the reactions and preoccupations of the public. The Arts and Crafts movement has been intensively studied and was a philosophy fundamentally opposed to the introduction of the synthetic dyes. The influence of this on practice is assessed along with the evidence from dye manuals for the extent to which the natural dyes were eclipsed by the synthetics.

In Chapter 4 the history of the development of the synthetic dyes is reviewed. Their chemistry is explored and the rationale behind the experimental materials and methods adopted later in the study is explained. Dyeing of textile samples to provide test samples is described. Chapter 5 outlines the theory of the vibrational spectroscopy methods used, infrared and Raman spectroscopy. Previously published work relating to their application in the area of cultural heritage is reviewed. Chapters 6 and 7 report the results of the investigations on the test samples and Chapter 8 extends these investigations to historical fabrics. Finally Chapter 9 reviews the overall conclusions of the study

## Chapter 2. Synthetic dyes, industrialisation and the expansion of commercial activity

### 2.1 Introduction

The nineteenth century was a period of rapid change and, having particular relevance for this study, the textile industries were a major part of the English industrial expansion of the time.<sup>35</sup> There was also a change in the meaning of the word ‘science’ over this period. Whereas it originally meant any branch of systematic study, by the mid nineteenth century it had become more restricted<sup>36</sup> and the Oxford English Dictionary attributes its first written use in this sense to W.G. Ward in the Dublin Review in 1867:

We shall...use the word ‘science’ in the sense which Englishmen so commonly give to it; as expressing physical and experimental science, to the exclusion of theological and metaphysical.<sup>37</sup>

Education was expanded to include greater sections of the population, both in age and in class, and wider ranges of subject matter. Technical education was available from an increasing number of institutions as an alternative to the traditional apprenticeship system in the manufacturing trades. These changes were happening all over Europe although at different rates in different countries. Naturally this rapid rate of change was unsettling and had undesirable consequences in terms of pollution and the growth of concentrated population centres and was therefore criticised by some. This chapter will examine these developments with respect to the synthetic dye industry in this period including a study of the development of the textile dyeing course at the Yorkshire College, the forerunner of Leeds University.

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<sup>35</sup> JENKINS, D. T. & PONTING, K. G. (1982) *The British Wool Textile Industry 1770-1914*, London, Heinemann Educational Books Ltd.

ROSE, M. B. (Ed.) (1996) *The Lancashire Cotton Industry. A history since 1700*, Preston, Lancashire County Books.

<sup>36</sup> ROSS, S. (1962) Scientist: The story of a word. *Annals of Science*, 18, 65-85.

<sup>37</sup> Oxford English Dictionary (2009), Oxford University Press, [<http://dictionary.oed.com/cgi/entry/50215796?>] Accessed online 28<sup>th</sup> July 2010.



Yorkshire College was initially chosen for study as references to it and to the instructor in dyeing there, John James Hummel, were found in the *Leeds Mercury* during searches of the database of 19<sup>th</sup>-century newspapers referred to in Chapter 1. Further investigation revealed a wealth of information which related to the foundation of the college and its progress throughout the rest of the century. Other colleges could have been researched in the same way but time constraints meant that increasing the size of the study was not an option. Secondary sources alone were therefore used for information about Owens College and other foundations from the time.<sup>38</sup> Yorkshire College was typical of the majority of the new colleges at the time in the motivations and identities of its founders. The increasing competition from European textiles in the second half of the nineteenth century led provincial industrialists to seek to improve their position, and providing better training for the population from which their workforce was drawn was considered one way of achieving this. The investment in these colleges sometimes came largely from one source such as Owens College or, in the case of the Yorkshire College, from multiple donations. The development of the colleges tended to gradually move away from vocational training to more academic fields with the addition of arts and pure science faculties and the Yorkshire College did follow this trend but was untypical in maintaining close links with the textile industries after it became the University of Leeds until the present day.<sup>39</sup> John James Hummel was not very representative of the staff employed by these institutions most of whom were chemists with doctorates. He never obtained a doctorate but had a very good grounding in practical chemistry and dyeing and probably had a flair for teaching. He was eventually created a professor but had to lobby hard to achieve this.

## 2.2 Chemistry in the nineteenth century

The chemical industry was already well advanced in England by the early nineteenth century and one of the largest economic sectors, textile production, consumed large

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<sup>38</sup> SANDERSON, M. (1975) *The Universities in the Nineteenth Century*, London and Boston, Routledge & Kegan Paul. This was the principal text used.

<sup>39</sup> The University of Leeds maintains studies in textile design and has a current partnership with Marks and Spencer plc. See [http://www.leeds.ac.uk/info/20024/research\\_and\\_innovation/1915/strategic\\_partnerships/6](http://www.leeds.ac.uk/info/20024/research_and_innovation/1915/strategic_partnerships/6) Accessed 19th Dec 2013

amounts of chemicals such as alkali and alum.<sup>40</sup> In another sector, the use of coal gas for lighting was advancing rapidly, producing large amounts of coal tar as a waste product. The chemical research leading to the introduction of synthetic dyes made a great difference to the working methods of the textile dyeing trade but it was certainly not the first time that chemistry was applied in this industry. The long-established extraction of natural dyes involved chemical manipulations, sometimes carried out by the producers of the dyes (as in the case of indigo and madder) and sometimes carried out by the dyers themselves (as with the logwoods).<sup>41</sup> Chemical modifications of natural dyes such as indigo sulphonc acid<sup>42</sup> and picric acid<sup>43</sup> also predated the exploitation of the coal tar dyes. These chemical processes however were carried out by guildsmen and craftsmen dyers and so were generally considered as part of the textile rather than the chemical industry.

This changed by the early nineteenth century with the application of science to industry with evidence based knowledge becoming the norm. Production methods were increasingly based on reproducible methodology subject to expertise rather than variable methods governed by the knowledge of the practitioner. Several other chemists had produced coloured compounds before Perkin's celebrated mauve was synthesised. For example, in 1834 Friedlieb Ferdinand Runge<sup>44</sup> (1795-1867) had produced red aurin from carbolic acid and deep blue pttacal from beechwood tar. Even Perkin had produced a bright red colour earlier in 1856 with his colleague Church during their researches into coal tar residues but it had not been pursued.<sup>45</sup>

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<sup>40</sup> HOMBURG, E., TRAVIS, A. S. & SCHROTER, H. G. (Eds.) (1998) *The Chemical Industry in Europe, 1850-1914. Industrial Growth, Pollution and Professionalization*, Dordrecht/Boston/London, Kluwer Academic Publishers.

<sup>41</sup> GRAFF, J.H.H.D. (2004) *The Colourful Past: The Origins, Chemistry and Identification of Natural Dyestuffs*. London, Archetype Press Pages 95 (madder), 236 (logwood), 253 (indigo)

<sup>42</sup> Also called indigo carmine. Ibid Page 258

<sup>43</sup> TRAVIS, A.S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*. London & Toronto, Associated University Presses Pages 41 - 43

<sup>44</sup> HOWARD, A. V. (1951) *Chambers's Dictionary of Scientists*, London & Edinburgh, W & R Chambers.

<sup>45</sup> GARFIELD, S. (2000) *Mauve. How one man invented a colour that changed the world.*, London, Faber and Faber Ltd. Page 44.

### 2.2.1 The teaching of chemistry

A prerequisite for industrial chemistry was relevant training but academic study of the physical sciences in England was seen more as a pastime for the leisured classes than a systematic study for any professional purpose except in the study of medicine. The only two universities in England at the start of the nineteenth century<sup>46</sup>, Oxford and Cambridge, were still controlled by the established Anglican Church and largely concerned with producing clergymen. The thrust of instruction was the liberal arts and studies in Natural Science were only initiated in 1848 at Cambridge and 1850 at Oxford<sup>47</sup>. Despite these reforms the courses were largely theoretical and there was still very little practical science carried out.<sup>48</sup> The only places where both basic and applied research were taught in England were the Royal College of Chemistry from 1845 and Owens College, Manchester under Schorlemmer from 1851.<sup>49</sup> Owens College was modelled on the Oxbridge format initially but instruction became much more practical in 1857 with the appointment of Sir Henry Roscoe (1833-1915) as Professor of Chemistry.<sup>50</sup>

There was however some patronage of the new materials sciences and Prince Albert (1819-1861) had a particular interest in their practical applications. Nevertheless, from early in the nineteenth century, England was widely perceived to be behind the rest of Europe in developing a mature chemical profession. In 1837 Justus Liebig (1803-1873), visiting from Giessen, condemned the lack of practical chemical training in England:

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<sup>46</sup> This study only considers University education in England. In the nineteenth century Scotland had several universities and their subject spread was much wider than in England. Some English students did study there but they could not cater for all those who wanted more than Oxford and Cambridge could offer.

<sup>47</sup> SANDERSON, M. (1975) *The universities in the nineteenth century*, London and Boston, Routledge & Kegan Paul. P. 75

<sup>48</sup> CARDWELL, D. S. L. (1972) *The Organisation of Science in England*, London, Heinemann Educational Books Ltd. p. 42. In 1825/26 Cardwell quotes a source discussing the new Mechanics' Institutes, one of which was to have a chemical laboratory, as saying 'in first-rate scientific institutions, attended by men of leisure, rank and education, the laboratories are seldom used'.

<sup>49</sup> SANDERSON, M. (1975) *The universities in the nineteenth century*, London and Boston, Routledge & Kegan Paul. Page 79. Owens College was founded in 1851 with a bequest of nearly £100,000 from the cotton merchant, John Owens (1790-1846). Schorlemmer (1834-1892) had studied at Heidelberg and Giessen.

<sup>50</sup> Ibid. Page 79. Roscoe took his degree at University College, London and his PhD under Bunsen (1811-1899) in Heidelberg. KARGON, R. H. (2004) Roscoe, Sir Henry Enfield. *Oxford Dictionary of National Biography*. Oxford, Oxford University Press.

England is not the land of science. There is only widespread dilettantism, their chemists are ashamed to be known by that name because it has been assumed by the apothecaries, who are despised.<sup>51</sup>

The first teaching at the Royal College of Chemistry was in temporary laboratories just off Hanover Square in London. The subscription list for the foundation was headed by the Queen's physician, Sir James Clark (1788-1870), Michael Faraday (1791-1867) and the Prince Consort. Prince Albert's influence was far-reaching in the new college and his interest was largely motivated by the improvements in agriculture that might develop from the study of chemistry. Its first director, probably nominated by Prince Albert, was August Wilhelm Hofmann (1818-1892) who had studied under Liebig. Hofmann was aware that the new sciences had to prove their worth in practical applications and his research career, whilst contributing greatly to fundamental understanding of organic chemistry, was shaped by the potential practical applications of his discoveries.<sup>52</sup>

A major emphasis of the time was on making good use of the wastes from established chemical processes and coal tar was one such product.<sup>53</sup> Chemists had found that different fractions could be distilled from this by the application of heat and Hofmann had already started to investigate one of the chemicals obtained, aniline. England was clearly a suitable place to pursue such studies due to the large amount of coal tar available. Chemistry had advanced to the point where the atomic composition of materials could be analysed and so similarities between substances could be determined although the structures of the molecules as we understand them today were not known.<sup>54</sup> Hofmann had determined similarities between aniline and naturally occurring alkaloids such as the medically important quinine and his research interests were in the synthesis of such natural compounds from the waste aniline. In fact the link between naturally occurring compounds and the constituents of coal tar were reinforced by the fact that aniline could also be

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<sup>51</sup> GARFIELD, S. (2000) *Mauve. How one man invented a colour that changed the world.*, London, Faber and Faber Ltd. Quoted page 20.

<sup>52</sup> Ibid. page 21

<sup>53</sup> CROOKES, W. (1863) Chemical products - The Application of Waste. *Popular Science Review*, 2:5, 58.

<sup>54</sup> KLEIN, U. (2005) Technoscience avant la lettre. *Perspectives on Science*, 13, 226. For example, it could be determined that one compound contained two more oxygen atoms than another and therefore it might be transformed into the second species by oxidation.

obtained from the breakdown of indigo, hence the name given to it, derived from the names for indigo in Sanskrit (*nila*) and Arabic (*an-nil*).<sup>55</sup>

Despite the fact that one of Hofmann's pupils was the first person to commercially exploit a synthetic dye, much of the chemical skill required to build on this innovation was found in Germany and not England whereas, at that time, England's textile industry was much larger than Germany's. Many chemists who had trained in German universities came to England for employment notably Heinrich Caro at Roberts Dale and Co.<sup>56</sup> and Otto N. Witt at Williams, Thomas and Dower, Brentford.<sup>57</sup>

Conversely English pioneers in chemistry had frequently obtained their degrees in German universities. For example, Lyon Playfair (1818-1898) worked under Liebig at Giessen and went on to be the Professor of Chemistry at the Royal Manchester Institution and chemist to the Geological Survey before entering a parliamentary career and being created 1<sup>st</sup> Baron Playfair.<sup>58</sup> Edward Frankland (1825-1899) studied under Bunsen in Marburg and subsequently became Professor of Chemistry at Owens College and finally at the Royal College of Chemistry.<sup>59</sup> Sir Thomas Edward Thorpe (1845-1925) started his studies in chemistry with Sir Henry Roscoe at Owens College but took his PhD at Heidelberg under Bunsen and ended his career as principal chemist at the new Government Laboratory.<sup>60</sup>

Thus the nineteenth century saw the start of professional chemical education, particularly in Germany. English institutions struggled to catch up and one such foundation in 1874 was the Yorkshire College of Science which ultimately became Leeds University. It was founded later than Owens College and had different initial aspirations being particularly

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<sup>55</sup> BALFOUR-PAUL, J. (1998) *Indigo*, London, British Museum Press. p. 258

<sup>56</sup> TRAVIS, A. S. (2008) What a wonderful Empire is the Organic Chemistry. *Bulletin of the History of Chemistry*, 33, 1-11.

<sup>57</sup> TRAVIS, A. S. (2006) Decadence, Decline and Celebration: Raphael Mendola and the Mauve Jubilee of 1906. *History and Technology*, 22, 131-152.

<sup>58</sup> GOODAY, G.J.N., 'Playfair, Lyon, first Baron Playfair (1818-1898)', *Oxford Dictionary of National Biography*, Oxford University Press, Sept 2004; online edn, May 2008  
[<http://www.oxforddnb.com/view/article/22368>, accessed 13 Sept 2010]

<sup>59</sup> HOWARD, A. V. (1951) *Chambers's Dictionary of Scientists*, London & Edinburgh, W & R Chambers.

<sup>60</sup> HAMMOND, P. W., 'Thorpe, Sir Thomas Edward (1845-1925)', *Oxford Dictionary of National Biography*, Oxford University Press, Sept 2004; online edn, Jan 2008  
[<http://www.oxforddnb.com/view/article/36514>, accessed 13 Sept 2010]

associated with instruction in the textile industries and so is very relevant to the present study.<sup>61</sup> The history of Leeds University has been published elsewhere<sup>62</sup> but its development is also well documented through contemporary newspaper reports possibly because Sir Edward Baines (1800-1890), an early supporter of the college and chairman of its council from 1880-1887, was also the editor of the *Leeds Mercury*.<sup>63</sup> This archive provides an alternative and perhaps more immediate narrative and is the primary source for the following analysis of the evolution of the Yorkshire College in the nineteenth century which concentrates on the course in textile dyeing run there. The changing educational aspirations of the College illustrate the attitudes in England to higher education in the last quarter of the nineteenth century.

### 2.2.2 The Yorkshire College

Support for the College came from a wide range of the middle and upper classes of Yorkshire with most support in Leeds itself. George Henry and Arthur Nussey, woollen manufacturers in Birstall were motivated to found a college in Leeds after their visit to the 1867 International Exhibition in Paris when they found that English woollen manufactories were no longer technically comparable to those of other countries.<sup>64</sup> Importantly Lord Frederick Cavendish (1836-1882) was recruited to be the chairman of the General Committee and other activists included Dr John Heaton (1817-1880), a prominent Leeds medical man,<sup>65</sup> Mr Titus Salt Jnr from the well-known industrial family, and, as previously mentioned, Sir Edward Baines MP. The Yorkshire College was thus typical of the foundations started by local men of influence to improve their cities and their businesses.

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<sup>61</sup> Owens College was founded on the model of Oxford and Cambridge as a purely academic institution but became much more vocational shortly afterwards.

<sup>62</sup> BERESFORD, M. W. (1975) Red brick and Portland Stone: a Building History. IN GOSDEN, P. H. J. H. & TAYLOR, A. J. (Eds.) *Studies in the History of a University 1874-1974*. Leeds, E.J. Arnold & Son Limited.

<sup>63</sup> SANDERSON, M. (1975) *The universities in the nineteenth century*, London and Boston, Routledge & Kegan Paul. Page 163

<sup>64</sup> Ibid. Pages 156-157

<sup>65</sup> TOSH, J. (2004) *Manliness and Masculinities in Nineteenth Century Britain: Essays on Gender, Family and Empire*, London, Routledge. Pages 129-147.

Although its foundation was discussed in the press in 1869<sup>66</sup> the first session of instruction at the College did not start until 26<sup>th</sup> October 1874.<sup>67</sup> The long delay was largely due to the difficulty of raising the necessary capital and this problem persisted throughout the independent history of the College. The proposal was to establish a College for ‘instruction in those sciences which are applicable to the industrial arts’ including dyeing’.<sup>68</sup> Evening classes were also proposed to supply instruction to ‘young men now engaged in business’.<sup>69</sup> There was an acceptance that the increasing competition from abroad was an issue and that ‘Manufacturers are now convinced that they must promote scientific education if they would keep pace with their continental rivals’.<sup>70</sup>

In 1871 an estimate of the funds required to establish the College and appeals for contributions were first published.<sup>71</sup> The fund was significantly increased by a donation from the Clothworkers’ Livery Company to establish a Professorship of Textile Fabrics.<sup>72</sup> It was proposed to run a series of courses on textile manufacturing, including weaving, and also ‘Scouring and Colour and Processes of Dyeing – to impart a sound theoretical and practical knowledge in chemistry applied to scouring and dyeing; to study the best ingredients, and the proper use of them by practical experiments’.<sup>73</sup> Thus textile dyeing was integral to the curriculum from the start. By 1874 £20,000 had been raised and this was considered enough to proceed. A constitution was approved,<sup>74</sup> and professors of Geology, Physics and Mathematics, Textile Industries (Prof. William Walker) and Chemistry (Prof. Thomas Edward Thorpe) were appointed<sup>75</sup> with courses starting in the autumn of that year.

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<sup>66</sup> ANON. *Sheffield and Rotherham Independent*. Sheffield. Nov 8th 1869

<sup>67</sup> ANON. *Leeds Mercury*. Leeds. Sep 24th 1874

<sup>68</sup> ANON. *Bradford Observer*. Bradford. Jan 25th 1870

<sup>69</sup> ANON. *Leeds Mercury*. Leeds. Jan 29th 1870 p. 12

<sup>70</sup> Ibid. Feb 25th 1870

<sup>71</sup> Ibid. Jul 6th 1871

<sup>72</sup> Ibid. Jun 6th 1873 p.3

<sup>73</sup> Ibid. Jul 6th 1873

<sup>74</sup> Ibid. May 1st 1874 p. 4

<sup>75</sup> Ibid. Jul 18th 1874 p. 7

Professor Walker proved to be a short-lived incumbent, resigning in early 1875.<sup>76</sup> Nevertheless the College was officially inaugurated in October 1875<sup>77</sup> and in early 1876 Mr Beaumont was appointed as an instructor, not a professor, to teach weaving classes.<sup>78</sup> John Beaumont (1821/2 – 1889) was a much more successful appointment, staying with the college until his retirement in 1889, and being succeeded by his son. He spent the summer of 1876 on a Continental tour of weaving schools to provide models for the development of the course in Leeds.<sup>79</sup>

Up to this date courses had been run in rented accommodation but in 1877 the Clothworkers' Company gave an additional £10,000 to purchase a suitable site and commence building.<sup>80</sup> The foundation stone was laid in October 1877.<sup>81</sup> In 1878 a department of coal mining was added<sup>82</sup> and in 1879 an instructor in dyeing, Mr J.J. Hummel (1850-1902), was appointed.<sup>83</sup> In the dye department, which opened in April 1880:

Not only will [the students] learn the “art and mystery” of dyeing fabrics, but with their own hands, and by the aid of the best appliances, will they have to carry out the theory into actual practice. This is the great and essential feature of the dyeing department.<sup>84</sup>

Thus, this first course in dyeing was intended to be a very vocational training aimed at existing and aspiring workers in the textile industries. It was supported by lectures and practical training in chemistry but, in contrast to the academic research taught at the Royal College, the attitude to dyeing was still largely empirical. The opening of this department

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<sup>76</sup> Ibid. Apr 24th 1875 p. 12. There is some mystery surrounding Walker's departure. Despite much encouragement he seems to have found the equipment supplied by the college inadequate and never delivered the lectures he was contracted for. GOSDEN, P. H. J. H. & TAYLOR, A. J. (Eds.) (1975) *Studies in the History of a University 1874-1974. To Commemorate the Centenary of the University of Leeds.*, Leeds, E.J. Arnold & Son Limited.

<sup>77</sup> ANON. *Leeds Mercury*. Leeds. Oct 7th 1875 p.5-6

<sup>78</sup> Ibid. Apr 22nd 1876 p.10

<sup>79</sup> Ibid. Sep 23rd 1876 p.12

<sup>80</sup> Ibid. Apr 17th 1877 p. 6

<sup>81</sup> Ibid. Oct 24th 1877 p.8

<sup>82</sup> Ibid. Mar 12th 1878 p.6

<sup>83</sup> Ibid. Oct 11th 1879

<sup>84</sup> Ibid. Apr 7th 1880 p.3



may also have been related to fierce criticism of the quality of the work of the dyers in the area in comparison to French work in the 1870s.<sup>85</sup>

Mr Hummel's inaugural lecture in 1880 was introduced by Mr Obadiah Nussey who explained:

Instructor Hummel states that his family have been dyers for generations, and that his father studied under Professors Chevrant and Dumas at the Gobelins, in Paris, and was engaged at dyeworks of the various kinds in Austria, Italy, Germany, and France. He was also engaged at the celebrated print works of the late Mr. James Thurlston, F.R.S., in Lancashire, along with Dr. Lyon Playfair. Mr. Hummel personally studied the chemistry of dyeing at the well-known Polytechnic School of Zurich, under Professor Bolley, where he gained the highest diploma in technical chemistry awarded by the institution. Subsequently he studied at the Royal Institution, Manchester, under the late Dr. Crace Calvert, and since 1869 he had been constantly engaged practically in the dyeing and printing of textile fabrics, successively as chemist, sub-manager, and managing partner, in Scotland and England. For some years, while engaged in Scotland and after the day's work, he conducted a class for the purpose of imparting a knowledge of chemistry in its application to dyeing to a number of young men already engaged in dyeworks, most of whom now hold responsible situations in dyeworks as foremen or managers.<sup>86</sup>

Despite his publication of a well respected manual of dyeing<sup>87</sup> and his tenure of the chair at the Yorkshire College until his death in 1902, little published information has been found about Hummel. He was a product of the international nature of the textile dyeing and printing trade with a foreign father who died before his birth, a Swiss step-father and English mother.<sup>88</sup> It is not clear whether the 'father' referred to in the biography given by Nussey was his birth or stepfather but most of his advancement was due to Swiss connections so his stepfather seems to have been highly influential in his life. He had been

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<sup>85</sup> JENKINS, D. T. & PONTING, K. G. (1982) *The British Wool Textile Industry 1770-1914*, London, Heinemann Educational Books Ltd. p. 180 quoting from Bradford Observer 1 Dec 1875

<sup>86</sup> ANON. *Leeds Mercury*. Leeds. Apr 13th 1880 p.6

<sup>87</sup> HUMMEL, J. J. (1885) *The Dyeing of Textile Fabrics*, London, Paris & Melbourne, Cassell and Company, Limited. The manual was reprinted in 1886, 1888, 1890, 1893 and 1896.

<sup>88</sup> He was born on 25<sup>th</sup> February 1850 at Moor Lane, Clitheroe. Birth Certificate; Certified Copy issued at the General Register Office 29<sup>th</sup> June 2010. His father had died in September 1849 after only a few months of marriage to his mother Mary, nee Bold. She subsequently remarried John Sieber who was a Swiss chemist working at a printworks. Information from 1841 and 1851 census data accessed via Ancestry.co.uk on 22<sup>nd</sup> and 23<sup>rd</sup> June 2010. John Sieber also died young and left an estate valued at "under £3,000" to Mary under a grant of probate on April 1861.

sent to study with another Swiss national, Gustavus Knecht,<sup>89</sup> in Everton, Liverpool where he was recorded in the 1861 census at the age of 11.<sup>90</sup>

At some point after this he spent three years in Zurich studying before returning to Manchester to work with Crace Calvert. According to the obituary written by his son<sup>91</sup> he was offered an assistantship there but turned it down in favour of a position at Messrs James Black and Co.'s dyeing and print works at Glasgow. He cannot be traced in the 1871 census but his obituary states that he remained at James Black for seven years and then, in 1875, moved to the Foxhill Bank Printing Company, Lancashire and then the Allander Print & Dye Works, Stirlingshire. At the time of his appointment at the Yorkshire College in 1879 he was working at the Nether Coal Dyeworks, Auchterarder, Perthshire.<sup>92</sup> It may have been while he was working in Stirlingshire that he met his wife, Wilhelmina Ure, and they were married on 19<sup>th</sup> Sept 1878 in Dumbarton according to the rites of the United Presbyterian Church. He was described on his marriage certificate as a Master Calico Printer.<sup>93</sup>

Hummel was obviously well versed in the latest developments in the dyeing industry and in his lecture gave an overview of it to the present. He pointed out that both Perkin and Verguin were carrying out chemical research when they made their discoveries, not engaged in the dye industry. Like Hofmann he was interested in the artificial synthesis of natural dyestuffs '.....one very important feature now introduced was the discovery by various workers of the pure colouring principles of the several dyewoods and the investigation of their properties.' The structure of indigo was now known and he predicted that those of logwood and brazilwood soon would be known. The outline of the course was given in which theory would be important but practice would also be critical. Chemistry

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<sup>89</sup> Gustavus Knecht was the father of Edmund Knecht who became Professor of Technical Chemistry at Manchester College of Technology in 1890. CARDWELL, D. S. L. (1972) *The Organisation of Science in England*, London, Heinemann Educational Books Ltd. p.174

<sup>90</sup> Census return accessed online via Ancestry.co.uk

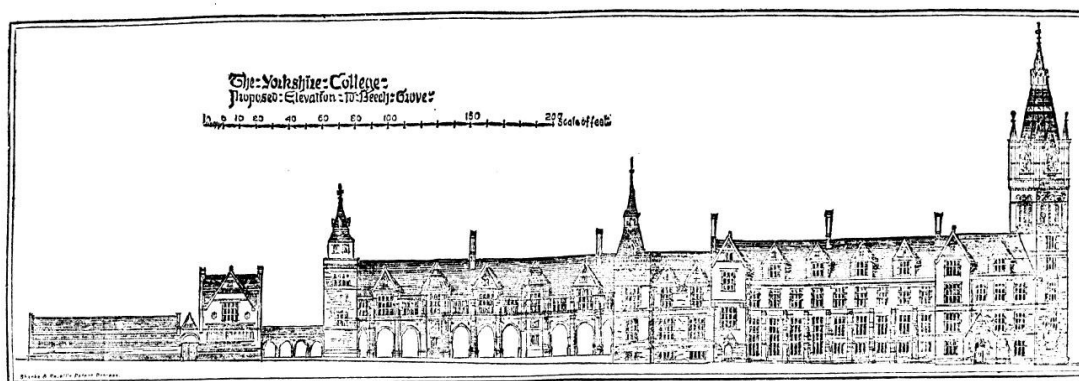
<sup>91</sup> HUMMEL, R. U. (1903) Obituary: John James Hummel. *Journal of the Chemical Society Transactions*, 83, 652-3.

<sup>92</sup> ANON. *Leeds Mercury*. Leeds. Oct 11th 1879

<sup>93</sup> Marriage certificate accessed via Ancestry.co.uk on 22<sup>nd</sup> June 2010. Wilhelmina's father, James Ure, is described as a Master Ironfounder.

was already taught in the College, of course, and experiments in dyeing would be added although the students would still have more to learn about large scale dyeing after completion of their training. As well as dyeing, the interactions between the dyes and fibres would be taught and methods for testing the purity of dyestuffs which was considered critical to the future career of the students.<sup>94</sup> It is notable though that, unlike his colleague Thorpe or Roscoe at Owens College, Hummel did not have a research degree.

After the formal lecture, Dr. Thorpe drew attention to a diagram on the wall of a list of approximately 40 colouring matters and their discoverers since 1856. He commented that almost all the names were German ‘.....scarcely a British name there...’. He put this down to the difference between the German and British systems ‘The majority of the men who had made these discoveries in regard to colouring matters were not practical dyers, but scientific chemists – professors of chemistry – in well-known German Universities, or their students.’<sup>95</sup> He was making the valid point that it was chemical research that was critical to industrial development whereas the course being inaugurated at the College was strictly vocational.



**Figure 2.1** Yorkshire College buildings in College Road Leeds, 1880<sup>96</sup>

<sup>94</sup> ANON. *Leeds Mercury*. Leeds. Apr 13th 1880 p.6

<sup>95</sup> Ibid. Apr 13th 1880 p. 6

<sup>96</sup> Ibid. Dec 2nd 1880 p.8 Image from 19<sup>th</sup> Century British Library Newspapers

In June 1880 representatives of the Clothworkers' Company came to inspect the new buildings. They visited the weaving class and also the Dyeing Department which was said to be '..... the first educational provision of the kind in this country.'<sup>97</sup> Both the dyeing and textile industries courses were well attended with a range of nationalities on the dyeing course. In a report of the opening of the new Textile and Dyeing Departments the numbers and origins of students are given as:

The number of entries for the dyeing classes of the opening session was 34, including students from Mexico and the West of England, besides those from Yorkshire..... The number of students for the dyeing lectures is 26, and in the dyehouse there are also 26, including students from Norway, Scotland and Wales.<sup>98</sup>

The opening of the new College buildings was also reported in the *Glasgow Herald*<sup>99</sup> and the article includes a report of the address by the Rt. Hon. Mr A.J. Mundella MP (1825-1897)<sup>100</sup> which sums up his feelings about the teaching of technical subjects and the comparison with Continental progress.

(Initially) .....they had great doubts about the object intended, and (that) they thought that the really practical place must be the workshop. Now, however, everybody seemed satisfied that while they could not dispense with practical workmanship, yet they knew there was something else which gave value to that experience. Look at the dyeing school of this Yorkshire College that day. He had in time paid money for dyeing; he had seen men testing alkalies and acids by dipping their fingers in them, but they did not by that process ascertain what they wanted with the skill and accuracy that the young men in our Yorkshire College were ascertaining it. .... The days of rule of thumb, they might depend upon it, were numbered..... those nations of the Continent who were producing such magnificent results in building machinery and apparatus were not doing it for any merely sentimental reason, or to make great progress in any branch of science. Their object was the very prosy, very practical one of self-interest. What they meant was to give industrial strength to those who they believed were the real source of the wealth of the nation. In giving instructions in those sciences which were applicable to industry, he might say that France

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<sup>97</sup> Ibid. Jun 19th 1880 p. 12

<sup>98</sup> Ibid. Dec 4th 1880 p.12

<sup>99</sup> ANON. *Glasgow Herald*. Glasgow. Dec 4th 1880 p.12

<sup>100</sup> Jonathan Spain, 'Mundella, Anthony John (1825–1897)', *Oxford Dictionary of National Biography*, Oxford University Press, 2004; online edn, Oct 2009 [<http://www.oxforddnb.com/view/article/19534>, accessed 19 Oct 2010]. Mundella was a liberal politician and a life-long campaigner for secondary and technical education. He had made his fortune in the hosiery trade.

and Germany were conducting an active competition with each other in this matter of arming for the industrial fight.

However much the necessity of instruction in technical subjects was recognised in order to compete with foreign business rivals, it remained difficult to actually raise money to fund the College which was in a constant state of deficit. In early 1880 the College appealed for more funding.<sup>101</sup> Although individually manufacturers seemed reluctant to part with hard cash, the Clothworkers' Company were consistent and generous benefactors. The Glasgow Herald noted with regard to new buildings opened in 1880:

The whole cost of the land, the erection of the buildings, and the fittings of the textile and dyeing departments have been defrayed by the Clothworkers' Company at a cost of about £15,000 and the site is a pleasant suburb of Leeds, hitherto known as Beech Grove.<sup>102</sup>

The students were either young men currently employed in the industry or younger men (14 to 18) who might have been inheriting a business in the textile industries or desirous of entering the trade. They might perhaps go on to study at University and in the calendar for the 1880/1881 session the general approach of the College was described as:

The various curricula have been arranged so as to provide complete courses of education in the subjects required for the London University Matriculation and Science, Arts, and Medical degrees; for scholarships at the Universities, and for various professions.<sup>103</sup>

The College was therefore more comparable to a modern secondary school than a University or Polytechnic.

By 1882 the facilities in the dyehouse had been extended to provide space for an expansion in the student numbers and more efficient apparatus. The range of work being carried out encompassed 'The dyeing of wool, cotton wool, calico, cotton yarn & silk, also calico printing and the preparation of the newer coal tar colours.'<sup>104</sup> No mention is made in the

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<sup>101</sup> ANON. *Leeds Mercury*. Leeds. Feb 10th 1880 p.8

<sup>102</sup> ANON. *Glasgow Herald*. Glasgow. Dec 4th 1880 p.12

<sup>103</sup> ANON. *Leeds Mercury*. Leeds. Sep 22nd 1880 p.2

<sup>104</sup> Ibid. Jun 26th 1882 p.3

prospectus of research on textile dyes although Hummel was actively investigating the structures and properties of natural dyes. A.G. Perkin (1861-1937)<sup>105</sup> was a student in 1881/2 and was working with Hummel on the discovery of new colouring matters from logwood and peachwood.<sup>106</sup>

The approach to the teaching of the textile industries and dyeing courses remained essentially technical and in 1882 it was proposed to alter the curriculum to facilitate students' entrance to the City and Guilds examinations in May.<sup>107</sup> The thrust of the course was to prepare students to become employable practical textile dyers, although the manufacture of coal tar dyes was also taught.<sup>108</sup> A major component of the training at the Yorkshire College is exemplified by the exact reproduction of a Government-specified colour, a highly technical skill rather than a creative process.<sup>109</sup> The teaching of chemistry at the College at that time covered coal mining, chemical technology and photography but there was a medical bias to the department.<sup>110</sup>

However by 1883 the aspirations of the College as a whole were changing from practical instruction in industries relevant to the local community to what were perceived by some to be loftier ambitions. At the Annual Meeting of the Board of Governors in that year proposals were put forward to extend the teaching to cover the arts as well as the sciences. There were two reasons for this. Firstly that instruction in foreign languages and classics was necessary for their students who wished to go on to attend university. Secondly the college wished to be incorporated in the Victoria University and would therefore need to provide instruction in these areas as well as literature to be considered. Although the extension of the teaching of the College to the arts was generally agreed there were those who were keen that the original foundation to supply education in technical subjects should

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<sup>105</sup> GARFIELD, S. (2000) *Mauve. How one man invented a colour that changed the world.*, London, Faber and Faber Ltd. Page 127 W.H. Perkin's son who had attended the Royal College of Chemistry in 1878

<sup>106</sup> ANON. *Leeds Mercury*. Leeds. Jun 26th 1882 p.3

<sup>107</sup> Ibid. Jun 26th 1882 p.3

<sup>108</sup> Ibid. Jun 23rd 1883 p.12

<sup>109</sup> Ibid. Jun 23rd 1883 p.12. It is ironic that this, in 1883, was a dyed fabric for military uniforms and the true weakness of the British position was finally revealed when war with Germany broke out in 1914 and the supply of dyes was cut off.

<sup>110</sup> GOSDEN, P. H. J. H. & TAYLOR, A. J. (Eds.) (1975) *Studies in the History of a University 1874-1974. To Commemorate the Centenary of the University of Leeds.*, Leeds, E.J. Arnold & Son Limited.p. 249

not be lost. Mr Greig spoke to this effect and pointed out that the College was established 'to supply education in technical subjects' and this foundation was not being fully adhered to. However he would not oppose the proposal as only a small amount of money was involved. The motion to extend teaching in the Arts was therefore carried unanimously.<sup>111</sup>

At this point it can be seen that a split was developing between the technical departments of the College and the newer, although more traditional, subjects. This was encouraged by the English university system which demanded qualifications in ancient and modern languages to allow admittance. The College also followed the English custom of seeing education as a means to transmit existing knowledge rather than stimulate original research. There was a certain amount of tension between the teaching staff in the academic and technical subject areas. In 1883 the heads of the technology departments complained unsuccessfully that they were not fairly represented in the governance of the College<sup>112</sup> although Beaumont had already been appointed professor in 1880/1 and Hummel was promoted soon after this in 1884/5.

The addition of more departments followed with the amalgamation with the local Medical School in 1884.<sup>113</sup> A new extension to the existing Textile Industries and Dyeing Departments in College Road was opened by the Prince and Princess of Wales in 1885, provoking a great deal of publicity and undoubtedly raising the profile of the College.<sup>114</sup> Again the Clothworkers' Company were generous donors with £30,000 given.<sup>115</sup>

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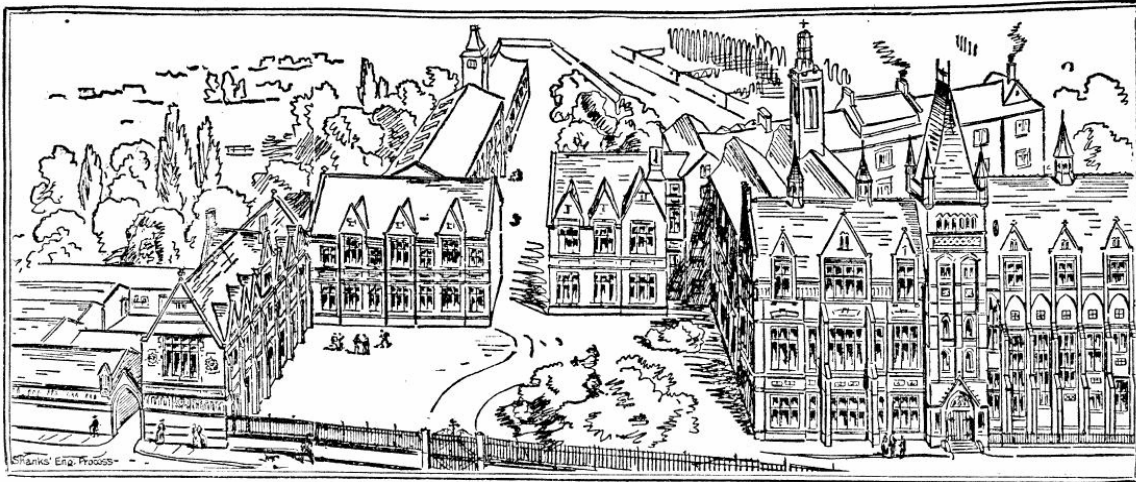
<sup>111</sup> ANON. *Leeds Mercury*. Leeds. Jul 12th 1883 p.8

<sup>112</sup> GOSDEN, P. H. J. H. & TAYLOR, A. J. (Eds.) (1975) *Studies in the History of a University 1874-1974. To Commemorate the Centenary of the University of Leeds.*, Leeds, E.J. Arnold & Son Limited. Pp. 197-200

<sup>113</sup> ANON. *Leeds Mercury*. Leeds. Aug 9th 1884 p.10

<sup>114</sup> ANON. *Daily News*. London. Jul 9th 1885

<sup>115</sup> ANON. *Leeds Mercury*. Leeds. Oct 3rd 1885 p.12



**Figure 2.2** A sketch of the existing and proposed new buildings in College Road in 1884.

The weaving sheds and dyeing department are on the far left. The proposed new dyeing department is towards the rear and left-hand side of the site in a T-shaped block. The chimney is disguised as a tower.<sup>116</sup>

In 1888 an Art Department was added to the broader range of subjects now on offer at the College. At the inauguration, the relevance of this addition to the original technical bias of the college was emphasised although the overall ambitions of the department were broader:

..... the primary intention of the department was to benefit the textile industries of the district, yet the committee had been broad enough in their views to provide also for the cultivation of general art study.<sup>117</sup>

The establishment of an Art Department no doubt also helped the College to achieve the long-held ambition of its General Council to be admitted to Victoria University in 1888. At the ‘Conversazione’ held to celebrate this great event the Marquis of Ripon gave the address during which he said:

From the very commencement of their work the council had kept a great ideal before them, holding very strongly the conviction that the College ought to occupy a high position in the educational system of the county, and always keeping in view the fact that that position would be considerably enhanced and strengthened if they could obtain a real and substantial union with the University.<sup>118</sup>

<sup>116</sup> Ibid. Oct 11th 1884 p.12

<sup>117</sup> Ibid. Jan 13th 1888 p.7

<sup>118</sup> Ibid. Feb 11th 1888 p.10



By 1890 the divide between the more technical and academic subjects became more institutionalised as the textile and dyeing students entered the City and Guilds Examinations and the others the London University matriculation examinations.<sup>119</sup> The technical subjects appeared to have been sidelined even more when Mr E. Woodhouse was reported the following year at the Annual Dinner of the College's Textile Society as saying:

.....it was not essentially a technical institution but the technical department was a valuable adjunct.....It must be an institution at which their youth could receive his education whether he were destined to be an independent gentleman or a cloth manufacturer.<sup>120</sup>

By this point in his career, Hummel's research interests had widened to include investigations in conjunction with the Royal Botanical Gardens, Kew on the evaluation of potential new dyestuffs<sup>121</sup> and research into the fastness of a large range of dyes.

Thus the Yorkshire College supplies an interesting study in the development of higher education in England. It was founded to supply a need to compete in the international textile industry and throughout the period under study the superiority of the German industry was constantly referenced. Although great attention was paid to the systems used on the continent the necessary lessons do not seem to have been drawn with regard to the integration of scientific research and industry. The college developed in two directions; towards technical instruction in textiles and dyeing and towards University level instruction in the traditional subjects of art, law and languages and the emerging field of medicine. Despite Thorpe's comments in 1880,<sup>122</sup> it missed the essence of the German model where scientific research methods were taught to enable industrial technical development. Thorpe was not alone in his opinion, the Second Report of the Royal Commissioners on Technical Instruction found that

The Englishman is accustomed to seek for an immediate return and has yet to learn that an extended and systematic education up to and including the

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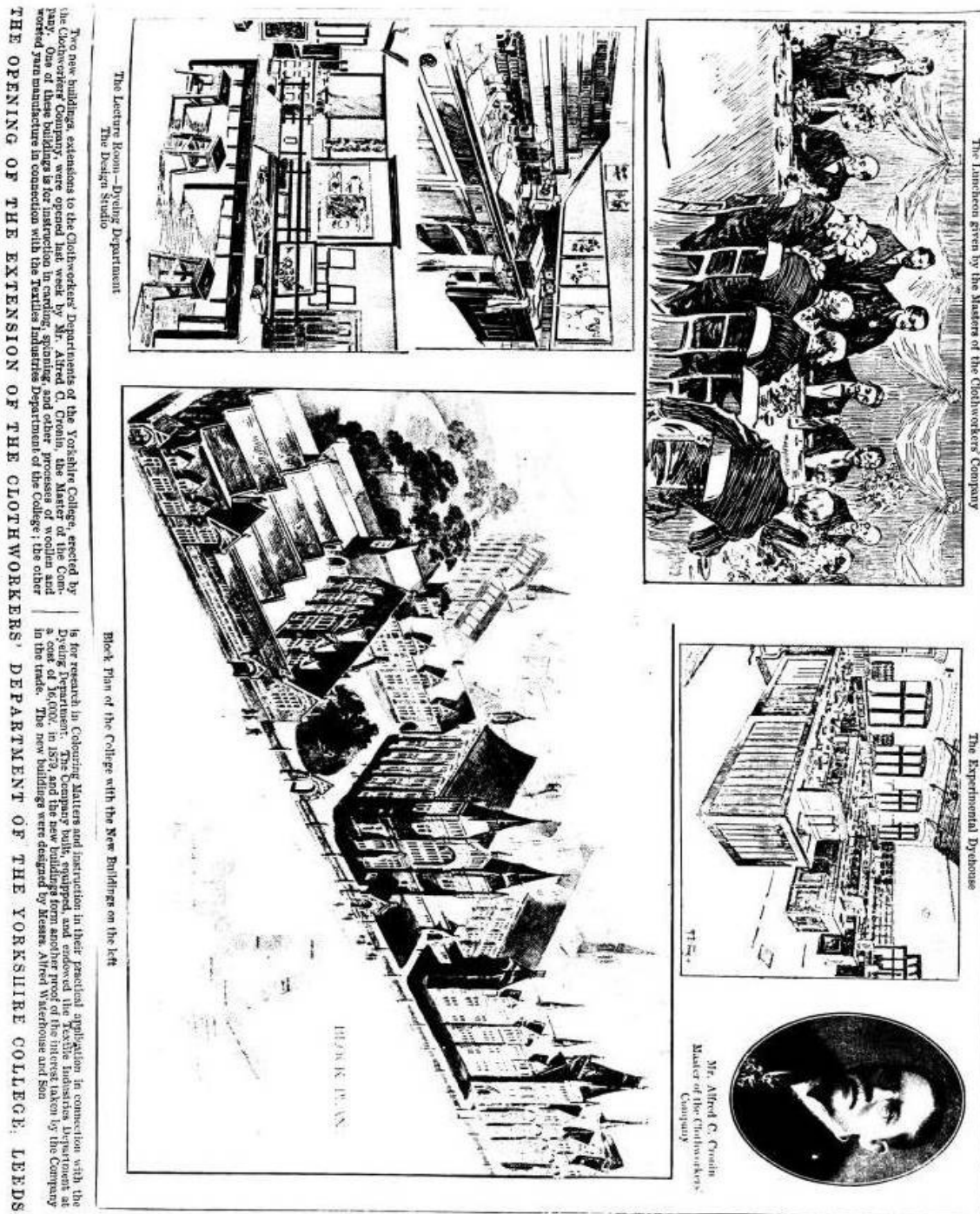
<sup>119</sup> Ibid. Feb 15th 1890 p.10

<sup>120</sup> Ibid. Apr 30th 1891 p.7

<sup>121</sup> HUMMEL, J. (1897) Letter from JJ Hummel to Sir William Thisleton-Dyer. *Archives: Directors' Correspondance*. London, Royal Botanic Gardens, Kew.

<sup>122</sup> Indeed, Thorpe did not succeed in establishing research degrees at the Yorkshire College and left in 1885.

methods of original research is now a necessary preliminary to the fullest development of industry.<sup>123</sup>



**Figure 2.3.** The extension to the dyeing department opened in 1900<sup>124</sup>

<sup>123</sup> Quoted in CARDWELL, D. S. L. (1972) *The Organisation of Science in England*, London, Heinemann Educational Books Ltd. p 133

<sup>124</sup> ANON. *The Graphic*. London. May 19th 1900

Germany only emerged as a unified political entity during the late nineteenth century. As it had previously been divided into several individual states, it had a number of universities in the 18<sup>th</sup> century as compared to England's two, Oxford and Cambridge which led to more competition between the institutions.<sup>125</sup> The systems in both countries at this time gave a great deal of the power in the running of the universities to the dons which resulted in resistance to change.<sup>126</sup> Both also existed within a specific religious milieu and one of their main functions was to produce clergymen, although in Germany the different religious backgrounds of individual nation states contrasted with the Anglican monoculture in England. The system was only finally changed in either case by the foundation of new universities. In Germany this movement started earlier and was motivated by the desire of the states to increase their student populations for economic reasons. In England, by contrast, although there were reforms at Oxford and Cambridge, the new foundations sprang up in the urban centres and many, such as the Yorkshire College, were initiated by industrial interest groups.

Original research was started by professors like Bunsen (1811-1899) in Heidelberg and Liebig (1803-1873) in Giessen much earlier than comparable studies began in England and it was at universities in Germany that many of the pioneering English research chemists were educated.<sup>127</sup> The standard of education of the students entering university was also much higher in Germany than in England thanks to the provision of much better and more universal schooling.<sup>128</sup> It was not until the second half of the nineteenth and the early twentieth centuries that the universities in England changed from self-governing institutions where a gentleman went to complete his education, to generators of input for the national

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<sup>125</sup> SANDERSON, M. (1975) *The universities in the nineteenth century*, London and Boston, Routledge & Kegan Paul. This discussion does not include the Scottish universities which operated on a slightly different model.

<sup>126</sup> Ibid. Page 5-7 In Oxford and Cambridge, the dons had a financial interest in the profit generated by the colleges and therefore the expense of installing laboratories and teaching science was a major disincentive to changing from the older liberal education. In both England and Germany the function of the traditional university was seen as to transmit an existing body of knowledge rather than carry out original research.

<sup>127</sup> MCCLELLAND, C. E. (1980) *State, society, and university in Germany 1700-1914*, Cambridge, Cambridge University Press. Page 151-152. Thomas Edward Thorpe obtained his PhD under Bunsen at Heidelberg, Edward Frankland also studied under Bunsen at Marburg and Lyon Playfair worked with Liebig at Giessen. This was in addition to German scientists moving to England, notably Hofmann and Caro in the case of the synthetic dye industry.

<sup>128</sup> Ibid.

economy. In 1900, after the opening of the latest extensions to the buildings of the Yorkshire College, Mr A.G. Lupton the President of the Council who was awarding the prizes was reported as referring:

....with pleasure to the number of their students who were taking a prominent part in the business and trade of the country, and contrasted the spirit of the present day with that of thirty years ago, when a college education was thought to totally unfit a man for entering into business.<sup>129</sup>

This could be seen as a tendency in Britain to attach a higher status to ‘gentlemanly’ subjects over commerce. Chemistry in this period was still seen as dirty work, not fit for gentlemen and even graduate level scientists were still doing fairly simple work.<sup>130</sup> The notions of class had changed during the industrial revolution from interest groups which were centred around industries such as agriculture or textiles to classes divided on the distribution of wealth, income and power<sup>131</sup> promoting the value of money over birth to determine social status. Nevertheless the newly moneyed classes in Britain still considered that a liberal University education gave more social cachet and satisfied their yearning for gentility. Unfortunately this did not translate into a change in status for research chemistry to a profession attractive to a gentleman until the twentieth century.

There was a continual struggle to raise money to finance the institution although the Clothworkers’ Company, arguably the leading ‘trade body’ in the textile industries, was a notable benefactor. Contemporaries commented on the differences of approach between England and Germany. Germany was seen to provide good, well-funded state education whereas in England Government funds were not forthcoming until the late nineteenth century. Yorkshire College received an annual Parliamentary grant of £1400, enough to cover operating losses, for an initial period of 5 years from 1890.<sup>132</sup> In 1897 they received

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<sup>129</sup> ANON. *Leeds Mercury*. Leeds. Nov 10th 1900

<sup>130</sup> DONNELLY, J. (1998) Structural Locations for Chemists in the British Alkali Industry, 1850-1910. IN HOMBURG, E., TRAVIS, A. S. & SCHROTER, H. G. (Eds.) *The Chemical Industry in Europe, 1850-1914: Industrial Growth, pollution, and Professionalization*. Dordrecht/Boston/London, Kluwer Academic Publishers. P. 212 & 217

<sup>131</sup> MORRIS, R. J. (1979) *Class and Class Consciousness in the Industrial Revolution 1780-1850*, London and Basingstoke, The Macmillan Press Ltd. Page 9

<sup>132</sup> ANON. *Leeds Mercury*. Leeds. Feb 15th 1890 p.10

£2200 out of a total grant of £25,000 given by Government to the University Colleges.<sup>133</sup> In contrast as early as 1868 Zurich Polytechnic had a state subsidy of £10,000 per annum.<sup>134</sup>

### 2.3 Expansion of the synthetic dye industry in the later nineteenth century

Thus, the discipline of chemistry emerged during the period under consideration in large part due to the synthetic dye industry. By reason of its different higher educational system and industrial development, Germany was better able to train personnel and develop a chemical industry. Pickstone<sup>135</sup> proposes a useful framework for the analysis of science in this period in a sociological context. The model divides science into four types; savant, analytical, experimental and techno-science through which the discipline broadly develops from the eighteenth century into the nineteenth. Over time which of these types is dominant changes but they overlap at any one time. Savant chemistry existed under private patronage and studied mostly external characteristics in order to classify the natural world. The synthetic dye industry during the period to 1860 can be classified in this way as new compounds were developed on the basis of process changes with little understanding of the underlying structures involved. This condition led to the long running patent disputes in this period. The next predominant type of analytical science was led by Hofmann who established the compositions of the basic dye types and was also prominent in the experimental phase corresponding to the systematic study of dye molecules in universities. Lastly in the techno-science phase the industrial research laboratories were established.

Whilst dye manufacturers did carry out research, especially in the early days of the industry, most of the work was carried out in independent laboratories.<sup>136</sup> It was only when the industry started to mature in Germany that dedicated research laboratories were set up in the factories. Perkin kept his research activities (as opposed to production development) separate from his factory and this was the pattern for several inventor-entrepreneurs. For

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<sup>133</sup> ANON. *Liverpool Mercury*. Liverpool. Jun 22nd 1897

<sup>134</sup> CARDWELL, D. S. L. (1972) *The Organisation of Science in England*, London, Heinemann Educational Books Ltd. p. 117.

<sup>135</sup> PICKSTONE, J. V. (1993) Ways of knowing: towards a historical sociology of science, technology and medicine. *British Journal for the History of Science*, 26, 433-458.

<sup>136</sup> TRAVIS, A. S. (1992) Science's powerful companion: A.W. Hofmann's investigation of aniline red and its derivatives. *British Journal of the History of Science*, 25, 27-44.

example, Girard maintained a research laboratory with his colleague De Laire in Paris on behalf of Société La Fuchsine and as a proprietor of the company could also be considered an inventor-entrepreneur.<sup>137</sup> Other companies, however, such as Brooke, Simpson & Spiller and Roberts, Dale & Co. did employ research or works chemists but not teams of researchers.<sup>138</sup>

### 2.3.1 The dye industry in England

The history of the synthetic dye industry has been comprehensively outlined by Travis<sup>139</sup> and will only be reviewed here to allow a comparison between the situations in England and Germany at the end of the nineteenth century.

By the last quarter of the nineteenth century the early English dye companies had undergone large scale reorganisations. The first, Perkin and Sons, sold its assets to Brook, Simpson and Spiller in 1873 but the latter firm did not prosper and was finally liquidated in 1905.<sup>140</sup> Burt, Boulton and Haywood manufactured alizarin from 1876 but were bought out by the British Alizarine Company in 1883.<sup>141</sup> This later organisation did persist and merged with the British Dyestuffs Corporation in 1931.<sup>142</sup> Roberts, Dale and Co. was not so fortunate, despite providing Heinrich Caro with his first experience with the synthetic dyes in 1859. Caro worked for the company until 1866 along with other development chemists. After this date these, mostly German, staff returned to their home country and the firm

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<sup>137</sup> HOMBURG, E. Ibid. The emergence of research laboratories in the dyestuffs industry, 1870-1900. 91-111. Société La Fuchsine was an alliance of French producers formed in 1863 to exploit a monopolistic patent for aniline red. It had failed by 1868. TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses. p.118

<sup>138</sup> Brooke, Simpson and Spiller employed RJ Friswell (1874-77?), R. Meldola (1877-85) and AG Green (1885-94). Roberts, Dale & Co. employed H. Caro (1859-66), AS Leonhardt (c1860 & c 1864-67), CA Martius (1863-65) and L. Schad (c1864-73).

<sup>139</sup> TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses.

<sup>140</sup> This firm had started life as Simpson, Maule and Nicholson in 1853 and by 1860 were one of the two major dye companies with Renard Frères. However they were badly affected by patent litigation and after two changes in proprietors bought Perkin's works in 1874 but sold it on in two years. Ibid.

<sup>141</sup> The British Alizarine Company was formed by a consortium of dyers to avoid the domination of the trade by the German controlled Alizarin Convention. Ibid. p.209

<sup>142</sup> MORRIS, P. J. T. & RUSSELL, C. A. (1988) *Archives of the British Chemical Industry 1750-1914. A Handlist*, Faringdon, Oxfordshire, UK, British Society for the History of Science.

suffered decline due to death and illness in the family of the proprietors and disastrous explosions at the works.<sup>143</sup>

The Holliday family were another firm which managed to persist into the twentieth century. Read Holliday owned the largest tar distillery in the north of England in the 1860s<sup>144</sup> and so the production of aniline dyes was a natural extension of this enterprise. Like Simpson, Maule and Nicholson, Thos. Holliday & Co. was caught up in patent litigation in the 1860s but, unlike the other company, they succeeded in the case of aniline red.<sup>145</sup> The company's most prosperous period was the 1870s after which it declined and was taken over by British Dyes Ltd in 1915.<sup>146</sup>

The Clayton Aniline Co. Ltd. was co-founded by Charles Dreyfuss in 1876. Initially it specialised in dye intermediates but from the late 1880s it manufactured primuline developed by Arthur George Green (1864-1941) who was the manager of the colour department from 1894 to 1901.<sup>147</sup> The company was taken over by the Society for Chemical Industry in Basle in 1911.<sup>148</sup> Claus & Reé Ltd. was formed in 1892 near Manchester but with Swiss backing. They made anthraquinone and azo dyes and were taken over by Levinstein's in 1917.<sup>149</sup>

The Levinstein family were initially heavily involved in the manufacture of synthetic dyes in Berlin and Milan.<sup>150</sup> Ivan Levinstein started manufacturing magenta dyes near Manchester in 1865. The company had a successful research programme and Ivan Levinstein campaigned vigorously for changes in English Patent law to protect the home

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<sup>143</sup> TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses. p. 156-157

<sup>144</sup> Ibid. p. 124

<sup>145</sup> Ibid. p. 216

<sup>146</sup> MORRIS, P. J. T. & TRAVIS, A. S. (1992) A History of the International Dyestuff Industry. *American Dyestuff Reporter*, 18.

<sup>147</sup> TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses. p. 217

<sup>148</sup> MORRIS, P. J. T. & RUSSELL, C. A. (1988) *Archives of the British Chemical Industry 1750-1914. A Handlist*, Faringdon, Oxfordshire, UK, British Society for the History of Science. Page 68

<sup>149</sup> Ibid. Page 67

<sup>150</sup> TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses. p. 131 & 135

manufacturers from foreign competition.<sup>151</sup> Levinstein's became the dominant English company in the early twentieth century.

### 2.3.2 The dye industry in Germany

Whilst the dye industry in England was much reduced by the last quarter of the nineteenth century in Germany, in contrast, it was thriving. Four of the most important companies were established in the 1860s. The Badische Anilin und Soda Fabrik (BASF) originated in Chemische Fabrik Dyckerhoff, Clemm & Co. in 1861 which was set up in Mannheim to produce fuchsine with Carl and August Clemm as the technical experts. Friedrich Engelhorn took control of the company in 1863 and the restructuring into BASF occurred in 1865 with investment from the Mannheim banking house of W.H. Ladenburg Söhne.<sup>152</sup> Expansion was rapid and BASF was one of the first companies to set up a professional research laboratory. Heinrich Caro joined the firm on his return from England in 1868 and controlled the research department.<sup>153</sup> By 1900 BASF had 6,485 employees and it expanded from a dye company to become associated with nitrogen fixation, high pressure chemistry and pharmaceuticals.<sup>154</sup>

The second important company started in the 1860s was Bayer and Co. It originated in Barmen in 1862 as a partnership between Johann Friedrich Westkott, a cotton dyer, and Friedrich Bayer, a dye merchant, who experimented with aniline dyes on their kitchen stoves. The business moved to Elberfeld and then had to be moved downstream onto the River Wupper after pollution incidents due to the production process for aniline red which used arsenic acid.<sup>155</sup> It had 4,200 employees by 1900 and later diversified into pharmaceuticals.<sup>156</sup>

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<sup>151</sup> Ibid. p. 144-149, 219, 244

<sup>152</sup> Ibid. p. 75

<sup>153</sup> Ibid. p. 178

<sup>154</sup> Ibid. p. 241

<sup>155</sup> Ibid. p. 74

<sup>156</sup> Ibid. p. 241



Hoechst was the third of these companies. In 1862 a partnership between two chemists, Eugen Lucius and Adolf Brüning, and two merchants, L. August Müller of Amsterdam and C.F. Wilhelm Meister, set up a dye works at Höchst near Frankfurt am Main. They initially traded as Meister, Lucius and Co. and then as Meister, Lucius and Brüning (MLB) from 1872.<sup>157</sup> By 1900 they had 3,555 employees and they also went on to become a major pharmaceutical company having supported Ehrlich's early work on biological tissue staining.<sup>158</sup>

The fourth and last of the major 1860s German quartet was Aktiengesellschaft für Anilinfabrikation (AGFA). It originated in an 1867 partnership between Carl A. Martius, a chemist, and Paul Mendelssohn-Bartoldy from a prominent banking family. Their first product was aniline red and Martius used Hofmann extensively as a consultant.<sup>159</sup> In 1900 they had 1,800 employees and they later became closely associated with photographic chemicals.<sup>160</sup> Leopold Cassella & Co. was also a major force in the German industry in the later nineteenth century. In the 1870s they sold aniline dyes manufactured by Leonhardt and were, at that time, specialists in natural colourants. By 1900 they had 1,800 employees, the same number as AGFA, but they did not continue to expand in the twentieth century as AGFA did.<sup>161</sup>

### 2.3.3 The trade in synthetic dyes

The dye manuals of the time list the suppliers of many of the dyes they describe and this data can be analysed to give an indication of which companies were commercially most active. The results for manuals from 1885 and 1893 are shown below. This does not give any data about market share by value, and not all dyes have a listed supplier, but does show the extent to which the different firms had penetrated the market based on their status as recommended suppliers in leading dye manuals.

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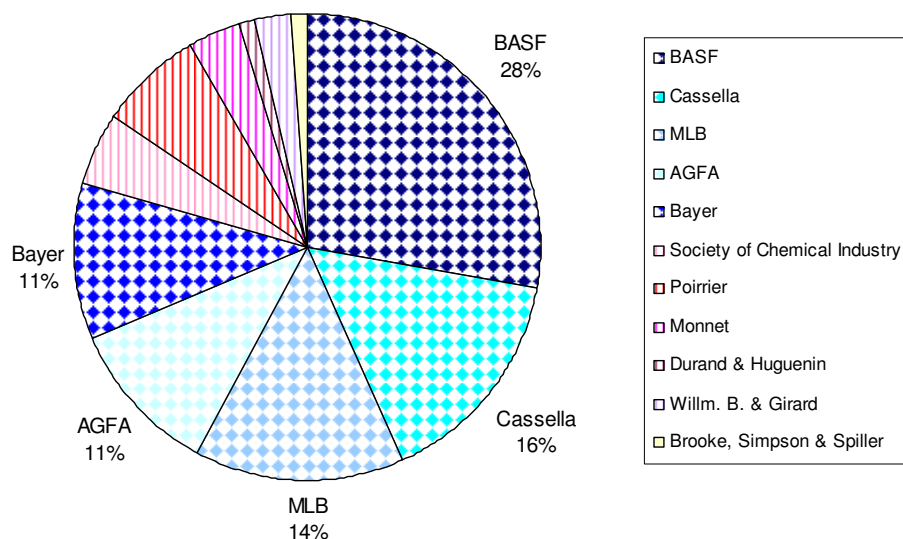
<sup>157</sup> Ibid. p. 75, 192

<sup>158</sup> Ibid. p. 230, 241. Paul Ehrlich (1854-1915) was a pioneer in the treatment of infectious disease.

<sup>159</sup> Ibid. p. 153, 212, 235

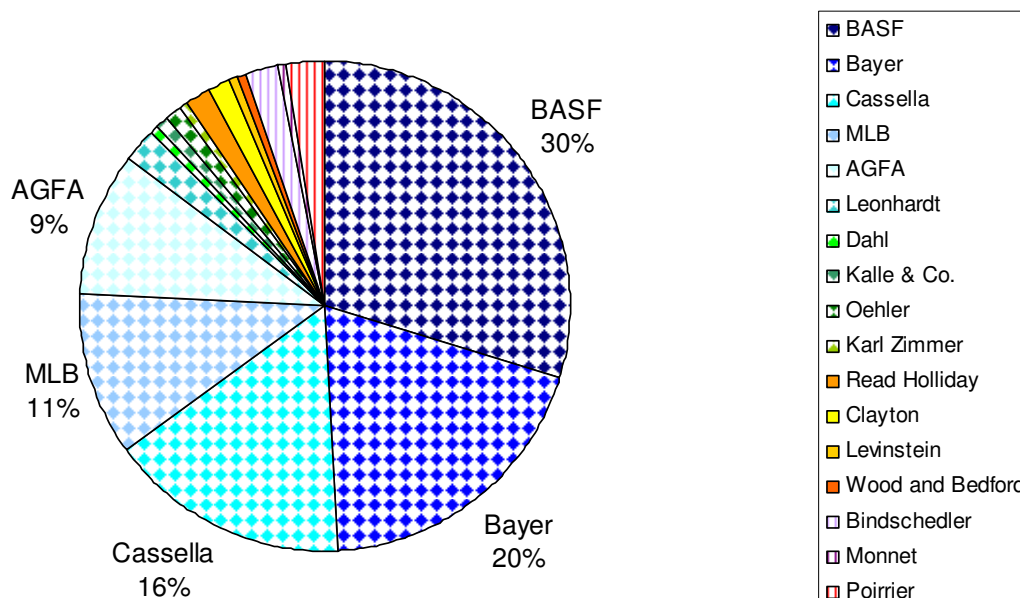
<sup>160</sup> Ibid. p. 241

<sup>161</sup> Ibid. pp. 97 & 241



**Figure 2.4** Percentage of dyes marketed by each firm listed in an 1885 dye manual.

German companies are shown in chequered blue, English in solid orange/yellow and French and Swiss in striped red/pink.<sup>162</sup>



**Figure 2.5** Percentage of dyes marketed by each firm listed in an 1893 dye manual.

German companies are shown in chequered blue/green, English in solid orange/yellow and French and Swiss in striped red/pink.<sup>163</sup>

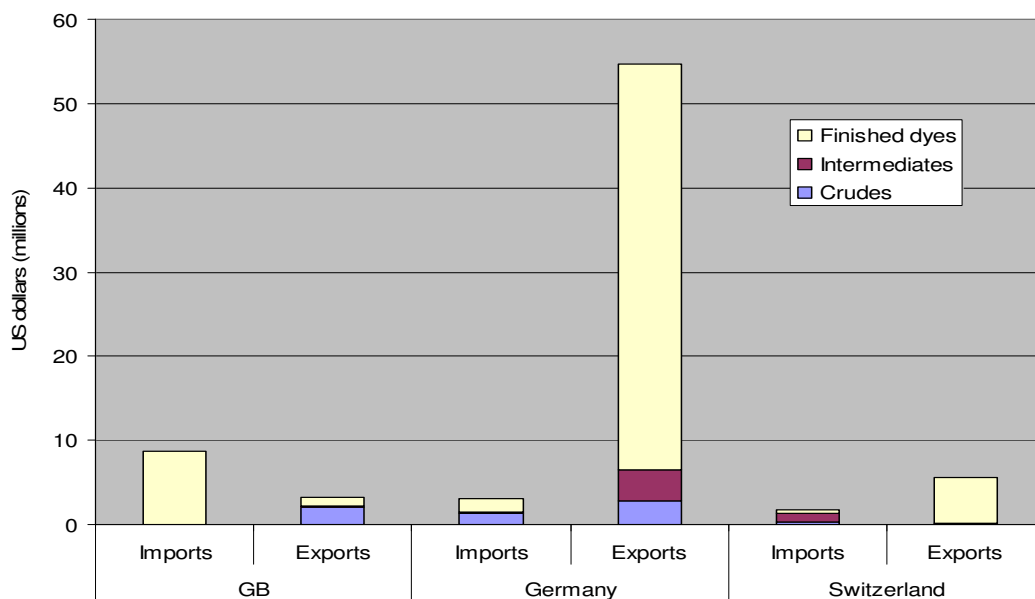
<sup>162</sup> HUMMEL, J. J. (1885) *The Dyeing of Textile Fabrics*, London, Paris & Melbourne, Cassell and Company, Limited.

The size of the German industry can be easily seen in these graphs with a few large firms dominating. France and Switzerland had a few companies but by 1900 France, like England, had ceased to be a major player in the field. Switzerland continued to prosper and some French companies re-located there. Although the data is only separated by a few years in the late nineteenth century, more firms are represented in the later set but the proportion of references not attributed to the major manufacturers remains roughly the same (20% in 1885 and 14% in 1893). It is however distributed between more enterprises in various countries in the later data set. Whereas in 1885 only one English firm is mentioned, Brooke, Simpson and Spiller, in 1893 four are referred to including the influential Levinstein. All of the four were in production by 1885 but it apparently took time to become established in the trade. Brooke, Simpson and Spiller, in contrast, had declined by 1893.

In 1914 Hesse produced a review of the synthetic dye industry for the Board of Directors of the General Chemical Company in New York. From the figures that he published it can be clearly seen that by 1912 Germany and Switzerland were net exporters of dyes and Britain a net importer (Figure 3.6). Germany was also exporting to Asia (24% of total exports) and North America (23%). In Europe her main markets after England were Austria, Italy, Belgium, France and the Netherlands.

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<sup>163</sup> KNECHT, E., RAWSON, C. & LOEWENTHAL, R. (1893) *A Manual of Dyeing: for the Use of Practical Dyers, Manufacturers, Students and all those interested in the Art of Dyeing*, London, Philadelphia, Charles Griffin and Company Ltd/J.B. Lippincott Company.



**Figure 2.6** Chart showing the values of imports and exports in the dye industry in Europe, 1912<sup>164</sup>

#### 2.3.4 The dye industry and pollution

The increasing level of industrialisation in the nineteenth century brought both benefits and problems. The chemical industry in general and the synthetic dye industry within this were certainly contributors to this situation. Pollution was a recognised problem although a certain level was tolerated as a necessary accompaniment to the increase in prosperity and life in a clean environment may have been seen as an impossible future. At the Annual Dinner of the Textile Society of the Yorkshire College in 1892 there was much discussion of the unsanitary conditions in Leeds. Alderman Ward said:

...he looked forward to the time when the River Aire would be, comparatively speaking, a pure stream – *laughter* – when the atmosphere we breathed would be clear, and when vegetation would thrive even in the centre of town.<sup>165</sup>

<sup>164</sup> HESSE, B. C. (1914) The Industry of the Coal-Tar Dyes: An Outline Sketch. *The Journal of Industrial and Engineering Chemistry*, 6, 1013-1027.

<sup>165</sup> ANON. *Leeds Mercury*. Leeds. Apr 28<sup>th</sup> 1892

Pollution in the German rivers was acute and it was said that the colours could be seen several miles from the dye works. Companies went to some lengths to hide their outfalls and low levels of arsenic contamination were tolerated. However the Dutch, downstream of the German factories, did lodge complaints about the effects on fisheries.<sup>166</sup> An early report of ill-effects to production workers was carried in the *Popular Science Review* where Dr Kreuser of Stuttgart described the men as developing bronchitis and ulcers which could be avoided by protective clothing, ventilation and better hygiene.<sup>167</sup> The unpleasant conditions in the factories may have been one of the reasons why chemistry was not an area of study favoured by the middle classes in England.<sup>168</sup> However, government enquiries and other investigations were not able to establish a specific nuisance related to the factories. Hummel includes in his dye manual a section of advice on sourcing water supplies for dyeing from rivers unpolluted by the other chemical industries.<sup>169</sup>

Workplace accidents were a hazard of the industry. Explosions at Roberts, Dale and Co. have already been referred to. Two accidents at Dan Dawson Brothers in Huddersfield were reported in the local press. In one case it was supposed that the wrong chemical had been added to the still and this resulted in an explosion and fire. In this case the worker involved survived with severe burns although there seemed to be more concern about the '7 or 800 pounds worth of damage' was done to the factory 'which was not covered by insurance'.<sup>170</sup> The worker who caught his overalls in some moving machinery in 1881 was even less fortunate and lost his life.<sup>171</sup>

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<sup>166</sup> HOMBURG, E., TRAVIS, A. S. & SCHROTER, H. G. (Eds.) (1998) *The Chemical Industry in Europe, 1850-1914. Industrial Growth, Pollution and Professionalization*, Dordrecht/Boston/London, Kluwer Academic Publishers. pp. 188-200 (Anderson)

<sup>167</sup> ANON. (1865) Medical Science: Effects of Aniline on Workmen employed in its Manufacture. *Popular Science Review*, 4, 249-250.

<sup>168</sup> HOMBURG, E., TRAVIS, A. S. & SCHROTER, H. G. (Eds.) (1998) *The Chemical Industry in Europe, 1850-1914. Industrial Growth, Pollution and Professionalization*, Dordrecht/Boston/London, Kluwer Academic Publishers. p. 212 (Donnelly)

<sup>169</sup> HUMMEL, J. J. (1885) *The Dyeing of Textile Fabrics*, London, Paris & Melbourne, Cassell and Company, Limited. Page 138

<sup>170</sup> ANON. *Leeds Mercury*. Leeds. Apr 6<sup>th</sup> 1877.

<sup>171</sup> ANON. (1881) Shocking Accident at Milnsbridge. *Huddersfield Daily Chronicle*. Huddersfield.

Perhaps the German factories were better organised and, for that reason safer. The group who were sent by the Royal Commission in 1882 to report on the chemical industry on the Continent were

... struck ..... with the substantially built, well-lighted, well-ventilated workshops, and above all, with the all-pervading cleanliness and neatness.<sup>172</sup>

The Commissioners were acquainted with the English chemical industries and no doubt with the conditions found there and so the fact that they commented favourably on those at Bindschedler and Busch can be taken to indicate that they were substantially different.

## 2.4 Conclusions

The history of the early development of the Yorkshire College illustrates the attitudes towards the teaching of chemistry in England at the time. Instruction at their inception was seen as closely allied to the relevant trades rather than the more research orientated institutions on the continent. The biography of Hummel demonstrates that personal connections with Germany or Switzerland could be pivotal in allowing young men to advance. Hummel, having spent some time studying at Zurich Polytechnic, progressed from working in various capacities in textile print works to become the first professor of textile dyeing at Yorkshire College. However, Hummel had some difficulty in obtaining his promotion to professor as he had not obtained a PhD and the applied subjects were not accorded the same status as pure research subjects. This attitude can be contrasted to the practical approach taken by European institutions where Hummel himself trained with Bolley at the Polytechnic School of Zurich.

There were many other colleges founded in England the middle part of the nineteenth century. The interest in the industrial towns and in Government in increasing the capacity

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<sup>172</sup> SAMUELSON, B. (1884) Second Report of the Royal Commissioners on Technical Instruction Vol. I. *Command Papers: Reports of Commissioners*. p. 223

of the home textile industry to compete overseas led to a general movement to improve the education of the workforce. Owens College in Manchester was a very similar foundation to the Yorkshire College. It opened slightly earlier in 1851 but was soon in decline with the same struggles for local support as at Yorkshire. Sir Henry Enfield Roscoe (1833-1915) was the first successful professor of chemistry there and he established a department of chemistry which prepared students for a career in research. This college, therefore, in common with others such as Durham, was concerned with the teaching of pure rather than applied subjects.<sup>173</sup> It has been seen that the Yorkshire College came under increasing pressure in the later nineteenth century to move to a similar type of curriculum including teaching in the arts. In this respect, it was unusual in maintaining its applied departments of dyeing and weaving.

The Yorkshire College had some general similarities with many other foundations of the nineteenth century in its local nature and its emphasis on relevance to trade. However, when examined closely there is evidence that it maintained this vocational nature after others had become much more academic. Certainly its instructor in dyeing, John James Hummel, was unusual in not having formal higher qualifications although his early history of contact with and study in Europe conformed to the normal course taken by English chemists of the time. Unlike the German foundations the English Colleges did not receive Government funds until they were well established. Crucially they developed from technical subjects towards classics and humanities rather than towards academic research in the technical subjects as their German equivalents did.

This chapter has examined new sources for the development of the teaching of chemistry and dye chemistry in the nineteenth century and has contributed to our knowledge of the complexity of this subject. The expansion of the industry in Germany and England has been outlined. The dominance of Germany has been well documented and additional data from nineteenth century dye manuals published in England analysed here supports this. Pollution was a recognised issue at the time and evidence for the problems of health and safety in the

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<sup>173</sup> KARGON, R.H. (2004-2009) Roscoe, Sir Henry Enfield *Oxford Dictionary of National Biography* Oxford, Oxford University Press

factories has been supplied from newspaper and periodical archives. The next chapter further examines the attitudes to the synthetic dyes in England and explores possible reasons for the emergence of Germany as the leading player in the synthetic dyestuffs trade.



## Chapter 3. The public perception of the new colours and their penetration into the market

### 3.1 Introduction

Thus the dye manufacturing industry expanded rapidly in the last quarter of the nineteenth century, particularly in Germany. This meant that both the products and the side effects made a strong impression on the public in Europe and the following section will examine the ways in which English consumers reacted. The increasing middle classes were providing a new market both for goods and ideas. Synthetic dyes were an aspect of the chemical industry which impinged directly on the public more than most. They were consumers of its products chiefly in the form of costume and furnishing textiles and the same individuals were also affected by the pollution produced by the industry.

There was also a continuing interest in self-improvement by various means such as reading, attending lectures, visiting museums and international exhibitions. Much of the literature concerning science was aimed at a broad spectrum of the educated middle class and families passed some of their leisure time sharing such sources.<sup>174</sup> The establishment of various institutions in this period provided public spaces in which subjects including science could be discussed and these were much used. In Manchester, which was typical of large towns in this respect, by 1840 there were several forums for instruction and discussion of science and the arts. The Literary and Philosophical Society was the most elevated as a learned society, the Royal Manchester Institution supplied the interests of the elite of the city, the Athenaeum was for the aspiring middle class and the Mechanics' Institution was for the working class.<sup>175</sup> Much more is known about the reactions of the middle classes to these new concepts and these are therefore best represented in this study. However, some of the comments intended for these audiences can also throw light on how the working classes viewed and consumed the new dyes.

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<sup>174</sup> TOPHAM, J. R. (2000) Scientific Publishing and the Reading of Science in Nineteenth-Century Britain: A Historiographical Survey and Guide to Sources. *Studies in the History and Philosophy of Science*, 31, 559-612. p. 573

<sup>175</sup> WACH, H. M. (1988) Culture and the Middle Classes: Popular Knowledge in Industrial Manchester. *The Journal of British Studies*, 27, 375-404.

Although undoubtedly many sections of the population did not discriminate between natural and synthetic dyes, they were seen among some of the middle class, particularly, as a symbol of the evils of the age. Many English dye firms had a vested interest in the continuing import and use of natural dyes, particularly indigo, and the productive textile sector was content to import dyes from Germany and allow the export of the raw material, coal tar, in large quantities in the opposite direction to fuel this expansion.

The Arts and Crafts movement illustrates the ambivalence shown by the English governing classes to the industrial world. There was, of course, a corresponding arts movement in Germany which paralleled the changes in England but this was set much more into an industrialised rather than a craft context. Hermann Muthesius (1861-1927) was a technical attaché to the German Embassy in London from 1896 to 1903 and published articles in Germany in which he commented that the ideas of Ruskin and Morris stressed the craft component too strongly and were anti-industrial.<sup>176</sup> The following section will analyse the 1862 London International Exhibition with reference to the presentation of the new dyes and the contrasting approaches of English and German exhibitors.

### 3.2 The 1862 London International Exhibition

The Exhibition was one of the earliest opportunities for the dye manufacturers to promote their new products directly to the public and it showcased both natural and synthetic dyes. Section I, Raw Materials, included four Classes. The first was 'Mining, quarrying, metallurgy, and mineral products', the second 'Chemical substances and products, and pharmaceutical processes' which included the dyes. Then followed Class 3 'Substances used for food, including wines' and Class 4 'Animal and vegetable substances used in manufactures'.<sup>177</sup> Interestingly, the natural dyes were included in the chemical section and not amongst the animal and vegetable substances which instead emphasised objects in which the original substance could still be seen, such as items made from ivory, basketwork, cocoa-nut matting and fleeces. Along with the application of steam power to agriculture and developments in glass manufacture, the

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<sup>176</sup> ULMER, R. (2005) Germany. IN LIVINGSTONE, K. & PARRY, L. (Eds.) *International Arts and Crafts*. London, V&A.

<sup>177</sup> JENKINS, D. T. & PONTING, K. G. (1982) *The British Wool Textile Industry 1770-1914*, London, Heinemann Educational Books Ltd.

invention of the new aniline dyes was quoted as a major justification for a new Exhibition.<sup>178</sup> These exhibits were in the annexe added to the permanent building of the exhibition on the Eastern Wing next to the foods. This was at some distance from the textile section which was shown in the south-eastern gallery on the south side of the great nave. Aniline dyes were however alluded to in the textile section:

Our stuffs are then dyed either with madder, with archils and other colour-bearing lichens, or, as is now more usual, with the aniline dyes from coal tar; they are dyed almost throughout by new and improved processes, of which the results, except in the black dyes, as before mentioned, are nowhere else to be surpassed. Messrs Butterworth and Brooks of Manchester have it duly remembered in the award of their medal that they were the first in the country to fix aniline colours on calicoes by a new method.<sup>179</sup>

Pharmaceutical drugs were shown as well as a wide range of dye products. The Illustrated Catalogue states:

A very interesting collection of chemicals, illustrating the improvements made in calico-printing and dyeing since 1851, has been formed at the suggestion of Dr. Lyon Playfair, by Mr. Robert Rumney of Manchester,<sup>180</sup> whose combined knowledge, as a chemist and manufacturer, rendered him peculiarly fitted for the work. In no department of applied chemistry have such strides been made within the last ten years as in dyeing and calico printing; and in the history of these useful arts, perhaps no similar period has been so fruitful in good results. A collection of products, illustrating the discovery of the coal-tar dyes formed by the first workman in this fertile field, Mr. W.H. Perkin, is also exhibited; in fact the various dyes are particularly well represented. The coal-tar series is most fully represented, and numerous specimens of the lichen and madder dyes are also exhibited. Altogether the specimens exhibited will tend to show that England has now become the dye-producing nation of Europe, instead of having to depend on Holland, France and other countries for the supply of lichen and madder dyes wherewith to ornament the produce of her millions of silk, woollen and cotton looms.<sup>181</sup>

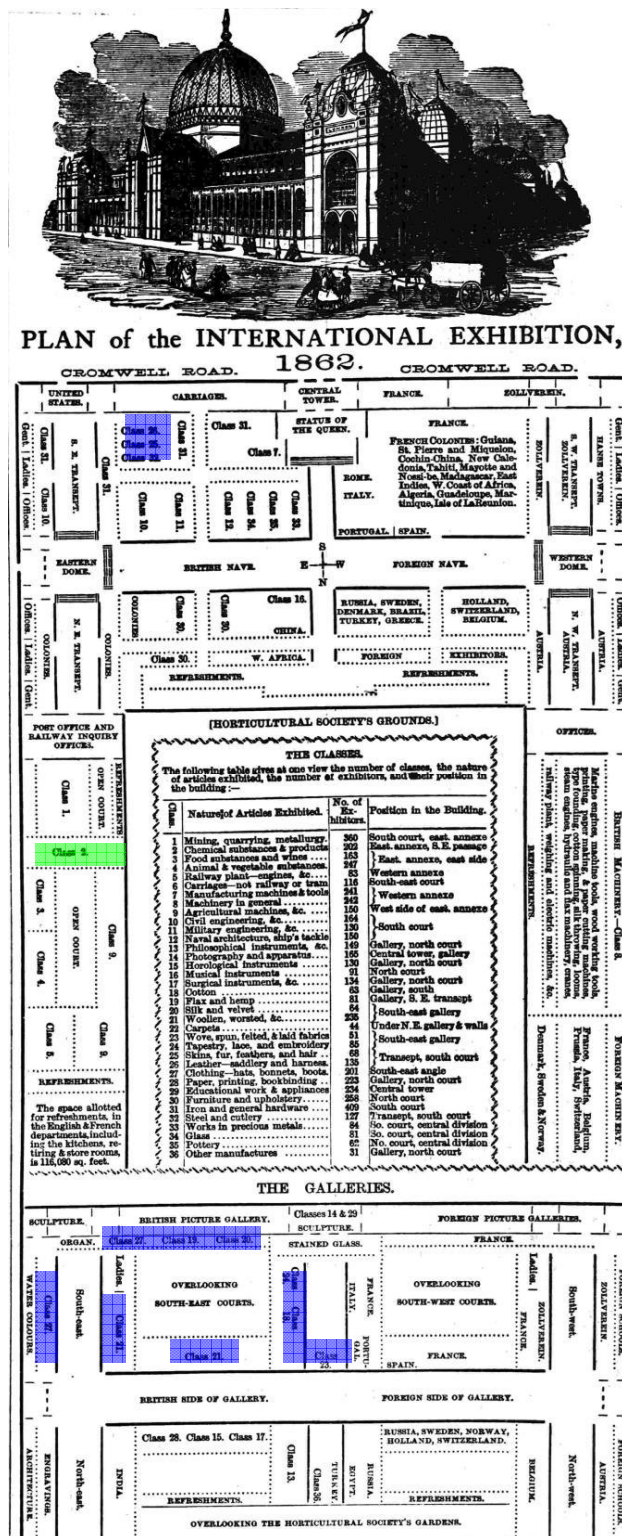
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<sup>178</sup> Ibid. Quoted in Hollingshead's review of the history of the 1862 exhibition in this volume, page 43

<sup>179</sup> ANON. (1862b) The International Exhibition. *Examiner*. London. Sep 27th

<sup>180</sup> Robert Rumney was a Manchester brewer who established the Ardwick Chemical Works in the town in about 1845. He made products for the calico printing industry. MORRIS, P. J. T. & RUSSELL, C. A. (1988) *Archives of the British Chemical Industry 1750-1914. A Handlist*, Faringdon, Oxfordshire, UK, British Society for the History of Science. Page 10

<sup>181</sup> JENKINS, D. T. & PONTING, K. G. (1982) *The British Wool Textile Industry 1770-1914*, London, Heinemann Educational Books Ltd. Quoted in Hollingshead's overview of the exhibition classes, p. 75



**Figure 3.1 Plan of the 1862 London International Exhibition.**

The synthetic dyes were shown as part of Class 2 (highlighted in green) and the textiles as Classes 18-27 (highlighted in blue). The Galleries were on the first floor.<sup>182</sup>

<sup>182</sup> ANON. *Cheshire Observer and General Advertiser: for Cheshire and North Wales*. Chester. Jun 7<sup>th</sup> 1862

What were referred to as the ‘larger and coarser kind of chemicals’ such as alum, soda and copperas were also shown in this area. The catalogue lists fifteen dye exhibitors out of a total of 202 in this class. One of the reviews highlights the coal tar products as being the most interesting in the chemicals section. In this review Hofmann is credited with the initial observation of the purple colour and Perkin with commercialising it. The manufacturers of coal tar dyes who have received medals are named but those who obtained medals for the extraction of dyes from lichens are not.<sup>183</sup>

Whilst the official descriptions are objective it is clear from journalistic accounts that the popular imagination was caught by the new dye substances and many of these were published. One of the more fanciful can be found in the periodical *All the Year Round* edited by Charles Dickens (Figure 3.2).

The German states exhibited together as their free trade block the Zollverein and *The Examiner* took a very poor view of their commercial attitude to the Exhibition:

With the bluntest honesty they exhibit together under the commercially attractive name of a Customs’ Union, set a large model of the Berlin Exchange before their threshold, make the most of their space, produce what they have to sell, price every item of it, and stand ready for instant traffic.<sup>184</sup>

This was intended to contrast in the mind of the reader with the artistic and educational displays of the British sections. The Zollverein exhibitors had to be constrained to remove a display of ‘the cheapest and rudest sort of German toys’<sup>185</sup> to a less conspicuous area. There were however some signs of future competition and dyes were on show in this section:

The Kingdom of Bavaria is strong in chemical colouring matters, among which is worthy of especial notice “Mittler’s gift-freies Grün,” a brilliant green for wall-papers, window blinds, or wreaths, entirely free from poison.<sup>186</sup>

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<sup>183</sup> ANON. *The Examiner*. London. Aug 9<sup>th</sup> 1862

<sup>184</sup> Ibid. 14th Jun 1862

<sup>185</sup> Ibid.

<sup>186</sup> Ibid.

Presently we come upon a case where a mag-

nificent gold-green crystal crown, like nothing in nature ever yet beheld, challenges public admiration as "acetate of rosaniline." And now I am coming upon dangerous ground. The metals were all very well, and even I, a confessed ignoramus, could make out something about them; but now when we are diving deeper into the chemical labyrinth, I must hold my end of the clue very firm, not to get utterly lost and bewildered. Well, this gold-green crown is called rosaniline; and rosaniline is aniline that turns a bright rose-red in alcohol; and aniline is got from the "basic oil of coal-tar," whatever that may be, and also in any quantity from indigo. This gold-green crown is very curious and very lovely. It is worth about four hundred pounds (at first the report went that it was worth a thousand), and one grain of it would dye a bucketful of water, deep magenta; and the whole crown itself would dye the Thames magenta from the sea to its source. Aniline is the material whence have been got the last two fashionable colours, mauve and magenta. A little way off, is a large bronze-coloured cylinder, called "solid purple aniline," worth eight hundred pounds, and capable of dyeing a nation's wardrobe the best shade of mauve. Mauve was originally sold at its weight in gold, for all that it was made of dirty bad-smelling coal-tar; but the secret has been found out now, and mauve and magenta fetch no more than some other dyes, though in the end a little dearer, because more fugitive than many others. In this case there are glass cups holding various coloured anilines: green, and blue, and yellow, and dull red, and purple, and dirty-looking mauve, all products of this basic oil of coal-tar under different conditions; as "precipitated," and "oxalate," and "sulphate," and "chloride," and "arseniate," and "crystallised," only I cannot fit the name and condition together. Then there is some "magenta powder," a beautiful mass of rainbow-coloured grains, like crushed peacock ore; and a curious blue fluid called ameline, which the label tells us is also got out of aniline; and there are aniline orange, and aniline deep purple, and cyanine blue from aniline, and opaline blue from aniline; and all these last are liquids, and very bright and clear. There is another very brilliant colour got from coal-tar, called rosolic acid, which, if any one could fix as a dye, would make his fortune. But as yet rosolic acid is fugitive and shy, and fades away after a few hours' exposure to the light. But it is such a crimson! A blood-red damask rose would look pale beside it.

**Figure 3.2** Review of the synthetic dyes display in the 1862 International Exhibition<sup>187</sup>

<sup>187</sup> DICKENS, C. (1862) Ignoramus at the Exhibition. *All the Year Round*, 560-561. Aug 23rd Reproduced from ProQuest British Periodicals Database accessed online 4<sup>th</sup> Feb 2010.

The 1862 exhibition was expressly not intended to be a platform for selling goods and these reports support the argument that one of the reasons for the triumph of Germany in the industrialisation of the synthetic dyes was their more forceful attitude to commerce than the English.

### 3.3 Evidence in printed sources for the public reaction to the new dyes: positive reactions

Some articles concerning synthetic dyes were published in the popular press before the 1862 exhibition and more were produced later. Many of the early references were either purely instructive with a positive attitude to this scientific advance or full of wonder. A series of articles published by Robert Hunt (1807-1887) in the *Art Journal* and *St. James's Magazine* in 1858<sup>188</sup>, 1859<sup>189</sup> and in 1861<sup>190</sup> outline the science behind the preparation of the new aniline dyes. Hunt was the editor of the 1867 edition of *Ure's Dictionary of Arts, Manufactures, and Mines* and a Fellow of the Royal Society and so had a scientific background as well as an interest in the popularisation of science.<sup>191</sup> The first article is a mixture of accurate information on murexide from guano as well as mauve from aniline and a fanciful account of a green dye produced from grass, perhaps reflecting the fact that this was a new field with little reliable information in the public domain. The next article concentrates on aniline colours and presents the data in a more rigorous manner whilst the third to appear adopts a slightly more homely tone and emphasises the link between the fossilised coal and the dyes as well as the utilisation of a previously discarded waste product from coal gas as the raw material.

In the early 1860's several other periodicals published similar articles with slightly varying emphases such as *Chambers's Journal of Popular Literature, Science, and Arts* on the preparation of mauve as well as murexide from guano<sup>192</sup> and short summaries

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<sup>188</sup> HUNT, R. (1858) Recent Applications to the Art of Dyeing. *Art Journal* (London), 41.

<sup>189</sup> HUNT, R. (1859) Colouring matters, especially those obtained from coal. Aniline Colours. The new colour 'mauve,' or Perkins's purple. *Art Journal* (London), 59, 335.

<sup>190</sup> HUNT, R. (1861) Mauve and Magenta. *St. James's Magazine*, 1.

<sup>191</sup> Alan Pearson, 'Hunt, Robert (1807–1887)', *Oxford Dictionary of National Biography*, online edn, Oxford University Press, Sept 2004 [<http://www.oxforddnb.com/view/article/14203>, accessed 25 Oct 2010 ]

<sup>192</sup> ANON. (1860) How we get Mauve and Tyrian Purple. *Chambers's Journal of popular Literature, Science and Arts*. Nov 17th

amongst general science themes.<sup>193</sup> A few of the articles predicted that these developments meant the end of importation of dyestuffs into England<sup>194</sup> and several of them emphasised that these products made good use of what had previously been waste.<sup>195</sup> As the decade progressed, articles on the same themes appeared in less specialised journals such as the *Wesleyan-Methodist Magazine*<sup>196</sup> along with a lengthy review of the topic in the *Popular Science Review*.<sup>197</sup> Many of these publications were widely read and the religious monthlies were extremely influential. The *Wesleyan-Methodist Magazine* sold more than 25,000 copies monthly in 1820, more than the *Edinburgh or Quarterly Reviews*.<sup>198</sup>

A Fine Art and Industrial Exhibition was held in Huddersfield in 1883. The categories of exhibits were 'Cloth Manufacturing Machinery', 'Mill Furnishing Department', 'Domestic Appliances' and 'Miscellaneous' and it was in the latter section that Brooke, Simpson and Spiller and Dan Dawson Brothers<sup>199</sup> were both awarded silver medals for coal tar dyes. Other silver medals in the same category were awarded for an eclectic mix including steam engines, pianos, adhesive enamelled letters and soap.<sup>200</sup> This illustrates well the dilemma that was faced when trying to categorise these new substances. They were classed as manufactured products, unlike the natural dyes which were processed but not seen as industrial, but did not fit easily into existing categories.

There was a wide variety of general public interest in the new dyes. Several groups of liberally educated people were interested enough to include displays of dyes or talks about the dyes in their meetings. For example, at the annual meeting of the Devon

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<sup>193</sup> ANON. (1861a) Contemporary Science. *London Review and Weekly Journal of Politics, Literature, Art, and Society*, 2, 175.

<sup>194</sup> ANON. (1861b) Science at Manchester. *Examiner*. London. ANON. (1863) Colour in the Coal Scuttle. *Leisure Hour*, 598, 373-375. CROOKES, W. (1863) Chemical products - The Application of Waste. *Popular Science Review*, 2:5, 58. ANON. (1861b) Science at Manchester. *Examiner*. London. Sep 7th 1861

<sup>195</sup> CROOKES, W. (1863) Chemical products - The Application of Waste. *Popular Science Review*, 2:5, 58. ANON. (1862a) Coal-tar. *London Journal*. London. Jul 12th

<sup>196</sup> ANON. (1865c) Varieties: The treasures of utility and beauty in coal. *Wesleyan-Methodist magazine*, 11, 740. Aug.

<sup>197</sup> PHIPSON, T. L. (1864) The Aniline Dyes. *Popular Science Review*, Jan.

<sup>198</sup> TOPHAM, J. R. (2000) Scientific Publishing and the Reading of Science in Nineteenth-Century Britain: A Historiographical Survey and Guide to Sources. *Studies in the History and Philosophy of Science*, 31, 559-612.

<sup>199</sup> Information on Brooke, Simpson and Spiller is given in section 3.3.1. Dan Dawson Brothers were an aniline dye manufacturer based at Milnsbridge, Huddersfield.

<sup>200</sup> ANON. (1884) Fine Art and Industrial Exhibition. *Huddersfield Chronicle and West Yorkshire Advertiser*. Huddersfield. Jan 12th



Association of Literature, Science and Art the topics ranged through archaeology, geology and economics and an exhibition of examples of coal tar dyes was shown.<sup>201</sup> In 1870 the St Columba Literary Association enjoyed a lecture on 'Recent Discoveries in Chemistry' given by Mr Matthew Cochrane, FCS which included sections on coal tar dyes and alizarine. More general audiences were addressed by public lectures, for example as in the series given in the Cutlers' Hall, Sheffield by Mr W. Baker entitled 'The Chemistry of the Earth',<sup>202</sup> and references can also be found in more general articles such as the description of Coventry published in *Leisure Hour*.<sup>203</sup> One group with a professional interest was the gas plant industry and examples of coal tar dyes were shown at meetings of gas plant managers<sup>204</sup> and at exhibitions of gas appliances.<sup>205</sup>

Lectures given to more specialist audiences were reported in the press as of interest to the general public. Hofmann's address to the Royal Institution in 1862 was reproduced in detail in the *London Review*.<sup>206</sup> Shorter accounts of lectures by Mr F. Field on 'Magenta and its derivative colours obtained from tar' given to the Royal Institution and Dr O.N. Witt on 'Colouring matters derived from diazo compounds' given to the Chemical Society were also published.<sup>207</sup> Several presentations to the British Association were reported in the London press or that local to the areas where meetings were held.<sup>208</sup> In 1887 the *Aberdeen Weekly Journal* took a very dim view of the address given by Sir Henry Roscoe, accounting it very dull '...thoroughly Manchesterian in its ideal of progress - which, after all, means only how we may best and most comfortably fill our bellies and clothe our backs' and pronouncing:

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<sup>201</sup> ANON. (1868) Devon Association of Literature, Science, and Art. *Trewman's Exeter Flying Post or Plymouth and Cornish Advertiser*. Aug 5th

<sup>202</sup> ANON. (1877) The Chemistry of the Earth. *Sheffield and Rotherham Independent*. Dec 11th

<sup>203</sup> ANON. (1872) A Midland Tour: Coventry. *Leisure Hour*, 778-782. Dec 7th

<sup>204</sup> ANON. (1864) The Scottish Association of Gas Managers. *Caledonian Mercury*. Sep 14th ANON.

(1879b) Gas Managers' Association. *Newcastle Courant*. Newcastle upon Tyne. Oct 10th

<sup>205</sup> ANON. (1880) The Exhibition of Gas Apparatus. *Glasgow Herald*. Glasgow. Sep 17th ANON. (1883) Gas Exhibition at Middlesborough. *York Herald*. York. Nov 5th

<sup>206</sup> ANON. (1862c) Learned Societies and Institutions: Royal Institution, 11th April, Dr Hofmann lectured "On Mauve and Magenta". *London Review and Weekly Journal of Politics, Literature, Art and Society*. London.

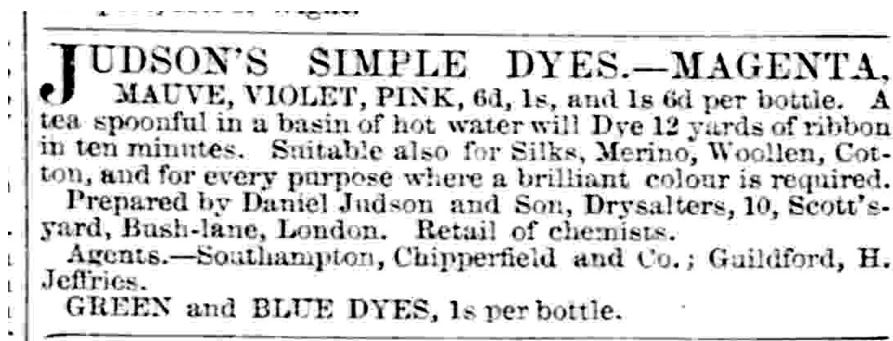
<sup>207</sup> ANON. (1865b) Royal Institution. *Morning Post*. London. May 17th (Fredeick Field was the chemist at Simpson, Maule and Nicholson.) ANON. (1879a) Chemical society. *Academy*. London. Mar 1st

<sup>208</sup> ANON. (1873) Chemistry: Report of the President's address to the Chemical Section of the British Association 'Alizarine'. *Athenaeum*. London. Sep 27th ANON. (1890a) British Association for the Advancement of Science. Meeting in Leeds. Chemical Section. *Leeds Mercury*. Sep 10th

We prefer the stuff that is "two-hundred-and-fifty times sweeter than sugar," the "coal-tar" dyes and the discovery of the "ten-millioneth" of "the diameter of a centimetre" yet!<sup>209</sup>

So the coal-tar dyes were still perceived as a slightly sensationalist topic in chemistry and also Manchester had become associated with a boorish quest to make money.

General books on chemistry with reference to aniline dyes and those more specifically on the new dyes were reviewed in the general press<sup>210</sup> whereas a more specialised dye monograph was reviewed in the *Bradford Observer* where there were likely to be interested trade readers.<sup>211</sup> The housewife was also a target audience and aniline dyes for the home market, particularly Judson's dyes, were advertised from as early as 1861.



**Figure 3.3.** Advertisement for Judson's Dyes, 1861<sup>212</sup>

<sup>209</sup> ANON. (1887) Report of the presidential address to the British Association given by Sir Henry Roscoe. *Aberdeen Weekly Journal*. Aberdeen. Sep 1st

<sup>210</sup> ANON. (1867) Ure's Dictionary. *Saturday Review of Politics, Literature, Science and Art*. Jul 13th

<sup>211</sup> ANON. (1869a) Aniline colours. *Bradford Observer*. Bradford. Jan 14th

<sup>212</sup> Reproduced from The Hampshire Advertiser, Oct 5<sup>th</sup> 1861. Accessed online from the Gale Database of Nineteenth Century British Library Newspapers Sep 14<sup>th</sup> 2010, Document Number R3208807127.

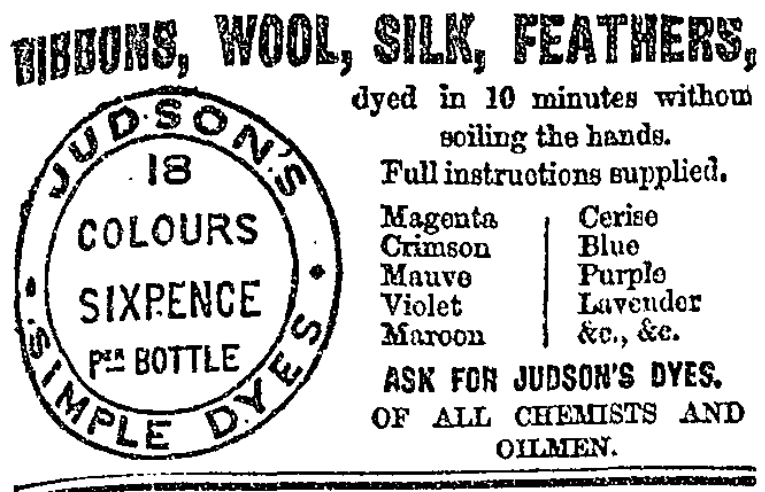


Figure 3.4 Advertisement for Judson's Dyes, 1873<sup>213</sup>

This long-lived brand was also frequently referred to in articles discussing the history of dyeing<sup>214</sup> or proposing the use of aniline dyes for colouring dried flowers<sup>215</sup> or freshening fabrics during spring cleaning.<sup>216</sup> Only one other brand has been identified in these archives and this was advertised to retailers rather than direct to the consumer.<sup>217</sup> Thus Judson's seems to have had a virtual monopoly on direct sales.

### 3.4 Evidence in printed sources for the public reaction to the new dyes: negative reactions

Increasing industrialisation in the mid nineteenth century led to problems with pollution which were recognised but not systematically measured or corrected until the twentieth century. The dye industry was only part of this problem but, due to the colour of many of its emissions, it was a highly visible one. The public, in particular the middle class

<sup>213</sup> Reproduced from The Daily News, August 15<sup>th</sup> 1873. Accessed via Gale online Database of Nineteenth Century British Newspapers, Sep 14<sup>th</sup> 2010, Document Number Y320355752.

<sup>214</sup> ANON. (1876) Dyes and dyeing. *Once a Week*. London. Oct 7th

<sup>215</sup> ANON. (1871a) Household Receipts: Colouring Grasses. *London Journal*. London. Mar 4th

<sup>216</sup> FROM OUR LADY CORRESPONDENT, L. (1893) Our Ladies' Letter. *Freeman's Journal and Daily Commercial Advertiser*. Dublin. Mar 20th

<sup>217</sup> CRAWSHAW, E. (1891) *A chat with my friends the chemists*. Pamphlet from the John Johnson Collection (Soap1 47a) in the Bodleian Library, University of Oxford. Accessed online via ProQuest LLC database 26<sup>th</sup> Oct. 2010.

public, were generally intrigued with the new dyes but there is some evidence of concern in the popular press of the time which is explored in the next section.

The groups who were targeted by the press fall into three main sectors. The first were the general public, with whom either an educational or sensational tone was adopted. Secondly, the housewife who could find tips on how to use the new dyes as well as warnings about health hazards and thirdly various special interest groups including the dyers and those leading the coal gas industry who had a professional interest in the uses of their waste.

By the mid 1860s reports on the medical side effects of the synthetic dyes were emerging. A report of the effects on workers' health has already been cited.<sup>218</sup> Potential harmful effects on consumers were also discussed in the press. Both the *Morning Post*<sup>219</sup> and the *Manchester Times*<sup>220</sup> carried an article by Professor Wanklyn suggesting that clothing coloured with these dyes could be injurious to health. He says that samples of magenta which he analysed contained arsenic and, although the levels used in dye production were by then reduced, the poison might be released as the dye faded. He also argues that some yellow dyes are strong irritants. On the other hand he concedes that the amounts of dye present in the textiles is small but suggests that highly coloured articles ought not to be worn next to the skin.

In 1879 Henry Carr published a book entitled '*Our Domestic Poisons; or, the Poisonous Effects of Certain Dyes and Colours used in Domestic Fabrics*'. This was reviewed in both *Popular Science Review*<sup>221</sup> and *Golden Hours*.<sup>222</sup> *Golden Hours* refers to the widespread use of aniline dyes in artificial flowers and reproduces Mr Carr's list of the symptoms of arsenical poisoning for their readers. In both reports green is cited as the most dangerous colour due to its association with arsenic. The *Popular Science Review* states that Mr Carr's motivation in publishing the pamphlet is to lobby for legislation to safeguard the public.

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<sup>218</sup> ANON. (1865a) Medical Science: Effects of Aniline on Workmen employed in its Manufacture. *Popular Science Review*, 4, 249-250.

<sup>219</sup> ANON. (1869b) Sock and shirt poisoning. *Morning Post*. London. Jan 23rd

<sup>220</sup> ANON. (1869c) Sock and shirt poisoning. *Manchester Times*. Jan 30th

<sup>221</sup> ANON. (1879c) Review of 'Domestic Poisons' by Henry Carr. *Popular Science Review*, 3:9.

<sup>222</sup> ANON. (1879d) Review of 'Our domestic Poisons' by Henry Carr. *Golden hours: an illustrated monthly magazine for family and general reading*, 12.

Even more concerning, perhaps, were many reports of the use of these new dyes for colouring foodstuffs. Adulteration of children's sweets was practised<sup>223</sup> and a case of the use of dye in jam was brought to court in Swansea but failed on a technicality.<sup>224</sup> The *Dundee Courier and Argus* in its report of the case alleges that the use of such dyes was widespread in the meat, jam and confectionary trades.<sup>225</sup> In contrast a later report from 1900 on the use of colouring in food makes no mention of the possible harmful side effects.<sup>226</sup> Further, in a review published in *The Speaker* in 1892 of the book 'Hygiene, Diseases, and Mortality of Occupations' by J.T. Arlidge, MD, FCRP, Dr Arlidge is quoted as saying that:

(A)lthough "aniline" is an "active poison," and injurious to aniline workers, yet that "aniline dyes," if free from arsenic and from undecomposed aniline, are in all respects harmless.<sup>227</sup>

Thus there was much concern when the aniline dyes were introduced about their safety and durability but by the end of the nineteenth century they had become accepted for regular use.

Nevertheless there were several publications in the latter part of the century which decried the use of the brightest aniline dyes, suggesting that they were a fashion indicating lower class associations.<sup>228</sup> Much earlier, in the 1860s, *Leisure Hour* had expressed disapproval for over-use of scarlet dyes<sup>229</sup> and the *Englishwomen's Domestic Magazine* had tried to persuade its readers that restrained colours and colour combinations were more sophisticated than the more gaudy versions whilst conceding that it was probably fighting a losing battle.<sup>230</sup> In January 1865 the fashion section lamented the tendency for a combination of colours in dress which it pronounced not

<sup>223</sup> ANON. (1871b) Ireland: Adulteration of Sweetmeats. *Bury and Norwich Post, and Suffolk Herald*. Bury St Edmonds. Feb 7th

<sup>224</sup> ANON. (1893a) Alleged adulteration of jam at Swansea. An important case breaks down. *Western Mail*. Cardiff. Jul 28th

<sup>225</sup> ANON. (1893b) Poisons in the Manufacture of Foods. *Dundee Courier and Argus*. Aug 8th

<sup>226</sup> ANON. (1900) *Northern Echo*. Darlington. Oct 13th

<sup>227</sup> ANON. (1892) Trade-Made Disease: Review of 'Hygiene, Diseases, and Mortality of Occupations' by J.T. Arlidge, M.D., F.R.C.P. London: Percival & Co. *Speaker*. Oct 22nd

<sup>228</sup> ANON. (1890c) Threats for the frivolous. *Merry England*, 14, ANON. (1890b) Queen Aniline. *Scots Observer*. Both these articles associate the aniline colours with 'the gutter' and 'London flower girls'. *Merry England* was aimed at a Roman Catholic audience so the sentiments expressed may indicate a view with a heavy religious bias.

<sup>229</sup> ANON. (1863) Colour in the Coal Scuttle. *Leisure Hour*, 598, 373-375.

<sup>230</sup> ANON. (1865) *English Women's Domestic Magazine* Pages 29 & 126. Accessed online <http://books.google.com/books> 2nd July 2010

suitable for 'persons in a middle station of life'. Combinations of yellow and blue or green and red were condemned as resembling a 'carnival disguise'. Later, in April, it found that '(T)he eccentric fashion of dresses composed of two different-coloured materials is gradually gaining ground' and suggested that combinations of one colour with black or two shades of the same colour were most acceptable.

Thus, despite disapproval in many quarters, the new fashions for bright, clear colours<sup>231</sup> dominated. The new dyes could, of course be used to produce subtle colour effects and were often combined together or with natural dyes to this effect.<sup>232</sup> By 1890 an article in the *Bristol Mercury* pronounced the triumph of the coal tar dyes in commercial use and predicted, correctly, that the latest discoveries would eventually even lead to the eclipse of natural indigo by a synthetic substitute.<sup>233</sup>

### 3.5 The Arts and Crafts Movement versus the synthetic dyes; the two Williams, Morris and Perkin

Although the synthetic dyes remained in widespread use for textile printing and dyeing, some sectors of fashion, as seen in the previous section, turned against really bright colours for costume and for home furnishing. The more subdued shades could be achieved with either natural or synthetic dyes but the Arts and Crafts Movement championed the use of the natural materials in harmony with their philosophy of encouraging craftsmanship in manufacture as a reaction to the increase in bulk production methods. Shops such as Liberty & Co. provided outlets where consumers could purchase textiles and other goods in this fashion. One prominent member of the movement who championed the use of natural dyes in furnishing fabrics was William Morris although there were other textile producers advertising their use of 'old-fashioned genuine honest' natural dyes (Fig. 3.5).

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<sup>231</sup> BONNER, H. B. (1886) Chats about Chemistry: Bleaching and Dyeing. *Our Corner*, 89-92. Feb This article describes the natural dyes at length but concludes with a short section on aniline dyes conceding that they have more 'depth, brilliancy and varied hues'.

<sup>232</sup> KNECHT, E., RAWSON, C. & LOEWENTHAL, R. (1893) *A Manual of Dyeing: for the Use of Practical Dyers, Manufacturers, Students and all those interested in the Art of Dyeing*, London, Philadelphia, Charles Griffin and Company Ltd/J.B. Lippincott Company. See for example Pattern Sheet No. 23

<sup>233</sup> STANDARD (1890) Coal Tar Products. *Bristol Mercury and Daily Post*. Bristol. Dec 12th



**Figure 3.5** Advertisement guaranteeing freedom from aniline dyes<sup>234</sup>

Reproduced from Longman's Magazine, October 1883

Morris' main objections to the synthetic dyes on artistic grounds were that the colours were not harmonious and, when they faded, changed colour very often. The new dyes were considered to be less fast than the natural dyes although the earliest, mauveine, was in fact more fast than previous versions of this colour.<sup>235</sup> Later dyes were often fugitive and were quickly discarded by the textile trade as this was discovered.

William Morris was a very close contemporary of William Henry Perkin. It is interesting to compare their biographies as they were both involved in textile dyeing in different ways and they could be said to epitomise the tensions in the late nineteenth century between the progressive and the conservative ideologies, even to the extent that Perkin represents a new-made middle class man and Morris the old order of the upper middle classes with inherited money and leisure time.

<sup>234</sup> Reproduced from Longmans's Magazine October 1883. Accessed via ProQuest online database British Periodicals [[http://gateway.proquest.com/openurl?url\\_ver=Z39.88-2004&res\\_dat=xri:bp:&rft\\_dat=xri:bp:article:e930-1883-002-12-02754B](http://gateway.proquest.com/openurl?url_ver=Z39.88-2004&res_dat=xri:bp:&rft_dat=xri:bp:article:e930-1883-002-12-02754B)] 7<sup>th</sup> Jul 2010.

<sup>235</sup> GARFIELD, S. (2000) *Mauve. How one man invented a colour that changed the world.*, London, Faber and Faber Ltd. This fastness of the dye was one of the factors which persuaded Pullar to use Perkin's product.

Table 3.1 Comparative biographies of Morris and Perkin

William Morris (1834-1896) <sup>236</sup>	William Henry Perkin (1838-1907) <sup>237</sup>
Father successful financier; family very comfortably off	Father successful builder; family relatively well off
Educated at Marlborough College and Exeter College, Oxford	Educated at City of London School & Royal College of Chemistry
Intended to enter the church but took articles with G.E. Street, the leading English Gothicist architect	Father intended him to train as an architect as his elder brother had
Left the office in 1856 to pursue painting and writing	Father invested in plant to manufacture mauveine
Set up the design company Morris, Marshall, Faulkner & Co. in 1861 with finance mostly from Morris	Business set up in 1857
Particularly successful in ecclesiastical commissions	Major products mauveine and alizarin
Company became Morris & Co. in 1875	Retired from business in 1874, devoting himself to research in his private labs and church activities
Joined the far left Democratic Federation in 1883	Awarded a knighthood in 1906 and travelled to America for a celebration of the 50 <sup>th</sup> anniversary of the discovery of mauveine
Well known as a prominent socialist and influential in the decorative arts. Had a very high public profile and a strong legacy of distinctive design.	Well known in professional chemical circles but did not have a high public profile

When he was still at the City of London School Perkin started to set up his home laboratory. The school seems to have been progressive in teaching chemistry at the early date of 1851 even though it was an addition to the normal curriculum and had to be paid for separately.<sup>238</sup> This was in contrast to the curriculum at Marlborough College where the subject range was more traditional and concentrated on those necessary for the young gentleman, such as the classics. Morris spent much of his time whilst at school reading and visiting antique and ancient sites in Wiltshire. Perkin was very enthusiastic in his immersion in chemistry, attending talks given by Henry Letheby (1816-1876) at the London Hospital and Faraday's (1791-1867) lectures at the Royal Institution.<sup>239</sup> The

<sup>236</sup> MACCARTHY, F. (2004-2009) Morris, William. *Oxford Dictionary of National Biography*. Oxford, Oxford University Press.

<sup>237</sup> TRAVIS, A. S. Ibid. Perkin, Sir William Henry.

<sup>238</sup> GARFIELD, S. (2000) *Mauve. How one man invented a colour that changed the world.*, London, Faber and Faber Ltd. Page 19

<sup>239</sup> Ibid. Page 19



Royal College of Chemistry was one of the first institutions to teach practical chemistry and had only been open for eight years under the direction of August Wilhelm von Hofmann (1818-92) when Perkin joined in 1853.<sup>240</sup> Hofmann was pivotal in the discovery of mauveine as he introduced the young Perkin to the chemistry of aniline<sup>241</sup> from which Perkin was given the task of producing quinine. This never succeeded but famously Perkin found that he had accidentally produced mauveine instead.<sup>242</sup>

Perkin never seems to have talked about the reasons for his decision to leave the Royal College of Chemistry to set up in business at the age of 20 with the aid of his father and brother. As the son of a builder and contractor he certainly had an advantage when setting up his chemical works and perhaps an entrepreneurial attitude inherited from his father. The fact that mauve was already a fashionable colour and therefore there was an obvious market may also have contributed to the decision.<sup>243</sup> Britain at the time was one of the main centres of the textile industry and therefore the infrastructure was available for practical implementation of the invention. Hofmann, although himself involved in various industrial applications of chemistry, was against the move. His participation was always as a professional consultant<sup>244</sup> and he may have felt that Perkin was limiting himself by investing his energies in the management of his own business and cutting off a promising research career. Indeed, the invention of a new textile colour perhaps seemed trivial beside the original intention of the research to synthesise the life-saving quinine.

Neither Morris nor Perkin followed the career paths initially laid out for them. Morris took longer than Perkin to establish his first company which was formed in 1861 and financed by himself. Perkin was unable to raise capital for his factory elsewhere and his father invested much of his savings to start the project. The choice of a suitable site was complicated by opposition to any chemical works near their home in London. They were therefore forced to settle on a piece of land then north of London at Greenford

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<sup>240</sup> Ibid. Page 21

<sup>241</sup> Hofmann remained a dominant figure in the synthetic dye industry throughout his career, training many of the chemists involved and carrying out much important research.

<sup>242</sup> GARFIELD, S. (2000) *Mauve. How one man invented a colour that changed the world.*, London, Faber and Faber Ltd. Page 43

<sup>243</sup> BALL, P. (2001) *Bright Earth. The Invention of Colour*, London, Penguin. Page 236.

<sup>244</sup> TRAVIS, A. S. (1992) Science's powerful companion: A.W. Hofmann's investigation of aniline red and its derivatives. *British Journal of the History of Science*, 25, 27-44.

Green in Middlesex which was purchased in 1857.<sup>245</sup> Construction took less than six months. Perkin also had to source suitable materials, design large scale processes and build suitable processing equipment. Despite the fact that mauve was a fashionable colour,<sup>246</sup> the success of the enterprise hung in the balance. The new colour was easy to apply to silk but could not be used on cotton and the very important cotton printing industry was not interested in it. However, both Queen Victoria (1819-1901)<sup>247</sup> and Empress Eugénie (1826-1920) soon wore the colour and its place in fashion was ensured.

Unlike Perkin, who showed immense tenacity and single mindedness in commercialising his new dye, Morris found it difficult to settle to any one profession. After taking his degree he was first articled to G.E. Street, one of the leading English Gothicist architects, but left the office in 1856 to pursue painting and writing.<sup>248</sup> He was always drawn to the crafts, however, and experimented with stone carving, clay modelling, woodcarving, manuscript illumination and embroidery. In 1861, with a group of friends, he set up Morris, Marshall, Faulkner & Co. as a design company.<sup>249</sup> They were particularly successful in commissions for re-decorating churches<sup>250</sup> and were always associated with wallpaper and tapestry designs. In this arena Morris found his true strength as a designer in the decorative arts.

Morris was always a romantic and continued to write epic poetry, journeying to Iceland where he was inspired by the Icelandic sagas.<sup>251</sup> The sources which he drew on for his designs were largely the medieval and the natural worlds and his attention to detail led him to try to manufacture all his products within the firm. The revivalist nature of the designs was carried through into Morris' interest in reviving the techniques of using natural dyes. This was the first aspect of manufacture which he brought in-house and he

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<sup>245</sup> GARFIELD, S. (2000) *Mauve. How one man invented a colour that changed the world.*, London, Faber and Faber Ltd. Page 55

<sup>246</sup> Even William Morris, when at Oxford in the early 1850's, wore purple trousers as did his friend Burne-Jones. MACCARTHY, F. (1994) *William Morris. A Life for Our Time.*, London, Faber and Faber. P. 56

<sup>247</sup> The fashion for strong colours between 1858 and 1860 is referred to by Ashelford ASHELFORD, J. (1996) *The Art of Dress. Clothes and Society 1500-1914*, London, National Trust Enterprises Limited. p. 121

<sup>248</sup> MACCARTHY, F. (1994) *William Morris. A Life for Our Time.* London, Faber and Faber. Page 102-108

<sup>249</sup> Ibid. Page 166

<sup>250</sup> Ibid. Page 176

<sup>251</sup> Ibid. Chapter 9, pages 278-310

was particularly interested in indigo dyeing from the natural plant material.<sup>252</sup> By 1881 the firm, which was now owned entirely by Morris, was carrying out its own dyeing and block printing and rug and carpet making and was about to set up a high-warp tapestry frame in new premises at Merton Abbey in south London.<sup>253</sup>

Morris & Co was becoming very successful at this time but the handcrafted nature of the production made the products expensive and therefore exclusive. This was not in tune with Morris' socialist ideology and was a cause of great distress to him.<sup>254</sup> His early exposure to the problems brought about by industrialisation in 'the Set' at Oxford was continued in his admiration of skilled handwork and the nobility of the craftsman. It culminated in his joining the Democratic Federation led by the Marxist Henry Mayers Hyndman in 1883<sup>255</sup> and subsequently to founding the Socialist League which envisaged the total overthrow of the status quo.<sup>256</sup> The manifesto argued for 'a change in the basis of Society – a change which would destroy the distinctions of classes and nationalities'.<sup>257</sup> Thus, although he was the manager of a sizeable commercial organisation at this point, Morris was committed to a far more Marxist vision of the future and had developed the youthful sense of the injustice of the capitalist system far more persistently than his colleagues of those earlier times.

Ever the romantic, Morris perhaps hoped that his utopian dreams could be realised by all in society uniting in a creative society where art and beauty were the most important values. However, other members of the Socialist league were more inclined to extreme anarchy and his views were sidelined.<sup>258</sup> He continued to speak and write in the socialist cause and became involved in the Arts and Crafts movements. Morris and Co. exhibited in the first Arts and Crafts Exhibition in 1888 and Morris gave a lecture on tapestry in association with the exhibition.<sup>259</sup> The productions of Morris and Co. were very successful in the 1890's and the firm employed about 100 people at Merton. His final

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<sup>252</sup> Ibid. Page 353

<sup>253</sup> Ibid. Pages 443-447

<sup>254</sup> Ibid. Morris had a few aristocratic clients but most were industrialists and entrepreneurs, often the same people who patronised his friends the pre-Raphaelite painters. Pages 411-412

<sup>255</sup> Ibid. Page 462

<sup>256</sup> Ibid. Page 504

<sup>257</sup> Ibid. Page 505

<sup>258</sup> Ibid. Page 554

<sup>259</sup> Ibid. Pages 592-596

production was the establishment of the Kelmscott Press in 1891.<sup>260</sup> Morris, despite personally being rather shy, was well-known in his life-time and his reputation, both as a political thinker and as a designer, persists until the present day.<sup>261</sup>

Both Morris and Perkin faced decisive moments mid-career in the 1870s. Although Morris, Marshall, Faulkner & Co. was successful and well-known in artistic circles it was not doing enough business to be commercially viable. In the early 1870s Morris took over more of the direction of the firm, expanding both the range of products and clientele as well as out-sourcing more of the production.<sup>262</sup> In 1875 the original partnership was eventually dissolved after some bitter disputes between the partners over the financial settlement and Morris continued trading as Morris and Co.<sup>263</sup>

Morris was very concerned with the methods of manufacture of his products and took great pains to re-introduce indigo dyeing with the natural rather than the synthetic product although the latter was much cheaper by this time. Morris actively disliked the synthetic dyes and stated in a lecture

It must be enough to say that their discovery while conferring the greatest honour on the abstract science of chemistry, and while doing a great service to capitalists in their hunt after profits has terribly injured the art of dyeing, and for the general public has nearly destroyed it as an art. Henceforward there is an absolute divorce between the *commercial process* and the *art* of dyeing. Anyone wanting to produce dyed textiles with any artistic quality in them must entirely forego the modern and commercial methods in favour of those which are at least as old as Pliny, who speaks of them as being old in his time.<sup>264</sup>

Wardle was pivotal in helping Morris in these experiments<sup>265</sup> and Morris based his desired palette on the antique textiles he so much admired. In his lecture on Arts and Crafts of 1889 he listed the colours he preferred and the dyes he used to achieve these

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<sup>260</sup> Ibid. Page 608

<sup>261</sup> A noted authority on Morris and his textiles, Parry, has published widely and to date including PARRY, L., (2005) *Textiles of the Arts and Crafts Movement*. London, Thames and Hudson. PARRY, L. (Ed.) (1996) *William Morris*, London, Philip Wilson Publishers Ltd. PARRY, L. (2013) *V&A Pattern: William Morris*, London, V&A Publishing.

<sup>262</sup> HARVEY, C. & PRESS, P. (1991) *William Morris: design and enterprise in Victorian Britain*, Manchester, Manchester University Press. Page 78

<sup>263</sup> Ibid. Page 90.

<sup>264</sup> MORRIS, W. (1889) *Of Dyeing as an Art* Arts and Crafts Lecture. Quoted in PARRY, L. (1983) *William Morris Textiles* New York, Crescent Books Page 39

<sup>265</sup> PARRY, L. (1983) *William Morris Textiles* New York, Crescent Books Page 40

which were all natural.<sup>266</sup> This approach inevitably made his products more expensive than those which were mass-produced with synthetic dyes. This meant that the main clientele for Morris and Co was the artistic middle class as well as the rich industrialists and provincial entrepreneurs that Morris met through his association with the Pre-Raphaelite painters.<sup>267</sup> His relations with his richer clients was difficult and he was aware that his position in selling mainly to the affluent was incompatible with the aspirations of the Arts and Crafts movement of providing goods design for all.<sup>268</sup>

Perkin had also made a very successful business from the manufacture of Mauveine and later alizarin, the major dye substance in madder, which he was able to exploit in England. However, when the competition from Germany within the industry became intense in 1873, the Perkins sold their works<sup>269</sup> and William Perkin retired from business in 1874 to devote himself to chemical research, particularly the production of perfumed compounds, and his church activities. His son,<sup>270</sup> writing in 1908, gave the principal reason for this decision as his father's dislike of an industrial career and his desire to pursue pure research.<sup>271</sup> His contributions to chemistry were widely recognised and he was prominent in the main chemical Societies of the time. The golden jubilee of the discovery of Mauveine was celebrated in both Europe and North America.<sup>272</sup> However, despite the fact that he was given a knighthood, there was no lasting appreciation of his work in the public mind as there was with Morris.

These two men therefore epitomise the polarisation in the dye industry in the late nineteenth century. Morris was highly influential in the circles of those who were

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<sup>266</sup> Ibid. Page 44

<sup>267</sup> MACCARTHY, F. (1994) *William Morris* London, Faber and Faber Ltd Pages 411-412

<sup>268</sup> Ibid. Page 412

<sup>269</sup> GARFIELD, S. (2000) *Mauve. How one man invented a colour that changed the world.*, London, Faber and Faber Ltd. Page 110

<sup>270</sup> This was his eldest son, William Henry Perkin (1860-1929). Two of Perkin's sons went on to become academic chemists, his oldest son was particularly influential doing much to establish effective chemical research at Oxford. Jack Morrell, 'Perkin, William Henry (1860-1929)', *Oxford Dictionary of National Biography*, online edn, Oxford University Press, Sept 2004  
[<http://www.oxforddnb.com/view/article/35478>, accessed 25 Oct 2010 ]

His younger brother, Arthur George Perkin (1861-1937) became professor of colour chemistry and dyeing at Leeds University. Jack Morrell, 'Perkin, Arthur George (1861-1937)', *Oxford Dictionary of National Biography*, online edn, Oxford University Press, Sept 2004  
[<http://www.oxforddnb.com/view/article/35476>, accessed 25 Oct 2010 ]

<sup>271</sup> SANDERSON, M. (1975) *The universities in the nineteenth century*, London and Boston, Routledge & Kegan Paul. Page 153

<sup>272</sup> GARFIELD, S. (2000) *Mauve. How one man invented a colour that changed the world.*, London, Faber and Faber Ltd. Page 3

powerful in British life. Many of them preferred to live in the kind of romantic surroundings he could create and subscribed to the Arts and Crafts preference for the natural over the synthetic and manufactured.<sup>273</sup> This, of course, was despite the fact that many of them derived their wealth from the very industrial processes which Morris was against. It was a source of great personal regret to Morris that his products, with their requirement for a high level of labour input, were much more expensive than the industrially produced alternatives and were therefore only accessible to the rich; his desire was to produce good design for all.<sup>274</sup> Morris may have been a reluctant businessman but he was an effective one. He was able to invest time and money in the early days of his business which paid off in reasonable returns later on.<sup>275</sup> Perkin was equally successful financially and the industry he founded went on to evolve into the international giant of the pharmaceutical industry.

In the second half of the nineteenth century the textile dyers were able to make use of both synthetic and natural dyes and combined them to produce the shade they required. They had to adapt their dyeing methods to accommodate the new dyes but technical assistance could be supplied by the dye manufacturers and most dyers used both categories simultaneously. Thus, an absolute distinction between the two types of dyes was not common at this time except within the Arts and Crafts movement. The overriding consideration was fashion, and whether a colour was produced with a natural or a synthetic dye was not important to the consumer. One example where this is clearly shown is in the arrangement of the exhibits at the 1862 International Exhibition in London where orchil dyes are shown in the chemistry section and not in the natural products section.<sup>276</sup>

### 3.6 The substitution of natural dyes by synthetics

In the preceding sections the themes of the expansion of the synthetic dye industry and the public reactions to it have been explored. This included an examination of the

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<sup>273</sup> NAYLOR, G. (Ed.) (1988) *William Morris by himself: designs and writings*, London, Macdonald & Co (Publishers) Ltd.

<sup>274</sup> MACCARTHY, F. (1994) *William Morris. A Life for Our Time.*, London, Faber and Faber. Page 445

<sup>275</sup> HARVEY, C. & PRESS, P. (1991) *William Morris: design and enterprise in Victorian Britain*, Manchester, Manchester University Press. Page 168

<sup>276</sup> (1862) *The International Exhibition of 1862, The Illustrated Catalogue of the Industrial Department. British Division Vol 1.*, London, Her Majesty's Commissioners.

resistance to the new dyes in some sectors of society taking the well-known example of William Morris as a case study. The question which naturally follows on from this discussion is to what extent did the synthetic dyes take market share from the naturals and how quickly did this happen?

Although several early articles had predicted the total demise of the natural dyes this was by no means the case. Some authors such as Macrae in 1880<sup>277</sup> suggested that madder was still an important dye and logwood remained in widespread use beyond the end of the nineteenth century. Dye manuals<sup>278</sup> still carried long sections on the natural dyes and Prof Hummel, for one, was researching the possibilities of new dye plants in connection with the Royal Botanic Gardens, Kew at the end of the century.<sup>279</sup>

Before the introduction of synthetic dyes, dyers were skilled in producing an infinite number of colours and shades by combining and manipulating the limited range of natural dyes. Jenkins and Ponting deduce from an examination of wool dyers' sample books that the range of shades did not increase after the introduction of the new dyes but it became easier to match colours as the synthetic dyes were more standard preparations.<sup>280</sup>

The development of the synthetic dye industry is typically characterised as the displacement of natural dyes by novel chemical compounds but many of the early researches were attempts to synthesise exact substitutes of natural dyes from different source compounds. Perkin's most successful dyes were a synthetic substitute for the mauve orchil and alizarin as a substitute for madder. In his inaugural address to the Yorkshire College in 1880, Hummel described the advances in artificial dyes in terms of the synthesis from coal tar products of the natural dyes alizarin and indigo and suggested that the next great advances would come from the replication of the logwoods

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<sup>277</sup> MACRAE, A. S. (1880) Competition between the aniline and madder dyes. *Science*, 1, 62-63.

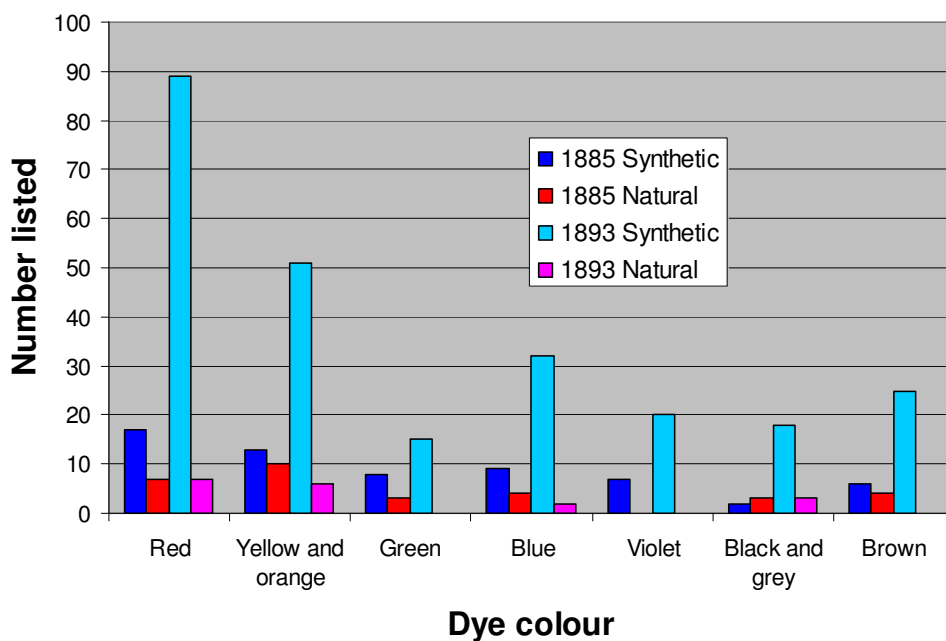
<sup>278</sup> KNECHT, E., RAWSON, C. & LOEWENTHAL, R. (1893) *A Manual of Dyeing: for the Use of Practical Dyers, Manufacturers, Students and all those interested in the Art of Dyeing*, London, Philadelphia, Charles Griffin and Company Ltd/J.B. Lippincott Company.

<sup>279</sup> HUMMEL, J. (1897) Letter from JJ Hummel to Sir William Thisleton-Dyer. *Archives: Directors' Correspondance*. London, Royal Botanic Gardens, Kew. Accessed online 21<sup>st</sup> Jun 2010.

<sup>280</sup> JENKINS, D. T. & PONTING, K. G. (1982) *The British Wool Textile Industry 1770-1914*, London, Heinemann Educational Books Ltd. p. 214

and brazilwood.<sup>281</sup> Most of his research was aimed at investigating potential new natural dyes or synthetic versions of the naturals.<sup>282</sup>

The dyes listed in Hummel's manual of 1885 and Knecht's of 1893<sup>283</sup> have been compared to see if any trends are evident in the uptake of synthetic dyes. Both books devote large sections to methods of dyeing with the natural compounds and so it can be deduced that these were by no means obsolete in the last decades of the nineteenth century. The earlier manual lists fewer dyes than the later one and has much less in the way of introduction and discussions on the dyeing trade. Both contain lists of methods for distinguishing the dyes present on samples of cloth and these have been used to provide the following analysis of the proportions of synthetic and natural dyes in common use (Figure 3.6). Presumably these lists reflect the methods which were thought of most value to textile dyers being the most likely to be commonly encountered and so it is these lists which are analysed here.



**Figure 3.6** Natural and synthetic dyes as listed in 1885 and 1893 analysed by colour.<sup>284</sup>

<sup>281</sup> ANON. *Leeds Mercury*. Leeds. Apr 13<sup>th</sup> 1880

<sup>282</sup> Ibid. Sep 16<sup>th</sup> 1896

<sup>283</sup> For the sake of brevity the dye manual by Knecht, Rawson and Loewenthal is referred to as 'Knecht'.

<sup>284</sup> KNECHT, E., RAWSON, C. & LOEWENTHAL, R. (1893) *A Manual of Dyeing: for the Use of Practical Dyers, Manufacturers, Students and all those interested in the Art of Dyeing*, London, Philadelphia, Charles Griffin and Company Ltd/J.B. Lippincott Company.



It can be seen that in all colour categories the number of dyes listed is much greater in the 1893 manual and this is due to the increase in the number of synthetics available. In some colours, for example red and black/grey, the numbers of natural dyes listed remains the same and, in fact, the same dyes are still in use. For natural green dyes, although there are three listed in the earlier manual, these are all compound dyes and so arguably both sources only list synthetic dyes for this colour. Despite the fact that in the middle of the nineteenth century murexide and orchil dyes were widely used to produce the fashionable mauve colour, only synthetic dyes are listed for violet colours in both these manuals. Orchil red is however listed in 1893 along with several synthetic orchil substitutes, all in the red section. Brown is also a category in which no natural dyes are listed in 1893 although roughly equal numbers are quoted in 1885. In every colour category there are far more synthetic dyes listed in the later source. This could reflect Hummel's interest in the natural colours leading him to give less prominence to the synthetics or could be due to a true increase in numbers with time.

Large sections of both manuals are devoted to the natural dyes but Knecht provides more commentary on their use and the state of the dye industry. Those still in use include logwood, fustic, quercitron bark and flavin, Persian berries, young fustic, turmeric, redwoods, madder, lichens, cochineal, kermes, lac and catechu. Fustic is said to be used on cotton for compound shades and on heavy woollens with logwood, indigo and alizarin. Quercitron bark and flavin (a preparation of quercitron bark) are listed but tartrazine (a synthetic) is said to be faster to light. Nevertheless the natural dyes are faster to milling and scouring and therefore have applications in some cases. Weld has largely been superseded by quercitron but is the best natural yellow on silk. Both have, though, apparently been largely overtaken by the coal-tar yellow colours. Persian berries are used for printing and gives orange and scarlet with cochineal or bright yellows and oranges when mordanted with tin on wool. However Knecht states that it is no better than quercitron and is more expensive.<sup>285</sup>

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HUMMEL, J. J. (1885) *The Dyeing of Textile Fabrics*, London, Paris & Melbourne, Cassell and Company, Limited.

<sup>285</sup> KNECHT, E., RAWSON, C. & LOEWENTHAL, R. (1893) *A Manual of Dyeing: for the Use of Practical Dyers, Manufacturers, Students and all those interested in the Art of Dyeing*, London, Philadelphia, Charles Griffin and Company Ltd/J.B. Lippincott Company. Pages 321-403. Edmund Knecht PhD FIC is described as the Head of the Chemistry and Dyeing Department of the Municipal

Several dyes are now being substituted by synthetic alternatives at least in some applications. Knecht states that Young fustic ‘...at the present day has practically fallen into disuse.’ Turmeric, on the other hand, although being fugitive to light, soaping and alkalies was still in use in large quantities for compound shades on wool, cotton and silk. The redwoods have now been overtaken for printing pinks and purples by the faster alizarin dyes. Cochineal, kermes and lac are now rarely used for dyeing silk where they have been overtaken by the coal-tar colours. Cochineal is now used mostly for dyeing woollen cloth. Catechu is now almost only used as a mordant for the basic coal-tar colours such as Bismarck brown, magenta and auramine. He lists six synthetic dyes specifically as substitutes for orchil and quinoline yellow as a substitute for picric acid. The latter was highly explosive which may have been the motivation for its substitution. Ironically we now characterise the lichen organism from which orchil is produced as being very susceptible to pollution so they it have been becoming scarce due to industrialisation in Europe.

Natural indigo was still used at this date (1893) of course as the synthetic version was uneconomic to produce. Knecht states that woad is still grown in Lincolnshire, the South of France and Hungary but was now never used alone for dyeing but in combination with indigo.<sup>286</sup> By this date madder had been largely superseded by artificial alizarin but dyeing recipes were still given. The lichen dyes orchil and cudbear were also still available from the firm of Marnas in France but were mostly now used for bottoming indigo and in compound shades.

It might seem an omission not to include a discussion of black dyes in this study as it coincides with the Victorian period (reigned 1837-1901) during the latter half of which, after the death of Prince Albert (died 1861), black was a dominant colour in fashion, led by the Court.<sup>287</sup> However, until the very last years of the nineteenth century there were no black synthetic dyes which could compete with logwood combined with an iron

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Technical School, Manchester and Christopher Rawson FIC FCS as late Head of the Chemistry and Dyeing Department of the Technical College, Bradford.

<sup>286</sup> Ibid. Page 321

<sup>287</sup> For a discussion of mourning see TAYLOR, L. (1983) *Mourning dress: a costume and social history*, London, George Allen and Unwin.

mordant or with the later improved chrome mordant.<sup>288</sup> As late as 1893, Knecht states that logwood is ‘perhaps the most important of dyestuffs’:

Logwood is very extensively employed in the dyeing of all textile fibres and all classes of fabrics. Immense quantities are used for dyeing wool, cotton and silk black...<sup>289</sup>

Notwithstanding the persistence of the natural dyes for industrial dyeing, a much larger part of the dye manual is devoted to the synthetic dyes. Knecht lists some 252 dyes, some of which might be similar compounds with different trade names. The majority of these are red with blues and blacks as the next largest category. He states in the introduction:

A new age was inaugurated for the art of dyeing by Perkins’ discovery of mauve in 1856. Almost numberless colouring matters have since been produced from coal-tar; relatively few have stood the test of time, and most of these will probably disappear from commerce before another thirty-five years have passed.....<sup>290</sup>

Some of the synthetic dyes are characterised as being resistant to road dirt (which was alkaline) and this was presumably of concern to the consumer.<sup>291</sup> One dye, resorcin blue, is said to have ‘a remarkable reddish fluorescence which is pronounced in gas light’.<sup>292</sup>

Thus the synthetic and natural dyes were used in combination or alongside each other for all of the nineteenth century. Each had its particular strengths and weaknesses and synthetic versions of the natural dyes tended to dominate as they were more consistent preparations than their natural counterparts. The synthetic dyes eventually replaced the natural dyes entirely in commerce although this did not happen until well into the

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<sup>288</sup> JENKINS, D. T. & PONTING, K. G. (1982) *The British Wool Textile Industry 1770-1914*, London, Heinemann Educational Books Ltd. p. 214. It is technically difficult to produce a satisfactory black dye as the chemical has to absorb all wavelengths of visible light to which the human eye is sensitive whereas each chemical structure will only absorb over a very narrow bandwidth. Therefore a black dye has to be a complex structure in order to appear a satisfactory colour. In many cases a combination of dyes such as indigo and madder was used.

<sup>289</sup> KNECHT, E., RAWSON, C. & LOEWENTHAL, R. (1893) *A Manual of Dyeing: for the Use of Practical Dyers, Manufacturers, Students and all those interested in the Art of Dyeing*, London, Philadelphia, Charles Griffin and Company Ltd/J.B. Lippincott Company. Page 345

<sup>290</sup> Ibid. Page 404

<sup>291</sup> Ibid. Page 553

<sup>292</sup> Ibid. Page 567

twentieth century. This was despite the reaction against the earliest of the new colours in some artistic circles and the establishment of at least one company (Morris & Co.) which successfully traded on the ethic of craft production of textiles into the twentieth century.

### 3.7 Summary of reasons for German supremacy

Much has been written about the early supremacy of England in the synthetic dye industry and how this lead was lost to Germany within about 20 years. Many reasons for this have been advanced, both at the time and more recently. The outbreak of the First World War was a shock to the authorities who discovered that, although England's textile industry was healthy enough, all the dyes were sourced from Germany and this supply was suddenly cut off. There were enquiries into the reasons for this decline and one published report<sup>293</sup> collated a series of papers written over the period from 1868 to 1914. In his introduction to this study, Gardner attributes the lack of Government support for the industry partly to its relatively low value (not more than £2million) in relation to the much larger textile trade as a whole. The list of factors he considered important in the loss of momentum to Germany are contrasted with those suggested by Travis and co-workers and the present study in Table 3.2 below.

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<sup>293</sup> GARDNER, W. M. (Ed.) (1915) *The British Coal Tar Industry:- Its Origin, Development and Decline*, London, Williams and Norgate.

Table 3.2 Summary of reasons suggested for the decline of the English synthetic dye industry compared with the German industry

Issue	Gardner 1915 <sup>294</sup>	Travis 1993 <sup>295</sup>	Current study
Patent system	<ul style="list-style-type: none"> <li>• No protection for English firms against German imports</li> </ul>	<ul style="list-style-type: none"> <li>• Intense competition in Germany due to lack of patent system stimulated the trade</li> </ul>	<ul style="list-style-type: none"> <li>• Certainly a factor, although not a major one</li> </ul>
Trade conditions	<ul style="list-style-type: none"> <li>• Excise restrictions on alcohol in England</li> <li>• English free trade policies (the fiscal system)</li> <li>• Apathy of English Governments towards industry (as opposed to commerce)</li> </ul>	<ul style="list-style-type: none"> <li>• Lack of investment</li> </ul>	<ul style="list-style-type: none"> <li>• Easier access to investment funds in Germany</li> <li>• Importance of indigo to English colonial economies</li> <li>• Arts and Crafts movement in England anti-industrial</li> </ul>
Business enterprise	<ul style="list-style-type: none"> <li>• Want of enterprise among English industrialists</li> </ul>	<ul style="list-style-type: none"> <li>• Greater technical and sales expertise in Germany</li> <li>• German firms able to consolidate and achieve a suitably large scale of operation</li> </ul>	<ul style="list-style-type: none"> <li>• Business enterprise not lacking in England</li> <li>• German firms more determined in selling and gave better technical support</li> </ul>
Cooperation	<ul style="list-style-type: none"> <li>• Want of cooperation among English industrialists</li> </ul>	<ul style="list-style-type: none"> <li>• German firms had good international links &amp; worked closely with academics</li> </ul>	<ul style="list-style-type: none"> <li>• Access to academic resources in Germany critical</li> <li>• Chemistry not an acceptable profession</li> </ul>
Lack of appropriate chemical education	<ul style="list-style-type: none"> <li>• Lack of well-trained chemists in England</li> <li>• Early neglect of science among the old English universities</li> </ul>	<ul style="list-style-type: none"> <li>• Lack of trained personnel</li> </ul>	<ul style="list-style-type: none"> <li>• Single most important factor</li> <li>• Secondary education was lacking in England</li> <li>• Chemists who were produced tended to be competent technicians rather than trained researchers</li> </ul>
Industrial research organisation	<ul style="list-style-type: none"> <li>• Early neglect of chemical research in England</li> </ul>	<ul style="list-style-type: none"> <li>• German research labs were not a significant factor as they only existed after the German lead was established</li> </ul>	<ul style="list-style-type: none"> <li>• Research and development was a critical factor even before it had become formally established in German industry</li> </ul>

Amongst the aspects of the economic environment in England which contributed to the emergence of Germany as the dominant player in the dye industry Gardner includes the patent systems. The latter is well accepted as a major factor. In England it had been

<sup>294</sup> Ibid.

<sup>295</sup> TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses.

developed largely to protect machinery from competition within the country and it was difficult to apply to chemical processes or products, particularly when these were ill-defined.<sup>296</sup> Much of the early development of dyes was motivated by the search for alternative processes to make the same product. Germany, being at the time a federation of relatively independent states, had no effective patent process and so there was no protection available for the foreign importers. However, German exporters were able to take out English patents which did not require them to manufacture in England. This last condition allowed foreign produced dyes to be protected and Levinstein, in particular, campaigned vigorously for the introduction of a clause requiring English patents to be worked in the country.

Overall trade conditions are also cited by Gardner including excise restrictions and the non-interventionist free trade policies of the Government. These are rightly considered of minor importance by Travis but there are some aspects of trade which he shows are relevant. One of these was the attitude to investment in the two countries.<sup>297</sup> Perkin had difficulty in raising the finance for his new factory to produce mauveine and eventually his father put his savings into the venture. A contributory factor in this may have been the very success of the English textile industry since these industrialists who could have invested in the new area preferred to re-invest in less speculative ventures. In Germany most of the new companies were formed with input from investment bankers. BASF procured investment from a Mannheim banking house and AGFA originated in a partnership between a chemist and a banker. Even those companies which were established in England suffered from a lack of continuing investment in research with the exception of Levinstein's which was the most successful. As Travis contends, German re-investment allowed consolidation and the achievement of a critical size.<sup>298</sup> BASF, the largest of the German firms by 1900, created a pivotal research department whereas the English industry was more concerned with producing returns for the investors than re-investing in the enterprise.

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<sup>296</sup> TRAVIS, A. S., HORNIX, W. J., BUD, R. & VAN DEN BELT, H. (1992) Why monopoly failed: the rise and fall of Societe La Fuchsine. *The British Journal for the History of Science*, 25, 45-63. The dispute which financially ruined the Société La Fuchsine was over patent rights.

<sup>297</sup> TRAVIS, A.S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*. London and Toronto, Associated University Presses. Page 234

<sup>298</sup> Ibid. Page 239

Travis further points to the excellent technical service provided by the German companies to back up their sales so that the English textile manufacturers did not need to employ their own chemists.<sup>299</sup> Jenkins and Ponting suggest that the woollen industry in England had a negative attitude to the 'scientific gentlemen at the universities and colleges'.<sup>300</sup> The best graduates from the Dyeing Department of the Yorkshire College in the early days either went to work in Germany or to teach in other technical departments.<sup>301</sup> Robert Haefley who was employed at the calico printers Edmund Potter & Co. in Manchester was perhaps more representative of the general type of individual working in England at that time. In the 1884 report of the Commissioners he described his work as developing the methods for printing the designs he received. This involved understanding the chemistry of the dyes to be used in order to combine them to produce the required effect although he testified that, in England, those carrying out his job were not usually trained as chemists and so proceeded more inefficiently by trial and error. He oversaw a laboratory of an analytical chemist and a lad who made up the colours under his direction.<sup>302</sup>

Another symptom of this devaluing of new production methods is shown in the Arts and Crafts movement pioneered by Morris whose socialism was closely allied to a rejection of the increasing industrialisation of the country. The Arts and Crafts Exhibition Society which was founded in 1887 in London was based on the premise that design production should move away from industrial to craft-based manufacture and took much inspiration from Morris.<sup>303</sup> His idealism led him to look for a return to an earlier and supposed more humane style of living and his thoughts were influential among many powerful sectors in the country. In contrast, outside Britain the Arts and Crafts movement embraced industrialisation.<sup>304</sup>

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<sup>299</sup> Ibid. p. 234

<sup>300</sup> Ibid. p. 218 No doubt this attitude would have been even more negative if they could have foreseen the synthetic textile fibres which would follow the dyes into the market in the twentieth century.

<sup>301</sup> CARDWELL, D. S. L. (1972) *The Organisation of Science in England*, London, Heinemann Educational Books Ltd. p. 175

<sup>302</sup> MATHER, W., SAMUELSON, B. & WARDLE, T. (1884) Second report of the Royal Commissioners on Technical Instruction. Vol. III. 1.--Notes on technical education in Russia, by William Mather. 2.--Report on the silk industry by Thomas Wardle. 3.--Scheme of technical education for Ireland, by Dr. Wm. K. Sullivan, D.S. C., Ph.D. 4.--Minutes of evidence, &c. relating to England, &c.

. *Command papers; Reports of Commissioners*. Pages 1-10

<sup>303</sup> LIVINGSTONE, K. & PARRY, L. (2005) *International Arts and Crafts* London, V&A Publications Page 12-13

<sup>304</sup> Ibid. Page 17

The factor of the English colonies was absent from the list produced in 1915. Hugill and Bachmann argue that this geopolitical factor was a major component in the competition.<sup>305</sup> Germany did not have access to the colonial products that England did and this acted as a spur to innovation. Thus, there was considerable investment in long-term research, both in industry and in the universities.<sup>306</sup> Whilst England's vision of the future was the maintenance of the status quo, Germany's was a new future where industry depended critically on scientific and technical input.

There was no want of enterprise among the British manufacturers (as Gardner claimed) but they seemed to lack the competitive drive of the Germans. This can be seen in the reports surrounding the 1862 International Exhibition in London where the German Zollverein group were prepared to sell their goods directly when the British contributors were content to merely exhibit. Britain too had a strong class culture where manual and professional workers were strictly divided. Perkin himself wrote that: 'for a scientific man to be connected with manufacturing was looked upon as *infra dig*'.<sup>307</sup> In Germany a new category of skilled worker (as opposed to a craftsman) was created who had practical and academic capabilities and who worked in potentially dirty and dangerous environments. The report of the Commissioners in 1882 though suggests that the Continental factories were better run than the English establishments and this may well be attributable to better trained workmen.<sup>308</sup>

Recently Schroter and Travis<sup>309</sup> have pointed out that national character traits are a factor considered important today in the analysis of economic performances around the world. For example, the Japanese culture is quoted as producing the very high levels of cooperation within their organisations. They apply this analysis to the nineteenth

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<sup>305</sup> HUGILL, P. J. & BACHMANN, V. (2005) The route to the techno-industrial world economy and the transfer of German organic chemistry to America before, during and immediately after World War I. *Comparative Technology Transfer and Society*, 3, 159-186.

<sup>306</sup> The development of an economic process for the synthesis of indigo is a well known example of this. The structure of indigo was published by Baeyer in 1868 but a commercial product was not available until 1897.

<sup>307</sup> GARFIELD, S. (2000) *Mauve. How one man invented a colour that changed the world.*, London, Faber and Faber Ltd. Page 47

<sup>308</sup> SAMUELSON, B. (1884) Second Report of the Royal Commissioners on Technical Instruction Vol I *Command Papers: Reports of Commissioners*. P. 223

<sup>309</sup> SCHROTER, H. G. & TRAVIS, A. S. (1998) An issue of different mentalities. National approaches to the development of the chemical industry in Britain and Germany before 1914. IN HOMBURG, E., TRAVIS, A. S. & SCHROTER, H. G. (Eds.) *The Chemical Industry in Europe, 1850-1914*. Dordrecht/Boston/London, Kluwer Academic Publishers.



century dye industry concluding that there were two fundamental differences between Britain and Germany which were important in the dominance of Germany. These were that there was much more cooperation between different sectors of society in Germany and there was greater economic vision amongst those with industrial influence in Germany. This vision in Germany led to the establishment of research laboratories both in industry and academia and, crucially, to cooperation between them.

Hummel demonstrates the importance of a network of European contacts in textile dyeing. It was his Swiss connections, no doubt, which enabled him to get an education at the prestigious Zurich Polytechnic which allowed him later to join the Yorkshire College eventually achieving the status of professor. As well as industry's distrust of clever scientists referred to earlier, there was also some distrust of foreign universities. Perkin was hesitant to allow his eldest son to study for a PhD in Würzburg as he regarded Germany as a dangerous centre of free thought.<sup>310</sup> German researchers were critical to the establishment of the English dye industry but they returned to Germany once employment was available there and no suitable replacements had been educated in England. Although a few English chemists had gained research degrees in Germany and Switzerland, they did not find employment in the English dye industry and there was no pool of chemists with various levels of research skills to staff development laboratories as in Germany. His research work also shows how important the natural products of the colonies were as a source of dyes in England.

Several of these points relate to chemical education and the analysis presented here certainly supports this as a major factor. The fact that many of the researchers at the beginning of the synthetic dye industry were educated in Germany, Switzerland or by German or Swiss nationals demonstrates that these countries had developed competent research and teaching groups much earlier than England and is often referred to in discussions of this topic.<sup>311</sup> A point which has not previously been raised with reference

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<sup>310</sup> MORRELL, J. (2004) Perkin, William Henry (1860-1929). *Oxford Dictionary of National Biography*. Online Edition, Sept 2004 ed. Oxford, Oxford University Press.

<sup>311</sup> See especially TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses. pp138-145; TRAVIS, A. S. (1998) Heinrich Caro and Ivan Levinstein: Uniting the Colours of Ludwigshafen and Lancashire. IN HOMBURG, E., TRAVIS, A. S. & SCHROTER, H. G. (Eds.) *The Chemical Industry in Europe, 1850-1914: Industrial Growth, Pollution, and Professionalization*. Dordrecht/Boston/London, Kluwer Academic Publishers.; and, for a more general examination of the chemical industries, MOKYR, J.

to synthetic dyes is that, as well as the university sector, the system of primary and secondary education in Germany was also better developed in the nineteenth century compared to the English system. In Prussia, universal primary education was introduced earlier than in England where compulsory education to age 10 was only introduced in 1876.<sup>312</sup> This meant that universities in Germany were able to accept an intake from a much larger base than those who could afford to buy schooling.

Thorpe, amongst others, recognised the central issue as that of training in research chemistry but he failed to establish research degrees at the Yorkshire College. The Council was initially concerned with providing technical training to produce workers for the local woollen industry and later with raising the status of the College by incorporation in the Victoria University which meant moving in the direction of an old-fashioned liberal education. The difference between the universities providing a liberal education for gentlemen contrasted with the new types of technical education as can be seen in the biographies of Perkin and Morris. By comparison in Germany there were both ancient universities providing a wide curriculum, including science, and technical high schools related to local industries.<sup>313</sup>

The lack of the right type of training for the new industries was a well-rehearsed argument at the time and strenuous efforts were made to improve the position both by trying to raise Government help and by starting local foundations which resulted in the civic universities of the northern cities.<sup>314</sup> These, though, were too focussed on training for immediate practical applications in industry. The dyeing students went on to take City and Guilds qualifications rather than degrees.<sup>315</sup> This missed the essential element of education in research skills in Germany and indeed the university system in England did not produce industrial research chemists until much later than the German system. In direct contrast, Hofmann and several other German chemists of the time moved

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(2001) The Industrial Revolution and the economic history of technology: Lessons from the British experience, 1760-1850. *The Quarterly Review of Economics and Finance*, 41, 295-311.

<sup>312</sup> BROCK, W. H. (1996) *Science for all: studies in the history of Victorian science and education*, Aldershot, Variorum. p 953

<sup>313</sup> SANDERSON, M. (1975) *The universities in the nineteenth century*, London and Boston, Routledge & Kegan Paul. Pages 143-144

<sup>314</sup> In England the main task of the established universities was the provision of graduates to administer the Empire.

<sup>315</sup> In 1882 the curriculum of the course was changed to facilitate students entering the City and Guilds examinations which were in May. ANON. *Leeds Mercury*. Leeds. Jun 26th 1882

between industry and academia and maintained links with their colleagues and students in both sectors. Travis maintains that the success of the German industry cannot be attributed to the industrial research laboratories as these were established after the lead had already been lost by England.<sup>316</sup> However, had the personnel and investment been available to staff such laboratories in England there might have been less of a dramatic shift in the industry and closer competition between the two countries. Under those circumstances it is no longer possible to predict now which of the two, if either, would have emerged as the stronger.

### 3.8 Conclusions

Thus the evidence presented in this study supports previous data that a major reason for the decline of the English synthetic dye industry was the lack of suitable education, particularly in research chemistry. New information about the early life of Professor Hummel supports previous work which has highlighted the importance of continental connections in the dye industry. Hummel's case shows that this effect operated at levels in the industry other than the industrial and academic research chemists usually cited and suggests that further research in industrial and census archives could be used to show to what extent foreign workers were important in English calico printing factories. In contrast to Hummel, Perkin never travelled abroad until he went to America for the 1906 Jubilee celebrations for the discovery of mauveine and was reluctant to allow his son to study abroad. The most important English overseas connections were with her colonies and this tended to bias both research, as undertaken by Hummel at Leeds, and the dyes used towards those natural products which were important to the colonial economies.

This study also shows the importance of the lack of funding for education in chemistry from the English government and even amongst the industrialists of the textile industry itself. The Yorkshire College never raised a sufficient proportion of its funding in Leeds and was heavily dependent on the London based Clothworkers' Company, many of whose members had ceased to be directly involved with clothworking. This may have been because these wealthy industrialists were not willing to risk their capital in a

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<sup>316</sup> TRAVIS, A.S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*. London & Toronto, Associated University Presses. Page 239

totally new branch of trade, closely associated as it was with their existing undertakings. The chemical industry needed substantial investment to produce novel equipment and reasonable working conditions which the English firms were not able or willing to provide. The lack of trained English employees at all levels was also an inevitable consequence of the lack of education.

The strong economic and political situation of England at this time was a handicap in developing this new industry. The profits from the textile trade were large, the colonies were a good source of natural resources and the Napoleonic wars had not produced such fundamental political change as in Germany. Therefore the bias was towards maintaining the comfortable *status quo* and furthermore this study shows that the English, but not that in Germany, Arts and Crafts movement was actively anti-industrial. Generally the attitudes towards the synthetic dyes analysed here show that the dyes were seen as a source of wonder more than a competitive opportunity. The evidence from the 1862 London International Exhibition shows clearly the more commercial attitude of the German contingent.

The extent of German penetration of the English market in the later nineteenth century is shown by the analysis of two English dye manuals. These sources also show additional evidence of the continuing importance of the natural dyes well after the introduction of the synthetics. This has been commented on previously but is often overlooked when the chemical dye industry is examined.

Indeed, whereas many previous studies of the dye industry have focussed on the history of science and technology, of education or the textile industries the aim of the present work has been to link these together and set these aspects of the industry in their social context. The expansion of industrialisation, industrial organisation and the reactions against these has been outlined. The coincident rise in levels of consumption amongst the increased population, particularly the middle classes, contributed to the success of the industry by providing a market for its products. This is particularly important in this study, linking as it does the use of the new dyes and the field of textile history.

The next chapters of the thesis introduce further disciplines into the discussion by introducing the chemistry of the dyes and describing the scientific analytical work carried out.

## Chapter 4. Introduction to the chemistry of the dyes and dyeing methods used in this study

### 4.1 Introduction

This chapter introduces the chemistry of textile dyes, particularly their structure as this is fundamental to the identification methods used. The methods used for dyeing the test fabrics will be described and their chemical interaction with the fibre explained.

There are a relatively small range of natural dyes, about 20 to 30 main compound types,<sup>317</sup> with the same or very closely related chemicals being sourced from similar organisms. This conformity in structure is due to the similarities in biochemical pathways found in living organisms. By contrast there are very many more synthetic compounds as these could be made by any process the chemist could devise. Indeed in the early days of the industry variability was introduced by the impure and poorly characterised starting materials and encouraged by commercial competition where patents were taken out on the synthetic method, not the product.<sup>318</sup>

As far as the dyers were concerned the important property of each of these compounds was the nature of the process used to dye the textiles and therefore the classification of the dye substances by this community is based on this distinction with five major classes of acid, basic, vat, mordant and direct dyes having been recognised from early times. Later, with the development of different forms of synthetic dyes and fibres, the categories of reactive and disperse dyes were added. The difference between these classes lies in the functional groups on the surface of the molecules. Chemists, however, classify the dye compounds on the basis of their structures and the differences mostly lie in the organisation of the

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<sup>317</sup> GRAAFF, J.H.H.D. (20004) *The Colourful Past: The Origins, Chemistry and Identification of Natural Dyestuffs*, London, Archetype Press. De Graaff lists 19 families of dyestuffs, some of which contain more than one coloured compound. Structures of the compounds are given in Appendix 5.

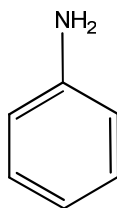
<sup>318</sup> MACLEOD, C. (1988) *Inventing the Industrial Revolution. The English patent system, 1660-1800*, Cambridge, Cambridge University Press.

backbones of the molecules. The dyes will be presented in the next sections grouped by their chemical classifications as this is the critical feature in terms of their identification.

#### 4.2 A brief description of the development of the synthetic dyes

The natural dyes had been available to the textile industry relatively unchanged for several centuries. There were a few new introductions, for example, Prussian blue in the mid eighteenth century<sup>319</sup> but the range of dyes used remained relatively static. By the nineteenth century the science of chemistry, although not yet very often referred to as such, was becoming a recognised discipline.<sup>320</sup> As discussed in Chapter 2 the early developments in the synthetic dye industry came about because investigators such as Hofmann were attempting to understand the nature of the chemical structures they were dealing with, comparing their structure with known useful plant-derived substances.<sup>321</sup> Chapter 2 introduced the developments in the study of chemistry in the second half of the nineteenth century and this section will describe in more detail the chemistry of the synthetic dyes and the development of the main types of compound.

It is now known that the basic building block of the compound from which the chemists were working, aniline, comprises a benzene ring substituted with an amine group, -NH<sub>2</sub> (Figure 4.1).<sup>322</sup>



**Figure 4.1. The structure of aniline**

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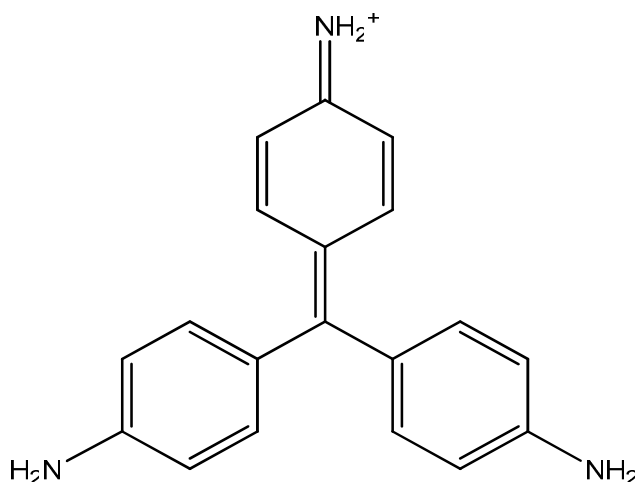
<sup>319</sup> SCHARFF, A. B. (1999) Synthetic dyestuffs for textiles and their fastness to washing. *ICOM 12th Triennial Meeting*. Lyon, ICOM-CC.

<sup>320</sup> CUNNINGHAM, A. & WILLIAMS, P. (1993) De-centring the 'big picture': *The origins of Modern Science* and the modern origins of science. *British Journal for the History of Science*, 26, 407-432. Cunningham and Williams discuss the development of our modern understanding of the concept of the sciences in the early nineteenth century.

<sup>321</sup> TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses.

<sup>322</sup> For an explanation of chemical diagrams see Appendix 2.

It was the reactions of this molecule with itself and other related aromatic<sup>323</sup> compounds that gave the first class of synthetic dyes, the triphenylmethanes. Hofmann was one of the leading figures in this area of investigation and it was he who first understood that the hydrogens of the amine group could be substituted to generate various new entities based on the rosaniline structure which has three substituted phenyl groups joined symmetrically by a central carbon atom (Figure 4.2).<sup>324</sup>



**Figure 4.2.** The structure of pararosaniline

The crucial analysis which led to this insight was carried out on the next dye after Mauveine to be discovered in 1859, aniline red. Hofmann found it to contain the equivalent of three aniline groups with two extra carbon atoms<sup>325</sup>. When the compound was reduced the colour was lost. The structure was not easily explained by reaction of aniline alone and it was during his experiments with very pure aniline that Hofmann realised that other

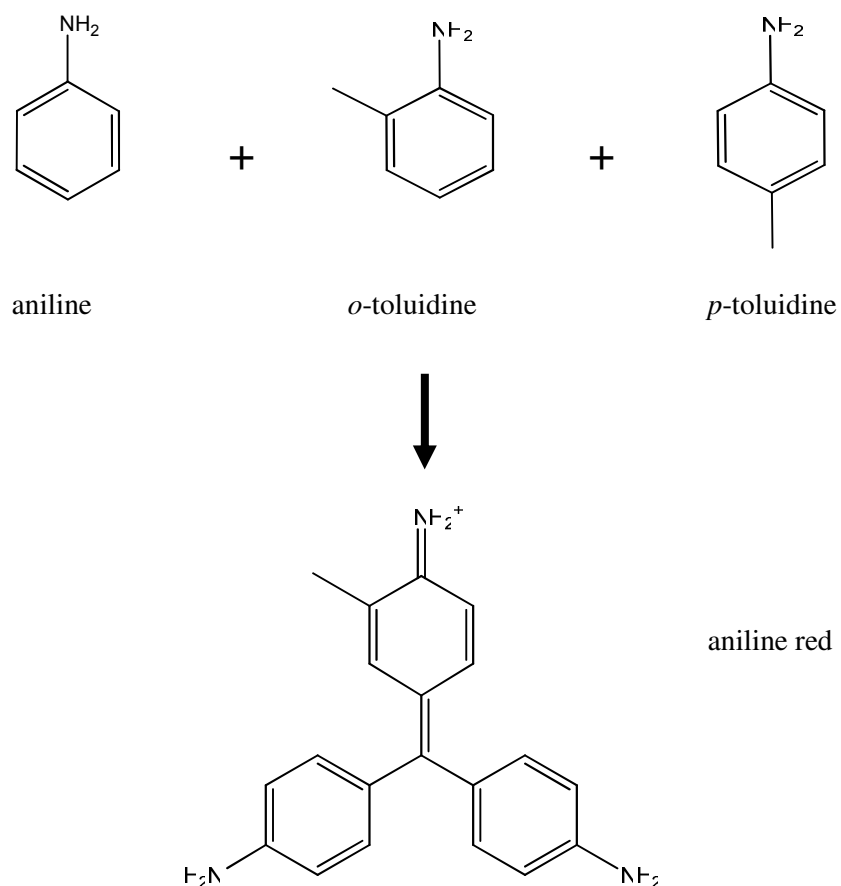
<sup>323</sup> Organic compounds are molecules in which multiple carbon (C) atoms are linked together to form chains with chemically active side groups attached. Occasionally other atoms such as oxygen (O), nitrogen (N) or sulphur (S) can be substituted for one or more carbon atom in the main chain. Where the chain is linear the compounds are termed 'aliphatic' but when there are circular formations they are termed 'aromatic'.

<sup>324</sup> Hofmann could not produce structural formulae for these compounds as, although the manner of combination of atoms into molecules was known, the cyclic nature of the benzene ring (C<sub>6</sub>H<sub>6</sub>) had not been deciphered. He could however determine the relative proportions of each atom in pure compounds and therefore deduce the components present in each structure.

<sup>325</sup> TRAVIS, A. S. (1992) Science's powerful companion: A.W. Hofmann's investigation of aniline red and its derivatives. *British Journal of the History of Science*, 25, 27-44.



related aromatic compounds were involved and these supplied the extra carbon atoms leading him to deduce the reaction shown in Figure 4.3.



**Figure 4.3.** Reaction leading to aniline red

There were at the time a number of red colours on the market, all manufactured from impure aniline by slightly different methods. This led to the extensive patent litigation in the 1860s during which the differences between the compounds were investigated but the

fact of whether they were distinct or identical was never established to the satisfaction of the courts.<sup>326</sup>

Once the basic configuration of the molecules was understood, structures for other colours which were produced either as by-products of the original oxidation reaction (yellow chrysaniline in 1863) or with different proportions of reactants (aniline blue in 1861 with excess aniline) could be proposed. For example, Hofmann's analysis of aniline blue led to the identification of its structure as triphenylated rosaniline, in other words a compound with each of the amine groups on the aniline rings substituted with a phenyl group. Further exploration of the use of other compounds to substitute the amine groups in the molecule gave rise to more colours such as Hofmann's violets (1863) which contained ethyl instead of phenyl groups.<sup>327</sup> Thus from this time the development of new dyes became better informed by the increasing understanding of the underlying chemistry than the previous approach which had been to repeat established syntheses with slightly different reactants in the hope of uncovering a new compound.

Chronologically, the next important discovery in the field of dye chemistry was the development of the class of azo dyes. Johann Peter Greiss (1829-1888)<sup>328</sup> was a key figure in this area as he had started research on the diazo reaction in 1858 at the Royal College of Chemistry.<sup>329</sup> The first azo dye to be introduced in 1863 was made by the action of nitrous acid on aniline and was initially called aniline yellow, soon to be changed to Field's yellow after the developer of the process.<sup>330</sup> In collaboration with Greiss, a brown version was

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<sup>326</sup> VAN DEN BELT, H. Ibid. Why Monopoly failed: the rise and fall of Societe La Fuchsine. 45-63. Several of the early dye manufacturers suffered severe economic losses due to these patent disputes.

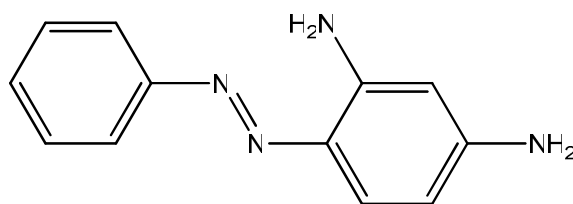
<sup>327</sup> TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*. London and Toronto, Associated Universities Presses. Page 73

<sup>328</sup> HOMBURG, E., TRAVIS, A. S. & SCHROTER, H. G. (Eds.) (1998) *The Chemical Industry in Europe, 1850-1914. Industrial Growth, Pollution and Professionalization*, Dordrecht/Boston/London, Kluwer Academic Publishers. Page 333

<sup>329</sup> TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses. p. 217.

<sup>330</sup> Frederick Field (1826-1885) developed this process while working at Simpson, Maule and Nicholson. USSELMAN, M. C. Field, Frederick (1826-1885). *Oxford Dictionary of National Biography*. Online edition ed. Oxford, Oxford University Press.

introduced by Caro<sup>331</sup> and Martius<sup>332</sup> in 1864 at Roberts, Dale & Co. in Manchester. It was therefore known as Manchester or, alternatively, Bismarck brown. Although Kekulé (1829-1896)<sup>333</sup> proposed the azo group (-N=N-) as the defining chemical structure in these dyes in 1866, it was not until 1875 that it was generally accepted that they were formed by the coupling of diazo intermediates to aromatic compounds. Otto Niklaus Witt (1853-1915)<sup>334</sup> produced London orange (Chrysoidine, see Figure 4.10) at Williams, Thomas & Dower in 1876. Despite having access to much of Greiss's development work, Caro at Badische Anilin und Soda Fabrik (BASF) showed very little interest in the azo dyes and it was the firm of Meister, Lucius and Brüning who capitalised on them, developing the red dye Ponceau.



**Figure 4.4.** The structure of chrysoidine

An important development of the azo dyes was the introduction of the first direct synthetic dye in 1884, discovered by Paul Böttiger.<sup>335</sup> This red dye could be applied directly to cotton without any mordant which obviously made the dyeing process easier and cheaper. Böttiger sold his patent to Aktiengesellschaft für Anilinfabrikation (AGFA) who marketed it as

<sup>331</sup> Heinrich Caro (1834-1910) was born in Posnan and came to England in 1857 to learn about new processes in calico printing. He worked for Roberts, Dale & Co, from 1859-1866 and joined BASF in 1868. TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses. p. 178.

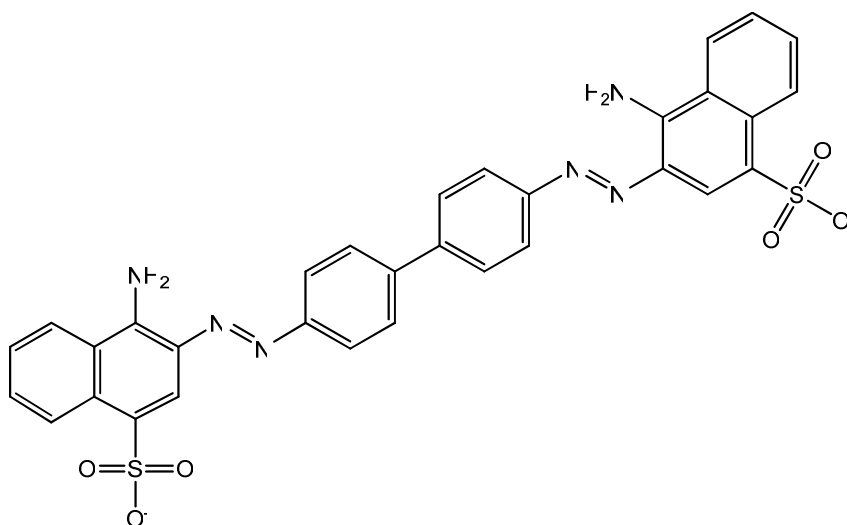
<sup>332</sup> Carl Alexander von Martius (1838-1920). He founded Aktiengesellschaft für Anilinfabrikation (AGFA) in 1867 in partnership with the banker Paul Mendelssohn-Bartoldy. Ibid. p. 235

<sup>333</sup> HOWARD, A. V. (1951) *Chambers's Dictionary of Scientists*, London & Edinburgh, W & R Chambers.

<sup>334</sup> HOMBURG, E., TRAVIS, A. S. & SCHROTER, H. G. (Eds.) (1998) *The Chemical Industry in Europe, 1850-1914. Industrial Growth, Pollution and Professionalization*, Dordrecht/Boston/London, Kluwer Academic Publishers. Page 344

<sup>335</sup> TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses. p. 216

Congo Red (Figure 4.11). A family of related dyes were then developed, the benzopurpurines.<sup>336</sup>



**Figure 4.5.** The structure of Congo Red

During this time the effort to reproduce natural dyes was ongoing. The first success was the synthesis of alizarin, the principle colouring matter of madder. Whereas the forgoing dyes were all based on aniline and its derivatives, this was based on another component of coal tar, anthracene.

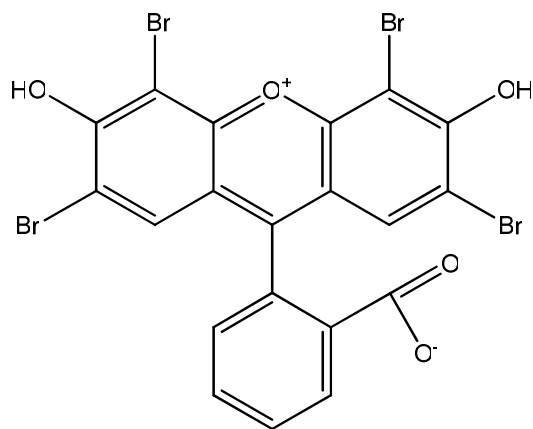
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<sup>336</sup> Ibid. p. 216. Direct dyes are long linear molecules which interact with the cellulose molecules by van der Waals and hydrogen bonding. Previous synthetic dyes had all been smaller molecules without this property.



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The first phthalein dye to be produced was eosin. This resulted from cooperation between the industrial chemist Caro and the academic Baeyer.<sup>340</sup> In 1874 Caro was able to brominate fluorescein producing a fluorescent pink dye eosin which was marketed by BASF.<sup>341</sup>



**Figure 4.7.** The structure of eosin

The last significant dye to be developed in the period under study was synthetic indigo. Baeyer was working on uric acid because it was related to the purple dye murexide. He then moved to investigate the structure of indigo by breaking it down stepwise to indole and published the first structure in 1868. Further details of the structure were defined with his co-worker Emmerling in the following year but he then allowed Kekule to pursue his own researches on the compound and it was not until 1876 that he returned to the compound with Caro. They made further progress towards a precise structure and developed several production methods but the syntheses were too expensive to make a commercial product. The correct structure was drawn by Baeyer in 1883 but it was not until 1890 that a new synthetic route starting from naphthalene was developed which was economic and the first commercial product was made at the BASF works in Ludwigshafen in 1897. Although this was slightly more expensive than natural indigo, it found buyers and

<sup>340</sup> Johann Friedrich Wilhelm Adolf von Baeyer (1835-1917) was an academic chemist working at Berlin, Strasbourg and Munich. HOWARD, A. V. (1951) *Chambers's Dictionary of Scientists*, London & Edinburgh, W & R Chambers.

<sup>341</sup> TRAVIS, A. S. (1993) *The Rainbow Makers. The Origins of the Synthetic Dyestuffs Industry in Western Europe*, London and Toronto, Associated University Presses. Page 213-214

as further improvements in the methods drove down costs the synthetic indigo took market share from the natural dye as alizarin had from madder.<sup>342</sup>

#### 4.3 Summary

Natural and synthetic dyes share their ability to interact with textile molecules to produce more or less permanent bonds. They also, of course, both have structures which cause them to appear coloured to the human eye. Those synthetic dyes which were direct substitutes for the natural compounds inevitably have the same structure and are therefore not capable of easy differentiation by chemical analysis. However, many of the synthetic dyes have structures which are quite different from any of the natural substances and therefore chemical analysis can be used to distinguish them. These include the triphenylmethanes based on rosaniline and the azo dyes and approaches to analysis will be discussed in Chapter 5.

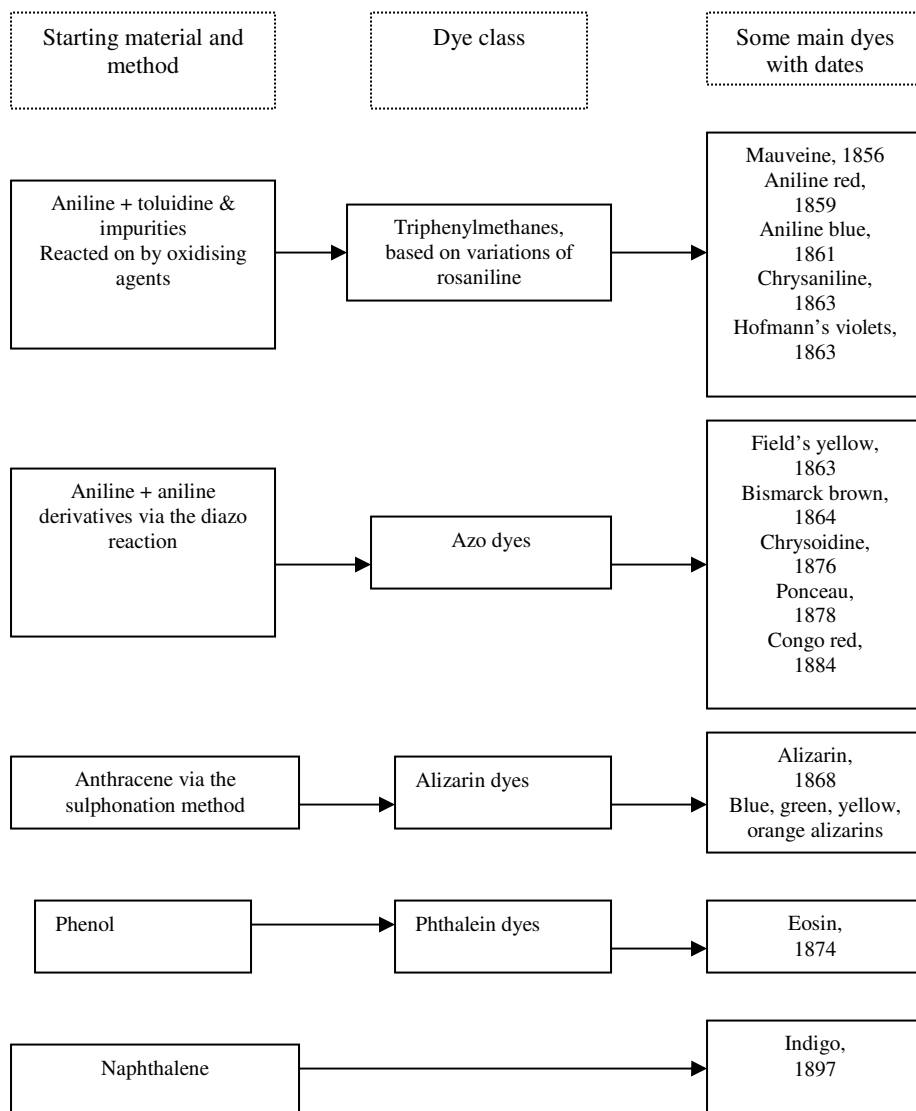
There was rapid development of new chemical entities for textile dyeing during the second half of the nineteenth century, summarised in Figure 4.14. Large markets were available both in Europe and in her colonies<sup>343</sup> and competition in these was fierce. This led to efforts both to produce the same dye by varying the production method and thus circumvent the patent and also to invent variations on existing compounds by changing the starting material or the reactants. Some of these dyes were products which were long-lived and commercially very successful. Others were soon superseded by new substitutes. The azos as a class were particularly successful and, in 1912, Hesse lists 921 dyes on the world market of which 462 were azo dyes.<sup>344</sup>

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<sup>342</sup> Ibid. Page 220-227

<sup>343</sup> See for example, accounts of the introduction of the synthetic dyes into the Indian textile industry such as BANERJEE, N. N. (1897) Dyes and Dyeing in Bengal. *Journal of Indian Art*, 7, 11-20. or THURSTON, E. (1897) The Cotton Fabric Industry of the Madras Presidency. *Journal of Indian Art*, 7, 54-60. In 1903 Steel, STEEL, F. A. (1903) The Doom of Indian Art. *Saturday Review of Politics, Literature, Science and Art*. regretted the substitution of natural with aniline dyes in Indian goods.

<sup>344</sup> HESSE, B. C. (1914) The Industry of the Coal-Tar Dyes: An Outline Sketch. *The Journal of Industrial and Engineering Chemistry*, 6, 1013-1027.



**Figure 4.8** Summary of main synthetic dye classes developed from 1856 to 1900

One of the major problems with the first of the synthetic dyes, Mauveine, was that it did not interact with the textile fibre in the same way that the natural dyes did. As a new class of



basic dye,<sup>345</sup> it reacted directly with protein fibres and so was easier to apply to these but Perkin had to develop new dyeing methods to use it with the cellulose fibre cotton. This was vital to the success of this first dye as in the second half of the nineteenth century cotton was a very popular fabric<sup>346</sup> whereas silk, as a luxury fabric, had a relatively limited market. Some of the next dyes to be developed were basic in character and needed further new dyeing methods to be developed. The textile dyers were willing to adapt their methods to exploit the new dyes as they became fashionable but there was also a constant search for synthetic substitutes for the natural dyes as there was a ready market for these using the dyers' original methods.

**Table 4.1.** Dyeing methods for synthetic dyes

Dyeing mechanism	Example dyestuffs
Acid	Orange II (chrysoidine), New coccine
Basic	Mauveine, Magenta/Fuchsine, Safranine, Malachite green
Direct	Congo red
Vat	Indigo
Mordant	Alizarin

#### 4.4 Preparation of test fabric samples

The dyes have been chosen on the basis of their date, current availability and suitability for dyeing on the chosen substrates. A range of chemical dye classes have been chosen to allow the demonstration of the ability of the method to differentiate within and between them. In some cases it has not been possible to establish an unequivocal date of introduction for a dye although a chronology can be assigned to most of them. Those which are considered to

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<sup>345</sup> Acid dyes have charged groups on the surface of the molecule which react with the textile fibre in acid conditions. Basic dyes also have charge groups but with the opposite charge and these react with the textile in neutral or basic conditions. Very few natural dyes are acid or basic.

<sup>346</sup> LEVITT, S. (1996) Clothing. IN ROSE, M. B. (Ed.) *The Lancashire Cotton Industry. A History since 1700*. Preston, Lancashire County Books.

have been in common use in the late nineteenth century by Schweppe<sup>347</sup> are shown in bold type.

Table 4.2 Dyes chosen for use in this study

Dye	Colour Index name	Chemical class	Date	Dyed on fabric
Safranine	Basic red 2	Azine	1859	✓
Pararosaniline chloride/Fuchsin basic	Basic red 9	Triarylmethane	1859	Not dyed
<b>Methyl violet 2B</b>	Basic violet 2	Triarylmethane	1861	✓
<b>Orange II</b>	Acid orange 7	Azo	1876	✓
<b>Malachite green</b>	Basic green 4	Triarylmethane	1877	✓ <sup>1</sup>
<b>New cocchine</b>	Acid red 18	Azo	1878	✓
<b>Victoria Blue B</b>	Basic blue 26	Triarylmethane	1883	✓
<b>Tartrazine</b>	Acid yellow 23	Azo	1884	✓
Fuchsin acid	Not found	Triarylmethane	Before 1885 <sup>2</sup>	✓
Methyl red	Acid red 2	Azo	Not known	3
Naphthol green B	Acid green 1	Nitroso/Fe complex	1885	✓
<b>Para red</b>	Not found	Azo	1889/90	3
<b>Rhodamine 6G</b>	Basic red 1	Xanthene	1892	✓
Flavazine L	Acid yellow 11	Azo	1892	✓
	Acid yellow 17	Azo	Not known	✓

1 – Dyed on silk only, as part of another study

2 – Fuchsin basic (also known as Aniline red) was introduced in 1859. Fuchsin acid (as Acid magenta) is listed in Hummel (1885)

3 – Dyeing of fabric with Methyl red and Para red was attempted but was not successful

Nineteenth century synthetic textile dyes are still in use in a range of applications, although not many included in this study are still used as dyes. They are however still readily obtainable and therefore can be used to create sample test fabrics for investigation. In addition to those above some samples of silk already dyed with Mauveine and Prussian blue were used for analysis.<sup>348</sup>

<sup>347</sup> Quoted in BARNETT, J. C. (2007) Synthetic organic dyes, 1856-1901: an introductory review of their use and related issues in textile conservation. *Reviews in Conservation*, 8, 67-77.

<sup>348</sup> These samples were kindly supplied by Prof A. Dronsfield, University of Derby

#### 4.4.1 Fabrics selected

Wool and silk were chosen as the test fabrics as they were both in common use in the nineteenth century. Silk was often used for fashionable dress, especially for the early synthetic dyes which were easy to dye on silk. Wool was used for dress and also accessories such as shawls<sup>349</sup> and underwear. Both were also much used for embroidery<sup>350</sup> and wool for furnishing textiles such as tapestries.<sup>351</sup> Thus these fibres are relevant for the study of both dress and textiles.

These are both protein fibres and are relatively simple to dye with the acid and basic early synthetic dyes. Protein fibres are very long molecules which have both negatively and positively charged surface groups and therefore the dye, under the right chemical conditions, can interact with the fibre. The dye is held to the fibre by the attraction between oppositely charged groups (electrostatic bond) and can be removed fairly easily if the chemical environment changes.

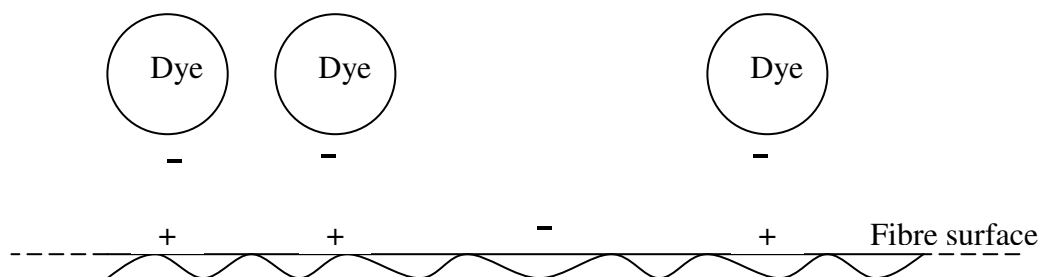


Figure 4.9 Diagram of the interaction of acid dyes with protein fibre

<sup>349</sup> MACKRELL, A. (1986) *Shawls, Stoles and Scarves*, London, B.T. Batsford Ltd. See especially Chapter 3 pages 48-79 which discusses 19<sup>th</sup> century shawls.

<sup>350</sup> HUIISH, M. (1970) *Samplers and Tapestry Embroideries*, New York, Dover Publications Inc. Page 171

<sup>351</sup> ANON. (1983) *The Burrell Collection*, Glasgow, HarperCollins. Pages 101-109

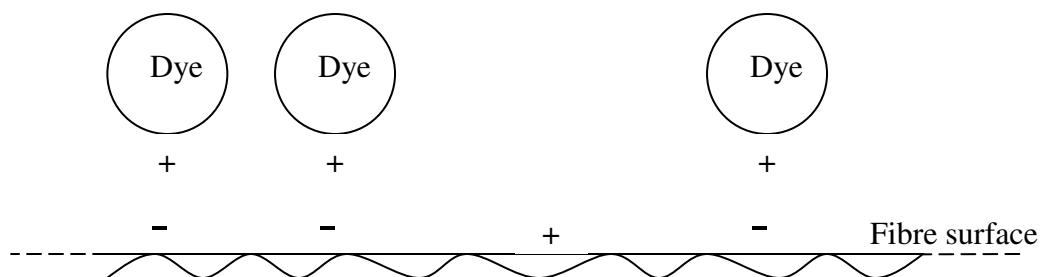


Figure 4.10 Diagram of the interaction of basic dyes with protein fibre

Acid dyes were applied to the fabric at low pH (acidic) conditions where the dye is negatively charged (Diagram 4.15) and basic dyes were applied at higher pH (basic) conditions (Diagram 4.16).

Plain weave fabrics were used for this study as the dye takes evenly to this type of weave and a flat surface is easier to analyse. Silk Habotai of medium weight was chosen as it is light enough to give a reasonable area of fabric for experimentation without having to apply a large weight of dye but is a dense enough weave to be practical for spectroscopy.

Wool sourced from Context Weavers was the other fabric chosen. It is also a plain weave produced as a reproduction of historic fabric and is therefore pure wool. It does contain high levels of lanolin as the yarn has not been extensively treated prior to weaving. Both fabrics however are bleached to give a pure white in the case of the silk and a cream white in the case of the wool.

#### 4.4.2 Pre-treatment of fabrics

The silk Habotai was not pre-treated before dyeing but the wool was scoured according to the method in the Textile Conservation Centre (TCC) Dyeing Manual<sup>352</sup>. Briefly the wool was heated with detergent to remove any natural oils or additives used during processing.

<sup>352</sup> ANON (2004) Dyeing Techniques Manual. Winchester, Textile Conservaton Centre.

These substances interfere with the interaction between the fibre and the dye and so must be removed. Although silk does contain the natural gum sericin this is not removed before dyeing as it can help to produce a more even dye.

#### 4.4.3 Fabric dyeing

The dyeing methods vary depending on the nature of the dye and are based on those used for acid dyes in the TCC manual<sup>353</sup> combined with methods adapted from a range of sources.<sup>354</sup>

For all dyeing, producing an even coverage of dye is problematic as the interaction of dye with the fabric can be very quick leading to areas of high dye density. For this reason additives are often used in the dyeing process to slow down this interaction and allow even dyeing. In these methods the additives used were sodium sulphate which binds to the charged silk fibres in solution and is gradually displaced by the dye during the dyeing process. Proprietary detergents are also used with specific compounds developed for particular fibres. Another factor which affects the dyeing process is the amount of liquid used in the dye bath, referred to as the liquor ratio. There should be enough liquid to allow full immersion of the fabric and effective stirring of the dye bath but if the dye is too dilute it will not be efficiently taken up by the fibres.

The concentration of dye used is expressed as depth of shade and calculated as a percentage based on the weight of the fabric. For example a 2% depth of shade would involve a dye bath where 2g of dye in solution is applied to 100g of fabric. However it should be noted that, unless the dye bath is completely used up during dyeing (exhausted), the actual concentration of dye in the fibres will be less than that implied by the depth of shade.

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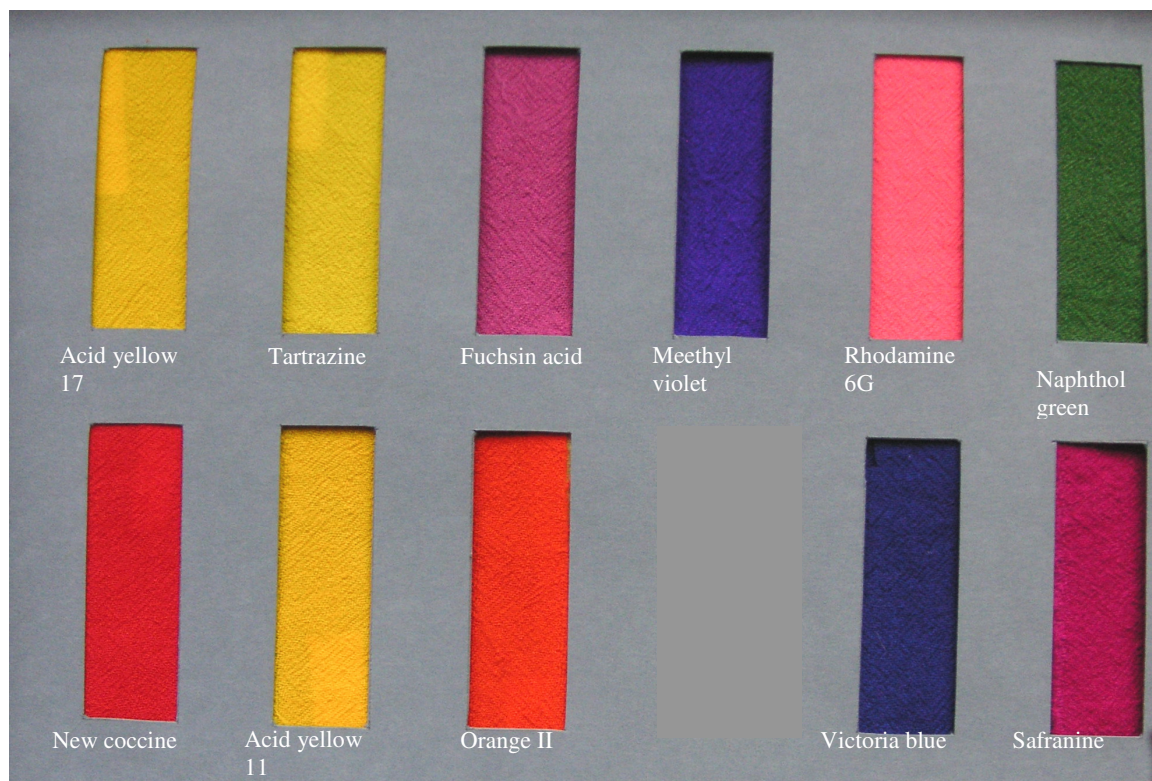
<sup>353</sup> CENTRE, T. C. (2008) Dyeing Techniques Manual. Winchester, University of Southampton.

<sup>354</sup> COOKSEY, C. J. & DRONSFIELD, A. T. (2003) Fischer, Doebner and the search for green. *Education in Chemistry*, 40, 46-52. GILES, C. H. (1974) *A laboratory course in dyeing*, Bradford, Yorks, The Society of Dyers and Colourists. SCHWEPPE, H. (1987) *Practical information for the identification of early synthetic dyes. Practical hints on dyeing with early synthetic dyes*, Washington, Smithsonian Institution. A method previously developed for basic dyes was also used (BAKER, R. M. (2005) The use of reflected visible light spectra to analyse dyed fabrics: the highs and lows of synthetic dyes. University of Southampton.)

The dye bath was heated in stages to a maximum of 90°C, held for a period and then cooled gradually. The fabric was then rinsed with softened water, decreasing the temperature of the water gradually. Full details of the dyeing process can be found in Appendix 1.

The method developed for dyeing with acid dyes was more complex. Various additives were tested in the dyeing process and Albegal FFA at 0.3 g/l was found to be effective in promoting dyeing. Sodium sulphate (Glauber's salt) at 10 g/l was also found to aid the process. Adding acetic acid at the start of the dyeing process and maintaining the pH at 4.5 was also found to be useful. Initially low depths of shade ranging from 0.1 to 1.5% were used as these are the ranges used in dyeing with modern synthetic dyes for textile conservation and were successful with the basic synthetic dye Malachite green. These did not produce a sufficient colour on the fabric so the depth of shade was increased finally up to 10% which was successful. It was not possible to dye the methyl red to this depth of shade, however, as its solubility in water was not high enough to produce a stock solution concentrated enough.

Figure 4.11 Dyed wool samples



#### 4.5 Summary

Fifteen dyes were identified as suitable for study. The criteria for this were that they were in use for textile dyeing before 1900 and they were still available as chemical compounds. One of the dyes, Acid yellow 17, is not known to have been used before 1900 but is included for its chemical similarity to two other dyes, Acid yellow 11 and Tartrazine. It was therefore considered that it would provide data on the sensitivity of the identification methods to small structural differences. Twelve of these dyes were successfully applied to silk and wool textiles.

The next chapter will outline the theory behind the vibrational spectroscopic methods used for the analysis of these samples.

## Chapter 5 Theory of vibrational spectroscopy and previous work using this method

This chapter introduces the theory behind the vibrational spectroscopy methods used in this study. Infrared (IR) spectroscopy will be discussed first, followed by Raman spectroscopy (RS) with its variations. The second part of the chapter summarises the work reported in the literature applying these techniques to dye and textile analysis. A short explanation of light, energy and colour can be found in Appendix 3.

The other main methods in current use for dye analysis are chromatographic. The principal method used with natural dyes is High Performance Liquid Chromatography (HPLC). This method along with fluorescence has also been applied to some synthetic dyes<sup>355</sup> but was not used in this study as it requires sampling of material from the textile under study and extraction of the dye from the fibre.<sup>356</sup> Although micro methods have been developed so that only a tiny sample is required, this method is therefore highly invasive and the aim of this study was to investigate the use of a technique which does not require sampling. Other methods have been used to analyse the dyes on textiles including chemical analysis<sup>357</sup> and Thin Layer Chromatography (TLC).<sup>358</sup> Both of these require a sample of the textile to be taken and the dye extracted into a solvent. They have been superseded by HPLC as they require the use of larger amounts of solvents which are difficult to handle for health and safety reasons and also HPLC allows the collection of the separated dye components which can then be subjected to further analysis to determine their structure. These further analyses include various forms of mass spectroscopy (MS).<sup>359</sup>

All molecules are in a constant state of movement in the form of symmetrical and asymmetrical bond vibrations, rotations around bonds and molecular bending. For any given molecule these form complex patterns which are characteristic of particular

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<sup>355</sup> BOMMEL, M.R.V., BERGHE, I.V., WALLERT, A.M., BOITELLE, R. & WOUTERS, J. (2007) High performance liquid chromatography and non-destructive three-dimensional fluorescence analysis of early synthetic dyes. *Journal of Chromatography A*, 1157, 260-272.

<sup>356</sup> GRAAFF, J.H.H.D. (2004) *The Colourful Past. Origins, Chemistry and Identification of Natural Dyestuffs* London, Archetype Publications page 35

<sup>357</sup> Ibid. Page 25

<sup>358</sup> Ibid. Page 26

<sup>359</sup> VERHECKEN, A. (2001) A Concise History of Dye Analysis. *Dyes in History and Archaeology*, 20, 1-22.



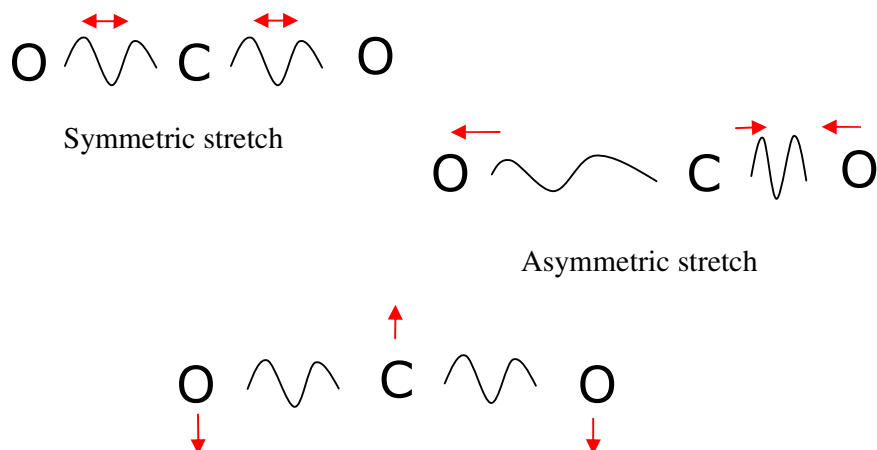
chemical functional groups and therefore produce very useful fingerprints. Rotational energy is only found in gases and so will not be referred to further in this discussion. There are three ways of measuring the vibrational fingerprint of a molecule; infrared absorption,<sup>360</sup> Raman scattering and inelastic neutron scattering. The last technique is highly specialised, requiring the use of a nuclear facility and is therefore not appropriate for studies of heritage material. Infra-red absorption and Raman scattering are discussed in the following sections.

### 5.1 Infra-red spectroscopy

In infrared spectroscopy a molecule is illuminated with a light from a continuous range of wavelengths within the infrared and it absorbs specific wavelengths indicative of its molecular structure. The energies of these vibrational frequencies are dependent on the mass of the atoms and the nature of the bonds between them. For example, for the simple molecule of carbon dioxide, CO<sub>2</sub>, conceptualised in a conventional simplistic form as tiny balls connected by springs, the vibrations can be shown by the red arrows in Figure 5.1.

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<sup>360</sup> Infrared wavelengths can also be emitted but this technique is not considered here.



Bend. There is a second bend possible with the carbon and oxygen atom moving in opposite directions in and out of the plane of the paper.

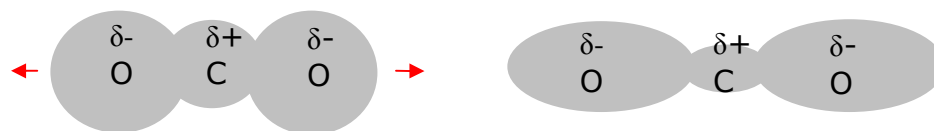
Figure 5.1 Molecular stretching modes of carbon dioxide (Adapted from Hendra et al 1991<sup>361</sup>)

In addition these vibrations cause changes primarily either in polarisation<sup>362</sup> (symmetrical stretches) or dipole moment<sup>363</sup> (asymmetrical stretches) as shown in Figure 5.2. Simplistically, these changes can be thought of as being caused by movement in the electron ‘cloud’ leading to changes in the degree of separation of the charges.

<sup>361</sup> HENDRA, P., JONES, C. & WARNES, G. (1991) *Fourier Transform Raman Spectroscopy: instrumentation and chemical applications*, Chichester, Ellis Horwood Ltd. Page 22

<sup>362</sup> Polarisation is the ease with which the electron cloud can be distorted by an external force such as a photon. In Figure 4a the elongated negative electron cloud can be thought of as more tightly bound to the positive nucleus and therefore as less mobile.

<sup>363</sup> Dipole moment is a measure of the asymmetry of the electron cloud, Figure 4b.



(a) Change in polarisability, Raman active



(b) Change in dipole moment, IR active

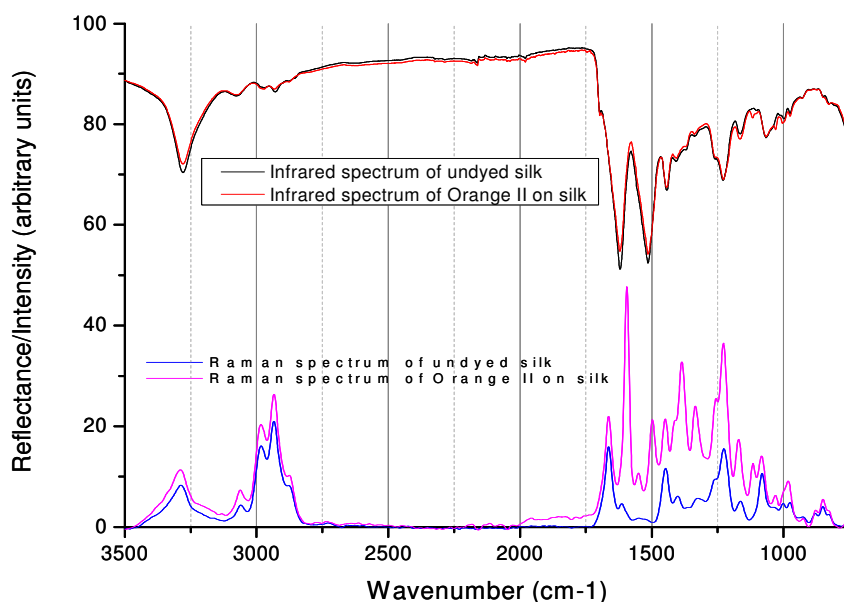
Figure 5.2 Electron cloud model of changes in (a) polarisability and (b) dipole moment produced by vibration (Adapted from Smith and Dent, 2005<sup>364</sup>).

The grey areas represent the 3-dimensional electron cloud which is formed around the positive atomic nucleus projected onto 2 dimensions;  $\delta+$  and  $\delta-$  denote a small surplus (-) or deficit (+) of electrons in that region.<sup>365</sup>

The changes in dipole moment give large signals in the IR spectrum whereas changes in polarisation do not. Thus some types of molecule are more easily analysed by IR spectroscopy than others. For very complex structures such as dye molecules some structural features will be detected more easily by IR spectroscopy and others by different types of spectroscopy such as Raman spectroscopy. Indeed to obtain the maximum amount of information both techniques can be used.

<sup>364</sup> SMITH, E. & DENT, G. (2005) *Modern Raman Spectroscopy. A Practical Approach*, Chichester, John Wiley and Sons Ltd.

<sup>365</sup> Electrons carry a negative charge so an area with slightly more electrons present will in fact have a negative potential with respect to other areas.



**Figure 5.3 Comparison of IR and RS spectra for Orange II dyed on silk.**

The IR spectra are absorbance spectra so the peaks show as reductions relative to the intensity of the illuminating beam set at 100%. The Raman spectra are scattered light and therefore the peaks appear as increases of intensity. Some peaks are seen in both, some in only one but the relative intensities in each are almost always different

## 5.2 Raman spectroscopy

Like IR spectroscopy, Raman spectroscopy depends on the vibrational energies of the molecule. However, it differs from IR spectroscopy in that it is a technique for measuring the light scattered from a sample.<sup>366</sup> Most of the light is scattered at the same wavelength as the incident light and therefore provides no information about the molecular structure of the sample. However, a very small amount of incident radiation interacts with the sample, losing or gaining energy, and is therefore scattered with a different wavelength. The discrete differences in wavelength between incident and scattered radiation provide information about the molecular bonding present in the sample. For this system to work the incident radiation must be of a single known wavelength and laser sources are ideal for this purpose. This incident radiation may be in the UV, visible or near infrared regions of the electromagnetic spectrum but the scattered light is in the mid-infrared.

<sup>366</sup> Scattering is also a much quicker process than absorption and therefore the Raman signal is transient.

As discussed in the section on IR spectroscopy, the molecular vibrations involved are different in nature from those involved in IR spectroscopy so complementary information is obtained. In Raman spectroscopy, the interaction with the oscillating dipole of the photon creates a large change in polarisability of the molecule and a small change in the dipole moment. This is most likely with symmetrical vibrations. In contrast, for infrared (IR) spectroscopy, the interaction with the oscillating dipole creates a large change in the dipole moment of the molecule and a small change in the polarisability. One particularly significant molecule, water, gives a very large signal in IR spectra and a very low signal in Raman so that aqueous solutions are simpler to study by Raman than IR.

Where it occurs, the change in wavelength between incident and scattered light is brought about by an interaction between the incident photons and the vibrational states of the molecules illuminated. The energy of the photon momentarily promotes the molecule into a higher virtual energy state and when it relaxes again to the normal state, energy in the form of radiation is released. Where the molecule relaxes to exactly the level it was originally in, whether that was the ground or excited state, no energy is exchanged between the photon and the molecule and the scattered radiation has the same wavelength as the incident radiation, giving rise to Rayleigh scattering (Figure 5.4b). However, if the molecule relaxes back to a different energy level from its original state, some energy is exchanged and the scattered light differs in energy, and thus wavelength, from the incident light.<sup>367</sup> If the molecule was originally in the ground state and is promoted to an excited state, the energy of the scattered light is lower and the wavelength longer than the incident light. This is referred to as Stokes radiation (Figure 5.4a). In the reverse case, where the molecule is originally in the excited state and relaxes to the ground state, the result is anti-Stokes radiation (Figure 5.4c). However, under normal conditions there are far fewer molecules in an excited state than in the ground state in a sample so anti-Stokes radiation is much less intense than Stokes radiation and is rarely measured.

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<sup>367</sup> Energy and wavelength are two properties of electromagnetic radiation. They are inversely related; as the wavelength increases, the energy decreases. Further details can be found in Appendix 3.

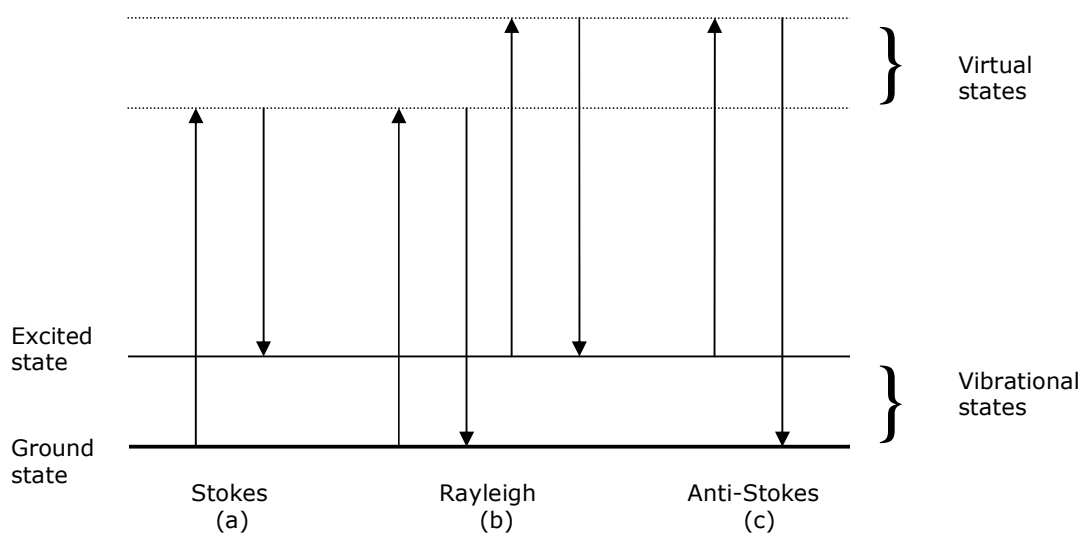


Figure 5.4 Energy level diagram showing the transitions involved in Rayleigh scattering and Stokes and anti-Stokes radiation

The precise difference between the ground and excited states, and thus the difference in wavelength between the incident and Stokes radiation, is dependent on the molecular bonds in the sample and so the measured wavelength differences provide information about the chemical structure of the sample. Raman spectra are plotted in terms of signal intensity against the wavenumber shift from the excitation radiation,  $\Delta\bar{\nu}$ , with wavenumber shift increasing to the left on the x-axis.

### 5.2.1 Resonance Raman spectroscopy

Although Raman spectroscopy is a very useful technique for analysis, the signals generated are very weak and so it presents a challenge to the spectroscopist. The emission can be enhanced if the wavelength of the exciting radiation is close to an electronic absorption band of the analyte. The polarisability, and hence the intensity of the Raman signal, is inversely proportional to the difference between the wavenumber of the exciting light and the energy difference between the ground and excited states. As this approaches zero, the polarisability increases and some peaks in the spectrum are greatly enhanced. By definition, dye molecules absorb light in the visible range as used for Raman so this can be a useful form of the technique. Only the vibrations coupled to

the chromophoric group<sup>368</sup> are intensified and the smaller the difference between the two energies, the stronger is the Raman intensity. This is termed resonance Raman spectroscopy (RRS) and was recently reviewed by Efremov et al.<sup>369</sup> Unfortunately, when the energy difference between the ground and excited states is exactly the same as the energy of the incident light, absorption can also occur producing fluorescence<sup>370</sup> which interferes with the measurement. Surface enhanced Raman spectroscopy is a method used to suppress fluorescence and this is discussed in the next section.

### 5.2.2 Surface enhanced Raman spectroscopy

Surface enhanced Raman spectroscopy (SERS) uses small colloidal metallic particles or surfaces roughened on the nano-scale to augment the Raman response of analytes in contact with the metal surface. The mechanism of enhancement is attributed to two effects; an electromagnetic component which contributes to local field enhancement and a chemical component which alters the polarisability of the analyte due to adsorption on the surface. There are several methods of producing such surfaces which normally involve either the use of colloidal metal solutions or vacuum-deposited, electrochemically roughened or lithographically produced surfaces.<sup>371</sup> In this study colloidal suspensions of silver nanoparticles have been used to produce the SERS effect. Resonance and surface enhanced effects can be combined using a resonant wavelength for the exciting laser and a noble metal surface and this is termed surface enhanced resonance Raman spectroscopy (SERRS).

SERS is a particularly useful technique for dye molecules as they generally contain unsaturated ring systems which may produce large amounts of fluorescence when irradiated with light in the visible and near infrared range. In addition, the colloid increases the signal intensity of the Raman spectrum and therefore increases the sensitivity of the technique. Another approach used to increase the signal intensity in

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<sup>368</sup> The chromophoric group is the part of the dye which absorbs visible light and thus gives it its colour.

<sup>369</sup> EFREMOV, E. V., ARIESE, F. & GOOIJER, C. (2008) Achievements in resonance Raman spectroscopy. Review of a technique with a distinct analytical chemistry potential. *Analytica Chimica Acta*, 606, 119-134.

<sup>370</sup> Fluorescence occurs when a photon is absorbed by a molecule and the energy is re-emitted at a longer wavelength.

<sup>371</sup> LAU, D., LIVETT, M. & PRAWER, S. (2008) Application of surface-enhanced Raman spectroscopy (SERS) to the analysis of natural resins in artworks. *Journal of Raman Spectroscopy*, 39, 545-552.

spectroscopy is to change the way the signal is processed in the instrument and this is described in the next section.

### 5.3 Equipment and experimental techniques

The following section briefly outlines the experimental techniques used, further details will be included in the experimental sections.

#### 5.3.1 Absorption/reflectance spectroscopy

Both UV-vis and IR spectroscopy are used in absorbance mode and the experimental arrangement can be shown schematically as in Figure 5.5.

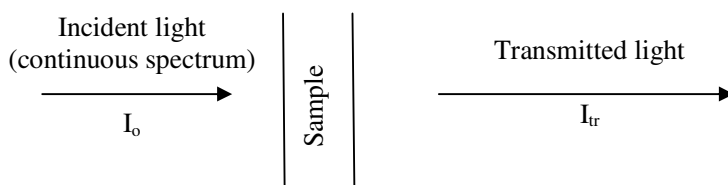


Figure 5.5. Diagram of experimental arrangement for absorbance spectroscopy

The transmitted light is always less than the incident light due to scattering as well as specific absorption by the sample. The transmitted light is analysed to produce a spectrum in the form of a graph of absorbance versus frequency. Where the sample is not transparent, such as a dyed textile, the light reflected is analysed in the same way as the light transmitted. Both scattering and absorption still cause reduction of intensity of reflected light compared to the incident light.

#### 5.3.2 Fourier Transform spectroscopy

In Raman spectroscopy, in particular, the intensity of signal generated is very low and therefore the most sensitive detection techniques are needed to generate a reasonable



signal-to-noise ratio. The most straightforward mechanism for separating the wavelengths of light collected in a spectrometer is that of the monochromator. In this system the light enters through a narrow slit and is collimated to produce a parallel beam which then strikes a diffraction grating which deflects the light according to its wavelength. This is then reflected onto an exit slit and onto the detector of the instrument. The exit slit may be narrow and the grating rotated to build up a spectrum, or wider with a position sensitive detector. Thus only a small section of the spectrum is collected at any one time.

The Fourier transform instrument uses an interferometer where the light entering from the sample is split into two beams of equal intensity, one of which is subjected to a variable optical delay, after which they are re-combined. This leads to interference between the two beams and this interference pattern can be expressed as a function of intensity against the length of the optical delay. This can then be mathematically converted by the Fourier transform to produce a spectrum of intensity against frequency. Higher resolutions can be achieved with an interferometer and, since the whole spectrum is collected simultaneously, the sensitivity of the instrument is increased.<sup>372</sup> Additionally, in this system no narrow slit is needed to increase the resolution, instead the light enters through a large circular hole typically 8mm in diameter compared with the slit width of 0.1mm.<sup>373</sup>

The signal to noise ratio can be improved by averaging a number of spectra since the noise is by definition random but the signal is fixed. The efficiency of this system however, relies on the spectra being accurately superimposed. Since the spectra are regulated by a laser with a very reliable frequency, successive spectra can be very accurately aligned in the interferometer whereas the mechanical wear present in a scanning monochromator can introduce errors of alignment. Thus the signal to noise ratio can be much higher with this type of instrument. For these reasons the Fourier transform (FT) system is used for both IR and Raman spectrometers.

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<sup>372</sup> HOLLAS, J. M. (2002) *Basic Atomic and Molecular Spectroscopy*, Cambridge, Royal Society of Chemistry.

<sup>373</sup> EDWARDS, H. G. M. & CHALMERS, J. M. (2005) Practical Raman Spectroscopy and Complementary Techniques. IN EDWARDS, H. G. M. & CHALMERS, J. M. (Eds.) *Raman Spectroscopy in Archaeology and Art History*. Cambridge, The Royal Society of Chemistry.

## 5.4 Summary of previous dye, pigment and textile analyses using spectroscopy

### 5.4.1 Ultraviolet and visible (UV-vis) reflectance spectroscopy

This analytical method is similar to IR spectroscopy except that the illuminating light is in the ultraviolet and visible region rather than the infrared. It has been used extensively for dye analysis although the studies carried out in the field of cultural heritage have concentrated on natural dyes.<sup>374</sup> The newer synthetic dyes are of chemical interest in applications where a change in their colour indicates a chemical reaction<sup>375</sup> or where they are used in photoactive systems<sup>376</sup> and are therefore reported in the literature in this context. In the field of dye development UV-vis spectroscopy is obviously critical to assess the functionality of the dye<sup>377</sup> and also to monitor changes in colour when functional dyes, such as those coupled to antibiotics, are synthesised.<sup>378</sup>

Although spectroscopy in the UV-vis region can provide useful chemical information, it is often combined or substituted with other methods to give more data. FT-IR is commonly used as such a complementary technique.

### 5.4.2 Infrared spectroscopy

This method has been applied to dyed textile samples but, since wavelengths in this region are absorbed by both coloured and colourless substances, the spectrum is usually

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<sup>374</sup> WITHNALL, R., CLARK, J. H., COOKSEY, C. J. & DANIELS, M. A. M. (1992) Non-destructive, *in-situ* identification of indigo/woad and shellfish purple by Raman microscopy and visible reflectance microscopy. *Dyes in History and Archaeology*, 11, 19-24.

CLEMENTI, C., NOWIK, W., ROMANI, A., CIBIN, F. & FAVARO, G. (2007) A spectrometric and chromatographic approach to the study of ageing of madder (*Rubia tinctorum* L.) dyestuff on wool. *Analytica Chimica Acta*, 596, 46-54.

FAVARO, G., CLEMENTI, C., ROMANI, A. & VICKACKAITE, V. (2007) Acidichromism and ionochromism of luteolin and apigenin, the main components of the naturally occurring yellow weld: a spectrophotometric and fluorimetric study. *Journal of Fluorescence*, 17, 707-714.

<sup>375</sup> CHIRILA, E., CARAZEANU, I. & DOBRINAS, S. (2000) Spectrometric studies about some dyes - anionic surfactant interactions in aqueous solutions. *Talanta*, 53, 271-275.

<sup>376</sup> KIMURA, M., FUKAI, T. & KINOSHITA, T. (2008) Synthesis and analysis of UV/visible spectra of carbocyanine dimer models. *Dyes and Pigments*, 77, 673-677.

NICOTRA, V. E., MORA, M. F., IGLESIAS, R. A. & BARUZZI, A. M. (2008) Spectroscopic characterization of thionine species in different media. *Dyes and Pigments*, 76, 315-318.

<sup>377</sup> GHARANJIG, K., ARAMI, M., BAHRAMI, H., MOVASSAGH, B., MAHMOODI, N. M. & ROUHANI, S. (2008) Synthesis, spectral properties and application of novel monoazo disperse dyes derived from *N*-ester-1,8-naphthalimide to polyester. *Dyes and Pigments*, 76, 684-689.

<sup>378</sup> MA, M., SUN, Y. & SUN, G. (2003) Antimicrobial cationic dyes: part 1: synthesis and characterization. *Ibid.* 58, 27-35.

dominated by the signals from the fibre which is present in much higher amounts than the dye. Nevertheless, some investigators have used algorithms to overcome this limitation. Chen et al.<sup>379</sup> produced a spectral library of 261 dye/textile combinations. They used a principal components analysis algorithm and successfully identified unknowns of both fibre type and dye including the closely related dyes C.I. Direct Yellow 50 and C.I. Direct Red 23. Gillard et al.<sup>380</sup> also produced a reference collection of dyed samples and tried four different search algorithms. They successfully identified the dye in an archaeological sample as indigo.

FT-IR has been extensively used for the identification of organic pigments on wall paintings, especially since the introduction of portable systems using fibre optics. Civici et al.<sup>381</sup>, for example, used a range of techniques but found that FT-IR was most useful for the pigments. The technique is also used for the analysis of pigments on paintings and Daniilia et al.<sup>382</sup> was able to identify Prussian blue, an 18<sup>th</sup> century pigment, on a painting and thus date it. The introduction of attenuated total reflectance FT-IR (ATR FT-IR)<sup>383</sup> and improvements in instrumental design have allowed increased spatial resolution in the method and this allowed Rizzo et al.<sup>384</sup> to perform paint cross section analyses. IR spectroscopy is also used for the analysis of pigments on pottery, for example in a study by Akyuz et al.<sup>385</sup> In one study, 24 paint pigments were examined and the IR method was found to be useful where fluorescence interferes with RS.<sup>386</sup>

IR spectroscopy has the advantage over UV-vis of producing distinctive molecular fingerprints but it suffers from substantial interference from other molecules present in

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<sup>379</sup> CHEN, C.-S., BROWN, C. W. & BIDE, M. J. (1997) Non-destructive near-infra-red analysis for the identification of dyes on textiles. *Journal of the Society of Dyers and Colourists*, 113, 510-56.

<sup>380</sup> GILLARD, R. D., HARDMAN, S. M., THOMAS, R. G. & WATKINSON, D. E. (1994) The detection of dyes by FTIR. *Studies in Conservation*, 39, 187-192.

<sup>381</sup> CIVICI, N. (2006) Non-destructive identification of inorganic pigments used in 16-17th century Albanian icons by total reflection X-ray fluorescence analysis. *Journal of Cultural Heritage*, 7, 339-343.

<sup>382</sup> DANIILIA, S., MINOPOULOU, E., ANDRIKOPOULOS, K. S., KARAPANAGIOTIS, I. & KOUROUKLIS, G. A. (2008a) Evaluating a Cumaean Sibyl: Domenichino or later? A multi analytical approach. *Analytica Chimica Acta*, 611, 239-249.

<sup>383</sup> This technique will be briefly explained in Chapter 6.

<sup>384</sup> RIZZO, A. (2008) Progress in the application of ATR-FTIR microscopy to the study of multi-layered cross-sections from works of art. *Analytical Bioanalytical Chemistry*, 392, 47-55.

<sup>385</sup> AKYUZ, S., AKYUZ, T., BASARAN, S., BOLCAL, C. & GULEC, A. (2008) Analysis of ancient potteries using FT-IR, micro-Raman and EDXRF spectrometry. *Vibrational Spectroscopy*, 48, 276-280.

<sup>386</sup> SILVA, C. E., SILVA, L. P., EDWARDS, H. G. M. & DE OLIVERA, L. F. C. (2006) Diffuse reflection FTIR spectral database of dyes and pigments. *Analytical Bioanalytical Chemistry*, 386, 2183-2191.

the sample such as the fibres and binders and since these, in most circumstances, are present in much larger concentrations than dye molecules, this can be a severe handicap.

#### 5.4.3 Raman spectroscopy

Like FT-IR, RS has been extensively used for pigment analysis in the cultural heritage field. Clark<sup>387</sup> lists spectral data for 15 blue pigments, 12 green pigments, 10 black pigments, 3 brown/orange pigments, 8 red pigments, 14 white pigments and 12 yellow pigments along with 16 organic pigments. Cheng et al<sup>388</sup> state that Raman microscopy is now the key technique to identify pigments on archaeological and historical artefacts in China and that many groups are building up libraries of reference spectra.

Smith and Clark, pioneers in this field, have produced two relatively recent reviews of this subject, one emphasising art history and conservation science<sup>389</sup> and the second concentrating on applications in archaeology.<sup>390</sup> The majority of studies in this area have been carried out on pigments on paper, applied to walls or in paintings. In an overview of studies of pigments on paper, in paintings or murals, Vandenabeele<sup>391</sup> has reviewed the identification of artists' materials and its use for dating. Table 5.1 summarises published work using RS for informing conservation decisions as well as contributing to attributions and dating.

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<sup>387</sup> CLARK, R. J. H. (2002) Pigment identification by spectroscopic means: an arts/science interface. *C.R. Chimie*, 5, 7-20.

<sup>388</sup> CHENG, X., XIA, Y., YANRU, M. & LEI, Y. (2007) Three fabricated pigments (Han purple, indigo and emerald green) in ancient Chinese artifacts studied by Raman microscopy, energy-dispersive X-ray spectrometry and polarized light microscopy. *Journal of Raman Spectroscopy*, 38, 1274-1279.

<sup>389</sup> SMITH, G. D. & CLARK, R. J. H. (2001) Raman microscopy in art history and conservation science. *Reviews in Conservation*, 2, 92-106.

<sup>390</sup> SMITH, G. D. & CLARK, R. J. H. (2004) Raman microscopy in archaeological science. *Journal of Archaeological Science*, 31, 1137-1160.

<sup>391</sup> VANDENABEELE, P. (2004) Raman spectroscopy in art and archaeology. *Journal of Raman Spectroscopy*, 35, 607-609.

VANDENABEELE, P. & MOENS, L. (2005) Overview: Raman Spectroscopy of Pigments and Dyes. IN EDWARDS, H. G. M. & CHALMERS, J. M. (Eds.) *Raman Spectroscopy in Archaeology and Art History*. Cambridge, The Royal Society of Chemistry.

Table 5.1. Summary of RS studies used as a tool in making conservation decisions or dating/attribution

In many of these studies complementary analytical techniques are also used with RS to confirm identity or extend the range of molecules detected

Reference	Application
(Wise and Wise, 2004)	Red pigment identified as Pigment Red 49 – known to have poor lightfastness. Underlayer of white zinc found in areas of degradation. Aniline dyes identified so limited display recommended.
(Civici et al., 2005)	Different ranges of pigments found in 17 <sup>th</sup> century Albanian icons compared with 15 <sup>th</sup> & 18 <sup>th</sup> century Greek icons.
(Magistro et al., 2001)	Similar pigments found in Byzantine & Greek 9 <sup>th</sup> to 13 <sup>th</sup> century manuscripts
(Brown and Clark, 2004)	Typical palette of pigments identified on 8 <sup>th</sup> century manuscripts, including the Lindisfarne Gospels.
(Bruni et al., 2001)	Compared 16 <sup>th</sup> century Eastern & Western manuscripts and found more use of lapis lazuli in the Eastern examples
(Froment et al., 2008)	Characteristic signatures for red & yellow earths from different sources
(Correia et al., 2007)	Identified range of pigments used by one artist from 1880 to 1884 & later pigments used during interventions
(Daniilia et al., 2008a)	Painting attributed to Angelica Kauffman rather than Domenichino on the basis of two of the pigments present
(Daniilia et al., 2008b)	Different proportions of pigments found in fragments of 2 wall paintings suggesting two artists
(Castro et al., 2004)	Identified ultramarine blue, not produced until 1828.
(Clark, 2002)	Egyptian papyri identified as fake due to later pigments identified
(Castro et al., 2008)	Variations in inks in stamps found to be contemporary
(Vila et al., 2007)	Able to identify the order of layers of inks in prints as an aid to identifying fakes
(Centeno et al., 2006)	Identified one pigment sensitive to acids/alkalis therefore avoid de-acidification of the paper substrate. Identified 2 water-soluble pigments.
(van der Werf et al., 2008)	Could distinguish between the original 13 <sup>th</sup> century ground and a later 16 <sup>th</sup> century ground in a panel painting
(Castriota et al., 2008)	Cobalt blue found indicating later alterations to a 16 <sup>th</sup> century fresco.
(Edwards et al., 2008)	Identified and prioritised areas of damage on frescos and also found evidence of microbiological damage
(Otieno-Alego et al., 2001)	Identified a bloom on paper as a bleaching residue not a pesticide residue, allowing handling
(Casadio et al., 2010)	Range of early synthetic organic pigments identified on prints with implications for display & treatment options

RS is also used in the field of forensic investigation for the analysis of pigments in pen inks<sup>392</sup> as well as for the comparison of dyed fibres.<sup>393</sup> Naturally these studies concentrate on modern dyes and paints in current use rather than historic examples. In the examination of cultural heritage both dyed and undyed fibres have been investigated with Raman spectroscopy. These have included wool,<sup>394</sup> canvas<sup>395</sup> and hemp<sup>396</sup> as well as heavily degraded archaeological textiles.<sup>397</sup> These papers are concerned principally with the study of the fibres themselves but a number of investigations have also been carried out on dyes and pigments either in solution or dyed into fibres.

A summary of recent papers describing the use of RS in the analysis of dyes and pigments is shown in Tables 5.2 and 5.3. Many investigations have been carried out on pigments rather than dyes but the principles of analysis and the applications are also relevant to dye analysis. The majority of studies in the area of cultural heritage have considered natural dyes (Table 5.2) whereas the studies carried out on the later synthetic dyes have been largely for the purpose of investigation of the techniques of RS or the chemistry of the dyes themselves (Table 5.3).

Raman spectroscopy was the chosen method for further investigation as it can be used to examine objects without taking a sample from them or causing any damage to them. These two criteria are very important in the field of textile conservation and textile art history as the artefacts are often unique and very precious. The owners will therefore prefer them to be intact after the investigation even if samples that might be taken can

<sup>392</sup> CLAYBOURN, M. & ANSELL, M. (2000) Using Raman Spectroscopy to solve crime: inks, questioned documents and fraud. *Science and Justice*, 40, 261-271.

MAZZELLA, W. D. & BUZZINI, P. (2005) Raman spectroscopy of blue gel pen inks. *Forensic Science International*, 152, 241-247.

<sup>393</sup> LEPOT, L., DE WAEL, K., GASON, F. & GILBERT, B. (2007) Application of Raman spectroscopy to forensic fibre cases. *Science and Justice*, xx, xxx-xxx, THOMAS, J., BUZZINI, P., MASSONNET, G., REEDY, B. & ROUX, C. (2005) Raman spectroscopy and the forensic analysis of black/grey and blue cotton fibres: Part 1. Investigation of the effects of varying laser wavelength. *Forensic Science International*, 152, 189-197.

<sup>394</sup> DOHERTY, B., MILIANI, C., VANDEN BERGHE, I., SGAMELLOTTI, A. & BRUNETTI, B. G. (2008) Micro-Raman spectroscopic study of artificially aged natural and dyed wool. *Journal of Raman Spectroscopy*, 39, 638-645.

<sup>395</sup> EDWARDS, H. G. M., NIKHASSAN, N. F., FARWELL, D. W., GARSIDE, P. & WYETH, P. (2006) Raman spectroscopic analysis of a unique linen artefact: the HMS Victory Trafalgar sail. *Ibid.* 37, 1193-1200.

<sup>396</sup> KOVOUR, S. K., SCHENZKE, K. & DIEPENBROCK, W. (2008) Orientation dependent FT Raman microspectroscopy on hemp fibers. *Macromolecular Symposia*, 265, 205-210.

<sup>397</sup> EDWARDS, H. G. M. & WYETH, P. (2005) Case Study: Ancient Textile Fibres. IN EDWARDS, H. G. M. & CHALMERS, J. M. (Eds.) *Raman Spectroscopy in Archaeology and Art History*. Cambridge, The Royal Society of Chemistry.

be very small. This type of method can also be used to monitor an object over time, for example to check for colour changes or fading, without causing any harm.<sup>398</sup> Also the application of this method to synthetic dyes in cultural heritage has not been systematically studied to date and provides a fruitful area of research for this study.

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<sup>398</sup> This approach has been used to monitor fading on textiles using UV/Vis spectroscopy. PRETZEL, B. (2000) *Determining the colour fastness of the Bullerswood carpet*. In ROY, A. & SMITH, P. (eds) Preprints from the IIC congress, Melbourne, 2000, *Tradition and Innovation: Advances in Conservation* London, IIC. Pages 150-154

Table 5.2. Summary of RS studies on natural dyes and pigments.

Dye	References	Comments
Indigo	(Withnall et al., 2005) (Shadi et al., 2003a) (Cheng et al., 2007) (Coupry et al., 1997) (Vandenabeele and Moens, 2003) (Andreev et al., 2001) (Koperska et al., 2011)	Vandenabeele & Moens could distinguish between natural and synthetic forms. Koperska et al examined stability Cheng et al studied indigo dye on silk Coupry et al identified structural changes on dyeing
Madder (alizarin & purpurin)	(Withnall et al., 2005) (Shadi et al., 2004) (Leona et al., 2006) (Baran et al., 2009) (Canamares et al., 2004) (Andreev et al., 2001) (Chen et al., 2006) (Koperska et al., 2011) (Whitney et al., 2006)	Leona et al used SERS to identify madder in a 16 <sup>th</sup> cent. tapestry Baran et al studied alizarin on a surface Withnall et al could not distinguish the spectra of alizarin and purpurin with SERRS but Shadi et al could. The latter group also claim semi-quantitative analysis Andreev et al used FT Raman Chen et al could identify alizarin extracted from a dyed textile Whitney et al used SERS
Tyrian purple, (dibromoindigo)	(Bruni et al., 2010) (Withnall et al., 1992)	Bruni et al used SERS on dye extracted from antique textiles Withnall et al carried out <i>in situ</i> analysis
Weld	(Jurasekova et al., 2008) (Teslova et al., 2007) (Corredor et al., 2009) (Andreev et al., 2001)	Jurasekova et al and Teslova et al used <i>in situ</i> detection with SERS Corredor et al used SERS to identify weld extracted from a textile
Cochineal	(Andreev et al., 2001) (Chen et al., 2006) (Koperska et al., 2011) (Whitney et al., 2006)	Whitney et al deposited a SERS active surface on the powder sample of dye
Lac	(Canamares and Leona, 2007) (Chen et al., 2006) (Whitney et al., 2006)	Canamares & Leona and Chen et al both used SERS on pure dye samples
Kermes	(Whitney et al., 2006)	
Berberine	(Leona and Lombardi, 2007)	Berberine was detected <i>in situ</i> on an antique textile fibre
Indigo carmine	(Shadi et al., 2003b) (Peica and Kiefer, 2008)	Peica & Kiefer used SERRS to characterise indigo carmine
Carotenoids/saffron/Cape Jasmine/curcumin	(Withnall et al., 2003) (Andreev et al., 2001) (Canamares et al., 2010) (Koperska et al., 2011)	Withnall et al used RRS directly on fruit and shellfish containing carotenoids Canamares et al used SERS and RS directly on dyed samples
Brazilwood	(Whitney et al., 2006)	Whitney et al used a silver film deposited directly onto the dye
Sepia (melanin)	(Centeno and Shamir, 2008)	SERS used on aqueous dye solution



Table 5.3. Summary of RS studies on synthetic dyes and pigments.

Reference	Dyes	Techniques used	Major findings
(Buzzini and Massonnet, 2004)	Modern green spray paints	FT-IR & RS	Identification of organic pigments by Raman
(Canamares et al., 2008)	Crystal violet	RS & SERS	Comparison of Raman & SERS
(Geiman et al., 2009)	Synthetic dyes in ballpoint pen inks	RS, FT-RS & SERS	SERS on TLC dye spots found most useful for a range of modern inks
(Ropret et al., 2008)	Yellow synthetic organic pigments (20 <sup>th</sup> C)	RS	Raman bands in the 1800-1000cm <sup>-1</sup> wavenumber difference range used for identification
(Shadi et al., 2001)	Nuclear fast red	SERS, SERRS	LOD determined. pH dependant change seen allowing assignation of bands to the -SO <sub>3</sub> H group.
(Lepot et al., 2008)	Modern fibres	RS	Direct analysis of the dyed fibre, especially cotton
(Massonnet and Stoecklein, 1999)	Red car paints	FTRS	Identification of car paints
(Mazzella and Buzzini, 2005)	Blue gel pen inks	RS	Two pigments identified in extracts of inks
(Munro et al., 1995)	Acidic monoazos	RRS & SERRS	Identification of pure dyes
(Poon et al., 2008)	Tattooing inks	RS & FT-IR	Identification of pigments in skin by comparison to reference spectra
(Salpin et al., 2006)	Modern synthetic dyes on wool	RS	Dyes and mixtures of dyes on the fibre analysed using reference spectra
(Sasic et al., 2005)	Rhodamine 6G	SERRS	Single molecule analysis
(Schulte et al., 2008)	20 <sup>th</sup> cent organic pigments	RS & FT-RS	Pigments identified by comparison with reference spectra
(Shadi et al., 2009)	Methyl green	SERRS	Conditions optimised and LOD established
(Thomas et al., 2005)	Modern cotton fibres	RS	Optimised wavelength and identified major dye on fibre
(Vandenabeele et al., 2000)	Database of modern azo pigments	RS	Identification protocol based on peaks established
(White, 2003)	Biro inks	SERRS	Stability of colloid treated dyes established
(White et al., 1996)	Reactive dye on cotton	SERRS	<i>In situ</i> analysis of dye on cotton fibre
(Almeida et al., 2010)	New coccine	FTRS, UV-vis, FTIR	Investigation of isomers of dye present in solution
(de Souza and Corio, 2010)	Alizarin Red S	SERS	Investigation of SERS effect
(Abbott et al., 2009)	Black reactive dyes on various fibres	RRS, UV-vis	Identification of dyes on the fibre
(Abbott et al., 2005)	Orange II	RRS, FTIR, UV-vis,	Structural study of Orange II

## Chapter 6 Infrared and surface enhanced Raman spectroscopy

### 6.1 Surface enhanced Raman spectroscopy of dye solutions

Much of the published work referenced in Chapter 5 used surface enhanced Raman spectroscopy to reduce fluorescence and increase sensitivity and therefore this method was tried with solutions of the synthetic dyes used in this study.

#### 6.1.1 Experimental

Silver colloid was produced using the method of Lee and Meisel<sup>399</sup> and added to 1mM aqueous solutions of dye. Drops of dye solution with and without silver colloid were spotted onto microscope slides and allowed to dry. The instrument used for analysis was a Renishaw Ramascope 2000 spectrometer with a HeNe laser at 632.8nm. The samples were examined in a Leica DMLM confocal microscope and the detector was a CCD camera. The microscope was focussed onto the edge of the dried dye spot where the concentration of dye was highest. The spectra from 100-3200 wavenumbers were obtained using an exposure of 10s and varying the laser power to avoid saturation of the detector but maintaining the same power for each dye with and without silver colloid. In these spectra fluorescence may cause saturation of the detector or a high and increasing or decreasing baseline.

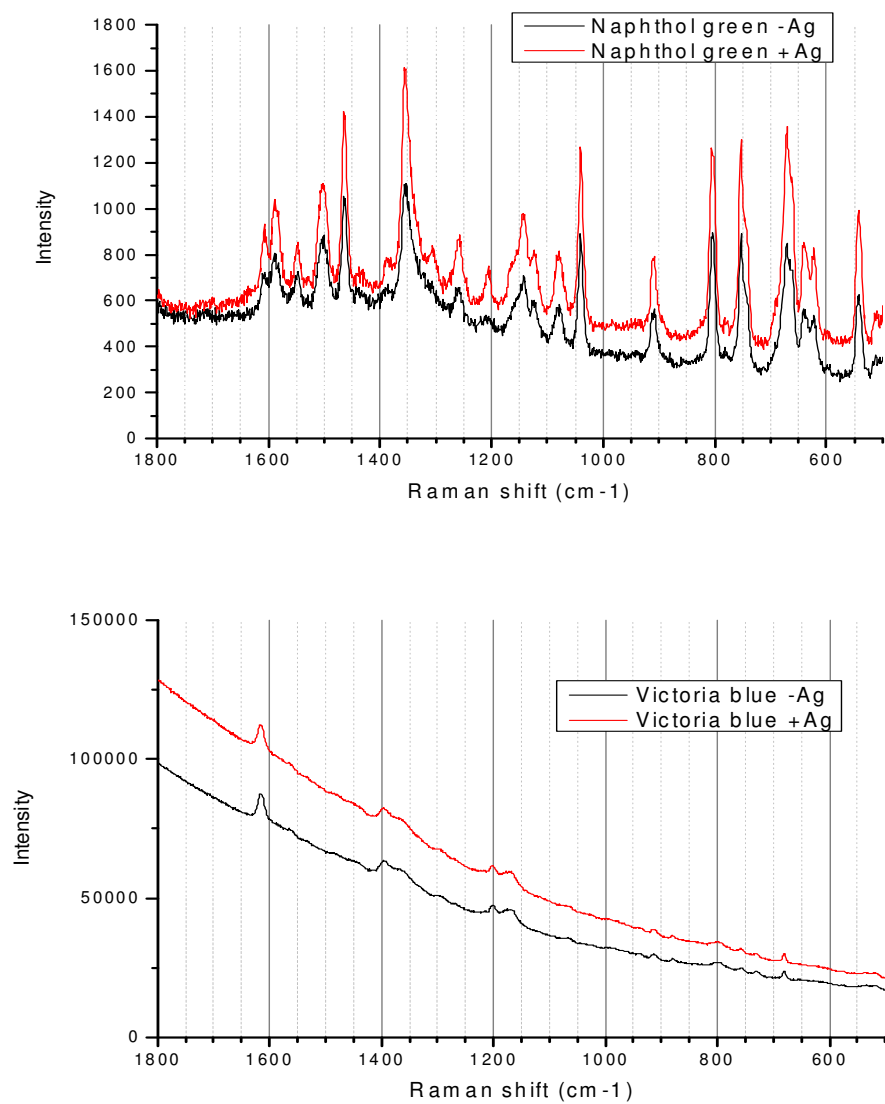
#### 6.1.2 Results

In some cases there was no difference between the spectra obtained with and without colloid (Figure 6.1). In the case of Naphthol green a reasonable signal is obtained which is not enhanced by the colloid. In contrast, the results for Victoria blue show fluorescence, exhibited by the rising baseline, which is not mitigated by the colloid and small poorly defined peaks which again are not enhanced by SERS. Neither of these dyes responds to the addition of colloid but Naphthol green nevertheless shows a reasonable spectrum.

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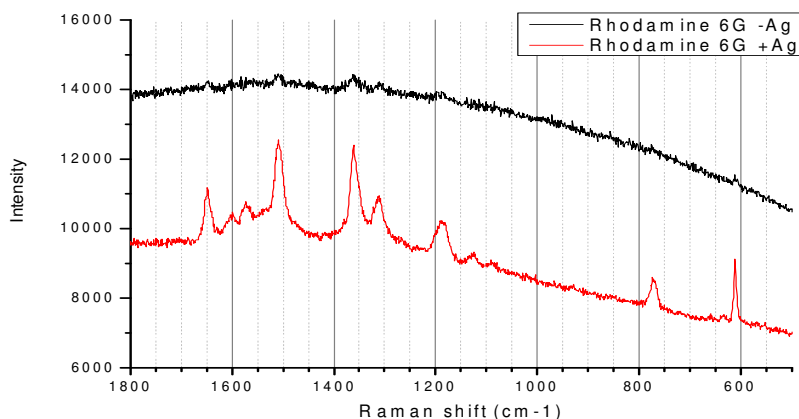
<sup>399</sup> LEE, P. C. & MEISEL, D. (1982) Adsorption and surface-enhanced Raman of dyes on silver and gold sols. *Journal of Physical Chemistry* 86, 3391-3395.

Figure 6.1 Spectra of Naphthol green and Victoria blue with and without silver colloid



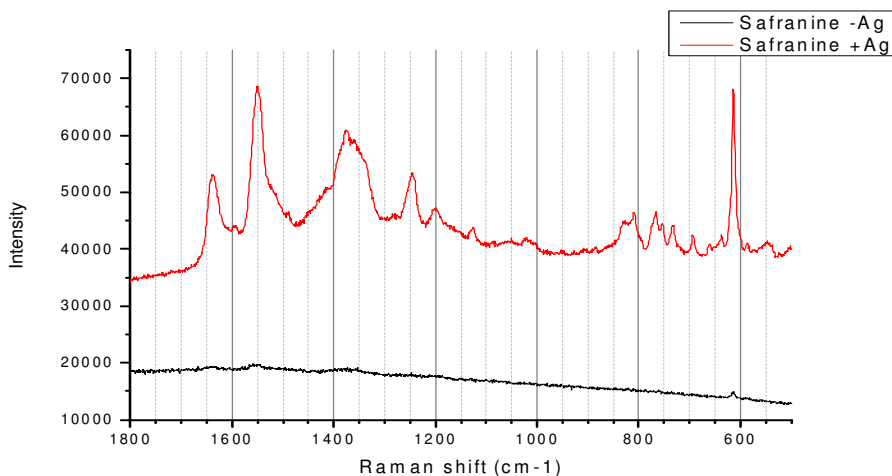
Rhodamine 6G is a dye which has been intensively studied in SERS mode and peak enhancements of many orders of magnitude have been observed.<sup>400</sup> A similar effect was seen in this study since the fluorescence was decreased and the peaks increased in the presence of the colloid (Figure 6.2) although the very great increase in intensity which is sometimes reported is not seen here.

Figure 6.2 Spectra of Rhodamine 6G with and without silver colloid



Safranine is a highly fluorescent dye like Rhodamine 6G which shows great peak enhancement in the presence of colloid (Figure 6.3).

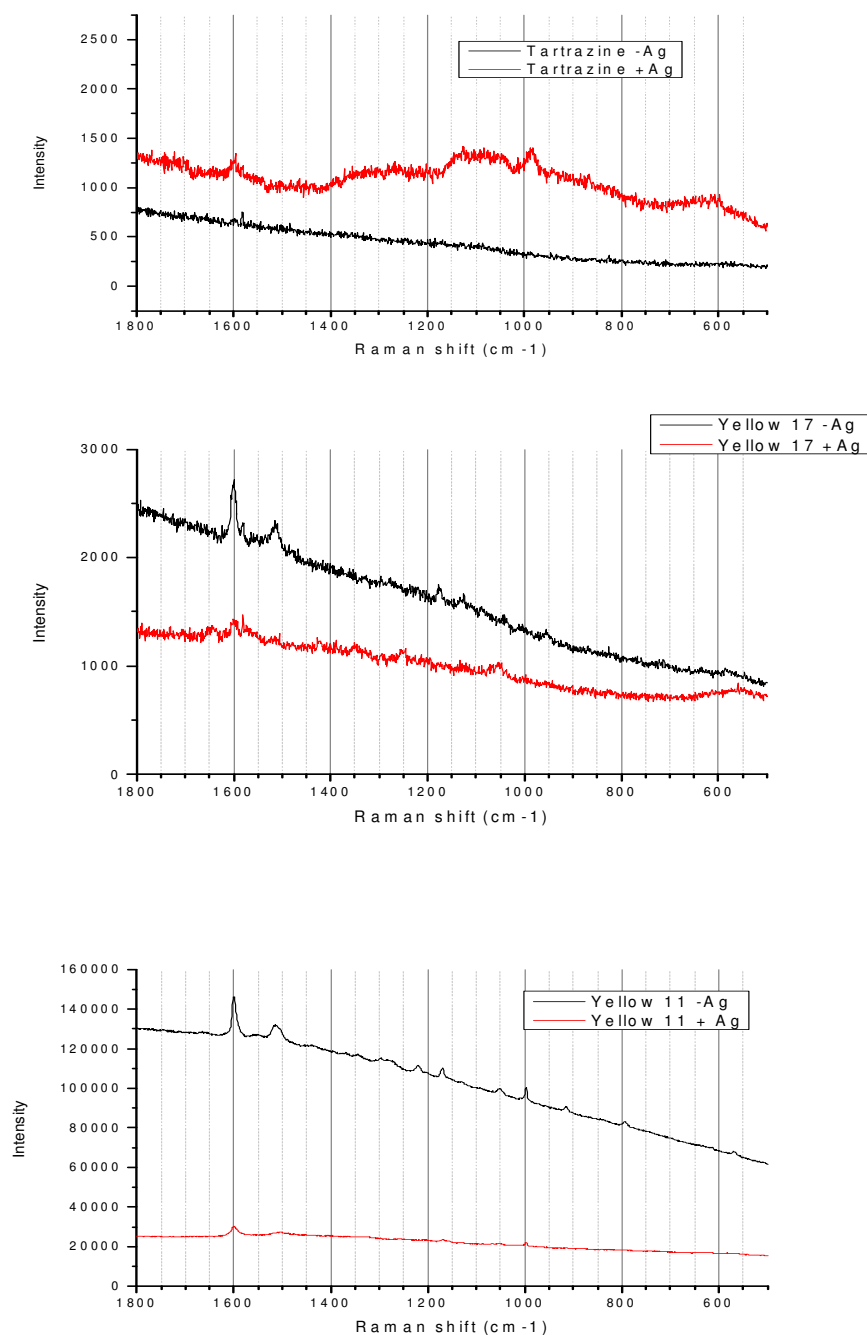
Figure 6.3 Spectra for Safranine with and without silver colloid



<sup>400</sup> See for example, CULHA, M., KAHRAMAN, M., TOKMAN, N. & TURKOGLU, G. (2008) Surface-enhanced Raman scattering on aggregates of silver nanoparticles with definite size. *Journal of Physical Chemistry C*, 112, 10338-10343.

The azo dyes Acid yellow 11, Acid yellow 17 and Tartrazine show variable results with little or no enhancement or fluorescence suppression in either Acid yellow 17 or Tartrazine. Acid yellow 11 shows suppression of fluorescence but, surprisingly, less well defined peaks in the presence of colloid (Figure 6.4).

Figure 6.4 Spectra for Tartrazine, Acid yellow 17, and Acid yellow 11 with and without silver colloid



### 6.1.3 Discussion and conclusions

The results for the addition of silver colloid to dye solutions show variable results. There are characteristic peaks for some dyes but not all and this method would require the extraction of the dye from the fabric if applied to intact textiles. The direct application of colloid to the textile was attempted but without success. Some studies do report the use of colloids on fibres and the identification of natural dyes in situ but these have used a pre-treatment of a sampled fibre with acid to increase the intimacy of the contact between the dye molecules and the colloid.<sup>401</sup> This method would therefore require both sampling and destructive testing whereas the goal of this study is to develop a method which could be applied to the intact sample.

### 6.2 Fourier transform infrared spectroscopy

A method which is not affected by fluorescence is IR spectroscopy. It has also been used in conjunction with RS in several of the published studies on synthetic dyes. In this study attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy was used. It is a well established technique for the study of textile fibres<sup>402</sup> and has also been applied to the identification of dyes and pigments but is complicated by the strong signals from the fabric when used on dyed textiles.<sup>403</sup> When examining organic dyes it offers the potential advantage of not being affected by fluorescence and was therefore explored in this study.

#### 6.2.1 Experimental

The equipment used was a ThermoScientific Nicolet iS10 running on Omnic software. The interferometer sensitivity was set at  $4\text{cm}^{-1}$  and 8 scans were averaged. The

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<sup>401</sup> LEONA, M. & LOMBARDI, J. R. (2007) Identification of berberine in ancient and historical textiles by surface-enhanced Raman scattering. *Journal of Raman Spectroscopy*, 38, 853-858.

<sup>402</sup> SATO, M. & SASAKI, Y. (2005) Studies on ancient Japanese silk fibres using FT-IR microscopy. IN WYETH, P. (Ed. *AHRB Research Centre for Textile Conservation and Textile Studies First annual Conference: Scientific Analysis of Ancient and Historic Textiles*. Winchester, Archetype Press.

GARSDIE, P. & WYETH, P. (2003) Identification of cellulosic fibres by FTIR spectroscopy. Thread and single fibre analysis by attenuated total reflectance. *Studies in Conservation*, 48, 269-275.

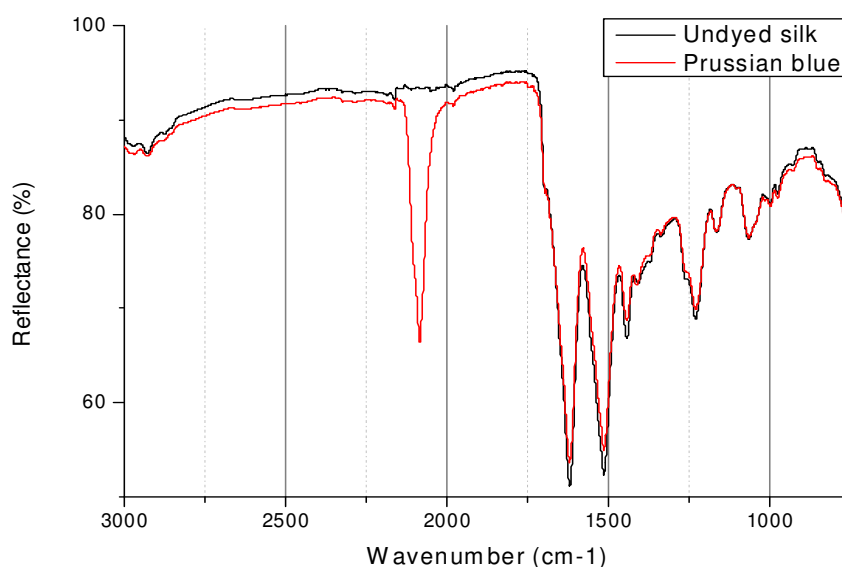
<sup>403</sup> KUCKOVA, S., NEMEC, I., HYNEK, R., HRADILOVA, J. & GRYGAR, T. (2005) Analysis of organic colouring and binding components in colour layer of art works. *Analytical Bioanalytical Chemistry*, 382, 275-282.

instrument is configured so that the IR beam enters a transparent crystal of high refractive index and is therefore internally reflected several times. The upper surface of the crystal is in contact with the sample and thus frequencies from the IR beam can be absorbed by it and a spectrum obtained. The sample must be in close contact with the crystal in order for the interaction with the beam to take place so pressure is applied by a clamp. The fabrics were folded to give four thicknesses and applied to the window of the machine using a pre-set torque lever to give reproducible pressure for each measurement. Undyed silk and wool were scanned as well as the dyed fabrics. The spectra were not processed and slight differences in equivalent peak heights for the fabric are due to normal spectral variation.

### 6.2.2 Results

In many cases no signal from the dye could be seen but there were a few strong results obtained. The most striking spectrum was seen for Prussian blue on silk (Figure 6.5) which showed a strong absorption at  $2085\text{cm}^{-1}$ . This dye is an exception for the compounds in this study as it is an inorganic synthetic compound (iron hexacyanoferrate) and generally the peaks seen for the organic dyes were small in comparison to the fibre peaks.

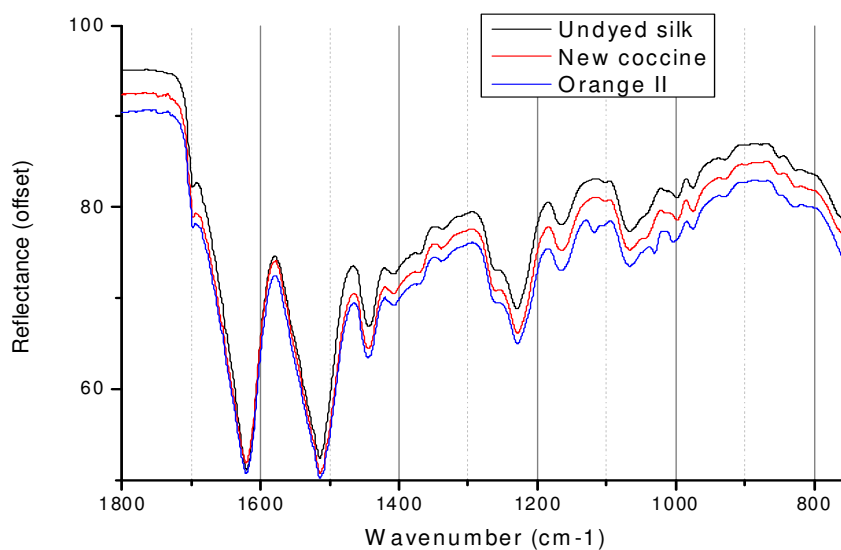
Figure 6.5 FT-IR spectrum for Prussian blue on silk



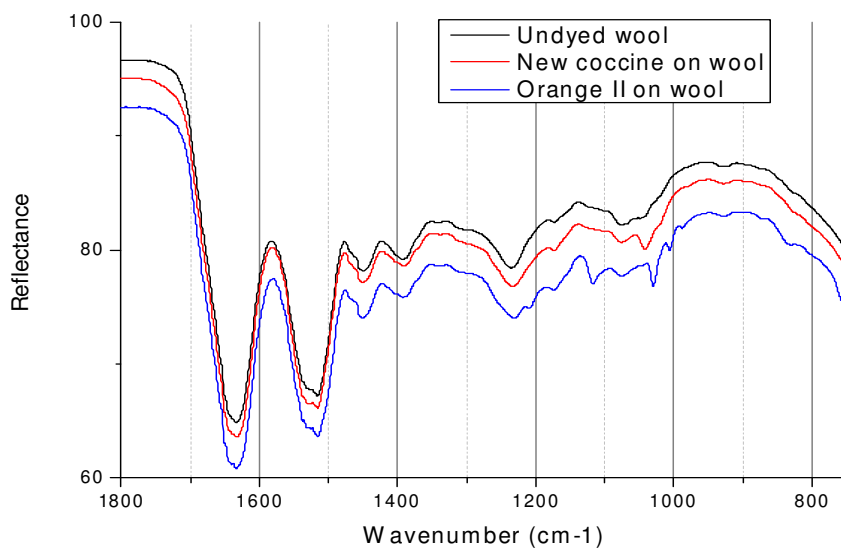
The azo dyes Acid yellow 11, Acid yellow 17 and Tartrazine gave no signal on either silk or wool but other azo dyes gave some small peaks. Orange II gave peaks at  $1118/1117\text{cm}^{-1}$  and  $1031/1030\text{cm}^{-1}$  on silk and an additional peak at  $1006\text{cm}^{-1}$  on wool. New coccine gave only one peak at  $1042\text{cm}^{-1}$  on wool and no peaks on silk (Figure 6.6).

Figure 6.6 FT-IR spectra for Orange II and New coccine dyes on silk and wool

(a) Dyes on silk



(b) Dyes on wool





For the triphenylmethane dyes, Fuchsin acid gave no signal distinguishable from the fibres. The results for the other dyes examined are given in Table 6.1 and Figure 6.7.

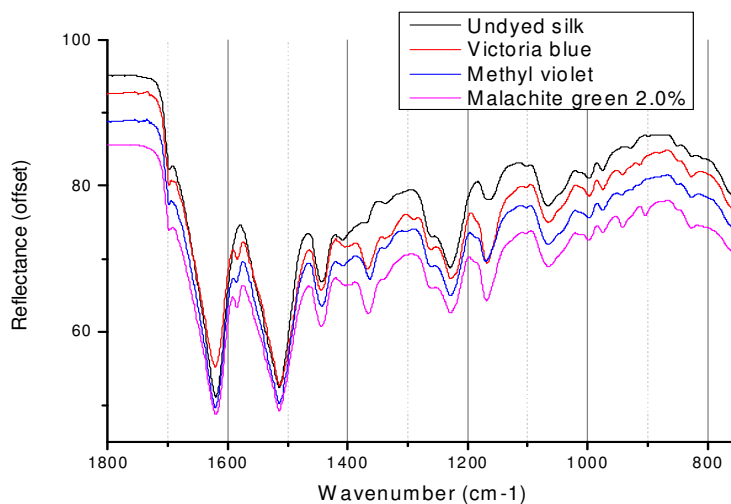
Table 6.1 FT-IR peaks for triphenylmethane dyes on silk and wool

Victoria blue on wool	Victoria blue on silk	Methyl violet on wool	Methyl violet on silk	Malachite green on silk
1170	1168	1173		
1369	1367		1363	1366
1583	1584	~1583*	1586	1585

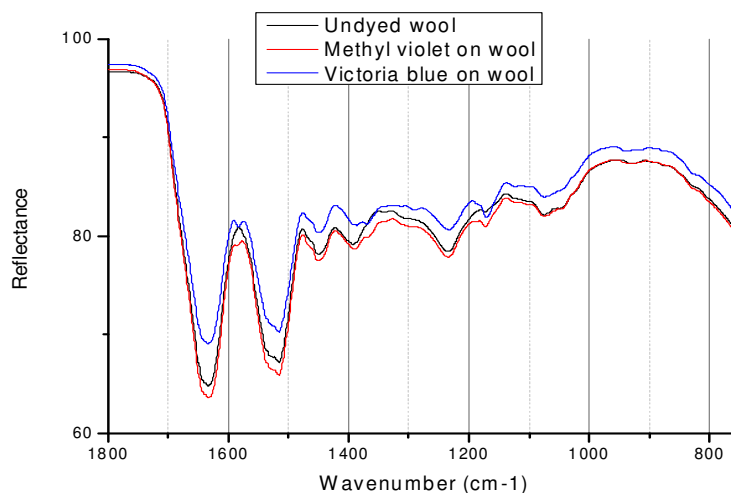
\*This shoulder was not well defined and hard to measure precisely.

Figure 6.7 FT-IR spectra for triphenylmethane dyes on silk and wool

(a) Victoria blue, Methyl violet and Malachite green on silk

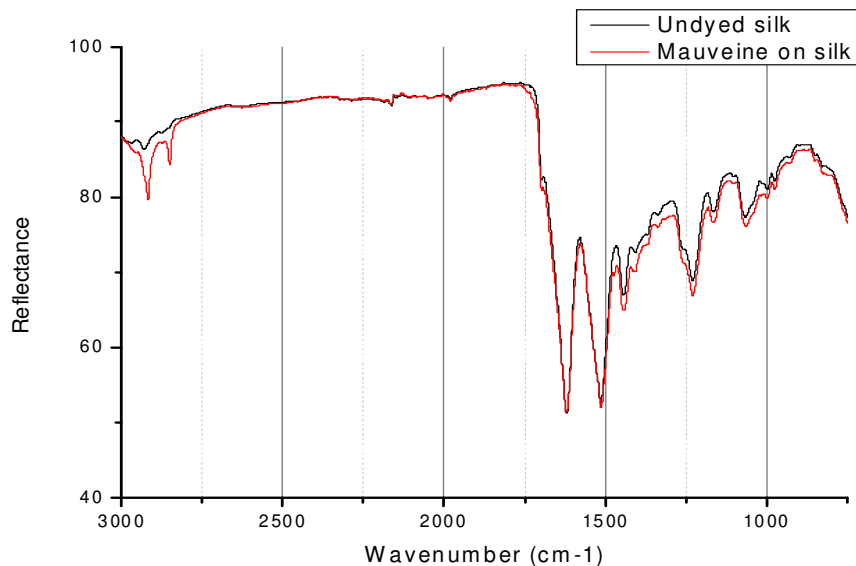


(b) Victoria blue and Methyl violet on wool



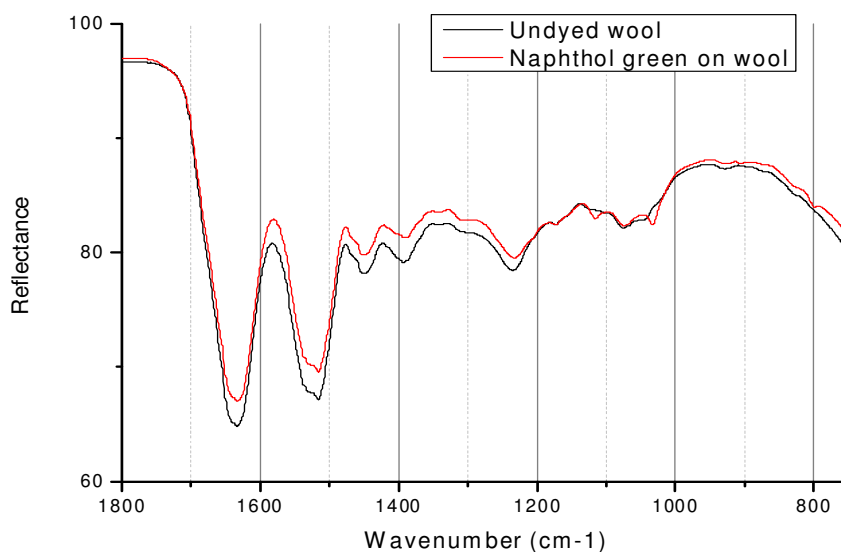
Mauveine on silk was also measured and gave a very different spectrum from the other dyes with peaks at 2850 and 2917 $\text{cm}^{-1}$  (Figure 6.8).

Figure 6.8 FT-IR spectrum for Mauveine dye on silk



Other dyes examined which gave no signal were Rhodamine 6G and Safranin. Naphthol green on silk gave no peaks other than those attributable to the fabric but on wool two minor peaks were seen at 1033 and 1116 $\text{cm}^{-1}$  (Figure 6.9).

Figure 6.9 FT-IR spectrum for Naphthol green on wool



### 6.2.3 Discussion and conclusions

In some cases dye spectra can only be seen on wool and not silk. This could be due to the higher infrared absorbance of the silk fabric in the spectral region of interest between 1400 and 1000cm<sup>-1</sup>. A summary of the presence of easily identifiable spectral signals for the dyes is shown below (Table 6.2).

Table 6.2 Summary of FT-IR dye spectra

Dye	Spectrum on wool	Spectrum on silk
Prussian blue	Not determined	Very strong
Orange II	Good	Good
New coccine	Good	No peaks
Acid yellow 11	No peaks	No peaks
Acid yellow 17	No peaks	No peaks
Tartrazine	No peaks	No peaks
Victoria blue	Good	Good
Methyl violet	Good	Good
Malachite green	Not determined	Good
Fuchsin acid	No peaks	No peaks
Mauveine	Not determined	Good
Rhodamine 6G	No peaks	No peaks
Safranine	No peaks	No peaks
Naphthol green	Good	No peaks

This technique requires no sampling of the textile and is non-destructive and therefore is very suitable for use with historic textiles. Thus for some dyes this technique can be useful for identification and this is particularly true for some of the triphenylmethane dyes which are likely to show fluorescence although the spectra obtained here for each dye are not distinctive enough to allow discrimination between them.

## Chapter 7 FT-Raman spectra

### 7.1 FT-Raman spectra of dye powders

The FT-Raman spectra of dye powders were obtained to determine which peaks were likely to be found on dyed textiles. In some cases these could be compared to previously published results but for many of the dyes no published spectra were found. A laser with a near infrared wavelength (1064nm) was used as this increase in wavelength decreases the amount of fluorescence obtained. Unfortunately the Raman spectrum, already weak, decreases rapidly as this wavelength increases.<sup>404</sup> The Fourier transform configuration of the instrumentation increases the sensitivity and so is a definite advantage in these experiments.

The analyses were carried out using a PerkinElmer 2000 NIR FT-Raman system with a diode pumped Nd:YAG laser, wavelength of 1064nm, running on PerkinElmer Spectrum® software. The system was set up to average 20-40 scans with a laser power of 50 to 300mW, an interferometer resolution of  $16\text{ cm}^{-1}$  and a J-stop resolution of  $14.95\text{cm}^{-1}$ . The optical path difference velocity was  $0.1\text{cm/s}$ . Dye powders were sandwiched between two microscope slides and held under light compression. Full experimental details are given in Appendix 4.

#### 7.1.1 Results and discussion

The spectra presented in this section have been offset with respect to each other to increase the clarity of the graphs but have not otherwise been processed. Some dyes showed significant fluorescence and the laser power was reduced in these cases. At high laser powers the amount of fluorescence produced saturates the detector and therefore no spectrum can be seen. Reducing the laser power does not abolish the fluorescence but reduces the total signal to a level where the spectral bands can be seen on top of it. Even where the baselines are not flat, baseline subtraction was not carried out as the distortion in

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<sup>404</sup> The intensity of the Raman spectrum decreases as the fourth power of the wavelength.

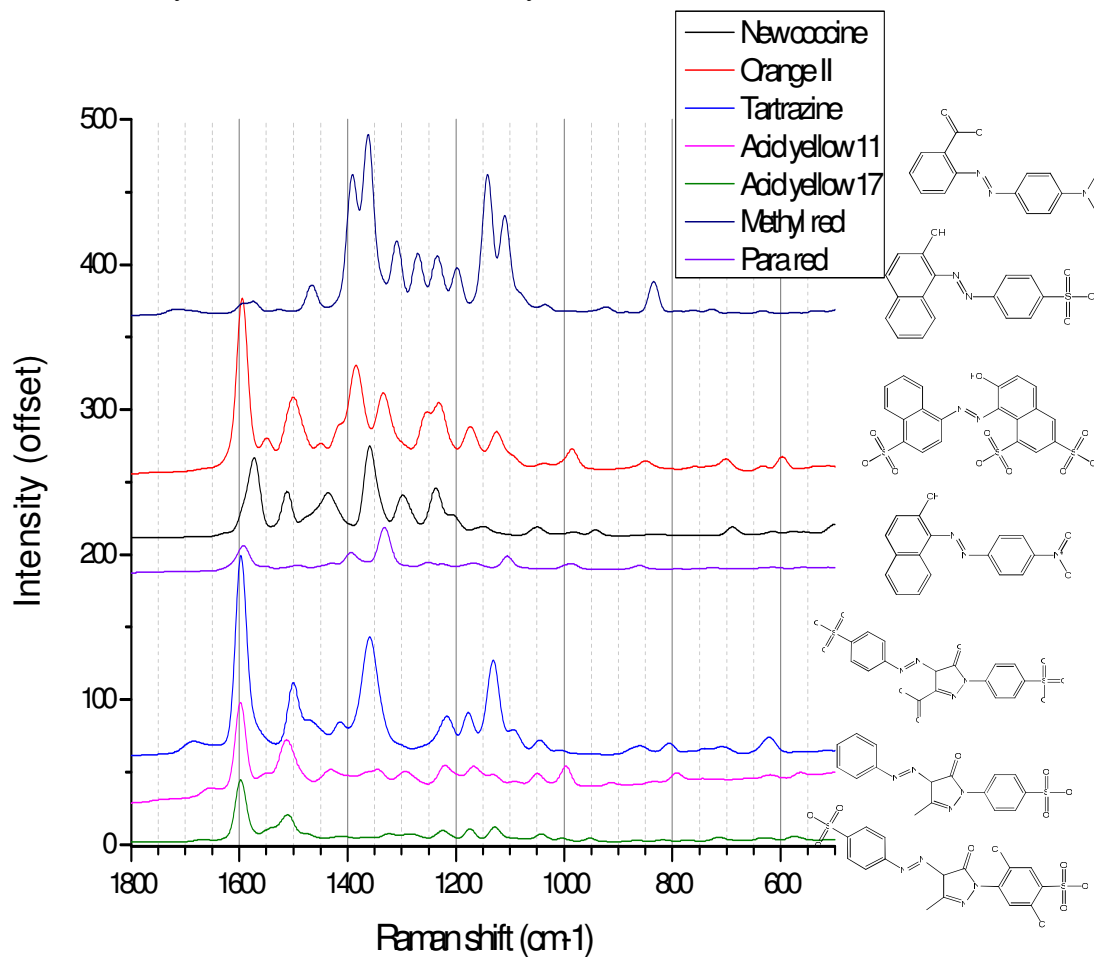
the section of interest ( $1800 - 500\text{cm}^{-1}$ ) was not intrusive. The minimal processing of the spectra shows the relative intensities of the Raman scattering for the individual dyes, although the variation in laser power has also to be taken into account.

This study does not seek to assign specific vibrations to each of the peaks seen. The aim of this work is to establish a method for distinguishing between the organic dyes studied by identifying clear differences in the spectral ‘fingerprints’ for each of the compounds. Spectra were collected over the range of Raman shift from  $200$  to  $3500\text{cm}^{-1}$  but the higher end of the range is dominated by the signal from the textile and the lower end shows fewer features. Therefore the section from  $1800$  to  $500\text{cm}^{-1}$  is presented throughout this work.

Figure 7.1. FT-Raman spectra for azo dye powders.

Spectra shown are raw data but are offset for ease of interpretation. Dye structures are shown in the order of the spectra, not the order of the legend.

Laser power: 300mW for Orange II, Tartrazine, Acid yellow 17, Para red, New coccine;  
200mW for Acid yellow 11; 50mW for Methyl red



**Table 7.1. Peak positions for azo dye powders compared.**

Published peak positions are given in brackets. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. Peak positions in red are those which are proposed for identification.

Methyl red	Para red	Orange II (Abbott et al. <sup>405</sup> )	New coccine (Almeida et al. <sup>406</sup> )	Tartrazine (Peica et al. <sup>407</sup> )	Acid yellow 11	Acid yellow 17
		(1622w)	(1607s)	(1682vw)		
	1592	1592 (1598vs)		1597 (1598vs)	1598	1597
			1572 (1574vs)			
				(1561sh)		
		1549 (1552w)			1548	
		(1510sh)	1512 (1515s)		1512	1511
		1500 (1499s)		1500 (1502s)		
		(1481w)	(1480w)			
1466			(1458m)	1472 (1470m)		
		1450 (1451w)	1436 (1441s)		1431	
		1414sh (1416m)	(1420m)	1414 (1415w)		1411
1391	1394	1384 (1385s)	(1401w)			
1362			1359 (1364vs)	1359 (1357s)		
	1332	1334 (1334m)	(1345m)		1344	1323
1309						
			1298 (1301m)		1293	1282
1270			(1286w)	(1271vw)		
		(1258m)				
		1253 (1250m)				
1234		1231 (1233s)	1237 (1241s)			
				1217 (1216m)	1220	1225
1198		(1210w)	1207sh (1207w)			
		1173 (1185s)		1177 (1177m)	1167	1174
1141						
		1125 (1123m)		1131 (1129s)	1132	1128
1110	1105	(1102m)				
				1094 (1093w)	1091	
		(1034w)	1050	1045 (1046vw)	1049	1042
		(1009w)		1008 (1010vw)	997	1003
		985 (991m)				
			942			952
					914	
				(880vw)		
		850		860 (861vw)		866
835					835	
						818
				806 (805vw)		
					792	
				(770vw)		772
				(738vw)		
				710 (718vw)		715
		701	690	(632w/m)		
				622 (617w/m)	620	630
		597				
					565	575

<sup>405</sup> ABBOTT, L. C., BATCHELOR, S. N., SMITH, J. R. L. & MOORE, J. N. (2009) Reductive reaction mechanisms of the azo dye Orange II in aqueous solution and in cellulose: from radical intermediates to products. *Journal of Physical Chemistry A*, 113, 6091-6103.  
<sup>406</sup> ALMEIDA, M. R., STEPHANI, R., DOS SANTOS, H. F. & DE OLIVEIRA, L. F. C. (2010b) Spectroscopic and Theoretical Study of the "Azo"-Dye E124 in Condensate Phase: Evidence of a Dominant Hydrazo Form. *Ibid.* 114, 526-534.  
<sup>407</sup> PEICA, N., PAVEL, I., CINTA PINZARU, S., RASTOGI, V. K. & KIEFER, W. (2005) Vibrational characterization of E102 food additive by Raman and surface-enhanced Raman spectroscopy and theoretical studies. *Journal of Raman Spectroscopy*, 36, 657-666.

The dye spectra show similarities and differences. All the dyes analysed have the common structural feature of an azo link between two aromatic groups. The simplest molecule, Methyl red, which has fewest substituted groups on the aromatic benzene rings shows the maximum intensity spectral peak close to  $1350\text{ cm}^{-1}$  which can be attributed to this azo group whereas this peak is either less prominent or absent for the other dyes. Para red, Orange II and New coccine form a structurally related group with one or two naphthalene groups. Para red produces a very low intensity spectrum but nevertheless the highest peak is close to  $1350\text{ cm}^{-1}$ . New coccine shows a duo of peaks of roughly equal intensity at about  $1350\text{ cm}^{-1}$  and  $1575\text{ cm}^{-1}$ . Orange II, however, has maximum intensity for a peak at approximately  $1600\text{ cm}^{-1}$  and shares this feature with the remaining dyes Tartrazine, Acid yellow 11 and Acid yellow 17. The last three dyes are another structurally related series with two phenyl groups joined by pyrazole and azo groups.

Table 7.1 also compares the results found here with published results for some of the dyes and these show good agreement. Most peaks not seen here are weak in intensity and indicate differences in sensitivity of the methods. The most prominent peak for all these spectra are at about  $1600\text{ cm}^{-1}$  which has been attributed to the phenyl groups in Tartrazine<sup>408</sup>. Tartrazine and Acid yellows 11 and 17 all show this peak at  $1597/8\text{ cm}^{-1}$  whereas Orange II and Para red have maxima at  $1592\text{ cm}^{-1}$  and the peak for New coccine, which has naphthalene groups in place of phenyls, is even further displaced at  $1572\text{ cm}^{-1}$ . Therefore the peak at this position is useful for identification. Three of the stronger bands for New coccine at  $1570$ ,  $1512$  and  $1360\text{ cm}^{-1}$  can be identified with those seen by Almeida and co-workers.<sup>409</sup>

The three related dyes, Tartrazine and Acid yellows 11 and 17, also show a consistent pattern of peaks at  $1217\text{--}1225\text{ cm}^{-1}$ ,  $1167\text{--}1177\text{ cm}^{-1}$  and  $1128\text{--}1132\text{ cm}^{-1}$ . These differ in their position and their relative intensity between the dyes and both these attributes can be used for identification.

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<sup>408</sup> Ibid.

<sup>409</sup> ALMEIDA, M. R., STEPANI, R., DOS SANTOS, H. F. & DE OLIVEIRA, L. F. C. (2010a) Spectroscopic and thermochemical study of the "Azo"-dye E124 in condensate phase: evidence of a dominant hydrazo form. *Journal of Physical Chemistry A*, 114, 526-534.



Figure 7.2. FT-Raman spectra for triphenylmethane dye powders

Spectra shown are raw data but are offset for ease of interpretation. Dye structures are shown in the order of the spectra not the order of the legend.

Laser power: 50mW for Methyl violet and Victoria blue; 250mW for Fuchsin acid; 100mW for Malachite green and Para rosaniline

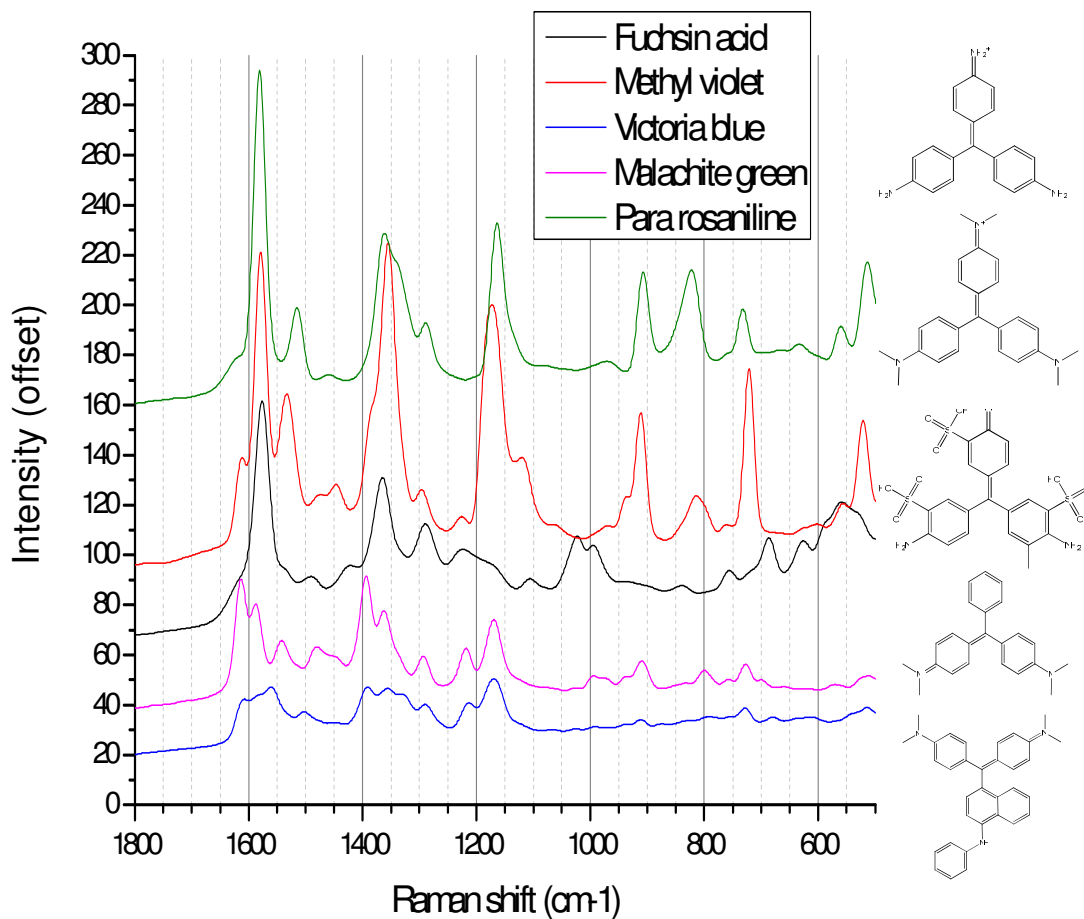


Table 7.2. Peak positions for triphenylmethane dye powders compared.

Published peak positions are given in brackets. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder

Peak positions in red are those which are proposed for identification.

Pararosaniline	Methyl violet (Cannamares et al. <sup>410</sup> )	Fuchsin acid	Malachite green	Victoria blue
	1611 (1617 w)		1613	1608
1581	1579 (1582 vs)	1576	1588	
				1560
	1533 (1536 w)		1542	
1515				
	(1480 vw)	1490	1481	
	1446 (1447 vw)			
	(1390 w)		1394	1391
1362	1355 (1357 s)	1365	1363	1356
1344(sh)	(1338 sh)			
1289	1296 (1299 vw)	1290	1293	1290
	(1228 vw)	1224	1218	1213
	(1185 m)			
1164	1173 (1170 m)		1170	1169
	1120(sh) (1133 sh)			
		1106		
		1023		
	(994 vw)	995		
	(973 vw)			
	936 (940 vw)			
907	911 (915 m)		910	
822	814 (621 vw)			
	(803 vw)		800	
	(767 vw)	756		
732	721 (724m)		727	728
		686		
	(628 vw)	626		
	(605 vw)			
560	556 (558 vw)			
513	521 (524 w)			

Most of the triphenylmethane dyes show a strong peak at about  $1600\text{cm}^{-1}$ , as seen in the azo dyes, characteristic of the phenyl group. They also show intense peaks at lower wavenumber differences which produce spectra which differ markedly from those for the azo dyes. The two dyes Methyl violet and Malachite green show three strong peaks between  $1800\text{cm}^{-1}$  and  $1000\text{cm}^{-1}$ . The exact positions vary between the two and can

<sup>410</sup> CANAMARES, M. V., CHENAL, C., BIRKE, R. L. & LOMBARDI, J. R. (2008) DFT, SERS and single-molecule SERS of Crystal Violet. *Journal of Physical Chemistry C*, 112, 20295-20300.

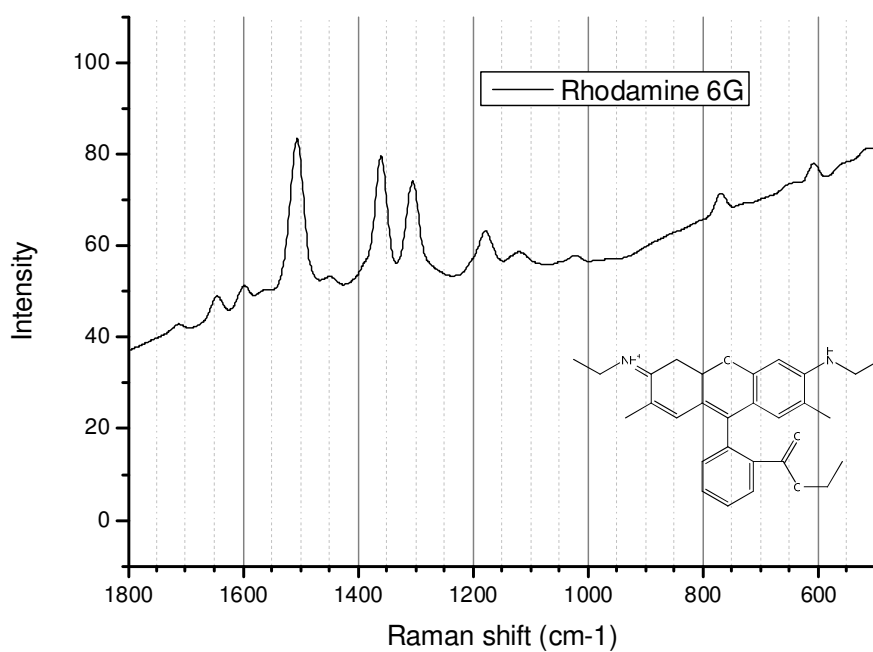
therefore be used for discrimination between them. Canamares et al<sup>411</sup> find only two strong peaks for Crystal violet but also report medium peaks at 1185 and 1170cm<sup>-1</sup>, the second of which corresponds to the third strong peak seen in these results.

Several of the other dyes showed substantial fluorescence and so were analysed at low laser power. For this reason the spectra have very different intensity ranges and are shown in separate figures (7.3 a-c) below.

Figure 7.3 FT-Raman spectra for Rhodamine 6G, Naphthol green and Safranine

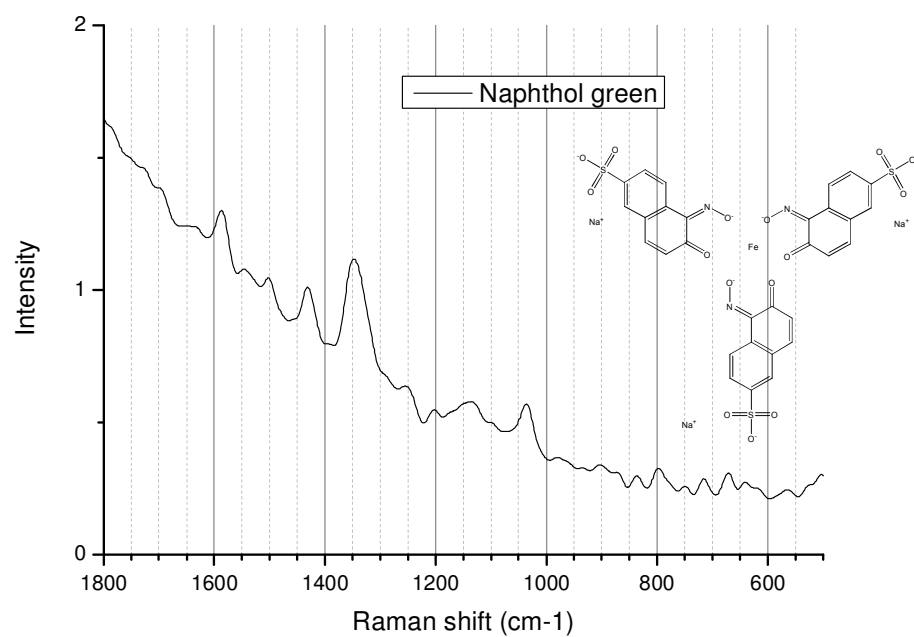
Laser power: 100mW for Rhodamine 6G; 75mW for Naphthol green; 15mW for Safranine

(a) Rhodamine 6G



<sup>411</sup> Ibid.

(b) Naphthol green



(c) Safranine

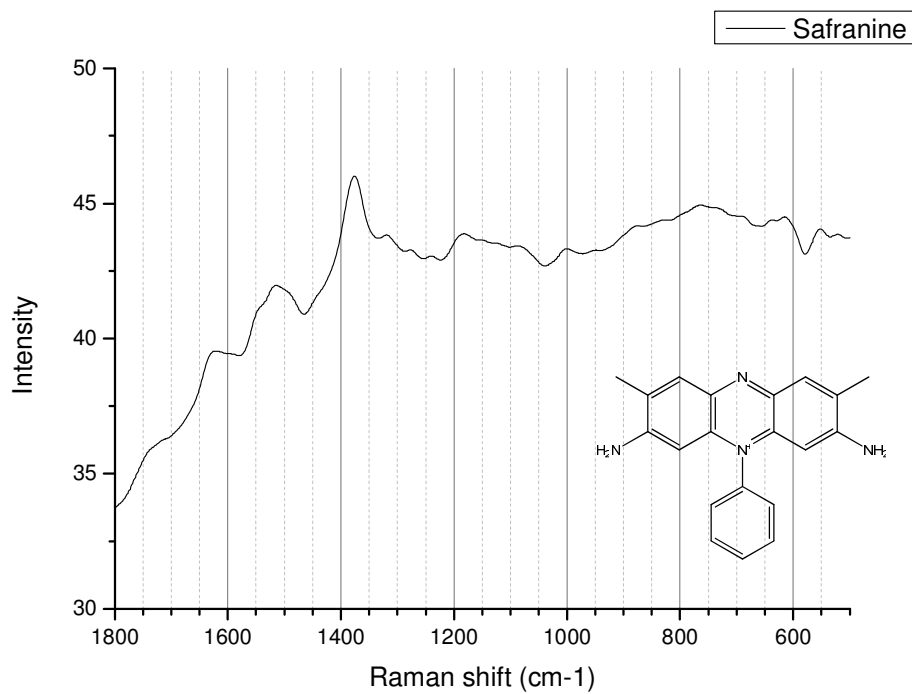


Table 7.3. Peak positions for other dye powders compared.

Published peak positions are given in brackets.

Peak positions in red are those which are proposed for identification.

Rhodamine 6G	Naphthol green	Safranine (Ciric-Marjanovic et al. <sup>412</sup> )
1711		
1645		
		(1632)
1597		
	1587	
		(1546)
1506	1502	(1505)
1449		
	1431	
1360		1376 (1420-1340 broad)
	1348	
1305		
		(1202)
1179		
1119		
	1036	
1022		
769		
608		

These dyes differ markedly in their structure from the others considered above and from each other. They are therefore not expected to show similarities and instead show marked differences. They are also different enough in spectral pattern to allow discrimination from the other dyes.

#### 7.1.2 Conclusions

The dye powders investigated here present characteristic ‘fingerprint’ spectra which can be used to distinguish the compounds. The fluorescence for some dyes meant that the laser power had to be reduced and only weak spectra were obtained. The next section of experimental work will examine the dyes on the fabric and investigate how closely they resemble the powder spectra.

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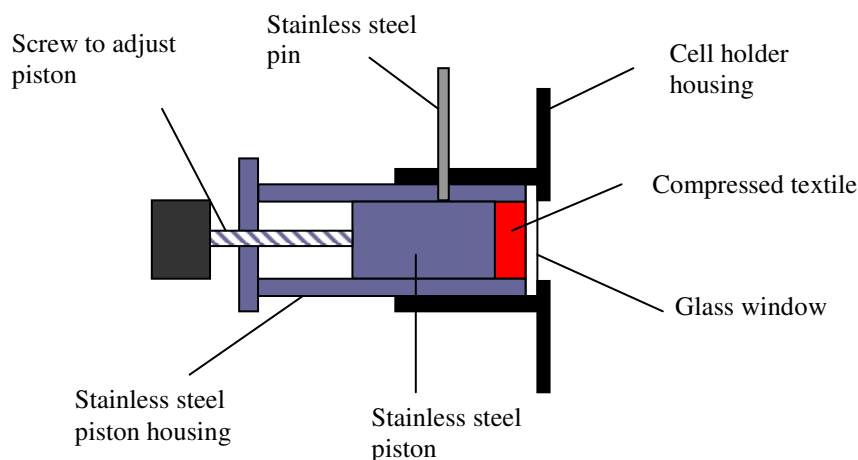
<sup>412</sup> CIRIC-MARJANOVIC, G., BLINOVA, N. V., TRCHOVA, M. & STEJSKAL, J. (2007) Chemical Oxidative Polymerization of Safranines. *Journal of Physical Chemistry B*, 111, 2188-2199.

## 7.2 FT-Raman spectra of dyed textiles

The method used for analysis of dye powders was applied to the samples of dyed silk and wool textiles. Pararosaniline was not used for dyeing and in other cases the fabric dyeing was completely unsuccessful or did not produce a sufficient concentration on the fabric. For these reasons no results can be presented for Methyl red or Para red. In other cases there was too much fluorescence seen to allow collection of a Raman spectrum and so no results are available for Victoria blue on either silk or wool or for Safranin on wool. No sample of Malachite green on wool was available.

The method followed was the same but with variations of the instrumental set-up which are listed in Appendix 4. Wool and silk fabrics were inserted in a sample holder and compressed (Figure 7.4). This maximized the volume of dyed sample within the laser spot and therefore increased the signal intensity. The holder is dismantled by removing the peg allowing the piston and piston housing to be removed from the shell of the holder. The glass window is also loose in the shell. The fabric sample was cut into circles of approximately 8mm (the same diameter as the piston) and inserted into a space created above the piston in the piston housing by withdrawing the piston into the body of the housing. With the glass window in place at the bottom of the shell of the holder, the assembled fabric, piston and piston housing was then re-inserted. The piston housing was then locked into the shell by means of the peg and the fabric compressed against the window by tightening the screw. The entire sample holder was manufactured to engage in a pre-existing fitment within the FT-Raman instrument which held the sample in an appropriate position in the laser beam.

Figure 7.4 Cross-sectional diagram of holder for textile samples.



### Data manipulation

The software package Origin® 8.1 was used for data manipulation. The baselines were manually subtracted from the spectra for dyed and undyed fabrics which were then normalised<sup>413</sup> with respect to the largest fabric peak (around  $3000\text{cm}^{-1}$  Raman shift). This peak was picked manually but the normalization could be performed by the software. The normalised undyed fabric spectra were then subtracted within the software from the dyed fabric spectra. The undyed spectra used for subtraction were obtained in the same experimental session as the dyed spectra in order to minimise any inaccuracies due to variations in instrument set up. The resultant spectra and the spectra obtained for the dye powders were then normalised on the strongest dye peak so that they could be compared.

#### 7.2.1 Results and discussion

The following section shows the results for the dyed textiles. The spectra have been manipulated to remove the textile spectrum and facilitate comparison. The subtraction of the baseline is performed manually from both the dyed and undyed spectra. Each baseline has to be subtracted individually as the fluorescence patterns are different for each sample

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<sup>413</sup> This operation allows comparison of related spectra. It consists of dividing the entire spectrum by the height of a peak which arises from a vibration seen in both spectra, resulting in a height of 1.0 for that peak and it corrects for minor variations in spectral intensity due to, for example, laser power variations.

and slight inaccuracies can produce negative peaks as seen in Figure 7.6 (Acid yellow 17).<sup>414</sup> Nevertheless, the results are still sufficiently clear to allow comparison of the spectra.

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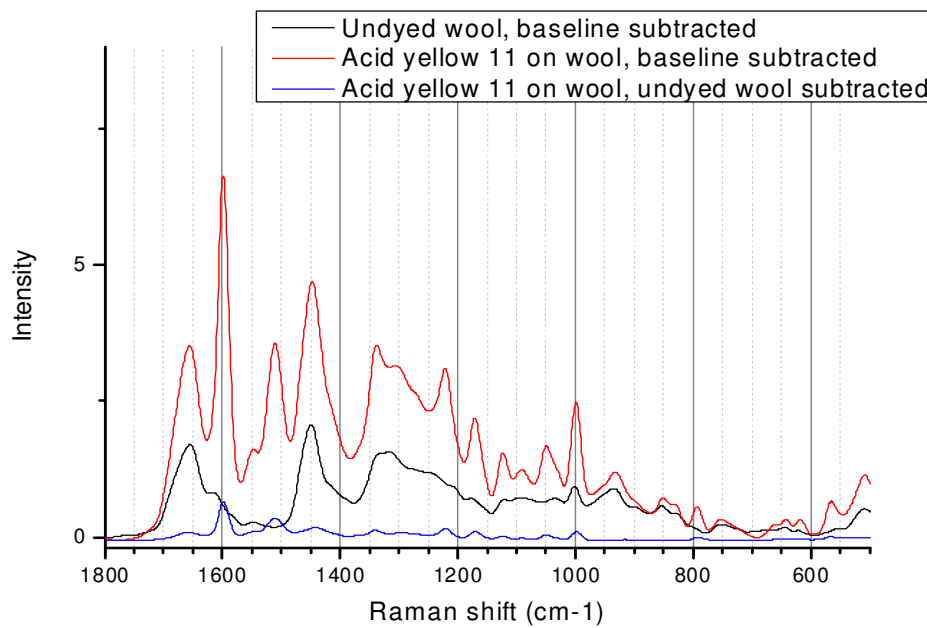
<sup>414</sup> The same phenomenon can also be seen in published spectra, for example SMITH, E. & DENT, G. (2005) *Modern Raman Spectroscopy. A Practical Approach*, Chichester, John Wiley and Sons Ltd., page 38.



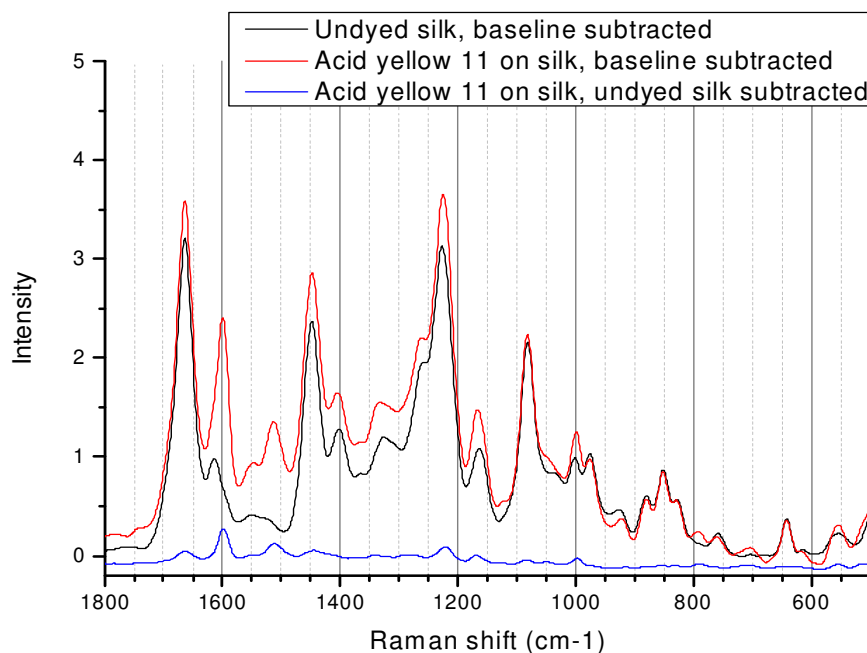
## Results for azo dyes

Figure 7. 5 Acid yellow 11 azo dye on silk and wool

(a) Comparison of spectra on wool. Undyed and dyed wool with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2932\text{cm}^{-1}$ .



(b) Comparison of spectra on silk. Undyed and dyed silk with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2934\text{cm}^{-1}$ .



(c) Comparison of spectra for Acid yellow 11 powder with the dye spectra extracted from silk and wool.

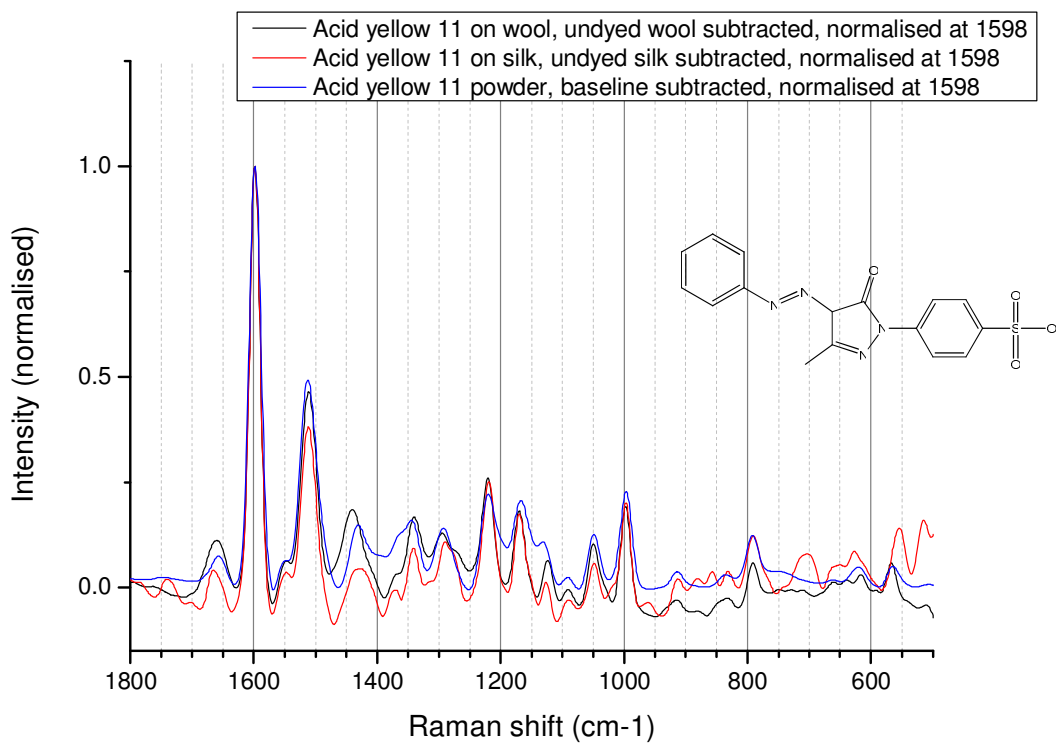
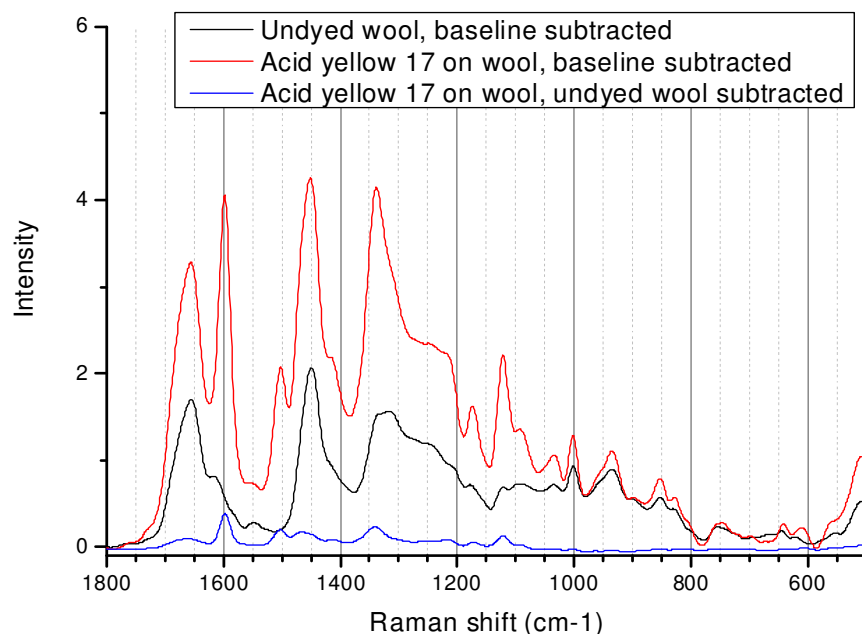


Table 7.4 Peak positions for Acid yellow 11 powder and on silk and wool

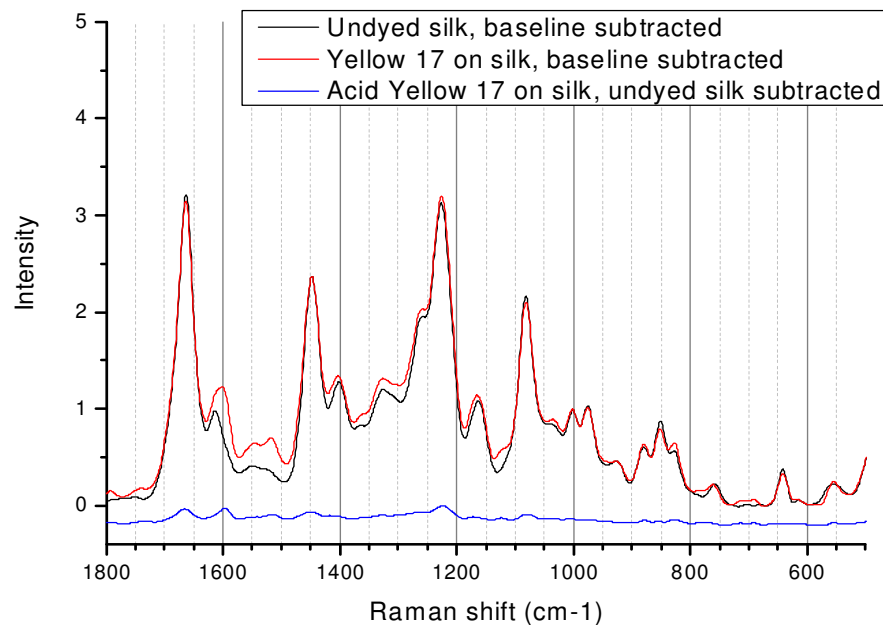
Acid yellow 11 powder		Acid yellow 11 with wool textile subtracted		Acid yellow 11 with silk textile subtracted	
Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity
1657	0.07	1660	0.11	1665	0.04
1598	1.00	1598	1.00	1598	1.00
1548(sh)	0.06	1547(sh)	0.06	1547(sh)	0.04
1512	0.49	1511	0.47	1512	0.38
1431	0.15	1440	0.18	1426	0.04
1344	0.16	1340	0.17	1341	0.09
1293	0.14	1295	0.13	1290	0.11
1220	0.22	1221	0.26	1219	0.25
1167	0.21	1170	0.18	1170	0.18
1132	0.11	1124	0.06	1127	0.01
1091	0.02	1094	-0.01	1090	-0.03
1049	0.13	1050	0.10	1049	0.06
997	0.23	998	0.19	997	0.20

Figure 7.6 Acid yellow 17 azo dye on silk and wool

(a) Comparison of spectra on wool. Undyed and dyed wool with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2932\text{cm}^{-1}$ .



(b) Comparison of spectra on silk. Undyed and dyed silk with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2934\text{cm}^{-1}$ .



(c) Comparison of spectra for Acid yellow 17 powder with the dye spectra extracted from silk and wool.

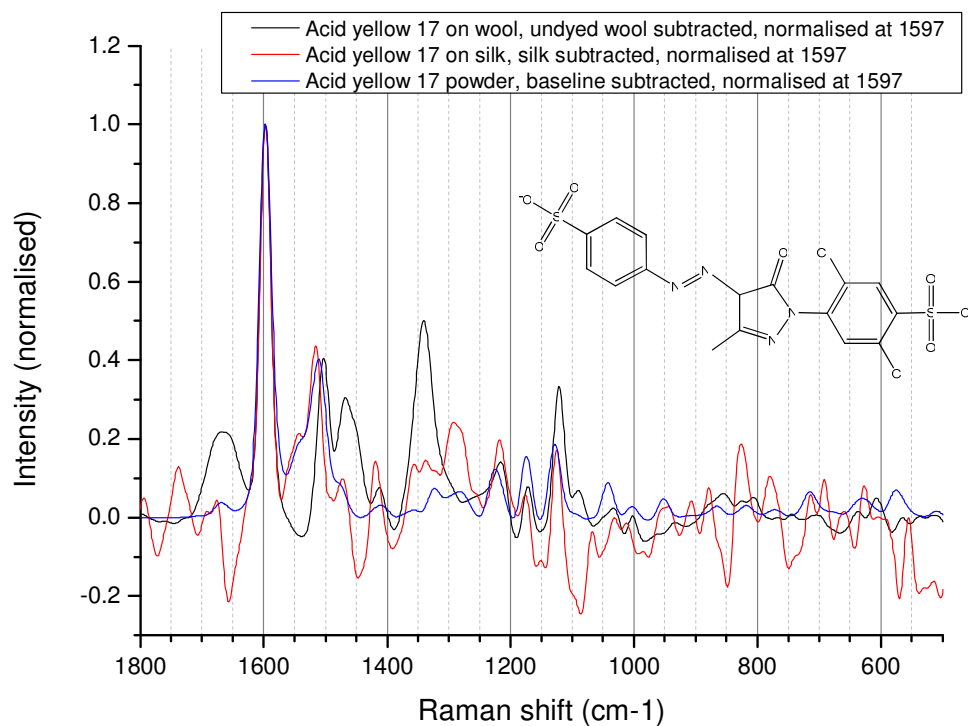
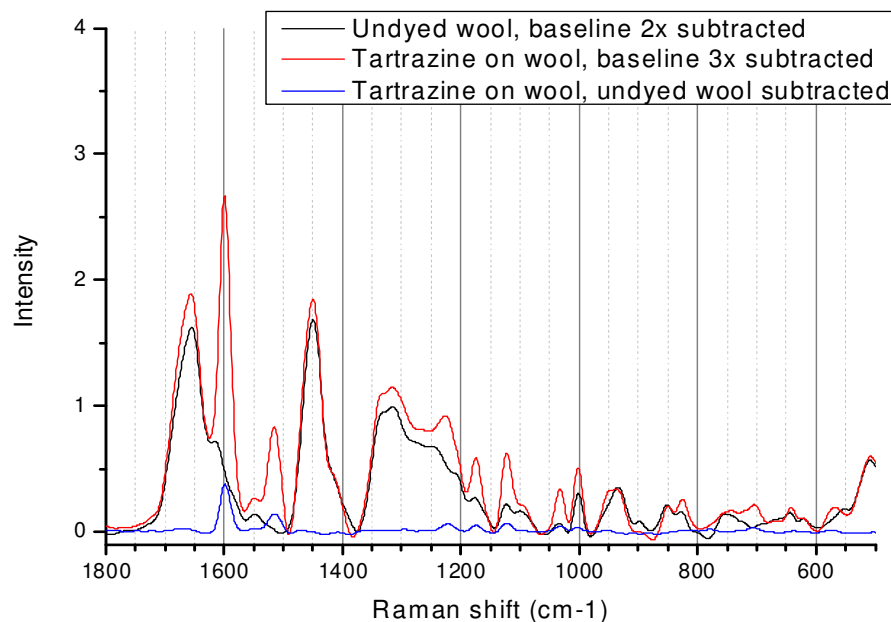


Table 7.5 Peak positions for Acid yellow 17 powder and on silk and wool

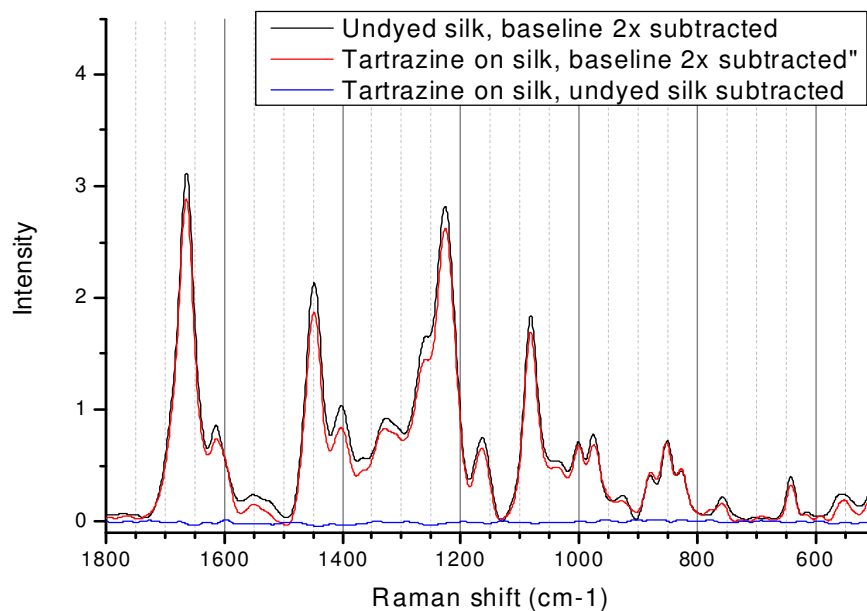
Acid yellow 17 powder		Acid yellow 17 with wool textile subtracted		Acid yellow 17 with silk textile subtracted	
Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity
1669	0.04	1668	0.22		
1597	1.00	1597	1.00	1597	1.00
1511	0.40	1503	0.41	1516	0.44
		1468	0.31	1472	0.10
1411	0.03	1413	0.08	1419	0.14
				1356	0.13
1323	0.07	1341	0.50	1337	0.15
1282	0.12			1292	0.24
1225	0.12	1216	0.14	1218	0.20
1174	0.16	1172	0.08	1176	0.06
1128	0.19	1121	0.33	1125	0.17
		1090 (sh)	0.07	1067	-0.04
1042	0.09	1033	0.02	1032	0
1003	0.03	1002	0	1012	-0.01

Figure 7.7 Tartrazine azo dye on silk and wool

(a) Comparison of spectra on wool. Undyed and dyed wool with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2932\text{cm}^{-1}$ .



(b) Comparison of spectra on silk. Undyed and dyed silk with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2934\text{cm}^{-1}$ .



(c) Comparison of spectra for Tartrazine powder with the dye spectra extracted from silk and wool.

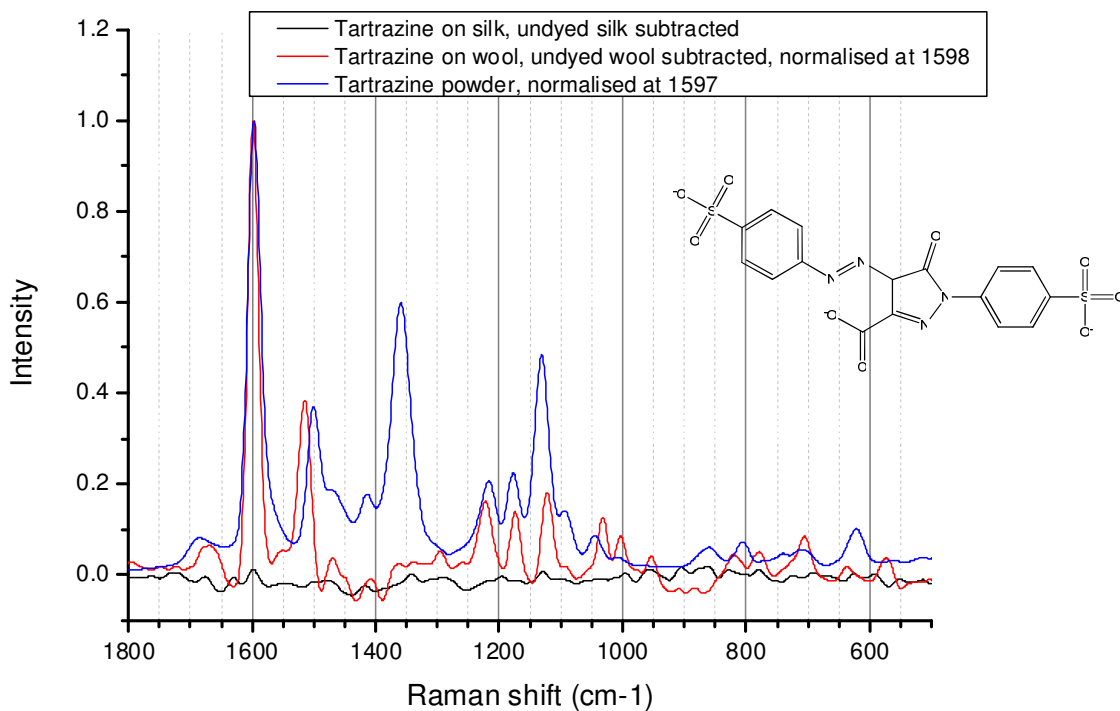


Table 7.6 Peak positions for Tartrazine powder and on wool

Tartrazine powder		Tartrazine with wool textile subtracted	
Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity
1684	0.08	1669	0.06
1597	1.00	1598	1.00
1500	0.37	1515	0.38
1470 (sh)	0.19	1470	0.04
1414	0.18	1408	-0.01
1359	0.60		
1217	0.21	1222	0.18
1177	0.22	1174	0.14
1131	0.48	1122	0.18
1094 (sh)	0.14	1093 (sh)	0.02
1045	0.09	1032	0.13
1008	0.04	1003	0.08

Figures 7.5, 7.6 and 7.7 for the related group of azo dyes show that in all cases a prominent peak at 1597/1598cm<sup>-1</sup> is seen on the dyed fabrics as it is for the powder. The trio of peaks

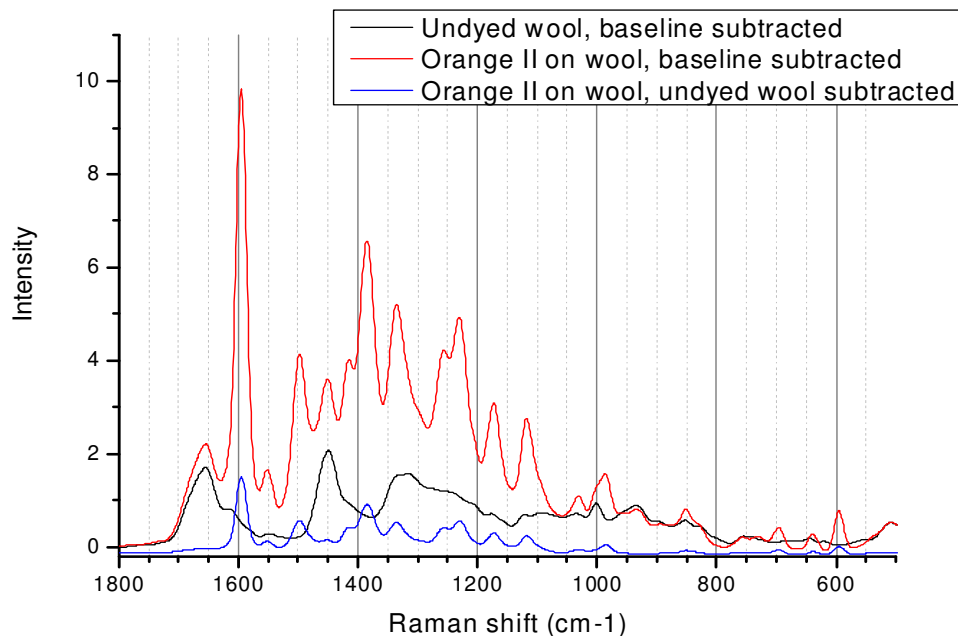
between  $1217\text{-}1225\text{cm}^{-1}$ ,  $1167\text{-}1177\text{cm}^{-1}$  and  $1128\text{-}1132\text{cm}^{-1}$  are also seen on the fibres although the spread of the peak positions is increased slightly.

The shifts in the peak positions could be due to changes in instrumental configuration. Where the resolution or other settings are changed, a consistent shift in peak positions may be seen. However, the changes seen here are neither consistently positive nor negative and therefore another explanation is more likely. The dyes interact via electrostatic forces with the fibre and this is likely to alter the electronic environment of the molecules which could account both for the slight changes in the vibrational energies seen in the peak shifts and in intensities. The acid groups of the molecules are the points of interaction with the fibre and the simplest molecule, Acid yellow 11 (Figure 7.5), has only one of these groups and therefore only one such attachment point. This is also the dye which shows the best correspondence between the three spectra and thus shows conservation of its vibrational energies under these different conditions. Acid yellow 17 (Figure 7.6) has two acid groups and therefore greater possible interaction with the fibre and this dye indeed shows greater differences between the spectra. Some of the peaks are significantly shifted and some only appear in one or two of the spectra.

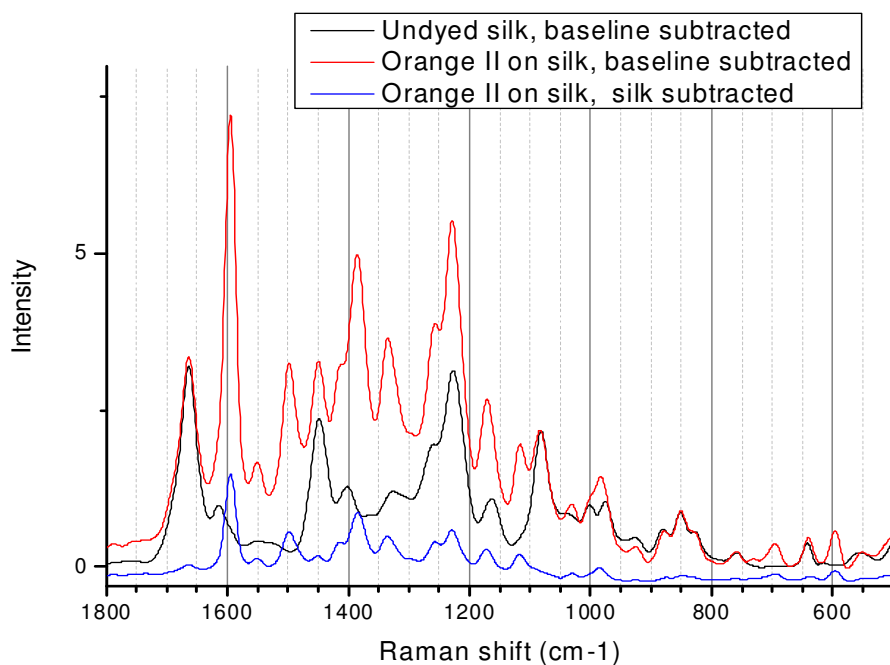
Tartrazine on silk shows virtually no vibrational energies due to the dye and there are a number of reasons why this might be so, for example, the concentration of dye on the fibres may be different. Although the same concentration of dye and the same dye procedure were used throughout the sample preparation, the level of uptake from the solution may vary depending on the dye and the fibre. Tartrazine (Figure 7.7) has three acid groups capable of interaction with the fibre and one molecule may therefore occupy more interaction sites than one molecule of the other dyes, limiting the total density of dye compound. In the powdered sample this dye gave the highest intensity spectrum of the three but it is the only one for which no reasonable spectrum for the dye could be extracted from the dyed silk textile. Possibly the Raman active vibrational energies have been suppressed by the close interaction with the silk fabric.

Figure 7.8 Orange II azo dye on silk and wool

(a) Comparison of spectra on wool. Undyed and dyed wool with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2932\text{cm}^{-1}$ .



(b) Comparison of spectra on silk. Undyed and dyed silk with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2934\text{cm}^{-1}$ .





(c) Comparison of spectra for Orange II powder with the dye spectra extracted from silk and wool.

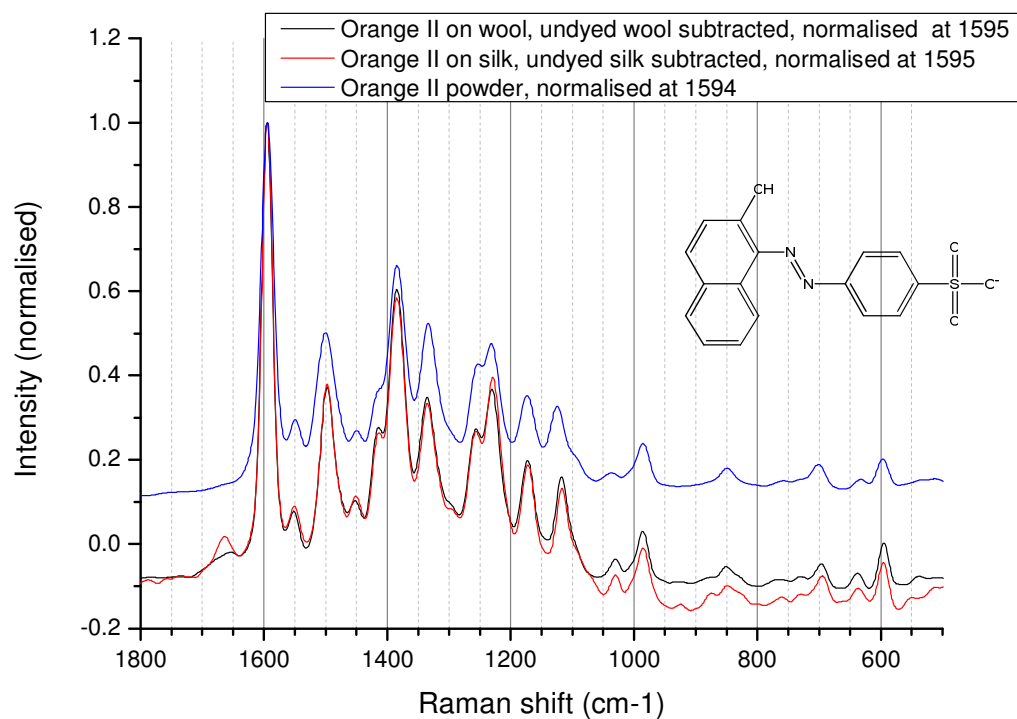
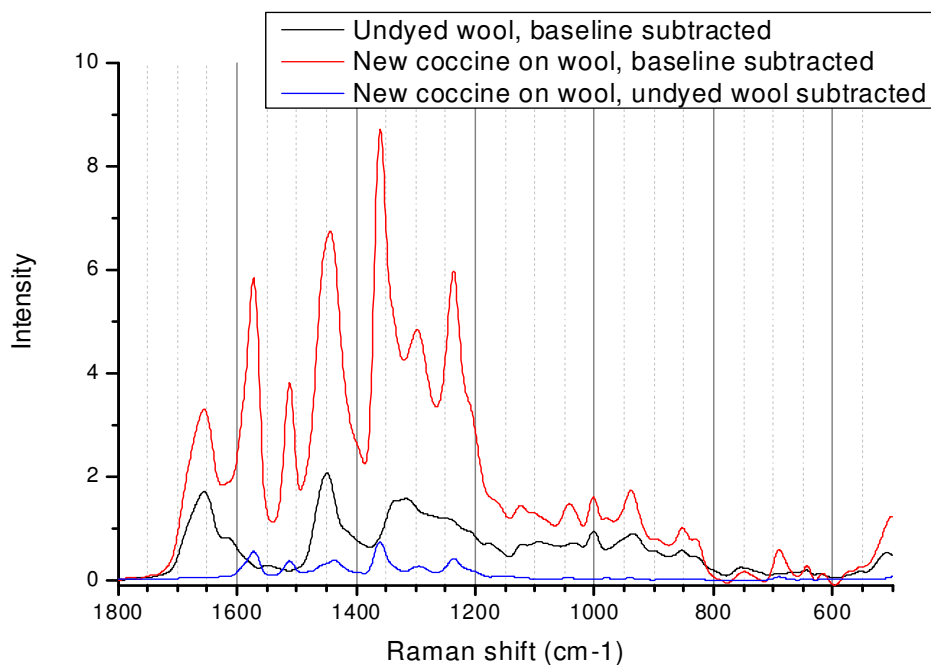


Table 7.7 Peak positions for Orange II powder and on silk and wool

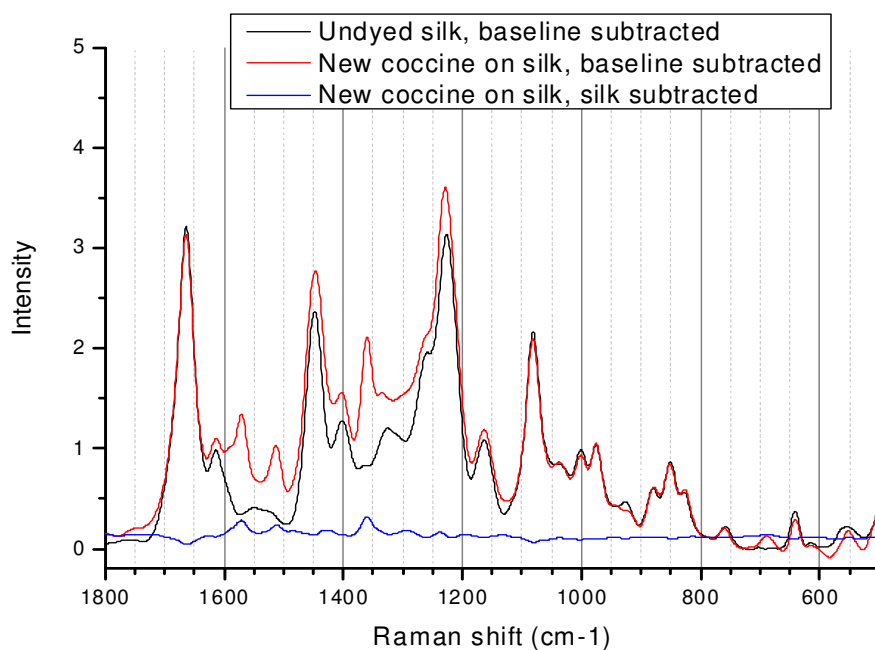
Orange II powder		Orange II with wool textile subtracted		Orange II with silk textile subtracted	
Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity
				1664	0.02
1594	0.30	1595	1.00	1595	1.00
1549	0.30	1552	0.08	1551	0.09
1500	0.50	1498	0.37	1498	0.38
1450	0.27	1452	0.10	1451	0.11
1414 (sh)	0.37	1414	0.28	1414	0.26
1384	0.66	1385	0.60	1385	0.58
1334	0.52	1336	0.35	1335	0.33
1253	0.43	1256	0.27	1256	0.27
1231	0.48	1230	0.37	1229	0.40
1173	0.35	1172	0.20	1172	0.19
1125	0.33	1118	0.16	1117	0.16
1037	0.17	1030	-0.04	1030	-0.07
985	0.24	986	0.03	985	-0.01
850	0.18	851	-0.05	849	-0.01
701	0.19	697	-0.05	695	-0.08
633	0.15	638	-0.07	637	-0.10
597	0.20	595	0.00	596	-0.04

**Figure 7.9 New cocchine azo dye on silk and wool**

(a) Comparison of spectra on wool. Undyed and dyed wool with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2932\text{cm}^{-1}$ .



(b) Comparison of spectra on silk. Undyed and dyed silk with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2934\text{cm}^{-1}$ .



(c) Comparison of spectra for New coccine powder with the dye spectra extracted from silk and wool.

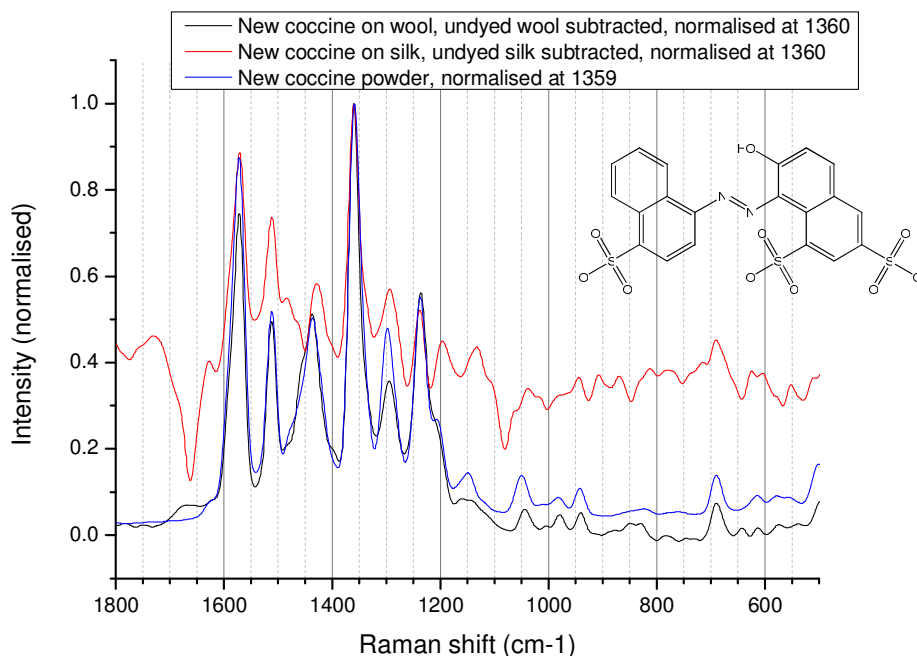


Table 7.8 Peak positions for New coccine powder and on silk and wool

New coccine powder		New coccine with wool textile subtracted		New coccine with silk textile subtracted	
Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity
				1627	0.40
1572	0.88	1572	0.75	1571	0.89
1512	0.52	1512	0.50	1512	0.74
				1484	0.55
1436	0.50	1437	0.51	1428	0.58
1359	1.00	1360	1.00	1360	1.00
1298	0.48	1295	0.36	1294	0.57
1237	0.55	1236	0.56	1238	0.52
1207 (sh)	0.27			1196	0.45
1149	0.14	1160	0.08	1132	0.44
1050	0.14	1044	0.06	1038	0.34
		1005	0.02		
982	0.09	980	0.05		
942	0.11	940	0.05		
690	0.14	690	0.07	690	0.45
		642	0.02		
615	0.09	613	0.02		

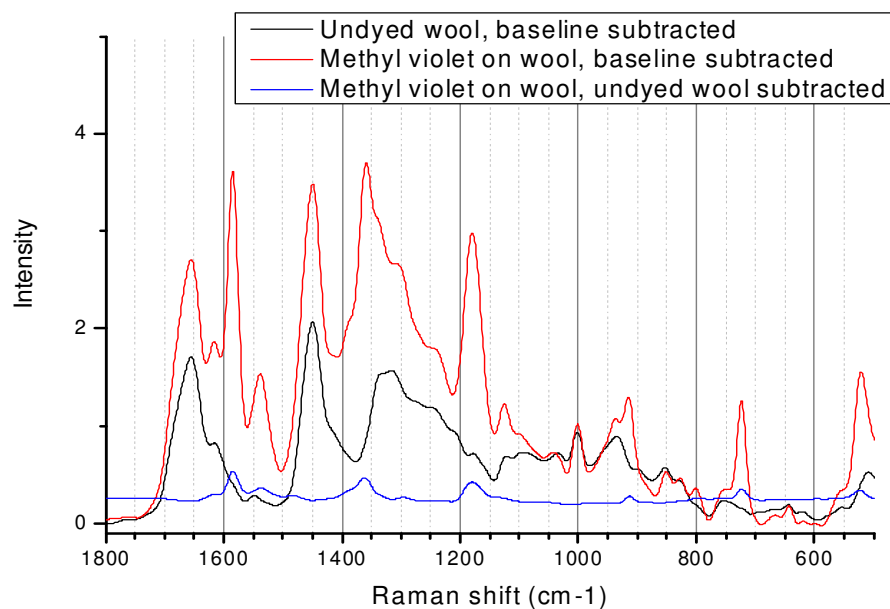
Orange II (Figure 7.8) and New coccine (Figure 7.9) are two further azo dyes which are structurally related to each other. They both show good correlations between the spectra for powder, silk and wool spectra, especially above  $1000\text{cm}^{-1}$ . Although New coccine has three

sulphonic acid groups and Orange II only one, there is not so much variation in intensity of the Raman spectrum seen between these dyes as between Acid yellows 11 and 17 and Tartrazine. Nevertheless, New coccine on silk does show the lowest intensity spectrum on silk.

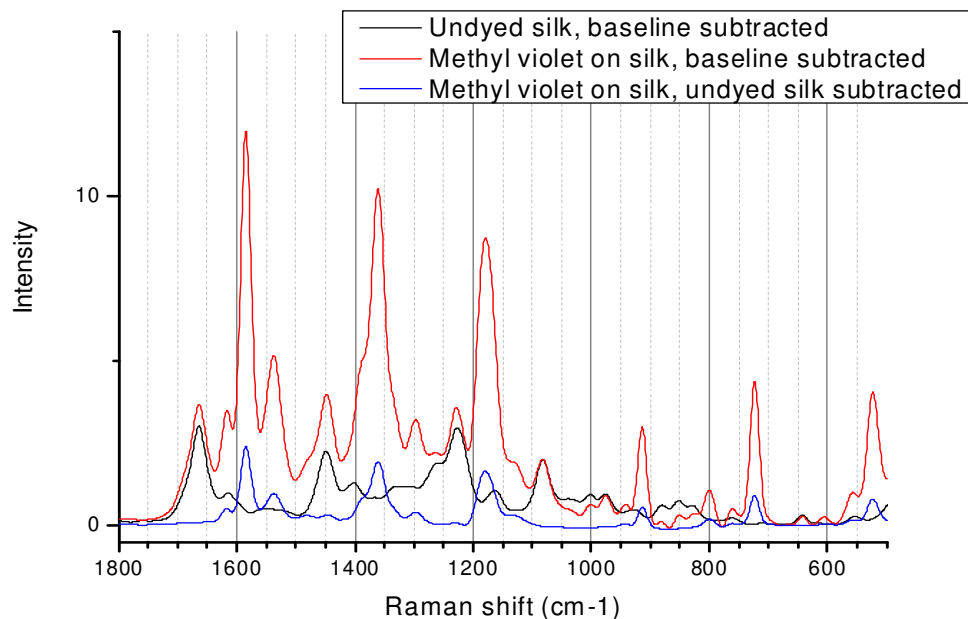
## Results for triphenylmethane dyes

**Figure 7.10 Methyl violet triphenylmethane dye on silk and wool**

(a) Comparison of spectra on wool. Undyed and dyed wool with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2932\text{cm}^{-1}$ .



(b) Comparison of spectra on silk. Undyed and dyed silk with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2934\text{cm}^{-1}$ .



(c) Comparison of spectra for Methyl violet powder with the dye spectra extracted from silk and wool.

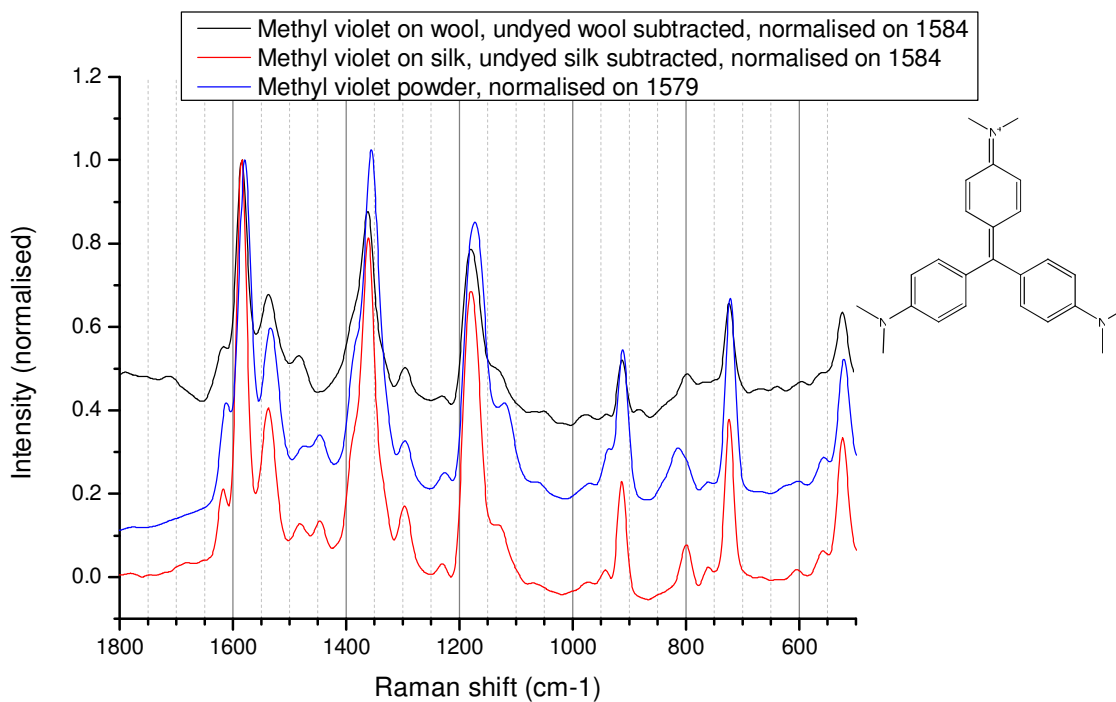
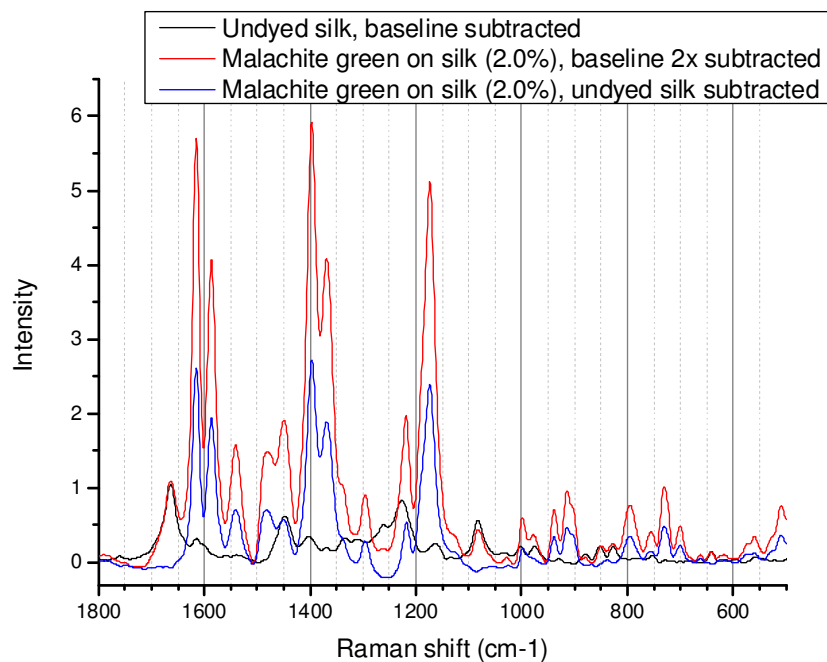


Table 7.9 Peak positions for Methyl violet powder and on wool and silk

Methyl violet powder		Methyl violet with wool textile subtracted		Methyl violet with silk textile subtracted	
Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity
1611	0.42	1616 (sh)	0.55	1617	0.21
1579	1.00	1584	1.00	1584	1.00
1533	0.60	1537	0.68	1537	0.40
1474 (sh)	0.31	1484	0.53	1482	0.13
1446	0.34			1446	0.13
1355	1.03	1362	0.88	1361	0.81
1296	0.33	1296	0.50	1297	0.17
1226	0.25	1231	0.43	1230	0.03
1173	0.85	1180	0.79	1180	0.69
1120	0.42			1134 (sh)	0.12
969 (sh)	0.22	976	0.39	972	-0.01
936	0.31	940	0.39	942	0.02
911	0.54	913	0.52	913	0.23
		883	0.40		
814	0.31				
		798	0.49	799	0.08
761 (sh)	0.23			761	0.02
721	0.67	723	0.66	723	0.38
602	0.23	595	0.47	604	0.02
556	0.29	562 (sh)	0.50	558	0.06
521	0.52	524	0.63	523	0.33

**Figure 7.11 Malachite green triphenylmethane dye on silk**

(a) Comparison of spectra on silk. Undyed and dyed silk with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2934\text{cm}^{-1}$ .



(b) Comparison of spectra for Malachite green powder with the dye spectra extracted from silk.

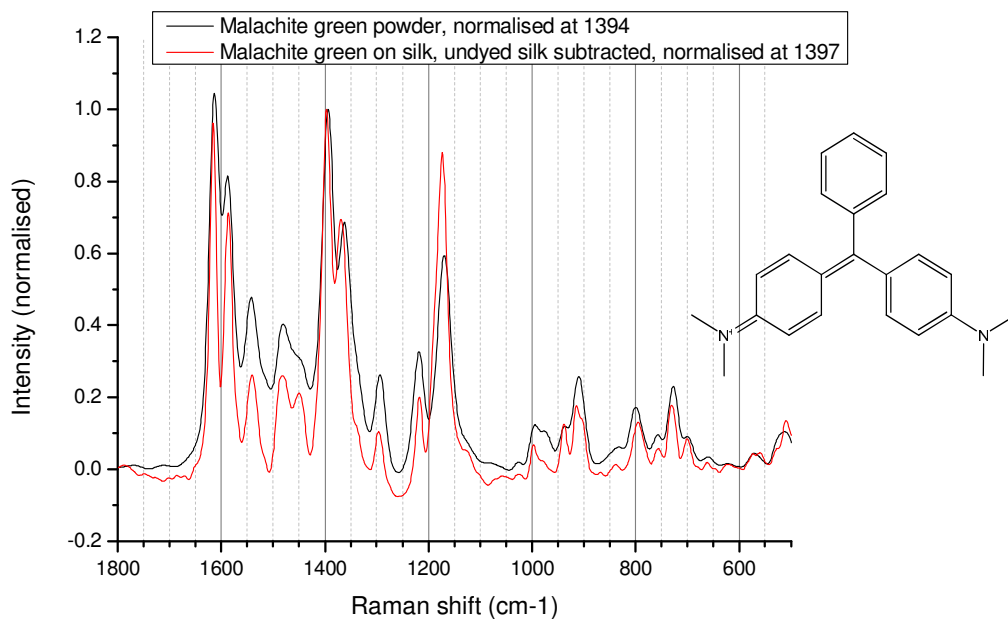
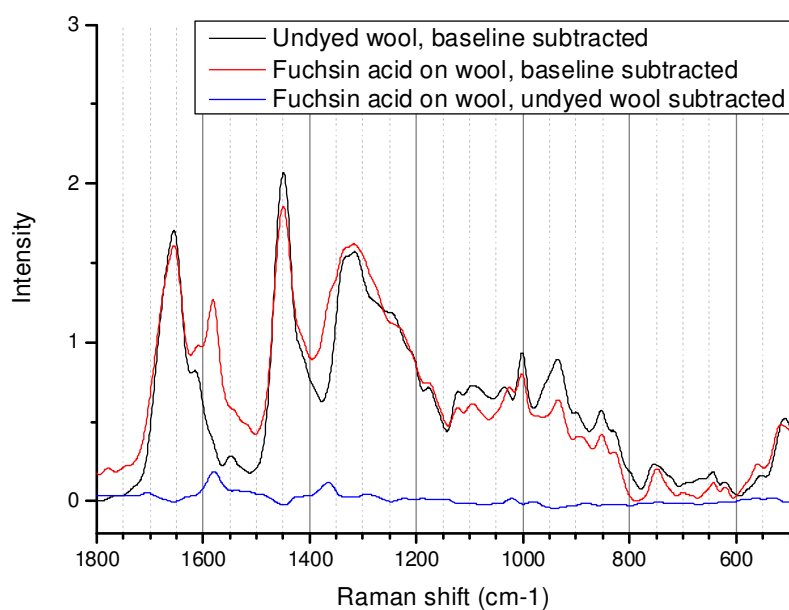


Table 7.10 Peak positions for Malachite green powder and on silk

Malachite green powder		Malachite green with silk textile subtracted	
Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity
1613	1.04	1616	0.96
1588	0.82	1587	0.71
1542	0.48	1540	0.26
1481	0.40	1482	0.26
		1450	0.21
1394	1.00	1397	1.00
1363	0.69	1369	0.70
1293	0.26	1296	0.11
1218	0.33	1217	0.20
1170	0.59	1173	0.88
994	0.12	997	0.07
977 (sh)	0.11		
937 (sh)	0.12	938	0.13
910	0.26	914	0.18
800	0.17	795	0.13
757	0.10	756	0.06
727	0.23	731	0.18
700	0.09	701	0.08

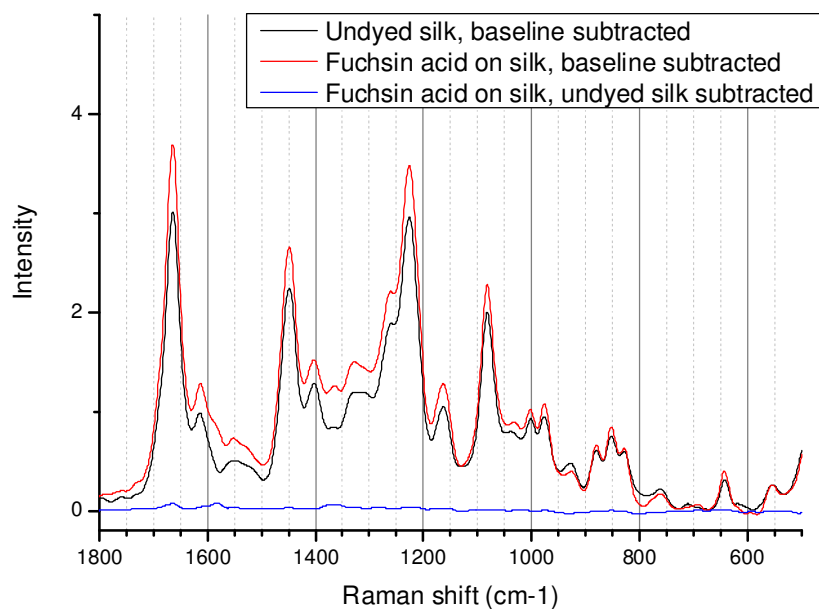
Figure 7.12 Fuchsin acid triphenylmethane dye on silk and wool

(a) Comparison of spectra on wool. Undyed and dyed wool with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at 2932cm<sup>-1</sup>.





(b) Comparison of spectra on silk. Undyed and dyed silk with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2934\text{cm}^{-1}$ .



(c) Comparison of spectra for Fuchsin acid powder with the dye spectra extracted from silk.

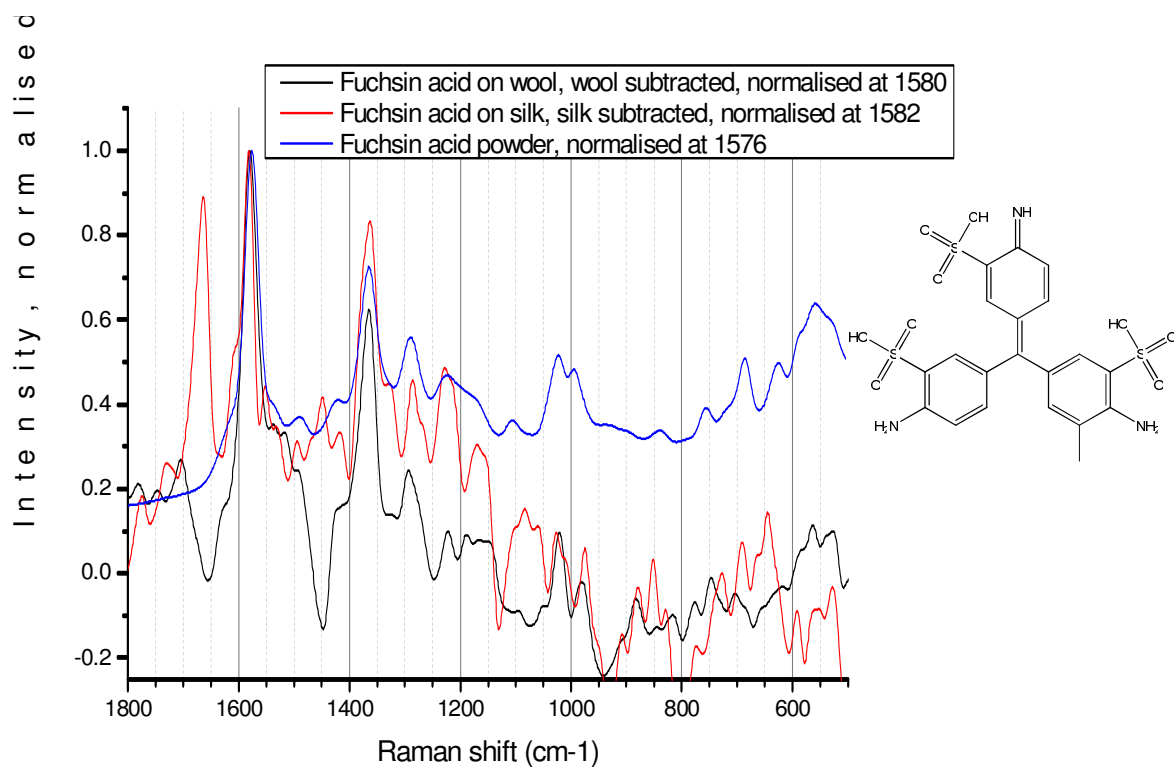


Table 7.11 Peak positions for Fuchsin acid powder and on silk and wool

Fuchsin acid powder		Fuchsin acid with wool textile subtracted		Fuchsin acid with silk textile subtracted	
Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity
		1704	0.27		
				1664	0.89
1576	1.00	1580	1.00	1582	1.00
				1552	0.44
1490	0.37			1495	0.31
				1449	0.42
				1418	0.33
1365	0.72	1365	0.62	1363	0.83
1290	0.56	1293	0.24	1286	0.46
1224	0.47	1222	0.10	1228	0.49
				1169	0.30
1106	0.36				
				1084	0.15
1023	0.52	1021	0.10	1027	0.10
995	0.48	981	-0.02	975	0.06

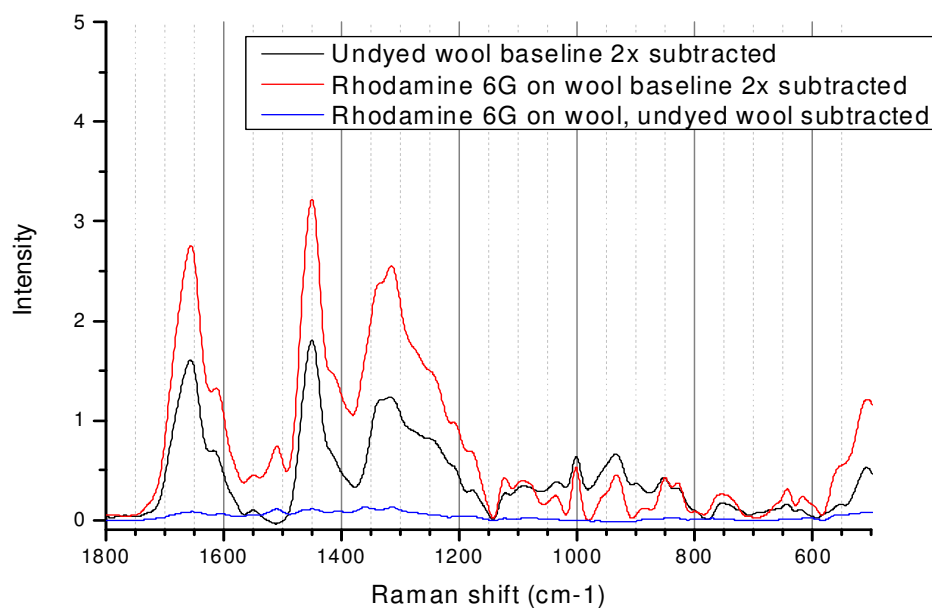
Methyl violet and Malachite green both show excellent agreement between the spectra under the different conditions. The peak position variations are very small and the relative intensities of the peaks are conserved. There is a good possibility that these dyes might be identifiable on fabric by FT-Raman spectroscopy.

Fuchsin acid, particularly on silk, shows very weak spectra and therefore the subtracted spectra show a high level of random variation. Nevertheless, two conserved peaks at about 1580 and 1365cm<sup>-1</sup> do emerge.

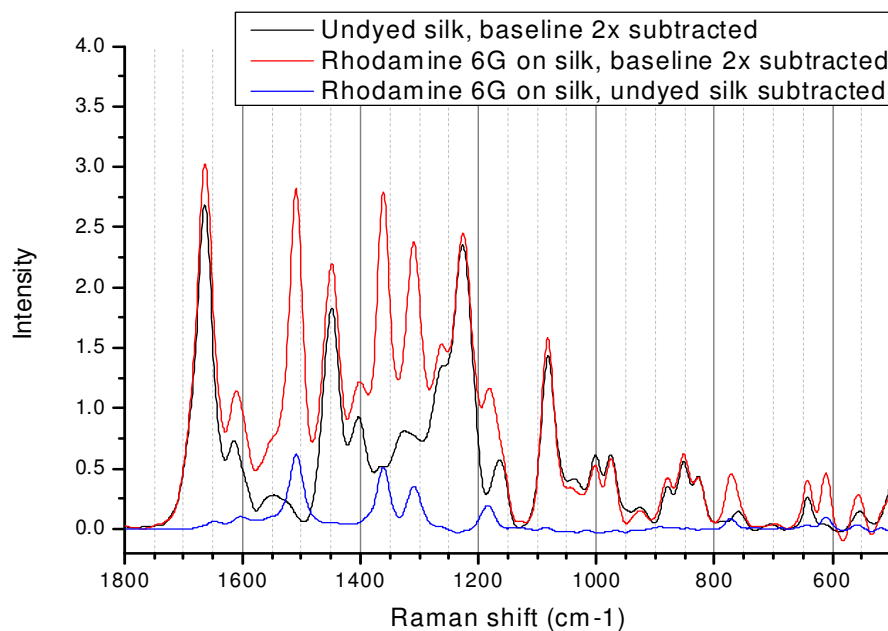
## Results for other dyes

**Figure 7.13 Rhodamine 6G on silk and wool**

(a) Comparison of spectra on wool. Undyed and dyed wool with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2932\text{cm}^{-1}$ .



(b) Comparison of spectra on silk. Undyed and dyed silk with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2934\text{cm}^{-1}$ .



(c) Comparison of spectra for Rhodamine 6G powder with the dye spectra extracted from silk and wool.

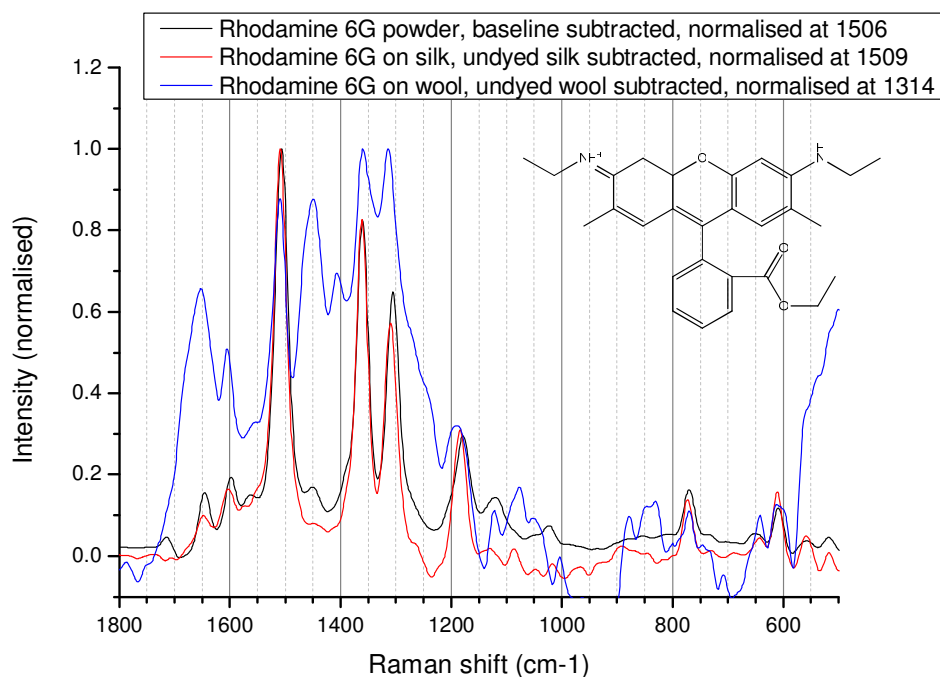


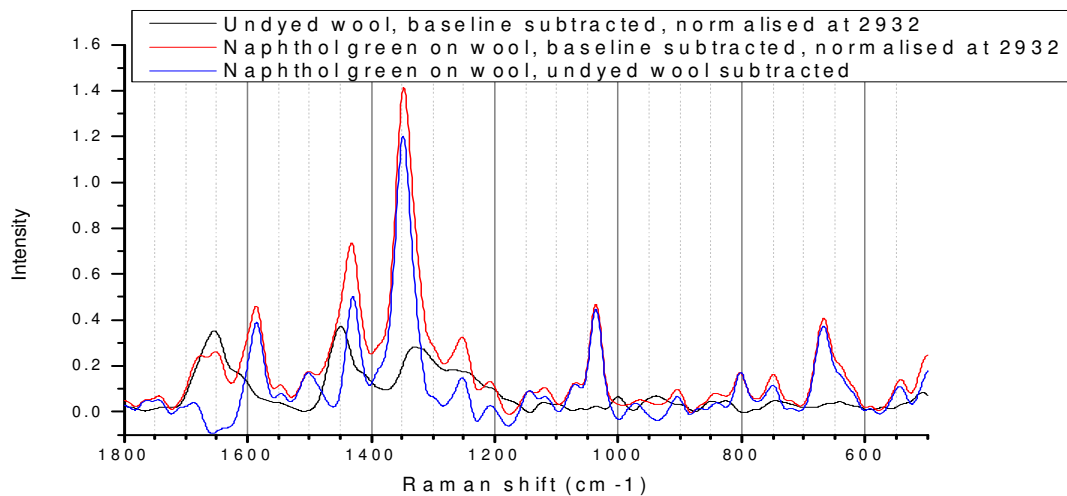
Table 7.12 Peak positions for Rhodamine 6G powder and on wool and silk

Rhodamine 6G powder		Rhodamine 6G with wool textile subtracted		Rhodamine 6G with silk textile subtracted	
Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity
1714	0.05				
1645	0.16	1652	0.66	1648	0.10
1595	0.19	1605	0.51	1603	0.16
1562	0.15	1553 (sh)	0.33	1573 (sh)	0.12
1506	1.00	1509	0.88	1509	1.00
1450	0.17	1449	0.88	1449 (sh)	0.08
		1406	0.69		
1360	0.83	1360	1.00	1361	0.83
1305	0.65	1314	1.00	1309	0.57
1179	0.30	1190	0.32	1184	0.31
1121	0.14	1122	0.11	1130	0.02
		1077	0.17	1087	0.02
		1052	0.09	1048	-0.03
1023	0.07			1017	-0.02
		1004	0.00		
770	0.16	770	0.11	773	0.14
		642	0.10	643	0.04
609	0.12	612	0.13	611	0.16

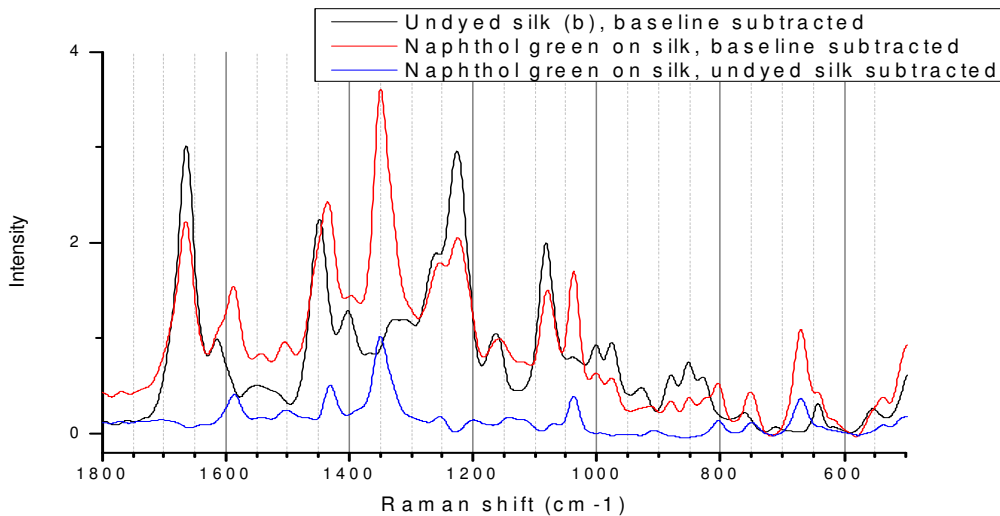
Rhodamine 6G on silk shows very good correlation with the powder spectrum but the dye on wool, whilst having many peak positions in common, shows greater variation in peak height.

Figure 7.14 Naphthol green dye on silk

(a) Comparison of spectra on wool. Undyed and dyed wool with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2932\text{cm}^{-1}$ .



(b) Comparison of spectra on silk. Undyed and dyed silk with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2934\text{cm}^{-1}$ .



(c) Comparison of spectra for Naphthol green powder with the dye spectra extracted from silk and wool.

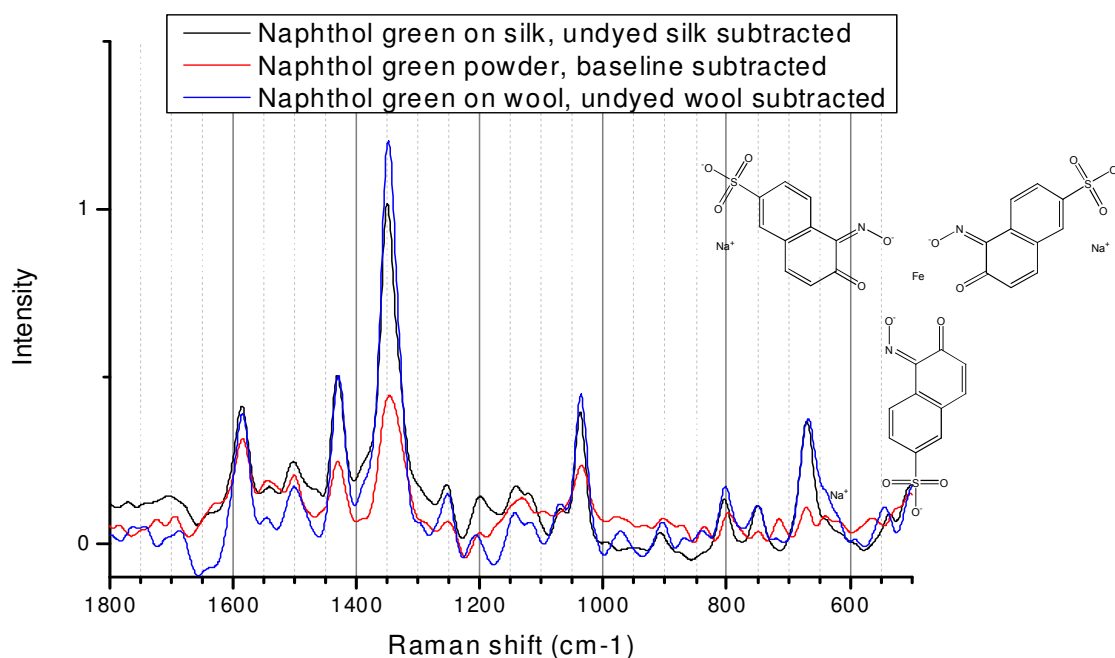


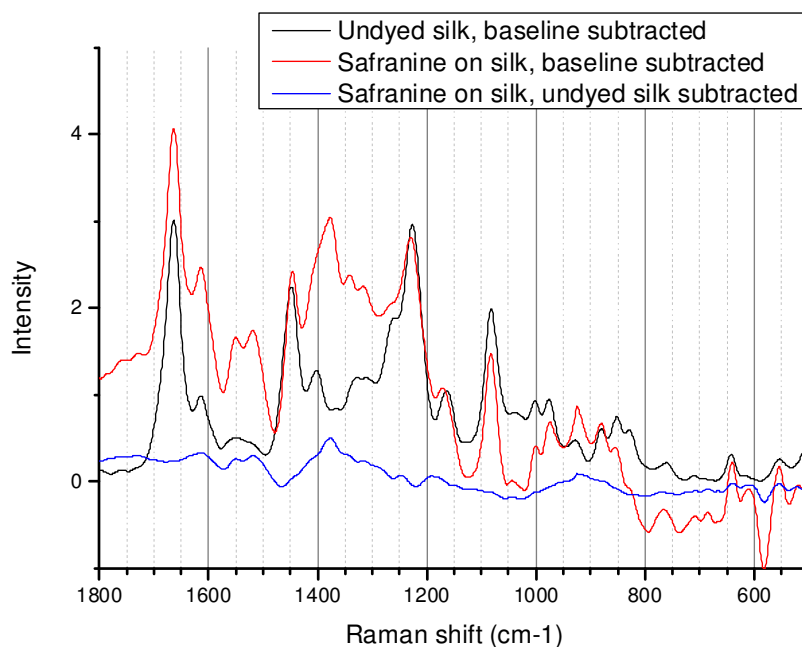
Table 7.13 Peak positions for Naphthol green powder and on silk and wool

Naphthol green powder		Naphthol green with silk textile subtracted		Naphthol green with wool textile subtracted	
Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Intensity
1585	0.31	1586	0.41	1585	0.39
1544	0.19	1541	0.17	1546	0.08
1501	0.20	1502	0.25	1500	0.17
1431	0.25	1431	0.50	1429	0.50
1347	0.44	1350	1.01	1348	1.20
1252	0.07	1254	0.18	1252	0.15
1201	0.03	1201	0.14	1207	0.03
		1142	0.17	1143	0.09
1132	0.14				
		1121 (sh)	0.15	1119	0.07
		1069	0.10	1070	0.12
1035	0.24	1037	0.39	1036	0.45
				972	0.04
903	0.08	908	0.03	904	0.07
873	0.06				
836	0.05			840	0.04
797	0.09	803	0.13		
749	0.04	750	0.11	750	0.11
715	0.07				
671	0.11	670	0.37	668	0.37

Naphthol green also shows excellent agreement between the spectra and should be identifiable on these fabrics.

Figure 7.15 Safranin on silk

(a) Comparison of spectra on silk. Undyed and dyed silk with the baseline subtracted and the dye spectrum obtained from these by subtraction of the fabric spectrum after normalisation of both with respect to the fabric peak at  $2934\text{cm}^{-1}$ .



(b) Comparison of spectra for Safranin powder with the dye spectra extracted from silk.

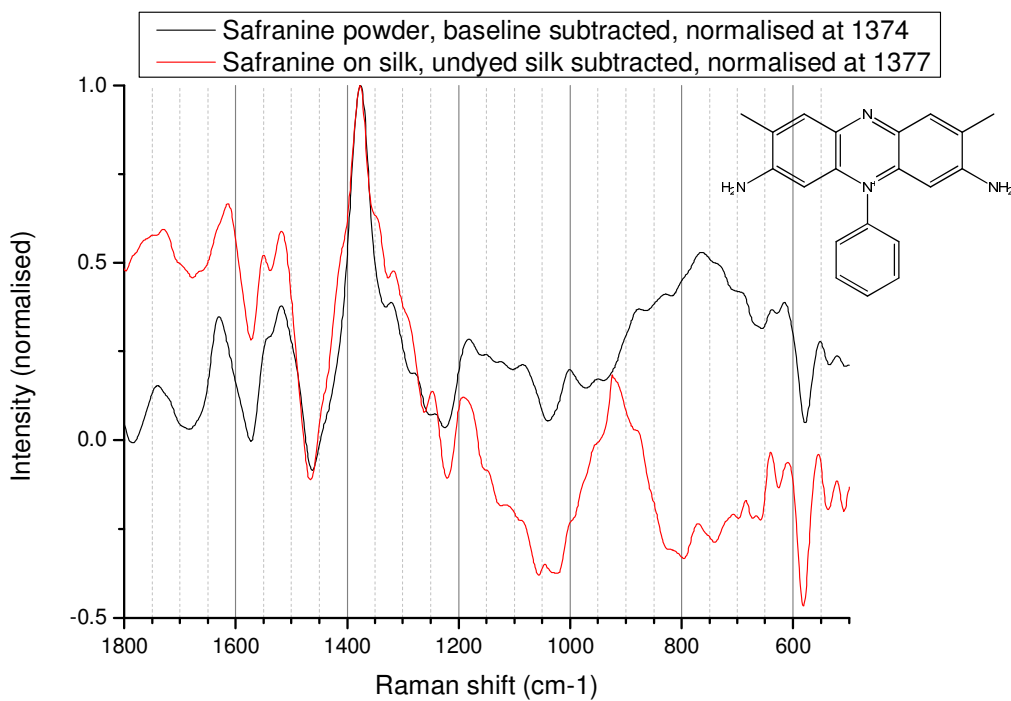


Table 7.14 Peak positions for Safranin powder and on silk

Safranin powder		Safranin with silk textile subtracted	
Raman shift (cm <sup>-1</sup> )	Normalised intensity	Raman shift (cm <sup>-1</sup> )	Normalised intensity
1740	0.15		
		1730	0.59
1630	0.35		
1540 (sh)	0.29	1550	0.52
1518	0.38	1518	0.59
1376	1.00	1377	1.00
1321 (sh)	0.39	1317 (sh)	0.48
1280 (sh)	0.19		
1243	0.07	1247	0.14
		1192	0.12
1181	0.28		

Safranin is a highly fluorescent dye and extraction of the dye spectrum was problematic. No spectrum on wool could be obtained. Nevertheless, the distinctive peak at 1376/7cm<sup>-1</sup> was seen in both the powder and silk spectra.



### 7.3 Conclusions

In most cases dye spectra could be successfully extracted from the dyed textiles and showed good correlation with the dye powder spectrum. Some differences could be attributed to the effect of the interaction between the dye and the protein fibre. The signals were often more intense on wool fabrics than silk and this might be due to the differences in the fibre structure. Wool has a more open microscopic structure<sup>415</sup> than silk and this allows the dye to penetrate further into the fibre increasing the possible uptake during dyeing. The greater concentration present would therefore produce a higher Raman signal.

Fluorescence is a well known problem with Raman spectroscopy and, although the use of the FT-Raman technique with an excitation frequency at 1064nm reduced the fluorescence, some dyes were still affected, particularly Victoria blue where no spectra for dyed samples could be collected.

The dyes studied can be clearly differentiated on the basis of their Raman spectra and this can be seen when the dyes are applied to silk and wool fabrics in many cases (Table 3). The most useful region for identification is between 1800 and 1000cm<sup>-1</sup>.

Table 7.15 Summary of results for dyes on fabrics

Dye	Spectrum on wool	Spectrum on silk
Acid yellow 11	Very good	Very good
Acid yellow 17	Good	Good
Tartrazine	Good	None
Orange II	Very good	Very good
New coccine	Very good	Very good
Methyl violet	Very good	Very good
Malachite green	Not determined	Very good
Fuchsin acid	Poor	Poor
Rhodamine 6G	Poor	Very good
Naphthol green	Very good	Very good
Safranine	Fluorescence problem	Poor

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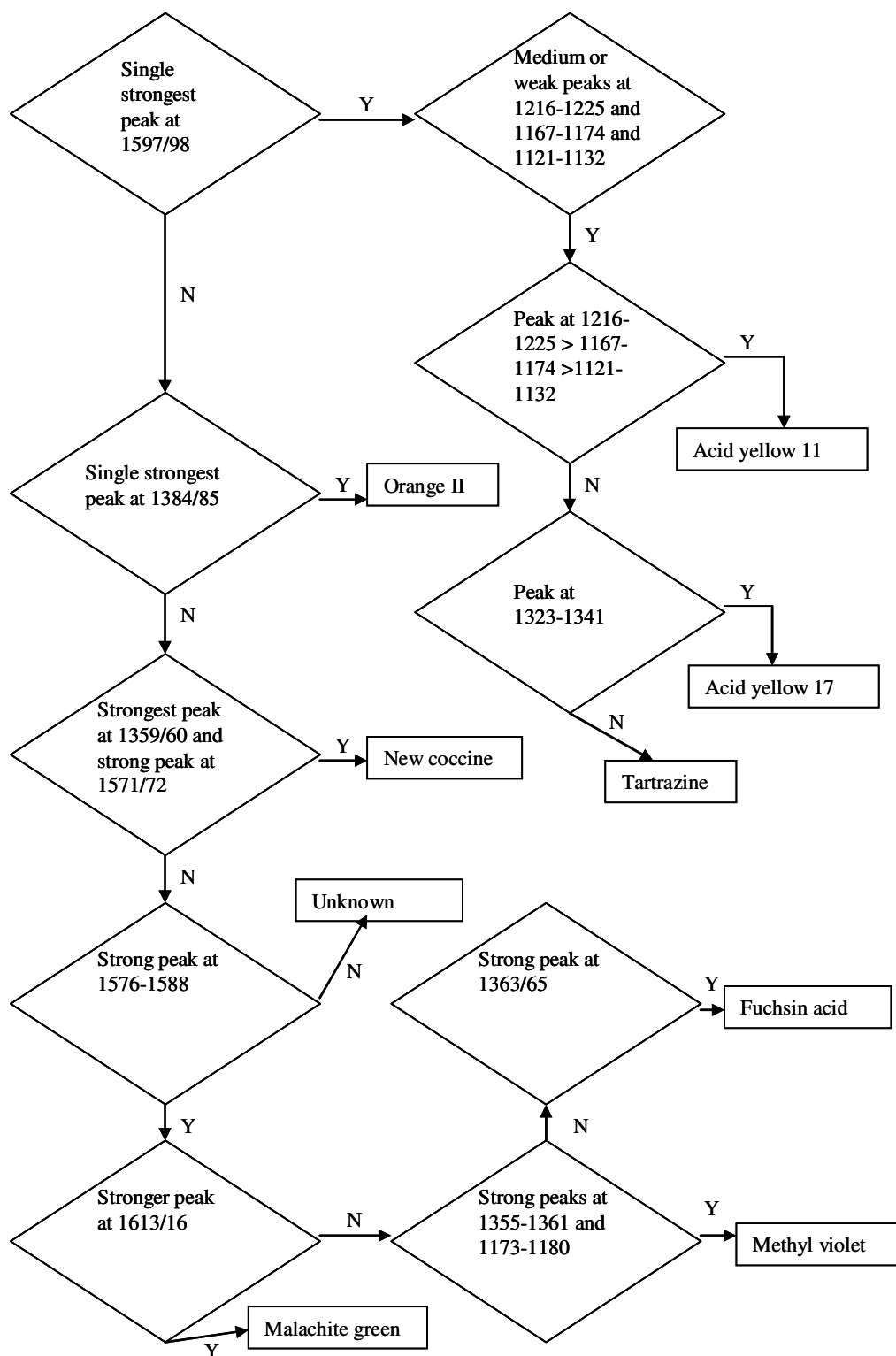
<sup>415</sup> TIMAR-BALAZSY, A. & EASTOP, D. (1998) *Chemical Principles of Textile Conservation*, Oxford, Butterworth-Heinemann. Pages 36-55

The most important factor affecting the quality of the extracted spectrum is the intensity of the dye spectrum relative to the fabric spectrum. Where there are only small differences between the undyed and dyed spectra the processing involving manual subtraction of the baseline and then instrumental subtraction of the fabric spectrum is very critical and can result in spurious negative peaks making distinguishing the significant peaks difficult. A computerised form of analysis such as principal components analysis might be of benefit.

The strong peak at about  $1600\text{cm}^{-1}$  is a very clear indicator of the phenyl group. One peak is not sufficient evidence to be able to assign a structure but other parts of the spectrum also give useful confirmation. The three intense bands at about  $1600$ ,  $1400$  and  $1200\text{cm}^{-1}$  are consistent for all the triphenylmethane dyes successfully examined here and are a useful indicator for them. A schematic chart for the identification of the azo and triphenylmethane dyes based on the results from this study is shown in Figure 7.16. Although in the system used here the fabrics had to be sampled to be physically placed inside the FT-Raman instrument, it is in principle possible to adapt this method to be used non-destructively with an FT-Raman microscope at the same laser wavelength.

For the modern test fabrics described in this chapter, the expected peaks were already known. To be usefully applied to the field of cultural heritage, the method must be capable of application to aged and unknown samples. The next chapter will describe its use on aged samples and on one sample where the dye is unknown.

Figure 7.16 Azo and triphenylmethane dye identification flow chart



## Chapter 8 Analysis of historic samples

The dye manual written by Knecht, Rawson and Loewenthal<sup>416</sup> is presented in three volumes, the third of which contains dyed samples of wool and cotton. A copy of this was in the possession of the author was therefore available for sampling and provided a convenient source for historic samples which can be confidently dated as from 1893 or before.



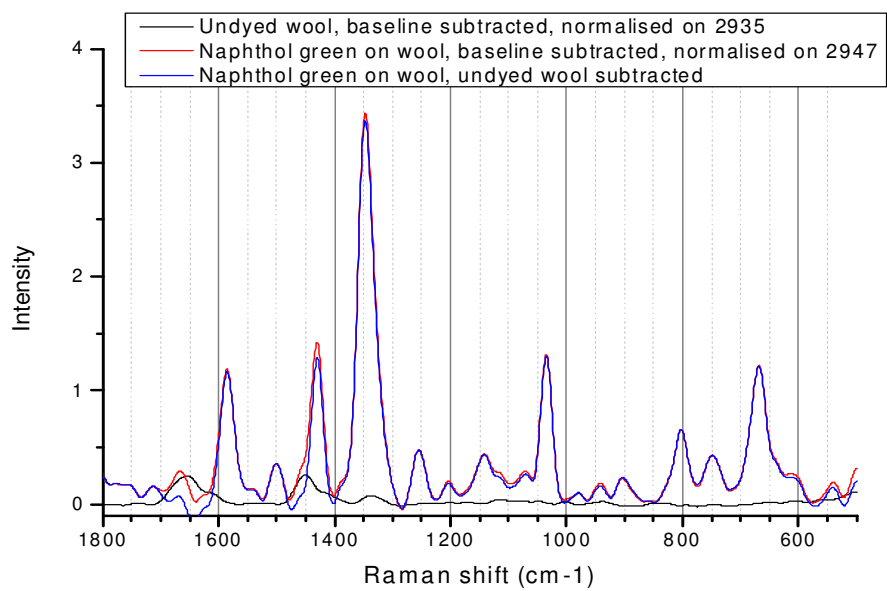
<sup>416</sup>KNECHT, E., RAWSON, C. & LOEWENTHAL, R. (1893) *A Manual of Dyeing: for the Use of Practical Dyers, Manufacturers, Students and all those interested in the Art of Dyeing; Specimens of Dyed Fabrics*, London, Charles Griffin and Company Limited.

The total dimensions of the samples were 4.5cm by 3cm. One side was gently dislodged from the paper and a narrow strip (approximately 3-5mm wide) was removed. The manual also contains samples of bleached wool and scoured wool before dyeing. The scoured wool was sampled similarly and was therefore available as an aged sample for direct comparison with the dyed samples.

The samples were inserted into the sample holder described in the previous chapter and analysed in the FT-Raman spectrometer as before. Details of the instrumental set up can be found in Appendix 4. Some samples were available with the same dyes discussed in Chapter 7 and therefore direct comparisons can be made between modern and historic samples. Other samples of dyes similar to the model systems used were analysed as well as an example of a natural dye. One fabric dyed with an unknown dye, not sourced from the dye manual, was also examined.

Figure 8.1 Naphthol green on wool

(a) Wool sample from 1893



(b) Modern samples

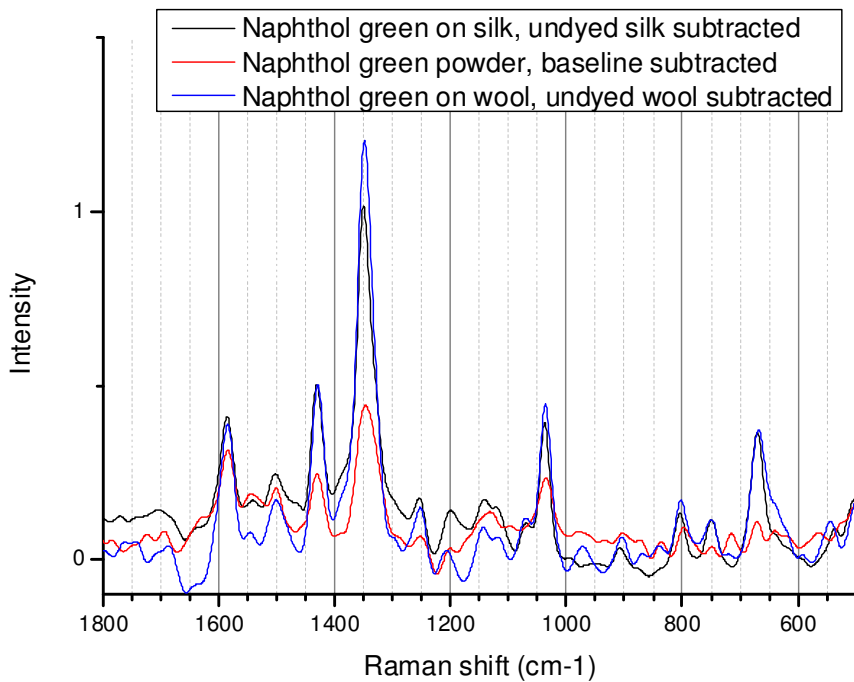


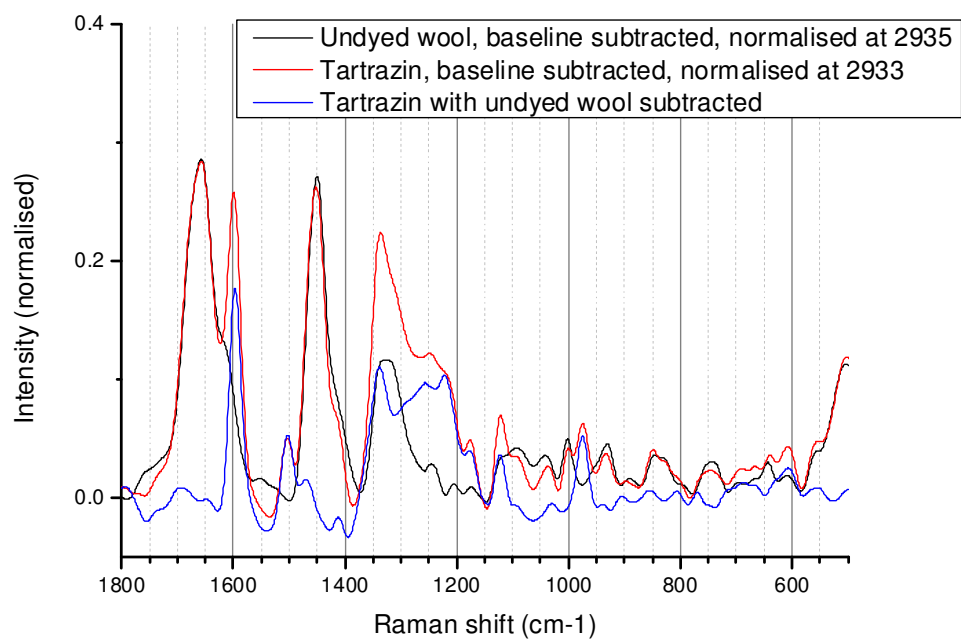
Table 8.1 Comparison of peaks for Naphthol green powder, on modern and on 1893 wool

Naphthol green powder	Naphthol green, wool subtracted, modern sample	Naphthol green, wool subtracted, 1893 sample
1585	1585	1586
1544	1546	1543(sh)
1501	1500	1500
1431	1429	1430
1347	1348	1347
1252	1252	1255
1201	1207	1204
1132	1143	1141
	1119	
	1070	
1035	1036	1035
	972	
903	904	903
873		
	840	
797	802	802
	750	
671	668	668

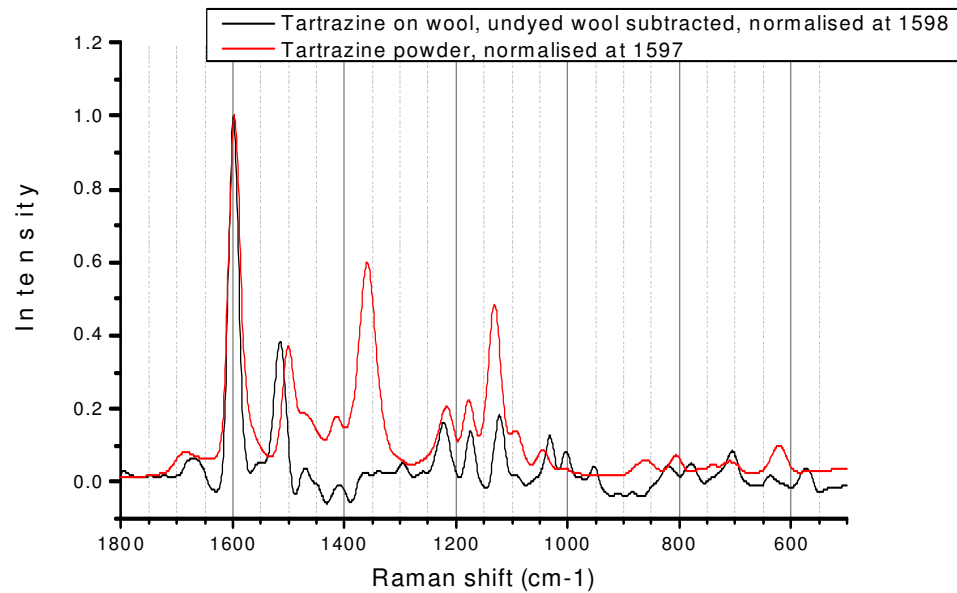
This sample is clearly identifiable as Naphthol green. The spectrum between 1600 and 1000cm<sup>-1</sup> is the most useful for comparison. Some of the peaks are not seen in the historic sample. In the 1893 sample the peak at 1119cm<sup>-1</sup> is present but only as a slight shoulder so is not listed in Table 8.1. Other peaks are also weak and so are not listed. The peak positions and relative intensities are the same for both modern and historic samples.

Figure 8.2 Tartrazine<sup>417</sup> on wool

(a) Wool sample from 1893



(b) Modern Tartrazine samples



<sup>417</sup> Tartrazin is the spelling used in the 1893 dye manual and is therefore used in the legend for the historic sample.



Table 8.2 Comparison of Tartrazine powder and on modern and 1893 wool samples

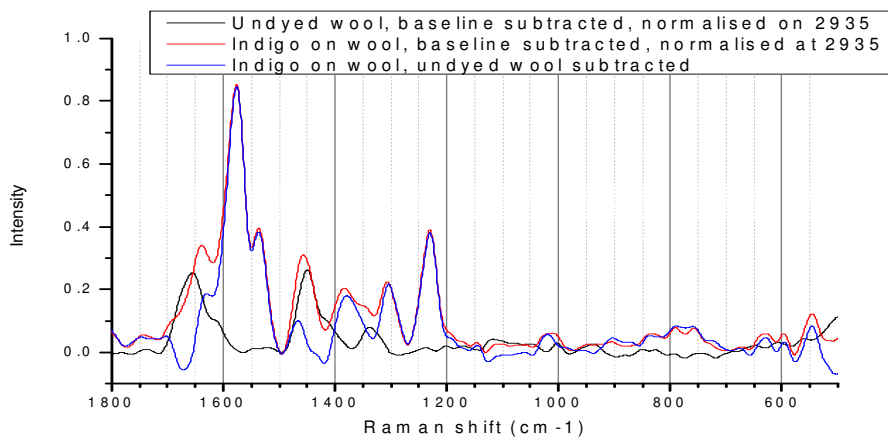
Tartrazine powder	Tartrazine, wool subtracted, modern sample	Tartrazine, wool subtracted, 1893 sample
1684	1669	
1597	1598	1599
1500	1515	1503
1470	1470	
1414	1408	
1359		
1217	1222	
1177	1174	
1131	1122	1121
1094	1093	
1045	1032	
1008	1003	975

The modern and historic spectra for Tartrazine on wool show fewer similarities than the corresponding spectra for Naphthol green but nevertheless there are strong peaks which can be used to identify the spectrum. The strongest peak at  $1599\text{cm}^{-1}$  is clearly seen as is the peak very close to  $1500\text{cm}^{-1}$ . The latter peak is closer to the result for powder than the modern wool and this suggests that comparative databases should include as many forms of the molecule as possible. The three peaks at approximately 1220, 1175 and  $1120\text{cm}^{-1}$  which were proposed as diagnostic for the modern dyes on wool are not all seen clearly here. The strongest of these three peaks at  $1120\text{cm}^{-1}$  is still apparent though and this could be useful for identification. The 1893 textile shows a poorly resolved spectrum in this area which might be due to degradation of the dye. Overall the spectrum from this historic wool sample can be unambiguously assigned to Tartrazine.

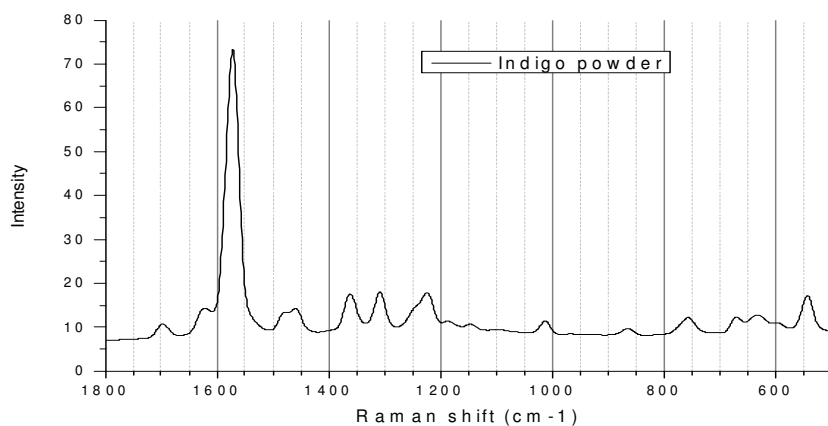
The main area of enquiry in this thesis has been the synthetic dyes but examinations of the dye manuals has shown that natural dyes were extensively used throughout the period. It was decided to test the indigo and indigo carmine samples from the manual since these could easily be encountered during testing of samples from the second half of the nineteenth century.

Figure 8.3 Indigo and indigo carmine on wool

(a) Indigo on wool 1893 sample



(b) Indigo powder spectrum



(c) Indigo carmine on wool

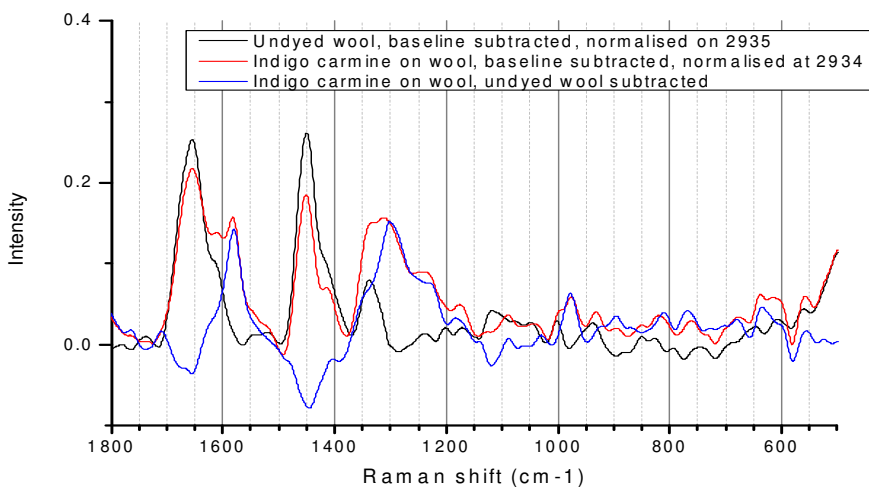


Table 8.3 Comparison of spectra for indigo powder and Indigo and Indigo carmine 1893 wool samples

Indigo powder	Indigo on wool, wool subtracted, 1893 sample	Indigo carmine on wool, wool subtracted, 1893 sample
1697	1702	1711
1622	1630(sh)	
1572	1576	1581
1477		
1459	1466	
1361	1378	
1308	1303	1303
1224	1230	
1013	1020	
		977
		896
864		
		810
756		768
670		
632	629	
597	593	
543	546	

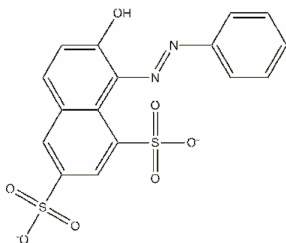
Indigo camine (which is a blue dye) is structurally very similar to indigo but is substituted with sulphonic acid groups. It might therefore be expected to share some vibrational energies with indigo and this is indeed seen at 1570 and 1300cm<sup>-1</sup> but the peak at 1570cm<sup>-1</sup> is much stronger than that at 1300cm<sup>-1</sup> for indigo whereas for indigo carmine the peaks have very similar intensities. Indigo carmine also lacks the peaks between these two which are clearly seen for indigo.

Strong FT-Raman spectra can be obtained for these two dyes which provide data enabling identification and distinction between these closely related dyes.

The 1893 dye manual did not contain any other samples of fabrics dyed with the compounds which had been used for the test samples in this study. This might indicate that these dyes had fallen out of popularity with the dyers by this date. Nevertheless a sample was present which was dyed with Orange G, a monoazo dye with similarities to Orange II. Certainly the colour on wool is comparable and therefore an ability to identify and distinguish between these dyes in practice would be of value.

Figure 8.4 Orange II and Orange G on wool compared

Orange G:



Orange II:

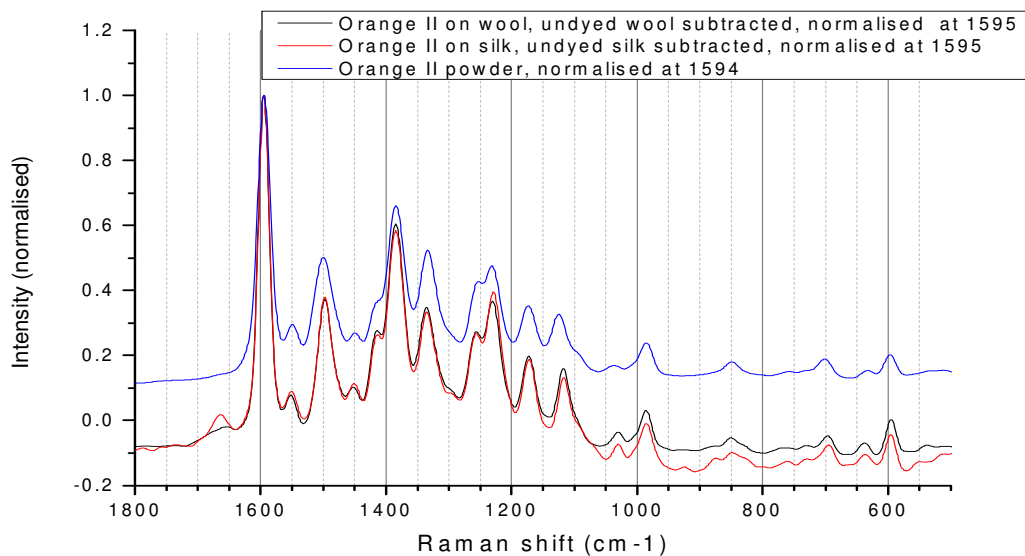
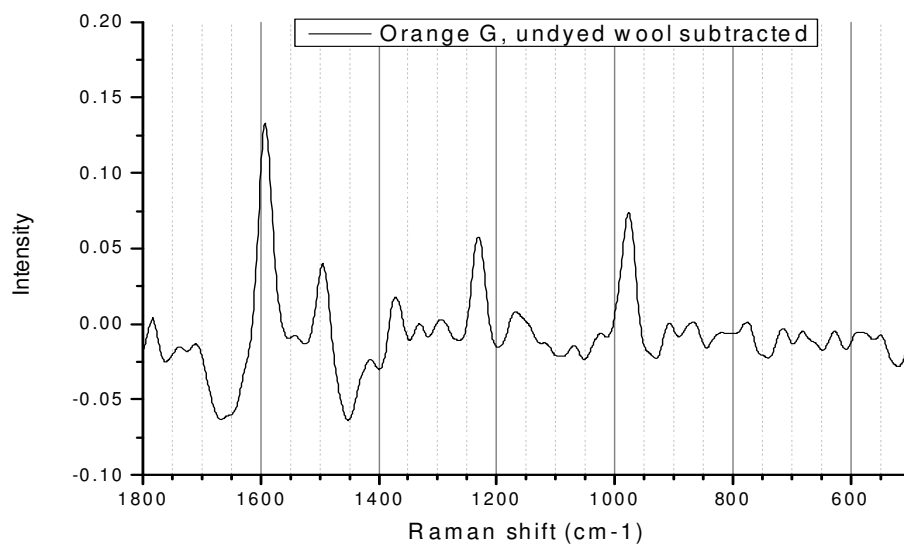
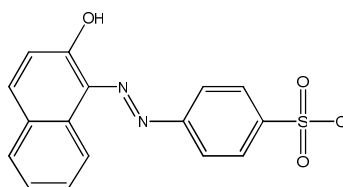


Table 8.4 comparison of peak positions for Orange II and Orange G on wool

Orange II on wool, wool subtracted, modern sample	Orange G on wool, wool subtracted, 1893 sample
1595	1593
1552	1542(sh)
1498	1495
1452	
1414	
1385	
	1371
1336	1331
	1294
1256	
1230	1231
1172	1168
1118	
1030	
986	976

Orange II and Orange G have a large degree of structural similarity. Both show the prominent peak at about  $1600\text{cm}^{-1}$  which is highly characteristic of the phenyl group and both show a peak very close to  $1500\text{cm}^{-1}$ . The peak just below  $1000\text{cm}^{-1}$  is quite different though with a much higher relative intensity in Orange G. The peaks at  $1375$  and  $1381\text{cm}^{-1}$  are also very different for these two dyes. Overall, the peaks for the historic Orange G sample are easy to identify whilst the dye is on the wool sample and, although fewer peaks are visible than for the modern Orange II, the differences between the spectra can be clearly seen.

Analysis of samples where the structure of the dye is known is very valuable to test the concept that FT-Raman is a technique which has applications in the field of cultural heritage. Samples such as these from dye manuals will be useful to establish a database for comparative purposes with unknowns. The identification of one unknown sample was attempted in this study. The sample was a piece of mauve silk. It was highly degraded in a manner which is characteristic of the effects of a treatment to increase the weight of silk. This treatment was used to produce a better drape for the fabric in wear and allowed a cheaper thin silk to imitate a heavier more expensive textile. It was very common in the late nineteenth and early twentieth centuries and tends to produce failure of the fibres in one direction of the cloth only, leaving slits where it has been folded or

areas of fraying. This damage lead to the inference that this piece of silk was late nineteenth or early twentieth century in date and could have been dyed with a synthetic dye relevant to this study.

The FT-Raman spectrum of a small piece of the sample was taken as before. A piece of modern silk had to be used to obtain the undyed fabric spectrum.

Figure 8.5 Shattered mauve silk

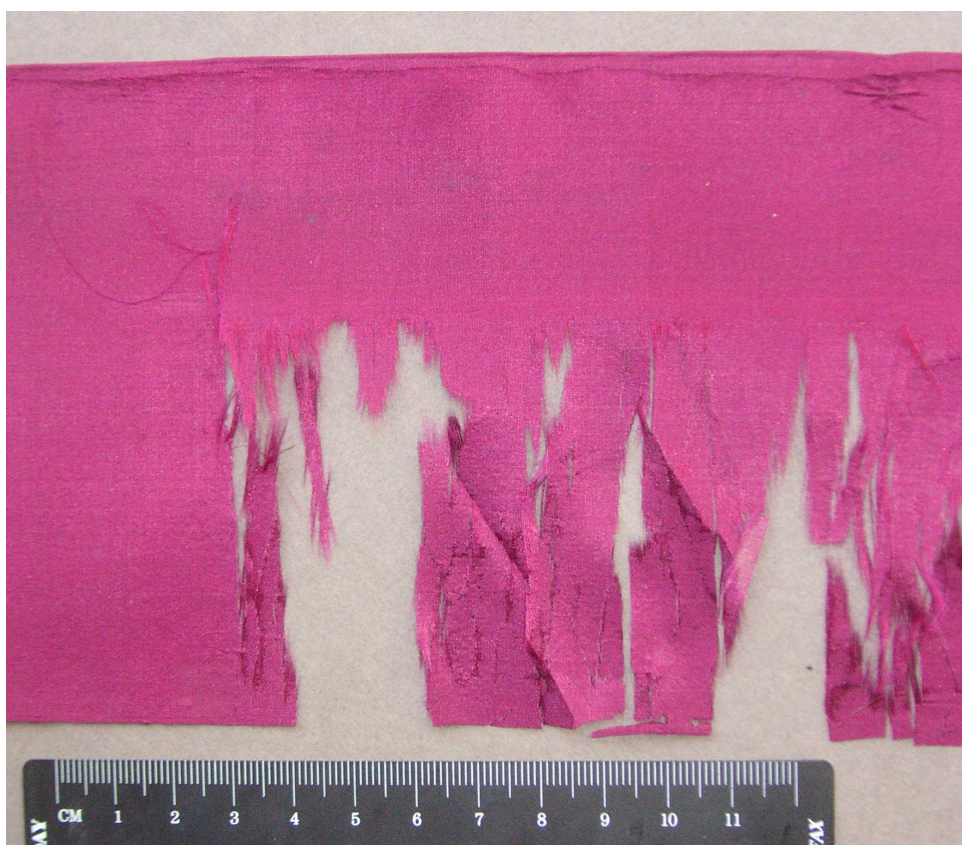
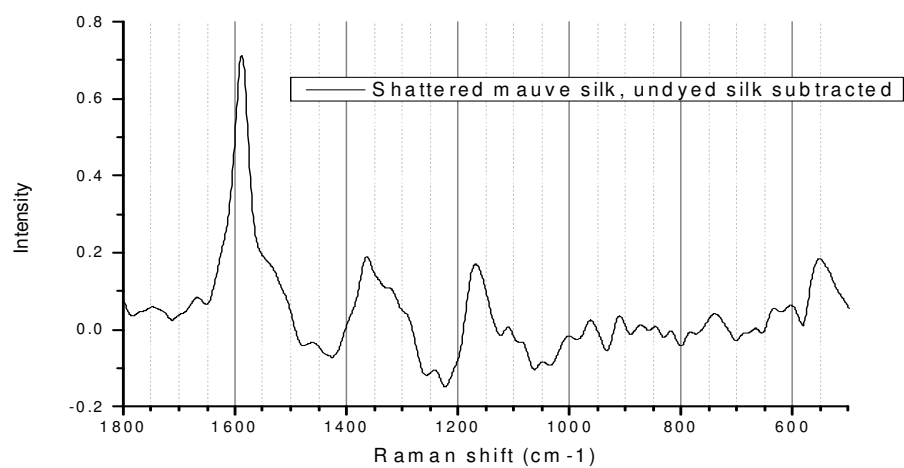
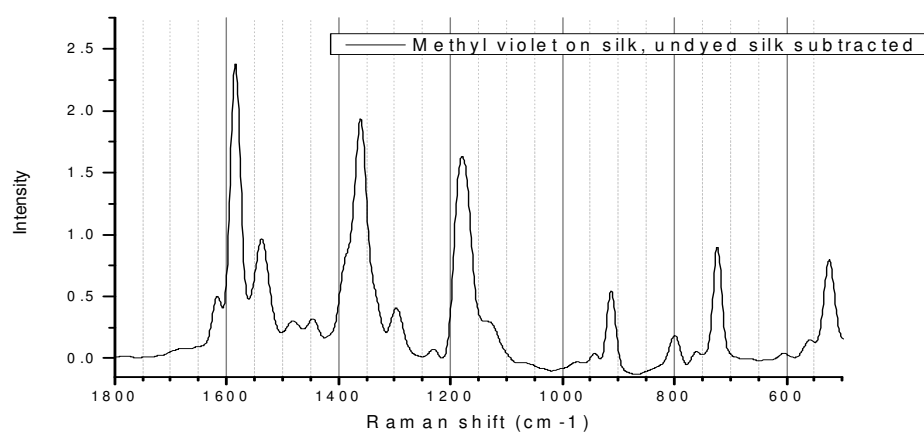


Figure 8.6 FT-Raman spectra for shattered silk and test samples on silk

(a) Shattered mauve silk with unknown dye



(b) Methyl violet on silk



(c) Fuchsin acid on silk

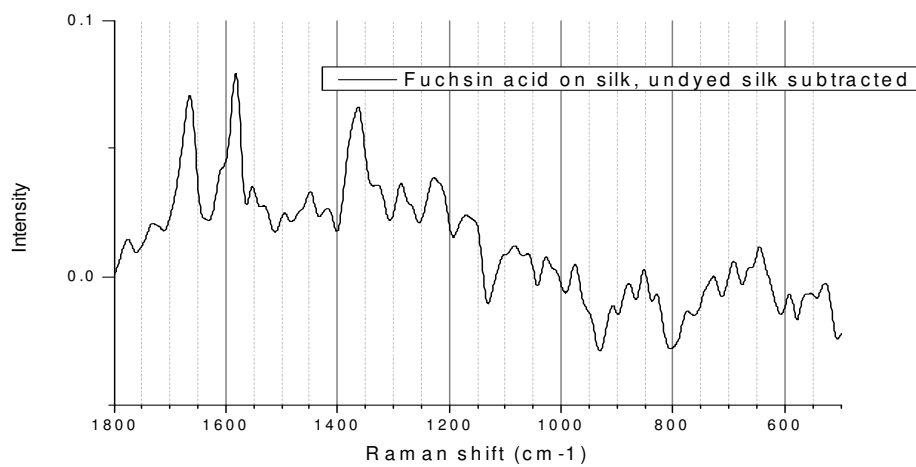


Table 8.5 Comparison of peak positions for shattered silk and candidate mauve dyes

Shattered silk	Methyl violet on silk	Fuchsin acid on silk
		1664
	1617	
1588	1584	1582
		1552
	1537	
		1495
	1482	
	1446	1449
		1418
1364	1361	1363
	1297	1286
	1230	1228
	1180	
1168		1169
	1134(shoulder)	
		1084
		1027
	972	975
	942	
	913	
	799	
	761	
	723	
	604	
552	558	
	523	

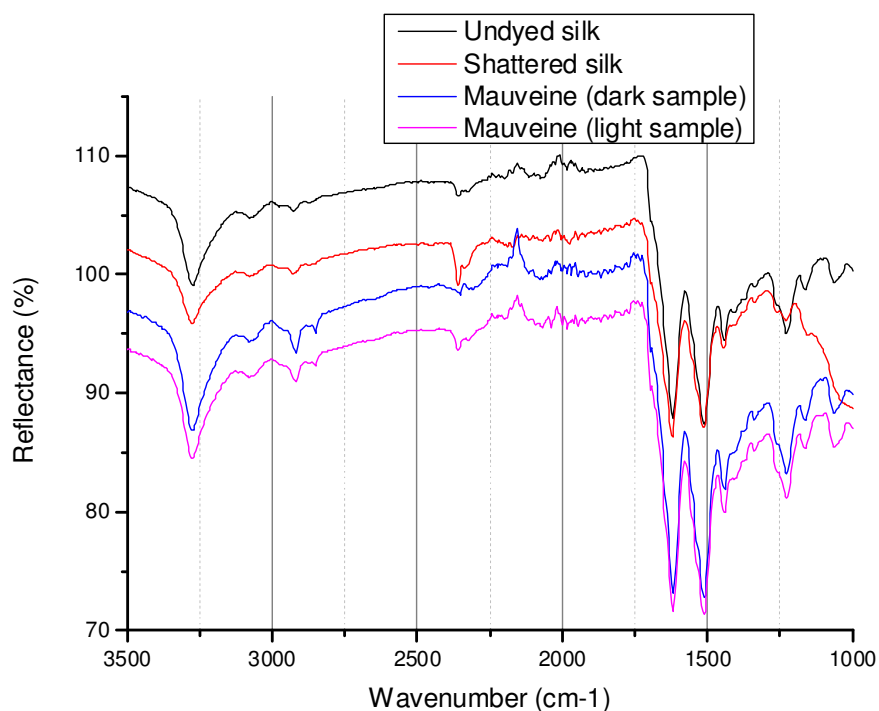
The shattered silk spectrum clearly shows the spectral pattern which has been found for the triphenylmethane dyes examined in this study with peaks of roughly equivalent intensity at about 1600, 1400 and 1200cm<sup>-1</sup>. The two candidate compounds available for comparison are Methyl violet and Fuchsin acid. The spectra for Fuchsin acid were unfortunately poor on silk and the dye spectrum extracted was therefore of poor quality. The peak positions for the unknown are more closely matched to those of Fuchsin acid than Methyl violet but the relative intensities are closer to the Methyl violet pattern. This therefore makes a secure identification with one or the other difficult. Nevertheless, it is probable that an aged sample of Fuchsin acid would give a very poor spectrum indeed in this system and therefore on balance the spectrum seems closer to Methyl violet. There were several variants of Methyl violet on the market in the nineteenth



century and this sample may be one of these or indeed a mixture as this approach was very common to produce the exact shade the dyer required.

Another dye which might be present on this fabric is Mauveine as this was also a dye of the triphenylmethane type, albeit a mixture of compounds.<sup>418</sup> It had not been possible to obtain a result with FT-Raman for this dye but it had given a distinctive FT-IR spectrum so the shattered mauve fabric was compared with this (Figure 8.7). The spectrum for the mauve silk does not match that for Mauveine as it is missing the peaks between 2750 and 3000cm<sup>-1</sup> and therefore that is not the dye on this fabric.

Figure 8.7 FT-IR spectra for shattered mauve silk and Mauveine on silk



From this analysis the dye on the shattered mauve sample can be identified definitely as a triphenylmethane dye and therefore a synthetic. When making an identification it is important to take all the factors relevant to the sample into consideration. In this case the dye has not faded and therefore it is unlikely to be Methyl violet itself as this was very fugitive to light. Mauveine was a much more stable dye and therefore it could be a

<sup>418</sup> BROWN, T. M., COOKSEY, C. J. & DRONSFIELD, A. T. (2000) Perkin's mauveine - a fortuitous discovery? *Education in Chemistry*, 37, 75-77.

strong candidate for the dye in this case but the spectroscopy results show that it is not present.

The results presented in this chapter show that the methods developed in Chapters 6 and 7 are applicable to older samples without problems due to fluorescence. The spectra for old and modern samples vary in how comparable they are. For Naphthol green the comparison is very close and the dye could be identified in an unknown sample with a great deal of confidence. For Tartrazine the similarity is not so great but the strong peaks are still observed and the dye could be identified. For the related dyes Orange II and Orange G, the spectra show similarities. Particularly the strong peak at about  $1600\text{cm}^{-1}$  is clearly seen for both samples but equally there are points of difference which arise due to the structural differences. The unknown mauve silk sample can be identified as a triphenylmethane dye using this system although the absolute assignment of a particular compound is not possible. However, the possibility of the presence of Mauveine can be discounted. The analysis of this sample shows that collecting data from both the Raman and infrared methods can be used to aid identification.

These results indicate that this method has definite potential for application to cultural heritage samples but there are also potential problems with the use of lasers which will be discussed the next chapter. The method as used in this study requires sampling of the object which is a drawback. The next chapter will also discuss possible methodological variations which could allow it to be truly non-sampling and non-destructive.

## Chapter 9 Conclusions

This study has analysed synthetic dyes both physically and in a historical sense. The overall area of interest for this research is the extent to which the nineteenth century textile dyes were utilised in the textile industry. The two major research strands of chemical investigation and historical research are, in turn, based on chemical methods, conservation science, textile conservation, dress and textile history and history of science. These inform each other, the historical investigation based on literature sources, including databases of contemporary publications, dye manuals and census information, suggests compounds for the physical investigation and the development of novel applications of spectroscopic methods will provide insights into the accuracy of the claims about objects.

The historical period addressed (1856-1900) is of interest because it was one of rapid change in many areas not least those of fashion, textiles and dyes. This thesis examines the developments in textile dyes in Britain, particularly in England, and compares them with those in Europe, especially in Germany. Whereas other European countries, such as France,<sup>419</sup> would be more important if the focus of this study were fashion itself, the production of textile dyes was contested chiefly between Germany and England and therefore these two countries form the basis for study. 1856 was a landmark date in the history of textile dyes as it was when William Henry Perkin first introduced a synthetic dye produced from the raw material of coal tar. This was a radical departure from the majority of dyes available up to that time which were sourced from plants, lichens, a few molluscs and insects<sup>420</sup> and led to the rapid growth of a new industry based on chemical processing in large factories. By 1900 the important blue dye indigo could be made synthetically and this marks the point where all the major natural dyes could be substituted by synthetic alternatives. Although many more synthetic dyes were developed in the twentieth century this therefore marks a suitable break point for a study of the early synthetic dye industry.

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<sup>419</sup> WILSON, E. & TAYLOR, L. (1989) *Through the Looking Glass. A history of dress from 1860 to the present day*. London, BBC Books. Page 22. Wilson & Taylor state that Paris had led western European fashion since the late seventeenth century and its dominance was increased by the development of the couturier there in the mid-nineteenth century.

<sup>420</sup> See Appendix 5 for structures and sources of natural dyes.

Knowledge of the dyes in common use in the nineteenth century and their structures is essential to systematically apply analytical procedures to historical textile objects. This study combines historical research on the dyes developed and, more importantly, used in this period together with the application of an analytical method for the identification of dyes on fabric which has hitherto not been used in this mode. This research will be discussed fully later in this chapter.

The sequence of the development of the synthetic dyes has been extensively studied and this research forms the starting point of this investigation. In this thesis digital databases were extensively used for research. These were found to offer a wide range of sources including newspapers, periodicals and pamphlets. Newspapers were mostly local publications and the immediacy of the newspaper reporting, although possibly presenting a biased view of events, gives an insight into the attitudes and preoccupations of the time and presents events in real time which hindsight might find too trivial to report. The periodicals accessed were aimed at a variety of audiences including families, women and religious groups. Some were intended to be broadly educational for the general population and included articles on the arts and the sciences whereas others were more for general entertainment. Census returns (for 1841, 1851, 1861, 1871, 1881 and 1891) and the registers of births, marriages and deaths were also accessed online as were government reports. The powerful search facilities allowed the investigation of a large number of different sources in a short space of time. These were exclusively English or British sources and therefore the attitudes expressed can only be seen from this perspective.

The periodicals and newspaper articles allow an overview of the reactions of different sectors of the public to the introduction of the new dyes as discussed in Chapter 3. This therefore took the scope of the study beyond the chronological data relating to the dye compounds into the wider responses in society. Whilst the evidence shows that many of the more educational publications presented the science as a beneficial advance, some of the periodicals were more populist in their approach. An example of this is the account of the synthetic dyes display in the 1862 London International Exhibition included in *All the Year*

*Round*.<sup>421</sup> Negative reactions to the dyes were divided between those who were concerned with adverse effects on health and those who objected to the colours produced by the dyes on aesthetic grounds. The health problems were produced both by pollution from the factories and by close contact with the dye compounds. Some of the chemicals used to produce the dyes were poisonous and this inevitably led to the suspicion that the dyestuffs could cause harm when textiles dyed with them were worn. This study did not research direct evidence of deaths due to this cause and, although articles were published citing this as a problem no strong evidence was produced in them.<sup>422</sup> Unfortunately, many of the dyes were indeed toxic when ingested<sup>423</sup> and there is evidence that they were used in foodstuffs which certainly would have been harmful.

Objections to the synthetic dyes on aesthetic grounds were widespread. Periodicals aimed at female readership such as the *Englishwoman's Domestic Magazine* were critical of strong colours and of several colours mixed in an outfit. The Arts and Crafts movement which was first formalised in London was a strong source of disapproval for the new dyes. It was strongly influenced by the ideas of William Morris who took great pains to revive the craft of dyeing with natural dyes for the textiles which he designed. His approach was inspired by socialist principles as well as his taste and he used craft based production methods for his decorative arts. These methods he considered more natural for the working man who was treated as an artisan rather than a production worker. The Arts and Crafts Movement was widespread through Europe but outside England it was not so heavily influenced by Morris and factory based production methods were not rejected.

It would be easy to imagine, reading the contemporary periodicals, newspapers and especially Morris' writings, that the natural dyes were completely superseded by the synthetics in the later nineteenth century. However, the examination of printed dye manuals from this period indicates that this was not in fact the case. The last of these to be published

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<sup>421</sup> DICKENS, C. (1862) Ignoramus at the Exhibition. *All the Year Round*, 560-561. Aug 23<sup>rd</sup> Accessed via ProQuest British Periodicals Database online 4<sup>th</sup> Feb 2010

<sup>422</sup> A definitive study of mortality due to the synthetic dyes would have to include a major survey of death records which was not possible in the time scale. Accidents in the dye factories have been commented on in Chapter 2.

<sup>423</sup> There are now known toxicological issues with the early synthetic dyes, many of which are carcinogenic.

in 1893<sup>424</sup> includes a full section on natural dyes with long passages on the use of the indigo vat. There has been published information on early dye methods as for example in Graaff who reproduces seventeenth century recipes<sup>425</sup> but the nineteenth century sources have not been published to date. A degree of chemical knowledge is required to interpret all these sources and those researchers who have looked at manuals so far seem to have concentrated on the natural dyes. Therefore this study may be the first to do so using the varied expertise of the investigator.

Morris could therefore have used dye manuals published in his own day as he was developing his knowledge of the use of natural dyes. Perhaps he was prejudiced against these sources as they were written for the manufacturing industry. It may also be that the trials carried out at Wardle's works in Leek were aimed at getting the exact effects that Morris wanted rather than re-inventing the dyeing and printing methods. However, it could hardly be claimed that the expertise had been lost, rather that the commercial dyers and printers preferred the advantages that the new dyes gave them. Certainly the samples of dyed fabrics in Knecht (1893) use the natural dyes in 5 of 60 (8%) samples of cotton and 12 of 84 (14%) samples of wool with an additional 5 wool samples using indigo extract in combination with a synthetic dye. Presumably these were to extend the range of shades and effects available.

John James Hummel's biography also emphasises the persistence of the natural dyes alongside the synthetics. There was no particular distinction drawn between the two, as can be seen also in the dye manuals. Both were in constant use and were often applied together. Hummel's correspondence with the Director of Kew Gardens shows that research into new sources of natural dyes, available through the large network of Englishmen living and working abroad, was ongoing into at least the late nineteenth century.

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<sup>424</sup> KNECHT, E., RAWSON, C. & LOEWENTHAL, R. (1893) *A Manual of Dyeing: for the use of Practical Dyers, Manufacturers, Students and all those interested in the Art of Dyeing*. London, Philadelphia, Charles Griffin and Company Ltd./ J.B. Lippincott

<sup>425</sup> GRAAFF, J.H.H.D. (2004) *The Colourful Past. Origins, Chemistry and Identification of Natural Dyestuffs* London, Archetype Press Ltd. Page 313ff.

Whilst the periodicals used were mostly published in London, the geographical spread of the newspapers was wide and facilitated this research of the Yorkshire College in the pages of the *Leeds Mercury*. This allowed this minor figure of the time, John James Hummel, to be rediscovered. He was an early instructor at Yorkshire College and although now hardly featuring in the official history of the University of Leeds and not meriting an entry in the Oxford Dictionary of National Biography he was well regarded at the time and his biography is instructive in the context of this study. His Swiss connections were pivotal in his early life in giving him the personal contacts to embark on a career as a textile printer. His training in Switzerland allowed him to start teaching in the works where he was employed and this led to his appointment at the Yorkshire College. The College was typical of many such institutions founded at about this time. In contrast to the only two universities then in England, Oxford and Cambridge, these were generally established in provincial manufacturing cities and were aimed at training young men<sup>426</sup> in the trades on which the local economies were based. Other similar institutions were Owens College in Manchester and Anderson's College in Glasgow. The financial backers were the local industrialists who were concerned at increasing competition from overseas and were seeking to develop a new workforce with the latest skills and design ideas. Like these other institutions there were early problems, in the case of the Yorkshire College mostly with funding and the teaching of the institutions gradually evolved into more academic areas and away from the original technical intentions. Unlike the others, though, the Yorkshire College maintained a Department of Dyeing under Hummel distinct from the chemistry teaching and the University of Leeds maintained its close ties with the local textile industry to a greater degree than the other universities founded at this time.

This theme of continental contacts is an echo of the well established history of the English synthetic dye companies which were largely staffed in the first instance by German chemists. The web of contacts outside and inside academia maintained by these men was one of the reasons for the success of the industry and the transfer of this success to Germany later in the century and Hummel's case demonstrated this same factor at work further down the hierarchy in the textile industries. This study proposes that another reason

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<sup>426</sup> Initially these were exclusively boys and men but over time a few women started to be admitted.

for the transfer of the lead in the synthetic dye industry from England to Germany was the antipathy in England to the new dyes exemplified by the Arts and Crafts movement. Although there was an equivalent aesthetic movement in Germany, evidence is presented that the importance given to the authentic production methods in England was unique and this may have unduly influenced the English attitude to factory production. Certainly the newspaper reports of accidents taken together with the Commissioners reports for the 1884 Royal Commission suggest that conditions were much more orderly and professional in the German factories. Lack of funding in England affected both the synthetic dye industry and chemical education, demonstrating the ambivalence to this area in the country.

The cultural heritage sector increasingly uses scientific methods for analysis of objects<sup>427</sup> and the preferred methodologies for obvious reasons are non-sampling and non-destructive. The Raman method developed here and applied to the dyed fabrics has been shown to be capable of identifying a number of dyes of different chemical types whilst the dye is still on the fabric. The established method for dye analysis has been to extract the dye and then to analyse it chemically. This is a method of long standing for natural dyes<sup>428</sup> and has recently been applied to synthetics.<sup>429</sup> However it requires sampling of the textile with subsequent destruction of the sample. This is not only harmful to the object but it limits the areas of investigation as samples have to be taken from an inconspicuous or already damaged area.

Raman spectroscopy applied to organic molecules such as the synthetic dyes is prone to problems of fluorescence which mask the Raman response. Several groups have investigated the use of colloidal silver particles to overcome this problem but this suffers from the drawback that a solution has to be applied to the fibre.<sup>430</sup> Using the long wavelength of 1064nm for the spectroscopy reduces the fluorescence of the molecules but

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<sup>427</sup> JANAWAY, R. C. & WYETH, P. (2004) Scientific Analysis of Ancient and Historic Textiles. *AHRC Research Centre for Textile Conservation and Textile Studies First Annual Conference*. London, Archetype

<sup>428</sup> GRAAFF, J. H. H. D. (2004) *The Colourful Past: The Origins, Chemistry and Identification of Natural Dyestuffs*, London, Archetype Press.

<sup>429</sup> BOMMEL, M. R. V., BERGHE, I. V., WALLERT, A. M., BOITELLE, R. & WOUTERS, J. (2007) High performance liquid chromatography and non-destructive three-dimensional fluorescence analysis of early synthetic dyes. *Journal of Chromatography A*, 1157, 260-272.

<sup>430</sup> CANAMARES, M. V. & LEONA, M. (2007) Surface-enhanced Raman scattering study of the red dye laccaic acid. *Journal of Raman Spectroscopy*, 38, 1259-1266.



also reduces the intensity of the spectral signal. The Fourier transform detection system is sensitive enough to detect these low level signals and therefore the system becomes practical.

Using this method the fluorescence of some of the organic dyes was still too strong to allow collection of a spectrum but nevertheless many of the dyes studied gave enough information to allow identification and it was shown that the method could be applied to historical samples successfully. Obviously this method could be applied to natural dyes as well as synthetics and indigo was investigated in this study. An unknown mauve silk was investigated and the dye class could be determined but not the precise dye. The use of infrared spectroscopy as well in this last investigation emphasises the usefulness of complementary forms of analysis. The FT-Raman method could potentially be applied to any part of the object without any need to disturb it. Areas sampled can be very specific as the laser spot is very small (0.2mm in the current study) and therefore multiple samples of different areas are possible. The experimental configuration adopted for the work reported here requires a sample of fabric to be placed inside the instrument and therefore hardly qualifies as non-sampling. However, alternative instrumentation using a microscope with an FT-Raman has been reported for the analysis of organic pigments<sup>431</sup> on paper without sampling. This could offer a methodology for the analysis of intact textiles. Casadio et al. use a high humidity chamber to enclose the prints which they are examining and this points to one of the potential drawbacks of this method. The laser spot, especially when concentrated by the lenses of a microscope, is very energetic and can therefore damage the object. Visible damage was only seen to one sample in this study, modern Naphthol green on silk. However, damage at the microscopic level was not tested. Care has to be taken to keep the laser power low and further work is needed to assess if any damage is caused to the textile under mild conditions.

Manual processing of the results was difficult, especially when the spectrum from the dye was weak compared to the fabric spectrum. Computerised principal components analysis

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<sup>431</sup> CASADIO, F., MAUCK, K., CHEFITZ, M. & FREEMAN, R. (2010) Direct identification of early synthetic dyes: FT-Raman study of the illustrated broadside prints of Jose Gaudalupe Posada (1852-1913). *Applied Physics A; materials science & processing*, 100, 885-899.

methods have been reported for pattern recognition in spectra and could be used to remove the element of operator error from the spectral analysis.<sup>432</sup>

This study shows that FT-Raman spectroscopy for the analysis of dyes is feasible and that the method can be applied to modern test samples and historic samples. More work needs to be carried out in assembling databases of Raman spectra as has been done for pigments and refinements in instrumentation and technique could no doubt lead to increases in spectral intensity and precision. The possibility that the technique could be applied directly to the object without sampling or pre-treatment is very encouraging for its application in cultural heritage.

In conclusion this thesis examines the competition between the natural and synthetic dyes in the second half of the nineteenth century. The impression given by Morris and others in the Arts and Crafts movement is that the synthetic dyes swamped the naturals after their introduction to the detriment of textile production. The historical part of this investigation suggests that the substitution of naturals by synthetics was not nearly as complete as this. Natural dyes continued to feature in dye manuals and Hummel and others continued to research natural dyes into the later nineteenth century. Certainly mechanisation took over in textile dyeing and printing and Morris' methods were the antithesis to this. The dyed samples and dye methods in the manuals suggest that natural dyes continued to be used even in combination with the synthetics. In the second part of this study a method was developed by which the synthetic dyes can be identified on fabric without the need to extract the dye. Although there was not time to investigate this in the present study this will allow surveys of late nineteenth century fabrics to determine how extensively synthetic dyes were in fact used and how long the natural dyes persisted.

#### Further work

There is much scope for further work on the themes explored in this study. The Raman technique requires further refinement and could be applied to dyes and pigments on cotton

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<sup>432</sup> ADAM, C. D. (2008) In situ luminescence spectroscopy with multivariate analysis for the discrimination of black ballpoint pen ink-lines on paper. *Forensic Science International*, 182, 27-34.

fabrics. Wool and silk, both protein fibres, were chosen in the present study for purposes of simplification and they were both widely used at the time. However, cotton was an increasingly popular fibre in the nineteenth century. The development of printing on cotton in the eighteenth century and the rise of the domestic cotton industry provided a ready source of fabric for dress<sup>433</sup> and so any comprehensive survey of dyes on fabrics would have to include this fabric. The study of the dye manuals shows that dye mixtures will be present in many, if not most, historic samples and these will be more complicated to analyse requiring computer analysis of spectra to separate signals due to separate compounds. An assessment of the prevalence of the synthetic or natural dyes in use might be accomplished by examining dated needlework samplers from the nineteenth century. In terms of art historical research, analysis of examples from the Aesthetic and Arts and Crafts movements would reveal whether these textiles are indeed free from synthetic dyes.

Research on dyeing and printing has made use of factory sample books<sup>434</sup> but much less is published on dye manuals perhaps because they are more technical than the older records and the historians who might encounter them cannot interpret them and conservation scientists do not consult the archives where the dye manuals are found. These sources have provided data on suppliers, the extent of use of synthetic as opposed to natural dyes as well as naturally aged dyed samples. The dye methods have not been fully utilised here and there is much more information which could be extracted from these volumes. This study suggests that these are a neglected resource for research. Census returns are a rich source of information about professions and places of origin and could be used to investigate the extent to which foreign workers were used at all levels in the English textile industry. In the case of Hummel, for example, his widowed mother re-married another cotton printer who lived very close by.

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<sup>433</sup> Levitt states 'The Victorian era saw more people than ever before entering the ranks of the lower-middle classes. Cotton gave the possibility of a starched white shirt and collar to the poorest clerk and cotton lace, satin and velvet brought the appearance of luxury within reach of many for Sunday-best.' LEVITT, S. (1996) *Clothing*. In ROSE, M.B. (Ed.) *The Lancashire Cotton Industry. A History Since 1700*. Preston, Lancashire County Books. Page 154

<sup>434</sup> See for example, SYKAS, P. A. (1998) The Public Require Spots: Modernism and the Nineteenth Century Calico Designer. *The Journal of the Textile Institute*, 89, 3-15.

Natural dyes which tend to be found on the oldest and most valuable textiles have been widely studied to date. There is a requirement to identify which are present to establish provenance and to date the objects and finding justification for spending time and money on these analyses is simple given the rarity and value of the pieces. However, the fabrics on which synthetic dyes are found are becoming older and interest in nineteenth century objects is growing amongst dress collectors and historians. It is hoped that the method developed here can be extended and applied to such collections and used to inform conservation. The results will contribute to aspects of nineteenth dress history allowing a review of the rate of spread of the synthetic dyes. New sources of information relevant to the study of dress history including nineteenth century newspapers and periodicals, now available in digital form, have been used here and these have been demonstrated to be valuable in this type of study.

This thesis challenges the simple view of synthetic dyes displacing naturals showing that the process was probably slow and piecemeal. Detailed information about the Yorkshire College and John James Hummel has been used to illuminate the struggles within the dye industry and the training of suitable workers in England. Although the industrialists realised that they were losing ground to the German firms, their efforts to catch up were too little, too late and the pharmaceutical industry which grew out of the synthetic dyes was firmly based in Germany and Switzerland.

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Daily News: London

The Examiner: London

Freeman's Journal: Dublin

Glasgow Herald: Glasgow

The Graphic: London

Huddersfield Daily Chronicle

Huddersfield Daily Chronicle and West Yorkshire Advertiser

Leeds Mercury: Leeds

Liverpool Mercury: Liverpool

London Review and Weekly Journal of Politics, Literature, Art and Society: London

The Manchester Times: Manchester

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## **Appendix 1**

### **Methods used for dyeing fabrics**

#### **Dye cycles**

All dyeing was carried out in beakers used as dye baths. Their temperature was controlled by immersing them in a thermostatically controlled water bath. The surface of the water bath was covered with polypropylene insulating spheres and at temperatures above 75°C the lid of the water bath was used to maintain the temperature.

The dye baths were continuously stirred to promote even (level) dyeing and the fabric was lifted out of the dye bath during dye and additive additions.

#### **Dyeing with basic dyes**

The liquor ratio used was 100:1 so 1g of fabric was used with a dye bath of 100ml total volume. Softened water was used to make up the difference in volume between the total of the additives and that of the dye bath. Acetic acid was used as an additive. The softened water was heated to 50°C in the dye bath and then the fabric was added and wetted completely. Acetic acid was added to 3% after 10 min and stirred well. After a further 10 min the dye was added and stirred well. A 1% (w/v) dye solution was used. The temperature of the dye bath was raised to 90°C over 30min and then maintained at that temperature for 30min. The dye baths were stirred regularly during this process and the volume maintained by addition of hot softened water.

The fabric was rinsed, first with hot softened water and then with progressively colder water. None of the dye baths was completely exhausted and, although the fabric was extensively rinsed, dye bleeding continued.

#### **Dyeing with acid dyes**

The same liquor ratio was used as for dyeing the basic dyes. Acetic acid, Albegal FFA™, and 10% (w/v) sodium sulphate (Glauber's salt) were used as additives.

The water and 0.3g/l Albegal FFA™ were heated to 50°C in the water bath and the fabric was then added and allowed to wet out. After 10 min the other additives, 1%

acetic acid and 10g/l sodium sulphate, were added. After a further 15 min the dye solution in softened water was added. A 0.5% (w/v) solution was used for most of the dyes except for Methyl red which was used at 0.02% (w/v).

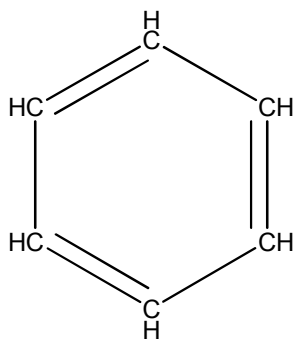
The temperature of the dye bath was raised to 70°C over 25 min and then held for 20-25 min during which time the pH of the bath was checked and adjusted to pH 4.5 as necessary with 10% acetic acid. The temperature of the bath was then raised to 90°C over 25-30 min and then held at that temperature for 25-30 min. The volume of the dye bath was monitored at these higher temperatures and hot softened water added as necessary to maintain the total volume. The pH was also checked and maintained at 4.5 as before. On completion of the dyeing, the dye baths were left to cool for 1 hour. The fabric was then copiously rinsed with softened water until dye bleeding had either stopped or become minimal. It was then rinsed in 1% formic acid solution to increase the wet fastness of the dye. As for the basic dyes, none of the dye baths were exhausted and some dye bleeding was seen in the final rinses.

## Appendix 2

### Brief guide to diagrammatic representations of chemical structures

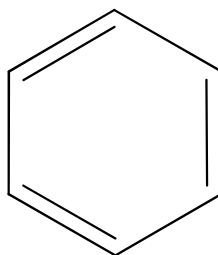
The chemical structures used in this thesis adopt certain common conventions. Normal chemical diagrammatic structures are shown with each atom identified by its chemical symbol and joined to each other atom by a line representing the covalent bond between the two. Each covalent bond signifies a pair of electrons shared between these atoms. Occasionally more than one pair of electrons is shared and then the bond becomes a double or even a triple bond denoted by two or three lines respectively.

Thus the structure for the benzene ring can be shown as below:

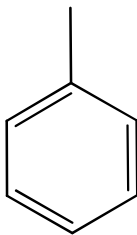


In this structure each carbon atom (C) must have four bonds in total and each hydrogen atom (H) must have one. In order to achieve this the carbon atoms are joined to their neighbours by alternate single and double bonds and each is joined to one hydrogen atom.

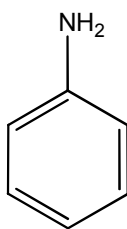
Large structures containing multiple carbon atoms can be very complex and are simplified by assuming a carbon atom at every junction of bonds and not showing the hydrogen atoms which complete the structure. The diagram for a benzene molecule is then drawn as shown below.



If a hydrogen atom is replaced by a methyl group ( $-\text{CH}_3$ ) it would be shown as in the diagram below.



However, other groups substituted on the carbon atoms of the ring would be shown explicitly as for aniline below where an amine ( $\text{-NH}_2$ ) group takes the place of the methyl group.





## Appendix 3

### A brief guide to light and colour

Light as perceived by our eyes is one small part of a continuous range of electromagnetic energy. The exact nature of electromagnetic energy is contradictory as it has some properties of waves and some of particles. The simplification that is of most use when considering spectroscopy is that the light energy is contained in short bursts of waves and these are referred to as photons. Each photon only contains light of one wavelength so that the whole spectrum is made up of photons at all possible wavelengths. The wavelength of the photon is inversely proportional to its energy according to equation 1 so that short wavelength photons have higher energy than longer wavelengths. This makes the wavelength of the light its most critical parameter and the sections into which the electromagnetic spectrum is divided are defined by wavelength.

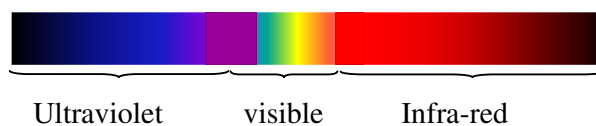
$$E = hc/\lambda \quad (\text{Eq 1})$$

*Where E is energy, h is Planck's constant, c is the speed of light and  $\lambda$  is wavelength.*

Wavelength and frequency are the most commonly used units for electromagnetic energy in everyday life. They are alternative ways of quantifying the wave function with the wavelength being the distance between successive peaks (or troughs) along the wave and the frequency ( $\nu$ ) the number of these peaks (or troughs) in a given distance or a given time. In spectroscopy an alternative unit, the wavenumber, is often used. This is related to the frequency of the wave and is a measure of the number of waves in one centimetre with units per centimetre ( $\text{cm}^{-1}$ ).

Wavelength and wavenumber are linked as shown below.

Wavelength (nm)	200	300	400	500	600	700	800	900	1000	1100	1200
Wavenumber (cm <sup>-1</sup> )	50000	33333	25000	20000	16667	14286	12500	11111	10000	9091	8333



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Figure A3.1 Spectrum of light in the visible region

### The chemistry of colour

All colour is produced by the modification by an object of the light incident on it. The range of light visible to the human eye is the spectrum from 400 to 700nm in wavelength and broadly equal amounts of light energy are present in sunlight at all these wavelengths. The effect of separating these wavelengths into a continuous spectrum can be seen, for example, in a rainbow. When illuminated with this broad range, coloured objects act on the light to specifically absorb some of these wavelengths and the human eye perceives the colour as the difference between the full spectrum and the reflected light. This energy absorption can occur by a variety of mechanisms such as physical diffraction in iridescence or chemical rearrangements within a molecule which lead to absorption of some wavelengths.<sup>1</sup> It is the latter mechanism which is important in the colour properties of dyes. The spectral distribution of the incident light is also critical in the perceived colour of an object as most sources of light do not contain all wavelengths of the visible spectrum in equal intensities and therefore some wavelengths which would normally be reflected and seen by the observer may not be present.

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<sup>1</sup> TILLEY, R. J. D. (1999) *Colour and optical properties of materials: an exploration of the relationship between light, the optical properties of materials and colour*, Chichester, John Wiley and Sons, Ltd.

Table A3.1 Wavelengths of coloured light<sup>2</sup>

Colour of reflected beam	Colour absorbed	Wavelength absorbed (nm) <sup>3</sup>	Energy of absorbed wavelengths (kJ)
None	Ultraviolet	<400	>300
Greenish yellow	Violet	400 – 430	472 – 277
Yellow-orange	Blue	430 – 490	277 – 247
Red	Blue-green to green	490 – 510	247 – 235
Purple-red	Green	510 – 530	235 – 223
Violet	Greenish yellow	530 – 560	223 – 214
Blue	Yellow	560 – 590	214 – 207
Greenish-blue	Orange	590 – 610	207 – 197
Blue-green to green	Red	610 – 700	197 – 176
None	Infrared	>700	<176

In addition, the perceived colours are not an inherent property of the light energy but a construction of a complicated set of receptors in the eye which in turn produce nerve impulses in the brain. This area is the subject of much research and has formed the basis of the measurement of colour for applications where customer perception is the most important criterion. Much research in recent years has greatly increased our understanding in this area but there are still some areas of uncertainty, for example concerning vision at low light levels and the exact processing of signals in the brain.<sup>4</sup>

Therefore there are three separate components involved in human perception of colour which are all critical to the end result; the spectrum of the incident light, the molecular nature of the object observed and the perceptual system of the observer. In UV-vis spectroscopy, the incident light is characterised so that its spectral distribution is known and the human detector is replaced with an electronic system. In this way the only variable remaining is the molecular structure of the analyte and this can then be determined.

<sup>2</sup> TIMAR-BALAZSY, A. & EASTOP, D. (1998) *Chemical Principles of Textile Conservation*, Oxford, Butterworth-Heinemann.

<sup>3</sup> 1 nanometre (nm) is 1 ten millionth of a centimetre

<sup>4</sup> BAYLOR, D. (1995) Colour Mechanisms of the Eye. IN LAMB, T. & BOURRIAU, J. (Eds.) *Colour: Art and Science*. Cambridge, Cambridge University Press.

MOLLON, J. (1995) Seeing Colour. IN LAMB, T. & BOURRIAU, J. (Eds.) *Colour: Art and Science*. Cambridge, Cambridge University Press.

## Appendix 4

### Spectroscopic experimental methods

#### Preparation of silver colloid

All solutions were prepared with purified water and glassware was rinsed with acid to clean before use.

250ml 1mM silver nitrate was placed in a round bottomed flask with a refluxing condenser attached and brought just to boiling point with the use of a heating mantle. 10ml 1%(w/v) trisodium citrate was added. The mixture was boiled gently for approximately 1 hour and then allowed to cool and stored in the dark in the fridge. It was centrifuged before use to concentrate.

#### Renishaw Ramascope 2000 (SERS)

The instrument was calibrated with a silicon slide using the 50x objective on the microscope. The samples were analysed with 10-30s scans using the 50x objective. The maximum laser power was 3mW and ranges of 10-50% were used. ThermoScientific Nicolet iS10 instrument with ATR attachment

The ATR window was cleaned with ethanol and a background reading of air taken. The samples were placed under the clamp arm and the clamp tightened to the torque point. The scans were taken with a interferometer resolution of  $4\text{cm}^{-1}$  and 8 scans were averaged.

#### PerkinElmer FT-Raman

The system was calibrated and the focus adjusted using a barium sulphate standard giving a high intensity peak at about  $1000\text{cm}^{-1}$  Raman shift. The instrumental settings used for each set of experiments is shown in Table 1. The laser power was measured using a separate meter.

**Table 1 Summary of FT-Raman settings**

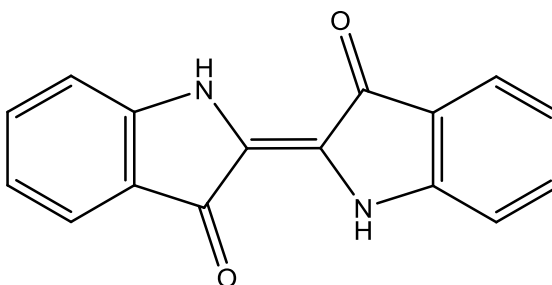
Date	Dyes/fabric	Settings
7 <sup>th</sup> Dec 10	Undyed wool Orange II on wool Tartrazine on wool New cocchine on wool Acid yellow 11 on wool Acid yellow 17 on wool Methyl violet on wool Fuchsin acid on wool Rhodamine 6G on wool	Interferometer resolution: 16cm <sup>-1</sup> J-stop image: 12.5mm J-stop resolution: 9.36cm <sup>-1</sup> 30 scans Laser power: 400mW nominal (~200mW actual) Optical path difference velocity: 0.1cm/s
8 <sup>th</sup> Dec 10	Undyed silk Orange II on silk Tartrazine on silk New cocchine on silk Acid yellow 11 on silk Acid yellow 17 on silk	Interferometer resolution: 16cm <sup>-1</sup> J-stop image: 12.5mm J-stop resolution: 9.36cm <sup>-1</sup> 30 scans Laser power: 400mW nominal (~200mW actual) Optical path difference velocity: 0.1cm/s
9 <sup>th</sup> Dec 10	Undyed silk Safranin on silk Methyl violet on silk Rhodamine 6G on silk Naphthol green on silk Fuchsin acid on silk	Interferometer resolution: 16cm <sup>-1</sup> J-stop image: 12.5mm J-stop resolution: 9.36cm <sup>-1</sup> 30 scans Laser power: 400mW nominal (~200mW actual) Optical path difference velocity: 0.1cm/s
30 <sup>th</sup> Mar 11	Undyed silk Malachite green on silk at 2%, 1.5%, 0.5%, 0.2%	Interferometer resolution: 8cm <sup>-1</sup> J-stop image: 11.55mm J-stop resolution: 8.0cm <sup>-1</sup> 60 scans Laser power: 400mW nominal (~200mW actual) Optical path difference velocity: 0.1cm/s
15 <sup>th</sup> Jun 11	Powders: New cocchine Orange II Tartrazine Acid yellow 11 Acid yellow 17	Interferometer resolution: 16cm <sup>-1</sup> J-stop resolution: 14.95cm <sup>-1</sup> 20 scans Laser power: 600 or 400mW nominal (~300 or 200mW actual) Optical path difference velocity: 0.1cm/s
16 <sup>th</sup> Jun 11	Powders: Safranin Methyl red Methyl violet Fuchsin acid Para red Naphthol green Victoria blue	Interferometer resolution: 16cm <sup>-1</sup> J-stop resolution: 14.95cm <sup>-1</sup> 20 scans Laser power: varied depending on fluorescence Optical path difference velocity: 0.1cm/s
26 <sup>th</sup> Jul 11	Dye manual samples: Scoured, undyed wool Orange G Rose Bengale Tartrazin	Interferometer resolution: 16cm <sup>-1</sup> J-stop resolution: 14.95cm <sup>-1</sup> 40 scans Laser power: 600mW nominal (~300mW actual) Optical path difference velocity: 0.1cm/s
4 <sup>th</sup> Aug 11	Dye manual samples: Scoured, undyed wool Indigo (woad) Cochineal Flavin Cudbear Indigo carmine Naphthol green Victoria blue R Victoria blue B Magenta Shattered mauve silk Undyed modern silk	Interferometer resolution: 16cm <sup>-1</sup> J-stop resolution: 14.95cm <sup>-1</sup> 20 or 40 scans Laser power: varied depending on fluorescence Optical path difference velocity: 0.1cm/s

## Appendix 5

### Structures of natural dyes

#### A5.1 Natural dyes

Perhaps the best known natural dye is indigo, the chemical structure of which is shown below (Figure A5.1).<sup>1</sup> The blue colour of this dye became one of the most iconic shades in our culture and received a phenomenal boost in the mid twentieth century when blue jeans became fashionable and indeed almost universal.<sup>2</sup>



**Figure A5.1.** The structure of indigo (indigotin)

Indigo is sourced from a range of dye plants from the woad and indigo families. It has to be extracted by a process involving fermentation of the plant material and subsequent oxidation leading to the precipitation of the insoluble compound shown above. Since the blue coloured compound is not water soluble it is reduced to a soluble form which is yellowish-green before it can be used as a dye. The whole process is very complex and requires a high degree of skill, appearing almost like magic to the uninitiated. This has led to the association of magical properties with the dye and folklore traditions around the process.<sup>3</sup>

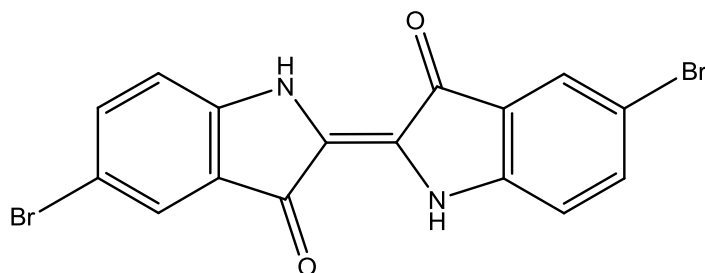
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<sup>1</sup> An explanation of the conventions used in the diagrammatic representations of the chemicals can be found in Appendix X

<sup>2</sup> PASTOUREAU, M. (2001) *Blue: the history of a color*, Chichester, Princeton University Press. BALFOUR-PAUL, J. (1998) *Indigo*, London, British Museum Press. Pastoreau charts the rise of the importance of the colour over time in the West although, as Balfour-Paul indicates, it has been a much-used dye in Eastern cultures for much longer.

<sup>3</sup> BALFOUR-PAUL, J. (1998) *Indigo*, London, British Museum Press. William Morris exploited this aspect of indigo dyeing to impress visitors to his dyeworks. MACCARTHY, F. (1994) *William Morris. A Life for Our Time.*, London, Faber and Faber.

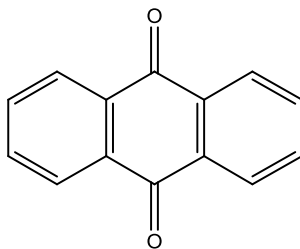
Another dye closely related chemically to indigo is Tyrian purple.<sup>4</sup> The fact that this dye only differs from indigo chemically by the addition of two atoms of bromine shows how sensitive the colour of a compound is to very small structural changes (Figure A5.2).



**Figure A5.2.** The structure of Tyrian purple (6,6'-dibromoinditgotin)

This dye is also sourced from a very different material from indigo being a secretion produced by a marine mollusc when stressed. Indigo carmine is another form of indigo with acid groups instead of bromine on the benzene rings. Although it is prepared from the natural dye indigo it does require chemical processing and so could arguably be classed as a synthetic dye. Some authors have characterised such dyes as 'semi-synthetic'.<sup>5</sup>

One of the next most common class of compounds found in natural dyes are the anthraquinones. The basic structure of this group is shown below (Figure A5.3).



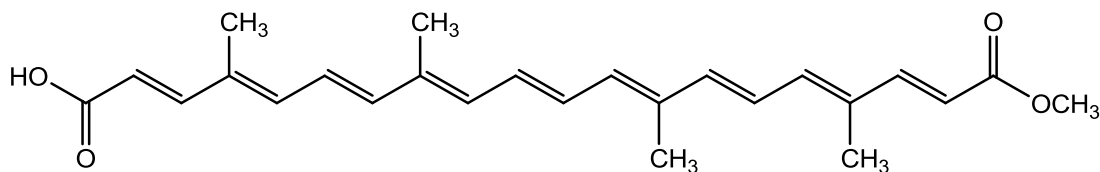
**Figure A5.3** The structure of anthraquinone

<sup>4</sup> This dye has several common names including 'shell-fish purple' and 'Imperial purple'.

<sup>5</sup> BARNETT, J. C. (2007) Synthetic organic dyes, 1856-1901: an introductory review of their use and related issues in textile conservation. *Reviews in Conservation*, 8, 67-77.

The red dyes madder, kermes, cochineal and lac are all examples of anthraquinone compounds. Kermes, cochineal and lac are found in insects whereas madder is another plant extract which has been almost as universally used as indigo. It was the dye used to produce the unusually fast Turkey Red, the secret of which was in the process of applying the dye to the linen or cotton cloth.<sup>6</sup> Madder contains the compounds alizarin, purpurin, acidic pseudopurpurin and xanthopurpurin in varying proportions of which the first two are predominant. These are all substituted with chemical groups added to one benzene ring of the anthraquinone molecule only. Kermes, cochineal and lac are acid anthraquinones, in the case of cochineal with one glycosylated form in the mixture. These are all substituted on both the benzene rings of the anthraquinone.

Another chemical class of natural dye is the carotenoids which give yellow/orange colours. These are long chain carbon compounds with many unsaturated bonds such as saffron and annatto sourced from a variety of plant types. A representative example is bixin, the structure of which is shown below (Figure A5.4).



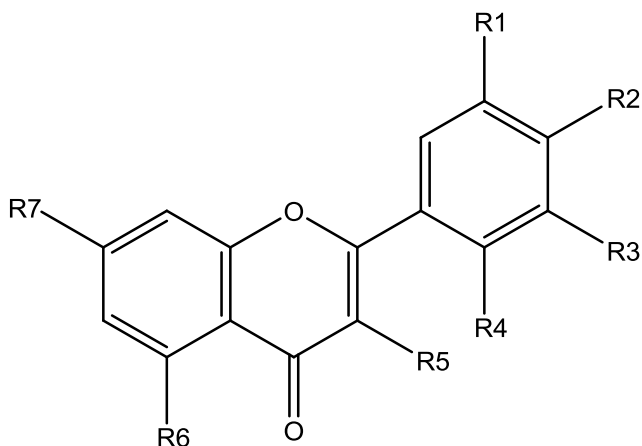
**Figure A5.4.** The structure of bixin, the principal colorant in annatto

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<sup>6</sup> GRAAFF, J. H. H. D. (2004) *The Colourful Past: The Origins, Chemistry and Identification of Natural Dyestuffs*, London, Archetype Press. Page 95.

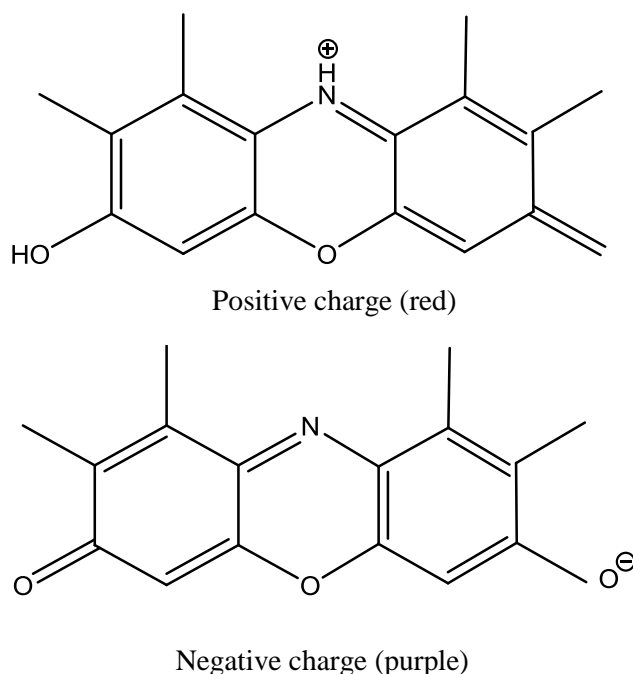


Far more commonly used, however, as yellow colorants are the flavonoids, of which an important example is weld. The multiple forms of this molecule, sourced from a range of plants, have a variety of different chemical groups in the positions shown as R1-R7 in Figure A5.5.



**Figure A5.5. The structure of flavonoid**

The only dye to produce a natural purple apart from Tyrian Purple is orchil sourced from lichens. This contains a variety of phenazones which are difficult to extract from the plant matter and involve a fermentation process as for indigo. Similar to indigo the dye compound is insoluble and the application is by a vat process. Orcein is the dye used on litmus paper and is red in acid solutions and blue/purple in alkaline conditions. This gives the dye a purple colour overall although this could be manipulated by the dyer by changing the pH conditions. The two chemical forms of the dye are shown in Figure A5.6 below.



**Figure A5.6 Structures of orchil**

The last major group of dyes are the redwoods which are divided into soluble redwoods comprising various forms of brazilin, and insoluble redwoods based on the more complex molecule santalin. As their name suggests these dyes produce red colours.

Other substances from natural sources have been used as dyes but are less important and have chemical structures related to those already discussed. These include black dyes. A good, stable black was a difficult colour to achieve with natural dyes. Almost always a mixture of dyes was used which might include indigo, madder, tannins and iron. Gallotanin dyestuffs are derived from barks and galls. These decompose in water to give sugars and acids and use iron mordants.

There are three methods used to apply these dyes to textile fibres which also depend on the chemistry of the molecules. Some of them which have charged groups, either acidic (negatively charged) or basic (positively charged), are able to interact directly with opposite charges on the fibre and are therefore classed as acid or basic dyes. The interaction with the fibre depends on the immediate environment being chemically correct to maintain the

required charged states and these dyes can therefore be fugitive in acidic or alkaline conditions. Direct dyes interact with the textile by weaker types of chemical bond and tend to be long molecules with multiple points of attachment. The most extensive class of dyes are the mordant dyes. These can be permanently attached to the textile fibres by the mediation of a further chemical, usually a metal, which will bind to both the textile fibre and the dye. These metals are added to the textile in the form of metallic salts either before or at the same time as the dye. The last class of dyes are the vat dyes, like indigo, which are reduced to allow them to dissolve and soak into the fibre, subsequently being precipitated in or on the fibre.

**Table A5.1.** Dyeing mechanisms for natural dyes

Dyeing mechanism	Dyestuffs
Vat	Indigo and Woad Orchil
Acid/basic	
Mordant	Anthraquinones (eg Madder, Kermes, Cochineal, Lac) Flavonoids (Weld etc) Soluble Redwoods (eg Brazilwood) Insoluble Redwoods (eg Red Sandalwood) Galls and tanins
Direct	Carotenoids (eg Annatto, Turmeric and Saffron) Indigo carmine

## Appendix 6

### Equipment and materials

#### Equipment:

PerkinElmer System 2000 NIR FT-Raman, diode pumped Nd:YAG laser and Spectrum software:

PerkinElmer Life and Analytical Sciences, Chalfont Road, Seer Green, Beaconsfield, Bucks, HP9 2FX, UK, +44 (0)1494 687515

Renishaw Ramascope 2000 with Renishaw HeNe laser at 632.8nm, Master Renishaw CCD detector and Leica DMLM confocal microscope

Renishaw plc, New Mills, Wotton-under-Edge, Gloucestershire, GL12 8JR, UK

[www.renishaw.com](http://www.renishaw.com)

#### Fabric sample holder:

Ventacon UK Ltd., Gable Cottage, Crawley, Hants, SO21 2PR, UK, +44 (0)1962 776314

#### FT-IR system:

ThermoScientific Nicolet iS10 FT-IR with ATR attachment:

Thermo Fisher Scientific, Fisher Scientific (UK) Ltd, Bishop Meadow Road, Loughborough, Leics, LE11 5RG, UK, 01509 231166, [www.fisher.co.uk](http://www.fisher.co.uk)

#### Fabrics

Silk (medium weight plain weave Habotai):

Whaleys (Bradford) Ltd., Harris Court, Great Horton, Bradford, West Yorkshire, BD7 4EQ, UK, +44(0)1274 576718, [info@whaleysltd.co.uk](mailto:info@whaleysltd.co.uk)

Wool (plain weave):

Context Weavers, Park Hill Holcombe Road BB4 4NP, UK, 01706 220917

#### Chemicals:

Dehypon LS45<sup>®</sup>:

Conservation Resources (UK) Ltd., Unit 2, Ashville Way, Off Watlington Road, Cowley, Oxford OX4 6TU, UK, +44 (0)1865 747755, [ConservArts@aol.com](mailto:ConservArts@aol.com)

Albegal<sup>®</sup> FFA: Town End (Leeds) PLC, Silver Court, Intercity Way, Stanningley, Leeds, LS13 4LY, UK, +44 (0)1132 564251

All other chemicals:

Fisher Scientific (UK) Ltd, Bishop Meadow Road, Loughborough, Leics, LE11 5RG, UK, 01509 231166, [www.fisher.co.uk](http://www.fisher.co.uk)