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Enlighten:Theses http://theses.gla.ac.uk/ theses@gla.ac.uk Turkey red dyeing in late-19th century Glasgow: Interpreting the historical process through re-creation and chemical analysis for heritage research and conservation

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Submitted in fulfillment of the requirement for the degree of Doctor of Philosophy

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Abstract

The dyed cotton textiles called Turkey red are a significant part of Scotland's cultural heritage and the legacy of its textile manufacturing industry, and were known for their exceptional colour and fastness to light and wash fading. This thesis is a multi-disciplinary investigation of the chemistry of these unique textiles in the context of 19th c. Scotland using historical material re-creations and modern analytical chemistry, situating the dyeing process in a historical context. This research is a significant contribution toward the continued preservation of historical Turkey red textiles.

Through a detailed, chemistry-focused examination of Turkey red methods published in English and French between 1785-1911, the key ingredients and steps for the process from a chemical perspective are identified (Chapter 1). The significance, chemistry, and previous research on the role of the oil (Chapter 2) and dye sources used (Chapter 3) are discussed to form the basis of the material re-creations and analysis. The oil is fundamental to and characteristic of the process, which is also noteworthy for being the first to replace a natural dye source (madder or garancine) with a coal-tar derived analogue (synthetic alizarin). Re-creations of dyed Turkey red, Turkey red oil, oiled calico, and synthetic alizarin provide experiential data and reference materials to test analyses prior to application on historical objects (Chapter 4).

The analysis of Turkey red oils by nuclear magnetic resonance (NMR) spectroscopy and high-performance liquid chromatography with mass spectrometry (HPLC-MS) (Chapter 5) provides information used to characterise, for the first time, how the oil and cotton fibres bond to form the basis of the Turkey red complex. This is studied using conservation-based diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and solid-state NMR (ssNMR) on replica and 19th c. pieces of Turkey red (Chapter 6). Dyes analysis of these samples by ultra high performance liquid chromatography with photodiode array (UHPLC-PDA) identifies chromatographic profiles of textiles dyed with natural or synthetic dye based on synthetic chemical markers. The presence of pigments on printed Turkey red is confirmed by infrared 4 Abstract

spectroscopy and scanning electron microscope with energy-dispersive X-ray (SEM-EDX) (Chapter 7).

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Foreword



La plus belle prérogative des sciences est d'éclairer la marche et de perfectionner les procédés des arts.¹

The greatest prerogative of the sciences is to enlighten the progress and perfect the practices of the arts.

Pa and Ma traded for a long time. The storekeeper took down bolts and bolts of beautiful calicoes and spread them out for Ma to finger and look at and price. Laura and Mary looked, but must not touch. Every new colour and pattern was prettier than the last, and there were so many of them! Laura did not know how Ma could ever choose. Ma chose two patterns of calico to make shirts for Pa, and a piece of brown denim to make him a jumper. Then she got some white cloth to make sheets and underwear. Pa got enough calico to make Ma a new apron. Ma said: 'Oh, no, Charles, I don't really need it.' But Pa laughed and said she must pick it out, or he would get her the [T]urkey red piece with the big yellow pattern. Ma smiled and flushed pink, and she picked out a pattern of rosebuds and leaves on a soft, fawn-coloured ground.²

Little House in the Big Woods, Laura Ingalls Wilder (1932).

Many years before I wrote this thesis, I read *Little House in the Big Woods* and wondered what the Turkey red must have looked like. I did not know that one day, I would have the opportunity to study, learn from, and re-create these brilliant, beautiful textiles that would have made a scandalously bright apron. Researching the blend of art and science involved in the production of these textiles has been a pleasure and I hope the outcomes will contribute to a greater awareness and appreciation of dyed and printed Turkey red.

¹ Jean Baptiste Vitalis, Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles, (Paris: Galerie Bossange Père, 1823).

² Laura Ingalls Wilder, Little House in the Big Woods, (New York, New York: Harper & Row, 1932), 96.

Image: University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/4. 1857-1863.

The continued preservation of heritage textiles is dependent on our understanding of their material composition and physical properties. Paradoxically, putting these objects on display for the appreciation of the public often shortens their life due to the detrimental effects of light exposure and fluctuations in temperature and humidity. The field of heritage conservation science applies modern chemical principles and non-invasive or micro-analyses to study these valuable textile artefacts. The information gained from this research improves conservation care and display practices, helping to maintain object integrity and preserve them for future generations.

The brilliant colour of Turkey red and how it is dyed have, for centuries, been a point of fascination to many.¹ Despite research and practical investigations extending back to the very beginnings of chemistry as a modern field during the Enlightenment, the chemistry of this notoriously complex process² has never been fully understood.³ To obtain quality Turkey red, a dyer needed a good deal of practical experience,⁴ but knowledge of the process was a jealously guarded industrial secret.⁵ Nevertheless, it spread across Europe through the use of spies⁶ and the publication of texts on the process starting in the mid-1700s,⁷ though it was said books alone were not enough to learn the process.⁸

In addition to its remarkable hue, it was renowned for its legendary fastness to washing, light exposure, and even bleaching.^{9,10} Dyeing and printing Turkey

¹ Carruthers, "A New Process of Dyeing Turkey Red," 123.

² Haller, "The Chemistry and Technique of Turkey Red Dyeing," 1417.

³ Zollinger, Color Chemistry: Syntheses, Properties, and Applications of Organic Dyes and Pigments, 255.

⁴ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 205.

⁵ Johnston, "The Secret of Turkey Red - Technology Transfer with a Scottish Connection," 298.

⁶ Lowengard, The Creation of Color in Eighteenth-Century Europe.

⁷ Mémoire contenant le procédé de la teinture du coton rouge-incarnat d'Andrinople sur le coton filé.

⁸ Chenciner, *Madder Red: a History of Luxury and Trade*, 189.

⁹ Ure, A Dictionary of Arts, Manufactures, and Mines, 793.

¹⁰ Arthur et al., "Seeing Red: Scotland's Exotic Textile Heritage," 6.

red was a major industry in the West of Scotland for about 150 years and thousands were employed in 'the Craft', as the trade was known in the Vale of Leven where many of the firms were located.¹¹ These firms, founded independently, became part of the United Turkey Red Company, Limited (UTR) in 1898. Their records in the Scottish Business Archive at the University of Glasgow form a significant part of the primary source material for this research.

During the time Turkey red was dyed in Europe, from the mid-18th to early 20th c., two major technological advances were made that reduced the production time from upwards of a month to only a few days.^{12,13} The invention of Turkey red oil, the first synthetic anionic surfactant,¹⁴ and synthetic alizarin, the first naturally occurring dye to be synthetically replicated,¹⁵ vastly improved the efficiency of the process but did not fundamentally alter its chemistry. The development of these products and their adoption by dyers occurred around the early 1870s, marking a transition between the 'old' process that used rancid olive oil and ground madder roots to the 'new' one, which substituted the novel chemical ingredients, though both produced Turkey red. To study the effects of these new ingredients in the context of the process, this research focuses on Turkey red dyed in the second half of the 19th c.

In addition to its connections with the field of chemistry, Turkey red was also tied to the growth of the chemical industry¹⁶ as the growing textile trade demanded larger quantities of ingredients and more cost-effective materials. The invention of synthetic alizarin was a significant step forward for Turkey red dyeing, but the synthetic dyes industry would eventually undermine it as well. It was not until the end of the 19th c. that chemists could produce a synthetic red dye whose fastness was even comparable to Turkey red, and not until after

¹¹ Fryer, *Behind the Vale*, 104.

¹² Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 587.

¹³ Leigh, "On the Estimation of Alizarin in Dyed Cotton Fabrics, and on an Attempt to Ascertain the Composition of Turkey-Red and Other Alizarin Lakes," 205.

¹⁴ Gunstone and Padley, *Lipid Technologies and Applications*, 788.

¹⁵ Travis, *The Rainbow Makers*, 164.

¹⁶ Macfarlan, "City of Glasgow," 165-167.

World War I that the development of naphthol dyes began to supersede Turkey red with production ending by 1936.¹⁷

Interest in the chemistry of the process diminished significantly with the decline in production.¹⁸ It did not entirely vanish, however, nor did general interest in the industry and the beautiful printed textiles preserved in collections around the world. A 2012 project at National Museums Scotland called Colouring the Nation explored the design, manufacture, and patterns of printed Turkey red found in their collections.^{19,20} Exhibitions on Turkey red were also shown at the Museum of Printed Textiles in Mulhouse²¹ and at the Collins Gallery in Glasgow.²² In addition, historical Turkey red can be found in the UK in the collections of the Victoria & Albert Museum (V&A), The National Archives, Glasgow Life, The Society of Dyers and Colourists, and the Museum of Science and Industry. Abroad, Turkey red is preserved in the collections of the Smithsonian, the Technical Museum of Vienna, and the Museum of Natural History in New York City, to name a few. A recent project supported by the West Dunbartonshire Council published a guide for a walk along the Leven with many former sites of Turkey red works marked,²³ and local historians continue to produce extensive accounts of the history of the industry.^{24,25}

Modern research on the chemistry of Turkey red addresses the colour complex^{26,27} but there has been no comprehensive investigation of the chemistry of the entire process until now. The unique nature of Turkey red, which is both a

¹⁷ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 504.

¹⁸ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 112.

¹⁹ Nenadic and Tuckett, "Colouring the Nation."

²⁰ Nenadic and Tuckett, Colouring the Nation: the Turkey Red Printed Cotton Industry in Scotland C. 1840-1940.

²¹ Jacqué et al., Andrinople: Le Rouge Magnifique.

²² Arthur et al., "Seeing Red: Scotland's Exotic Textile Heritage."

²³ The River Leven Heritage Trail.

²⁴ Fryer, Behind the Vale.

²⁵ MacKay, Bleachfields Printfields and Turkey Red.

²⁶ Kiel, "Metaalcomplexen Van Alizarinerood."

²⁷ Soubayrol, "Préparation et étude structurale des complexes formés entre l'aluminium et l'alizarine: Importance de la nature du solvant et de la base utilisés sur le degré de condensation de l'aluminium et l'agencement moléculaire."

process and a product but technically not a dye²⁸ in that it exists only on cotton fibres, complicated previous work. Historical research was limited to empirical, extractive analytical techniques that could not effectively characterise the complex,²⁹ which must be characterised *in situ* on the fibres. The development of modern instrumental analytical tools in recent decades presents a new opportunity to study and characterise historical Turkey red. This work will hopefully improve our understanding of these textiles and how they can be displayed without causing them further damage, a serious concern in the conservation of heritage textiles.

The research in this thesis aims to improve our understanding of the chemistry of historical Turkey red by addressing the following questions:

1. What are the essential steps and ingredients in making Turkey red and is it possible to dye it following a historical process?

2. What is the composition of the oil used in Turkey red dyeing, and can it be characterised on historical Turkey red through conservation-based analysis?

3. Which red dyes are present on historical Turkey red, and can they help determine object provenance?

These questions are answered by a process-based, cross-disciplinary approach combining an extensive review of historical publications, historical research, and archive material with modern chemical analytical techniques. The historical literature provides knowledge of how Turkey red was dyed, making it possible to design conservation-based analyses to study and characterise the historical textiles. This work contributes to the field of heritage conservation science by improving the knowledge of these unique textiles and laying a foundation of analytical work that will be expanded upon to gather more information about the robustness of historical Turkey red to light exposure, a significant concern for historical textiles. The approaches taken in this thesis are:

²⁸ Brackman, Clues in the Calico: a Guide to Identifying and Dating Antique Quilts, 63.

²⁹ Crookes, A Practical Handbook of Dyeing and Calico-Printing, 323-324.

1. Review of historical literature on the process of Turkey red dyeing and archival research of primary source material from the Turkey red industry to gain an understanding of how it was dyed and insight from experienced dyers.

2. Review of research on the Turkey red process and related topics, such as the components of madder and synthetic alizarin, to identify possible ways to characterise the complex and determine provenance.

3. Re-creation of Turkey red oil, synthetic alizarin, and dyed Turkey red following historical processes to obtain samples for testing by analytical techniques and to determine how technical processes are transmitted through text.

4. Non-invasive analysis of historical and replica textiles to characterise the Turkey red complex and gather information about object provenance.

5. Analysis of dyes extracted from micro samples of replica and historical 19th c. Turkey red to determine which components are present.

The structure of the thesis is as follows:

Chapter 1 discusses the approach of historical re-creations and the Turkey red process based on the literature and archive material reviewed, considering how knowledge was communicated, the significance of technological developments in ingredients, considerations for materials and equipment in a re-creation, and a history of the process to set a context for this work. An approach for the re-creation of Turkey red is identified and the analytical approach for characterising the complex *in situ* on historical pieces is discussed.

Chapter 2 addresses the role of oil in Turkey red dyeing, including the composition of the oils used, historical understanding of its chemistry, how products like Turkey red oil were made, and how this can be used to characterise Turkey red. This is used for the experimental re-creation of Turkey red oil and the *in situ* analysis of Turkey red presented in later chapters.

Chapter 3 gives an overview of the dyes used for Turkey red, the transition from a naturally sourced dye to a synthetic one, and how synthetic alizarin was manufactured in the late 19th c. This lays the framework for the experimental re-creation of synthetic alizarin and the analysis of dyes on historical textiles to determine which components are present and whether any can be used to establish object provenance or date of manufacture.

Chapter 4 presents the experimental re-creations of Turkey red oil, dyed Turkey red, and synthetic alizarin with a discussion of how actually implementing a historical process differs from simply reading it in a text. The preparation of oiled calico samples for the *in situ* characterisation of the complex is also included here.

Chapter 5 discusses the analysis of historical, replica, and modern Turkey red oil by ¹H nuclear magnetic resonance spectroscopy (NMR), ¹³C NMR, and high performance liquid chromatography with mass spectrometry (HPLC-MS) and proposes their composition based on these results, which helps the subsequent investigation of how the oil and cotton fibres bond in the dyeing. This also confirms the success of the re-creation and whether the composition of the product has changed since the decline of the Turkey red industry.

Chapter 6 answers the how the oil and cotton bond in Turkey red dyeing through a non-invasive *in situ* analysis of historical and replica samples by comparing two techniques, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), with supporting results by ¹³C ssNMR. This chapter also investigates how aluminium ions are incorporated in the oiled cotton and the nature of this complex by ²⁷Al ssNMR.

Chapter 7 presents the UHPLC analytical results of dyes extracted from historical and replica dyed fibres as well as historical and modern reference samples of dye sources to identify components characteristic of a natural or synthetic dye source based on the discussion in Chapter 3. The analysis of some black fibres by UHPLC is also included. This work identifies the pigments anticipated from the literature on yellow, green, and blue areas of printed Turkey red by FTIR spectroscopy and SEM-EDX, with a discussion of the fastness implications for the dyes and pigments present.

This research improves upon our knowledge of the chemistry of the unique Turkey red process and the historical pieces preserved in many museum and archive collections, contributing to a better understanding of the textile legacy of this once great Scottish industry. It also explores how industrially valuable processes were recorded and communicated and how materials used for dyeing can help with interpreting and dating heritage Turkey red.

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Author's declaration

I declare that, except where explicit reference is made to the contribution of others, that this dissertation is the result of my own work and has not been submitted for any other degree at the University of Glasgow or any other institution.

Julie H. Wertz

Note on Translation

Unless otherwise stated, all translations are my own and intended for clarity and understanding.

Abbreviations

°Bé	degrees Baumé
°Tw	degrees Twaddle
AOE	Archibald Orr Ewing & Co.
ATR-FTIR	Attenuated total reflectance Fourier transform infrared spectroscopy
СТС	Centre for Textile Conservation
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
FACE	Fatty acid cellulose ester
FFA	Free fatty acid
H.F.	Historisches Farbstoffsammlung (historical dyes collection)
HPLC	High performance liquid chromatography
MS	Mass spectrometry
NMR	Nuclear magnetic resonance spectroscopy
PDA	Photodiode array
SEM-EDX	Scanning electron microscope-energy dispersive X-ray
spg	Specific gravity
ssNMR	Solid-state nuclear magnetic resonance spectroscopy
TLC	Thin-layer chromatography
TU Dresden	Technisches Universität Dresden
UHPLC	Ultra high performance liquid chromatography
UTR	United Turkey Red Company, Limited
UV-Vis	Ultraviolet-visible light spectroscopy
V&A	Victoria & Albert Museum

1 The Turkey red dyeing process and its history in Scotland

This chapter discusses the approach of reconstructing historical materials following historical methods, referred to here as historical reconstructions or recreations, which is used to understand the chemistry and fundamental characteristics of the Turkey red dyeing process. The information is gathered from historical methods reviewed for this project and the opinions, thoughts, and research of 19th c. dyers and chemists on how the process affected the quality of the final product. Firsthand source material comes from archive manuscripts on Turkey red dyeing, helping to connect the publications to the historical textiles in archive and museum collections that are studied in this work. The conclusions from this review form the basis for the experimental recreation of dyed Turkey red in Section 4.3.3 and the chemical analysis of replica and historical Turkey red in this thesis. This approach was chosen to fulfil the aims of this project and answer the research questions outlined later in this chapter because it provides practical insight into Turkey red dyeing, considers previous research and experimentation on the topic, and generates replica samples for analytical testing to ensure conservation-based testing of historical pieces.

Historical concerns over secrecy in the industry raise the question of whether published texts were representative of industrial practices or if authors were withholding information vital to the process in their books and recipes. Peel, who worked at United Turkey Red (UTR) in the mid-20th c. (after Turkey red production ended), explains that the highly specialised technique was protected even within firms and 'few inside the works themselves knew anything more than the broad outline or general method.' He acknowledges that methods by Berthollet, Papillon, and Hummel were published but says 'these accounts did not reveal "know how" nor new developments.'¹ Acquiring knowledge of Turkey red from an experienced firsthand source was not possible for this project since production ended about 80 years ago, so the re-creation work sought to test whether his assertion holds true. Doubtless, there are many refinements and adjustments to the process born of experience that have been lost with time.

¹ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 502.

Other sources say it was not enough to obtain a recipe for Turkey red from a book² and that 'practical experience is the only reliable guide'.³ One aim of this research is to explore whether it is possible to dye and characterise Turkey red from the texts reviewed for this project, testing these assertions. Whether it is of the same quality as 19th c. Turkey red and how this is quantified is another question entirely.

To improve conservation and display practices for historical Turkey red, more about its chemistry must first be determined, which in turn requires a study of the unique dyeing process. This chapter also provides a discussion of the properties of Turkey red according to the literature as well as a history of Turkey red dyeing in Scotland to set a context for the historical pieces analysed in this work.

1.1 Material reconstruction methodology

The re-creation of historical materials and processes is a useful approach that can answer a variety of questions by filling in gaps in physical and textual evidence. Materials re-creation from past processes is most commonly seen in the field of experimental archaeology,^{4,5} but has also found value creating reference samples in investigative research of historical materials by scientific analysis and for comparative modelling studies with historical objects as a valuable resource when object sampling is restricted.^{6,7,8} Reviving the use of a heritage object, such as restaging a scientific experiment using a historical apparatus, lends insight into past challenges and provokes discussion about our perceptions of history.⁹ Assumptions may also be tested, as shown by a practical re-creation of yarn spun from replica 12th c. spindles, where it was found that

² Chenciner, Madder Red: a History of Luxury and Trade, 189.

³ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 205.

⁴ Carrell, "Replication and Experimental Archaeology."

⁵ Harding, Experiment and Design: Archaeological Studies in Honour of John Coles.

⁶ Carlyle and Witlox, "Historically Accurate Reconstructions of Artists' Oil Painting Materials."

⁷ Dik et al., "Early Production Recipes for Lead Antimonate Yellow in Italian Art."

⁸ Quye, Hallett, and Carretero, "Wrought in Gold and Silk": Preserving the Art of Historic Tapestries.

⁹ Eggen et al., "Reconstructing Iconic Experiments in Electrochemistry: Experiences From a History of Science Course."

although archaeologists and textile historians believed heavier spindles were associated with producing heavier yarn, in reality the spinner was the significant variable.¹⁰ Dress historians re-make garments from historical patterns and from fragile objects when a more robust version is needed.¹¹ On a larger scale, a historical reconstruction may serve as a visitor attraction by providing an immersive, contextual experience, like Colonial Williamsburg.

Many factors must be considered in a historical re-creation. Authenticity, and therefore the validity and usefulness of the results, must be evaluated alongside the goals of the experiment. Reynolds emphasises that a true experimental replica must have a clear aim that it fulfils, and that it uses the same materials as the original.¹² His description is a useful foundation but does not address when material changes are unavoidable, for example health and safety constraints or sourcing problems. Hopkins addresses a material change that affects the aesthetic of her replica but notes aesthetics were not a factor in her questions, thereby fulfilling Reynolds' criteria.¹³ In an object intended for display, the aesthetic factor would more significant, shifting the priorities of the re-creation. The suitability of materials for a re-creation, given changes over time in supplies, production, environment, etc., forces a balance between the modern and the past.¹⁴ In this research, the aim to reproduce and characterise dyed Turkey red calico as faithfully as possible presented modern health and safety concerns that required adaptations to the method. As in Hopkins's work,¹⁵ these changes are made in a way to minimise their effect on the research questions, or else their influence is acknowledged and discussed.

Replica objects are made for a variety of reasons, possibly to stand-in for a fragile original,¹⁶ as a handling item for visitors to engage with,¹⁷ or, as with this

¹⁰ Kania, "The Spinning Experiment: Influence on Yarn in Spinning with a Hand-Spindle."

¹¹ Davidson and Hodson, "Joining Forces: the Intersection of Two Replica Garments."

¹² Reynolds, "The Nature of Experiment in Archaeology ."

¹³ Hopkins, "Using Experimental Archaeology to Answer the Unanswerable: a Case Study Using Roman Dyeing."

¹⁴ Carlyle and Witlox, "Historically Accurate Reconstructions of Artists' Oil Painting Materials."

¹⁵ Hopkins, "Using Experimental Archaeology to Answer the Unanswerable: a Case Study Using Roman Dyeing."

¹⁶ Morena, "Definitions of Authenticity: a Study of the Relationship Between the Reproduction and Original *Gone with the Wind* Costumes at the Harry Ransom Center."
research, to explore the making process itself and obtain samples for analysis. The idea of re-creating an object to learn about how it was made has existed for more than 100 years, though previous work was often subjective and removed from historical context.¹⁸ By studying an object alongside related historical documentation, our understanding of what it is and how it was made is enhanced and expanded.¹⁹ The process of a re-creation is valuable itself for providing unanticipated results not found in the textual record, and, it should be noted, a personal experience for the experimenter(s).²⁰ By re-creating oil paints following historical methods, the HART (Historically Accurate Reconstructions Techniques) project found flaws in certain paints that echoed documented complaints by painters in the literature.²¹ A reconstruction of dyeing apparatus in Pompeii identified unknown problems and missing information through practical experimentation.²² Another group found their initial attempt to re-create a voltaic pile was unsuccessful because they neglected to read Volta's description of his invention, which contained valuable details on its construction.²³

A reconstruction may be carried out through analysis of an original artefact and extrapolation of a method,²⁴ or through the interpretation of historical recipes. This research uses the latter approach, but the work is not as straightforward as choosing a recipe and executing it. Source material must be found, its provenance considered, and the content analysed and interpreted, which may involve multiple sources to account for variations in practice or incomplete methods.^{25,26} A useful representative method considers the intent

- ²² Hopkins, "Using Experimental Archaeology to Answer the Unanswerable: a Case Study Using Roman Dyeing."
- ²³ Eggen et al., "Reconstructing Iconic Experiments in Electrochemistry: Experiences From a History of Science Course."
- ²⁴ Ellis, Newman, and Barsanti, "Replication of Glazed Quartzite From Kerma, Capital of Ancient Kush (Sudan)."

¹⁷ Lithgow, "Sustainable Decision Making-Change in National Trust Collections Conservation."

¹⁸ Gold, "Reconstruction and Analysis of Bismuth Painting."

¹⁹ Carlyle and Witlox, "Historically Accurate Reconstructions of Artists' Oil Painting Materials."

²⁰ Eggen et al., "Reconstructing Iconic Experiments in Electrochemistry: Experiences From a History of Science Course."

²¹ Carlyle and Witlox, "Historically Accurate Reconstructions of Artists' Oil Painting Materials."

²⁵ Dik et al., "Early Production Recipes for Lead Antimonate Yellow in Italian Art."

²⁶ Carlyle and Witlox, "Historically Accurate Reconstructions of Artists' Oil Painting Materials."

behind each step over individual details,²⁷ finding a balance between authenticity and a reasonable undertaking for the experimenter. This allows for flexibility in practical considerations like sourcing appropriate materials and addressing challenges. In a re-creation of lead antimonate yellow, an ambiguous historical term that could be interpreted in multiple ways was narrowed down to two likely modern equivalents through historical and contextual analysis.²⁸ A detailed study of 16th and 17th c. bismuth-painted boxes reviewed historical texts and analysed objects to understand their structure, comparing the results to previous research on the items for a more complete understanding.²⁹ The Modeling of Damage in Historic Tapestries (MODHT) project made replica tapestry samples using traditional materials and techniques for analytical testing that would have been unethical on the originals.^{30,31,32} This data gathered from these model samples, acknowledging the limitations of re-creations, provides valuable information by proxy on historical tapestries. In this project, a comprehensive approach evaluating methods, archival texts, objects, previous research, and historical re-creations is applied to Turkey red textiles.

Multiple perspectives may be helpful in a historical reconstruction when certain aspects are outwith the specialist area of the experimenter. The Pompeii dyeing experiment, a collaboration between archaeology and engineering, found that for archaeologists, 'how' the dye vat worked centred around its use in a practical, social, and economic context whereas for the engineers 'how' meant the effect of external influences on the object itself.³³ The project assumed Pompeian dyers used a lead kettle because it was a cheap and malleable material, but did not consider its potential chemical effect on the dyeing

²⁷ Hopkins, "Reconstructing the Dyeing Industry of Pompeii Through Experimental Archaeology:the Challenges and Rewards of a New Approach."

²⁸ Dik et al., "Early Production Recipes for Lead Antimonate Yellow in Italian Art."

²⁹ Gold, "Reconstruction and Analysis of Bismuth Painting."

³⁰ Peggie, "The Development and Application of Analytical Methods for the Identification of Dyes on Historical Textiles."

³¹ Hacke, "Investigation Into the Nature and Ageing of Tapestry Materials."

³² Quye, Hallett, and Carretero, "Wrought in Gold and Silk": Preserving the Art of Historic Tapestries.

³³ Hopkins, "Using Experimental Archaeology to Answer the Unanswerable: a Case Study Using Roman Dyeing."

process until the experiment was discussed with experienced dyers.³⁴ The recreation and analysis of Turkey red in this project considers both the history and chemistry of the process since one aspect alone may diminish the value of the work—a chemist alone may take the process and re-creation out of historical context, while a historian alone would not have the scientific expertise to undertake an analysis. Experiencing the sights and smells of a historical process gives the researcher a more comprehensive understanding of the work that was done, the challenges faced, and the environment in which these items were made.

1.1.1 Considerations for Turkey red re-creations

One of the challenges with the re-creation of synthetic alizarin and Turkey red is the scale of the original recipes. For synthetic alizarin, some sources have no scale but use ratios;³⁵ industrially, it was manufactured by tons in purpose-built, largely closed systems.³⁶ This research is conducted at a bench scale rather than in tons, but the scaling down is considered acceptable here because the processes were originally developed at this scale. The use of closed vessels and high temperatures pose more of a challenge in this work. In addition to the attendant health and safety concerns, the cost of a high-pressure reaction vessel was prohibitive and modern techniques like microwave systems are not consistent with historical practices. Having to use borosilicate glass makes it possible to observe the reaction, an important part of the re-creation experience, but does potentially affect the reaction conditions. Scale is also a factor in the Turkey red re-creation. Due to the size of vessels available (1 and 2 L beakers), the scale of the re-creation is much smaller than what a dyer would typically use. The intent of the re-creation is a characterisation and a successful dyeing is prioritised over an optimised process, which has more significance on a production scale. When taking into consideration ranges of quantities, concentrations, etc. for ingredients in this work, an excess is favoured to avoid an incomplete dyeing. Fewer methods were found for making Turkey red oil, so

³⁴ Hopkins, "The Importance to Archaeology of Undertaking and Presenting Experimental Research: a Case Study Using Dyeing in Pompeii."

³⁵ Caro, Graebe, and Liebermann, Improvements in Preparing Coloring Matters.

³⁶ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar."

the addressing gaps for the re-creation was more challenging and involved consulting modern source material.

Measurements are another consideration. Although today chemists use molarity to measure concentration, in the historical literature solutions are measured by density, using a hydrometer. Density (mass/volume) is related to molarity (mol./volume), but is also temperature-dependent. Some texts do not specify which hydrometer scale is used, though at low concentration the difference may have minimal effect on the process. French authors tend to use the Baumé (°Bé) scale while English authors use Twaddle (°Tw). These scales can be converted to specific gravity (spg), a modern and dimensionless expression of concentration as a ratio of the solution density to the density of water. Twaddle is converted to specific gravity by the equation ((°Tw x 5) + 1000)/1000).³⁷ The replica work in this research uses a Twaddle hydrometer for consistency with the literature.



Figure 1-1 Twaddle hydrometer used to measure solutions following 19th c. methods.

As discussed earlier, a few points must be addressed regarding the use of modern materials to re-create a historical process. One concern is quality, since reagent impurities may influence the outcome of a reaction. Modern reagents can be obtained at a variety of purities depending on the needs of the analyst. Although one might think standards were lower historically, chemists began to develop analytical tests for reagent composition and purity in the 18th c.³⁸ and by the 19th c. were aware of and able to address undesirable impurities in purchased reagents.³⁹ Perkin describes the extensive treatments done at his works to distil anthracene and sufficiently purify it for alizarin manufacture.⁴⁰

³⁷ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 876.

³⁸ Szabadváry, *History of Analytical Chemistry*, 150.

³⁹ Smith, "Laboratory Notes. Preparation of Pure Carbonate of Soda, Pure Carbonate of Potash, and Absolute Alcohol.."

⁴⁰ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar."

For the late-19th c. focus of this research, reagent inconsistencies are not a significant concern and in this work any grade of reagent purchased from a chemical supplier was sufficiently pure to be suitable for these re-creations. Sourcing, on the other hand, poses another challenge, since some ingredients like rancid olive oil and bullock's blood are no longer commonly available.

Water supply is an important concern in textile dyeing, both in terms of volume and quality. Metals and salts dissolved in the water can influence the dyeing process, and contaminants like iron cause discolouration in Turkey red.⁴¹ The vessels and tools used may also affect the process in a similar manner to the water quality, such as when Papillon's method cautions against even using iron nails in a bucket to avoid any leeching into the dye bath.⁴² Hopkins also addresses the issue of water supply in a dyeing re-creation and assesses the hardness and metal content of historical and modern sources.⁴³ To minimise any effect from the water, the re-creations use ultrapure water when possible. When a larger volume is required, the use of tap water is justified since this research was conducted in the same region where United Turkey Red operated and the softness of the water is expected to be similar, acknowledging for the possible effect of modern treatment additives.

By reconstructing historical materials following historical methods, a better understanding is obtained of the practices used to create historical textiles like Turkey red, contributing to their further conservation and appreciation. Considerations must be made while interpreting historical sources for missing information, sourcing historically appropriate reagents and equipment, and modern health and safety standards. These factors are addressed by a thorough literature review of Turkey red dyeing methods and previous research on the technique and its chemistry. For these re-creations, consideration was given to each ingredient, step, and piece of equipment used to control for extra variables like contamination and impurities. The work was done to be as true as possible to the historical texts, following specifications when given and making careful deviations (e.g. using glass vessels) when the change was not anticipated to have

⁴¹ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 205.

⁴² "V. Account of the Process Followed by M. Pierre Jacques Papillon for Dyeing Turkey Red."

⁴³ Hopkins, "Reconstructing the Dyeing Industry of Pompeii Through Experimental Archaeology:the Challenges and Rewards of a New Approach."

an impact on the outcome, though it is acknowledged any deviation has the potential to affect the re-creation unless confirmed otherwise.

1.1.2 Survey of Turkey red methods and textiles

This research reviewed published methods and archive manuscripts for Turkey red dyeing, and uses pieces of 19th c. Turkey red in museum and archive collections for primary material evidence. Published methods in English and French were studied, the earliest being a 1765 account from the French government that was probably the first widely distributed method for the production of Turkey red in Europe. The latest one, from 1911, shows how dyers tried to economise the time it took to dye Turkey red as quicker, less labour-intensive synthetic dyes took over the market in the early 20th c. Previous commentary and analysis of Turkey red, much of it research predating the decline of the industry in the 1930s, was also reviewed. This established what dyers and chemists more familiar with the process had found significant and attempted to characterise, and to gain insight into how their approaches were and were not successful in revealing the mysteries of Turkey red.

To explore the correlation between published texts and industrial practices, manuscripts from Turkey red dyers were sought in archive collections. One of the aims of this research was to locate historical Turkey red objects with corresponding notes from the dyer, but no dyeing notes were found in the UTR collection. A ledger titled *Turkey Red Dyeing Calculation Book, Lennoxbank A.O.E 1873*⁴⁴ (called 'AOE dyestuffs ledger' here) does not contain directions for dyeing, but its entries from 1873 to 1892 list the quantities and prices of ingredients used in Turkey red dyeing at three dye works operated by the Archibald Orr Ewing (AOE) firm.

⁴⁴ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.

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This ledger makes it possible to track how ingredients were used over nearly 20 years during a period when the industry was expanding and adapting to new technologies. In addition to the AOE dyestuffs ledger, manuscripts on the Turkey red process from J&P Coats, Ltd. dating from the early 20th c. were found at Paisley Central Library (Paisley, Scotland, UK).^{45,46,47,48} The collection does not contain any textiles and Coats was better known for thread manufacture than Turkey red dyeing, but the documents show practices consistent with published methods and the AOE ledger. A notebook from Foxhill Bank Print Works dated from 1830-1840s was also found in the V&A Textiles and Fashion Collection⁴⁹ that

⁴⁵ Brennan, Tannahill, and Percy, *Turkey Red Process for Cotton Yarn*. 1/9/3.

⁴⁶ Tannahill, *Turkey Red Dyeing*. 1/9/3.

⁴⁷ Collin, Turkey Red Process for Cotton Yarn. 1/9/3.

⁴⁸ Straugh, Recipe From Mr Straugh. 1/9/3.

⁴⁹ Book of Dye Recipes and Samples of Printed Cotton Made by Foxhill Bank Printworks England 1830-1840s. T.8-1978.

contains an 'old' process for Turkey red. This text also corroborates that published methods did document actual industrial practices.

The historical textiles examined and analysed for this work come from a variety of sources. Some are found in textile dyeing manuals, which do not always record the provenance of the sample, and are referenced by the text they are found in. The largest set is from the UTR collection at Glasgow University, which has nine books containing samples of Turkey red (ca. 1850s-1900) spanning the period of interest for this research. Based on the irregular presentation of the samples (roughly cut, uneven shapes) and the frequent occurrence of off-register prints, these volumes were likely internal records for UTR. The sample pattern books are listed in Table 1-1 with dates ascribed based on inscriptions and stationer's labels in the volumes. A second collection in the Victoria and Albert Museum (V&A) Textiles and Fashion Collection contains a mixture of loose (as opposed to pasted in books) pieces from UTR, some German, Swiss, and Italian handkerchiefs, a remarkable dress, and a few other miscellaneous pieces. The analysis of these objects is discussed later in this thesis.



Figure 1-3 Turkey red textiles mounted in a sample pattern book, 1886-1888. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/6. Image courtesy of Lesley Richmond.

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Book	Date	
UGD 13/8/1	after 1867	
UGD 13/8/2	1856-1861	
UGD 13/8/3	1857-1858	
UGD 13/8/4	1857-1863	
UGD 13/8/5	after 1867	
UGD 13/8/6	1886-1888	
UGD 13/8/7	1887	
UGD 13/8/8	1878	
UGD 13/8/9	1899-1902	

Table 1-1 Sample pattern books from Glasgow University UTR collection.

1.2 Deconstructing the methods

This section discusses the broad conclusions from the review of historical Turkey red methods and identifies key themes and developments. The process by which a method was chosen for the re-creation is discussed and a proposed definition of Turkey red is given.

1.2.1 Defining Turkey red

The initial intent was to use the Turkey red methods reviewed to generate one all-encompassing method representative of the process. This approach was not feasible because the quantities of ingredients were determined for a set weight of cotton, and not all steps appear in all processes. Furthermore, technological developments in ingredients resulted in a distinction between 'old' and 'new' processes, which is discussed further in Section 1.2.3. Many processes contain repeated steps, or even repeated sets of steps, convoluting the order of operations. Vitalis offers two similar methods for Turkey red; the *marche en gris* has fewer repeated steps and dyed a lower-quality product than the *marche en jaune⁵⁰* in Figure 1-4, indicating quality was connected to a sufficient quantity of ingredients on the fibres.

⁵⁰ Vitalis, Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles, 246.

Marche en jaune.	Translation
Débouilli.	Scouring.
Bains de fiente.	Dung baths.
Bains blancs.	White baths.
Sels.	Salts.
Dégraissage.	Degreasing.
Engallage.	Galling.
Alunage.	Aluming.
Lavage d'alun.	Washing the alum.
Bains blancs.	White baths.
Sel.	Salt.
Dégraissage.	Degreasing.
Engallage.	Galling.
Alunage.	Aluming.
Lavage d'alun.	Washing the alum.
Garançage.	Maddering.
Avivage.	Brightening.
Rosage.	Clearing.

Figure 1-4 The *marche en jaune* Turkey red process from Vitalis with translation by this author.

A more useful means to evaluate the methods was developed based on a description by Knecht, who says Turkey red is the result of a series of operations—oiling, sumaching, mordanting, dyeing, and clearing.⁵¹ Looking at the broad characteristics of a process and breaking it into modules rather than the specifics of an individual recipe made it easier to identify which steps are fundamental to Turkey red and which appear to be at the discretion of the dyer. The repeated steps, which become less common over time in the methods reviewed, appear to be compensation for lower-quality ingredients or limited experience. As dyers became familiar with the process, they would be better at accomplishing in fewer steps what originally had taken sixteen.

The conclusion from this research is that there are five fundamental ingredients in Turkey red dyeing— cotton, oil, aluminium, calcium, and dye. There is a prescribed series of steps— 1) oiling, 2) mordanting, 3) dyeing, and 4) clearing, where the dyed cotton is vigorously cleaned to remove unbound dye components. Preparation of the cotton with oil was necessary, and when comparing Turkey red methods to other dyeing techniques it is obvious that this is also characteristic of Turkey red and not practiced with other colours.

⁵¹ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 588.

The step called sumaching, which refers to the application of tannins—either from oak galls or sumac⁵²—is not studied in this research. Tannins are polyphenolic compounds that contain many –OH groups and chelate with metals.⁵³ They were known to improve the uptake of colour by attracting more mordant,⁵⁴ probably by complexing with the metal salt. The use of tannins in dyeing was not restricted to Turkey red,⁵⁵ and they were not always used in the process.⁵⁶ Tannins probably served as a secondary mordant by attracting more aluminium, but they are not studied in this project because the review did not determine them to be necessary for the process and unlike the oiling, tannins are not particular to Turkey red.

Two more notorious ingredients in the process, dung and blood from sheep and cattle, were similarly determined to be non-essential assistants based on inconsistencies in their use. To keep the scope of this characterisation manageable, the research focuses on the essential aspects of Turkey red listed above and does not include dung and blood, though they are discussed in the literature review to provide a complete understanding of the process. Further investigation into these intriguing and evidently beneficial ingredients is recommended. Calcium, on the other hand, is not an ingredient in every method but was determined to be vital to the process.⁵⁷ Around the late 18th c., as the process spread across Europe, dyers became aware that if calcium was not naturally present in the water used, then it must be added, usually in the form of chalk,⁵⁸ a discovery claimed by Haussmann. Ure explains that after moving from Rouen to Logelbach, Haussmann found his dyeing was unsuccessful due to the decreased calcium content in the water. Avignon madder was found to contain enough calcium to make the additive unnecessary,⁵⁹ which may explain

⁵² Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 267.

⁵³ Hagerman, *The Tannin Handbook*.

⁵⁴ Hummel, *The Dyeing of Textile Fabrics*, 227-232.

⁵⁵ Duerr and Turnbull, *Bleaching and Calico-Printing* : a *Practical Manual*, 53.

⁵⁶ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 204.

⁵⁷ Haussmann, "XXXII. Observations on Maddering; Together with a Simple and Certain Process for Obtaining, with Great Beauty and Fixity, That Colour Known Under the Name of the Turkey or Adrianople Red," 171.

⁵⁸ Hummel, *The Dyeing of Textile Fabrics*, 433.

⁵⁹ Ure, A Dictionary of Arts, Manufactures, and Mines, 791.

why chalk is not included in every recipe. Where it was not an additive, mostly in the form of chalk, the dyer was likely working with calciferous water that naturally supplied sufficient calcium to the dye bath.

As with any dyeing technique, the cellulosic fibres must first be scoured of their natural waxes and oils. Cotton is the only fibre mentioned in the literature, though technically it would be possible to dye linen as well,⁶⁰ but with more difficulty due to its more crystalline polymeric structure. The scoured fibres are treated with oil suitable for dyeing purposes until a sufficient amount is attached to the fibres. This step is followed by applying aluminium to the oiled fibres, and then finally the dyeing takes place in a bath with the colorant and calcium present. The last step, clearing, removes all excess compounds not sufficiently bonded to the fibres. Even experienced dyers did not always produce Turkey red of the best quality,⁶¹ so a definition based on its chemistry rather than its fastness is appropriate. For this research, Peel's description of Turkey red as a combination of calcium-aluminium-alizarin lake combined with a fatty acid on vegetable fibre⁶² is a useful working definition.

Much of the literature claims that prior to 1810, Turkey red could only be dyed on yarn and not cloth.^{63,64,65} A comparison of methods from before and after that date does not reveal any marked differences to the modern reader. Furthermore, Parliamentary records from 1786 report dyeing Turkey red 'in the Piece',⁶⁶ meaning woven items, and a 1798 article by Pallas mentions cloth,⁶⁷ so the pre-1810 divide may be less significant than implied by the literature. Tarrant says the difference was due to difficulties oiling woven fibres compared

⁶⁰ Berthollet, *Elements of the Art of Dyeing*, 127.

⁶¹ Schaefer, "The History of Turkey Red Dyeing," 1412.

⁶² Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 496.

⁶³ Bremner, *The Industries of Scotland* 299.

⁶⁴ Jacqué et al., Andrinople: Le rouge magnifique 15.

⁶⁵ Leigh, "On the Estimation of Alizarin in Dyed Cotton Fabrics, and on an Attempt to Ascertain the Composition of Turkey-Red and Other Alizarin Lakes" 205.

⁶⁶ Great Britain House of Commons, "Journals of the House of Commons" 467.

⁶⁷ Pallas, "II. the Genuine Oriental Process for Giving to Cotton Yarn or Stuff the Fast or Ingrained Colour, Known by the Name of Turkey Red, as Practised at Astracan" 10.

to yarn hanks,⁶⁸ rather than a difference in process, a logical explanation consistent with the findings from this research.

A laborious and time-consuming aspect of the process was that the cotton had to be dried between nearly every step, which in Scotland was seasonal work prior to improved indoor drying techniques. Tarrant says this development occurred in the 1830s⁶⁹ while Peel writes that Scottish firms took up indoor drying around 1841.⁷⁰ A less refined method must have been available before then, however, because directions in the 1804 publication of Papillon's method recommend 'stove' drying⁷¹ as does the 1830s-40s Foxhill Bank book.⁷² The origins of indoor drying aside, all the processes reviewed for this project included drying after nearly every step, which Jenny says improves the process.⁷³

As mentioned in the introduction, a fundamental characteristic of Turkey red is that it is not technically a dye, but a process.⁷⁴ The result of this process, also called Turkey red, is a textile product coloured by a chemical complex that does not exist without the fibre onto which it is dyed. This means one cannot have a bottle or packet of Turkey red, only Turkey red yarn or fabric. This has significant implications for analytical characterisation, discussed further below.

1.2.2 Historical research and in situ analysis

This project takes into consideration the historical analytical work on the characterisation of Turkey red, much of it being made by empirical assays that are now long obsolete. Ultimately, chemists were unable to completely answer how Turkey red formed because they lacked the ability for *in situ* analysis, though some of their research laid the foundation for this work. These investigations and how they influence the analyses here are discussed in the literature reviews.

⁶⁸ Tarrant, "The Turkey Red Dyeing Industry in the Vale of Leven" 41.
⁶⁹ ibid., 43.

⁷⁰ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline."

⁷¹ "V. Account of the Process Followed by M. Pierre Jacques Papillon for Dyeing Turkey Red."

⁷² Book of Dye Recipes and Samples of Printed Cotton Made by Foxhill Bank Printworks England 1830-1840s. T.8-1978.

⁷³ Jenny, "Mémoire sur la fabrications du rouge d'Andrinople," 759.

⁷⁴ Brackman, Clues in the Calico: a Guide to Identifying and Dating Antique Quilts, 63.

Research on the chemistry of Turkey red sharply declined when the industry shut down in the 1930s,⁷⁵ though some interest persisted.⁷⁶ A doctoral thesis by Kiel on alizarin lake complexes from the 1960s includes analysing the lake on Turkey red.⁷⁷ This is the only published *in situ* analysis of Turkey red, but the focus was on the lake and did not attempt to characterise the oil. As early as 1916, Leigh observed that analyses of *in vitro* preparations, like studying the lake in a test tube, were 'purely speculative work' that led to erroneous conclusions. He writes 'the lake must be analysed as it exists on the fibre.'⁷⁸ His assessment of Turkey red analysis was correct, though it was not until Kiel's time that analytical instruments capable of this research were developed, and not until this project that a comprehensive analytical characterisation of Turkey red, for the first time with a heritage conservation-based approach, has been undertaken.

One useful analytical technique for dyes and textile research is chromatography, which is not an *in situ* analysis. This technique allows the separation of dyes extracted from a textile fibre and their identification by comparison to reference compounds. It was not developed until the late 1930s⁷⁹ and therefore does not feature in the historical research on Turkey red. Extracting the dyes does not reveal the nature of the complex but still provides valuable information as to whether light-sensitive compounds are present, making the small sample required justifiable for improved conservation practices. Certain dyes may also serve as chemical markers, which may be the case with Turkey red (discussed further in Section 1.2.3). To date, no dyes analysis of historical Turkey red has been published, though there have been many studies of madder and madder-dyed textiles.^{80,81,82} These investigations

⁷⁵ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 112.

⁷⁶ Haller, "Constitution of Turkey Red."

⁷⁷ Kiel, "Metaalcomplexen van Alizarinerood."

⁷⁸ Leigh, "On the Estimation of Alizarin in Dyed Cotton Fabrics, and on an Attempt to Ascertain the Composition of Turkey-Red and Other Alizarin Lakes," 213.

⁷⁹ Stahl, "The Historical Development of the Method."

⁸⁰ Henderson, Rayner, and Blackburn, "Isolation and Extraction of Lucidin Primeveroside From Rubia Tinctorum L. and Crystal Structure Elucidation."

⁸¹ Mouri and Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC."

⁸² Derksen, Niederländer, and van Beek, "Analysis of Anthraquinones in Rubia Tinctorum L. by Liquid Chromatography Coupled with Diode-Array UV and Mass Spectrometric Detection."

identified hydroxyanthraquinone colourants, which is expected to be the case for Turkey red as well since madder was traditionally the dye source. This research aims to identify dyes on Turkey red and whether any can be linked to madder or synthetic alizarin as the dye source, possibly revealing information about their age or provenance.

1.2.3 Technological advances and Turkey red

The methods surveyed for this project encompass the period from when the entire process was done by hand with rancid olive oil and madder roots to an era where the much of the dyeing was done with the aid of machinery and manufactured ingredients replaced naturally-sourced ones. The transition toward modern ingredients is of interest to this project because of the affect it could have on the chemistry of the process. If these advances resulted in chemically different artefacts, then a single conservation practice for Turkey red may not be suitable. Technological advances in equipment permitted oven drying and steaming the cotton, an improvement first mentioned in 1885,⁸³ but Turkey red was still dyed before their use. This indicates that while they may have improved the efficiency of the process for the dyer, and perhaps improved the quality of the final product, they did not fundamentally change the overall process.

Traditionally, cotton to be dyed Turkey red was first treated with a bath of rancid olive oil mixed with alkali and, frequently, sheep or cow dung as well. The task involved steeping the cotton in the bath, wringing, and drying it multiple times before carefully washing to remove excess oil that did not adhere to the fibres. The development of Turkey red oil in the early 1870s⁸⁴ (castor oil treated with sulfuric acid and neutralised) cut the oil treatment down to one step: steeping the cotton in a bath of water and Turkey red oil, then wringing, drying, and rinsing. In the literature, a Turkey red method using rancid olive oil is sometimes called an 'old' or an emulsive oil process, while those using Turkey red oil are a 'new' or sulfated oil process. The distinction was unnecessary until the development of the 'new' process and it is used consistently in publications and archive material once the two co-exist.

⁸³ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton."

⁸⁴ Markley, Fatty Acids: Their Chemistry, Properties, Production, and Uses, 1735.

The other significant transition in Turkey red dyeing, synthetic alizarin, also occurred around this time. Dyers replaced the ground madder traditionally used in the dye bath with the more concentrated product, which lowered costs and did not have the woody impurities of madder. Synthetic alizarin was commercially available in 1869,⁸⁵ so its use in Turkey red was fairly concurrent with the development of the 'new' oiling process. In terms of time saved when dyeing, the impact of synthetic alizarin was not as significant as Turkey red oil was, but its price and convenience compared to madder drove its increased use. This transition implies a collection of 19th c. Turkey red may have pieces dyed with madder and with synthetic alizarin, which, depending on the individual molecules present, may have separate display and conservation requirements.

The general impression from the literature is that the 'old' and 'new' processes both dyed Turkey red, and that good colour could be achieved with madder or synthetic alizarin. The research questions for this project on the chemistry of the oil and the identification of a natural or synthetic dye source aim to address these technological advances and whether they had an impact on the chemistry of the process. This will also help determine whether 'old' and 'new' process Turkey red are the same chemical complex and can be treated similarly or whether further classification of collections is needed before treatment or display.

1.2.4 Vessels and fibre preparation

The tools used in the dyeing as well as the ingredients can influence Turkey red. It was important that equipment like vessels be free from iron,⁸⁶ a condition also applied to the alum used.⁸⁷ Iron was known to dull the red colour, so Turkey red dyers often used copper vessels instead.⁸⁸ The water used for dyeing would ideally have a low mineral content to ensure no interference in the process.⁸⁹

⁸⁵ Travis, "Between Broken Root and Artificial Alizarin: Textile Arts and Manufactures of Madder," 2.

⁸⁶ "V. Account of the Process Followed by M. Pierre Jacques Papillon for Dyeing Turkey Red."

⁸⁷ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour."

⁸⁸ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton."

⁸⁹ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 58.

Advance bleaching the cotton prior to dyeing Turkey red was generally considered unnecessary for a successful outcome and only a good scouring was required;^{90,91} Knecht even says it was potentially harmful to the process.⁹² For Turkey red intended to be discharge printed, lightly bleaching the fabric may have improved the quality of the print since white areas would be revealed, so to a point it may not have been detrimental. The effect of bleaching on the chemistry is beyond the scope of this project. The use of bleach on Turkey red after it is dyed, another matter, is discussed in Section 1.3.2.

1.2.5 Hummel's process for dyeing Turkey red

To re-create dyed Turkey red for this project, one published method was chosen that represented the fundamental characteristics of the process and had clear directions, measurements, and ingredients specified. After weighing considerations regarding sourcing ingredients, clarity, time, provenance of the method, and the method itself, the Turkey red dyeing process in John James Hummel's *The Dyeing of Textile Fabrics*⁹³ (1886) was selected.

Hummel provides methods for the 'old' and 'new' processes, both using synthetic alizarin as the colorant, which had by this time superseded madder. To keep the experimental work and analysis manageable, and because no rancid olive oil like *huile tournante* could be sourced, only the 'new' process is recreated in this work, but samples are dyed with madder and synthetic alizarin. The details of the 'old' and 'new' processes and their chemistry are discussed further in Chapter 2.

The credibility of the text comes from Hummel's extensive experience in the dyeing industry and as a Professor of Dyeing at Yorkshire College (later part of Leeds University). His father worked as a chemist in the print works of James Thomson at Primrose (Clitheroe, England, UK), where Turkey red was printed,⁹⁴ and was well acquainted with significant figures of the textile industry like

⁹⁰ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton."

⁹¹ Hummel, *The Dyeing of Textile Fabrics*, 85.

⁹² Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 96.

⁹³ Hummel, *The Dyeing of Textile Fabrics*.

⁹⁴ Thomson, "Specification of the Patent Granted to James Thomson for a Method of Producing Patterns on Cloth Previously Dyed Turkey Red, and Made of Cotton or Linen, or Both."

Daniel Koechlin, Walter Crum, John Mercer, and Frederick Steiner. Hummel's stepfather was John Sieber, an accomplished Swiss technical chemist with an expertise in the application of colouring matters who succeeded Hummel senior at Primrose. Sieber later worked at Irwell Springs, the Turkey red works of Mercer & Greenwood, near Bacup (England, UK), so it is possible young Hummel was familiar with the process for most of his life. Hummel studied at Zürich Polytechnic and received a technical diploma, returning to England and taking a job as a chemist in the James Black & Co. printworks in Alexandria (Scotland, UK). During his time there, he began using artificial alizarin to replace madder. After Alexandria, he was the sub-manager at Foxhill Bank Print Works in Church, Lancashire. This works is also the origin of one of the manuscripts reviewed for this project,⁹⁵ though it predates Hummel's tenure. He worked at two more Scottish dye works before applying to be an instructor in dyeing at Yorkshire College in 1879. Hummel was progressive and open about sharing processes and recipes in an industry where skill was traditionally gained through laborious experience and practices were carefully guarded.⁹⁶

Hummel's experience, background, and reputation for sharing his methods along with the clarity of the method itself make it a good historical process to attempt translating into a modern method for re-creation. It contains all the requisite features of a Turkey red process and uses ingredients that can be obtained for this project.

1.2.6 Summary

Trying to define a process as singular and inscrutable as Turkey red through historical publications seemed, at the outset, daunting. First, the literature contains many cautionary statements about practical experience as the only reliable guide,⁹⁷ and that learning about the process or acquiring a recipe was insufficient instruction to produce true Turkey red.⁹⁸ Learning the technique from someone within the Turkey red industry was not an option for this project

⁹⁵ Book of Dye Recipes and Samples of Printed Cotton Made by Foxhill Bank Printworks England 1830-1840s. T.8-1978.

⁹⁶ Walker, "The Life and Influence of Professor J.J. Hummel."

⁹⁷ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 205.

⁹⁸ Chenciner, Madder Red: a History of Luxury and Trade, 189.

since production in Scotland ended about 80 years ago, so the methods and texts were carefully deciphered and evaluated to compensate for the absence of instruction. Developments and adaptations to the process, namely Turkey red oil and synthetic alizarin, raised questions of whether these new ingredients yielded a product with a different chemistry. The range of British and French sources reviewed, written over a 150-year period, introduce a variety of practices and ingredients in which it can be difficult to see a method to the madness.

Historical research, commentary, and analysis were also reviewed to gather information and avoid replicating previous unsuccessful analyses, many of which were extractive and useless to characterise a complex that exists only on the fibre. This review was vital to gain an understanding of the process and revealed key concerns for a successful dyeing, like the absolute necessity of sufficient oil on the fibre. The technique became more accessible when a method was reviewed with the questions *what is the intent of this step*? and *what chemical reactions could occur*? in mind. This approach, coupled with an investigation into the composition of Turkey red oil, made it possible to compare the chemistry of the 'old' and 'new' oiling processes to determine whether they had the same purpose and if these findings can be applied to all Turkey red.

It is unclear why, historically, acquisition of a Turkey red method did not guarantee a successful dyeing. It may be the case that dyers were so unfamiliar with the process, which appears to be unique in its lengthy and prescribed preparation of the fibres, that any misunderstanding or lack of information caused a failure. The quality of ingredients would also have had an impact on the process, which may have discouraged an inexperienced dyer who would not have known what to look for. Factors that affect the quality, including the dyer's familiarity with the process, are another fascinating aspect of Turkey red still to be investigated. The experimental re-creation and analysis of Turkey red dyed with Hummel's method for this project explores whether the process can be learned and executed without demonstration. The work generates samples that are valuable in the characterisation of Turkey red, another goal for this project. The historical Turkey red dyeing methods and archive texts are summarised in an annotated bibliography in Appendix B.

1.3 Properties of Turkey red

One cannot help but notice when reading about Turkey red the degree of acclaim in the literature regarding its quality, durability, and colour. This research aims to elucidate more on the chemistry of Turkey red, but an investigation into its properties as a dyed textile is beyond the scope of this project. These attributes of Turkey red are discussed in here to underscore the historical significance of the textile and exactly why it was worth so much effort to produce. Hopefully, future research will be able to expand upon the findings from this project to quantify and explain some of its incomparable quality.

1.3.1 Brilliant colour

It was described as having 'a lustre' that was difficult to imitate⁹⁹ and the brightest colour that could be dyed on vegetable fibres.¹⁰⁰ Crookes says 'Turkey-red are very readily recognised by the peculiar fiery and deep tone of the colour'¹⁰¹ and Cain writes it is 'the most important application of the mordant dye to cotton'.¹⁰² Although there are persistent misconceptions about natural dyes only producing muted colours, cellulosic fibres are less susceptible to dyeing and the colour is much redder than the result of a non-Turkey red process.

Most of the Turkey red viewed for this research has been printed, a process discussed further in Section 1.4. The printed yellow, green, blue, black, and white—the typical Turkey red colourway seen in the images below—are as vivid as the red, creating the vibrant calicoes that, after more than 100 years, are still as lovely as they were hailed to be in the 19th c.

⁹⁹ Berthollet and Berthollet, *Elements of the Art of Dyeing and Bleaching*, 326.

¹⁰⁰ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 40.

¹⁰¹ Crookes, A Practical Handbook of Dyeing and Calico-Printing, 326.

¹⁰² Cain and Thorpe, The Synthetic Dyestuffs and the Intermediate Products From Which They Are Derived, 36.



Figure 1-5 19th c. floral and paisley Turkey red piece, after 1867. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/5.



Figure 1-6 19th c. peacock with flowers Turkey red motif. Image courtesy of the V&A, T.133(23)-1976.



Figure 1-7 Germany Turkey red handkerchief depicting Fame distributing gymnastic honours, ca. 1880-1899. Image courtesy of the V&A, 1802-1899.

1.3.2 Fastness

In addition to being an attractive shade, Turkey red was known as a textile exceptionally fast to both washing and light exposure.¹⁰³ It was very durable against soaping,¹⁰⁴ which might be explained by the use of soap in the final step of the dyeing process. Hofenk de Graff says Turkey red has a light fastness of blue wool standard 5-6 (on a scale of 0-8),¹⁰⁵ but no experimental data is included. Peel describes Turkey red as able to tolerate boiling under pressure with sodium carbonate or soap, rubbing on white linen without transferring colour, and 2 $\frac{1}{2}$ years of British daylight without fading.¹⁰⁶ The latter seems unusually low considering the low average light levels in Britain and that much of the export market for Turkey red was to India and other sunnier places¹⁰⁷ speaks more for its light fastness. It is worth nothing that the origins of the technique are likely Indian as well (see Section 1.5.1). Turkey red is consistently

¹⁰⁴ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 205.

¹⁰³ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 502.

¹⁰⁵ Hofenk de Graff, van Bommel, and Roelofs, *The Colourful Past*, 108.

¹⁰⁶ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 502.

¹⁰⁷ Arthur et al., "Seeing Red: Scotland's Exotic Textile Heritage."

described as the fastest in the literature,^{108,109} but it is not yet known how this is quantified in modern conservation terms. The image below, of Turkey red in a private collection that had been displayed in direct sunlight for many years, shows that although it had remarkable fastness, it is still susceptible to damage from light exposure. Through this research, a better understanding about the chemistry of Turkey red improves our display practices of these unique and remarkable textiles.



Figure 1-8 Turkey red print with some light damage, c. early 20th c. Turkey red from R.A. Peel, printer at United Turkey Red. Private collection of Susan Prentice.

Rub fastness, meaning the colour does not transfer with abrasion, was an important feature of quality Turkey red.¹¹⁰ It was also known for was its resistance to bleaching,¹¹¹ which made it attractive to Irish linen finishers

¹⁰⁸ Cooper, A Practical Treatise on Dyeing, and Callicoe Printing: Exhibiting the Processes in the French, German, English, and American Practice of Fixing Colours on Woollen, Cotton, Silk, and Linen, 286.

¹⁰⁹ Ure, A Dictionary of Arts, Manufactures, and Mines, 793.

¹¹⁰ Carruthers, "A New Process of Dyeing Turkey Red," 124.

¹¹¹ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 205.

because the colour would not transfer to the white yarn while weaving, and the red bands they wove could withstand bleaching.¹¹²



Figure 1-9 Towel woven with Turkey red borders, ca. late 19th c. © Julie H. Wertz, private collection.



Figure 1-10 The woven pattern on the towel borders made with plain warms and Turkey red weft. © Julie H. Wertz, private collection.

In *the Statistical Account of Scotland*, Burns writes that Turkey red yarn was woven with unbleached cotton or linen, and that when bleached together it

¹¹² Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 502.

'acquires more beauty and lustre by this trying operation.'¹¹³ There is some discussion in the literature from the 1880s that the 'new' process Turkey red was not as resistant to bleaching as that of the 'old',¹¹⁴ but this may have been a transitional period of adaptation between the two processes¹¹⁵ because the point is not continually raised. The beauty of Turkey red speaks for itself, but much remains to be answered in terms of quantifying the fastness with modern methods. Hopefully this research will contribute to our understanding of Turkey red so this may be further researched for the benefit of collections worldwide.

1.4 Discharge printing

The oiling required for Turkey red precludes the direct application of red areas in printed textiles—fabric was solid Turkey red after dyeing. A technique called discharge printing was, according to much of the literature, developed in 1811 by a Mulhouse dyer name Daniel Koechlin.¹¹⁶ This involved selectively removing the red through a chemical process, leaving white areas that could be printed over with other colours. Koechlin found that by adding a weak acid, like citric or tartaric, to the hypochlorite bleach Turkey red was normally resistant to, the colour rapidly disappeared.^{117,118} By mixing the acid in a paste, using gum, starch, or pipe clay,^{119,120} the design could be applied with carved blocks and later with cylinders. Much of the Turkey red preserved in collections is printed, leading one to imagine that historically, most it was as well. According to Tarrant, half of the Turkey red dyed was left plain red,¹²¹ and its relative absence in collections is probably due to print samples having been reserved as design records.

The literature is not completely in accord on Koechlin's contribution. In an 1824 letter to *The Glasgow Mechanics' Magazine*, John Miller states he developed a means of discharge printing in 1802 while working for Monteith,

¹¹³ Burns, "Parish of Barony of Glasgow," 115.

¹¹⁴ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton."

¹¹⁵ Hummel, *The Dyeing of Textile Fabrics*, 444.

¹¹⁶ Jacqué et al., *Andrinople: Le rouge magnifique*, 10.

¹¹⁷ Bremner, *The Industries of Scotland*.

¹¹⁸ Schaefer, "The History of Turkey Red Dyeing," 1415.

¹¹⁹ The Dyer and Colour Maker's Companion, 42.

¹²⁰ Duerr and Turnbull, *Bleaching and Calico-Printing* : a Practical Manual, 42-43.

¹²¹ Tarrant, "The Turkey Red Dyeing Industry in the Vale of Leven," 45.

Bogle and Co.^{122,123} George Roger or Rogers (both are used), manager of Monteith's Barrowfield works, is also connected to the process for that same year and possibly as far back as 1792, though with little evidence to support the claim.^{124,125} Credit for the process was evidently of enough interest that it was disputed in early 1824^{126,127,128,129} and at no point is Koechlin mentioned in these sources. Who exactly developed the discharge printing of Turkey red, or whether it was developed independently in more than one location, may remain a mystery but is beyond the scope of this project.

As discussed earlier, finished Turkey red was known for its resistance to chlorine bleach, which contributed to its reputation for fastness. Printers applied the weakly acidified paste with engraved blocks, plates, or rollers to discharge the red dye for the desired pattern. An aqueous solution of bleaching powder (calcium hypochlorite, Ca(ClO)₂) was applied and the colour removed only where the acidic paste contacted the fabric. The historical literature says that blue was applied by mixing Prussian blue pigment dissolved in acetic acid with the paste. Yellow was obtained by adding a lead salt to the paste and developing the colour with a chromium salt solution, which precipitated lead chromate. Green was the result of overprinting yellow and blue. Black was achieved in a few ways, sometimes by printing Prussian blue without discharging the underlying red or by printing a black dye like logwood or aniline black over the red.^{130,131} Pink, the only colour that was not obtained by the discharging process, was effectively a light red made by using less aluminium. Patterns of pink and red, called 'two reds' in some of the UTR sample pattern books, were

¹²² Miller, "Statement Relative to the Discharging Process of Turkey Red, by Means of Presses."

¹²³ "On the Process for Discharging Turkey-Red."

¹²⁴ Tarrant, "The Turkey Red Dyeing Industry in the Vale of Leven," 42.

¹²⁵ Arthur et al., "Seeing Red: Scotland's Exotic Textile Heritage," 6.

¹²⁶ "Notices to Correspondents," 1824b.

¹²⁷ "Discharging of Turkey-Red."

¹²⁸ "Notices to Correspondents," 1824d.

¹²⁹ "Notices to Correspondents," 1824e.

¹³⁰ Crookes, A Practical Handbook of Dyeing and Calico-Printing, 594-597.

¹³¹ Duerr and Turnbull, *Bleaching and Calico-Printing* : a *Practical Manual*, 42-43.

obtained by applying more aluminium mordant with a block where red was desired.¹³²



Figure 1-11 Unusual Turkey red print over stitched-in thread, purpose unknown. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/5.

Printed Turkey red has a characteristic colourway of red, yellow, green, blue, white, black, and sometimes pink. The low water solubility of Prussian blue and lead chromate gave the printed product the same reputation for fastness as plain Turkey red. The details of the chemistry of discharge printing are not addressed in this thesis but may be worth further investigation in future research. The literature and surviving textiles do not indicate that other dyes beyond those discussed (actually pigments, save logwood) were used in Turkey red prints, perhaps because differences in fastness would have resulted in uneven fading.

1.5 The history of Turkey red dyeing in Scotland

This section outlines the history of Turkey red dyeing with an emphasis on the development of the industry in Scotland as the focus of this project to provide a context for the process being analysed.

¹³² Storey, "Turkey Red Prints," 34-35.

1.5.1 Origins and arrival in Western Europe

The exact origins of Turkey red dyeing are undocumented, though it is proposed to have been developed in or around India.^{133,134} This is consistent with some of the dyeing in the *kalamkari* technique practiced in India, where milk (a source fat like oil, and possibly calcium), aluminium, and madder are used. Indonesian dyeing techniques for cotton using plant seed oil, symplocos leaves (aluminium), and root bark from *Morinda citrifolia* L (source of anthraquinone dyes like madder)¹³⁵ support a south Asian origin. The dyeing was practiced in Turkey and the Levant, where it was sold to Western Europe, hence the name.¹³⁶ It is occasionally called Adrianople red or *rouge Andrinople* after the modern-day city of Edirne, formerly called Adrianopolis,¹³⁷ where the dyeing was practiced in what is now northwest Turkey.



Figure 1-12 Locations where Turkey red was dyed in Greece and Turkey. Image generated in Google Maps.

European dyers recognised the demand for imported Turkey red and sought a means to produce it independently. Spies were employed and sent to Greece and Turkey to learn the process,¹³⁸ which has been called the first case of

¹³³ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 111.

¹³⁴ Sandberg, *The Red Dyes*, 101.

¹³⁵ Cunningham et al., "Hanging by a Thread: Natural Metallic Mordant Processes in Traditional Indonesian Textiles."

¹³⁶ Berthollet, *Elements of the Art of Dyeing*, 127.

¹³⁷ Cardon, Natural Dyes: Sources, Tradition, Technology and Science, 116.

¹³⁸ Lowengard, The Creation of Color in Eighteenth-Century Europe.

industrial espionage and of globalisation.¹³⁹ Regardless of whether it was the first, it was certainly a significant landmark in the modern era as overseas trade expanded and manufacture moved toward the Industrial Revolution. Even into the late 19th and early 20th centuries after decades of production and countless publications, dyers used proprietary methods and kept them strictly secret.^{140,141} Schaefer writes that it was 'not enough to acquire some knowledge of the method or even to secure possession of a recipe.'¹⁴²

In 1746, French industrialists d'Haristoy and Goudard were assisted by Greek Turkey red dyers from Smyrna in setting up Western Europe's first Turkey red works at Darnétal, near Rouen, and Aubenas in Languedoc. Not long after, two more works were established in Nîmes by a dyer called Eymard and in Saint-Chamond by Charles Flachat.¹⁴³



Figure 1-13 Locations of first Western European Turkey red dye works in France. Image generated with Google Maps.

¹³⁹ Boot et al., *Turkish Red & More*.

¹⁴⁰ Crookes, A Practical Handbook of Dyeing and Calico-Printing, 325.

¹⁴¹ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 499.

¹⁴² Schaefer, "The History of Turkey Red Dyeing," 1412.

¹⁴³ Cardon, Natural Dyes: Sources, Tradition, Technology and Science.

Flachat, a Lyonnais businessman, went to Adrianople in 1748 and engaged the services of a master dyer and some workers, returning to France with them around 1756.^{144,145} Schaefer says it was more likely the case that French dyers had gained some knowledge of the process but were unable to drastically improve it prior to the arrival of the experienced Greek dyers.

1.5.2 Turkey red dyeing in England

Similar tactics were employed in Britain as well. In 1753, John Wilson, a cotton velvet and piece dyer in Ainsworth, near Manchester,¹⁴⁶ sent an agent to Smyrna to learn the Turkey red process. Although successful, Wilson was disappointed that it was not suited to the dyeing he did and found 'the tediousness of so many operations, and the exactness required, every time rendered it of no more value to me' than a basic madder dyeing method.¹⁴⁷ Nevertheless, he received two prizes from the Society of Arts in 1761 and 1763 for producing Turkey red.¹⁴⁸

The French government published a method for Turkey red dyeing in 1765,¹⁴⁹ making knowledge of the process even more widely available. This, and Wilson's efforts, must not have been sufficient to establish production in Britain because Parliament offered a prize for successfully dyeing Turkey red. French dyers Louis and Abraham Borelle demonstrated their method to the Manchester Chamber of Commerce in 1784 and were awarded a prize of £2500 in 1786. A second claim to the prize was made in 1785 by Pierre Jacques Papillon,^{150,151} a Rouennais dyer who was pre-empted by the Borelles but who would have an instrumental role establishing the Turkey red industry in Scotland.

¹⁴⁴ Schaefer, "The History of Turkey Red Dyeing," 1412.

¹⁴⁵ Sandberg, *The Red Dyes*, 102.

¹⁴⁶ Aikin, A Description of the Country From Thirty to Forty Miles Round Manchester, 164.

¹⁴⁷ Wilson, An Essay on Light and Colours, and What Colouring Matters Are That Dye Cotton and Linen, 20.

¹⁴⁸ Lowengard, The Creation of Color in Eighteenth-Century Europe.

¹⁴⁹ Mémoire contenant le procédé de la teinture du coton rouge-incarnat d'Andrinople sur le coton filé

¹⁵⁰ Great Britain House of Commons, "Journals of the House of Commons."

¹⁵¹ Tarrant, "The Turkey Red Dyeing Industry in the Vale of Leven," 39.

One reason the process may have been difficult to transfer, aside from its astonishing complexity, was the different British climate. Schaefer writes that adaptation of the Eastern method was required for dyeing in Western Europe.¹⁵² Henry Monteith reported in an 1834 survey of labour practices that Turkey red was generally not dyed during 'severe winter weather', ¹⁵³ indicating even ambient temperature had a consequential role. Aside from the obvious challenges drying cotton in a cool, damp climate, relative humidity and water quality may also have had effect. Any differences or adaptations are not apparent from a review of the processes or the literature, implying that subtle adaptations in handling or preparation were more likely than a complete overhaul of the process.

The scale of the Scottish industry was much larger than Turkey red production in England, but there were still some significant operations in the Manchester area. Frédéric Steiner, an Alsatian dyer, purchased part of a works at Church in 1836 from the family of Robert Peel.¹⁵⁴ Peel was the inventor of carding cylinders and worked with Hargreaves on the spinning jenny. The Foxhill Bank works was founded in the late 1700s and later owned by the Peels, then Steiner.¹⁵⁵ Historical Turkey red from Church and Foxhill Bank is analysed as part of this research. Primrose, James Thomson's mill where Hummel was born, was located nearby.

¹⁵² Schaefer, "The History of Turkey Red Dyeing," 1408.

¹⁵³ "Factories Inquiry Commission: Supplementary Report of the Central Board of H. Maj. Commissioners Appointed to Collect Information in the Manufacturing Districts, as to the Employment of Children in Factories, and as to the Propriety and Means of Curtailing the Hours of Their Labour. Part II.."

¹⁵⁴ Jacqué et al., Andrinople: Le rouge magnifique, 55.

¹⁵⁵ Ashmore, The Industrial Archaeology of Lancashire.



Figure 1-14 Approximate sites of Turkey red works in Lancashire. Image generated in Google Maps.

1.5.3 Turkey red dyeing in Scotland

John Wilson was not the only British dyer hoping to profit from Turkey red. In 1732, an association called the Red Society was founded in Glasgow. Their minute book, in the Mitchell Library archives (Glasgow, Scotland, UK) states their purpose was for 'better regulating of the dying of reed linnen & Cotton yearn madder red'.¹⁵⁶

¹⁵⁶ Minutes of the Red Society. T-TH15/26.

espon the 24 of mainh 1732 about this time several of comon of the incom very un grazgon Gorba in the regulating of ree Cinnen For having Taken 10 our 0 01 pour shall ar ne Denro pany cf e themselves goods 70 Eure cu Chosen Con cing ne

Figure 1-15 First page from 'Minutes of the Red Society', dated March 1732. $\ensuremath{\mathbb{C}}$ Glasgow City Council: Archives T-TH15-26.

Their charter, dated 1759 and written on a large piece of parchment, mentions

the 'Encourageing the Dying Mader Red'.¹⁵⁷

¹⁵⁷ Charter of the Red Society. T-TH15/25.

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Figure 1-16 The Charter of the Red Society, dated 1739. © Glasgow City Council: Archives T-TH-15-25.

Figure 1-17 Inset from the Charter of the Red Society describing their purpose of improving madder dyeing on cotton. © Glasgow City Council: Archives T-TH-15-25.

It is not clear if a 'proper method' of dyeing red meant Turkey red, but it is probably the case since it was considered the best way to obtain red on cotton and simple madder dyeing as done on wool would have been known.

The textile industry was already established in the Glasgow area by the mid-18th c.¹⁵⁸ Dalquhurn, a bleaching operation, was founded west of the city in the Vale of Leven in 1715. Pollockshaws Printfield was built in 1742 near Auldhouse Burn in what is now the Pollockshaws area on the south side of Glasgow, later becoming a collection of textile operations. Cotton spinning began at Rothesay on the Isle of Bute in 1778 and not long after was practiced in other parts of Scotland. In 1783, the New Lanark cotton mills, at the time the largest in

¹⁵⁸ Wertz, "Turkey Red Textile Dyeing in Glasgow: a Cross-Disciplinary Investigation Into Scotland's Bygone Industry."

Britain, were founded by socialist reformer Robert Owen, his father-in-law David Dale, and Richard Arkwright, who made significant contributions to cotton spinning.¹⁵⁹ Turkey red was not dyed at New Lanark, but Dale's involvement in the cotton industry meant he would have a part elsewhere.

David Dale was born in 1739 and as a young man worked as a herder and a weaver's apprentice before becoming a travelling peddler that purchased linen yarn spun by farmers' wives. In Glasgow, he worked as a clerk in a drapery store and expanded the business, importing yarn from Holland and running a shop above the Tolbooth on High Street.¹⁶⁰ As a prominent businessman, he was instrumental in establishing the first branch of the Royal Bank of Scotland in Glasgow.¹⁶¹ He founded the Blantyre Mills, located southeast of Glasgow, for cotton production with his partner James Monteith,¹⁶² whose family would also figure prominently in the dyeing of Turkey red.

Another of Dale's business partners, George Macintosh, was born in the same year in Newmore, north of Inverness.¹⁶³ He made his way to Glasgow and became a clerk at a tannery, eventually becoming the head of a shoe factory. He knew of lichen dyeing from his Highland youth and established a cudbear dye works on land east of Glasgow Cathedral in 1777. The site had walls ten feet high and was operated by Highland workers, consuming 250 tons of lichen annually and generating a noxious smell due to the urine required for the process.¹⁶⁴ While in London in 1785 he met and hired Papillon, bringing him back to Glasgow to establish the Dalmarnock Turkey red works on the bank of the Clyde;¹⁶⁵ the site was located between modern-day French Street and the Rutherglen Bridge.¹⁶⁶

¹⁵⁹ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 496-497.

¹⁶⁰ Eyre-Todd, *History of Glasgow*, 314.

¹⁶¹ McLaren, "David Dale, Scott Moncrieff and the Royal Bank of Scotland in Glasgow, 1783-1806."

¹⁶² Anderson, "Parish of Blantyre," 322.

¹⁶³ Carment, "Parish of Rosskeen," 268.

¹⁶⁴ Eyre-Todd, *History of Glasgow*, 305.

¹⁶⁵ Burns, "Parish of Barony of Glasgow," 114.

¹⁶⁶ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 498.



Figure 1-18 Approximate location of Dalmarnock Turkey red works, later called Barrowfield. Image generated in Google Maps.

Dale and Macintosh published an advertisement in the Glasgow Mercury that December for dyeing cotton yarn Turkey red at 3 s. per pound and no fewer than 60 pounds per consignment.¹⁶⁷ Macintosh's son, Charles, made significant contributions to the chemical industry in Scotland and was involved in the manufacture of sugar of lead (lead acetate), an alum works at Hurlet, bleaching powder (calcium chloride) production at St Rollox, various other chemicals, and the invention of waterproof fabric used to make jackets still called Mackintoshes today.

By 1787 Papillon had left Dalmarnock due to 'his unhappy temper' while Macintosh continued producing and improving the Turkey red process. Papillon was briefly attached to various dyeing enterprises, but never again found success.¹⁶⁸ He repeatedly petitioned the Board of Manufactures for financial support of his failing works and in 1790 agreed to disclose his process in writing to the Board, to be made public after 12 years, in exchange for funds. The process was examined by eminent chemist Dr Joseph Black for validity and sealed for the duration; the Board opened it in 1802 but with various delays it was not published until 1804.¹⁶⁹ The method appeared in the *Philosophical*

¹⁶⁷ Arthur et al., "Seeing Red: Scotland's Exotic Textile Heritage," 6.

¹⁶⁸ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 497.

¹⁶⁹ Johnston, "The Secret of Turkey Red - Technology Transfer with a Scottish Connection," 297.
Magazine,¹⁷⁰ though the Borelle method had already been published by Thomas Henry of Manchester in 1790.¹⁷¹ American chemistry professor Thomas Cooper writes in his dyeing manual that he thought little of Papillon's method, which does unusually include oil of vitriol (sulfuric acid) and sal ammoniac (ammonium chloride), calling them 'manifestly deceptions'.¹⁷² Edward Bancroft, a physician, chemist, and double agent during the American Revolution assessed Papillon's method and noted these irregularities, concluding they 'indicate a want of chemical knowledge in M. Papillon' and that they were included to add novelty to the recipe.¹⁷³ By helping George Macintosh establish a successful Turkey red works, Papillon made a much larger contribution to the industry than the later dissemination of his method.

In 1792, the son of James Monteith, also called James, purchased Blantyre Mill in its entirety from Dale¹⁷⁴ and eventually started dyeing Turkey red there as well, making Blantyre the only works where cotton was spun, woven, and dyed Turkey red. Between the First and Second *Statistical Account of Scotland* (about 50 years), the population of the parish grew from 1040 to 3000, largely credited to the Blantyre works.¹⁷⁵ His younger brother, Henry Monteith, took over Blantyre in 1802¹⁷⁶ and purchased Dalmarnock from Dale and Macintosh in 1805, renaming it Barrowfield. He had established a weaving factory a few years earlier in nearby Bridgeton and with these enterprises founded the basis of a red-andwhite discharge printed bandana empire.¹⁷⁷ The handkerchiefs were exported globally and came to be known as 'Monteiths' in some places;¹⁷⁸ Scottish physician and chemist Andrew Ure published a detailed description of 'the Great

¹⁷⁰ "V. Account of the Process Followed by M. Pierre Jacques Papillon for Dyeing Turkey Red."

¹⁷¹ Henry, "Considerations Relative to the Nature of Wool, Silk, and Cotton, as Objects of the Art of Dying; on the Various Preparations, and Mordants, Requisite for These Different Substances; and on the Nature and Properties of Colouring Matter. Together with Some Observations on the Theory of Dying in General, and Particularly the Turkey Red," 380.

¹⁷² Cooper, A Practical Treatise on Dyeing, and Callicoe Printing: Exhibiting the Processes in the French, German, English, and American Practice of Fixing Colours on Woollen, Cotton, Silk, and Linen, 297.

 ¹⁷³ Bancroft, Experimental Researches Concerning the Philosophy of Permanent Colours, 188-189.

¹⁷⁴ Eyre-Todd, *History of Glasgow*, 312.

¹⁷⁵ Anderson, "Parish of Blantyre," 323-326.

¹⁷⁶ Tarrant, "The Turkey Red Dyeing Industry in the Vale of Leven," 41.

¹⁷⁷ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 499.

¹⁷⁸ Arthur et al., "Seeing Red: Scotland's Exotic Textile Heritage," 6.

Bandana Gallery' of Monteith's operation, which in 1824 printed 224 bandanas every ten minutes.¹⁷⁹



Figure 1-19 A traditional white polka dot patterned Turkey red handkerchief. Man's handkerchief or bandana sample, c. 1867-1870, Archibald Orr Ewing & Co. Reproduced courtesy of Glasgow Museums, 1876.128.b.15.

Monteith died in 1848, incredibly wealthy from Turkey red, and after his son and heritor retired in 1873 Barrowfield was demolished. Production at Blantyre continued until 1904, when the firm was liquidated and acquired in 1925 as the Livingstone Scottish National Memorial (today the David Livingstone Centre) in honour of its famous son, the explorer and missionary who was born at the mill and worked there in his youth. A Turkey red shirt of his worn during his time in Africa can be seen on display in the museum.

By the early 1800s, increasing air pollution in Glasgow made it more difficult to bleach and dry cloth outdoors, and the quality and supply of water with increased industry on the Clyde was likely a concern as well. The Vale of Leven, through which the River Leven flows south from Loch Lomond into the Firth of Clyde west of Glasgow, had been identified as a good site for textile production as far back as 1770, when William Stirling and Sons moved their operation there and founded the Cordale calico print works.¹⁸⁰ The Leven is fed by rainwater that has first collected in Loch Lomond, where most of the particulates settle,

¹⁷⁹ Ure, "Description of the Great Bandana Gallery."

¹⁸⁰ Tarrant, "The Turkey Red Dyeing Industry in the Vale of Leven," 43.

making the river an abundant source of clear, soft water ideal for textile production.¹⁸¹ More firms were soon established and the Vale became the centre of the textile dyeing and printing industry in the West of Scotland.

1.5.4 The Scottish industry and United Turkey Red

Calico bleaching, dyeing, and printing operations on the banks of the Leven expanded after Dalquhurn was founded in 1715. A table provided in MacKay's detailed history *Bleachfields Printfields and Turkey Red* shows the growth of the industry.¹⁸²

Year	Works	Location	Туре
1715	Dalquhurn	Renton	Bleaching, later TR dyeing
1768	Levenfield	Alexandria	Printing
1770	Cordale	Renton	Printing
1772	Milton	Jamestown	Bleaching, then TR dyeing
1784	Levenbank	Jamestown	Printing, later TR dyeing
1785	Ferryfield	Alexandria	Bleaching, then printing
1785	Dalmonach	Bonhill	Printing
1790	Croftengea	Alexandria	Bleaching, later TR dyeing and printing
1793	Bonhill Printing Co.	Bonhill	Printing
1795	Kirkland	Bonhill	Bleaching, then printing
pre- 1838	Dillichip	Bonhill	Printing, then TR dyeing

Table 1-2 Bleaching, printing, and dyeing operations in the Vale of Leven. Italicised names are works that later became part of United Turkey Red.

¹⁸¹ Stewart, "Parish of Bonhill," 445.

¹⁸² MacKay, Bleachfields Printfields and Turkey Red, 11.



Figure 1-20 Approximate locations of textile works in the Vale of Leven. Glasgow is to the southeast. Image generated in Google Maps.

The Turkey red industry became the largest employer in Dunbartonshire, the name of the region where the firms were located. By the 1860s, acquisitions and amalgamations had brought the various works under the ownership of five firms, three of which were major Turkey red producers that later formed United Turkey Red.¹⁸³ These firms wielded immense economic power over the lives of their employees. Most families had at least one member employed in the industry¹⁸⁴ and loyalty to a firm was maintained by jeopardising the employment of relations if an individual expressed a desire to leave.¹⁸⁵ Turkey red was pervasive in the Vale, even for those not working in the industry. Describing his childhood playing on the banks of the Leven in the early 20th c., Tom Gallacher writes 'We jumped back from the odd jets of steam which spurted from its banks and were drawn to the gaping sluice gates which took giant gulps of fresh water and spat it out—blood red.'¹⁸⁶

The three principal Turkey red dyers in the Vale were William Stirling & Sons, John Orr Ewing & Co., and Archibald Orr Ewing & Co., who produced enough

¹⁸³ ibid., 14.

¹⁸⁴ Fryer, Behind the Vale, 104.

¹⁸⁵ Tuckett and Nenadic, "Colouring the Nation: a New in-Depth Study of the Turkey Red Pattern Books in the National Museums Scotland," 169.

¹⁸⁶ Gallacher, "The Secret of the Vale."

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textiles to dominate the world market.¹⁸⁷ To give an idea of the scale, William Stirling & Sons was valued at around £208,000 in the first half of 1882,¹⁸⁸ the equivalent of roughly £10 million in 21st c. currency.¹⁸⁹ The specialisation of the industry made it sensitive to changes in the market and in the 1890s the government of India imposed increased tariffs to help foster growth of the domestic textile industry, jeopardising the market share of Scottish Turkey red. To counteract this, the firms amalgamated in October 1897 to form the United Turkey Red Company Limited, a near monopoly under which each firm maintained its individual trademark and operations.¹⁹⁰ Alexander Reid & Sons of Milngavie (between Glasgow and Loch Lomond) also joined but did not produce Turkey red.¹⁹¹



Figure 1-21 Turkey red bale labels from UTR, late 19th c. From left: UGD 13/7a/3/5a, UGD 13/9/4, UGD 13/5/3.

By the time United Turkey Red formed, synthetic red dyes like Paranitraniline Red, of a lower quality than true Turkey red, were in use.¹⁹² In 1914, Naphthol Reds had become available and were in limited use by the firm, producing better results than Para reds.

¹⁸⁷ Arthur et al., "Seeing Red: Scotland's Exotic Textile Heritage," 6.

¹⁸⁸ Private Ledger, William Stirling & Sons. UGD 13/3/1.

¹⁸⁹ "Currency Converter."

¹⁹⁰ Tarrant, "The Turkey Red Dyeing Industry in the Vale of Leven," 45.

¹⁹¹ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 501.

¹⁹² Tarrant, "The Turkey Red Dyeing Industry in the Vale of Leven," 45.



Figure 1-22 Paranitraniline Red (left) and Naphthol Red.

The improvements in azo dyes after World War I was the final blow to Turkey red, whose laborious and time-consuming process could not compete with the new product and by 1936 production ceased.¹⁹³ The firm continued dyeing and printing other calico products until 1961, when it was taken over by the Calico Printers' Association (CPA), which eventually closed the works and liquidated the equipment. Through the CPA, surviving papers from United Turkey Red were acquired by the University of Glasgow, the Society of Dyers and Colourists, National Museums Scotland, and the City of Manchester.¹⁹⁴

Since United Turkey Red was an amalgamation under which the individual firms dyed their own Turkey red, the textiles analysed for this research may have been produced by different firms or at different works. Only one of the books containing Turkey red was made after 1897 (UGD 13/8/9), when United Turkey Red formed. The AOE dyestuffs ledger clearly originates from the Archibald Orr Ewing firm, while a sample pattern book (UGD 13/8/6) contains a slip for Alexandria Works, linking it to John Orr Ewing & Co.

¹⁹³ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 504.

¹⁹⁴ Tuckett and Nenadic, "Colouring the Nation: a New in-Depth Study of the Turkey Red Pattern Books in the National Museums Scotland," 164.

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	Alexandria Dorks,	
Name, Engaged at		
Hours W	Vorking,	

Figure 1-23 Slip from the Alexandria Works found in UGD 13/8/6, 1886-1888. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/6.

None of the other books contain definite indications of where the samples were dyed, nor does the analytical data identify any distinguishing features. This thesis does not attempt to provide a full history of United Turkey Red or of dyeing in the Vale of Leven and only aims to set a historical and geographical context for the process and textiles discussed in this research. For further reading on these topics, Peel's *Turkey Red Dyeing in Scotland: Its Heyday and Decline*,¹⁹⁵ Tuckett and Nenadic's *Colouring the Nation*,¹⁹⁶ MacKay's *Bleachfields Printfields and Turkey Red*,¹⁹⁷ and Tarrant's chapter in *Scottish Textile History*¹⁹⁸ are recommended.

1.6 Summary

The use of material reconstruction from historical processes is a valuable approach in the characterisation of heritage objects, enabling a better understanding of their conservation and display needs. The experience of recreation brings a process to life in a way that only reading about it cannot, and allows the experimenter to test the validity of a method and how processes were communicated. An evaluation of Turkey red methods reviewed for this project found that while individual methods may have distinctive ingredients or follow

¹⁹⁵ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline."

¹⁹⁶ Nenadic and Tuckett, "Colouring the Nation."

¹⁹⁷ MacKay, Bleachfields Printfields and Turkey Red.

¹⁹⁸ Tarrant, "The Turkey Red Dyeing Industry in the Vale of Leven."

slightly different steps (e.g. the 'old' and 'new' oiling processes), they share the same essential qualities characteristic of Turkey red dyeing—cotton prepared with oil and aluminium, then dyed in a madder or synthetic alizarin bath containing calcium. To facilitate replicating a historical Turkey red process to create samples for analysis, J.J. Hummel's method in *The Dyeing of Textile Fabrics* was selected for its clarity, precise measurements, and the reputation of its author. The other methods reviewed during this research were also taken into consideration to ensure Hummel's method did not fail to address anything significant. This chapter begins to answer the question for this project regarding the essential steps of the Turkey red process, which will be tested practically in the experimental re-creation and analysis of Turkey red later in this thesis.

In addition to the complex and unique nature of the process, the professed fastness of Turkey red to light and wash fastness contribute to its fabled status as a dyed textile. No other process yielded such a brilliant red on cotton, let alone one that was touted to be durable. This research does not address these colour and durability properties, but instead contributes to our understanding of the chemistry of Turkey red. This opens the possibility to eventually deciphering whether, and how, historical Turkey red is more robust to light exposure and the intrinsic link between fastness and quality. It also offers the opportunity to explore reviving or adapting the process as a modern craft industry.

The body of literature on the history of the Turkey red industry in Britain and elsewhere is extensive. The summary provided in this chapter gives context for this research and underscores the importance of Turkey red dyeing and printing in Scotland, but only provides a brief glimpse of the complex history that the recommended sources recount in much greater detail. The following chapters discuss the ingredients, practices, and chemistry of the Turkey red process to provide a framework for the re-creation and analytical work.

2 Oil and the oiling process in Turkey red dyeing

It is widely acknowledged in the historical literature that preparing the scoured cotton with oil is crucial to the successful dyeing of Turkey red.^{1,2,3} Interestingly, a review of other dyeing processes for cotton, wool, and silk indicates that no other technique depends on oiling the fibres in the same way. Oil may occasionally be used as a finishing agent in other processes, but the pretreatment of cotton with fats is characteristic of Turkey red in the mind of anyone who is familiar with it. Descriptions of Alizarin Red, the lower-quality and cheaper alternative to Turkey red, indicate the oil is directly responsible for the higher quality of Turkey red,⁴ underscoring its importance. Furthermore, it was established in the introduction to this thesis that Turkey red exists only on cellulosic fibres and cannot be extracted intact for analysis. Therefore, in situ analysis, that is to say non-extractive, is the most accurate way to characterise Turkey red textiles. Although it is clear the oiling of cotton fibres is key to producing Turkey red, exactly what happens between the oil and the cotton has never been fully understood.^{5,6} Previous research on the chemistry of the oil was conducted by necessity through extractive methods because modern instrumental techniques were not available at the height of interest in Turkey red.^{7,8}

In the early 1870s, a new chemical product called Turkey red oil was adopted by dyers, replacing the traditional rancid olive oil and instigating a change in how the dyeing was done, from the 'old' to the 'new' process. To answer the question for this project regarding the composition and role of the oil in Turkey red, this chapter reviews how oil was used applied to the cotton, the ideas and

¹ Berthollet and Berthollet, *Elements of the Art of Dyeing and Bleaching*, 341.

² Hummel, *The Dyeing of Textile Fabrics*, 233.

³ Carruthers, "A New Process of Dyeing Turkey Red," 124.

⁴ Cooper, A Practical Treatise on Dyeing, and Callicoe Printing: Exhibiting the Processes in the French, German, English, and American Practice of Fixing Colours on Woollen, Cotton, Silk, and Linen, 299.

⁵ Schützenberger, *Traité des matières colorantes*, 281.

⁶ Sandberg, *The Red Dyes*, 106.

⁷ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 589.

⁸ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour."

research of past chemists and dyers, and the transition from the 'old' to the 'new' process from a chemist's perspective to evaluate whether the chemistry of the overall process was altered. It also discusses methods to make Turkey red oil, used in Section 4.1.1 for the historical re-creation, and auxiliary ingredients like blood and dung. The conclusions from this chapter inform the hypotheses on the composition of the oil, determined experimentally in Chapter 5, and its role in the dyeing process (see Chapter 6).

2.1 Introduction

Some of the earliest European publications on Turkey red, dating from the late 18th c., shows dyers knew oil is fundamental to dyeing Turkey red.⁹ They were aware of its contribution to the colour¹⁰ and that it was 'an undisputed fact' that without oil, aluminium and alizarin produced dull colours.¹¹ Even the less expensive 'Alizarin Reds' or 'madder reds' on cotton, lower-quality, more economical alternatives to Turkey red, were improved with oil treatment, though less than was used for Turkey red.^{12,13} In a method for Alizarin Red, Hummel includes an oil treatment, but it is applied after the aluminium and alizarin rather than before,¹⁴ as in Turkey red. These reds were 'essentially different' from Turkey red, less bright and less fast but much quicker to produce.¹⁵

The oil treatment was labour-intensive, time-consuming, costly, and involved drying the fibres after each application. Naturally, this part of the process was the most obvious place for improvements and the expense of manufacturing Turkey red likely encouraged its makers to try and cut costs. Some cheaper and quicker methods with shortcuts, like combining two steps by adding a metal salt to the oil bath, still used the oil bath first and sometimes repeated the

⁹ Berthollet, *Elements of the Art of Dyeing*, 164.

¹⁰ Schützenberger, *Traité des matières colorantes*, 281.

¹¹ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 206.

¹² Cooper, A Practical Treatise on Dyeing, and Callicoe Printing: Exhibiting the Processes in the French, German, English, and American Practice of Fixing Colours on Woollen, Cotton, Silk, and Linen, 300.

¹³ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 106.

¹⁴ Hummel, *The Dyeing of Textile Fabrics*, 451.

¹⁵ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 603.

treatment anyway.¹⁶ The cost cutting may also have affected the product since combining these steps is inconsistent with traditional Turkey red processes. According to Hummel, a better result is obtained when fibres are oiled *before* aluminium is applied.¹⁷ A quicker single-bath dyeing recipe nevertheless required the same oil preparation¹⁸; it seems the oiling was more difficult to shorten than everything else. Another 'improved' method says, 'the best results have been obtained with goods oiled in the usual manner',¹⁹ so even improvers acknowledged the limitations of shortcuts. These processes appeared largely during the decline of the Turkey red industry in the early 20th century^{20,21} and are not considered for this research because they are too different from a traditional method.

Besides trying to shorten the oiling process, chemists also sought to understand the composition of the oil. By the second half of the nineteenth century, dyers and chemists were confident that fatty acids were the essential constituent in the oil to make Turkey red.^{22,23,24} Up to this point, study of its chemistry was largely based on empirical findings by reacting fibres and extracts with various other compounds. Their conclusions, reached by trial-and-error experimentation and based on 19th c. chemical knowledge, can be improved upon with the modern analytical approach used in this research.

The fascinating and complex role of oil in the chemistry of Turkey red was never fully understood before the process became obsolete in the textile dying industry. Despite interest in the question from esteemed dyers and chemists like Knecht, Berthollet, Hummel, and Persoz, the exact chemistry of this step has yet to be determined.²⁵ Liles explains, 'Turkey red is the most complex of any

¹⁶ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 503.

¹⁷ Hummel, *The Dyeing of Textile Fabrics*, 161.

¹⁸ Carruthers, "A New Process of Dyeing Turkey Red," 123.

¹⁹ Farbwerke Meister Lucius & Brüning, Manufacture and Application of Alizarine Products for Directly Dyeing Vegetable Fibres.

²⁰ Hurst, "Recent Progress in Dyeing," 73.

²¹ Fährmann, Process of Dyeing Turkey Red.

²² Jenny, "Mémoire sur la fabrications du rouge d'Andrinople," 834.

²³ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 588.

²⁴ Crookes, A Practical Handbook of Dyeing and Calico-Printing.

²⁵ Hurst, "Recent Progress in Dyeing," 138.

dye known, ancient or modern, and its entire chemistry has never been totally confirmed, mostly because it was entirely replaced by much cheaper fast vat and developed reds by 1910-40, at which point further study of its chemistry ceased.'²⁶ Today, instrumental techniques have advanced to the point where non-invasive or micro-analytical techniques can provide better analysis than ever before. This is especially timely since Turkey red production has ceased and these textiles have become museum objects. More knowledge of their properties and robustness is needed in order to best preserve what remains for future generations.

2.1.1 Terminology

The inconsistent use of terminology in the literature can be challenging at times. For clarity, this section explains a few of the terms that are frequently used in the literature and this work. One of the key topics in this research, the oil, is a good example. Besides 'oil', it is called in various texts 'oils', 'fatty matter', 'fatty bodies', 'oily matter', 'oleaginous matter', '*corps gras*', and '*huile*', among others. In Turkey red dyeing the oil was usually of vegetable origin, but in some places alternatives like milk were used, hence the references to fats (oils being a type of fat). Vegetable oils are triglyceride molecules, as shown in Figure 2-1, a combination of fatty acids (Figure 2-2) and glycerol, and in most cases, they are liquid at room temperature.



Figure 2-1 Triglyceride molecule The three carbon atoms of the glycerol are in the centre with myristoleic (top), palmitoleic (bottom right), and hexanoic (left) acids attached.

²⁶ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 112.

The structure of fatty acids is a long chain of carbon atoms bonded with primarily single bonds, although double bonds (unsaturated fats) also occur. Fats can be broken down into free fatty acids (FFAs) and glycerol by hydrolysis. There is a systematic nomenclature for fatty acids, but here they are referred to only by their trivial names (e.g. oleic acid in lieu of cis-9-octadecenoic acid) for ease of reading.



Figure 2-2 Oleic acid

Rancid is another term that appears frequently in this chapter because of the use of rancid olive oil in the 'old' process. It is defined as 'the characteristic, unpalatable odour and flavour of edible fats and oils following oxidative or hydrolytic degradation',²⁷ describing a breakdown to glycerol and FFAs. The chemistry of the process related to Turkey red dyeing is discussed further in Section 2.4. Many methods, especially for the 'old' process, refer to a 'ley', or in French *lessive*, an aqueous solution of sodium (occasionally potassium) carbonate. The origin of ley comes from Middle English and refers to 'alkalized water' made from plant ashes or strong alkaline solutions used for washing.²⁸

The oil is called a 'mordant' in some texts, another term whose definition is relevant to this chapter and the research overall. It comes from Latin *mordere*, 'to bite', because a mordant 'bites' onto the fibre and holds the dye. The most common mordants are metals like aluminium, iron, chromium, tin, titanium, or copper, though other substances like tannins and oils can also be used.²⁹ Parks, an early twentieth-century dye chemist, says mordants are substances strongly adsorbed by the fibres, which in turn strongly adsorb the dye.³⁰ By this definition, the oil could be considered a mordant if it links the colour complex to the fibre. In the literature reviewed for this research, both oil and aluminium are called mordants, and the oil is also called an auxiliary agent. In this work,

²⁷ Robards, Kerr, and Patsalides, "Rancidity and Its Measurement in Edible Oils and Snack Foods. a Review."

²⁸ Oxford University Press, "Lye, N.1."

²⁹ Patel, "Natural Dyes," 412.

³⁰ Parks, "The Chemistry of Turkey Red Dyeing," 492.

'mordant' is used to mean 'a compound that stays on the fibre and improves the dyed colour'.

2.2 Historical use of fats in textile dyeing and early investigations

According to Hummel, the use of fatty substances in dyeing dates to 'the ancient Hindoos, when intending to dye calico red by means of Madder, were in the habit of first steeping the cloth in milk and then exposing it to the sun.'³¹ This practice is reflected in the Indian textile printing tradition known as *Kalamkari*. Schützenberger also attributes the use of fat to India, where he says buffalo or ewe's milk is applied before exposing the goods to sunlight.³² Liles credits the use of oils in textile processes to India and says that although it is unknown when they were first used, a process like Turkey red probably emerged in the 1500s.³³ A late 18th c. account describes Turkey red dyeing at Astracan with fish oil,³⁴ so populations appear to have adapted to a local, abundant oil source. Dyers today in Indonesia use a variety of seed oils native to southeast Asia in a process that is strikingly similar to Turkey red.³⁵ Hofmann de Keijzer,³⁶ Driessen,³⁷ and Crookes³⁸ also describe dyeing techniques like Turkey red in Indonesia and southeast Asia.

This research does not aim to identify the origins of Turkey red dyeing, but the accounts of practices in Southeast Asia are consistent with the comments in the dyeing texts. It is not unreasonable to imagine the use of fat to prepare cotton originating in Indonesia or India and being used in madder dyeing, eventually becoming Turkey red as the process was refined and disseminated.

³¹ Hummel, *The Dyeing of Textile Fabrics*, 233.

³² Schützenberger, *Traité des matières colorantes*, 280.

³³ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 113.

³⁴ Pallas, "II. the Genuine Oriental Process for Giving to Cotton Yarn or Stuff the Fast or Ingrained Colour, Known by the Name of Turkey Red, as Practised at Astracan."

³⁵ Cunningham et al., "Hanging by a Thread: Natural Metallic Mordant Processes in Traditional Indonesian Textiles."

³⁶ Hofmann-de Keijzer and van Bommel, "TLC and HPLC Analysis of Red and Violet Cotton Yarns of Indonesian Textiles," 73.

³⁷ Driessen, "Étude sur le rouge turc, ancien procédé."

³⁸ Crookes, A Practical Handbook of Dyeing and Calico-Printing, 327.

2.2.1 In vitro and in situ

The study of historical Turkey red dye posed a challenge to 19th c. chemists because the dye complex is an intrinsic part of the fibre itself. Their analyses did not completely answer their questions because existing methods, such as extraction, were unsuited to the nature of Turkey red. Extractive analyses could identify FFAs, but not how they were bonded, which was also the case with laboratory-scale *in vitro* experiments using Turkey red ingredients in solution.^{39,40,41} Because these experiments ignored the fact that Turkey red exists only on the fibres, a characteristic acknowledged at the time, they were unable to answer how the FFAs were attached to the cotton.

An *in vitro* analysis assumes the chemistry of Turkey red is independent of the chemistry of the cellulose, which is inconsistent with descriptions of the product and the nature of the process. Since Turkey red cannot be isolated and only exists on the fibre, preparing it in a beaker will not completely replicate the complex. Extractive and *in vitro* work is informative in some respects, such as the colorant analysis via chromatography in Chapter 7, but for the study of the oil an *in situ* approach is recommended here.

2.3 Oils used historically

Different types of oil were used at various times and places, indicating that the property of oil, in general, was more important than the type of oil used. Historically, vegetable oils were primarily used. Bancroft says sesame oil, hog's lard or 'any other greasy or oil matter' were suitable,⁴² but Jenny is slightly more conservative, saying there are very few suitable oils and only the ones that quickly become rancid and form an emulsion with carbonate solutions are useful.⁴³ Drying oils like linseed oil, which have a higher degree of unsaturation, were unsuitable because they blackened the colour⁴⁴ and increased the risk of

³⁹ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés.

⁴⁰ Parks, "The Chemistry of Turkey Red Dyeing."

⁴¹ Knecht, Rawson, and Loewenthal, A Manual of Dyeing.

⁴² Bancroft, Experimental Researches Concerning the Philosophy of Permanent Colours, 199.

⁴³ Jenny, "Mémoire sur la fabrications du rouge d'Andrinople," 776.

⁴⁴ Schaefer, "The History of Turkey Red Dyeing," 1409.

spontaneous combustion.⁴⁵ This section summarises the fats mentioned in the literature for dyeing Turkey red.

2.3.1 Rancid olive oil, or huile tournante

The oil used in the 'old' process to dye Turkey red is often called *huile tournante*, a French name that also appears in English texts. *Huile tournante* describes olive oil that is rancid and has 'turned', hence the name, though it is also called Gallipoli oil.⁴⁶ Rancidity occurs by two routes, oxidative and hydrolytic. Hydrolytic rancidity is when a water molecule reacts with a triglyceride to free a fatty acid, a process accelerated by heating.⁴⁷ The products of oxidative rancidity include triglyceride hydroperoxides.⁴⁸ Since FFAs and glycerides are the proposed composition of Turkey red oil, it is more reasonable to conclude *huile tournante* is the product of natural hydrolytic rancidity. The most common fatty acid in olive oil is oleic acid, comprising from 65-85% of the fatty acids by weight.⁴⁹

Olive oil tended to become rancid more easily than other oils, making it the most used,⁵⁰ and it was also abundant in Europe. Schaefer says *huile tournante* was produced by pressing olive oil into cisterns and letting impurities settle to the bottom. After the pure oil on top was siphoned off, the oil for Turkey red was left at the bottom.⁵¹ Jenny says the oil should be extracted using hot water and that with few exceptions, olive oil was the only one used in Europe for Turkey red dyeing,⁵² which is consistent with published texts and archival

⁵⁰ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 27-31.

⁴⁵ Vitalis, Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles, 238.

⁴⁶ Cooper, A Practical Treatise on Dyeing, and Callicoe Printing: Exhibiting the Processes in the French, German, English, and American Practice of Fixing Colours on Woollen, Cotton, Silk, and Linen, 20.

⁴⁷ Vaclavik and Christian, "Fat and Oil Products," 245-246.

⁴⁸ Robards, Kerr, and Patsalides, "Rancidity and Its Measurement in Edible Oils and Snack Foods. a Review."

⁴⁹ Spangenberg, Macko, and Hunziker, "Characterization of Olive Oil by Carbon Isotope Analysis of Individual Fatty Acids: Implications for Authentication."

⁵¹ Schaefer, "The History of Turkey Red Dyeing," 1409.

⁵² Jenny, "Mémoire sur la fabrications du rouge d'Andrinople," 757.

material from the era.⁵³ The best oil for dyeing came from the region around Genoa, Italy, as well as Languedoc and Provence in the south of France,⁵⁴ and in Naples it was pressed from fermented olives.⁵⁵

Hummel says *huile tournante* is 'simply olive oil more or less rancid, and hence well adapted for producing a tolerably permanent emulsion.'⁵⁶ It was thick and acidic, and had a rancid taste and smell,⁵⁷ described as a characteristic odour of butyric, valeric, and caproic acids.⁵⁸ According to Vitalis, *huile tournante* is full of mucilage,⁵⁹ a thick gluey glycoprotein produced by many plants.⁶⁰ The literature on *huile tournante* indicates a higher content of mucilage made the oil better for dyeing.⁶¹ Vitalis describes three tiers of olive oil—virgin, common, and *tournante*, the latter containing a good deal of mucilage that makes the virgin and common oils less suitable for dyeing.⁶² According to Jenny, olives fermented before pressing yielded useful oil and fermentation in the presence of mucilage produced *huile tournante*,⁶³ probably when acids produced by the reaction caused triglyceride hydrolysis.

Today, *huile tournante* is difficult to obtain because its desirability has shifted. No longer used for textile dyeing, it is refined and sold as an inferiorgrade olive oil for cooking purposes. The closest product this project could source was *huile de bourbes* ('mud' oil), olive oil that has sediment, but it was not rancid and could not be used. In the past, when olive oil was not sufficiently

⁵⁶ Hummel, *The Dyeing of Textile Fabrics*, 234.

⁵⁸ Jenny, "Mémoire sur la fabrications du rouge d'Andrinople," 763.

⁶⁰ Anderson and Lowe, "The Composition of Flaxseed Mucilage."

⁶² Vitalis, Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles, 118.

⁵³ Book of Dye Recipes and Samples of Printed Cotton Made by Foxhill Bank Printworks England 1830-1840s. T.8-1978.

⁵⁴ Chaptal, *L'art de la teinture du coton en rouge*, 57.

⁵⁵ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 30.

⁵⁷ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 29.

⁵⁹ Vitalis, Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles, 118.

⁶¹ Cooper, A Practical Treatise on Dyeing, and Callicoe Printing: Exhibiting the Processes in the French, German, English, and American Practice of Fixing Colours on Woollen, Cotton, Silk, and Linen, 296.

⁶³ Jenny, "Mémoire sur la fabrications du rouge d'Andrinople," 759.

rancid for Turkey red, dyers and chemists explored ways to render it more suitable. They could manipulate insufficiently rancid oil by adding a quantity of oleic acid. Hummel recommends 5-15 per cent oleic acid (weight or vol. unspecified)⁶⁴ while Chateau uses less acid but heats the mixture.⁶⁵ Liles, in his modern dyeing text, recommends the use of 5-10 mL of oleic acid in an oil bath because of difficulties obtaining rancid olive oil in the modern day.⁶⁶ The addition of oleic acid, a fatty acid, and heat in this process induces hydrolysis in the olive oil, effectively increasing its rancidity. The technique does not appear to have been widely used, but it is documented in the literature and included in this discussion because it is applied to one of the oiled calico sample sets in Section 4.2.4.

2.3.2 Turkey red oil

From the early 19th c., chemists sought an alternative to *huile tournante*, which could be expensive to obtain and was often inefficient.⁶⁷ The first chemical treatment to manufacture oil useful for dyeing, adding sulfuric acid to olive oil, dates to Frémy in 1831,⁶⁸ with similar work by Runge in 1834.⁶⁹ More work followed by Kayser in 1846⁷⁰ and then Mercer and Greenwood the next year, who took out a patent.⁷¹ Persoz also cites prepared oil research done by Achard,⁷² so by the mid-1800s a steady interest had developed in these products. Dépierre writes that treated olive oil was sold by the English around 1873,⁷³ though Hurst says it was not frequently used.⁷⁴

⁶⁴ Hummel, *The Dyeing of Textile Fabrics*, 436.

⁶⁵ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 31.

⁶⁶ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 121.

⁶⁷ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 29.

⁶⁸ Radcliffe and Medofski, "The Sulphonation of Fixed Oils."

⁶⁹ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 589.

⁷⁰ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2^{me} partie, L'alizarine artificielle et ses dérivés, 214.

⁷¹ Burton and Robertshaw, Sulphated Oils and Allied Products, 17.

⁷² Persoz, Traité théorique et pratique de l'impression des tissus, 335.

⁷³ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 224.

⁷⁴ Hurst, *Textile Soaps and Oils*, 139.

Research ensued to determine which oils made the best 'sulphated oil'. Knecht says castor oil treated with sulfuric acid was better suited for dyeing than olive oil.⁷⁵ The exact date that castor oil began to be used, and who first proposed it, is uncertain. Storey writes the discovery is credited to Walter Crum, a Glaswegian industrialist, in 1864,⁷⁶ though other sources say he did not use it in the textile industry until 1875.⁷⁷ Leigh says Wuth and Storck worked it out independently of each other in 1870.⁷⁸ According to Knecht, Wuth worked on the sodium salt while Storck developed the ammonia salt, and Wuth's product was sold in Manchester from 1876.⁷⁹ The exact date and credit of the discovery was of enough concern that, in 1909, the Société Industrielle de Mulhouse put together a commission to review various claims and stories.⁸⁰

As cheaper alternatives to castor oil, cottonseed and corn oils were also investigated, but they yielded dark-coloured, unsuitable products.⁸¹ These oils contain more double-unsaturated fatty acids,⁸² making them chemically more like drying oils than olive or castor oil. The use of drying oils, like linseed oil, was discouraged for Turkey red because of the blackening effect it had on the colour.^{83,84} In general, cutting castor oil with cheaper alternatives was never beneficial to the dyer. Castor oil treated with sulfuric acid became known as Turkey red oil,⁸⁵ also referred to as alizarine oil, oleine, soluble oil, dyeing oil, red oil,⁸⁶ and sulfated castor oil. It is also called a 'prepared' oil and is made by treating castor oil with sulfuric acid, then washing out the excess acid and neutralising it. Similar to the effect of oleic acid added to olive oil, the sulfuric acid induces glyceride hydrolysis and increases the fatty acid content.

⁷⁵ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 600.

⁷⁶ Storey, The Thames and Hudson Manual of Dyes and Fabrics, 73.

⁷⁷ Markley, Fatty Acids: Their Chemistry, Properties, Production, and Uses, 1735.

⁷⁸ Leigh, "On the Estimation of Alizarin in Dyed Cotton Fabrics, and on an Attempt to Ascertain the Composition of Turkey-Red and Other Alizarin Lakes," 209.

⁷⁹ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 161.

⁸⁰ Brandt et al., "Sulfoléates et rouge turc par le procédé rapide, priorités."

⁸¹ Hurst, "Recent Progress in Dyeing," 143.

⁸² Gunstone, *Fatty Acid and Lipid Chemistry*, 69.

⁸³ Bancroft, Experimental Researches Concerning the Philosophy of Permanent Colours, 199.

⁸⁴ Schaefer, "The History of Turkey Red Dyeing," 1409.

⁸⁵ Storey, The Thames and Hudson Manual of Dyes and Fabrics, 73.

⁸⁶ Hurst, *Textile Soaps and Oils*, 139.

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The transition to Turkey red oil occurred from 1870-1875,^{87,88} and resulted in the 'new' process, in contrast with the *huile tournante* 'old' process. Turkey red oil had a higher fatty acid content than *huile tournante*,⁸⁹ so more was applied in each treatment, decreasing the time required to adequately prepare the cotton. Sansone writes *huile tournante* required three oil treatments while Turkey red oil needed only one.⁹⁰ Verbong credits Turkey red oil for enabling the reduction in dyeing time from six to eight weeks to one week or less,⁹¹ and Haller says the number of steps was reduced from seventeen to six. It was sold in various concentrations diluted with water, often around 50%, but at higher concentrations if freight costs were involved.⁹²

Besides shortening the dyeing process, Turkey red oil was the first synthetic anionic surfactant and it soon was also used as a mordant for basic colours in cotton dyeing, wool oiling, and for its soap-like properties.⁹³ Although Turkey red is no longer in production, the textile industry still uses Turkey red oil as a wetting, levelling, and dispersing agent in dyeing and as a finishing agent to impart softness improve silkiness and drape in cellulose fabrics.⁹⁴ Outwith textiles, it is used for inks, industrial detergents, leather treatment, and as a lubricant additive for cutting oils and hydraulic fluids.⁹⁵ It also is safe for skin contact and mixes well with water, making it a good base for bath-oil products.⁹⁶ Today, Turkey red oil is one of the most common anionic surfactants used in industry because of the availability of raw materials and simple, low-cost production.⁹⁷ This project benefits from the continued use of Turkey red oil because it offers an opportunity to examine whether the production method

- ⁸⁹ Haller, "The Chemistry and Technique of Turkey Red Dyeing," 1418.
- ⁹⁰ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 204.

⁹² Hurst, Textile Soaps and Oils, 139.

⁸⁷ ibid., 139.

⁸⁸ Radcliffe and Medofski, "The Sulphonation of Fixed Oils," 23.

⁹¹ Verbong, "Turksrood," 282.

⁹³ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 167.

⁹⁴ Panda, The Complete Book on Textile Processing and Silk Reeling Technology, 447.

⁹⁵ LaFalce, "Sulfated Castor Oil Production."

⁹⁶ Gunstone and Padley, *Lipid Technologies and Applications*, 788.

⁹⁷ Nawaby, Kruus, and Dabek-Zlotorzynska, "Determination of Anionic Surfactant Turkey Red Oil by Capillary Electrophoresis with Direct UV Detection," 401.

differs from the historical texts and makes it possible to compare commercial samples to historical and replica ones.

2.3.3 AOE Dyestuffs ledger

The entries in the AOE Dyestuffs Ledger date from 1873 to 1892 and provide firsthand insight to the transition from the 'old' to 'new' process in the Archibald Orr Ewing firm. The ledger entries only distinguish between 'old' and 'new' process for 1873-1874, but some later entries have values for 'both processes'. Castor oil does not appear at all. Remarkably, no mention of Turkey red oil is found until the last six months of 1883, when the Levenbank Works used 'olive oil & alizarin oil', entered as one quantity. It was used again at Levenbank, which dyed cloth, over the next two years, though not consistently and not at Milton or Dillichip, where yarn was dyed. The first entries for those date from the last six months of 1886, when 'oleine' is introduced. By 1887, the use of Turkey red oil is steady, though olive oil never entirely disappears. Figure 2-3 illustrates the figures for oil consumption from the ledger, but because we do not know enough about why it was kept or how the firm did their dyeing, it may never be known for certain why the Archibald Orr Ewing firm continued to use olive oil, which this record shows was still used into the 1890s.



Oil used to dye 110 lbs. Turkey red yarn, Dillichip works 1873-1892

Figure 2-3 Oil used for Turkey red dyeing at three works in the Archibald Orr Ewing firm. Data from AOE dyestuffs ledger, University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/4/1.

The graphs show that olive oil appears most often; these figures occasionally include a small quantity of palm oil that was recorded as well,⁹⁸ perhaps as a supplement or for experimental purposes. Entries for 'vitriol', or sulfuric acid, appear throughout the ledger. Although the first two entries mention an 'old' and 'new' process, Turkey red oil is not listed as an ingredient. As discussed regarding Papillon's method,⁹⁹ sulfuric acid is not generally used in Turkey red, so the firm may have been making their own sulfated oil, which Hurst says some firms did.¹⁰⁰ There are no dyeing instructions, so the purpose of sulfuric acid can only be speculated upon.

⁹⁸ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.

 ⁹⁹ "V. Account of the Process Followed by M. Pierre Jacques Papillon for Dyeing Turkey Red."
¹⁰⁰ Hurst, *Textile Soaps and Oils*, 140.

Since the distinction between 'old' and 'new' is not maintained throughout the ledger and Turkey red oil does not appear until 1883, it is unclear which process was followed. According to Sansone, in 1885 the 'new' process was more common, but the 'old' process had not been completely abandoned and 'some of the Scotch firms still adhere to it' because it produced the fastest colours to light, washing, and bleaching.¹⁰¹ The continued use of ruminant dung in the ledger, which was characteristic of the 'old' process, also supports this. Another possible explanation for the olive oil is that the firm was using the Steiner process, discussed later, which used hot olive oil and which Peel says was used at the John Orr Ewing firm as of 1898.¹⁰² Although the John Orr Ewing and Archibald Orr Ewing firms operated separately, the Orr Ewings were brothers and with the dissemination of technology by this time it is likely the firms followed similar dyeing practices. The ledger may show the Archibald Orr Ewing firm was one of the Scottish firms that continued the 'old' process because they felt it made a higher-quality product, or that they were using a modified Steiner process, but production notes would provide a better understanding of the inhouse practices.

The replica and analytical work in this research focuses on the 'new' process because *huile tournante* could not be sourced and because of the late-19th c. focus on the developing chemical industry and Turkey red oil. The conclusion from the review of the literature, based on descriptions of the 'old' and 'new' processes, the oils, and the transition between the processes is that that both yield Turkey red and can be considered chemically similar.

2.4 Suitability of oils for Turkey red

The historical literature addresses the issue of suitable oil for Turkey red dyeing, for which dyers had various tests for even though precise analytical techniques were unavailable at the time. By the mid-1800s, chemists and dyers knew oils were composed of glycerol and fatty acids¹⁰³ (see FIGURE 2-1), and that the

¹⁰¹ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 205.

¹⁰² Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 501.

¹⁰³ Persoz, Traité théorique et pratique de l'impression des tissus, 344.

latter contributed to the success of the dyeing.^{104,105} Furthermore, they were aware the process to make Turkey red oil was for 'the splitting up of the glycerides and setting the fatty acids at liberty'.¹⁰⁶

Without a doubt, high-quality Turkey red depended on high-quality oil— Chaptal says the beauty and evenness of the colour on the fibre was particularly affected.¹⁰⁷ This means a high content of FFAs— for olive oil, the opposite of quality food oil, which has a low acid content. Hurst writes he identified some *huile tournante* with up to 20% FFA content,¹⁰⁸ for comparison, cold-press extra virgin has a maximum of 1.0% fatty acids and the lowest-quality food oil has a maximum acidity of 1.5%.¹⁰⁹ The standard test for *huile tournante*, which was used before the significance of fatty acids was fully understood, was to assess its ability to form a milky emulsion with a weak aqueous carbonate solution or 'ley'.^{110,111} An emulsion is a fine dispersion of microdroplets of one liquid into another, the two not being miscible;¹¹² in this case oil and water with the fatty acids acting as emulsifiers. This is why in some places *huile tournante* is referred to as 'emulsive oil' and the 'old' process as the 'emulsive' process. The emulsion became obsolete with the 'new' process because Turkey red oil is fully miscible with water.

To test *huile tournante*, a few drops of the oil were added to a weak ley, which should produce said milky emulsion.^{113,114,115} Furthermore, the emulsion

- ¹⁰⁸ Hurst, *Textile Soaps and Oils*, 139.
- ¹⁰⁹ Spangenberg, Macko, and Hunziker, "Characterization of Olive Oil by Carbon Isotope Analysis of Individual Fatty Acids: Implications for Authentication."
- ¹¹⁰ Pallas, "II. the Genuine Oriental Process for Giving to Cotton Yarn or Stuff the Fast or Ingrained Colour, Known by the Name of Turkey Red, as Practised at Astracan," 6.
- ¹¹¹ Chaptal, *L'art de la teinture du coton en rouge*, 57-58.
- ¹¹² Vaclavik and Christian, "Fat and Oil Products," 263.
- ¹¹³ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 27.
- ¹¹⁴ Chaptal, *L'art de la teinture du coton en rouge*, 56.

¹⁰⁴ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 270.

¹⁰⁵ Duerr and Turnbull, *Bleaching and Calico-Printing* : a *Practical Manual*, 84.

¹⁰⁶ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 263.

¹⁰⁷ Chaptal, *L'art de la teinture du coton en rouge*, 55.

¹¹⁵ Persoz, Traité théorique et pratique de l'impression des tissus, 345.

must hold for some time and not separate.^{116,117,118} This was effectively a test for the oil bath in the 'old' process, which was a large-scale batch of *huile tournante* and ley emulsion. The leys were made with potassium or, more frequently, sodium carbonate (called 'soda').

In the late 18th c., soda was obtained by burning seaweed, kelp¹¹⁹ or saltwort, a plant that grows well in brackish environments along the Mediterranean coast, producing ash with a high sodium carbonate content. The finest was called 'Barilla', 'Barilla salsola', or 'Alicante Barilla', Alicante being a Spanish port on the Mediterranean where the plant was harvested.^{120,121} By the late 1700s, the demand from the growing textile, soap, and glass industries had outpaced the natural supply and the Leblanc process to make sodium carbonate from brine was developed shortly before the French Revolution, freeing dyers from their dependence on imported Barilla. By 1818, Charles Tennant, in partnership with George Mackintosh's son Charles Mackintosh, had produced 100 tons of soda using this process at his St Rollox works outside of Glasgow,¹²² probably supplying the local Turkey red industry.

2.5 Making Turkey red oil

This section discusses the process historically used to make Turkey red oil in three phases: sulfation, washing, and neutralisation. This information is used to re-create Turkey red oil as part of this research. There are many more methods available for dyeing Turkey red than there are for making Turkey red oil, and most texts are as non-specific as "add sulfuric acid to castor oil and stir", adding an additional layer of uncertainty to the re-creation. The method from Scheurer-Kestner in Knecht's *A Manual of Dyeing* (1893) was the only one found that was reasonably complete and clear to the modern reader, and was chosen for this and its consistency with the broad descriptions in other texts. The method was

¹¹⁶ Crookes, *Dyeing and Tissue Printing*, 76.

¹¹⁷ Schützenberger, *Traité des matières colorantes*, 282.

¹¹⁸ Mémoire sur la fabrications du rouge d'Andrinople," 758.

¹¹⁹ Reed, "Acid Towers and the Control of Chemical Pollution 1823-1876."

¹²⁰ Chaptal, *L'art de la teinture du coton en rouge*, 62.

¹²¹ Chenciner, Madder Red: a History of Luxury and Trade.

¹²² Reed, "Acid Towers and the Control of Chemical Pollution 1823-1876," 101.

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supplemented with other historical and modern source material when necessary, which is referenced accordingly in this section. Since the oil is still manufactured today, an industrial chemist was consulted who confirmed, by telephone, that the same process is still used.¹²³ This means the replica and historical samples can be reliably compared to a modern commercial one.

The methods are sometimes a challenge to interpret for the modern reader with no physical descriptions of the reaction and undefined variables like solution concentration. Additionally, by the 1890s, the 'new' process was well established and dyers were accustomed to making and working with Turkey red oil. The equipment used to make Turkey red oil could occasionally be a source of contamination. Lead tanks,¹²⁴ or iron tanks lined with lead were used, or smaller batches were made in wooden or ceramic containers.¹²⁵ Some sources said that the oil must rest if a zinc or lead vessel was used so contaminants could settle out.¹²⁶ This project uses borosilicate glass beakers, so contamination is not a concern. The experimental re-creation of Turkey red oil for this project is presented in Section 4.1.1.

2.5.1 Sulfation

The first step in making Turkey red oil, sulfation, is controlled by the ratio of oil to acid, with time and temperature being secondary factors. This is done with concentrated sulfuric acid, about 96-98%. Enough time to react with sulfuric acid is needed to release an adequate quantity of FFAs, but over-reacting the mixture can produce undesired effects. It was important not to let the reaction mixture overheat and adversely affect the product, so the temperature was monitored to ensure it did not rise above 35-40 $^{\circ}$ C.^{127,128} Too much heat produced sulfur dioxide (SO₂), which darkened the product and affected the dyeing.¹²⁹

¹²³ LaFalce, "Sulfated Castor Oil Production."

¹²⁴ Duerr and Turnbull, *Bleaching and Calico-Printing* : a *Practical Manual*, 84.

¹²⁵ Radcliffe and Medofski, "The Sulphonation of Fixed Oils," 23.

¹²⁶ Mémoire sur la fabrications du rouge d'Andrinople," 779.

¹²⁷ Duerr and Turnbull, *Bleaching and Calico-Printing* : a Practical Manual, 84.

¹²⁸ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 161.

¹²⁹ Cain and Thorpe, The Synthetic Dyestuffs and the Intermediate Products From Which They Are Derived, 292.

oil and made it difficult to mix the acid. Rather than risk this, it was better to add the acid incrementally and let the heat dissipate between additions.¹³⁰ The reaction with the acid causes the oil to turn from clear, straw-yellow to an opaque, dark brown viscous fluid.^{131,132} This is a common result of reactions with sulfuric acid, which is an effective dehydrating agent. This colour does not persist in the finished oil, which undergoes further changes during washing and neutralisation.¹³³

A typical method to make Turkey red oil involved reacting a quantity of castor oil with a percent of its weight, around 15 to 40, of concentrated sulfuric acid, more being required in the winter¹³⁴ probably due decreased reactivity and difficulty stirring. The Scheurer-Kestner method uses one part sulfuric acid to three parts castor oil and lets it react for 12 hours.¹³⁵ Other sources say 'overnight'¹³⁶ or no less than 24 hours,¹³⁷ so practices varied considerably. More unusual methods recount olive oil and sulfuric acid reacting for 24 to 28 hours¹³⁸,¹³⁹ but this is inconsistent with the other literature reviewed. This recreation uses overnight as a guideline since it fits within the figures found in the literature.

The 1:3 ratio of acid to oil by weight from Scheurer-Kestner has a scientific basis—three fatty acid-glycerol bonds in a triglyceride must be hydrolysed for maximum efficiency of the reaction.¹⁴⁰ Had they been able to calculate this by molar mass (approximating castor oil as triricinolein), they would have found they were not far from the molar ratio for the two compounds.

¹³⁰ Radcliffe and Medofski, "The Sulphonation of Fixed Oils," 23.

¹³¹ ibid., 26.

¹³² Grün and Woldenberg, "Investigation of the Essential Constituent of Turkey-Red Oil and Its Derivatives," 495.

¹³³ Burton and Robertshaw, Sulphated Oils and Allied Products, 1.

¹³⁴ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 160.

¹³⁵ ibid., 165.

¹³⁶ Duerr and Turnbull, *Bleaching and Calico-Printing* : a *Practical Manual*, 84.

¹³⁷ Hurst, Textile Soaps and Oils, 144.

¹³⁸ Hummel, *The Dyeing of Textile Fabrics*, 234.

¹³⁹ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 221.

¹⁴⁰ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 166.

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1.0 g $H_2SO_4 \times \frac{\text{mol } H_2SO_4}{98.08 \text{ g}} \times \frac{1 \text{ mol triricinolein}}{3 \text{ mol } H_2SO_4} \times \frac{933.34 \text{ g}}{\text{mol triricinolein}} = 3.2 \text{ g triricinolein}$ Figure 2-4 Calculation of sulfuric acid to make Turkey red oil.

Hurst recommends a minimum of 1:5 acid to oil by and says intact triglycerides in the oil had the benefit of decreasing frothing when mixed with oil,¹⁴¹ so some unreacted oil may have been desirable.

2.5.2 Washing

Surprisingly, washing is the most important step when making Turkey red oil.¹⁴² Once the acid has reacted enough with the oil, the excess must be washed out or else the product would be ruined.¹⁴³ The composition of the oil was constantly changing as hydrolysis and sulfation occurred, so the reaction was stopped when the FFA content was suitable and before it went too far.¹⁴⁴ Washing also prevents any remaining acid in the Turkey red oil from having a detrimental effect on the cellulose fibres.

The oil was washed by liquid-liquid extraction, because although sulfuric acid is water soluble, the oil is not. Shaking the oil with water extracts the acid, and when the phases separate the aqueous acid mixture can be drained off. To accomplish this, it was made in a vessel with a tap on the bottom, possibly sloped to ensure optimal drainage.¹⁴⁵ Other water-soluble compounds like glycerol were also removed during washing.^{146,147} Most sources do not indicate the water was heated, although Scheurrer-Kestner uses water at 40 °C for the first wash.¹⁴⁸ One says the washing was conducted 'at the highest temperatures',¹⁴⁹ a

¹⁴¹ Hurst, *Textile Soaps and Oils*, 146.

¹⁴² Trask, "Sulfonation and Sulfation of Oils," 570.

¹⁴³ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 160.

¹⁴⁴ Trask, "Sulfonation and Sulfation of Oils," 570.

¹⁴⁵ Hurst, *Textile Soaps and Oils*, 144.

¹⁴⁶ Burton and Robertshaw, Sulphated Oils and Allied Products, 17.

¹⁴⁷ Gunstone, *Fatty Acid and Lipid Chemistry*, 206.

¹⁴⁸ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 165.

¹⁴⁹ Trask, "Sulfonation and Sulfation of Oils," 570.

practice the industrial source said was used at his firm,¹⁵⁰ but this is not done in this work since it is uncommon in the historical literature.

The oil was sometimes washed with a salt solution instead of, or in addition to, plain water. This was done with 'common salt' (sodium chloride, NaCl) or Glauber's salt (sodium sulfate decahydrate, Na₂SO₄ • 10 H₂O);¹⁵¹ the sulfate produced better results and may have stabilised the product.¹⁵² Some methods wash with water and then salt,^{153,154} others placed little importance on its use.¹⁵⁵ The industrial chemist confirmed the salt was necessary to remove excess acid, and that although chloride anions destabilised the oil-water interface during washing, the firm uses NaCl because it is cheaper than Na₂SO₄.¹⁵⁶ For this recreation the sulfate was chosen since the scale did not make cost a concern and it was acknowledged to be the superior choice. Concentrations of the solution are frequently unspecified, but Radcliffe recommends a saturated solution,¹⁵⁷ which is roughly 16 g anhydrous Na₂SO₄ per 100 mL water.¹⁵⁸ After washing, the oil should be 'a uniform mass of a creamy colour without any dark streaks'.¹⁵⁹

2.5.3 Neutralisation

The final neutralisation step addressed the residual acid not removed through washing, since the product was still very acidic. This was done with a strong base, typically sodium hydroxide (NaOH) or ammonia (NH₃),¹⁶⁰ which yielded fatty acid salts. The ammonium salts were more likely to break down, which was thought to improve the uptake of fatty acids¹⁶¹ and eliminate ammonia as it

¹⁵⁰ LaFalce, "Sulfated Castor Oil Production."

¹⁵¹ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 160.

¹⁵² Burton and Robertshaw, Sulphated Oils and Allied Products, 18.

¹⁵³ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 165.

¹⁵⁴ Radcliffe and Medofski, "The Sulphonation of Fixed Oils," 23.

¹⁵⁵ Hurst, *Textile Soaps and Oils*, 144.

¹⁵⁶ LaFalce, "Sulfated Castor Oil Production."

¹⁵⁷ Radcliffe and Medofski, "The Sulphonation of Fixed Oils," 26.

¹⁵⁸ Okorafor, "Solubility and Density Isotherms for the Sodium Sulfate-Water-Methanol System."

¹⁵⁹ Hurst, *Textile Soaps and Oils*, 144.

¹⁶⁰ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 161.

¹⁶¹ Hummel, *The Dyeing of Textile Fabrics*, 444.

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volatilised.¹⁶² For this project, NaOH was selected to avoid introducing another variable (ammonium ions) and any hazards from evolved gaseous ammonia, and because the modern commercial Turkey red oil is a sodium salt.

Care in precise neutralisation was important¹⁶³ since too acidic a product would damage the fibres and too extreme a pH in either direction could affect subsequent dyeing steps. The historical literature does not provide much detail on neutralisation in terms of concentrations or physical changes to look for. Hurst uses an aqueous solution NaOH at 40 °Tw,¹⁶⁴ roughly 1.2 spg¹⁶⁵ or an 18% solution.¹⁶⁶ A modern preparation of isoricinoleic acid uses 50% aq. NaOH (w/w or w/v unspecified).¹⁶⁷ Stronger alkali decreases the amount of added water, but in a small-scale batch may over-adjust the pH.

To neutralise the oil, the alkali solution is added dropwise with continuous stirring to avoid unreacted aqueous pockets in the oil. As the oil is neutralised, the creamy and opaque substance becomes more transparent, with the process ending when the oil is clear. The final volume will be greater than the initial quantity of oil, possibly up to twice as much,¹⁶⁸ in part because of retained water—according to Burton about 35%.¹⁶⁹

2.5.4 Summary

Based on the historical literature and the conversation with the industrial source, the process of making Turkey red oil—sulfation of castor oil followed by washing and neutralisation—appears to be standard and consistent. This is valuable information for the re-creation, because it validates a comparison of the analytical results on the composition of the replica, commercial, and historical Turkey red oils. The review identified Scheurer-Kestner's method

¹⁶² Hurst, *Textile Soaps and Oils*, 146.

¹⁶³ Burton and Robertshaw, Sulphated Oils and Allied Products, 18.

¹⁶⁴ Hurst, *Textile Soaps and Oils*, 145.

¹⁶⁵ O'Neill, Chemistry of Calico Printing, Dyeing, and Bleaching, 12.

¹⁶⁶ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 186.

¹⁶⁷ Ahmad and Singh, "Surface Active Properties of Sulfonated Isoricinoleic Acid," 205.

¹⁶⁸ Hurst, "Recent Progress in Dyeing," 144.

¹⁶⁹ Burton and Robertshaw, Sulphated Oils and Allied Products, 18.

provided by Knecht as a useful representative recipe for the re-creation, taking other sources into consideration to complete it.

No documents exist on the products of Turkey red oil in the Glasgow University archives, but an early 20th c. process is preserved in the Coats Archives at Paisley Central Library (Paisley, Scotland, UK). The documents are later than the period of interest for this project, but the directions are consistent with the published literature on Turkey red oil, corroborating that practices in the dyeing works were similar to what was published on the topic. *Recipe from Mr Straugh*, dated 16 April 1908, reacts sulfuric acid with an initial 3:1 ratio of olive to castor oil, then the next day adds twice the original weight in castor oil.¹⁷⁰ A letter from the firm dated 13 December 1943 summarises the other material available in the collection and says, 'comparing these three records, there is really very little difference'. The author writes:

The quantities and proportions given in Mr. Strauch's (sic) recipe are those which obtained over a long period of years and were only altered within comparatively recent times. The alteration was that as Olive Oil was more expensive, more and more Castor Oil came to be used until finally we were using 75% Castor Oil and only 25% Olive Oil. The actual process of making remains substantially the same.'¹⁷¹

The inclusion of olive oil in the Straugh recipe is more consistent with the AOE dyestuffs ledger than with published literature on Turkey red oil and Turkey red dyeing, which favours castor oil. The above quotation from the Coats Archive shows eventually the price of olive oil costed it out of use for making Turkey red oil, but perhaps the AOE ledger was written when it was still cost-effective to use, or else Sansone was correct about some Scottish firms adhering to the old process.

Turkey red oil today, which can be purchased from industrial sources as well as craft suppliers for the making of bath oils, is alternately described as amber coloured, dark brown, and light yellow, which shows how much the final product can vary while still being Turkey red oil. The only chemical supplier that sells Turkey red oil is Sigma-Aldrich; according to a certificate of analysis, a 10%

¹⁷⁰ Straugh, *Recipe From Mr Straugh*. 1/9/3.

¹⁷¹ Brennan, Tannahill, and Percy, *Turkey Red Process for Cotton Yarn*. 1/9/3.

aqueous solution of their product has a pH of 7-8, making it neutral to slightly basic, and it has a 16-20% water content.¹⁷²

2.6 Composition and chemistry

Since its invention, dyers and chemists were interested in the composition of Turkey red oil and performed empirical experiments to investigate it, such as mixing it with ether and boiling it with water.¹⁷³ We now know that finished Turkey red oil is a complex mixture of compounds with varying properties,¹⁷⁴ often forming emulsions and micro-emulsions.¹⁷⁵ Markley says the quality of the raw materials, reaction time, stirring, temperature, concentrations, and catalysts all affect the reaction, and that many side reactions occur during the process.¹⁷⁶ This section summarises previous research on the topic consistent with the analytical results from this research in Chapter 5.

2.6.1 Reactions between castor oil and sulfuric acid

The primary and most important reaction when making Turkey red oil is glycerol hydrolysis. Chemically speaking, good reason exists for choosing castor oil, from the seeds of the *Ricinus communis* plant, to make Turkey red oil.¹⁷⁷ It is unusual for an oil in that it is nearly a pure compound largely made of the trigylcerides of ricinoleic acid,¹⁷⁸ experimentally determined to be 87% of the fatty acid content with oleic acid following at 7%.¹⁷⁹ Since the overwhelming majority of castor oil is composed of ricinoleic acid triglycerides, castor oil is sometimes described as triricinolein.¹⁸⁰

¹⁷² "Certificate of Analysis."

¹⁷³ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 165.

¹⁷⁴ Radcliffe and Medofski, "The Sulphonation of Fixed Oils," 23.

¹⁷⁵ Gunstone and Padley, *Lipid Technologies and Applications*.

¹⁷⁶ Markley, Fatty Acids: Their Chemistry, Properties, Production, and Uses, 1736.

¹⁷⁷ Duerr and Turnbull, *Bleaching and Calico-Printing* : a Practical Manual, 84.

¹⁷⁸ Naughton, "Production, Chemistry, and Commercial Applications of Various Chemicals From Castor Oil," 65.

¹⁷⁹ Nawaby, Kruus, and Dabek-Zlotorzynska, "Determination of Anionic Surfactant Turkey Red Oil by Capillary Electrophoresis with Direct UV Detection."

¹⁸⁰ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 160.



Figure 2-5 Ricinoleic acid

The structure of ricinoleic acid is similar to oleic acid—cis-9-octadecenoic acid except that ricinoleic acid has a hydroxyl at the 12-carbon, giving it 'a diversity of uses shared by no other fat.'¹⁸¹

Physically, castor oil is a clear, pale yellow liquid more viscous than other oils. The hydroxyl group gives castor oil its viscosity—in a similar manner to adhesives, the hydrogen bonding of the hydroxyl groups results in stickiness and decreased flow. The unique reactivity of castor oil can be attributed to its high proportion of ricinoleic acid and its hydroxyl, which alters the physical properties of the oil and how it reacts with sulfuric acid.

First, as other triglycerides, the sulfuric acid hydrolyses the glyceride bonds to release FFAs.¹⁸² The degree of glycerol hydrolysis determines the FFA content of Turkey red oil and therefore its usefulness in the dyeing process. Experiments in the 19th c. found the average composition of Turkey red oil to be 20-27% FFAs, 25% sulfated compounds and partial glycerides, and the rest water.¹⁸³ The glycerol, which is water soluble, is extracted in the washing step and is not a significant component in Turkey red oil,^{184,185} nor was it thought to have a role in the dyeing process.¹⁸⁶ In this research, its presence (or absence) is a useful indicator of whether glycerol hydrolysis has occurred.

After the triglycerides are hydrolysed, the sulfuric acid reacts with the hydroxyl group, if present, and the double bond.¹⁸⁷ Reaction with the hydroxyl produces a sulfate ester and releases a water molecule,¹⁸⁸ but the esters tend to

¹⁸¹ Achaya, "Chemical Derivatives of Castor Oil," 758.

¹⁸² Trask, "Sulfonation and Sulfation of Oils."

¹⁸³ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 161.

¹⁸⁴ ibid., 164.

¹⁸⁵ Hurst, *Textile Soaps and Oils*, 157.

¹⁸⁶ Persoz, Traité théorique et pratique de l'impression des tissus, 176.

¹⁸⁷ Burton and Robertshaw, Sulphated Oils and Allied Products, 26.

¹⁸⁸ LaFalce, "Sulfated Castor Oil Production."

hydrolyse back to hydroxyls.^{189,190} The oil has around 8% SO₃, which contributes to its surfactant properties,¹⁹¹ and indicates around 35% sulfated fatty acids.



Figure 2-6 Sulforicinoleic acid The product of an addition reaction between sulfuric acid and ricinoleic acid. The sulfate group hydrolyses back to a hydroxyl.

The sulfated compounds were known to hydrolyse during textile processes that used heat,¹⁹² as they would have been treated for Turkey red. Since *huile tournante* would not have contained sulfated compounds and the 'old' and 'new' processes yielded comparable Turkey red, they are not presumed to be significant in the dyeing as minor components of the oil treatment. The reaction between the double bond and the acid also produces a sulfate ester on one of the carbons,¹⁹³ as shown below.



Figure 2-7 Sulfate ester on olefinic bond

When these hydrolyse, the double bond is permanently broken,¹⁹⁴ an effect discussed in the analysis of Turkey oil for this project.

¹⁸⁹ Trask, "Sulfonation and Sulfation of Oils," 569.

¹⁹⁰ Gebhart and Mitchell, Neutralization of Sulphonated Organic Esters.

¹⁹¹ Naughton, "Production, Chemistry, and Commercial Applications of Various Chemicals From Castor Oil," 69.

¹⁹² Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 590.

¹⁹³ Burton and Robertshaw, Sulphated Oils and Allied Products, 31.

¹⁹⁴ Markley, Fatty Acids: Their Chemistry, Properties, Production, and Uses, 1736.

2.6.2 Properties and polymerisation

Turkey red oil has uses as a surfactant, detergent, and emulsifier.^{195,196} Its emulsive properties were the primary reason it was developed for Turkey red dyeing, but the other properties, such as decreasing surface tension, may also affect the process. The oil was a significant development in surfactant technology.¹⁹⁷

Side reactions that occur in finished Turkey red oil are helpful in identifying the freshness of the oil. As such, they are used in this research to help characterise the historical oils. Ricinoleic acid, the primary component of Turkey red oil, autopolymerises as it ages and must be made fresh.¹⁹⁸ Chemists in the late 19th c. found polymers containing up to five ricinoleic acids formed in Turkey red oil.¹⁹⁹ Autopolymerisation of FFAs produces estolides, compounds formed when the carboxyl group of a fatty acid links to another fatty acid chain.²⁰⁰

Figure 2-8 Ricinoleic acid estolide

The compound above has an estolide number of three and depicts the bond formation described by Isbell.

After six weeks at room temperature in a loosely closed container, a sample of ricinoleic acid had contained 50% estolides of various numbers,²⁰¹ however, they are not anticipated to be a significant presence on Turkey red fibres since these conditions are not characteristic of the oiling process. Furthermore, the formation of estolides decreases the overall FFA content, meaning there are fewer (but also larger and potentially more sterically hindered) molecules

¹⁹⁵ Subrahmanyam and Achaya, "Structure and Surfactance-Evaluation of Ricinoleyl Alcohol."

¹⁹⁶ Nawaby, Kruus, and Dabek-Zlotorzynska, "Determination of Anionic Surfactant Turkey Red Oil by Capillary Electrophoresis with Direct UV Detection."

¹⁹⁷ Storey, The Thames and Hudson Manual of Dyes and Fabrics, 89.

¹⁹⁸ Achaya, "Chemical Derivatives of Castor Oil," 758.

¹⁹⁹ Hurst, *Textile Soaps and Oils*, 149.

²⁰⁰ Isbell, "Chemistry and Physical Properties of Estolides."

²⁰¹ Hawke and Kohll, "The Auto-Reactions of Ricinoleic Acid Part I. Reactions at 180° C, 147° C, 122.3° C and Room Temperature."
available to bond to the cellulose. Estolides are a product of ageing, forming slowly at lower temperatures (they are typically produced under much harsher conditions²⁰²) and are discussed here as an indicator of the sample age for some of the historical Turkey red oils.

The discussion shows Turkey red oil is a complex mixture of fatty acids and glycerides, some with a sulfate ester, and that the composition varies based on the reaction conditions. The 'active' ingredient in the oil, fatty acids, determined its usefulness to a Turkey red dyer. In this research, ¹H and ¹³C NMR are used to analyse samples of Turkey red oil to determine its composition and fatty acid content.

2.7 Historical research on the role of the oil

The role of the oil in Turkey red dyeing has been of interest to dyers and chemists since chemistry emerged as a field in the 18th c. Various hypotheses were proposed and sometimes subject to analysis, evolving from more 'magical' explanations of animalisation toward modern chemical principles. This section discusses these ideas and previous research on the topic.

Animalisation, the earliest theory, was the idea that cotton fibres could be treated to become more like animal fibres.^{203,204} The thought behind this was that wool and silk, both which dye more readily than cotton,²⁰⁵ do so because they are animal products. By applying oil or blood, glue, and other ingredients of animal origin,²⁰⁶ the cotton attracted dye more like wool than untreated cotton.²⁰⁷ The 'animal' fibres, wool and silk, are protein fibres that have a different chemistry than 'vegetable' fibres like cotton and linen, which are

²⁰² Isbell, Kleiman, and Plattner, "Acid-Catalyzed Condensation of Oleic Acid Into Estolides and Polyestolides."

²⁰³ Cooper, A Practical Treatise on Dyeing, and Callicoe Printing: Exhibiting the Processes in the French, German, English, and American Practice of Fixing Colours on Woollen, Cotton, Silk, and Linen, 287.

²⁰⁴ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 269.

²⁰⁵ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 18.

²⁰⁶ Pallas, "II. the Genuine Oriental Process for Giving to Cotton Yarn or Stuff the Fast or Ingrained Colour, Known by the Name of Turkey Red, as Practised at Astracan," 11.

²⁰⁷ Driessen, "Étude sur le rouge turc, ancien procédé," 178.

cellulosic. Wool has an amorphous structure, and silk is semi-irregular, but cellulose has a crystalline form whose increased rigidity makes it more resistant to dyeing. Since the cellulose would not be converted to protein by this treatment, the idea of 'animalisation' is better described as a treatment that makes cellulose fibres dye more like protein fibres.²⁰⁸

The oil was also thought to have a varnishing effect on the fibres, forming a protective coating.^{209,210} Turkey red was said to have a lustre,²¹¹ so although not a varnish in the hard, lacquered sense, the hydrophobic nature of the fatty acid chain may create a protective barrier on the fibre that improved its finish. In the 1960s, Kiel and Heertjes conducted some of the only modern analytical work on Turkey red as part of a study of alizarin lake complexes and concluded the oil functioned as a water-repellent barrier, based on the results of a dry sulfuric acid test on historical Turkey red samples removed from copies of dyeing manuals by Dépierre (1892), Persoz (1846), and Schützenberger (1870).²¹² Their destructive analysis did not reveal the nature of the bonds.

The idea that the oil helped attract more aluminium^{213,214} is consistent with the sequence of the dyeing steps and the reagents present. This also explains why oiled cotton appeared to dye more like animal fibres, because more aluminium resulted in a deeper colour. An 1885 investigation of Turkey red describes a 'fatty alizarate of alumina lake', which did not take the cellulose into account, but was a reasonable explanation for the conventions of the time.

²⁰⁸ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 272.

²⁰⁹ Hummel, *The Dyeing of Textile Fabrics*, 436.

²¹⁰ Niederhäusern, "Rapport sur le travail de M. F. Driessen: 'Etude sur le rouge turc, ancien procédé', et sur le contenu de deux plis cachetés, nos 700 et 1276, déposés pqr le même auteur," 187.

²¹¹ Berthollet and Berthollet, *Elements of the Art of Dyeing and Bleaching* 326.

²¹² Kiel and Heertjes, "Metal Complexes of Alizarin v-Investigations of Alizarin-Dyed Cotton Fabrics," 100.

²¹³ Hummel, *The Dyeing of Textile Fabrics*, 233.

²¹⁴ Niederhäusern, "Rapport sur le travail de M. F. Driessen: 'Etude sur le rouge turc, ancien procédé', et sur le contenu de deux plis cachetés, nos 700 et 1276, déposés pqr le même auteur," 187.

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Figure 2-9 'Fatty alizarate of alumina lake' from Journal of the Society of Dyers and Colourists. $^{\rm 215}$

A lake is a complex of colorant with a metallic oxide,²¹⁶ so a more accurate description would be that the oil anchors more lake to the fibres. The oil does not appear to contribute directly to the colour of Turkey red because both plain and oil-treated cloth before dyeing are white,^{217,218} but after dyeing, plain cloth merely turns pink, while oil-treated cloth dyes to a deep red. Experimental work by Karadag et al. determined the amount of dye bonded to the cotton increases with the number of oil treatments,²¹⁹ supporting this hypothesis. Kiel and Heertjes determined the oil was not part of the lake complex, and did not attempt to explain how the fibre was involved,²²⁰ which this research finally addresses.

By the mid-19th c., chemists hypothesised that the aluminium formed a metal soap complex with the bonded fatty acids,²²¹ but they were unable to identify it on the fibre. Metal soaps form when the carboxylate group of a fatty acid reacts with a metal to form -COOM.²²² A soap is the sodium or potassium salt of a fatty acid, whereas a metal soap has a heavier metal ion.²²³ Aluminium soaps, like those that would form in Turkey red, are insoluble in water, which may contribute to its wash fastness. This would be as aluminium ricinoleate, or

²¹⁵ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 206.

²¹⁶ Oxford University Press, "Lake, N 6."

²¹⁷ Berthollet, *Elements of the Art of Dyeing*, 149.

²¹⁸ Vitalis, Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles, 238.

²¹⁹ Karadag and Dolen, "Re-Examination of Turkey Red," 586.

²²⁰ Kiel and Heertjes, "Metal Complexes of Alizarin v-Investigations of Alizarin-Dyed Cotton Fabrics," 98-100.

²²¹ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 139.

²²² Patel, "Natural Dyes," 414.

²²³ Bossert, "The Metallic Soaps," 10.

aluminium oleate in the 'old' process, since oleic acid is the major component of olive oil.²²⁴



Figure 2-10 Aluminium oleate



Research techniques in the 19th c. could not take into account the cellulose fibres because they lacked the ability to perform *in situ* analysis. Dyers were aware they did not understand how the oil was bonding to the fibres,²²⁵ but predicted that metal soaps were forming based on the results of experiments in solution^{226,227} and that this was the basis of Turkey red.²²⁸ Typically, the fibres were oiled, and then the aluminium was applied. An unusual method from Haussmann combines the two,²²⁹ but this was said to produce unlevel dyeings due to the badly fixed mordant.²³⁰ The poorer quality may be due to fact that aluminium soaps precipitated in the dye bath, rather than adhering to the oil on the cotton fibre, as in the traditional method. The order of steps indicates that the oil bonds to the fibres in such a way that it is still possible to form a metal soap as well, so when the oil bonds to the fibre prior to the addition of aluminium, it does so in a way that leaves the carboxylate group available to react.

²²⁴ Spangenberg, Macko, and Hunziker, "Characterization of Olive Oil by Carbon Isotope Analysis of Individual Fatty Acids: Implications for Authentication."

²²⁵ Hummel, *The Dyeing of Textile Fabrics*, 436.

²²⁶ Noelting and Binder, "Rapport de MM. E. Noelting et F. Binder sur un mémoire de M. Fischli, sur la théorie de la fabrication du rouge d'Andrinople, présenté pour le concour au prix no. III."

²²⁷ Parks, "The Chemistry of Turkey Red Dyeing," 500.

²²⁸ Hummel, *The Dyeing of Textile Fabrics*, 155.

²²⁹ Haussmann, "XLIII. Observations on Maddering; Together with a Simple and Certain Process for Obtaining, with Great Beauty and Fixity, That Colour Known Under the Name of the Turkey or Adrianople Red," 260.

²³⁰ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 212.

The formation of aluminium soap is a logical conclusion given the compounds present, however, until now, there have been no *in situ* analytical results to support this explanation. The experimental work on this topic is presented in Section 6.7.

2.8 Free fatty acids and cellulose

By now the following points have been established— in both 'old' and 'new' processes: 1) the oil bath contains FFAs that 2) adhere to the cellulose fibre and 3) Turkey red exists only on the fibre. This section discusses bonding between the FFAs and cellulose, which is investigated experimentally by the *in situ* analytical work in Chapter 6.

The well-preserved condition of the historical samples indicates no degradation or damage to the cellulose polymer, and the dyeing conditions are not expected to cause any significant changes either. The structure of cellulose is fundamental to the chemistry of Turkey red dyeing. Cellulose, the most abundant naturally occurring organic polymer, is a polysaccharide with the empirical formula $(C_6H_{10}O_5)_n$. It can be more specifically described as a chain of 1,4- β -D-glucan,²³¹ shown below. Each ring is structurally identical, as denoted by the brackets around the glucose monomer in Figure 2-11, though the alternating orientation (e.g. AVAV) in 3-dimensional space is considered a dimer by some sources like Chettra because hydrogen bonding between cellulose hydroxyls is affected by ring orientation. Each ring has three hydroxyl groups, which is where the oil is expected to bond.



Figure 2-11 Structure of cellulose with brackets enclosing D-glucose.

²³¹ Chettra, "Microscopy and Surface Chemical Investigations of Dyed Cellulose Textiles," 12.

Wool and silk, which have fewer hydroxyl groups, cannot undergo these same reactions. Linen is even more crystalline than cellulose, and according to Berthollet required twice as much oiling as cotton,²³² so uptake of oil in Turkey red dyeing is affected by the fibre structure.

The historical literature documents how dyers and chemists were aware some reaction occurs during the oiling process and attempted to explain what was happening. One early explanation of the bonding was oxidation, because the oiled cotton would sometimes, if left carelessly while being dried, spontaneously combust due to the evolved heat,^{233,234,235} a well-known phenomenon for oily materials. Polymerisation is another proposed explanation,²³⁶ but as discussed earlier, estolides cannot form on Turkey red if the carboxyl has bonded to the cellulose. Considering the conditions of the oiling process and the functional groups present, -COOH (fatty acid) and -OH (cellulose), there are two plausible bond formations. A hydroxyl and a carboxyl can condense to form an ester, in this case a fatty acid cellulose ester (FACE).



Figure 2-12 Proposed ester formation between cellulose hydroxyl and fatty acid carboxyl.

FACEs are prepared using microcrystalline cellulose, fatty acids, and organic solvents like pyridine or p-toluenesulfonyl chloride,^{237,238} making them quite

²³² Berthollet and Berthollet, *Elements of the Art of Dyeing and Bleaching*, 337.

²³³ Persoz, Traité théorique et pratique de l'impression des tissus, 333.

²³⁴ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 198.

²³⁵ Schützenberger, *Traité des matières colorantes*, 283.

²³⁶ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 160.

²³⁷ Jandura, Kokta, and Riedl, "Fibrous Long-Chain Organic Acid Cellulose Esters and Their Characterization by Diffuse Reflectance FTIR Spectroscopy, Solid-State CP/MAS."

different from the Turkey red practices. Based on the harsher conditions needed to form the ester bond, it is unlikely this reaction would occur on cotton fibres when oiling for Turkey red. A more likely explanation is the fatty acid adsorbing to the cellulose via hydrogen bonding. The bond between the acid carbonyl and cellulose hydroxyl can form instantly and does not require hydrolysis, unlike ester formation.





This also leaves the carboxyl of the FFA available to attract aluminium. Hydrogen bonds are not as strong as ester bonds, which could explain why excessive washing will remove the oil,²³⁹ and they do not alter the cellulose polymer through hydrolysis.

To investigate the nature of the oil-cellulose bond in Turkey red, samples of oiled calico and replica Turkey red were prepared for *in situ* analysis. These samples evaluate a range of variables in the oiling process and the results are compared to those from historical samples to determine similarity and characterise the complex for the first time ever.

2.9 Preparing the oil baths

In the 'old' process, used exclusively prior to the 1870s, the oil treatment was prepared by making an emulsive mixture of *huile tournante*, soda ley, and often

²³⁸ Freire et al., "Surface Characterization by XPS, Contact Angle Measurements and ToF-SIMS of Cellulose Fibers Partially Esterified with Fatty Acids."

²³⁹ Berthollet, *Elements of the Art of Dyeing*, 162.

ruminant dung,^{240,241} sometimes called 'green liquor'²⁴² or 'gray steep'.²⁴³ Subsequent baths made without dung were called 'white baths'²⁴⁴ and were supposed to look like thick milk with no oil floating on the surface.²⁴⁵ Preparation of the bath depended on the quality of the individual ingredients.²⁴⁶ Directions in some methods suggest a requisite level of familiarity with the process^{247,248,249} based on how materials should look or behave, subjective assessments not always clearly described in the text and difficult for a modern experimenter to make. Papillon, the dyer who helped George Mackintosh found the Scottish Turkey red industry in 1785, included gum arabic, ammonium chloride, and sulfuric acid in his method.²⁵⁰ These unusual ingredients may have been emulsive assistants,²⁵¹ indicating that Papillon may not have been a good dyer or had difficulty practicing in Scotland, and are why Cooper strongly disapproved of Papillon's method for Turkey red.²⁵²

Occasionally the oil bath was heated,^{253,254} which Jenny says accelerates the impregnation of the cotton with oil,²⁵⁵ undoubtedly making the lengthy process

- ²⁴³ "V. Account of the Process Followed by M. Pierre Jacques Papillon for Dyeing Turkey Red."
- ²⁴⁴ Persoz, Traité théorique et pratique de l'impression des tissus, 189.
- ²⁴⁵ Berthollet, Éléments de l'art de la teinture, 153.
- ²⁴⁶ Vitalis, Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles, 120.
- ²⁴⁷ Mémoire contenant le procédé de la teinture du coton rouge-incarnat d'Andrinople sur le coton filé, 1.
- ²⁴⁸ Berthollet, *Elements of the Art of Dyeing*, 147.
- ²⁴⁹ Cooper, A Practical Treatise on Dyeing, and Callicoe Printing: Exhibiting the Processes in the French, German, English, and American Practice of Fixing Colours on Woollen, Cotton, Silk, and Linen, 287.
- ²⁵⁰ "V. Account of the Process Followed by M. Pierre Jacques Papillon for Dyeing Turkey Red."
- ²⁵¹ Jenny, "Mémoire sur la fabrications du rouge d'Andrinople," 760.
- ²⁵² Cooper, A Practical Treatise on Dyeing, and Callicoe Printing: Exhibiting the Processes in the French, German, English, and American Practice of Fixing Colours on Woollen, Cotton, Silk, and Linen, 287.
- ²⁵³ Hummel, *The Dyeing of Textile Fabrics*, 429.
- ²⁵⁴ Henry, "Considerations Relative to the Nature of Wool, Silk, and Cotton, as Objects of the Art of Dying; on the Various Preparations, and Mordants, Requisite for These Different Substances; and on the Nature and Properties of Colouring Matter. Together with Some Observations on the Theory of Dying in General, and Particularly the Turkey Red," 381.

²⁴⁰ Cooper, A Practical Treatise on Dyeing, and Callicoe Printing: Exhibiting the Processes in the French, German, English, and American Practice of Fixing Colours on Woollen, Cotton, Silk, and Linen, 297.

²⁴¹ Schützenberger, *Traité des matières colorantes*, 282.

²⁴² Hummel, *The Dyeing of Textile Fabrics*, 428.

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more efficient. One of the more notorious features of the 'old' process was the use of ruminant dung and, occasionally, intestinal fluid,^{256,257} in the oil bath. Surprisingly, dung is a regular entry in the AOE dyestuffs ledger all the way through its end in 1892,²⁵⁸ indicating the 'old' process may still have been in use, though without production notes this can only be speculation. Several hypotheses on the chemical role of the dung were proposed by dyers and chemists, which are discussed in Section 2.10.1.

In some 'old' process methods, oils baths from previous dyes were recycled because they made the new bath more effective.²⁵⁹ This practice is also documented in the Collin process from the Coats Archive, where the excess oil was pressed out and collected after each application to be re-used in subsequent treatments.²⁶⁰ These practices likely evolved out of economy and were found to improve the efficiency of future baths, probably because FFAs in the old bath would have had an effect similar to adding oleic acid to olive oil and promoting triglyceride hydrolysis. The addition of FFAs, as a pure additive or from the old baths, would promote triglyceride hydrolysis and release FFAs in the new bath. This was the aim of the oil bath—to disperse fatty acids for even and thorough application to the cotton.

The development of water-soluble Turkey red oil made it much simpler to disperse fatty acids in the oil bath, improving the speed and efficiency of the oiling process. This became known as the 'new' method and bought about great savings of cost and time. The baths were made only with water rather than a soda ley²⁶¹ because the oil was water-soluble, decreasing reagents used and preparation time, and animal products like dung and intestinal juice were less used. In Hummel's 'new' process, a cold solution of Turkey red oil diluted with

²⁵⁵ Jenny, "Mémoire sur la fabrications du rouge d'Andrinople," 789.

²⁵⁶ Mémoire contenant le procédé de la teinture du coton rouge-incarnat d'Andrinople sur le coton filé.

²⁵⁷ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 224.

²⁵⁸ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.

²⁵⁹ Persoz, Traité théorique et pratique de l'impression des tissus, 177.

²⁶⁰ Collin, Turkey Red Process for Cotton Yarn. 1/9/3.

²⁶¹ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 600.

water was applied to the fibres.²⁶² Historical sources recommend a bath of roughly 5-10% aq. Turkey red oil,²⁶³ while a modern dyer uses around a 3% solution, which he says is less than what was used historically but gives better results.²⁶⁴ Other modern methods, including a re-creation of Turkey red,²⁶⁵ use undiluted Turkey red oil.²⁶⁶ This indicates that the degree of dilution, which also depends on the water content of the oil, was more a question of efficient reagent use than a precise figure to be followed, but a systematic study is recommended. The conclusion from this review is that the outcome of both oiling processes was the same, and Turkey red from the 'old' and 'new' methods can be reliably compared.

2.10 Oil application to cotton

Pre-treatment of cotton with oil was imperative for Turkey red dyeing and unique to the process. To apply the oil, the cotton was saturated in the bath, the excess liquid removed, and then dried. This is consistent across all methods,^{267,268,269} with slight variations in handling. The technique is often described as 'tramping', an Anglicised form of *tremper*, French for 'to soak, steep, immerse'.²⁷⁰ Occasionally, the cotton was left in the bath for a period rather just saturated,^{271,272} but this practice was less common.

Into the 19th c., Turkey red dyeing was largely done by hand. This meant handling hanks of cotton yarn or 100-lb lengths of calico in and out of baths, soaking wet and laden with oil, then drying the cotton and possibly repeating the

²⁶² Hummel, *The Dyeing of Textile Fabrics*, 443.

²⁶³ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 205.

²⁶⁴ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 117.

²⁶⁵ Karadag and Dolen, "Re-Examination of Turkey Red."

²⁶⁶ Fereday, *Natural Dyes*, 28.

²⁶⁷ Chaptal, L'art de la teinture du coton en rouge, 95.

²⁶⁸ Berthollet and Berthollet, *Elements of the Art of Dyeing and Bleaching*, 328.

²⁶⁹ Hummel, *The Dyeing of Textile Fabrics*, 443.

²⁷⁰ Oxford University Press, "Tramp, v. 1."

²⁷¹ Henry, "Considerations Relative to the Nature of Wool, Silk, and Cotton, as Objects of the Art of Dying; on the Various Preparations, and Mordants, Requisite for These Different Substances; and on the Nature and Properties of Colouring Matter. Together with Some Observations on the Theory of Dying in General, and Particularly the Turkey Red," 381.

²⁷² "V. Account of the Process Followed by M. Pierre Jacques Papillon for Dyeing Turkey Red."

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whole process. Mechanisation of the oiling step in the latter part of the 19th c. greatly simplified the work and by the 1880s it was almost completely mechanised.²⁷³ Hummel describes a tramping and wringing machine developed by Messrs. Duncan Stewart and Co. of Glasgow and includes many exceptional technical drawings.²⁷⁴ Descriptions of machinery are found in the Coats Archive documents as well.^{275,276,277}



Figure 2-14 Tramping machine for oiling yarn from Hummel.²⁷⁸

To ensure a sufficient quantity of adsorbed fatty acids,²⁷⁹ the oiling step was repeated multiple times in the 'old' process^{280,281} due to the lower fatty acid content of *huile tournante*. More repetitions were required in the winter than in the summer,²⁸² so the process was subject to temperature and humidity, which in

²⁷³ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 205.

²⁷⁴ Hummel, *The Dyeing of Textile Fabrics*, 429.

²⁷⁵ Tannahill, *Turkey Red Dyeing*. 1/9/3.

²⁷⁶ Straugh, Recipe From Mr Straugh. 1/9/3.

²⁷⁷ Collin, Turkey Red Process for Cotton Yarn. 1/9/3.

²⁷⁸ Hummel, *The Dyeing of Textile Fabrics*, 430.

²⁷⁹ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 588.

²⁸⁰ Ure, A Dictionary of Arts, Manufactures, and Mines, 793.

²⁸¹ Persoz, *Traité théorique et pratique de l'impression des tissus*, 189.

²⁸² Verbong, "Turksrood," 275.

Scotland could sometimes mean a suspension of Turkey red production.²⁸³ Experience was required to know when the cotton was sufficiently oiled²⁸⁴ because the work was variable, depending on the cloth, the oil, and the season.²⁸⁵ Methods for the 'new' process do not repeat the oil application,²⁸⁶ or repeat it once;²⁸⁷ a modern text recommends four to six applications for *huile tournante* and one to two for Turkey red oil.²⁸⁸ There is no test or visual cue for determining when the cloth is sufficiently oiled other than to continue dyeing it to see what happens. Years of practice and observation allow an experienced dyer to judge when this occurs, but the literature provides no guidance for the reader. The analytical work on the oil and cotton may help find a way to experimentally determine the quantity of oil on the fibres.

An alternative technique used to apply oil for dyeing Turkey red, the Steiner Process, does not use a solution of fatty acids like the *huile tournante* and Turkey red oil processes do. It was developed in the mid-19th c. and practiced in Manchester and Scotland, and involved baths of hot, not rancid olive oil to prepare the cotton.^{289,290} The rest of the process was much the same as the others. The colour was considered to be beautiful and fast,²⁹¹ and samples by the Steiner process in dyeing manuals by Dépierre and Crookes are as lovely as samples from the other processes. It could not be applied to yarn due to difficulties handling the fibres in hot oil.²⁹² One proposed explanation of its chemistry is that the head rapidly oxidised the fats,²⁹³ but re-creation of the process is difficult due to a lack of documentation, perhaps because Steiner was

²⁸³ "Factories Inquiry Commission: Supplementary Report of the Central Board of H. Maj. Commissioners Appointed to Collect Information in the Manufacturing Districts, as to the Employment of Children in Factories, and as to the Propriety and Means of Curtailing the Hours of Their Labour. Part II.," 142.

²⁸⁴ Jenny, "Mémoire sur la fabrications du rouge d'Andrinople," 788.

²⁸⁵ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 277.

²⁸⁶ Hummel, *The Dyeing of Textile Fabrics*, 443.

²⁸⁷ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 600.

²⁸⁸ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 118.

²⁸⁹ Jacqué et al., Andrinople: Le rouge magnifique, 34.

²⁹⁰ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 501.

²⁹¹ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 596.

²⁹² Driessen, "Étude sur le rouge turc, ancien procédé," 169.

²⁹³ Jacqué et al., Andrinople: Le rouge magnifique, 48.

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more successful than others at guarding his industrial practices. The original records from Steiner describing his process were lost in a fire at an industrial archive in 1950,²⁹⁴ and documentary evidence of the process involves purposebuilt machinery no longer extant. For these reasons, it is not re-created in this project but the process is mentioned because a Steiner sample of historical Turkey red²⁹⁵ is included in the *in situ* analysis of Turkey red.

All the excess oil not bound to the fibre must be removed before the aluminium is applied²⁹⁶ or the quality of the final product is affected. Excess oil leaves the fibres greasy and not rub fast,²⁹⁷ because the loose oil would attract and transfer colourant. Oil that was not washed off in advance could disperse in the next bath and diminish the quality of the textile²⁹⁸ by competing with the oils bound to the fibre and forming complexes in solution. This is consistent with the earlier discussion of the one-step oil and alum bath that produced inferior dyeings. Removing the excess oil in the 'old' process, often called 'salting',^{299,300} involved repeated washings in a weak soda ley, like the one used to make the oil bath.^{301,302,303} The ley forms an emulsion with the oil on the fibres, in a reversal of the oil application, initially removing unbound oil. Care had to be taken not to overdo this step and remove the bound FFAs.³⁰⁴ After the salting, the cotton was rinsed well in water to remove any salts.^{305,306} In the 'new' process, far less work was needed due to the water-solubility of Turkey red oil and the difference in triglyceride content compared to *huile tournante*. Hummel's process does not

³⁰² Chaptal, L'art de la teinture du coton en rouge, 95.

²⁹⁴ ibid., 52.

²⁹⁵ Crookes, A Practical Handbook of Dyeing and Calico-Printing, 327.

²⁹⁶ Hummel, *The Dyeing of Textile Fabrics*, 437.

²⁹⁷ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 116.

²⁹⁸ Carruthers, "A New Process of Dyeing Turkey Red," 124.

²⁹⁹ Vitalis, Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles, 238.

³⁰⁰ Schützenberger, *Traité des matières colorantes*, 288.

³⁰¹ Haussmann, "XLIII. Observations on Maddering; Together with a Simple and Certain Process for Obtaining, with Great Beauty and Fixity, That Colour Known Under the Name of the Turkey or Adrianople Red," 261.

³⁰³ Berthollet and Berthollet, *Elements of the Art of Dyeing and Bleaching*, 329.

³⁰⁴ Hummel, *The Dyeing of Textile Fabrics*, 439.

³⁰⁵ Chaptal, *L'art de la teinture du coton en rouge*, 96.

³⁰⁶ Mémoire contenant le procédé de la teinture du coton rouge-incarnat d'Andrinople sur le coton filé.

include any washing, but applies a steaming treatment instead.³⁰⁷ In general, to remove excess oil from cotton prepared with Turkey red oil, only washing with warm water was required.³⁰⁸

In both processes, the cotton was dried after each application of oil, one of the main reasons the process was so lengthy. With the number of repetitions required by the 'old' process, this made Turkey red dyeing in Scotland seasonal work prior to the invention of indoor drying,³⁰⁹ which is not difficult to imagine given the challenge of drying large quantities of cotton in the Scottish climate. Drying, in fact, takes place between nearly every step in a Turkey red process. The fibres were usually hung to dry on poles or sticks when dried.^{310,311} By the early 19th c., drying in ovens or stoves became more common.



Figure 2-15 Cross-section of stove for Turkey red from Hummel³¹²

Temperatures ranged from 50 to 70 °C^{313,314,315} and the cotton was generally left for 12-24 hours,³¹⁶ although Hummel uses only one to two.³¹⁷ Some believed air

³⁰⁷ Hummel, *The Dyeing of Textile Fabrics*, 443.

³⁰⁸ Carruthers, "A New Process of Dyeing Turkey Red," 126.

³⁰⁹ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline," 499.

³¹⁰ Pallas, "II. the Genuine Oriental Process for Giving to Cotton Yarn or Stuff the Fast or Ingrained Colour, Known by the Name of Turkey Red, as Practised at Astracan."

³¹¹ Vitalis, Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles, 236.

³¹² Hummel, *The Dyeing of Textile Fabrics*, 441.

³¹³ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 205.

³¹⁴ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 593.

³¹⁵ Hummel, *The Dyeing of Textile Fabrics*, 431.

³¹⁶ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 117.

³¹⁷ Hummel, *The Dyeing of Textile Fabrics*, 443.

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drying still yielded a better, more fast textile,^{318,319} but opinions were divided and others though heat drying was necessary, especially in cold or damp weather.³²⁰ Those who promoted oven drying said the hot, dry fibres readily absorbed more liquid and encouraged the adsorption of oil,³²¹ pushing the oil deeper into the fibre.³²² The use of heat increased the risk of spontaneous combustion in the oiled cloth, however, which motivated dyers to build their drying facilities some distance from the dye works.³²³ There is no qualitative assessment of air-dried and oven-dried Turkey red, so the effect on fastness remains unknown, but the experimental work in this research assesses the effect of heat as a variable in the oiling process.

The application of pressurised steam, which was developed in England and used in wool dyeing³²⁴ and calico printing,³²⁵ started to be applied to Turkey red in the 1880s. It was the only instance of steam used in calico dyeing.³²⁶ Directions specified steaming at 2-8 psi for around 60-90 minutes,^{327,328} though the Tannahill document in the Coats Archive uses considerably higher pressures of 2 atmospheres,³²⁹ about 30 psi.

³²² Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 192.

³¹⁸ Henry, "Considerations Relative to the Nature of Wool, Silk, and Cotton, as Objects of the Art of Dying; on the Various Preparations, and Mordants, Requisite for These Different Substances; and on the Nature and Properties of Colouring Matter. Together with Some Observations on the Theory of Dying in General, and Particularly the Turkey Red," 381.

³¹⁹ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 593.

³²⁰ Chateau, "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour," 137.

³²¹ Jenny, "Mémoire sur la fabrications du rouge d'Andrinople," 781.

³²³ Sandberg, *The Red Dyes*, 106.

³²⁴ Schaefer, "The History of Turkey Red Dyeing," 1413.

³²⁵ O'Neill, Chemistry of Calico Printing, Dyeing, and Bleaching, 164-165.

³²⁶ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 702.

³²⁷ Hummel, *The Dyeing of Textile Fabrics*, 443.

³²⁸ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 600.

³²⁹ Tannahill, *Turkey Red Dyeing*. 1/9/3.



Figure 2-16 Steaming chamber for yarn from Hummel.³³⁰

Steaming was also thought to help the oil penetrate the fibre,³³¹ subjecting the cotton to temperatures above 100 °C because of the elevated pressure. Condensed steam on the fibres may have gently washed them or made the bonding conditions more favourable. The effect of steam on oil uptake is investigated briefly in this research.

2.10.1 Ruminant dung, bullock's blood, and substitutes

Nothing captures the imagination quite like the historical use of ruminant dung and blood in Turkey red dyeing. Although these substances were plentiful and cheap, they would have been no more pleasant to work with in the past as they are imagined to be now. The conclusion from the review of Turkey red methods in this research was that these 'animal' substances probably benefitted the dyeing process as auxiliaries but, based on inconsistent use, were not required for a successful dyeing. The chemistry of their role in the dyeing process has not been determined by modern analysis, and this project does not attempt to do so, but their notoriety and association with the process, and the historical interest in their purpose, merit a brief discussion.

³³⁰ Hummel, *The Dyeing of Textile Fabrics*, 445.

³³¹ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 243.

In the 'old' process, dyers often included sheep or cow dung in the oil bath and blood in the dye bath.^{332,333,334} It is unclear which process was followed for most of the AOE dyestuffs ledger, but it records both reagents still in regular use until it ends in 1892.³³⁵ They are neither included in every Turkey red process nor unique to it; in fact, they were also commonly used in the printing of calico and dyeing of other colours.^{336,337,338} Cooper writes that although animal substances were often left out, he believed they produced deeper and more fast colour, and because of their low cost there was no reason to omit them.³³⁹



Figure 2-17 Dung used for Turkey red dyeing at three works in the Archibald Orr Ewing firm, 1873-1892.

Cloth dyeing was practiced at Levenbank, while yarn dyeing was done at Milton and Dillichip. Data from *Turkey Red Dyeing calculation book AOE Lennoxbank*, University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/4/1.

Printers sometimes kept herds of cattle to maintain a supply of dung,

although it was often inconvenient for them.³⁴⁰ Figure 2-17 shows, on average,

consistent use of dung for dyeing cloth and yarn, with it eventually being disused

³³² "V. Account of the Process Followed by M. Pierre Jacques Papillon for Dyeing Turkey Red."

- ³³⁵ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.
- ³³⁶ Hummel, *The Dyeing of Textile Fabrics*, 238.
- ³³⁷ Duerr and Turnbull, *Bleaching and Calico-Printing* : a *Practical Manual*, 39.
- ³³⁸ O'Neill, Chemistry of Calico Printing, Dyeing, and Bleaching, 164.
- ³³⁹ Cooper, A Practical Treatise on Dyeing, and Callicoe Printing: Exhibiting the Processes in the French, German, English, and American Practice of Fixing Colours on Woollen, Cotton, Silk, and Linen, 285.

³³³ Hummel, *The Dyeing of Textile Fabrics*, 433.

³³⁴ Vitalis, Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles, 238-244.

³⁴⁰ Crookes, Dyeing and Tissue Printing, 244.

for yarn dyeing in the late-1880s. This is consistent with increased use of Turkey red oil in yarn dyeing (see Figure 2-3) and continued use of olive oil, characteristic of the 'old' process, for cloth. Bullock's blood is added to the dye bath in most recipes, and sheep's blood was used as well.³⁴¹ In the mid-1860s, the Dalquhurn Works of William Stirling & Sons used 130,000 gallons of bullock's blood annually.³⁴² Later in the 19th c., the blood was sometimes replaced with powdered blood albumen.^{343,344} The AOE dyestuffs ledger records the consistent use of blood in Turkey red dyeing, and the transition to blood albumen in their yarn dyeing operation from the late 1870s to the late 1880s. Cloth dyeing at Levenbank continued to use blood and did not adopt albumen.³⁴⁵





Data from Turkey Red Dyeing calculation book AOE Lennoxbank, University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/4/1.

³⁴¹ Berthollet, *Elements of the Art of Dyeing*, 154.

³⁴² Bremner, *The Industries of Scotland*, 301.

³⁴³ O'Neill, Chemistry of Calico Printing, Dyeing, and Bleaching, 166.

³⁴⁴ Hummel, *The Dyeing of Textile Fabrics*, 437.

³⁴⁵ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.



Figure 2-19 Blood albumen used for dyeing Turkey red yarn at Milton and Dillichip, 1873-1892. Data from *Turkey Red Dyeing calculation book AOE Lennoxbank*, University of Glasgow

Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/4/1.

It is unknown when or why these ingredients began to be used in textile dyeing, but like role of the oil, an early explanation for their purpose was animalisation.³⁴⁶ The original inclusion of blood has been ascribed to belief in its magical properties and potential to improve the red colour.³⁴⁷ By the mid-1800s chemists recognised the action of blood and dung as chelating agents for unbound mordant to prevent it from spreading to undesired areas on calico prints and to keep it from forming lake complexes in the dye bath.^{348,349,350} Once this was understood, the dung was replaced by chemical substitutes called 'dunging salts' like arsenates, silicates, and phosphates.³⁵¹ Compounds like phosphates are ingested by livestock and largely excreted in their manure,³⁵² and when complexed with aluminium they form water insoluble compounds that precipitate out of a dye bath. The transition to chemical substitutes is seen in Hummel's 'fixing' step, where the cotton, after being treated with alum, is soaked in a sodium phosphate solution.³⁵³ To prepare blood for dyeing, it was

³⁴⁶ Vitalis, Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles, 236.

³⁴⁷ Schaefer, "The History of Turkey Red Dyeing," 1411.

³⁴⁸ Persoz, Traité théorique et pratique de l'impression des tissus, 486.

³⁴⁹ O'Neill, Chemistry of Calico Printing, Dyeing, and Bleaching, 311.

³⁵⁰ Berthollet and Berthollet, *Elements of the Art of Dyeing and Bleaching*, 461.

³⁵¹ Crookes, A Practical Handbook of Dyeing and Calico-Printing, 297.

³⁵² Barnett, "Phosphorus Forms in Animal Manure."

³⁵³ Hummel, *The Dyeing of Textile Fabrics*, 443.

collected and stirred with twigs to remove the fibrin, strained of clots, and diluted with water, noxious work that stank and posed a public health risk. The ability to extract blood albumen, the desired component, was an improvement for the Turkey red dyers but still a fairly unpleasant process itself.³⁵⁴

According to Tarrant, using dunging salts makes the product Alizarin Red rather than Turkey red,³⁵⁵ but this is not consistent with the historical literature on the process. The conclusion from this research is that the use of dung, blood, and their respective chemical substitutes improved the quality of the overall dyeing by adding a measure of control, but that they are not fundamental to the Turkey red process.

2.10.2 Aluminium

In a traditional Turkey red method, aluminium is applied to the cotton after it is prepared with oil. This was often accomplished with a solution of alum (potassium aluminium sulfate); the best had minimal iron content and came from pits near Rome.^{356,357} The alum was dissolved and mixed with a carbonate solution (a ley) to make the bath basic.^{358,359} Alternatively, aluminium acetate was also used, and is supposed to be better for cellulosic fibres.³⁶⁰ This was often obtained by making 'red liquor', where a mixture of alum, lead acetate, and ley solutions were combined to make aqueous aluminium acetate with precipitated lead sulfate.³⁶¹ The purpose of both of these baths was to imbue the oiled calico with aluminium ions, which form the basis for the colour complex in the dyeing step. This research does not attempt to investigate the differences between alum and aluminium acetate, but the difference may have a bearing on the cost

³⁵⁴ "12th Annual Report of the Medical Officer of the Privy Council."

³⁵⁵ Tarrant, "The Turkey Red Dyeing Industry in the Vale of Leven," 87.

³⁵⁶ Mémoire contenant le procédé de la teinture du coton rouge-incarnat d'Andrinople sur le coton filé.

³⁵⁷ Schaefer, "The History of Turkey Red Dyeing," 1407.

³⁵⁸ Henry, "Considerations Relative to the Nature of Wool, Silk, and Cotton, as Objects of the Art of Dying; on the Various Preparations, and Mordants, Requisite for These Different Substances; and on the Nature and Properties of Colouring Matter. Together with Some Observations on the Theory of Dying in General, and Particularly the Turkey Red," 385.

³⁵⁹ Hummel, *The Dyeing of Textile Fabrics*, 443.

³⁶⁰ Liles, The Art and Craft of Natural Dyeing: Traditional Recipes for Modern Use, 21.

³⁶¹ Napier, A Manual of Dyeing Receipts for General Use, 15.

and efficiency of the process, and possibly the quality of the product. The recreation work uses alum since it was a common and acceptable reagent for Turkey red dyeing.

2.11 Summary

After the decline of the Turkey red industry, persistent questions remained, from dyers and chemists alike, about the chemistry behind the oiling of cotton for Turkey red, a treatment fundamental to its dyeing and unique to the process. These occupy a large portion of the literature on the process and have, until now, been unanswered. This chapter discusses the oiling processes in the Turkey red methods reviewed and previous research on its chemistry to help answer the research question for this project on the role of the oil. The conclusions are that despite variations, the 'old' and 'new' processes were chemically similar and that the 'new' process, by using Turkey red oil, was a more efficient incarnation of the process that used *huile tournante*.

Historical research on the oil in Turkey red shows dyers and chemists understood the purpose of the treatment was to impart fatty acids to the cellulose fibres, but they had no way to characterise the bond *in situ* without the analytical instruments available today. They could not quantify the effect of the oil on the textile or its exact role, but with their knowledge and experiments determined it formed a protective coating of some kind and increased the attraction of aluminium to the fibres, improving the colour. This research aims to determine the composition of Turkey red oil using modern analytical techniques and to understand the chemistry of the oil in the overall process. The experimental work includes re-creating Turkey red oil following a historical method and subsequent analysis of replica, commercial, and historical samples of Turkey red oil in Chapter 5. In Chapter 6, oiled calico and Turkey red are analysed *in situ* to characterise the fatty acid-cellulose bonds and identify how the aluminium is affixed to finally answer what the part of the oil is.

3 Dyes used in 19th c. Scottish Turkey red

During the early 1870s, in addition to technical developments in the oiling process, Turkey red was at the forefront of the textile industry's transition from natural to synthetic dye sources. It is an unusual case for being such a large consumer of a single dyestuff, which traditionally had been sourced from the madder root—for an idea of the scale, in 1859, the Dalguhurn works alone consumed enough madder to dye 18 million yards of Turkey red cloth and 800,000 pounds of yarn.¹ The successful commercial synthesis of alizarin, the major component of *Rubia tinctorum* L., in 1869 made it the first naturally occurring dye to be replicated,² bringing about a rapid collapse of the madder industry.³ The significantly higher concentration of dye in synthetic alizarin and the absence of woody impurities that made up the bulk of ground madder appealed to dyers, though they had already started to address these drawbacks from the mid-1800s by using a concentrated madder product called garancine. Entries in the AOE dyestuffs ledger show the transition, from 1873-1892, between madder, garancine, and synthetic alizarin, which the firm appears to have readily applied in favour of madder, though they continued to use garancine until the mid-1880s.⁴ Comparison between the literature, which implies a rapid and complete transition to synthetic alizarin, and firsthand material from the ledger entries showing actual industrial practices, provides a more complete picture of how Turkey red dyers practiced their craft.

Dyestuffs identification is an important technique in the care and display of historical textiles, whose condition may swiftly deteriorate under light exposure if certain compounds are present. Some compounds may also serve as chemical markers that indicate where or when a textile was dyed. Research on natural dyes is a well-established field and many studies have characterised compounds found in madder roots, ^{5,6,7,8,9} and on textiles dyed with madder.^{10,11,12} The review

¹ Peel, "Turkey Red Dyeing in Scotland Its Heyday and Decline."

² Fieser, "The Discovery of Synthetic Alizarin."

³ Chenciner, *Madder Red: a History of Luxury and Trade.*

⁴ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.

⁵ Derksen et al., "High-Performance Liquid Chromatographic Method for the Analysis of Anthraquinone Glycosides and Aglycones in Madder Root (Rubia Tinctorum L.)."

⁶ Chenciner, *Madder Red: a History of Luxury and Trade*; Bányai et al., "HPLC Analysis of Alizarin and Purpurin Produced by Rubia Tinctorum L. Hairy Root Cultures."

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for this research did not find any published analyses or identifications of dyes on Turkey red, a significant gap this project aims to redress. Furthermore, only recently has research begun on the characterisation of late-19th c. synthetic dyes,^{13,14} a significant development in the field of organic chemistry that revolutionised the textile industry, and no study of early synthetic alizarin has yet been published. Madder roots contain a mixture of hydroxyanthraquinone dyes in addition to alizarin (1,2-di-hydroxyanthraquinone), like purpurin and pseudopurpurin (1,2,4-tri-hydroxyanthraquinone and 1,2,4-trihydroxyanthraquinone-3-carboxylic acid, respectively). Late-19th c. chemists found this was also the case with synthetic alizarin, though they initially anticipated a pure product. Synthetic alizarin was soon found to contain hydroxyanthraquinone dyes that were not found in madder,¹⁵ like anthrapurpuin and flavopurpurin (1,2,7-tri-hydroxyanthraquinone and 1,2,6-trihydroxyanthraquinone), so while both dye sources yielded Turkey red, their chemical profiles varied.

This chapter discusses the use of madder, *garancine*, and synthetic alizarin in Turkey red dyeing, how the latter two were manufactured, and which anthraquinone dyes may be found on textiles. The information is used to answer the question for this project regarding the identification of dye sources and whether this can be used to determine object provenance or age through the application of conservation-based dyes analysis on historical Turkey red in Chapter 7 and an attempted re-creation of 19th c. synthetic alizarin in Chapter

- ¹² Hofmann-de Keijzer and van Bommel, "TLC and HPLC Analysis of Red and Violet Cotton Yarns of Indonesian Textiles."
- ¹³ van Bommel et al., "High-Performance Liquid Chromatography and Non-Destructive Three-Dimensional Fluorescence Analysis of Early Synthetic Dyes."
- ¹⁴ Liu et al., "Identification of Early Synthetic Dyes in Historical Chinese Textiles of the Late Nineteenth Century by High-Performance Liquid Chromatography Coupled with Diode Array Detection and Mass Spectrometry."

¹⁵ Perkin, "XVI.-on Artificial Alizarin."

⁷ Schaefer, "The Cultivation of Madder;" Golcu et al., "Isolation of Colour Components From Rubia Tinctorum L.."

⁸ Henderson, Rayner, and Blackburn, "Isolation and Extraction of Lucidin Primeveroside From *Rubia Tinctorum* L. and Crystal Structure Elucidation."

⁹ Mouri and Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC."

¹⁰ Ahn and Obendorf, "Dyes on Archaeological Textiles: Analyzing Alizarin and Its Degradation Products."

¹¹ Farizadeh et al., "Kinetic Studies of Adsorption of Madder on Wool Using Various Models."

4. Although this project does not perform any light fastness tests, identifying which dyes are found on historical Turkey red enables future studies to determine the robustness of these hydroxyanthraquinones for improved conservation practices.

To clarify a point of terminology often used ambiguously in the historical literature, "synthetic alizarin" is used here to refer to the synthetic dye product that was a mixture of hydroxyanthraquinone dyes. It was frequently called "artificial alizarin" or just "alizarin" as well, but here alizarin refers only to the actual alizarin molecule, 1,2-di-hydroxyanthraquinone.



Figure 3-1 Alizarin, or 1,2-di-hydroxyanthraquinone.

Additionally, for a long time it was alternately spelled *alizarine* at the discretion of the author¹⁶ (*purpurine*/purpurin is seen as well¹⁷), but this is only preserved in direct quotations.

3.1 Colour

This section briefly explains colour theory in order to provide an understanding of how the structure of a molecule affects the perceived colour and the separation of mixed dyes. Coloured molecules have a series of alternating single and double bonds called a conjugated system in which electrons in the pi orbitals of double bonds are shared around the molecule across bonds. The pi electrons are excited by absorbing specific energies from visible light, relating to different wavelengths depending on the number and arrangement of double bonds in the molecule.¹⁸ Although many anthraquinone isomers exist, the base

¹⁸ Allen, *Colour Chemistry*.

¹⁶ Travis, *The Rainbow Makers*.

¹⁷ Roscoe, On the Artificial Production of Alizarine, the Colouring Principle of Madder.

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structure of anthraquinone dyes is 9,10-dioxoanthracene (Figure 3-2), which is commonly called anthraquinone and referred to as such in this work. Its parent molecule, anthracene, has a conjugated system from its three adjoining benzene rings. Adding two central carbonyls alters the conjugated electron system, resulting in a pale yellow colour.



Figure 3-2 Anthracene (left) and anthraquinone structures with numbered locations for possible substitution of functional groups.

Colour is influenced by the length of the conjugated double bond system and the presence of electron-donating groups like hydroxyls, carbonyls, amines, and sulfonic acids.^{19,20,21} Madder dyes can be described collectively as hydroxyanthraquinones since -OH is by far the most common substituent; a few have -COOH or -CH₃ groups as well. Hydroxyls are effective electron donors and major colour contributors that have a strong absorption band in the visible light spectrum.²² This means hydroxyanthraquinone dyes with similar structures nonetheless have distinct colours based on the number and positions of the hydroxyls. In chromatography, these hydroxyls affect how the molecule interacts with the mobile and stationary phases, separating a mixture into individual components that, thanks to their colour, can be detected using UV and visible light.

Purpurin, flavopurpurin, and anthrapurpurin are all isomers of trihydroxyanthraquinone, but the differences in -OH position yields subtly different hues and separate retention times in chromatography, making it possible for this research to separate and identify dyes from Turkey red textiles and early

¹⁹ Hofenk de Graff, van Bommel, and Roelofs, *The Colourful Past*.

²⁰ Griffiths, Colour and Constitution of Organic Molecules.

²¹ Allen, *Colour Chemistry*.

²² Gordon and Gregory, Organic Chemistry in Colour.

synthetic alizarin samples. Anthraquinone dyes are polygenetic, meaning they produce different colours depending on the mordant used,²³ in the case of Turkey red complexing with aluminium and calcium to produce the signature bright red. As shown in the figure below, they are also pH sensitive and have applications as indicator compounds.



Figure 3-3 Solutions of alizarin, anthrapurpurin, and purpurin in methanol (from left)



Figure 3-4 The same dyes diluted with aqueous sodium carbonate solution

3.2 Madder

Madder root has been used to dye textiles since the ancient $era^{24,25,26}$ and, prior to the development of synthetic alizarin, was one of the most important dye sources available. By the time Turkey red dyeing was established in Western Europe in the mid-18th c., dyers relied on the cultivated *R. tinctorum* for its

²³ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2^{me} partie, L'alizarine artificielle et ses dérivés.

²⁴ Bhardwaj and Jain, "Indian Dyes and Dyeing Industry During 18th-19th Century."

²⁵ Hofenk de Graff, van Bommel, and Roelofs, *The Colourful Past*.

²⁶ Travis, "Between Broken Root and Artificial Alizarin: Textile Arts and Manufactures of Madder."

increased colouring capacity. The amount imported by the United Kingdom every year valued about £1,000,000²⁷ (about £45 million in 2005 currency²⁸). Out of all the dyes in madder, alizarin was the most abundant in *R*. *tinctorum* and historically the most significant.

3.2.1 Madder use in Europe

R. tinctorum originated in the Middle East and Mediterranean Basin and has since been naturalised in Europe, China, Japan, Malaysia, Mexico, South America, Africa, and the west coast of North America.²⁹ Dyer's madder, as it was also called, was a cultivar bred over centuries to produce the best red colour with the most dye.³⁰ It has a higher concentration by weight of dye molecules, though R. *cordifolia* and R. *peregrina* have a wider variety of colouring molecules.³¹ Farming massive quantities of dried and ground madder root required by the Turkey red industry was possibly even more labour-intensive than Turkey red itself, since quality roots were obtained by careful cultivation over a period of two to three years, followed by harvesting and meticulous drying, fermentation, and milling.³²

²⁷ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar."

²⁸ "Currency Converter."

²⁹ Cardon, *Le monde des teintures naturelles*.

³⁰ Schaefer, "The Cultivation of Madder."

³¹ Chenciner, Madder Red: a History of Luxury and Trade.

³² Schaefer, "The Cultivation of Madder."



Figure 3-5 *Rubia tinctorum* at the Botanischer Garten KIT, Karlsruhe, Germany. Image © H. Zell, Wikimedia Commons

In the 16th and 17th c., before Turkey red was dyed in Europe, the climate and soil of the Dutch islands of Zeeland yielded the best madder in Europe.³³ Dutch madder was thought to be of the highest quality, but French production was strong because the government promoted the industry,³⁴ which expanded there throughout the 19th c.³⁵ Madder was also grown on the coasts of the Caspian Sea,³⁶ in Italy, Turkey, and India, and Britain, though not very well in the latter.³⁷ More information on the history and cultivation of madder can be found in Chenciner,³⁸ Schaefer³⁹, and Travis.^{40,41}

³³ ibid.

³⁴ Mellor and Cardwell, "Dyes and Dyeing 1775-1860," 266.

³⁵ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 576.

³⁶ Pallas, "II. the Genuine Oriental Process for Giving to Cotton Yarn or Stuff the Fast or Ingrained Colour, Known by the Name of Turkey Red, as Practised at Astracan," 5.

³⁷ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar," 573.

³⁸ Chenciner, *Madder Red: a History of Luxury and Trade.*

³⁹ Schaefer, "The Cultivation of Madder."

⁴⁰ Travis, "Between Broken Root and Artificial Alizarin: Textile Arts and Manufactures of Madder."

⁴¹ Travis et al., "Technology in Decline: a Search for Useful Concepts."

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Sketch-map showing the location of the species Rubia, of madder dyeing, and of Turkey red dyeing. By Gustav Schaefer.





Figure 3-6 Map of historical global *Rubia* cultivation and use Map by Gustav Schaefer. Originally published in *CIBA Review*.⁴²

Britain was the largest consumer of madder in the mid-19th c., its textile industry taking about a third of world export.⁴³ It was in such demand that dyers had to ensure they were not purchasing product adulterated with dirt, ground brick dust, or other plant matter. The practice was common enough that chemists were urged to find a way to test for foreign substances.⁴⁴ The need to import vast quantities of dyestuff, the price, and the risk of purchasing adulterated madder no doubt fuelled the desire among dyers for an alternative product.

The development of synthetic alizarin heralded the end of widespread madder cultivation. In 1868, the year before alizarin was commercially produced, a hundredweight of madder cost thirty shillings and would drop to eight shillings within a few years.⁴⁵ French madder farmers suffered as profits

⁴² Schaefer, "The Cultivation of Madder," 1398.

⁴³ Chenciner, *Madder Red: a History of Luxury and Trade*, 83.

⁴⁴ Travis, "Between Broken Root and Artificial Alizarin: Textile Arts and Manufactures of Madder," 10.

⁴⁵ Schaefer, "The Cultivation of Madder," 1406.

collapsed, fields were unsown, and peasants starved, and although they protested, the change was irreversible.⁴⁶ The uncertainty faced by the madder growers of France is highlighted in a report on the queries from the Vaucluse Agricultural Society (in southeast France) on the manufacture of artificial alizarin. Concerns of the farmers in 1873 were [author's translation]:

- Are the manufacturers of Mulhouse using artificial alizarin?
- Are the colours obtained from this product of a good shade?
- What is the price per kilogram?
- Does the product serve for printing and dyeing?
- What should madder growers fear now?
- What should they fear for the future?⁴⁷

Their fears were not unfounded, and within ten years madder cultivation went into a global decline.⁴⁸ By the 1890s it had virtually vanished, unable to compete with synthetic alizarin for price, purity, concentration, and quality of colour.⁴⁹

3.2.2 Formation of anthraquinones in madder

The roots of the madder plant are where the dyes are found and must be of a certain maturity, from three to seven years old depending on where they were cultivated, to contain a useful amount of colouring material—older plants contained a wider variety of colorants.⁵⁰ The tap and side roots are covered by a thick rind-like skin containing little dye. Inside, a softer substance surrounding woody fibres at the heart of the root contains most of the colorant.⁵¹ A detailed study of madder is beyond the scope of this project, but further reading on the topic can be found in Colin,⁵² Decaisne,^{53,54} and Chenciner.⁵⁵

⁴⁶ Chenciner, *Madder Red*: a History of Luxury and Trade, 83.

⁴⁷ Brandt, "Rapport présenté au nom du comité de chimie par M. Brandt, sur la valeur comparée de l'alizarine artificielle et de la garance."

⁴⁸ Chenciner, Madder Red: a History of Luxury and Trade, 83.

⁴⁹ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 577.

⁵⁰ Cardon, *Le monde des teintures naturelles*, 102.

⁵¹ Derksen, "Red, Redder, Madder: Analysis and Isolation of Anthraquinones From Madder Roots (Rubia Tinctorum)," 3.

⁵² Colin and Robiquet, "Nouvelles recherches sur la matière colorante de la garance."

⁵³ Decaisne, Nouvelles recherches sur la matière colorante de la garance.

⁵⁴ Decaisne, "On the Root of the Madder."



Figure 3-7 Dried and cut madder roots. Image © Julie H. Wertz





Interest in madder during the first half of the 19^{th} c. was strong since it had great commercial value as a dyestuff. The biochemistry of madder roots influences its colouring power based on which dyes develop during the roots' maturation. Different species of madder contain different colourants—*R*. *cordifolia* is a different mixture of dyes than *R*. *tinctorum*—and relative amounts can also vary based on age of the plant, cultivation, and climate. Preparing madder to be useful for dyeing was so laborious because in the roots, the dyes

⁵⁵ Chenciner, *Madder Red: a History of Luxury and Trade.*

are largely present in the form of glycosides,⁵⁶ meaning bound to a sugar by a bond that must be hydrolysed for the aglycone dyes to be useful.⁵⁷

Although the sugar, primeverose, a disaccharide of xylose and glucose, was not identified until the 1930s, research on the components of madder dates to the early 19th c. and chemists knew that a sugar was present.^{58,59} Early work found that yellow fluid expressed from fresh roots turned red when exposed to the atmosphere, and the depth of colour corresponded to the age of the root.⁶⁰ Alizarin was first isolated in 1826 by French chemists Colin and Robiquet, who named it after *ali-zari*, which was what the roots were called in the Levant.⁶¹



Figure 3-9 Alizarin-2-B-primeveroside The form in which alizarin occurs in madder roots, ruberythric acid. Alizarin is on the left with primeverose bound to the 2-hydroxyl.

Obviously, madder growers had developed the ability to hydrolyse the glycoside bond to free the dyes long before the chemistry of the process was understood. The roots also contain an enzyme, erythrozyme, which does this naturally. It is destroyed by high heat, however, which explains why better quality madder roots dried slowly in the sun had more colouring power than those kiln-dried at a higher temperature.^{62,63} Fermentation also induces glycoside hydrolysis, which

⁵⁶ ibid., 135.

⁵⁷ Derksen et al., "Chemical and Enzymatic Hydrolysis of Anthraquinone Glycosides From Madder Roots," 137.

⁵⁸ Richter, "Anthraquinone Colouring Matters: Ruberythric Acid," 1702-1707.

⁵⁹ Cooksey and Dronsfield, "Edward Schunck: Forgotten Dyestuffs Chemist?," 192.

⁶⁰ Decaisne, "On the Root of the Madder," 270.

⁶¹ Colin and Robiquet, "Nouvelles recherches sur la matière colorante de la garance," 241.

⁶² Travis, "Between Broken Root and Artificial Alizarin: Textile Arts and Manufactures of Madder," 12.

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could be encouraged with the addition of lime (calcium oxide or calcium hydroxide)⁶⁴ or by pouring water on bags of madder.⁶⁵

Anthraquinones in madder are secondary metabolites, a low molecular weight product with no obvious function in cell growth synthesized for a finite period by cells that are no longer growing,⁶⁶ and have been proposed as having a biological role in plant defence.⁶⁷ This also applies for other *Rubiaceae* members like *Galium* and *Cinchona*,⁶⁸ and different biosynthetic pathways in various plant species produce different mixtures of anthraquinones. In *R. tinctorum*, this is via the shikimate pathway.^{69,70} Analysis of madder extracts has identified compounds with substitutions on both outer rings of the anthraquinone,⁷¹ but the majority occur on only one ring. This may have implications for making distinctions between dye sources based on the synthetic pathway for manufactured alizarin, discussed later in this chapter.

The number of anthraquinones identified in madder roots has increased over time as analytical techniques have become more sensitive. Early work identified six, nineteen were known by the mid- 20^{th} c.,⁷² and recent research has identified 36, 15 which have a role in dyeing.⁷³ To have tinctorial properties, a

- ⁶⁴ Travis, "Between Broken Root and Artificial Alizarin: Textile Arts and Manufactures of Madder," 12.
- ⁶⁵ Chenciner, Madder Red: a History of Luxury and Trade, 167.
- ⁶⁶ Hobson and Wales, "'Green' Dyes," 42.
- ⁶⁷ Pankewitz, "General Introduction and Thesis Outline."
- ⁶⁸ Caro et al., "Natural Hydroxyanthraquinoid Pigments as Potent Food Grade Colorants: An Overview."
- ⁶⁹ Eichinger et al., "Quantitative Assessment of Metabolic Flux by ¹³C NMR Analysis. Biosynthesis of Anthraquinones in Rubia Tinctorum."
- ⁷⁰ Derksen, "Red, Redder, Madder: Analysis and Isolation of Anthraquinones From Madder Roots (Rubia Tinctorum)," 8.
- ⁷¹ Mouri and Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC."
- ⁷² Burnett and Thomson, "Naturally Occurring Quinones. Part XV. Biogenesis of the Anthraquinones in Rubia Tinctorum L. (Madder)," 2438.
- ⁷³ Henderson, Rayner, and Blackburn, "Isolation and Extraction of Lucidin Primeveroside From *Rubia Tinctorum* L. and Crystal Structure Elucidation," 105.

⁶³ Chenciner, Madder Red: a History of Luxury and Trade, 136.

hydroxyanthraquinone needs an -OH at position C1 or C4 (see Figure 3-2) and at least one more -OH at another position to generate an orange-red colour.⁷⁴

3.2.3 Important hydroxyanthraquinone dyes in madder

Alizarin (Figure 3-1) has the molecular formula $C_{14}H_8O_4$ and a molar mass of about 240 g/mol. It is only moderately soluble in water and begins to dissolve around 70 °C,⁷⁵ which is consistent with Turkey red methods heating the dye bath to this temperature. On wool and silk, alizarin dyes bright, deep colours with metal mordants like aluminium and iron by forming a lake complex, but for cotton and Turkey red the oil treatment is required to achieve this degree of colour.

Purpurin is typically the next most abundant dye in madder after alizarin and was also isolated by Colin and Robiquet in 1826.⁷⁶ The third –OH at position 4 makes purpurin a deeper red hue than orangey-red alizarin.



Figure 3-10 Purpurin (1,2,4-tri-hydroxyanthraquinone)

In paintings, purpurin lakes are less light fast, making madder lakes less fast than those made with pure alizarin,^{77,78} which has implications for conservation if this applies to dyed textiles as well. Purpurin colours were considered to be less

⁷⁴ Derksen, "Red, Redder, Madder: Analysis and Isolation of Anthraquinones From Madder Roots (Rubia Tinctorum)," 18.

⁷⁵ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2^{me} partie, L'alizarine artificielle et ses dérivés, 88.

⁷⁶ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 576.

⁷⁷ Schweppe and Winter, "Madder and Alizarin," 114.

⁷⁸ Kirby, Spring, and Higgitt, The Technology of Eighteenth- and Nineteenth-Century Red Lake Pigments.

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wash fast as well,⁷⁹ and it was used less due to its higher cost when synthesised dyes were adopted.⁸⁰

Most madder contains alizarin and purpurin, and the relative amounts deposited on the fibre can be influenced with a change in temperature; dye baths above 85 °C have a higher relative amount of purpurin. This is due to the decarboxylation of pseudopurpurin, which increases the purpurin yield, a process that also occurs when the roots are dried.⁸¹



Figure 3-11 Pseudopurpurin (1,2,4-tri-hydroxyanthracene-3-carboxylic acid)

Historically, madder was known to stain the bones of livestock red when the tops, which had no use in dyeing, were used as feed. The effect was harmless to the animals and also tended to give a reddish shade to their milk and a yellow one to the resulting butter.⁸² These effects are largely from pseudopurpurin,⁸³ which has also been shown to increase bone mineral density in rats.⁸⁴ Alizarin is known to have an antimicrobial and antibacterial effect,⁸⁵ so using madder tops as feed for cattle may have been both cheap food and a convenient preventative medicine. The tendency to complex with calcium can also be seen in the Turkey red process, where calcium is a requisite ingredient. Madder grown in soil with a higher calcium content produces red roots with a larger quantity of dye,

⁷⁹ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar," 574.

⁸⁰ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. ^{2me} partie, L'alizarine artificielle et ses dérivés, 69.

⁸¹ Hofenk de Graff, van Bommel, and Roelofs, *The Colourful Past*, 93-98.

⁸² Schaefer, "The Cultivation of Madder," 1399.

⁸³ Richter, "Vital Staining of Bones with Madder."

⁸⁴ Wu et al., "Dietary Pseudopurpurin Effects on Bone Mineral Density and Bone Geometry Architecture in Rats."

⁸⁵ Golcu et al., "Isolation of Colour Components From Rubia Tinctorum L.."

whereas madder grown in calcium-poor soil makes for a yellower dyed textile,⁸⁶ so the influence of calcium extends beyond the dyeing process to the dye source itself.

There are other hydroxyanthraquinones in madder that act as dyes, but the focus of this research on Turkey red dyed with early synthetic alizarin and madder puts them beyond the scope of this work. Their identification is further complicated by a lack of commercial reference standards, necessitating prior isolation and identification from natural sources before the results can be compared to textile samples. One compound, however, is worth note. Although the naturally-sourced dyes are frequently perceived to be safer than their modern chemical replacements, madder can contain a significant quantity of lucidin (1,3-dihydroxy-2-hydroxymethylanthraquinone), a genotoxin that poses difficulties in using the extract for dyeing purposes.⁸⁷

3.3 Garancine

The amount of madder consumed by the Turkey red industry, its cost, and the transport required to ship it to Scotland motivated dyers and chemists to find a more efficient dye source. For a few decades in the mid- to late-1800s, concentrated madder products like *garancine*, *garanceux*, *fleur de garance*, and Kopp's green alizarin existed and were used by various textile industries. Of these semi-synthetic products, in the sense that they are made from chemical treatment of a natural product, *garancine* was used the most for Turkey red.

Garancine was first prepared by Colin, Robiquet, and Lagier in 1828 and patented in France.^{88,89} It was made by treating ground madder with concentrated sulfuric acid, which broke down some of the woody material and increased the tinctorial power without affecting the colour.⁹⁰ *Garancine* was less bulky, easier to store, and cheaper to transport because of its higher

⁸⁶ Schaefer, "The Cultivation of Madder," 1399.

⁸⁷ Derksen, "Red, Redder, Madder: Analysis and Isolation of Anthraquinones From Madder Roots (Rubia Tinctorum)," 26.

⁸⁸ Lagier, Robiquet, and Colin, Procédés d'épuration de la garance.

⁸⁹ Society of Dyers and Colourists, *Colour Index*, 3237.

⁹⁰ Crookes, A Practical Handbook of Dyeing and Calico-Printing, 257.
concentration. Within about ten years it had been adopted in the French dyeing centres of Rouen and Alsace.⁹¹ Around 30-40 parts *garancine* could be obtained from 100 parts of madder and it had 4-5x more colouring power, though some thought it was not always as nice or as fast.⁹² The AOE dyestuffs ledger records the use of *garancine* into 1886,⁹³ showing that for more than a decade the firm used it alongside synthetic alizarin when dyeing Turkey red.

Making *garancine* involved soaking madder in eight to ten times its weight of cold water, letting it stand twelve hours, then draining off the excess water and mixing the sludge with about 1/3 the original weight of madder of concentrated sulfuric acid. This was boiled for four to five hours, diluted with cold water, filtered, and washed again until no longer acidic. The *garancine* was pressed into cakes, then dried and ground into a powder.⁹⁴



Figure 3-12 Bottle of historical garancine from Catalyst Science Discovery Centre. © Catalyst Science Discovery Centre.

There are similarities between making *garancine* and synthetic alizarin, processes that both use concentrated sulfuric acid as a reagent. A recent re-

⁹¹ Chenciner, *Madder Red: a History of Luxury and Trade*, 131.

⁹² Crookes, A Practical Handbook of Dyeing and Calico-Printing, 260.

⁹³ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.

⁹⁴ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 388.

creation made a sample of *garancine* for comparison to historical samples,⁹⁵ but it was made refluxing madder with hydrochloric acid according to an 1860 French patent by Jean-Henri Fabre. This method is not documented in the literature reviewed for this project, so it is uncertain whether their results are representative of *garancine* samples in general. A sample of historical *garancine* (formerly in the Leeds University Department of Colour Chemistry collection, now at the Museum of Science and Industry, Manchester) analysed for two different papers contained alizarin and purpurin as well as some unidentified peaks.^{96,97} These may be unreferenced madder components, but it is also plausible different molecules are produced when the madder is boiled with sulfuric acid that could serve as chemical markers for that particular dye source

3.4 Synthetic alizarin dye

Synthetic alizarin was the first synthetic dye to be significantly fast to light and washing because it had the same properties as the naturally sourced molecule. It had an advantage over madder because it did not contain any of the impurities from the plant that dulled the colour.⁹⁸ The textile industry was initially divided, however, when it came to adopting it over madder. Knecht explains that dyers accepted the synthetic product because it fit into their established processes, but weavers were more reluctant because yarn dyed with the artificial product was greasy and difficult to size. This was because dyers had not yet compensated for the increased concentration of colorant in synthetic alizarin by decreasing the amount of oil used, more of which was needed when dyeing with madder. Once this was overcome, adoption of synthetic alizarin was common and by 1873 some dye works were using it exclusively.⁹⁹ Synthetic alizarin is used in the AOE dyestuffs ledger from its beginning in 1873; the last entry for madder is 1874.¹⁰⁰

⁹⁵ Cuoco et al., "Characterization of Madder and Garancine in Historic French Red Materials by Liquid Chromatography-Photodiode Array Detection."

⁹⁶ Hofenk de Graff, van Bommel, and Roelofs, *The Colourful Past*.

⁹⁷ Kirby, Spring, and Higgitt, The Technology of Eighteenth- and Nineteenth-Century Red Lake Pigments.

⁹⁸ Chenciner, Madder Red: a History of Luxury and Trade, 265.

⁹⁹ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 587.

¹⁰⁰ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.



Figure 3-13 Figures taken from AOE dyestuffs ledger show the transition from garancine to synthetic alizarin for cloth dyeing. Madder used in the first three entries is not shown. Data from AOE dyestuffs ledger, University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/4/1.

The colours dyed with synthetic alizarin were slightly different, but this was acceptable to dyers who were already accustomed to products like *garancine*.¹⁰¹ The reds were brighter and more intense, purples more blue-toned, and blacks deeper.¹⁰² One modern commentary notes madder-dyed textiles have a more nuanced hue than those dyed with synthetic alizarin,¹⁰³ but in the 19th c. the brilliance of colour may have been preferred. It is also worth noting that improvements in chemical processes mean modern synthetic alizarin is not the same mixture of dyes that it was in the late 19th c., when the colour may have been more nuanced. Research in the late 19th c. comparing Turkey red dyed with madder and synthetic alizarin concluded that the latter was less fast, possibly due to the new colorants not found in madder,¹⁰⁴ but the test is not robust by modern standards and warrants further investigation.

¹⁰¹ Travis, "Between Broken Root and Artificial Alizarin: Textile Arts and Manufactures of Madder," 17.

¹⁰² Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar," 577.

¹⁰³ Chenciner, *Madder Red: a History of Luxury and Trade*, 267.

¹⁰⁴ Sansone, "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton," 208.

3.4.1 Anthrapurpurin and flavopurpurin

Initially, processes to make synthetic alizarin were not very tightly controlled in terms of reagent ratios, temperatures, and time. Variations in these conditions during the synthetic process yielded two hydroxyanthraquinone dyes in addition to alizarin that had not been previously seen before, anthrapurpurin (also called isopurpurin) and flavopurpurin.¹⁰⁵



Figure 3-14 Structures of anthrapurpurin (left) and flavopurpurin

The literature does not indicate that purpurin was a significant component of synthetic alizarin. It appears to have first been obtained synthetically by alizarin oxidation around 1874^{106,107} and was more expensive than anthrapurpurin and flavopurpurin.¹⁰⁸



Figure 3-15 Modern reference standards of alizarin, anthrapurpurin, and purpurin. Image $\ensuremath{\mathbb{C}}$ Julie H. Wertz

¹⁰⁵ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar."

¹⁰⁶ Lalande, "Synthesis of Purpurin."

¹⁰⁷ Rosenstiehl, "Synthesis of Purpurin, and on Certain Analogous Colouring Matters."

¹⁰⁸ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 585.

Anthrapurpurin was discovered by Auerbach, who named it isopurpurin, around 1872.¹⁰⁹ It was subsequently described by Perkin, who called it anthrapurpurin.¹¹⁰ Perkin did extensive research on the molecule in terms of its properties and how it was synthesised, which improved chemists' ability to control the synthesis.^{111,112} He believed anthrapurpurin was as important, if not more so, than alizarin. Flavopurpurin forms in a similar manner to anthrapurpurin. It is less abundant than anthrapurpurin in synthetic alizarin, and less research has been published on flavopurpurin in general.¹¹³ Dépierre ranks the major hydroxyanthraquinone dyes, from bluish to reddish hue, in the order of alizarin, anthrapurpurin, flavopurpurin, and purpurin.¹¹⁴ Once chemists were able to control the synthesis and manipulate the yield ratios, dyers were able to take advantage of the slight colour variations between these dyes by picking a mix ratio that produced the desired shade of red.

The natural occurrence of anthrapurpurin and flavopurpurin is unclear based on the available literature, most of which is from the late 19th c. and discusses anthrapurpurin and flavopurpurin in the context of synthetic alizarin. For modern research, one paper lists flavopurpurin as a main anthraquinone glycoside present in *Rubia tinctorum*,¹¹⁵ but their dyeing study did not perform any identifications, so the origin of this information is unclear. Flavopurpurin was isolated from *Morinda pandurifolia* and identified by ¹H and ¹³C NMR data.¹¹⁶ A review of natural hydroxyanthraquinoid pigments lists both,¹¹⁷ but a source is only provided for anthrapurpurin, *Cinchona succirubra*.¹¹⁸ None of these studies

- ¹¹¹ Perkin, "XV.- on Anthrapurpurin."
- ¹¹² Perkin, "XXXI.-on the Formation of Anthrapurpurin."

- ¹¹⁴ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2^{me} partie, L'alizarine artificielle et ses dérivés, 69.
- ¹¹⁵ De Santis and Moresi, "Production of Alizarin Extracts From Rubia Tinctorum and Assessment of Their Dyeing Properties."
- ¹¹⁶ Ruksilp et al., "Biochemical Systematics and Ecology."
- ¹¹⁷ Caro et al., "Natural Hydroxyanthraquinoid Pigments as Potent Food Grade Colorants: an Overview."
- ¹¹⁸ Khouri and Ibrahim, "Purification and Some Properties of Five Anthraquinone-Specific Glucosyltransferases From Cinchona Succirubra Cell Suspension Culture."

¹⁰⁹ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar."

¹¹⁰ Auerbach, *Anthracen*, 203.

¹¹³ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar," 577-579.

referencing naturally occurring anthrapurpurin and flavopurpurin contain scientific evidence that they are found in madder roots, making them useful to distinguish natural from synthetic colorant as potential indicators in the dating of historical textiles.

3.4.2 Synthetic alizarin in the late 19th c.

Today, synthetic alizarin is sold as a dry powder, but in the late-19th c. it went to market in the form of a paste. This was because dry alizarin powder caused irregular dyeing and spotting due to its difficulty dispersing in the dye bath.¹¹⁹ The paste was made with water, glycerine, or Turkey red oil^{120,121} and was initially available in concentrations of 10-15% dye;¹²² by the turn of the century most products were at 20% concentration.¹²³ It was occasionally sold at higher concentrations, usually 40% and sometimes up to 80%, to save on freight costs,¹²⁴ but probably diluted before use. The concentration of synthetic alizarin used in the AOE dyestuffs ledger is not consistently recorded, but 10% and 20% both appear. A shift in price per pound values and the quantities used imply the firm perhaps transitioned to the 20% paste around 1883.¹²⁵ This is consistent with the increased 20% synthetic alizarin production that year shown in Figure 3-29.

¹¹⁹ Perkin, "Methods of Analysis Employed in the Manufacture of Alizarin," 86.

¹²⁰ Duerr and Turnbull, *Bleaching and Calico-Printing* : a Practical Manual, 110.

¹²¹ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2^{me} partie, L'alizarine artificielle et ses dérivés, 64.

¹²² Auerbach, Anthracen, 153.

¹²³ Cain and Thorpe, The Synthetic Dyestuffs and the Intermediate Products From Which They Are Derived, 118.

¹²⁴ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 585.

¹²⁵ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.





Different varieties of alizarin paste were sold with varying quantities of alizarin, anthrapurpurin, and flavopurpurin. A mixture of 45% alizarin and 55% flavopurpurin was considered good for Turkey red. This would have balanced the 'blue' tone of alizarin with the 'red' tone of flavopurpurin. Products like Alizarin B, for *bleu* or *blau*, were pure or nearly pure alizarin used for dyeing violets and pinks,¹²⁶ and Badische Anilin und Soda Fabrik (BASF) produced chemically pure alizarin sold as Alizarin V (for violet).¹²⁷ Alizarin G, for *gelb*, the German word for yellow, was another common formulation. The paste brownish-yellow, hence the name, but produced redder shades than alizarin on its own. It contained higher concentrations of anthrapurpurin and flavopurpurin, of which the ratio could be adjusted to give redder or yellower hues, respectively.^{128,129} 'Red' branded synthetic alizarin was actually 85-90% anthrapurpurin.¹³⁰

The manufacturers may have done this by manipulating the reaction conditions, but exactly how the different shades were prepared is unclear. The proliferation of synthetic alizarin mixes was such that Perkin lamented 'much of the manufacturer's time is occupied with preparing these; moreover, he is

¹²⁶ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 68-69.

¹²⁷ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 585.

¹²⁸ ibid., 586.

¹²⁹ Duerr and Turnbull, *Bleaching and Calico-Printing* : a Practical Manual, 110.

¹³⁰ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 98.

forced to keep a considerable stock of colour on hand.¹³¹ A few examples include Alizarin R, RA, GA, V, VX, SX, SGX, though the labels had little actual value.¹³²

One of the aims of this research is to identify individual components of late-19th c. synthetic alizarin on historical Turkey red. A set of historical synthetic alizarin samples kindly provided by the TU Dresden Historisches Farbstoffsammlung (H.F.; 'historical dyes collection') serves as a valuable set of references from the same era in which the textiles were dyed. The samples 'Alizarin PA' and 'Alizarinrot WG' are example of this ambiguous naming system, which may have served the purpose of letting a buyer know, for example, that purchasing Alizarinrot WG from BASF would consistently produce a particular shade.



Figure 3-17 'Alizarinrot WG BASF Teig 20%' and 'Alizarin P.A. Prag' from the TU Dresden Historisches Farbstoffsammlung. Samples prepared by Dr Horst Hartmann.

The UTR archive documents reviewed for this project do not indicate any specific variety of alizarin, e.g. V or B, being used, making it difficult to connect this information to the historical textiles. The AOE ledger provides

¹³¹ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar," 597.

¹³² Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 69.

concentrations and amounts of alizarin paste used, but not the manufacturer.¹³³ The archive contains three contracts for synthetic alizarin, one from 1898 between the British Alizarine Company and two in 1899 and 1900 between Meister Lucius & Brüning. The British Alizarine contract agreed upon a supply 500 tons of synthetic alizarin at 20% strength to United Turkey red for 6 d. per pound and includes an extensive list of 'qualities' they made, though with no descriptions.¹³⁴



Figure 3-18 Varieties of synthetic alizarin produced by The British Alizarine Company and sold to United Turkey Red in 1898. © University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/5/13/3/4.

The 1899 contract with Meister Lucius & Brüning includes a separate letter promising United Turkey Red an additional 5% allowance of product and requesting the favour remain a secret between the two firms.¹³⁵ Both the 1899 and 1900 contracts stipulate the dye manufacturers would not make their 'brand RX' more than 10% of their monthly shipment.¹³⁶

¹³³ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.

¹³⁴ Contract for Artificial Alizarine- 500 Tons to UTR Co. Ltd From the British Alizarine Co. Ltd. UGD 13/5/13/3/4.

¹³⁵ Correspondence Between UTR Co. Ltd and Meister Lucius and Brüning, Frankfurt Re. Contract to Supply Alizarine. UGD 13/5/13/6/20.

¹³⁶ Letter From Meister, Lucius & Brüning to UTR Co. Ltd Glasgow Re. Contract for Sale of Alizarine. UGD 13/5/13/7/38.

to be delivered of our brand RX not to 10% - ten percent - of our actual months ry, accidents excepted. Each months delivery to be

Figure 3-19 Contract between Meister Lucius & Brüning and United Turkey Red limiting the quantity of their RX brand of synthetic alizarin. © University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/5/13/7/38

An 1896 trade publication from the manufacturer lists a variety of alizarin dyes; by this point the name was used to refer to compounds like Alizarin Yellow G, an azo dye. This was because manufacturers used the name 'alizarin' to indicate dyes used in conjunction with or in processes where anthraquinones were used.¹³⁷ Versions of the hydroxyanthraquinone dye alizarin from Meister, Lucius & Brüning include Nr. 1B new, Nr. 1, 2A bl. Bl., 2A, 2AW, 2BW, 1W, RX, 2W, 3W, 3GW, 4FW, SDG, GG, F, paste, Nr. 1 powder.¹³⁸

Dyed Patterns	Employment	Commercial Name	Year of introduc- tion	Mode of solution	Methods of Dyeing		
					Wool	Cotton	Silk
Alizais Rel No. 2 poeter.	I contrarying und see Tortgered and plan here yes use water of the second secon	Alizarin Red (Nr 1B new, Nr 1, a Abl, bu, 2a, 2a,W, BW, GW, BW, KX, aW, GW, GW, FW, SDG, GG, F, paste, Nr 1 powder)	1869/70	Make intra gamp and to the doe last broads due to broads der colours are der colours are der colours are der colours are der colours are der colours and der colours are der colours and der colours are der colours and der colours are der c	1. Marchen with dark synapsical balance in the second synapsical balance in the second synapsical synapsica	In each of the second s	Mardan aith airs airs an an airs an airs an airs an airs an airs an airs an airs an airs an airs an airs airs airs airs an airs an airs an airs airs airs airs airs airs airs airs airs

Figure 3-20 1896 trade publication from Meister Lucius & Brüning with descriptions and samples of pieces dyed with synthetic alizarin.

In the J&P Coats archive, Dr Collin's notes mention 'alizarine 1 extra' from Bayer for their 'Turkey Red Blue Shade', 'Alizarine V₂' from BASF for their 'Turkey Red Medium Shade', and 'SX' from BASF for 'Turkey Red Yellow Shade'.¹³⁹

¹³⁷ Gurr, Synthetic Dyes in Biology, Medicine, and Chemistry, 354.

¹³⁸ Farbwerke Meister Lucius & Brüning, The Coal Tar Colors of Farbwerke vorm. Meister Lucius & Brüning. A: General Part.

¹³⁹ Collin, Turkey Red Process for Cotton Yarn. 1/9/3.



Figure 3-21 Varieties of synthetic alizarin used to dye Turkey red by J&P Coats ca. early 20th c. © Coats.com, Paisley Central Library, Records of J&P Coats Limited, 1/9/3

The literature indicates there is little significance to be found in the various names for 19th c. synthetic alizarin mixtures. The limited range of dyes expected to be found (primarily alizarin, anthrapurpurin, flavopurpurin) means there are only so many potential ratios of colourant in any blend, information that is too general to help determine textile provenance when variables like dye uptake mechanisms are taken into consideration as well. The case may be different, however, for other synthetic dyes, and future research should take into consideration the naming conventions of manufacturers in the event it does have significance for that product.

3.5 History of synthetic alizarin

Chemists of the late 19th c. considered the development of synthetic dyes derived from coal tar to be one of the best and most surprising discoveries of contemporary chemistry.¹⁴⁰ Concentrated madder products like *garancine* made the process more efficient for dyers, but still depended on the amount of cultivated madder on the market, for which the demand had not decreased. The development of *mauveine* and the triphenylamine (aniline) dyes encouraged chemists to search for a means to synthesise alizarin as well in order to meet the insatiable demand of the market, much of it from Turkey red dyeing. This research focuses on synthetic alizarin, but a good overview of the development

¹⁴⁰ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 1.

of early synthetic dyes can be found in Travis's comprehensive work *The Rainbow Makers*.¹⁴¹

The history of early synthetic alizarin industry is largely set in two countries— England and Germany. In England, Perkin first synthesised *mauveine*, and it was through him that connections between the English and German synthetic dye industries initially formed. His early research was done under August Wilhelm Hofmann, the German chemist who worked in England for a number of years and contributed much to the understanding of aniline-derived dyes.¹⁴² While Perkin's discovery was not backed up by years of research, in Germany discoveries were published in technical journals and communicated to other organic chemists, laying scientific foundations for the field through research on the nature of organic substances.¹⁴³ Homberg gives a good overview of the development of dye research laboratories, including German ones as well.¹⁴⁴

Although most remembered for his invention of *mauveine*, Perkin contributed significantly to the synthetic dye industry with his work on alizarin. Shortly after he developed an industrially successful method to manufacture alizarin, he retired. In Scotland, dyes were not manufactured on any significant scale until the early 20th c., but there are still connections to Perkin.¹⁴⁵ After accidentally inventing *mauveine*, he sent a sample to Scottish dyer Robert Pullar to test its viability as a dye.¹⁴⁶ Perkin was also a close personal friend of Glasgow dry goods merchant Robert Hogg, and it was to Hogg that Perkin sent his first samples dyed with his synthetic alizarin. Later, Perkin sold his wares in Glasgow through Hogg.¹⁴⁷ In 1869, Perkin was offered the Chair of Applied Chemistry at Anderson's College, now part of the University of Strathclyde, but turned it down because of a dispute with the Chair of Chemistry.¹⁴⁸ Courses in dyeing were offered at the College from the early 1900s, but these would be the application of dye to

¹⁴¹ Travis, *The Rainbow Makers*.

¹⁴² Loughlin, "Synthetic Red Dyes in Commercial Production Between 1860 and 1900," 28.

¹⁴³ Mellor and Cardwell, "Dyes and Dyeing 1775-1860," 277.

¹⁴⁴ Travis et al., "The Emergence of Research Laboratories in the Dyestuffs Industry, 1870-1900."

¹⁴⁵ Fox, Dye Makers of Great Britain 1856-1976, 158.

¹⁴⁶ Garfield, Mauve: How One Man Invented a Colour That Changed the World.

¹⁴⁷ Hogg, Correspondence. YL1999.2/1/14.

¹⁴⁸ Peel, "Dyeing Education in Glasgow From Anderson's University (1796) to the Royal College of Science and Technology (1958)," 491.

textiles rather than the development of new dyes,¹⁴⁹ highlighting the significance of the textile industry in Scotland. A detailed account of Perkin's life and work can be found in Garfield's *Mauve: How One Man Invented a Colour That Changed the World*¹⁵⁰, and in the accounts of Holme¹⁵¹ and Rowe.¹⁵²

Alizarin was first isolated from madder in 1828, but its structure could not be discerned¹⁵³ until Kekulé worked out the structure of benzene in 1865.¹⁵⁴ This was a step forward, but alizarin still proved elusive due to some misconceptions about its skeletal structure. From the mid-19th c., the primary hypothesis on the structure of alizarin was that it had a phthalic acid precursor, and therefore a naphthalene parent hydrocarbon, a belief that was a persistent red herring in the search for its structure.^{155,156}



Figure 3-22 Phthalic acid (left) and naphthalene

The structure would finally be discovered in the laboratory of German chemist Adolph Baeyer, who completed his PhD in Heidelberg in 1858 under the guidance of Robert Bunsen, followed by a period of research with Kekulé. In 1860, he obtained a teaching position in applied chemistry with an emphasis on dyes and dyeing at the Gewerbe Institute in Berlin. In his lab, Baeyer and his students established a tradition of breaking down molecules of industrial interest and using that information to devise ways to synthesise them. The work was done by

¹⁴⁹ ibid., 490.

¹⁵⁰ Garfield, Mauve: How One Man Invented a Colour That Changed the World.

¹⁵¹ Holme, "Sir William Henry Perkin: a Review of His Life, Work and Legacy."

¹⁵² Rowe, "The Life and Work of Sir William Henry Perkin."

¹⁵³ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 387.

¹⁵⁴ Chenciner, Madder Red: a History of Luxury and Trade, 265.

¹⁵⁵ Fieser, "The Discovery of Synthetic Alizarin," 2613.

¹⁵⁶ Travis, "Between Broken Root and Artificial Alizarin: Textile Arts and Manufactures of Madder," 12-17.

research assistants Carl Graebe, who had worked at the aniline dye factory of Meister, Lucius & Co. (later Meister Lucius & Brüning), and Carl Liebermann, who had worked in the Mulhouse calico printing industry. Both were qualified chemists. In early 1868, at the suggestion of Baeyer, Graebe and Liebermann attempted to find a useful precursor to alizarin by distilling it with zinc dust to reduce it. The pair worked through the weekend and before presenting their discovery of alizarin's structure that Monday evening at the meeting of the German Chemical Society.^{157,158} They found the parent hydrocarbon was in fact anthracene (see Figure 3-2), not naphthalene. As it happens, naphthalene and anthracene both yield phthalic acid upon oxidation, making it difficult to determine the starting molecule and no doubt contributing to the confusion.¹⁵⁹

Finally, the structure of alizarin was known. It was the first dye that chemists fully understood the structure of, making it possible to attempt synthesis.¹⁶⁰ Since Graebe and Liebermann had a head start as the discoverers of its structure, they were able to propose a synthetic route not long after and filed for a patent on the process in Britain in December 1868.¹⁶¹ They initially attempted to use sulfonation and hydrolysis reactions, based on recent research, but did not succeed and patented an alternative method. It started with anthracene, which was treated with nitric acid to produce anthraquinone, then brominated and finally hydroxylated to alizarin. There was little commercial value in it, however, due to the cost of bromine and a low yield.¹⁶²

¹⁵⁷ Travis, *The Rainbow Makers*, 168-172.

¹⁵⁸ Graebe and Liebermann, "Ueber Alizarin und Anthracen," 49.

¹⁵⁹ Travis, "Between Broken Root and Artificial Alizarin: Textile Arts and Manufactures of Madder," 17.

¹⁶⁰ Dronsfield, Brown, and Cooksey, "Synthetic Alizarin- the Dye That Changed History."

¹⁶¹ Liebermann and Graebe, Coloring Matters.

¹⁶² Travis, *The Rainbow Makers*, 176.



Figure 3-23 Graebe and Liebermann's bromination synthetic route

Rights to the patent were secured by BASF. Their technical director, Heinrich Caro, had worked in Britain making aniline dyes in the early days after *mauveine* and was instrumental in the rapid expansion of the German dye industry.¹⁶³ Caro, Graebe, and Liebermann hoped to improve the process yield at BASF by overcoming the earlier anthraquinone sulfonation problem. The firm had an unused supply of mixed anthraquinones available, so Caro begin experimenting with them.¹⁶⁴ He was successful with anthraquinone sulfonation where Graebe and Liebermann had not been, because they had not applied sufficient heat— an accidental discovery of Caro's after he left a mixture of sulfuric acid and anthraquinone over a Bunsen burner and found traces of alizarin in the charred crust. Repeating the experiment with fuming sulfuric acid (also called oleum; SO_3 in H₂SO₄) and high heat yielded the desired product, anthraquinone sulfonic acid. When heated with strong alkali, the sulfonic acid group or groups are hydrolysed, becoming hydroxyls.¹⁶⁵



Figure 3-24 Anthraquinone-2-sulfonic acid, the precursor to alizarin in synthesis

¹⁶³ Travis, "Colour Makers and Consumers: Heinrich Caro's British Network."

¹⁶⁴ Travis et al., "Technology in Decline: a Search for Useful Concepts."

¹⁶⁵ Travis, The Rainbow Makers, 176-179.

On June 25th, 1869, Caro, Graebe, and Liebermann filed for a British patent on anthraquinone sulfonation and hydrolysis to synthesise alizarin.¹⁶⁶ Public knowledge of the alizarin structure meant that they were not the only chemists researching its synthesis. Remarkably, Perkin applied for a British patent on the same method the following day.¹⁶⁷

As a student under Hofmann, Perkin learned how to distil anthracene from coal tar and studied its oxidation and chlorination. He was also interested in synthesising natural products, a background that gave him an advantage in his alizarin research.¹⁶⁸ Interestingly, Travis says there is no indication Perkin was aware of the correct structure of alizarin until early 1869, making his patent the product of fairly quick work.¹⁶⁹ He had found the same anthraquinone sulfonation route as the Germans, but delayed filing his application so he could send cloth samples dyed with synthetic alizarin to his friend Robert Hogg in Glasgow, which he did on May 20th, 1869. The Germans had registered their signatures regarding the discovery at the Berlin patent office on June 15th. Based on this, Perkin asserted that although the German patent was filed first, he had discovered the process before them.¹⁷⁰ The London office, in what was later said to be a show of favouritism, asked the German inventors to rewrite part of their application and sealed Perkin's first, on August 24th, 1869. Shortly thereafter, the Prussian Royal Polytechnic Commission refused Graebe and Liebermann a patent on the grounds that it was too similar to the initial bromination route, leaving them without exclusive rights in some parts of Germany.^{171,172} Caro, Graebe, and Liebermann's British patent was finally sealed on January 11th, 1870.

During the summer of 1869, Perkin continued his alizarin research and on November 17th filed for a British patent on synthesis by anthracene chlorination,

¹⁶⁶ Caro, Graebe, and Liebermann, Improvements in Preparing Coloring Matters.

¹⁶⁷ Perkin, Improvements in the Manufacture of Coloring Matter Suitable for Dyeing and Printing.

¹⁶⁸ Fieser, "The Discovery of Synthetic Alizarin," 2628.

¹⁶⁹ Travis, *The Rainbow Makers*, 180.

¹⁷⁰ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar."

¹⁷¹ Holme, "Sir William Henry Perkin: a Review of His Life, Work and Legacy," 244.

¹⁷² Travis, The Rainbow Makers, 179-182.

sulfonation, and oxidation to anthraquinone sulfonic acids.¹⁷³ The process yielded a higher ratio of anthrapurpurin to alizarin.¹⁷⁴ It was sealed on January 7th, 1870, meaning Perkin held two British patents to synthesise alizarin before the Germans had been granted their first.





Alizarin was not the only manufactured dye to be subject to patent disputes as inventors struggled to document reactions and products they could not always fully or reliably describe. The near-simultaneous patent filings in Britain made an awkward situation, especially since BASF held only a British patent for anthraquinone sulfonation. Seeking to avoid future court cases, Caro and Graebe travelled to London with Friedrich Engelhorn, the founder of BASF, to meet with Perkin. The two parties agreed in March 1870 to honour each other's patents and to divide the alizarin market, giving Perkin a monopoly in Britain and BASF the mainland European market.¹⁷⁵ Later that year, however, the outbreak of the Franco-Prussian War hampered the German dyes industry and for a period Perkin operated largely without competition in alizarin manufacture.¹⁷⁶ Research continued into the early 20th c. on new synthetic processes to make alizarin as manufacturers looked for cheaper, more efficient reaction conditions. More than 40 patents were filed for alizarin synthesis from the late 1860s to the early

 ¹⁷³ Perkin, Improvements in the Manufacture of Coloring Matter Suitable for Dyeing and Printing.
¹⁷⁴ Travis, The Rainbow Makers, 187.

¹⁷⁵ ibid., 183.

¹⁷⁶ Welham, "The Early History of the Synthetic Dye Industry," 148.

1890s, but they had little commercial value and anthraquinone sulfonation remained standard.¹⁷⁷

This research studied the patents of Caro, Graebe, Liebermann, and Perkin in order to learn more about the early alizarin industry, which grew from the Turkey red dyers' need for more dyestuff than what could be supplied through madder cultivation, closely connecting the two industries. Synthetic alizarin also introduced anthrapurpurin and flavopurpurin, dyes not found in madder, to Turkey red, making them potential chemical markers for synthetically dyed textiles. The study of synthetic alizarin for this project is used to attempt a recreation of the alizarin synthesis as practiced in the late 19th c., in order to explore how industrially valuable processes were documented and communicated and what sort of information was omitted. The experience of recreation adds an additional layer of understanding to interpretations of the texts alone, and hopefully provides material for analysis and comparison.

3.6 Principal synthetic routes for alizarin dye

Between Perkin and Caro, Graebe, and Liebermann, patents on alizarin synthesis were held for routes proceeding via sulfonation, chlorination and sulfonation, and bromination, though the latter had no commercial value.¹⁷⁸ The former two produced anthraquinone sulfonic acids, which were then hydroxylated. Anthraquinone or anthracene were used as starting materials; anthracene reacted more easily than anthraquinone but also had to be oxidised to anthraquinone to complete the process. This section discusses the patents and reaction conditions to identify a method for the historical re-creation of synthetic alizarin in this project. Patents were filed first in Britain and later in the US for the same processes; the following list summarises the British patents and provides the analogous US patent number when applicable. They are ordered by date of application, rather than issue, since it is more representative of the date of invention. Figure 3-26 compares the routes of the processes.

¹⁷⁷ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 45.

¹⁷⁸ Fieser, "The Discovery of Synthetic Alizarin," 2626.

- Liebermann, Charles, and Charles Graebe. 18 Dec. 1868. Coloring Matters. GB 3850, issued June 15, 1869. (US 95,465/US 4,321)^{179,180,181}
- Caro, Heinrich, Charles Graebe, and Charles Liebermann. 25 Jun. 1869. Improvements in Preparing Coloring Matters. GB 1936, issued January 11, 1870. (US 153,536)^{182,183}
- Perkin, William Henry. 26 Jun. 1869. Improvements in the Manufacture of Coloring Matter Suitable for Dyeing and Printing. GB 1948, issued August 24, 1869.¹⁸⁴
- Perkin, William Henry. 17 Nov. 1869. Improvements in the Manufacture of Coloring Matter Suitable for Dyeing and Printing. GB 3318, issued January 7, 1870. (US 127,426)^{185,186}





Dye makers wanted their starting materials to be as pure as possible to avoid wasting potentially valuable regents on impurities.¹⁸⁷ The parent hydrocarbon for alizarin synthesis, anthracene, was a previously useless extract from coal tar that made it a cheap starting material for chemists. Large quantities were collected from tar distillers, who had no use for the product, until its value as a precursor for dye synthesis was known. Although cheap, the anthracene had to

¹⁷⁹ Liebermann and Graebe, Coloring Matters, GB 3850.

¹⁸⁰ Graebe and Liebermann, Improved Process of Preparing Alizarine, US 95465.

¹⁸¹ Graebe and Liebermann, Improvement in Dyes or Coloring-Matters from Anthracene, US 4321.

¹⁸² Caro, Graebe, and Liebermann, Improvements in Preparing Coloring Matters, GB 1936.

¹⁸³ Caro, Liebermann, and Graebe, Improvement in the preparation of coloring matters from anthracene, US 153536.

¹⁸⁴ Perkin, Improvements in the Manufacture of Coloring Matter Suitable for Dyeing and Printing, GB 1948.

¹⁸⁵ Perkin, Improvements in the Manufacture of Coloring Matter Suitable for Dyeing and Printing, GB 3318.

¹⁸⁶ Perkin, Improvement in the Manufacture of Coloring Matters from Anthracene, US 127426.

¹⁸⁷ Barnett, Anthracene and Anthraquinone, 74.

be distilled from pitch and purified to be useful.¹⁸⁸ Had there not been such an abundance of these hydrocarbons, the early synthetic dyes industry would have been very different.¹⁸⁹ To produce anthraquinone for a starting material, anthracene was oxidised under harsh conditions, often with chromic acid or potassium dichromate in acetic or sulfuric acid.^{190,191} Other oxidising agents like nitric acid in acetic acid could be used¹⁹² but were less common.

Today, about 80% of anthraquinone dye manufacture today is via anthraquinone sulfonic acids, similar to the route used by 19th c. chemists.¹⁹³ Although electrophilic substitution of anthraquinone is difficult due to the deactivating effect of the two carbonyl groups, anthraquinone sulfonation is an effective means to synthesise substituted anthraquinones.¹⁹⁴ The reaction between sulfuric acid and anthraquinone occurs at very high temperatures; modern literature cites 200 °C¹⁹⁵ but figures from 250-280 °C appear in the patent specifications.¹⁹⁶ With a harsher reagent like oleum (about 20% SO₃ in conc. H₂SO₄), the reaction takes place around 150 °C.¹⁹⁷ The products of sulfonation are anthraquinone sulfonic acids and water.¹⁹⁸ An alternative route, reversing the first two steps, was to sulfonate anthracene, which requires less extreme conditions without the carbonyl groups of anthraquinone, then oxidise it to anthraquinone sulfonic acid.

¹⁸⁸ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar," 585.

¹⁸⁹ Mellor and Cardwell, "Dyes and Dyeing 1775-1860," 278.

¹⁹⁰ Barnett, Anthracene and Anthraquinone, 73.

¹⁹¹ Perkin, "Methods of Analysis Employed in the Manufacture of Alizarin," 83.

¹⁹² Graebe and Liebermann, Improved Process of Preparing Alizarine.

¹⁹³ Bien, Stawitz, and Wunderlich, "Anthraquinone Dyes and Intermediates," 514.

¹⁹⁴ Gordon and Gregory, Organic Chemistry in Colour, 67.

¹⁹⁵ Venkataraman, *The Chemistry of Synthetic Dyes*, 59.

¹⁹⁶ Caro, Graebe, and Liebermann, Improvements in Preparing Coloring Matters.

¹⁹⁷ Bien, Stawitz, and Wunderlich, "Anthraquinone Dyes and Intermediates," 515.

¹⁹⁸ Venkataraman, *The Chemistry of Synthetic Dyes*, 51.



Figure 3-27 Anthracene sulfonation synthetic route also specified by Caro, Graebe, and Liebermann.

The patent says this reaction takes place from 100-150 $^{\circ}$ C.¹⁹⁹ After sulfonation, oxidation was done by boiling the product with manganese dioxide (MnO₂). The literature on alizarin synthesis indicates this route was used less often than anthraquinone sulfonation but no explanations are made as to why.

The product(s) of the sulfonation reaction, and how they could be manipulated, were analysed and debated. In anthraquinone sulfonation, anthraquinone-2-sulfonic acid initially forms, followed by a mixture of 2,6- and 2,7- disulfonic acids that increase in yield at higher temperatures. These disulfonic acids are the precursors to flavopurpurin and anthrapurpurin. They are more water-soluble than the monosulfonic acid that produces alizarin and can be separated from a mixture at this stage to increase the purity of the final product.^{200,201}



Figure 3-28 Anthraquinone-2,7-disulfonic acid (left) and anthraquinone-2,6-disulfonic acid. The precursors to anthrapurpurin and flavopurpurin in alizarin synthesis.

¹⁹⁹ Caro, Graebe, and Liebermann, Improvements in Preparing Coloring Matters.

²⁰⁰ Barnett, Anthracene and Anthraquinone, 176.

²⁰¹ Venkataraman, *The Chemistry of Synthetic Dyes* 60.

As chemists better understood the reactions taking place, they were able to manipulate the synthesis conditions to control the product. With less acid and lower temperatures, the monosulfonic acid that produces pure alizarin is the major product.²⁰² More acid and higher temperatures produces the di-sulfonic acids.²⁰³. Some used oleum for better reactivity at a lower temperature, a successful practice that became more common. The son of William Perkin, Arthur George Perkin, describes a "blue sulfonation", which yielded a higher ratio of alizarin, and a "scarlet sulfonation", which yielded a mixture of anthrapurpurin and flavopurpurin using more oleum and higher temperatures. The product mixture could be altered by manipulating the quantity of acid and the temperature of the reaction.²⁰⁴ There is not as much historical research on anthracene sulfonation, but it was thought the reaction produced anthracene-1-and -2-sulfonic acids,²⁰⁵ which modern research has confirmed.²⁰⁶ This means the route yields dye mixtures with a higher ratio of alizarin.

Oleum proved to be a useful reagent in anthraquinone sulfonation, but it is a dangerous substance due to its SO₃ content and extreme reactivity. Perkin developed his anthracene chlorination route to avoid having to use oleum, which had to be imported from Germany and at great expense due to its hazardous nature.²⁰⁷ The method exposed purified anthracene spread in lead chambers to chlorine gas, which was generated in wooden barrels by reacting calcium chloride with hydrochloric acid. Anthracene chlorination released hydrochloric acid gas,²⁰⁸ producing mostly 9,10-dichloroanthracene.²⁰⁹ The chlorine substituents made it easier to sulfonate the hydrocarbon, which was done by heating concentrated sulfuric acid to 130-150 °C and slowly adding the dichloroanthracene. When the reaction was complete it was diluted with water and boiled with MnO₂ to oxidise the anthracene, yielding anthraquinone sulfonic

²⁰² Perkin, Improvement in the Manufacture of Coloring Matters from Anthracene, 580.

²⁰³ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 37.

²⁰⁴ Perkin, "Methods of Analysis Employed in the Manufacture of Alizarin," 84.

²⁰⁵ Barnett, Anthracene and Anthraquinone, 62.

²⁰⁶ Gore, "Abnormal Substitution Reactions of Anthracene and Phenanthrene."

²⁰⁷ Travis, *The Rainbow Makers*, 183.

²⁰⁸ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar."

²⁰⁹ Gordon and Gregory, *Organic Chemistry in Colour*, 13.

acids²¹⁰ in a manner similar to the German chemists' patent for anthracene sulfonation and oxidation. Nearly ten years later, Perkin gave a lecture to the Royal Society where he said the temperature was raised to 260 °C after the dichloroanthracene was added to the acid, and that the acid was also responsible for oxidation to anthraquinone,²¹¹ indicating he continued making adaptations and improvements after he received his patent. He felt dyes produced by anthracene chlorination produced a more even colour and the anthraquinone sulfonation was too difficult to control,²¹² but because he had a monopoly on the process it is unclear whether anyone shared his opinion.

Regardless of the previous synthetic route, the final step of hydroxylation, historically called 'caustic fusion', was the same. It was done by adding either sodium or potassium hydroxide to the anthraquinone sulfonic acids with a small quantity of water, then heating it to around 180 °C;²¹³ modern literature says that the reaction can be carried out at 150-220 °C.²¹⁴ Closed, pressurised vessels were often used,²¹⁵ which would create a significant safety risk for the recreation. The reaction conditions, which varied from 180 °C for 24 hours in closed metal tubes²¹⁶ to 180-260 °C 'for about one hour' in an unspecified vessel,²¹⁷ vary significantly and make it difficult to design the re-creation. To obtain the dye, the reaction mixture was diluted with water and run into a vessel of acidified water, which neutralised the excess alkali and precipitated the dye. This mixture was boiled to agglomerate the colorant, then cooled, filtered, washed, and collected.²¹⁸

²¹⁰ Perkin, Improvements in the Manufacture of Coloring Matter Suitable for Dyeing and Printing, GB 3318.

²¹¹ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar," 589.

²¹² ibid., 597.

²¹³ ibid., 577.

²¹⁴ Bien, Stawitz, and Wunderlich, "Anthraquinone Dyes and Intermediates," 531.

²¹⁵ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 578.

²¹⁶ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar," 592.

²¹⁷ Caro, Graebe, and Liebermann, Improvements in Preparing Coloring Matters.

²¹⁸ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar."

The language of the patent specifications, and of supplementary historical publications on the topic, is often vague or incomplete to a modern reader, though whether this is the result of intentional omissions or presumably tacit knowledge is unknown. Out of the three synthetic routes documented in the patents, only anthracene sulfonation and oxidation has conditions plausible for the re-creation. The extreme temperatures in excess of 250 °C required for anthraquinone sulfonation and the hazards posed by oleum and chlorine put these routes beyond the scope of this project for the amount of specialist equipment and precautions required. The method published by Caro, Graebe, and Liebermann²¹⁹ still uses hazardous substances and high temperatures, and by necessity the re-creation must make adaptations like avoiding closed or pressurised vessels. The experimental work and a discussion of the process are included in Section 4.5.

3.7 The alizarin industry and 19th c. Scottish Turkey red

Synthetic alizarin is credited as the real success of the synthetic dyes industry.²²⁰ Its development had been fueled by demand from the Turkey red industry for more colorant, and they embraced the product. Industrial manufacture of synthetic alizarin began in 1869 by the mid-1870s had superseded madder in the Turkey red industry,²²¹ a transition captured in the AOE dyestuffs ledger.²²² Early product was consumed almost entirely by the Turkey red industries of Glasgow and Manchester.²²³ Dépierre provides figures for alizarin production and consumption for the late 19th c. The massive British textile industry had an insatiable appetite for dyes and in 1887 consumed 43% of the global alizarin output (Russia, the next highest, used a mere 18%). Figure 1-30 shows data for European alizarin production from 1869-1887. Output went from 1000 kg in 1869

²¹⁹ Caro, Graebe, and Liebermann, Improvements in Preparing Coloring Matters.

²²⁰ Mellor and Cardwell, "Dyes and Dyeing 1775-1860," 277.

²²¹ Travis, "Between Broken Root and Artificial Alizarin: Textile Arts and Manufactures of Madder," 17.

²²² Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.

²²³ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar," 597.

to 24,000,000 kg in 1890, with Germany producing the vast majority by that time. By the 1890s, some Glasgow dyers used 1500 kg of 10% alizarin per day.²²⁴



Figure 3-29 European production figures for 20% alizarin from Dépierre.

When Perkin agreed with the German chemists in 1870 to divide the alizarin market, he acquired exclusive rights over the biggest alizarin market in the world.²²⁵ He use the anthracene chlorination process at his Greenford Green works, which he noticed few continental manufacturers did,²²⁶ though his bias toward the process eventually affected his market share. German researchers had worked out the required synthesis conditions to obtain alizarin, flavopurpurin, and anthrapurpurin, whereas Perkin's process yielded primarily anthrapurpurin and could not meet the demand for the other dyes. By 1873, the demand for synthetic alizarin was higher than the production output of Perkin & Sons.²²⁷ Competition arrived on the market as German product, imported illicitly by labelling it as madder extract or garancine, rendering patent protection nearly useless. In 1873, Friedrich Bayer, a former dyestuffs merchant who had founded a chemical works in Elberfeld, invited representatives from the largest

²²⁴ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 80-82.

²²⁵ Holme, "Sir William Henry Perkin: a Review of His Life, Work and Legacy," 244.

²²⁶ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar," 597.

²²⁷ Cliffe, "Pacta Conventa- the Last Days of Perkin & Sons," 318.

Scottish Turkey red firms to a lavish dinner at his works to curry business. That year, increased market competition drastically reduced the market price of alizarin,²²⁸ a shift unfortunately not documented by the AOE dyestuffs ledger because it begins that year.²²⁹

Unable to meet the demand for synthetic alizarin without expanding the Greenford Green works, Perkin and his brother, Thomas Dix Perkin, decided to sell. It was purchased in 1874 by the firm Brooke, Simpson & Spiller, who within the year had sued the Perkins for misrepresentation. The dispute appears to have arisen from tensions between the firm and the Perkins, who agreed to a six-month consultancy, and from gross mismanagement and the elimination of cost-saving measures on the part of the new owners, such as extracting useful reagents from waste material. The suit was unsuccessful and Brooke, Simpson & Spiller sold their rights to tar distillers Burt, Bolton & Haywood in 1876. Since the Greenford Green site's capacity was limited, they later moved most of the operation to a new factory at Silvertown.^{230,231,232} The disastrous sale meant that by 1880, less than 10% of the demand for alizarin in Britain was being met,²³³ making it even easier for Turkey red dyers to look abroad for their supply.

In the mid-1870s, the demand for raw materials and the ability to supply them resulted in a market flooded with low-quality anthracene, driving down the price of alizarin and frustrating all manufacturers. To relieve the pressure, the British and Germans came to an agreement in 1881 called The Alizarin Convention, forming a cartel that included all major European alizarin producers. This set a lowest price for all alizarin products and set quotas for each company based on output in 1881.²³⁴ Burt, Boulton & Haywood were the only British members. The patents they had acquired with Greenford Green were set to expire in 1883, raising the concern that competition from other British firms was imminent. To protect their interests, the Alizarin Convention tried to

²²⁸ Travis, *The Rainbow Makers*, 192-195.

²²⁹ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.

²³⁰ Rowe, "The Life and Work of Sir William Henry Perkin," 559.

²³¹ Cliffe, "Pacta Conventa- the Last Days of Perkin & Sons."

²³² Cliffe, "Litera Scripta Manet - the Alizarin Debacle."

²³³ Welham, "The Early History of the Synthetic Dye Industry," 149.

²³⁴ Travis, The Rainbow Makers, 201-202.

extend the patents and consumer contracts with a 50% price increase. Instead of being intimidated into cooperation, consumers like the Scottish Turkey red firms decided to source their own alizarin, forming The British Alizarine Company in 1883 with £200,000 in capital. They bought Silvertown from Burt, Boulton & Haywood and began manufacture at a capacity of 600-700 tons per year, about one-fifth of what British textiles were consuming, and reduced the price from 2s. 6d. to 1s. 10d. per lb. at 20% strength. They managed to regain around half the market share by 1885, (see Figure 3-30) when the Alizarin Convention broke down and the price fell to 11d. per lb.²³⁵



Figure 3-30 Source of alizarin used at Alexandria Turkey red works, 1880-1885. The Alexandria works in Dumbarton used over two million pounds of 10% alizarin per year, which was approximately one-sixth of British consumption.²³⁶

The British Alizarine Company survived partly through the market of its shareholders and by improving the quality of its product.²³⁷ The post-Convention market was difficult as prices for alizarin plummeted; in the AOE dyestuffs ledger the price per pound for alizarin is 1s 4 $\frac{1}{2}$ d. at the beginning of 1885 and 9 $\frac{1}{2}$ d. at the end of 1886²³⁸ (see Figure 3-16). Poor-quality anthracene still plagued the British industry, decreasing yields and profit margins. In 1886,

²³⁵ Welham, "The Early History of the Synthetic Dye Industry," 149.

²³⁶ ibid., 150.

²³⁷ ibid., 149.

²³⁸ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.

Archibald Orr Ewing became chairman of British Alizarine and succeeded in making the firm productive and profitable again,²³⁹ though an 1887 survey of dye consumers showed that 90% of the dye used in the West of Scotland was of German origin.²⁴⁰ To compete with the increased reputation and quality of the British Alizarine product, German manufacturers attempted to buy off the firm on terms they found completely unacceptable. They then proposed another cartel like the Alizarin Convention, with terms that did not interest British Alizarine, which was effectively founded as an alizarin co-op for British dyers. In May 1900, the two groups came to an agreement of terms for a second Alizarin Convention, again setting prices and quotas.²⁴¹

In Glasgow, British alizarin was traded through Henderson, Hogg & Co, who were based at 26A Renfield Street in the late 19th c. This was the firm of Robert Hogg, Perkin's close friend and business associate, who wrote to Perkin in a letter that synthetic alizarin was more readily adopted by Turkey red dyers than printers.²⁴² The German industry was represented in Glasgow from 1875, when Friedrich Bayer set up a distributor, Bryce & Rumpff, for his product.²⁴³ The overall impression from the literature is that, based on quality and price fluctuations, Scottish Turkey red dyers consumed both British and German synthetic alizarin.

3.8 Dyeing Turkey red

Compared to the preparatory steps for the fibres, actually dyeing Turkey red was relatively simple. The cotton by this point had been prepared with oil, possibly tannins, and then aluminium. It was important to ensure the fabric was thoroughly washed of excess aluminium so that a lake did not form in the dye bath.²⁴⁴ After dyeing the final step was clearing, which removed any compounds not securely bound to the fibres.

²³⁹ Fox, Dye Makers of Great Britain 1856-1976, 117-118.

²⁴⁰ Travis, "Colour Makers and Consumers: Heinrich Caro's British Network," 316.

²⁴¹ Welham, "The Early History of the Synthetic Dye Industry," 150.

²⁴² Cliffe, "The Dyemaking Works of Perkin & Sons," 317.

²⁴³ Travis, *The Rainbow Makers*, 197.

²⁴⁴ Knecht, Rawson, and Loewenthal, A Manual of Dyeing, 702.

When madder was used, the quantity employed by Turkey red dyers varied somewhat, generally around two pounds per pound of cotton being recommended.^{245;246;247;248} The ground madder was placed in the requisite volume of cold water, with chalk and often with bullock's blood as well. Turkey red methods do not say to treat the madder in any particular way, e.g. soaking it in water prior to dyeing, but this may have been a tacit understanding for an experienced madder dyer. For methods that use synthetic alizarin, dyers employed around 150-200 g of the 10% strength per kg²⁴⁹ or 75-90 g/kg of the 20% paste.²⁵⁰ The requisite calcium was usually added in the form of chalk (CaCO₃) if not already present in the water supply. The bath was prepared in much the same manner with the alizarin and calcium dispersed in cold water, then the cotton added.

Dyeing, relative to the lengthy preparation of the fibres with oil and aluminium, simply involved putting the dye and calcium in a sufficient volume of water, adding the fibres, and heating it. The outcome was certainly much more exciting, however, as the white cotton went into the bath and emerged a brilliant, deep red hue. The dye bath was heated to a low boil over the course of an hour, then held at temperature until the colour was satisfactory, about 1-2 hours more.²⁵¹ Hummel says to keep the bath cold for 30 minutes, then slowly raise the temperature to 70 °C over an hour and hold until the colour is developed.²⁵² It was known that hydroxyanthraquinones really start to dye the fibres around 70-80°C,²⁵³ which is consistent with the solubility of alizarin in

²⁴⁹ Hummel, *The Dyeing of Textile Fabrics*, 443.

²⁵² Hummel, *The Dyeing of Textile Fabrics*, 443.

²⁴⁵ Mémoire contenant le procédé de la teinture du coton rouge-incarnat d'Andrinople sur le coton filé.

²⁴⁶ Vitalis, Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles, 242.

²⁴⁷ Henry, "Considerations Relative to the Nature of Wool, Silk, and Cotton, as Objects of the Art of Dying; on the Various Preparations, and Mordants, Requisite for These Different Substances; and on the Nature and Properties of Colouring Matter. Together with Some Observations on the Theory of Dying in General, and Particularly the Turkey Red," 386.

²⁴⁸ Haussmann, "XLIII. Observations on Maddering; Together with a Simple and Certain Process for Obtaining, with Great Beauty and Fixity, That Colour Known Under the Name of the Turkey or Adrianople Red."

²⁵⁰ Dépierre, Traité de la teinture et de l'impression des matières colorantes artificielles. 2me partie, L'alizarine artificielle et ses dérivés, 395.

²⁵¹ Ure, A Dictionary of Arts, Manufactures, and Mines, 796-797.

²⁵³ Crookes, A Practical Handbook of Dyeing and Calico-Printing, 247.

water mentioned earlier. After the colour was satisfactory, the cotton was removed and rinsed, then washed and dried prior to the final clearing step. This is where blood, discussed in Section 2.10.1, was included, and although not an essential ingredient, it appears to have had a useful auxiliary role improving the quality of the dyeing. When using madder or *garancine*, the cotton had to be washed of particulates as well as excess dye.

The clearing step was the final stage to finish dyed Turkey red cotton. The purpose of the step was to remove excess compounds that had not fully adhered to the fibres, as well as colour impurities. Clearing was believed to remove yellow-toned compounds from madder that interfered with the colour, so products like *garancine* did not need as much clearing.²⁵⁴ With the adoption of synthetic alizarin, dyers also found an even less severe clearing was required²⁵⁵ as fewer natural impurities were present, though the step was never abandoned.

Early methods had the cotton boiled, for a period of hours with varying duration, in a covered vessel with a bath of water or soda ley and dissolved olive oil soap.^{256,257} Bran was also used as an alternative,^{258,259} but soap is more common. The vessel was eventually changed to a closed, pressurised system that improved the fastness and lustre of the product,²⁶⁰ probably by raising the temperature at which the solution boiled. Tin salts, usually tin(II) chloride, were sometimes added to the clearing step to improve the colour as well,²⁶¹ but were not considered essential. Chemists in the 19th c. believed the salts formed a quantity of lake with tin rather than aluminium, possibly replacing iron impurities,²⁶² or else as tin soaps on the fibre without an attached lake.²⁶³

²⁵⁴ ibid., 274.

²⁵⁵ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 587.

²⁵⁶ Berthollet, *Elements of the Art of Dyeing*, 157.

²⁵⁷ "V. Account of the Process Followed by M. Pierre Jacques Papillon for Dyeing Turkey Red."

²⁵⁸ Haussmann, "XLIII. Observations on Maddering; Together with a Simple and Certain Process for Obtaining, with Great Beauty and Fixity, That Colour Known Under the Name of the Turkey or Adrianople Red," 264.

²⁵⁹ Ure, A Dictionary of Arts, Manufactures, and Mines, 793.

²⁶⁰ Schaefer, "The History of Turkey Red Dyeing," 1413.

²⁶¹ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 590.

²⁶² ibid., 591.

Many of the hydroxyanthraquinone dyes, including alizarin and purpurin, are sensitive to pH (see Figure 3-4). In a clearing bath with a carbonate solution, exposure to the alkali may account for some of the desired shift in colour as well as removed impurities. Olive oil soap was made from olive oil and lye, so the pH may have been raised even without the use of carbonate. The sodium fatty acids from the soap may have replenished or augmented any fatty acids removed from the fibre during the clearing process. The exact role of the tin salts has not been fully understood, and their use appears to be auxiliary rather than requisite based on their inconsistent appearance in Turkey red methods. For this research, clearing in a pressurised vessel was not possible due to inadequate equipment and the attendant safety risk. A trial with a domestic pressure cooker resulted in a violent emission of purple caustic slime from the safety vent valve, but in theory a larger vessel may be practicable. The earlier covered vessel method was used since it was historically suitable and overall quality was a secondary concern in this work.

3.8.1 Lake complex

It has long been known that the complex that creates the brilliant red colour in Turkey red is a lake of alizarin, aluminium, and calcium,²⁶⁴ though a more comprehensive definition includes the other hydroxyanthraquinone dyes that complex as well. A variety of structures for this complex have been proposed, such as the one from Fierz-David and Rutishauser below, published in the 1940s.²⁶⁵

²⁶³ Parks, "The Chemistry of Turkey Red Dyeing," 503.

²⁶⁴ Hummel, *The Dyeing of Textile Fabrics*, 450.

²⁶⁵ Fierz-David, "Composition and Constitution of Turkey Red," 57-58.



Figure 3-31 Lake structure proposed by Fierz-David and Rutishauser.

Decades later, in their extensive research on alizarin lakes, Kiel and Heertjes were dissatisfied with the Al-O-Ca-O-Al bridge suggested in the former model.²⁶⁶ Their investigation by infrared spectroscopy in the 1960s proposed the following structure with a 1:1:2 ratio of Ca-Al-alizarin, which does not specifically place the calcium ions within the complex:



Figure 3-32 Lake structure proposed by Kiel and Heertjes.

In the early 1990s, Wunderlich et al. did a crystallographic analysis of the complex, but as it was crystallised from a DMF/water mixture, ²⁶⁷ the conditions are not representative of the Turkey red dye bath. Research shortly afterward by Soubayrol *et al.* proposed a 'sandwich' type structure from an aqueous

²⁶⁶ Kiel and Heertjes, "Metal Complexes of Alizarin I -the Structure of the Calcium-Aluminium Lake of Alizarin," 78.

²⁶⁷ Wunderlich and Bergerhoff, "Konstitution und Farbe von Alizarin-und Purpurin-Farblacken."

medium with the same ratio found by Kiel and Heertjes, but one that accounts for the position of the calcium ions as well.^{268,269}





Figure 3-33 'Binuclear closed structure' Turkey red lake complex by Soubayrol et al. Image from Delamare,²⁷⁰ published online at http://books.openedition.org/pcjb/docannexe/image/605/img-16.jpg.

The results of their analysis by ²⁷Al solid-state NMR (ssNMR) found aluminium had a coordination number of six in the complex and proposed the 'binuclear closed structure' pictured above. The complex also includes water molecules, whose presence could be detected based on the analytical technique used. Analysis of replica Turkey red by ²⁷Al ssNMR is presented in Section 6.8 and compared to these findings. This project does not attempt to characterise the lake complex, but based on the chemistry of the dyeing process, the work of Soubayrol *et al.* is used as a reference for the *in situ* analysis of the aluminium in this research.

3.9 Summary

The transition from naturally sourced dyes to industrially manufactured ones marked a huge shift in textile production, chemistry, and technological progress. Turkey red was the first established dyeing technique to be affected by the transition, when madder roots were replaced with synthetic alizarin, but overall the change in ingredients did not fundamentally alter the chemistry of the process. The vast quantities of madder required by the Turkey red industry fuelled the synthesis of alizarin, which in turn sparked the expansion of the synthetic dyestuffs industry when chemists realised it was possible to replicate industrially valuable compounds. There is a large body of published research on

²⁶⁸ Soubayrol, Dana, and Man, "Aluminium-27 Solid-State NMR Study of Aluminium Coordination Complexes of Alizarine."

²⁶⁹ Soubayrol, "Préparation et étude structurale des complexes formés entre l'aluminium et l'alizarine: Importance de la nature du solvant et de la base utilisés sur le degré de condensation de l'aluminium et l'agencement moléculaire."

²⁷⁰ Delamare and Monasse, "Le rôle de l'alun comme mordant en teinture. Une approche par la simulation numérique."

madder extracts and madder-dyed textiles, but relatively little work has been done thus far on the early synthetic dyes, including alizarin. The analysis of dye components on textile fibres allows for a better understanding of the light fastness properties of the object and whether especially sensitive compounds are present. For Turkey red, detecting dyes that are specific to synthetic alizarin helps determine the age of the textile based on when it could have been dyed.

This chapter discusses the rise of the synthetic alizarin industry in the late 19th c. and its connections to Scottish Turkey red, as well as how the alizarin was actually produced. This is used for the historical re-creation aspect of this project, which aims to learn more about how processes were documented and communicated, and what products they yielded. Although considered a 'natural' dyeing technique because of its association with madder, the rise of synthetic alizarin and its adoption by dyers shows this is a misconception. The discussion of individual dye components, specifically anthrapurpurin and flavopurpurin, is applied to the chromatographic analysis of replica and historical Turkey red in Chapter 7.

Dye	Structure	C.I. Number	C.I. Description	
Natural alizarin/ ruberythric acid	1,2-di- hydroxyanthraquinone, ß- 2-alizarin primeveroside	75330	Natural Red 6, 8, 9, 10, 11, 12	
Natural purpurin	1,2,4-tri- hydroxyanthraquinone	75410	Natural Red 16, 8	
Natural pseudopurpurin	1,2,4-tri- hydroxyanthraquinone-3- carboxylic acid	75420	Natural Red 14, 9, 8	
Alizarin	1,2-di- hydroxyanthraquinone	58000	Mordant Red 11	
Purpurin	1,2,4-tri- hydroxyanthraquinone	58205	Mordant dye	
Pseudopurpurin	1,2,4-tri- hydroxyanthraquinone-3- carboxylic acid	58220	Pigment	
Flavopurpurin	1,2,6-tri- hydroxyanthraquinone	58240	Mordant Red 4	
Anthrapurpurin	1,2,7-tri- hydroxyanthraquinone	58255	Mordant dye	
Rubia tinctorum	-	-	Natural Red 8	
Rubia peregrina	-	-	Natural Red 8	
Rubia cordifolia	-	-	- Natural Red 16	
Garancine	-	-	Natural Red 10	

Table 3-1 Table of natural and synthetic dyes discussed in this chapter.C.I. data taken from The Colour Index, 3rd edition.

²⁷¹ Society of Dyers and Colourists, *Colour Index*.

4 Re-creation of Turkey red and related materials following historical processes

The practice of re-creating historical materials and processes as a means to understand both objects and techniques was discussed in the introduction as one of the significant aspects of this project, which aims to replicate and characterise dyed Turkey red calico and two main ingredients, Turkey red oil and alizarin dye. One of the research questions for this project addresses how processes are communicated through text and across time, and whether they contain sufficient information to enable a successful re-creation. The material discussed thus far on the dyeing of Turkey red, making Turkey red oil, and synthesising alizarin, is put into effect here to experimentally test whether the desired materials can be obtained following historical processes. This chapter describes and discusses the re-creations of Turkey red oil, dyed Turkey red, and synthetic alizarin attempted for this project.

4.1 Replica Turkey red oil

The re-creation of Turkey red oil following the method from Scheurer-Kesner in Knecht¹ was undertaken to experience the process of making the oil as Turkey red dyers might have, and to obtain a sample for analysis and comparison. Supplementary information was taken from a modern study on isoricinoleic acid² when the historical method did not specify a solution concentration. As discussed in Section 2.5, based on the review of method to make Turkey red oil, three parts castor oil and one part sulfuric acid were left overnight to react with the mixture not allowed to rise above 35 °C. The oil was washed with warm water and then aqueous sodium sulfate per Scheurer-Kesner's method, then neutralised.

There is little physical description of the process in the literature and a few attempts were needed before an acceptable sulfated castor oil was obtained from this exercise. One preliminary batch was not allowed given enough time to react and yielded an inhomogeneous product. Another was not sufficiently

¹ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 160.

² Ahmad and Singh, "Surface Active Properties of Sulfonated Isoricinoleic Acid."
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neutralised and when applied to calico, the excess acid in the oil caused holes to appear in the fabric.



Figure 4-1 Trial batches of replica Turkey red oil. Both batches are insufficiently neutralised and contain excess sulfuric acid, indicated by turbidity (left) and inhomogeneity (right).

4.1.1 Reagents and equipment

Ultrapure water at 18.2 M Ω resistivity (Millipore Direct-Q UV 3) was used for preparing neutralisation and washing solutions. Castor oil (general purpose grade), anhydrous sodium sulfate (Na₂SO₄, reagent grade), and pH 1-14 indicator paper were purchased from Fisher; concentrated sulfuric acid (H₂SO₄, ACS grade 95.0%-98.0%) was purchased from Sigma-Aldrich; sodium hydroxide (NaOH, analytical) was purchased from Acros Organics. All vessels used to prepare solutions and sample were made of borosilicate glass. The stir rods, thermometer, and separating funnel were also made of glass.

4.1.2 Experimental re-creation of Turkey red oil

Castor oil (54.4 g, ca. 60 mL) was weighed in a glass beaker and concentrated H_2SO_4 (18.1 g) was weighed in a separate flask. Portions of acid about 1 mL in volume were added dropwise with a pipette to the oil while stirring it with a glass rod. The temperature was monitored with a glass thermometer after each addition of acid to ensure it did not exceed 35 °C. The reaction with the acid caused the oil to become dark brown and opaque, as described in the literature, and although still viscous it was less so than the castor oil. Acid was added and stirred thoroughly approximately every 20 minutes over a period of 4.5 hours so

evolved heat could disperse between additions. The single-phase mixture was left to react overnight.



Figure 4-2 Castor oil before (left) and after the sulfuric acid was added.

Per Scheurer-Kestner's method, 400 mL of ultrapure water was heated to 40 °C in a large beaker. The oil was added to the water and stirred, immediately changing from tarry, greenish brown to creamy pale yellow. Within a few minutes, two phases became distinct—a milky white aqueous layer and an opaque yellow oil layer on top, similar to descriptions in the literature. The left image in Figure 4-3 shows the separating phases in the background and a portion that has been transferred into a separating funnel. When stirring and transferring the oil, a fatty odour was present and the viscosity after washing had been further reduced.



Figure 4-3 Washing the sulfated oil of excess acid (left) and the oil separating from the sodium sulfate wash.

When the mixture in the funnel had separated into two distinct phases, the lower aqueous layer was drained away until a portion of the oil layer passed through the funnel, and then the oil transferred to a beaker. Anhydrous Na_2SO_4 (24.2 g) was dissolved in ultrapure water (200 mL) and the oil added to this solution and mixed well. It was left overnight, stirred again in the morning, and then transferred to a separating funnel and left to separate again before the aqueous layer was drained off.

To make a neutralising solution, NaOH (4.2 g) was weighed and dissolved in ultrapure water (30 mL). This is less concentrated than the 50% (w/v) solution specified by Ahmad et al.,³ and was chosen so the neutralisation progressed more slowly and the pH could be monitored. The pH was checked by adding a drop of oil to about 2 mL of ultrapure water, mixing it, and testing with pH 1-14 indicator paper. Initially, the paper indicated the pH was 1. At this point, the oil was cloudy, butter yellow, and much less viscous than castor oil.

Around 0.3 mL of NaOH solution at a time was added dropwise to the oil and stirred after each addition with a glass rod. The first few additions produced no effect, but after about 1.5 mL was added the oil became clear where the alkali made contact, then clouded again after stirring. To test the pH, a drop of oil was added to 1 mL of water and checked with indicator paper. As the pH approached neutral, the oil became clearer, slightly more viscous, and the colour darkened to a golden yellow. These physical changes were consistent with those discussed in the review, and corresponded to the decrease in free acid. The neutralisation was stopped when a drop of oil in water showed the pH was 7. Final pH was confirmed with a pH 6.0-7.7 test strip from Fisher. The entire neutralisation process took around an hour to complete, though this was with a very slow addition of base and frequent pH checks.



Figure 4-4 Neutralising sulfated castor oil From left: Before adding NaOH (left), during the process (centre), and the finished oil (right).

4.1.3 Discussion

The successful replica Turkey red oil did not separate, become turbid, or create holes in the calico to which it was applied. The experimental re-creation shows how few details of the process are provided in historical texts, making it difficult at times to determine quantities or concentrations to use. Chemists in the 19th c. did not have pH indicator paper to confirm the excess acid had been neutralised, though the fairly obvious physical changes seen in this re-creation were probably sufficient for an experienced manufacturing chemist to recognise whether the reaction was proceeding as intended. The few physical descriptions in the literature were recognised during the experiment, indicating consistency with the historical product. This sample is analysed and compared to historical and modern commercial samples of Turkey red oil in Chapter 5 to determine and compare their compositions.

4.2 Replica oiled calico

Samples of calico prepared with Turkey red oil (TRO) were made to study the bonds between fatty acid and cellulose without aluminium or dye present, simplifying the data. The three sample sets presented in this section were designed to test the variables of oil type, concentration, effect of heat exposure, and the effect of washing on the oiled calico. The results from the analysis of these samples is used to characterise the bond, and compared to results from historical and replica Turkey red to confirm similarity or identify any further changes. Results from the analysis of these samples by Fourier 184 Chapter 4 • Re-creation of Turkey red and related materials following historical processes transform infrared spectroscopy (FTIR) and solid-state nuclear magnetic resonance spectroscopy (ssNMR) are presented in Chapter 6.

4.2.1 Reagents and preparation

Ultrapure water at 18.2 M Ω resistivity (Millipore Direct-Q UV 3) was used to prepare solutions and rinse. To dry the samples, an Espec environmental chamber with the humidity controls turned off and a Heraeus accelerated ageing oven were used. Sodium oleates and ricinoleic acid were purchased from Sigma-Aldrich. Turkey red oil sodium salt (microscopy grade) was purchased from Fluka, replica Turkey red oil was made as described in Section 4.1.2, and a historical Turkey red oil sample was provided by Debbie Bamford (DB TRO). Coco-oleic 2-ethylhexyl ester estolides were provided by Dr Steven Cermak of the United States Department of Agriculture. Following historical methods, solution concentrations were measured by density with a Twaddle hydrometer (0-24 $^{\circ}$ Tw.) from Brannan. Initial scouring was done with commercial soda crystals (Na₂CO₃) and liquid soap flakes from Dri-Pak. Soda solutions for washing samples were prepared with sodium carbonate from Sigma-Aldrich.

4.2.1.1 Scouring

The cotton used for these samples was organic calico purchased from Whaleys Bradford (Bradford, England, UK). A bath was prepared in a large, stainless-steel kettle with tap water (8 L) and commercial soda crystals (40 g), following a scouring recipe for cotton from Fereday.⁴ The cotton was simmered for one hour, during which the water turned dark yellow-brown and developed a waxy, fatty odour. This was drained off and replaced with a fresh scouring bath of Na₂CO₃ (5 g/L (aq.)). The second bath was simmered for 90 minutes, after which the water was light brown and slightly turbid. The calico was removed and washed in a domestic washing machine on the cotton setting (60 °C). To avoid introducing detergents to the fibres, the calico was washed with liquid soap flakes and then air dried prior to use.

⁴ Fereday, *Natural Dyes*, 21.

4.2.2 Sample set A01: Oiled calico test of treatments and time points

This sample set tests different oil treatments to evaluate whether the composition of the oil influences the amount bonded to the fibre and the effect of the heat treatment on oil uptake. To assess the effect of steaming, one time point was duplicated and subjected to an additional steam treatment. A control set for heat was left at room temperature to determine the extent of the reaction without heat. The oil concentration and oven temperature (60 $^{\circ}$ C) remained constant. The oil treatments were [1] Fluka TRO and [2] replica TRO with [3] water as a control. Knowing the variable water content of Turkey red oil on a production scale would be valuable to calculate optimal dilution for efficiency, but it does not apply to the scope of this work. To obtain useful samples for characterisation, an excess of oil was used and mixed with water at a 1:1 ratio to ensure a sufficient quantity was present. To study the effect of heat, the time points selected covered a longer period of time than was practiced in 'new' Turkey red processes in case the changes were subtle. They were placed in the oven and removed after 1, 4, 10, and 21 days. The samples at room temperature were left for 30 days to compensate for the cool, damp Glasgow climate.

Swatches of scoured and washed unbleached cotton calico were cut into 3 cm x 5 cm strips and separated into three treatment groups. For [1], Fluka TRO (2.05 g) was thoroughly mixed with water (2.06 g). For [2], replica TRO (2.05 g) was mixed with water (2.03 g). The control samples [3] were prepared with only water. Each set of samples was placed in a glass dish and the treatment applied dropwise with a pipette until each swatch was saturated. The excess oil was removed by gently squeezing the samples under finger pressure, then they were placed in clean glass dishes separated by treatment and put in the oven.

At each time point, samples were removed from the oven and rinsed in flowing water until the runoff, initially opalescent and frothy, was transparent and no longer contained bubbles, then the pieces left to air dry. With progressing time points, the oiled samples were stiffer and yellowed upon removal from the oven. These changes mostly disappeared after washing, save for some slight yellowing on the longer samples. Before washing, the calico felt greasy and increasingly tacky with longer heat exposure. All samples had a fatty smell. The second set of 4-day samples was not washed, but placed on a wire rack in a stainless steel pressure cooker (Fagor 4 qt) with 300 mL water and heated to an operating pressure of 15 psi for 90 minutes. Afterward, the samples were rinsed in flowing water and air-dried. In Table 2, pre- and post-treatment weights show that oiled samples increased more than the slight variation seen in the controls. The increase in weight generally corresponds to the duration of heat treatment.

Treatment	Ambient	1-day	4-day	4-day+steam	10-day	21-day
[1] Fluka	4.8	6.9	4.6	7.2	17.9	26.5
[2] Replica	7.0	9.6	9.3	11.2	17.4	25.0
[3] Water	no value	0.4	0.7	1.0	1.4	1.0

Table 2 Percent weight increase of samples after oil treatment (weights in g).



Figure 4-5 Calico samples (A01 4-day) prior to washing. From left: Water [3], replica Turkey red oil [2], Fluka Turkey red oil [1].



Figure 4-6 Calico samples (A01 4-day) after washing away the excess oil. Same order as above.

4.2.3 Sample set A02: Oiled calico test of concentration and washing

This sample set was designed to examine the effect of the oil concentration, and whether washing with water or soda ley (aq. Na_2CO_3) had an impact on oil uptake. The samples were treated with diluted replica TRO and controls prepared with water. Treatments of 10%, 25%, and 50% TRO in water (w/w, not accounting for the water content of the oil) were prepared according to Table 3 and the samples were placed in the oven at 60 °C.

Oil (g)	0.76	1.25	1.52
Water (g)	6.79	3.79	1.56
Conc.	10.1%	24.8%	49.4%

Table 3 Calculation of varied oil concentration treatments in water.

After three days, the samples were removed, washed thoroughly in flowing water, and left to air dry. Each sample was cut in half to make a 'salt' set, which was given an additional washing with soda ley. These samples were washed individually in 40 mL aliquots of 2 °Tw aq. Na₂CO₃ by working them vigorously by hand for 30 seconds, repeated three times each, and then rinsing well in flowing ultrapure water. The samples were placed in the oven at 60 °C to dry for three hours.

4.2.4 Sample set A05: Oiled calico test of time points with isotope-tagged oil

To prepare samples for analysis by a complementary technique to FTIR, the A05 sample set was designed using isotopic oleic acid for analysis by ¹³C ssNMR, an *in situ* tool that provides more details about the oil-cellulose bond type—e.g. ester, carboxylic acid. The strong bulk cellulose signal relative to the amount of oil present, and the low natural abundance of ¹³C meant that the C1 signal of the fatty acid had to be amplified with an isotope, though for cost purposes it had to be diluted to 30% w/w with olive oil. The discussion in Section 2.3 mentioned the occasional treatment of olive oil with oleic acid to make it more *huile tournante*, so this preparation is consistent with historical practice. Isotopic oleic acid-1-¹³C (Sigma-Aldrich, 99% ¹³C) (669 mg) was mixed with olive oil (1.6 g, Cooperative l'Oulibo) and two drops of ultrapure water to assist the emulsion. The mixture was creamy, opaque, and greenish yellow.

To determine how quickly the bonds formed, time points of 0, 3, 12, 24, and 72 hours were chosen. If the 0 h time point (sample treated and immediately washed, no heat) had oil present, this indicates rapid uptake by the fibres. Two control sample sets were prepared using only water and only olive oil (no oleic acid). Calico swatches 3 cm x 2 cm were placed in glass dishes and the treatment applied dropwise until saturated. The 0 h samples were then rinsed individually in aliquots of 2 °Tw aq. Na₂CO₃ until the runoff was clear and not frothing, then air-dried. The heated samples were placed in the oven at 60 °C, removed at the appropriate time points, and washed and dried in the same way.

4.2.5 Sample set A06: Treatment test of oiled calico samples

The purpose of this sample set is to compare the FTIR spectra of oiled calico treated with Turkey red oils and known reference compounds like ricinoleic acid to see if the oils and fatty acids produce the same spectral bands. Treatments for this sample set include Fluka TRO, replica TRO, DB TRO, dry sodium oleate, ricinoleic acid, estolides, and water as a control. For the TRO samples, about 0.5 g of oil was diluted to 2.0 g using ultrapure water (ca. 25% conc.) and mixed well; the DB sample was more difficult to disperse than the others. For ricinoleic acid and the estolides, about 0.5 g was weighed and a drop of water added to test solubility, which was negligible. A drop of 2 °Tw aq. sodium carbonate was then tested in each. The ricinoleic acid produced a finely dispersed white precipitate of sodium ricinoleate while the estolides were discarded without further preparation because they were too inconsistent with the Turkey red dyeing process to yield useful results. About 0.5 g of dry sodium oleate was weighed and diluted with 2.2 g ultrapure water to make a clear yellow solution.

Two samples apiece were treated and the controls prepared with ultrapure water. The samples were placed in separate glass dishes in a Heraeus accelerated ageing oven at 60 °C for 24 hours, then removed. The samples were washed in flowing water until they no longer felt slimy, which was straightforward for the TRO samples, the sodium oleates, and the control. The ricinoleic acid/sodium ricinoleate sample was persistently sticky and required being rinsed in 2 °Tw soda ley and then flowing water before it lost this quality. The samples were left to air dry and room temperature. The difficulty in both

treating and rinsing the ricinoleic acid calico samples is intriguing and may indicate something about why Turkey red dyers appear to have never adopted using purified fatty acids when Turkey red oil was so much easier.

4.3 Dyeing Turkey red

The culmination of this research on the process and chemistry of Turkey red dyeing is the dyeing re-creation following a 19^{th} -c. process. The discussion of the methods in Chapter 1 identified Hummel's 'new' process as a sound representative recipe, taking into account information from other sources as well. One of the significant messages in the literature is that Turkey red cannot be learned from a book, but must be taught. This re-creation tests this assertion, since there are no surviving dyers from the 19^{th} c. industry to demonstrate the process. The calico was treated in the same manner prior to the dyeing step, when the samples were divided in two groups, one dyed with synthetic alizarin and one with madder. The madder dye bath was prepared for dyeing based on historical recipes using madder (Chapter 3). For clarity, the term 'alum' is used here to indicate potassium aluminium sulfate dodecahydrate (KAl(SO₄)₂•12H₂O). The re-creation is presented in three parts—first, the reagents used and a version of Hummel's scaled-down process in modern terms, followed by a description and then a discussion of the re-creation.

In this section, the historical process from Hummel is summarised in a modern experimental format along with a list of materials used in the recreation. The original text is included in Appendix B. This re-creation incorporates the five fundamental ingredients (cotton, oil, aluminium, calcium, alizarin/madder) in the prescribed order of application for Turkey red. To keep the experimental and analytical work manageable, it does not include variations like ruminant dung, tannins, blood in the dye bath, or alternative ingredients like aluminium acetate. It is recommended these alternative preparations are explored to determine their impact on the quality of the product, along with testing the efficiency of reagent use for an optimisation of the process. To assist the characterisation and achieve a successful dyeing, quantities of reagents are sometimes used in excess, lowering the efficiency of the process, though with the small scale of this work this is not a significant concern. This re-creation of Turkey red was designed to yield samples to test analytical techniques in order

to characterise the oil on the fibres and identify dye molecules, two of the research questions for this thesis. Analysis of the oil by FTIR is presented in Chapter 6 and of the dyes by ultra high performance liquid chromatography with photodiode array detection (UHPLC-PDA) in Chapter 7.

4.3.1 Materials and equipment

To prepare solutions and baths for dyeing, ultrapure water at 18.2 M Ω resistivity (Millipore Direct-Q UV 3) was used. Due to the large volume required, the samples were washed between steps with flowing tap water. To remove any trace compounds, a final rinse was given with flowing ultrapure water. To ensure an adequate and consistent supply, the Fluka Turkey red oil sodium salt was used for these samples. Ground *Rubia tinctorum* L. was purchased from Couleur Garance (Lauris, France); Turkey red oil sodium salt (microscopy grade) was purchased from Fluka; potassium alum (KAl(SO₄)₂•12H₂O, reagent grade) and purpurin (90% dye content) were purchased from Sigma-Aldrich; sodium carbonate (Na₂CO₃, \geq 99.5 % purity) was purchased from Fisher; calcium carbonate (CaCO₃, 99% purity) was purchased from Alfa Aesar; alizarin (97% purity) was purchased from Acros Organics; olive oil Marseille soap was purchased from l'Occitane en Provence.

4.3.2 Hummel's 'new' process for dyeing Turkey red in modern terms

This method is based on Hummel's 'new' Turkey red method, with some directions for solution preparation taken from the 'old' process in *The Dyeing of Textile Fabrics*, J.J. Hummel, 1886.⁵ To make this recipe accessible to the widest possible audience, values are given in weight and concentration rather than moles and molarity. Hummel gives quantities of ingredients per weight of dry cotton, which this method also does, but scaled to a more accessible 100 g from the 500 kg of the original text. When a range is given, e.g. 15-20% weight, the higher value was taken for consistency and clarity. **Bold** steps are essential, *italic* steps are supplementary.

⁵ Hummel, *The Dyeing of Textile Fabrics* 427-453.

The method starts with scoured cotton. Hummel's process uses an oven for drying between steps, which this research was able to replicate through the use of specialist accelerated-ageing equipment. If using enclosed heat to make Turkey red, care should be taken so a fire does not occur. Air-drying between steps is an acceptable alternative, save for the impact of heat on oil uptake. To compensate for this, the oil can be left for a longer period (testing of time points based on climate recommended). The madder dyeing bath is an adaptation of the dye bath from Hummel's 'old' process, which differs from the 'new' process by its inclusion of bullock's blood. It is included here along with a proposed substitution of blood albumen based on an experimentally determined albumen content in cattle blood,⁶ but this variable was not tested during this project. The synthetic alizarin is replaced with a quantity of madder per weight cotton taken from other Turkey red processes.^{7,8} Directions for making a paste of synthetic alizarin are included to compensate for modern dry synthetic alizarin powders being more difficult to disperse in water.

- 1. Oiling
 - Soak the dry cotton thoroughly in a cold or tepid bath of aqueous Turkey red oil at a concentration of around 90 g/L. Prepare a volume adequate to thoroughly saturate the cotton.
 - Gently wring the excess and dry at 75 $\,^\circ\text{C}$ for 1-2 hours or in the air for longer.

2. Steaming

• Steam the dry cotton at 2-5 psi for 60-90 minutes.

3. Aluming

- Measure a volume of water sufficient to allow the cotton movement and heat it to about 70 $^\circ\text{C}.$
- Dissolve alum (ca. 95 g/L) in the water and allow the solution to cool.
- To make the solution basic, slowly add dropwise concentrated or saturated aq. Na_2CO_3 (about 30 g/L at 25 °C) while stirring. When the white precipitate no longer dissolves back into solution, no more carbonate is needed.
- The final solution should measure 8 °Tw (1.04 spg). If high, dilute with water; if excessively low, add a more concentrated alum solution to adjust (may require more Na₂CO₃).

⁶ Alberghina et al., "Reference Intervals for Total Protein Concentration, Serum Protein Fractions, and Albumin/Globulin Ratios in Clinically Healthy Dairy Cows."

⁷ Le Pileur d'Apligny, *L'art de la teinture des fils et étoffes de coton*, 139.

⁸ Persoz, Traité théorique et pratique de l'impression des tissus, 182.

- Heat the solution to around 40 °C, submerge the cotton, and leave for 2-4 hours, stirring occasionally to ensure level uptake. Remove from the bath and wring.
- Proceed to (4) *fixing*, or dry and proceed to (5a/5b) **dyeing**.

4. Fixing

- Make a solution of sodium phosphate (10 g/L) in enough water to cover the fibres, heat to 40-50 °C, and steep the cotton for 30 minutes.
- Remove, rinse well, and dry.

5a. Dyeing with synthetic alizarin

- Prepare a volume of cold water sufficient to allow the cotton movement to ensure level dyeing. Weigh the alizarin and add enough water to make a paste, and then disperse the paste in the bath. The quantity needed for high-concentration modern synthetic alizarin is about 2 g per 100 g of dry cotton. For 500 g cotton, around 10 g of 97% alizarin is used.
- Add to the bath calcium carbonate (2 g/kg cotton).
- Submerge the cotton in the bath and leave cold for 30 minutes. Slowly raise the temperature to 70 °C over 60 minutes, then hold until the colour is satisfactory or the bath is exhausted.
- Wash the cotton well, wring, and dry.
- Proceed to 6 or 8.

5b. Dyeing with madder

- Weigh a quantity of ground madder (*R. tinctorum* L) approximately 2x the dry weight of the cotton to be dyed. Add enough water so the madder is saturated and covered, then soak overnight to extract water-soluble components. Filter to collect the madder and discard the liquor with its undesired components. For 500 g dry cotton, 1 kg madder is used.
- Prepare a volume of cold water sufficient to allow the cotton movement, which ensures level dyeing. Add the soaked madder.
- Add to the bath calcium carbonate (2 g/kg of cotton).
- *Optional*: Add to the bath 300 g bullock's blood or 9 g blood albumen per kg of cotton.
- Add the cotton to the bath and leave cold for 30 minutes. Begin slowly raising the temperature to 70 °C over 60 minutes, then to 100 °C over 30 minutes. Hold for 30-60 minutes, checking the colour is satisfactory and the bath is not exhausted.
- Wash the cotton well, wring, and dry.
- Proceed to 6 or 8.

6. Second oiling

- Saturate the cotton with a solution half the concentration of the initial oil treatment (see Step 1).
- Wring the excess and dry at 75 $^\circ\text{C}$ for 1-2 hours.

7. Second steaming

• Steam the dried cotton at 2-5 psi for 60-90 minutes.

8. Clearing

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- Weigh sodium carbonate and vegetable soap (Castile, Marseille, etc., cut or flaked) (3 g/100 g cotton each) and add to a volume of water large enough for the cotton to move freely. Boil for 4 hours at 3-4 psi or for 12 hours in a covered and vented vessel, replacing water as needed.
- Wash, wring, and dry.

4.3.3 Experimental re-creation of Turkey red

Squares of scoured calico (see Section 4.2.1) 5 cm x 5 cm were cut with pinking shears to minimise fraying during the dyeing process. Fluka TRO (25 g, 82% oil (Sigma-Aldrich, product 16316, lot 1453189V)) was mixed with ultrapure water (50 mL) to make a solution of about 400 g/L, roughly 5x the concentration specified by Hummel. The calico was placed in a glass dish and saturated with the oil, then gently wrung and laid on bamboo mats (see Figure 4-7). The mats were placed in an oven at 75 °C for 24 hours to ensure sufficient heat exposure. The calico was slightly yellowed, greasy, sticky, and smelled fatty.



Figure 4-7 Calico squares oiled in preparation for dyeing Turkey red.

To steam the samples, the pieces were placed in a ceramic dish with a loose cover of aluminium foil to allow air circulation but prevent condensation from dripping onto the calico (see Figure 4-8). About 300 mL water was placed in the bottom of an aluminium pressure cooker (Prestige 3 L) that operates at 10 psi according to the manufacturer label. The covered dish was placed on foil balls to keep it above the heat source, then the system closed and heated to pressure for 60 minutes. After depressurising the cooker, the calico was removed and

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rinsed well in flowing water so no excess oil contaminated the aluminium bath. The fabric was no longer yellowed, greasy, or stiff.



Figure 4-8 A small-scale means to steam oiled calico under pressure as practiced in Hummel's method.

The alum bath was made by heating ultrapure water (1 L) to around 70 $^{\circ}$ C and dissolving alum (100 g). After the solution cooled, saturated aq. Na₂CO₃ was added dropwise with stirring. After the first few drops (about 1 mL total), the clear, colourless solution appeared slightly opalescent and white (Figure 4-9). With further stirring the precipitate was re-dissolved (Figure 4-10).



Figure 4-9 The alum solution before (left) and after adding carbonate solution.



Figure 4-10 Precipitate forming and dissolving in the alum solution as carbonate is added.

In solution, alum and Na₂CO₃ react to form aluminium hydroxide (Al(OH)₃) and carbon dioxide. To become part of the cellulose-fatty acid complex, the aluminium ions must be in solution, so the precipitate is undesirable. When flocculation persisted after stirring, no more alkali was added (Figure 4-11). The density of the final solution should be 8 °Tw (1.04 spg). This solution initially measured 10 °Tw. and was diluted accordingly with water.



Figure 4-11 Persistent flocculation in the adjusted alum solution.

The alum bath was divided into portions and each heated to 50 $^{\circ}$ C, slightly higher than the recommended temperature (40 $^{\circ}$ C) but within a reasonable range for the process. Maintaining a low temperature for small volumes proved difficult with the available equipment, which afforded little control. The dried calico samples were submerged in the baths and stirred intermittently with a glass rod (Figure 4-12).



Figure 4-12 Applying alum to oiled calico samples.

The baths became semi-opaque, and more white precipitate appeared, possibly aluminium soaps forming with unbound oil that was not washed off. After 4 hours, the calico was removed, wrung, and dried in the oven at 75 °C., then rinsed well in flowing tap water and air-dried.

The samples were separated into three groups: [1] synthetic alizarin, [2] madder, and [3] synthetic purpurin. Each set had three samples and weighed approximately 2 g total. For each dye bath, ultrapure water (800 mL) was put in a large glass beaker. Using high-concentration synthetic dyes (90-97%), approximately 40 mg alizarin or purpurin is needed per replicate. Alizarin powder was weighed and mixed with a few drops of water to make a paste, which was then added to the dye bath (Figure 4-13). For the quantity of cotton, only 4 mg CaCO₃ is required, which was too low to weigh accurately with the available balance. The literature indicates excess calcium is not harmful to the process because it is not consistently measured as an ingredient, and not measured at all in methods where the author appears to have depended on

calciferous water. As such, a small lump (about 15 mg) was added to the dye bath and stirred. The same preparation was followed with another bath using purpurin and $CaCO_3$ (Figure 4-15).



Figure 4-13 Prepared calico entering a dye bath made with synthetic alizarin.

The samples were placed in their respective baths and left at room temperature for 30 minutes (Figure 4-14), then moved to hot plates and the temperature slowly raised while monitoring with a glass thermometer and stirring regularly to assist level dyeing. The vessels were covered with large watch glasses to reduce evaporation. After 90 minutes, the temperature reached 70 °C. This is slightly longer than the 60 minutes specified by Hummel and others, but caution was taken in this work in case accidental overheating affected the dyeing and because the hot plates were difficult to control.



Figure 4-14 Calico in the cold alizarin dye bath after 30 minutes.



Figure 4-15 A purpurin dye bath as the temperature is raised to 70 $^{\circ}$ C.

The temperature was held for 60 minutes and the baths stirred regularly. The colour of the baths began to deepen as the temperature was raised, and colour developed on the calico.



Figure 4-16 Calico being dyed Turkey red with the alizarin dye bath in the background.



Figure 4-17 Turkey red dyed with synthetic alizarin being removed from the dye bath.

After 60 minutes, the colour had deepened to a vivid red in the alizarin samples. Surprisingly, the colour of the purpurin samples was much lighter and pinkish, compared to the alizarin samples. The pieces were rinsed thoroughly in flowing water and dried at room temperature.

To prepare the madder bath, ground madder (6 g) was weighed and soaked overnight in water (30 mL). The next day, the water was drained off and the madder transferred to a bath of ultrapure water (800 mL) in a large beaker with about 15 mg of CaCO₃. The fabric was placed in the bath and left cold for 30 minutes.



Figure 4-18 Dyeing Turkey red with madder.

The beaker was placed on a hot plate and covered with a watch glass to reduce evaporation, then heated to 70 °C over 75 minutes with regular stirring. The bath had an earthy smell from the ground madder, which coated the fabric in brown bits and made it more difficult to see development of the colour. The temperature was raised to 100 °C over 30 minutes, then boiled for an additional 30 minutes, when the colour was satisfactory. The calico was removed, rinsed well in flowing water, and left to air dry. At this point, the madder samples were slightly darker than the synthetic alizarin ones.



Figure 4-19 Turkey red dye baths with alizarin (left) and madder.



Figure 4-20 Turkey red dyed with madder (left), synthetic alizarin (centre), and purpurin. The madder used produced a slightly brick red, the alizarin a pure red, and purpurin a pinkish-red.

Replicating the clearing step was difficult, partly due to the available equipment and partly because of the step itself. Although a commercial pressure cooker was suitable for the steaming step, when tested for clearing, the frothing soap solution began to erupt from the safety vent valve and nearly put out the heat source (a domestic gas stove was used for the pressure cooker because the electric hot plate did not produce enough heat to maintain operating pressure). Clearing was not always done in pressurised vessels, and in some early texts closed (but not sealed) boilers are described, though these methods often have the cotton boiled for of 12 hours, which is impractical for this re-creation. Since the samples are small, and to avoid any hazards that may occur with a closed system, clearing was performed with lidded aluminium kettle (2 L) for a shorter time.

The samples were kept separate by dye during the clearing process. For each set, tap water (500 mL) was placed in the kettle and 2 g each Na₂CO₃ (Dri-Pak) and flaked olive oil Marseille soap added. The samples were submerged and the temperature raised to a gentle boil with the lid on, but vented to release steam. The samples were lifted out of solution by the froth generated from the boiling soap, so they were held under the surface by placing bamboo skewers across the top of the water. Eventually, the froth dissipated and the clearing bath, which had turned medium red, could be seen. The samples were boiled for 60 minutes (periodically replacing water to compensate for evaporation), then removed, rinsed well in flowing water, and left to air dry. A study of the impact of the clearing process on fastness is recommended to determine whether its effect is

to push the complex further into the fibre, to thoroughly scrub the fibres of unbound dye complex, or potentially both.



Figure 4-21 Finished Turkey red dyed with madder (top), alizarin (middle), and purpurin (bottom).

4.3.4 Discussion and conclusion

Experiencing the sights, smells, and challenges of dyeing Turkey red to gain a more complete perspective than could be obtained through reading was valuable and insightful. The text of Hummel's 'new' method uses fairly clear terminology and measurements, making it a good representative recipe, but as is often the case the method occasionally seemed incomplete to a modern reader. An indepth understanding of the process from the range of dyeing methods and supplementary texts reviewed for this project was vital to the re-creation of such a complicated dyeing technique. The broad survey of the literature made it possible to work around unclear statements and directions by comparing and connecting texts, providing as complete and thorough of an understanding of the process as possible.



Figure 4-22 Replica Turkey red dyed for a public engagement project.

There are few physical descriptions of the dyeing process in the historical texts. The experience of seeing precipitates form and dissolve in solutions, the colour change of the dye baths, and the brilliant red colour developing on the calico were exciting manifestations of the chemistry taking place. The oil lent the calico a faint, fatty odour that persisted until the clearing step, while the madder bath had a woody smell that did not linger. Other sights and smells, like rancid olive oil, ruminant dung, steeped sumac or gall nuts, and fresh bullock's blood, were absent from this re-creation but no doubt would have contributed to the experience. One clearing bath, when boiling too vigorously, spilled out of the kettle and left a large purple puddle of slimy, viscous carbonate/soap solution, making it abundantly clear how messy a large-scale dyeing would be. This may also explain why some believed a works should be exclusively Turkey red⁹—the necessary soap and oil could be contaminants in other processes.

Hummel's method is good, but as with the other texts more description would make a significant difference to a non-expert Turkey red dyer. The literature emphasises how time-consuming it was to dye Turkey red, especially for the 'old' process. Even using the 'new' process with small samples that took very little time to wash and dry, much of the dyeing process involved waiting time in the oven, time in each bath, time to clear—with little required from this dyer beyond observation, though on a production scale there is more to be observed and managed. This re-creation of Turkey red focused on the

⁹ Chenciner, Madder Red: a History of Luxury and Trade, 201.

fundamental ingredients of the process, to create samples for testing conservation-based analyses prior to their application on historical pieces. To keep the replica pieces similar to the historical ones, the re-creation followed a 19th-c. method and used the ingredients it specified as much as possible.

The legendary fastness of Turkey red has not yet been investigated using modern, quantitative methods, but the information about its chemistry and characteristics gathered from the re-creation and replica samples is a significant step toward being able to do so. It is the recommendation of this work that further research on the fastness of Turkey red or any attempt at production evaluates the auxiliary steps not addressed in this research, like tannins, additional oiling, alternative sources of aluminium and calcium, additional steaming, etc. Turkey red was superseded in the 1930s by manufactured red dyes that were quicker and cheaper to use, but in today's world of diminishing resources and rising concern over the environment there may also be potential to revive a dyeing technique that produced such a durable, brilliant colour.

4.4 Madder dyed calico

To test oil as a variable in the dyeing process for comparison to Turkey red samples, a piece of calico was dyed using madder and aluminium (without oil or calcium) following recipe 52 for vegetable fibres from Fereday.¹⁰ This method consists of a tannic acid treatment, alum bath, and finally dyeing with madder. The calico used is described in 4.2.1 and the alum and madder in 4.3.1. Tannic acid (ACS grade) was purchased from Sigma-Aldrich.

4.4.1 Experimental

Tannic acid (0.2 g) was weighed and dissolved in ultrapure water (500 mL). A piece of scoured calico (1.5 g) was added and bath heated to 80 °C over 1 hour, then the temperature lowered slightly to 60 °C and held for 1 hour. It was left to cool overnight and the next day re-heated to 80 °C, then removed and rinsed in flowing water. A bath was made with alum (0.8 g) in ultrapure water (500 mL) and the damp calico added. The temperature was raised to 60 °C over 1 hour, then held for 90 minutes. Again, the calico was left overnight as the bath

¹⁰ Fereday, *Natural Dyes*, 76.

Chapter 4 \bullet Re-creation of Turkey red and related materials following historical processes 205 cooled. The next day, it was re-heated to 60 °C over 1 hour, then left to cool again, and finally removed and rinsed well in flowing water.

Ground madder (3.2 g) was mixed with cold water (10 mL) and left overnight to soak. The next day, the water was drained away and the madder added to a bath of ultrapure water (500 mL). The calico was added and the temperature raised to 80 °C over 1 hour, then raised to boiling and held for 2 hours. It was left to cool overnight and the next day re-heated to 65 °C over 1 hour. The bath was then cooled and the calico removed, rinsed, and air-dried.

4.4.2 Discussion

Comparing the replica Turkey red samples to cotton dyed with madder reveals the effect of oil on the colour. Without it, the colour produced by madder on cotton is a dusty, muted pink without any of the brilliance of Turkey red. Samples kindly donated by another dyer, Debbie Bamford, show the same effect. In Figure 4-23, replica Turkey red dyed with madder is compared to calico and poplin (from Bamford) dyed with madder.



Figure 4-23 Replica Turkey red dyed with madder (left), calico dyed with madder (centre), poplin dyed with madder by D. Bamford. The Turkey red sample is the only one that received an oil treatment.

A piece of Turkey red dyed by Bamford with rancid olive oil and madder, shown in Figure 4-24, has a deeper and more characteristic colour than the unoiled poplin sample. It is lighter than the pieces prepared with Turkey red oil for this project, probably due to the lower fatty acid content in the natural material.



Figure 4-24 Replica Turkey red dyed with madder (left) and synthetic alizarin (centre) by J. Wertz next to a sample dyed by D. Bamford with madder and rancid olive oil.

The calico samples dyed with madder and without oil are useful references in the *in situ* analysis of Turkey red and provide a clear visual indication of how vital oil is to the process. They also provide the opportunity to test, as asserted in the literature, the increased resistance of Turkey red to bleaching.¹¹ In Figure 4-25, five drops of common household bleach (ca. 3-6% aq. sodium hypochlorite) were added to pieces of replica Turkey red and madder-dyed calico. The left two images, taken before and five minutes after the application of bleach, show no visible effect on the Turkey red. At this point, drops of white vinegar (ca. 5% aq. acetic acid) were applied and a white area began to appear on the Turkey red as well.

¹¹ Carruthers, "A New Process of Dyeing Turkey Red."



Figure 4-25 Trial discharging of replica Turkey red (top) and madder-dyed calico. From left: Initial samples (left), after five minutes with bleach, immediately after adding vinegar, 15 seconds after vinegar (right).

The results of this experiment were consistent with claims in the literature about its increased resistance to bleaching. The chemical conditions of the discharge process (a weak acid plus bleach to make hypochlorous acid) effectively removed the colour on both samples, more rapidly on the non-Turkey red piece. Further investigation into this property of Turkey red and the chemistry of its discharge printing is suggested from this experiment.

4.5 Synthesis of alizarin

A re-creation of synthetic alizarin following a 19th c. patented method was attempted to test how the process was documented and communicated, and to obtain a reference sample with a similar composition to what 19th c. dyers used since modern alizarin is of a higher purity. The challenges discussed in Chapter 1 regarding hazardous substances, equipment, and temperatures meant for the scope of this project, the re-creation was based on a less-used anthracene sulfonation and oxidation route patented by Caro, Graebe, and Liebermann.¹² It was ultimately unsuccessful and did not yield any alizarin or other dyes. Fortunately, samples of 19th c. synthetic alizarin kindly provided by the TU Dresden Historical Dyes Collection (Historisches Farbstoffsammlung) served as

¹² Caro, Graebe, and Liebermann, Improvements in Preparing Coloring Matters.

references for the dyes analysis of historical and replica Turkey red, so the unsuccessful re-creation did not impact the dyes analysis. This section describes how the route was chosen and the work undertaken with a discussion of the experience and where the synthesis may have deviated from the intended route.

As usual, finding a useful representative recipe often requires inferences and assumptions by the reader to overcome 'missing' information and various challenges posed by language and terminology. Reagents in the original patent text are measured in ratios of parts, so the initial weight of anthracene in the re-creation was chosen for the desired scale of this reaction and the other reagents adjusted accordingly. To keep the work accessible to a wider audience and to maintain consistency with the original text, modern units like moles are not used here. Specified reaction times range from 'three hours' to a less helpful 'boil the whole strongly for some time'. This, coupled with a general lack of physical descriptions in the literature, makes it difficult to gauge whether the reaction is proceeding as intended. In the historical texts, reaction completion was often determined by taking a portion and proceeding with the next step(s), so a chemist experienced with the process likely knew what to look for. In this re-creation, intermediate testing was done by thin-layer chromatography (TLC) and ¹H and ¹³C nuclear magnetic resonance (NMR) to gather more information.

4.5.1 Equipment and reagents

The size and shape of vessels is rarely described; many used closed vessels, which cannot be accommodated in this work. The re-creation was carried out using borosilicate glassware, which is consistent with the patents specifying glass or porcelain vessels inert to the acid.^{13,14} Round-bottom flasks of different sizes were used with a Teflon-coated magnetic bar. Open flames are no longer common in organic chemistry laboratories and a jacketed system was not available, so the flasks were heated in an open oil bath containing high-temperature silicone oil and controlled with a thermal probe. All high-temperature work was carried out in a fume cupboard and a water-cooled condenser open to the air was attached to the flask to reduce evaporation and

 ¹³ Perkin, Improvements in the Manufacture of Coloring Matter Suitable for Dyeing and Printing.
¹⁴ Caro, Graebe, and Liebermann, Improvements in Preparing Coloring Matters.

Chapter 4 • Re-creation of Turkey red and related materials following historical processes 209 as a safety measure. Standard PPE was used and extra care taken in the handling of highly corrosive and carcinogenic substances.

The following reagents were used for the experimental work. Anthracene (97% purity) and 9,10-anthraquinone-2-sulfonic acid sodium salt hydrate (97% purity) was purchased from Alfa Aesar; sulfuric acid (H_2SO_4 , 95-97%) was purchased from Fluka; manganese (IV) dioxide (MnO_2), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), and calcium hydroxide ($Ca(OH)_2$) were purchased from Sigma-Aldrich; and glacial acetic acid was purchased from VWR. Tap water was used for diluting and washing the product.

4.5.2 Experimental re-creation of early synthetic alizarin

This section discusses the experimental re-creation of synthetic alizarin and adaptations made to the procedure as the work proceeded, based on the specifications in "Preparing Coloring Matters" by Caro, Graebe, and Liebermann,¹⁵ A copy of the original patent is included in Appendix D.

In a fume hood, anthracene (1.0 g), a pale, greenish-white crystalline solid, was weighed into a 50 mL round-bottom flask with a Teflon-coated stir bar. H_2SO_4 (2.2 mL) was measured with a syringe and added slowly to the anthracene. On contact, the clear, colourless acid turned bright yellow and then started to blacken.



Figure 4-26 Anthracene, anthracene with sulfuric acid, and the blackened mixture prior to heating (from left)

An open water-cooled condenser was attached to the flask, which was placed in the oil bath and heated to 100 $^{\circ}$ C. Initially, the blackish mixture was too thick to

¹⁵ ibid.

be stirred. It became more fluid after 20 minutes heating, but some stuck to the wall of the flask that, for safety reasons, could not be opened to stir it in.



Figure 4-27 The anthracene-sulfuric acid mixture while heating

After 3 hours, the temperature was raised to 150 °C and held for 1 hour. Material on the flask wall began to melt back into the mixture. The heat was removed and the reaction left to cool overnight, yielding a brown-black sludge with some liquid in the centre. It is unknown how the reaction should look at this point, but the blackening is consistent with sulfuric acid reactions such as in the making of Turkey red oil, and with descriptions of reactions with sulfuric acid in other processes.¹⁶ An intermediate sample was taken to determine whether the desired anthracene-2-sulfonic acid had formed.

With the flask in the cold oil bath to absorb evolved heat, water (15 mL) was added down the condenser, producing no visible reaction. MnO_2 (3 g) was added and the flask swirled, loosening the thick substance on the bottom. The system heated to 110 °C, then after 30 minutes the temperature was increased to 120 °C, with reflux starting at 115 °C. The patent only says complete oxidation is needed, but does not say how long this takes. During reflux, the mixture was a bubbling, brown-black liquid with solid visible on the bottom of the flask. No visible changes had occurred after four hours, so the heat was removed and an intermediate sample taken. Reflux was resumed for another 1.5 hours, still with no visible changes, so the heat was removed and the system left to cool overnight.

¹⁶ Perkin, "The History of Alizarin and Allied Colouring Matters, and Their Production From Coal Tar," 589.

The cooled reaction mixture was a red-brown solution with brown sediment. It was swirled and transferred to a 250 mL conical flask. In the patent, excess acid was neutralised with concentrated aq. $Ca(OH)_2$. After adding 5 mL of the solution, it became clear the volume of alkali solution needed to neutralise the acid would be difficult to evaporate in the next step. For this work, small portions (ca. 0.25 g) of dry $Ca(OH)_2$ were added directly to the flask and stirred, then the pH checked with pH 1-14 paper. After about 5 g $Ca(OH)_2$, the pH was in the low alkali range as directed by the patent.

Solid MnO₂ and precipitated calcium sulfate were collected by vacuum filtering the mixture through filter paper on a Büchner funnel. Saturated aq. Na₂CO₃ was slowly added to the filtrate (about 4 mL total) while stirring until no more CaCO₃ precipitated, then the solid was filtered out as before. Approximately 150 mL of filtrate was collected, and should contain dissolved anthraquinone sulfonic acids.



Figure 4-28 After oxidation, the product of the reaction should be dissolved anthraquinone sulfonic acids.

The patent uses evaporation to remove water and isolate the soluble anthraquinone sulfonic acids. The filtrate was transferred to a 250 mL roundbottom flask, which was placed in the oil bath, a stir bar added, and the condenser attached. The temperature was set to 130 °C, boiling began at 119 °C. During the first hour, the red-brown colour became bluish, then changed to deep purple, and a dark amorphous crust formed around the edge. 212 Chapter 4 • Re-creation of Turkey red and related materials following historical processes



Figure 4-29 The apparatus to remove water from the reaction mixture.



Figure 4-30 Crust forming on the wall of the flask as the solution changes colour during evaporation.

The large volume of water was difficult to remove by this method, taking around 4 hours to complete. For 19th c. manufacturers, purpose-built systems like those described by Perkin¹⁷ and a familiarity with the process probably made this step less of an obstacle. The expected product, anthraquinone-2-sulfonic acid, is pale grey when pure, so the remaining solid, an amorphous, purple-black crust, contains other compounds as well. None of the literature describes the reaction at this stage so it is unknown whether this is typical.

¹⁷ ibid.



Figure 4-31 The reaction product after evaporating the water.

Based on the weight of the solid in the flask, NaOH (5.1 g) dissolved in water (3 mL) was added down the condenser with the flask in the cold oil bath to absorb evolved heat. With the column open at the top and a shield in place as an additional safety measure against explosions, the system was heated to 190 $^{\circ}$ C.



Figure 4-32 The initial hydroxylation reaction.

The reaction boiled vigorously and the volume initially increased, then decreased with evaporation. After one hour, the heat was removed and the flask left to cool overnight. According to Perkin, after hydroxylation of anthraquinone sulfonic acid the reaction should be a deep purple fluid that thickens with cooling,¹⁸ which accurately describes this product.

¹⁸ ibid., 592.

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Figure 4-33 The boiling hydroxylation reaction.

Perkin's treatment of his reaction product yielded a precipitate of the desired dye, which was the expectation for this re-creation.

To finish the synthesis, about 150 mg of product, a deep purple paste, was dissolved in 2 mL of water. The purple solution became red-orange as glacial acetic acid was dropped in and stirred (about 1 mL total). A precipitate formed as expected.



Figure 4-34 Aqueous solution of hydroxylation product before (left) and after adding glacial acetic acid.

The precipitate was collected by filtering through cotton wool in a glass pipette, followed by washing with water. It transpired that the apparent colour did not belong to the precipitate, but was from the solution. When washed, the precipitate was an unknown white solid. The colour change of the solution indicates pH-sensitive compounds are present, but no coloured compounds were in the precipitate.



Figure 4-35 Final precipitate in solution (left), washing precipitate by filtering on cotton wool (centre), dried final reaction product.

A larger preparation was made by dissolving about 1 g of the reaction product in water (20 mL), precipitating with drops of glacial acetic acid, and collecting
the solid on filter paper with a Büchner funnel. Figure 4-36 shows how the precipitate colour changes as the solution is washed away—the purple ring is solution retained by the filter paper.



Figure 4-36 Precipitate before (left) and after washing with water.

The precipitate appeared to contain no hydroxyanthraquinone dyes, which are yellowish to reddish solids. The white solid appeared to only be soluble in highly alkaline water, similar to the solvent from which it was precipitated. Identification of the unknown precipitate was not pursued further because it went beyond the scope of the project.

4.5.3 Conclusion

Although the synthesis re-creation did not yield any dye, it was an interesting and informative experience that made it possible to see how the reaction progressed, from unanticipated colour changes to an unexpected precipitate. The re-creation tested how industrially valuable processes were documented and communicated. Practical matters like how to efficiently transfer material between vessels, how long to run a reaction and recognise its progress, and what vessels to use are not well documented, forcing inferences based on common sense or current laboratory practice. It was difficult to assemble a method that was historically true, complete, and compliant with health and safety standards, and to execute it without experience, expert guidance, or detailed descriptions in the texts. The re-creation underscored how challenging developing these synthetic processes must have been to those who pioneered them. It is not clear exactly where the synthesis deviated from the intended route. This pathway is not referenced as often as the other, more hazardous routes, and may have been less efficient. The small scale of the reaction could also be a factor, although the original text does not specify one. Based on the conditions specified in the patent and other alizarin synthesis methods, plus the experience gained from the actual re-creation, it may be the case that heat produced by the available equipment was insufficient to carry out the desired reactions, or else closed vessels were vital to the synthesis. Further investigation was outwith the scope of the project, but may offer more insight into this historically significant chemical manufacturing process.

4.6 Summary

Re-creations are a useful way to improve our understanding of the practices, reagents, and skills involved in making materials of historical interest. The process gives the experimenter the opportunity to connect textual records to practical experience, and may be useful to generate materials for analytical testing. The work is also useful for understanding how processes were communicated in the 19th century, and how they are interpreted and revived today. That such industrially valuable processes like Turkey red dyeing were so freely published raises the question as to whether authors were disclosing the complete specifications, yet the work presented in this chapter indicates that successful re-creation, at least with respect to the appearance of the final product, is indeed possible.

Based on the literature reviewed and discussed in the first three chapters of this thesis, this project attempted to re-create Turkey red oil, oiled calico, dyed Turkey red, and 19th c. synthetic alizarin, although this was clearly unsuccessful. In each experiment, it was unclear at some point whether things were proceeding correctly due to a general lack of description in the texts, for example when initial batches Turkey red oil were un-homogeneous or overly acidic. Making Turkey red oil brought to life the sights and smells not recorded in the text, an experience that improved understanding of the method when visual cues corresponded to chemical changes in the product. Dyeing Turkey red involved lengthy periods of waiting while the calico remained white, before the colour was finally developed in the dye bath—an immensely satisfying outcome

after reading so many texts about the process. The failed alizarin synthesis revealed some of the challenges faced by the chemists who initially developed the processes, and by modern chemists attempting to re-create historical industrial processes, which rely on large-scale specialised methods that are difficult to re-create in modern chemistry labs.

In addition to the experience of re-creation, the samples of Turkey red oil, oiled calico, and Turkey red have value in testing analytical techniques for characterisation, especially if the work may harm the object or there is limited historical sample available. Had it been successful, the alizarin synthesis would also have provided a reference sample, but fortunately samples from the TU Dresden collection could be used in lieu. In Chapter 5, analysis of replica, commercial, and historical Turkey red oils is presented for a characterisation of the oil treatments and a comparison between modern and historical samples. This is followed by in situ analysis of oiled calico and historical and replica Turkey red in Chapter 6 to finally understand the oil-cellulose bond, and to determine similarity of the replica Turkey red to the historical pieces. In Chapter 7, analysis of reference samples and dye extracted from Turkey red fibres investigates whether the hydroxyanthraquinone profile can be used to determine object provenance. This work contributes toward answering all three research questions for this project. Understanding the chemistry of such a complex and unusual textile and process like Turkey red benefits from a review and re-creation prior to analysis, making the technique somewhat less mysterious but no less fascinating.

5 Analysis and characterisation of Turkey red oil

The introduction to this thesis established that oil is fundamental to the successful creation of Turkey red and that the manner of its use is unique to the process. Chapter 2 discussed the 'old' *huile tournante* process giving way to the 'new' Turkey red oil process and previous research on the chemistry of the oils. The chapter concluded that the two oils had a similar composition, a mixture of free fatty acids (FFAs), and that the higher concentration of FFAs in Turkey red oil relative to *huile tournante* made it more efficient at adequately oiling the cotton. An experimental re-creation of Turkey red oil in Section 4.1 yielded a product that is physically similar to the commercial sample and descriptions in the literature of the historical product. Chemists and dyers in the 19th c. understood that good dyeing oil had a high FFA content based on analytical techniques available to them, but no study has yet confirmed their work using modern experimental tools within the context of textile dyeing.

The aim of this work is to answer the question for this project regarding the composition of the oil and its overall chemistry within the Turkey red complex. Confirming which compounds are present in the oil provides a better understanding of how it bonds to the cellulose fibres. This chapter discusses the analysis and characterisation of Turkey red oils by ¹H and ¹³C nuclear magnetic resonance spectroscopy (NMR) and high performance liquid chromatography with mass spectrometry (HPLC-MS), building upon the foundation laid by 19th-c. chemists to investigate its role in the dyeing process.

5.1 Samples

5.1.1 Turkey red oils

Four samples of Turkey red oil were analysed for this project. The replica Turkey red oil (TRO) in Section 4.1 was prepared using castor oil treated with sulfuric acid, then washed with water and aq. sodium sulfate (Na₂SO₄) and neutralised with aq. NaOH. The sample of commercial Turkey red oil sodium salt was purchased from Fluka Sigma-Aldrich. The oil is clear, light golden yellow with moderate viscosity.

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A sample of historical TRO of unknown date was kindly provided by Debbie Bamford (DB), a dyer in Sheffield. It was given to her by someone whose family member worked in the textile dyeing industry, and nothing else is known of its provenance, other than it is not newly made. The oil is golden yellow, fairly turbid but still translucent. It is almost gelatinous, thicker than the commercial TRO but less viscous than castor oil.



Figure 5-1 Historical Turkey red oil donated by Debbie Bamford (left) and in the Society of Dyers and Colourists collection.

The Society of Dyers and Colourists (SDC), Bradford, UK, generously allowed a sample of their historical TRO to be taken for this research. The bottle has a glass stopper and a paper label affixed that appears to be original. The oil inside is a dark amber liquid, fairly viscous. About 0.5 mL was taken.

5.1.2 References

Samples of triglyceride oils were analysed for comparison to the TROs to learn more about the sulfuric acid reaction that produces them, and a sample of estolides was analysed to investigate what happens to TRO as it ages. Ultimately, no sample of *huile tournante* could be found, so it is not included in this analysis, but the conclusions from the review are that the 'old' and 'new' processes had the same chemistry and therefore *huile tournante* is expected to be a mixture of fatty acids as well.



Figure 5-2 Olive oil reference from Cooperative l'Oulibo.

Olive oil (*huile de bourbes*, or 'mud oil') was kindly donated by Cooperative L'Oulibo in Bize-Minervois, France. The oil was greenish-yellow and slightly turbid with fine, light brown particulate at the bottom of the bottle. The bottle was received in early 2013 and stored in a cupboard. Castor oil was purchased from Fisher. Ricinoleic acid (≥99%) was purchased from Sigma-Aldrich and received in a glass ampoule, consistent with its tendency to polymerise with exposure to air. Coco-oleic estolide 2-ethylhexyl ester (see Figure 5-6) was a gift from Dr Steven Cermak at the USDA Agricultural Research Service (Peoria IL, USA). The sample is a clear, light yellow oily fluid that is less viscous than the olive oil.

5.2 NMR analysis

Analysis by NMR provides information about the structures of molecules in the sample, in this case ¹H and ¹³C atoms. The technique is potentially non-destructive, depending on the possibility of recovering the sample from the solvent, but since it requires a very small sample size (in this case, about one drop), it is suitable for conservation-based research. The technique is discussed in further detail in Appendix A and the full spectra are included in Appendix E.

5.2.1 Instrument and acquisition

The spectra were taken on a Bruker AVIII 500 MHz NMR spectrometer. The ¹H spectra were taken at 500 MHz and each sample was scanned 16 times. The instrument was set to 125 MHz for ¹³C nuclei and each sample was scanned 1024 times. The accompanying TopSpin software from Bruker was used to process the spectra and peaks were identified using the automatic peak-picking algorithm. Chemical shifts were assigned relative to the solvent signal; in ¹H NMR CHCl₃ appears as a single peak at 7.28 ppm and in ¹³C NMR, the solvent signal is a triplet with the central peak at 77.36 ppm.

5.2.2 Sample preparation

For the reference samples ricinoleic acid, castor oil, olive oil, and estolides, 1 drop of sample was added to a glass vial with 1 mL chloroform-d (CDCl₃, Cambridge Isotope Laboratories). A small spatula of anhydrous Na₂SO₄ (Sigma-Aldrich) was added to remove any trace water, then the vial shaken. Freeflowing Na₂SO₄ crystals in the vial, as opposed to clumping, indicate a dry sample. The liquid was drawn off the Na₂SO₄ with a pipette and filtered into an NMR tube through cotton wool to trap any particulates.

The TRO samples, due to their higher water content, required more aggressive drying than could be accomplished with Na₂SO₄. When water is in a sample, the H atoms can exchange with the solvent to form HDO, which appears as a broad, shifting peak that can obscure other signals. Azeotropes, a mixture of two or more liquids that maintains its proportions during distillation, so one is not boiled away before the other, are a useful drying technique. Water in trace quantities does not evaporate easily even under vacuum, but an azeotrope of toluene and water is easier to remove. To dry the TROs, 2-3 drops of sample were added to a 100 mL glass round-bottomed flask with ca. 20 mL of toluene (Fisher), then swirled to dissolve. The DB and SDC samples, probably due to their age, solvated with more difficulty. The flask was placed on a Buchi Rotovapor and the water-toluene mixture evaporated under vacuum until the volume was constant. The same amount of toluene was added again and the evaporation repeated to ensure dryness. The sample was reconstituted from the wall of the flask by adding ca. 1 mL CDCl₃ and swirling it around to collect the sample, then

pipetting it into an NMR tube through cotton wool. Toluene was also evaporated from an empty flask and then rinsed with CDCl₃ to check for any residual toluene signals in the samples. The spectra for the commercial and SDC samples show trace signals for toluene (see Appendix E), indicating insufficient evaporation. Toluene appears in ¹H NMR spectra in CDCl₃ around 2.36, 7.17, and 7.25 ppm and in ¹³C NMR spectra around 21.5, 125.3, 128.3, 129.1, and 137.9 ppm.¹ These signals could potentially affect the interpretation of the C9/C10 region around 130 ppm, but that is not a significant aspect of this research. After drying the samples using toluene, the shifting HDO peak was no longer present in the DB and SDC spectra.

5.2.3 ¹H NMR Results

This analysis identifies the various proton environments in the samples, which are referred to by the carbon atom to which they are attached—e.g. a reference to 'H9' means the proton attached to the carbon atom at position 9 on the fatty acid chain. Figure 5-3 shows the numbered structure of ricinoleic acid (9Z, 12R)-12-hydroxyoctadec-9-enoic acid), the most common fatty acid in castor oil. The molecule would have two additional fatty acids for the R groups. These numbers are used to refer to the constituent atoms of the molecule and also apply to oleic acid (Figure 5-4).



Figure 5-3 Ricinoleic acid triglyceride



Figure 5-4 Structure of oleic acid

¹ Gottlieb, Kotlyar, and Nudelman, "NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities."

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In the earlier discussion of oils in Chapter 2, the idea of autopolymerisation reactions between FFAs in the oil forming estolides, a known condensation product of fatty acids,² was mentioned. Estolides form spontaneously, but slowly, at room temperature,³ so their presence can be linked to the age of the sample. Fatty acids with an -OH readily form an estolide bond and are well-suited to polymerisation⁴. Figure 5-5 depicts triricinoleic estolide, which could form in Turkey red oil.



Figure 5-5 Structure of triricinoleic estolide

The presence of estolides can be detected by the estolide methine proton at H12 (labelled H_m), which appears around 4.8 ppm for polyestolides in CDCl₃.⁵ The reference sample of coco-oleic 2-ethylhexyl estolides⁶ (Figure 5-6) has an H_m peak at 4.87 ppm (see Figure 5-9). The H* signal marked in the figure below corresponds to a signal in the spectrum that does not appear in the TRO samples because no ethylhexyl group is present.



Figure 5-6 Coco-oleic estolide 2-ethylhexyl ester

² ibid., 569.

³ Hawke and Kohll, "The Auto-Reactions of Ricinoleic Acid Part I. Reactions at 180° C, 147° C, 122.3° C and Room Temperature," 1.

⁴ Isbell, "Chemistry and Physical Properties of Estolides."

⁵ Isbell and Kleiman, "Characterization of Estolides Produced From the Acid-Catalyzed Condensation of Oleic Acid."

⁶ Cermak, Biresaw, and Isbell, "Comparison of a New Estolide Oxidative Stability Package."

5.2.3.1 ¹H spectra of castor and olive oils and ricinoleic acid

The ¹H NMR spectra for castor oil and olive oil are consistent with published spectra for these substances that were used to assign the chemical shifts.^{7,8,9} The peak assignments for castor and olive oil proton NMR are shown in Table 5-1. Knowing the spectra of starting materials will be useful to identify differences in the spectra of Turkey red oils and therefore what chemical changes have occurred.

¹ H chemical shift, δ ppm					
Position	Olive oil	Castor oil	Ricinoleic		
		Castor on	acid		
2	2.31	2.29	2.31		
3	1.61	1.59	1.62		
4-7	1.27	1.28	1.30		
8	2.02	2.02	2.03		
9	F 24	5.51	5.52		
10	5.54	5.40	5.41		
11	2.01	2.19	2.21		
12		3.58	3.63		
13	1.26-1.30	1.44	1.46		
14-17		1.28	1.30		
18	0.88	0.86	0.88		
α	4.13-4.32	4.11-4.29	_		
ß	5.27	5.24	_		

Table 5-1 ¹H NMR assignments for castor and olive oils and ricinoleic acid.

⁷ Xia and Larock, "Castor Oil-Based Thermosets with Varied Crosslink Densities Prepared by Ring-Opening Metathesis Polymerization (ROMP)."

⁸ Sacchi, Addeo, and Paolillo, "¹H and ¹³C NMR of Virgin Olive Oil. an Overview."

⁹ Lie Ken Jie and Cheng, "Confirmation of the Carbon Chemical Shifts of Ethylenic Carbon Atoms in Methyl Ricinoleate and Methyl Ricinelaidate."





Figure 5-7 1 H NMR spectra of olive and castor oils, and ricinoleic acid. Spectra taken in CDCl₃ and aligned using the solvent signal at 7.28 ppm.

Full ¹H spectra of reference compounds ricinoleic acid, castor oil, and olive oil are shown in Figure 5-7. The signal from glycerol hydrogens (2 H α and 1 HB) is useful to determine whether glycerides or FFAs are present. In castor oil, H α glycerol appears from 4.22-4.29 ppm and in olive oil from 4.13-4.32 ppm. HBglycerol is at 5.24 and 5.27 ppm for castor and olive oils, respectively. The integrated areas of these peaks (see Appendix E) is around 0.40 for HB and 0.73 for each H α peak, consistent with the expected 1:4 ratio in a triglyceride molecule. These signals indicate castor and olive oil are mostly triglycerides, whereas the ricinoleic acid has neither H α nor HB. Glycerol, a water-soluble compound, is not expected to be a significant component of Turkey red oil, so these signals should be different in those samples. There is no H1 proton, so changes to the carboxyl carbon must be studied with ¹³C NMR.

Oleic acid, (9Z)-octadec-9-enoic acid, has the same basic structure as ricinoleic acid, but without an -OH on C12. In olive oil, the alkene (H9 and H10) protons are in almost the same environment and produce a signal at 5.34 ppm. In castor oil and ricinoleic acid, the -OH group causes the signal to split into distinct H9 and H10 environments and shift downfield. It also has this effect on neighbouring H13 and H11 protons (see Table 5-1).

The signal in castor oil at 3.58 ppm is from H12, the carbinol proton, appearing in ricinoleic acid at 3.63 ppm. When the integral of this peak is set to 1.00, the integral value of the H18 peak is 3.40 in castor oil and 3.26 in ricinoleic acid, consistent with a proportion of about 87% ricinoleic acid cited in

the literature¹⁰ and indicative of a higher proportion of hydroxy fatty acids in the ricinoleic sample. The olive oil spectrum does not have a carbinol signal, consistent with its lack of ricinoleic acid content.

5.2.3.2 ¹H spectra of Turkey red oils

In TRO, the bond between glycerol and the fatty acid carboxyl is hydrolysed in the sulfation process.¹¹ When this bond is hydrolysed, the proton environments are changed on the fatty acid and the glycerol, which shows in the spectrum. In castor oil, sulfuric acid reacts with the -OH on ricinoleic acid before it attacks any alkene carbons.¹² These effects—triglyceride hydrolysis, substitution of the -OH, changes to the alkene bond—are summarised in Table 5-2. The peak clusters, decreased resolution, and appearance of peak shoulders in the spectra are consistent with changes indicating a mixture has formed, as expected due to the variable nature of the reaction with sulfuric acid. Peak assignments were made with the help of published spectra for castor oil and ricinoleic acid.^{13,14,15}

¹ H chemical shift, δ ppm						
Position	Castor oil	Ricinoleic acid	Fluka	DB	SDC	Replica
9	5.51	5.52	5.42-	5.42-	5.34-	5.41-5.54
10	5.40	5.41	5.55	5.55	5.54	
12	3.58	3.63	3.63	3.63	3.62	3.62
α-glycerol	4.11- 4.29	-	4.17	-	-	4.13-4.28
B-glycerol	5.24	_	-	_	_	5.26
H _m	-	_	4.90	4.89	4.89	_

Table 5-2 Relevant ¹H NMR peak assignments for Turkey red oils compared to castor oil.

¹⁰ Nawaby, Kruus, and Dabek-Zlotorzynska, "Determination of Anionic Surfactant Turkey Red Oil by Capillary Electrophoresis with Direct UV Detection," 401.

¹¹ Burton and Robertshaw, Sulphated Oils and Allied Products, 21.

¹² Trask, "Sulfonation and Sulfation of Oils," 569.

¹³ Xia and Larock, "Castor Oil-Based Thermosets with Varied Crosslink Densities Prepared by Ring-Opening Metathesis Polymerization (ROMP)."

¹⁴ Lie Ken Jie and Cheng, "Confirmation of the Carbon Chemical Shifts of Ethylenic Carbon Atoms in Methyl Ricinoleate and Methyl Ricinelaidate."

¹⁵ Orfanakis et al., "Characterization of Polyglycerol Polyricinoleate Formulations Using NMR Spectroscopy, Mass Spectrometry and Dynamic Light Scattering."

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Figure 5-8 Segment of ¹H NMR spectra of Turkey red oils and castor oil. Spectra taken in CDCl₃ and aligned using the solvent signal at 7.28 ppm.

In Figure 5-8, the spectra for the TRO samples have shifts consistent with the spectrum for ricinoleic acid, whereas for castor oil the peaks are slightly upfield, as discussed for Figure 5-7. The signals for H α and H β in castor oil (4.11-4.29 ppm, 5.24 ppm, respectively) are much clearer and sharper than the same signals in the Fluka and replica TRO samples. No H α and H β appear in ricinoleic acid or the historical DB and SDC samples. The replica TRO has the strongest H α signal relative to H9/H10 out of the TRO samples and a low H β peak at 5.26 ppm, indicating triglyceride hydrolysis occurred, but to a lesser degree compared to the other TROs. It is slightly downfield from the H β signal in castor oil, possibly the effect of the sulfuric acid reaction altering the glyceride. The results are consistent with the conclusion that making Turkey red oil breaks the glycerol bonds, and that most glycerol is removed in the washing process. The residual glycerol signals and the asymmetric peak shapes indicate mono- and diglycerides are present. Further confirmation of triglyceride hydrolysis is discussed with the ¹³C NMR spectra.

The H12 carbinol signal appears at 3.58 ppm in castor oil and 3.63 ppm in ricinoleic acid, consistent with this shift in the TRO samples, though there it is broader and weaker relative to the ricinoleic acid. Some peaks in the castor oil samples are shifted relative to the peaks in the other samples, probably the effect of its triglyceride bonds. The series of broad, low peaks in the TRO spectra (black boxes in Figure 5-8) are fairly consistent across the samples and do not appear in any of the reference spectra. Peak broadening may be indicative of a mixture forming, the effect of water, hindered rotation or the

result of new proton environments producing signals. The samples were dried, but the possibility for residual water must be considered. The spectra for the oils and estolides, which are larger molecules than FFAs, do not have these peaks although they would be subject to more hindered rotation. Sulfuric acid reacts preferentially with an -OH to form sulfate esters after reacting with triglyceride bonds.¹⁶ A characterisation of natural chlorosulfolipids found the ¹H NMR signal for a central carbinol on a lipid chain shifts downfield about 0.77 ppm (3.76 ppm to 4.53 ppm) when the -OH becomes -OSO₃H.¹⁷ The series of weak signals in the TRO samples downfield of the H12 carbinol may be the result of sulfate ester formation or the polymerisation of free glycerol;¹⁸ they do not appear in the reference spectra that were not treated with sulfuric acid (non-TRO samples). This analysis does not attempt further identification of these peaks since polyglycerols are not expected to affect the oiling process for Turkey red and the degree of sulfate ester formation does not appear to be significant in the dyeing texts based on the usefulness of the 'old' and 'new' processes.

The alkene proton signals in castor oil (5.40 and 5.51 ppm) and ricinoleic acid (5.41 and 5.52 ppm) are again much stronger and sharper than in the TRO samples, where the peaks are broader and less resolved. The sulfate esters resulting from sulfuric acid reacting with this bond are prone to hydrolysis, yielding a hydroxy fatty acid.¹⁹ This analysis does not attempt to determine to what extent the alkene is substituted since it is a secondary reaction to triglyceride hydrolysis. Some of the additional peaks in this area may be the result of estolide alkenes as well (discussed below).

¹⁶ Trask, "Sulfonation and Sulfation of Oils," 569.

¹⁷ Kawahara et al., "Absolute Configuration of Chlorosulfolipids From the Chrysophyta Ochromonas Danica."

¹⁸ Orfanakis et al., "Characterization of Polyglycerol Polyricinoleate Formulations Using NMR Spectroscopy, Mass Spectrometry and Dynamic Light Scattering."

¹⁹ Trask, "Sulfonation and Sulfation of Oils," 569.

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Figure 5-9 Segment of ¹H NMR spectra of Turkey red oils and estolide reference. Spectra taken in CDCl₃ and aligned using the solvent signal at 7.28 ppm.

Figure 5-9 shows the TRO samples compared to the ¹H spectrum for the reference sample coco-oleic 2-ethylhexyl ester (Figure 5-6). The estolides have a clear estolide methine (H_m) signal at 4.87 ppm, which is not present in the oils or ricinoleic acid spectra in Figure 5-7 (though the discussion in Section 5.2.4.1 suggests otherwise), and an Ha signal indicating small portion of estolides have alkenes (not pictured in estolide structure). The H* signal from the 2-ethylhexyl ester is particular to the structure of this preparation and not expected to be seen for ricinoleic estolides likely to form in Turkey red oil. In the replica TRO sample, which was a few months old at the time of analysis, a very faint peak can be seen if the signal is amplified. The Fluka sample has a signal at 4.90 ppm indicating estolide formation, consistent with its date of manufacture (lot 1453189V, quality control release Nov. 2009). The historical DB and SDC samples each have a strong peak at 4.89 ppm, with weak signals in the Fluka TRO and faint ones in the replica TRO. Ricinoleic acid tends to self-polymerise and must be made fresh²⁰ if a high quantity of FFAs is desired, as in oiling for Turkey red. The formation of estolides reduces the quantity of FFAs available to bond to the cellulose, and estolides are not expected to become part of the oiling process based on the conditions of the oiling process, which are not conducive to rapid estolide formation based on the literature.²¹ Many dyeing firms, especially those

²⁰ Achaya, "Chemical Derivatives of Castor Oil," 758.

²¹ Isbell, Kleiman, and Plattner, "Acid-Catalyzed Condensation of Oleic Acid Into Estolides and Polyestolides."

with chemists, made their own TRO on-site,²² avoiding the problem of polymerisation in the oil.

5.2.3.3 ¹H NMR summary

The proton NMR spectra for castor and olive oil were characteristic of triglycerides, with castor oil containing a high proportion of ricinoleic acid. The spectrum of ricinoleic acid was consistent with that of castor oil, minus the glyceride peaks, and some peaks were slightly shifted between the two samples as a result of this difference. The TRO spectra show the reaction with sulfuric acid hydrolyses the glycerol bonds, releasing FFAs. The sulfuric acid next attacks any -OH groups, followed by the alkene, potentially forming sulfate esters that would likely hydrolyse. The changes in the alkene peaks (H9/H10) are consistent with changes to these proton environments when compared to the spectra for castor oil and ricinoleic acid. Turkey red oil, the product of the sulfation process, is much less viscous than castor oil, reflecting the changes to the -OH and alkene environments seen in these spectra. The spectra also show autopolymerisation reactions between FFAs that occur as TRO ages produce estolides, which decrease the usefulness of the oil for the Turkey red process, evidence of why dyers preferred fresh oil. Although estolide formation reduces the available quantity of FFAs and do not appear to have a role in the dyeing of Turkey red, they are not assessed quantitatively here. The quantity of estolides in the Fluka TRO did not prove to be an impediment to its usefulness in Turkey red dyeing for this research (see Section 4.3) and a dye house would have been unlikely to have ingredients lying around for an extended period to go to waste. These results support the conclusion that TRO is a mixture of FFAs and that the historical, commercial, and replica samples have similar compositions.

5.2.4 ¹³C NMR Results

Spectra for ¹³C can be more difficult to obtain due to low relative abundance of the isotope (ca. 1%), resulting in weaker signals. Some weaker signals in these samples are difficult to distinguish or not visible above the noise, but in general the ¹³C support the conclusions from ¹H NMR spectra.

²² Hurst, *Textile Soaps and Oils*, 140.

5.2.4.1 ¹³C spectra of castor and olive oils and ricinoleic acid

The chemical shifts in ¹³C NMR spectra for castor and olive oil and ricinoleic acid are consistent with those published in the literature.^{23,24,25,26} The peak assignments are given in Table 5-3.

¹³ C chemical shift, δ ppm				
Position	Olive oil	Castor oil	Ricinoleic acid	
1α	173.4	173.5	170.6*	
1B	173.0	173.0	179.0	
2	34.3	34.2	34.4	
3	24.8	25.1	25.0	
4-7	29.0-27.7	29.2-29.9	29.2-29.8	
8	27.5	27.4	27.6	
9	129.9	133.3	133.4	
10	130.3	125.6	125.3	
11	27.5	35.6	35.6	
12		71.7	72.0	
13	20.2.20.4	37.1	37.0	
14	27.3-30.1	25.9	25.9	
15		29.1-29.6	29.2-29.6	
16	32.1	32.2	32.1	
17	22.9	22.8	22.9	
18	14.3	14.3	14.7	
a	62.4	62.3	-	
β	69.2	69.1	_	

Table 5-3 ¹³C NMR peak assignments for castor and olive oils

*Weak signals at 174.0 and 74.0 ppm (see Figure 5-11 and Figure 5-12) consistent with C1 estolide and C_m carbons indicating trace polymerisation has occurred.

²³ Gunstone et al., "Fatty Acids. Part 50. ¹³C Nuclear Magnetic Resonance Studies of Olefinic Fatty Acids and Esters."

²⁴ Husain et al., "Quantitative Determination of Castor Oil in Edible and Heat-Abused Oils by ¹³C Nuclear Magnetic Resonance Spectroscopy."

²⁵ Lie Ken Jie and Cheng, "Confirmation of the Carbon Chemical Shifts of Ethylenic Carbon Atoms in Methyl Ricinoleate and Methyl Ricinelaidate."

²⁶ Sacchi, Addeo, and Paolillo, "¹H and ¹³C NMR of Virgin Olive Oil. An Overview."



Figure 5-10 ¹³C NMR spectra of castor and olive oils and ricinoleic acid. Spectra taken in CDCl₃ and aligned using the central solvent signal at 77.36 ppm.

In Figure 5-10, signals for the Ca and CB glycerol carbons are present in castor oil at 62.3 and 69.1 ppm, respectively, and in olive oil at 62.4 and 69.2 ppm, confirming the oils are triglycerides. Ricinoleic acid has no such peaks. Unlike the ¹H spectra, which had no H1 signal, the C1 signal can be used to identify fatty acids or glycerides. In both castor and olive oils, the C1a signal is around 173.4 ppm and the C1B signal is at 173.0 ppm; this should shift when the glycerol bonds are hydrolysed. This is evident in the ricinoleic acid spectrum, which has a large C1 signal at 179.6 ppm as well as a small C1 at 174.0 ppm, indicative of minor estolide components (see Appendix E).

The C12 signal in castor oil appears at 71.7 ppm and in ricinoleic acid at 72.0 ppm, distinct due to the effect of the –OH and shifted due to the difference between triglycerides and FFAs. The –OH also causes slight shifts in the signals for C11, C13, and C14, which does not happen in olive oil since the –CH₂– environments are identical. This effect is also seen on the alkene carbons. In castor oil and ricinoleic acid, the C9 and C10 signals are around 133 ppm and 125

ppm, respectively. The same signals in olive oil are 129.9 ppm for C9 and 130.3 for C10, much closer due to the absence of the -OH. Both samples also have other smaller peaks in this region from various mono- and polyunsaturated minor component fatty acids.

5.2.4.2 ¹³C spectra of Turkey red oils

The ¹³C NMR spectra of Turkey red oils are consistent with the published spectra for ricinoleic acid and castor oil that were used to make peak assignments.^{27,28,29} These spectra also support the conclusions from the ¹H NMR spectra.

¹³ C chemical shifts, δ ppm						
Position	Castor oil	Ricinoleic acid	Fluka	DB	SDC	Replica
1 (FFA)	-	179.6	180.5/182.6*	180.3	180.6	179.2
1 (estolide)			174.2	174.0	173.p	174.2
1α	173.5		173.5	-	-	173.5
1B	173.0		172.0	I	1	173.5
9	133.3	133.4	134.4*	133.6*	133.6*	133.5
10	125.6	125.3	125.6*	125.5*	125.6*	125.5
12	71.7	72.0	71.8	71.9	71.9	71.8
α	62.3	-	62.4	1	1	62.4
В	69.2	-	weak	-	_	69.1
Cm	-	74.0	74.0	74.0	74.0	_

Table 5-4 Relevant ¹³C NMR peak assignments for Turkey red oils compared to castor oil. * There are multiple signals in this area due to the mixed nature of the samples; the strongest is represented in the table.

²⁷ Husain et al., "Quantitative Determination of Castor Oil in Edible and Heat-Abused Oils by ¹³C Nuclear Magnetic Resonance Spectroscopy."

²⁸ Lie Ken Jie and Cheng, "Confirmation of the Carbon Chemical Shifts of Ethylenic Carbon Atoms in Methyl Ricinoleate and Methyl Ricinelaidate."

²⁹ Orfanakis et al., "Characterization of Polyglycerol Polyricinoleate Formulations Using NMR Spectroscopy, Mass Spectrometry and Dynamic Light Scattering."



Figure 5-11 Portion of 13 C spectra of Turkey red oils and castor oil, ca. 165-185 ppm. Spectra taken in CDCl₃ and aligned using the central solvent signal at 77.36 ppm.

In Figure 5-11, the castor oil spectrum shows two distinct C1 α and C1 β signals around 173 ppm. Ricinoleic acid has a C1 signal at 179.6 ppm consistent with the absence of glyceride bonds. This C1 FFA signal appears in the TRO samples around 180 ppm. In the Fluka and replica TRO, C1 signals from FFAs, and glycerides are present, and in Fluka there is an additional signal at 182.6 ppm consistent with a fatty acid sodium salt. The DB and SDC samples also have a C1 fatty acid signal around 180 ppm. A C1 estolide signal is present in some samples around 174.0 ppm and discussed later in this section. The C1 fatty acid signal for ricinoleic acid and the replica TRO are much closer in chemical shift when compared to the other TRO samples.



Figure 5-12 Portion of ¹³C NMR spectra of Turkey red oils and castor oil, ca. 60-85 ppm. Spectra taken in CDCl₃ and aligned using the central solvent signal at 77.36 ppm.

The spectra show the Fluka and replica TRO samples still contain glycerol, though much less relative to the castor oil (see Figure 5-12). The ricinoleic and TRO samples have a C12 signal around 71.8 ppm, appearing in castor oil slightly

upfield at 71.7 ppm, again consistent with the slight shifts seen in the ¹H spectra. Fluka TRO has an additional unidentified signal at 72.5 ppm. The black boxes A and B highlight minor unidentified components in the Fluka and replica TRO samples. They are not consistent with the blank spectrum for toluene (see Appendix E) or its signals in CDCl₃, so they are not obviously contaminants. If they are the result of minor component formation from the sulfuric acid reaction as proposed in the discussion of the ¹H NMR spectra, they may indicate new carbon environments relative to the ricinoleic acid or castor oil. The aforementioned study of chlorosulfolipids determined the ¹³C chemical shift of a centrally-located carbon shifts about 5 ppm downfield when an -OH becomes an -OSO₃H.³⁰ The peaks in box A may be the result of glycerol sulfates and in box B fatty acid sulfate esters, but further analysis is required to draw any conclusions.

Changes to the allylic carbons are shown in Figure 5-13. The Fluka, DB, and SDC samples all have multiple small signals on either side of C9 and C10, plus various small signals from reactions on other minor component fatty acids. In the Fluka and SDC samples, some of these low peaks may be from trace toluene left after drying. The signals for C9 and C10 in all TRO samples show not all alkenes are attacked during sulfation.



Figure 5-13 Portion of 13 C NMR spectra of Turkey red oils and castor oil, ca. 115-140 ppm. Spectra taken in CDCl₃ and aligned using the central solvent signal at 77.36 ppm.

³⁰ Kawahara et al., "Absolute Configuration of Chlorosulfolipids From the Chrysophyta Ochromonas Danica."

The estolide methine carbon (C_m) produces a signal in polyestolides around 74 ppm³¹ (Figure 5-14). The Fluka, DB, and SDC samples have a signal at 74.0 ppm, consistent with the value for C_m , supporting the evidence in the ¹H NMR spectra that the FFAs spontaneously form estolides over time. In the reference sample coco-oleic 2-ethylhexyl ester, C_m appears at 74.4 ppm due to the different estolide structure—in TROs, polyricinoleic estolides are anticipated to form. No C_m signal is visible in the replica TRO due to its freshness and the low relative abundance of ¹³⁻C, but the C1 estolide signal around 174.0 ppm in Figure 5-11 is consistent with trace amounts in ricinoleic acid and the TRO samples.



Figure 5-14 Portion of ¹³C NMR spectra for Turkey red oils and estolides, ca. 55-85 ppm. Spectra taken in CDCl₃ and aligned using the central solvent signal at 77.36 ppm.

5.2.4.3 ¹³C NMR summary

The results of the ¹³C NMR analysis support the conclusions from the ¹H spectra, showing the olive and castor oils are triglycerides, while the TROs have almost no glycerol signals. The triglyceride oils have signals for C1a and C1B around 173 ppm (see Figure 5-10), whereas in ricinoleic acid a C1 signal for FFAs appears at 179.6 ppm. In the TRO samples, it can be seen around 180 ppm, consistent with glycerol hydrolysis of castor oil to produce FFAs. Additional C1 signals around 173 ppm are evidence of remaining glyceride compounds. The reaction with sulfuric acid may produce some minor components based on small peaks around 72 ppm and 78 ppm in the replica and Fluka TRO samples. The alkene bonds undergo some hydrolysis but are not completely removed; a variety of

³¹ Isbell and Kleiman, "Characterization of Estolides Produced From the Acid-Catalyzed Condensation of Oleic Acid."

compounds result from sulfuric acid attacking this bond on different FFAs. The presence of estolides in some samples is confirmed by the C_m signal at 74.0 ppm.

5.2.5 Composition of Turkey red oil based on NMR analysis

The ¹H and ¹³C NMR spectra show the reaction between sulfuric acid and castor oil causes glycerol hydrolysis and various reactions between the acid and the alkene bond and ricinoleic acid -OH groups. Although no sample of rancid olive oil was available for this research, some reasonable conclusions may be drawn from this work. Since Turkey red oil is composed of FFAs, and the 'old' and 'new' Turkey red processes both yielded Turkey red, the oil called *huile tournante* was likely the product of hydrolytic rancidity in olive oil that increased the quantity of FFAs.



Figure 5-15 Reactions between castor oil and sulfuric acid.

Comparing the ¹H and ¹³C NMR spectra of the TRO samples and reference compounds provides some indication of how the reactions proceed. The biggest changes are seen in the signals from glycerol and the fatty acid bonds to it, which undergo the most changes when castor oil reacts with sulfuric acid. Changes to peaks in the C9 and C10 region show the sulfuric acid reacts with some of the alkene bonds, a similar effect seen in the ¹H NMR spectra for the H12 signal. A large portion of Turkey red oil is a mixture of FFAs, which will autopolymerise over time to form estolides, as shown in both sets of spectra. Based on what is known about the reactivity of sulfuric acid and castor oil, it appears the reaction time was long enough to hydrolyse most of the glycerol bonds and some of the -OH and alkenes. The reaction time with sulfuric acid has an outcome on the composition of Turkey red oil, with the proportion of FFAs in the final product being more significant than the sulfonation side-products. The results support the conclusions from the review in Chapter 2.

5.3 HPLC-MS

As a complementary technique to NMR, which can have difficulty distinguishing mixed samples like TRO, HPLC-MS was chosen because it allows the analyst to separate mixtures of compounds from small samples. The MS detector is used because the FFAs are not UV-active enough to be detected optically. Depending on the sample, the technique may be destructive, but since it requires minimal sampling the results are usually worth the sacrifice. The purpose of this was to determine more specifically the FFA and triglyceride composition of the Turkey red oils. The technique is discussed in further detail in Appendix A and the full report is included in Appendix F.

5.3.1 Instrument and acquisition

Samples for analysis were sent to the Dipartimento di Chimica e Chimica Industriale at the University of Pisa in Pisa, Italy, and analysed by Dr Ilaria Degano and Dr Jacopo La Nasa. Their report (Appendix F) gives the amounts of triglycerides and fatty acids and fatty acid profiles of the samples. Since the conclusion from this research, based on the variety of oil and fat sources used, is that the type of fatty was not significant to the process, the profiles are considered beyond the scope of this research.

Chromatography was done on an Agilent 1200 Infinity HPLC equipped with a Poroshell 120 EC-C18 column (50 mm [incorrect in the report as 5.0 mm] x 3.0 mm i.d., 2.7 μ m particle size) and a Zorbax Eclipse Plus C18 guard column (12.5 mm x 4.6 mm i.d., 5 μ m particle size). The column temperature was set to 45 °C. A gradient elution with methanol (eluent A) and isopropanol (eluent B) was

programmed as follows: 90% A for 5 minutes, linear gradient to 90% B in 25 minutes, 90% B for 5 minutes with a 0.3 mL/min flow rate. The sample injection volume was 1 μ L and after each sample the system was re-equilibrated for 10 minutes.

Mass spectrometry was done on an Agilent 6530 Accurate-Mass Q-TOF LC/MS system with a Jet Stream ESI interface. In the ESI the conditions were: drying gas (N₂, purity >98%) 350 °C and 10 L/min; capillary voltage 4.5 kV; nebulizer gas 35 psig; sheath gas (N₂, purity >98%) 375 °C and 11 L/min. MS and MS/MS spectra were acquired in positive mode in the range of 100-1700 m/z. The fragmenter was set at 200 V, nozzle voltage at 1000 V, skimmer voltage at 65 V, octapole RF at 750 V. The collision energy for MS/MS experiments was set at 50 V and the collision gas was N₂ (purity 99.999%). Data were collected by auto MS/MS acquisition with an MS scan rate of 1.03 spectra/sec and an MS/MS scan rate of 1.05 spectra/sec; only one precursor was acquired per cycle (relative threshold 0.010%).

5.3.2 Sample preparation

The sample preparation was omitted from the report for HPLC-MS and can be found in this article by the same group.³² 3-5 mg of sample was dissolved in 500 μ L n-hexane in an ultrasonic bath at 60 °C for 5 minutes. The extracted lipid fraction was dried under nitrogen flux, diluted with 500 μ L of the mobile phase and filtered through a 0.45 μ m PTFE filter. 10 μ L of the filtrate was diluted to 1 mL.

5.3.3 HPLC-MS Results

The triglyceride profile of castor oil shows 74.6% of the sample is triricinoleic triglycerides, which is consistent with the NMR results and the known composition of castor oil. Olive oil had a high proportion of trioleic triglycerides at 30.0%, and contained no ricinoleic glycerides. The total amounts of triglycerides were higher in these oils than in the Turkey red oils, which had more FFAs.

³² La Nasa et al., "Core Shell Stationary Phases for a Novel Separation of Triglycerides in Plant Oils by High Performance Liquid Chromatography with Electrospray-Quadrupole-Time of Flight Mass Spectrometer."



Figure 5-16 Normalised amount (%) of soluble triglycerides and free fatty acids. Legend: TAG = Tri(acyl)glycerides FA: Fatty acid

The results in Figure 5-16 were obtained by normalising the sum of all peak areas toward the weight sample and the dilution factor of the sample. The high proportion of triglycerides in castor oil became FFAs when it was made into replica TRO ('CastorSolf'). The FFA content of the olive oil is slightly higher than the acceptable acid content for fresh olive oils,³³ which is consistent with it being *huile de bourbes* rather than food-grade oil. The results also found the Fluka (TRO-Sigma), DB, and SDC samples had a higher degree of polymerisation than the other oils (see Appendix F). This analysis supports the conclusion from the NMR analysis that in TRO samples the proportion of FFAs to triglycerides is fairly high.

5.4 Summary

This aim of these analyses was to experimentally determine the composition of Turkey red oil using robust, modern analytical techniques to confirm the conclusions of 19th c. dyers and chemists that fatty acids were the major component in the oil. To achieve this, reference samples of castor and olive oils and of ricinoleic acid were compared to four Turkey red oils, two of historical origin, one commercial, and one replica. The results are indicative the historical re-creation of Turkey red oil following a 19th c. method successfully produced a material with the same chemical composition as the other samples. This shows

³³ Spangenberg, Macko, and Hunziker, "Characterization of Olive Oil by Carbon Isotope Analysis of Individual Fatty Acids: Implications for Authentication."

the texts contain accurate directions for making the oil, possibly indicating the value of knowledge exchange was greater than the benefits of maintaining secrecy, at least for some.

The results from the ¹H and ¹³C NMR analysis and the HPLC-MS profile support the proposition that Turkey red oil is a mixture of FFAs with some partial glycerides, but that most triglycerides are hydrolysed in the sulfation process. Quantitation of these compounds is beyond the scope of this project and this research does not explore the composition of Turkey red oil in detail since it is not thought to be significant within in the context of Turkey red dyeing, though an optimisation of the process may benefit from such an investigation. Dyers do not appear to have gone through great lengths to test their oil and did not appear to have much difficulty acquiring oil of suitable quality. Confirming that the composition of Turkey red oil is largely FFAs addresses part of the research question for this project about the role of the oil. This information is then used to form a hypothesis on the reactivity between Turkey red oil and cellulose. The carboxylic acid of FFAs is the most reactive, as shown by the formation of estolides, so this is thought to be what bonds to cellulose. The good condition of historical Turkey red textiles indicates the oil does not affect the cellulose polymer, so a reaction is more likely to occur with the numerous -OH groups of the glucose units. Now that it has been confirmed the purpose of the oiling steps in the Turkey red process is to apply FFAs to the cotton, in situ experimental work can determine what changes take place on the textile.

6 *In situ* analysis of oiled calico and Turkey red textiles

Prior to this research, the ability to identify Turkey red textiles was limited to confirming the presence of alizarin on bright red cotton textiles. This does not take into account the oil, which is an ideal chemical marker to look for since preparation with oil is imperative to the Turkey red process and characteristic of it in that it does not appear in other dyeing techniques. Historically, research on the oil was by necessity done through extraction from the fibres and analysis, but since Turkey red exists only on the fibre, the information gained is incomplete. When Turkey red production in Scotland ended in the 1930s, prior to the development of the instrumental analyses now available, so did most research on its chemistry. These textiles are now valuable historical objects and further research on them requires an emphasis on non-invasive techniques in order to ensure their continued preservation.

With these conditions in mind, Fourier transform infrared spectroscopy (FTIR) was chosen as a tool to characterise Turkey red in situ due to its ability to distinguish organic bonds and its applications for surface analysis. The technique was previously applied to Turkey red in the 1960s, in a doctoral thesis on metal complexes of alizarin, and found evidence of oil on the fibres.¹ The historical samples were destructively prepared as KBr pellets, a technique not suited to conservation-based analysis, and the work did not attempt to characterise any of the oil bonds. In the last fifty years, no further work has been published on the topic. Modern FTIR instruments now allow rapid, non-invasive analysis with no sample preparation, making it possible to re-visit and examine the role of the oil in Turkey red. This research compares the application of two FTIR techniques, attenuated total reflectance (ATR) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Analyses were done of replica Turkey red, historical pieces from the United Turkey Red (UTR) collection at Glasgow University (GU) and the Centre for Textile Conservation (CTC) Karen Finch reference collection, 19th c. dyeing manuals in the GU Special Collections, and a fibre from an unusual dress in the Victoria & Albert Museum (V&A) collection.

¹ Kiel, "Metaalcomplexen van Alizarinerood," 191.

Analysis by ¹³C solid-state NMR (ssNMR) was chosen to complement the FTIR results. The chemical shift for a carbonyl carbon (C1) can distinguish a carboxylic acid (R-COOH), carboxylate (R-COO⁻), or ester (R-COOR), which may be less clear in FTIR spectra. The technique is similar to traditional NMR and results are interpreted using the same chemical shift references. Furthermore, ssNMR does not require solvation, so it can be used for *in situ* analysis on the cellulose fibres.

The conclusion from the literature review and the analysis of Turkey red oils is that the free fatty acids (FFAs) in the oil form bonds with the hydroxyl groups of cellulose fibres in the oiling process for Turkey red. This chapter investigates the nature of this bonding and its role in the process, which has been of interest to dyers and chemists since the late 18^{th} c.² The work in this chapter addresses the questions for this project regarding whether the FFA-cellulose bond can finally be characterised, with an emphasis on conservation-based analysis, and whether Turkey red can be re-created from a historical recipe by comparing the replica samples to 19^{th} c. textiles.

6.1 FTIR spectroscopy

Interpreting FTIR spectra may be difficult due to overlapping bands, depending on what materials and therefore bonds are present. Organic bonds are distinguished in FTIR spectroscopy by the position and shape of spectral bands. Carbonyls (C=O) are particularly FTIR active and easy to identify. The v_{asym} (C=O) band around 1744-1700 cm⁻¹ is especially useful for FFA characterisation since cotton scoured for dyeing has been stripped of its natural waxes and cellulose has no carbonyl groups, so except for adsorbed water around 1640 cm⁻¹, the only bands that appear in this region should be from an oil treatment. Fatty acids should be easily identified by their carbonyl group, and to an extent as well by the aliphatic carbon chain. The position of these bands also indicates what types of bonding occur. Alizarin molecules also have two carbonyl groups; the bands for aromatic carbonyls appear in a different range from aliphatic ones³ and will not interfere with the oil analysis. To address this potential for confusion, in this

² Berthollet, *Elements of the Art of Dyeing*, 164.

³ Pretsch, Bühlmann, and Badertscher, *Structure Determination of Organic Compounds*.

research samples prepared with either, neither, or both compounds were analysed and compared.

This project compares the application of ATR and DRIFTS techniques. Recent developments in handheld FTIR instruments⁴ mean analysis can be done with minimal disruption to the object. DRIFTS analysis previously required samples to be powdered, making it destructive in the case of Turkey red, but newer handheld instruments require only surface contact and have more potential for heritage object research. Published investigations thus far include DRIFTS analysis of built heritage⁵ and painting layers.⁶ Characterisations of textile degradation and treatments by DRIFTS have been preliminary⁷ and no studies have yet been published, the results presented in this chapter being a novel application of DRIFTS to heritage textiles. The handheld instruments also make it possible for researchers to overcome the limitations of an object that cannot be analysed on an ATR interface. The relatively new handheld DRIFTS devices are less common, however, than the fairly standard ATR instruments. For reasons of instrument availability and individual sample configurations (i.e. mounted or loose textile), spectra of replica and historical Turkey red were taken with the handheld DRIFTS instrument and, when possible, the ATR instrument as well. The depth of penetration below the object surface also differs between DRIFTS and ATR, possibly providing some contrast between what is detected closer to the surface and further in the bulk fibre.⁸ The aim was not to directly compare the two techniques, but rather to see if both could be useful and what were the advantages and disadvantages of each. The information provided by the two techniques is compared here within in the context of oiled cotton evaluation and Turkey red identification. The details of FTIR spectroscopy and the specifics of the individual techniques are discussed in Appendix A.

⁴ Higgins, Rein, and Seelenbinder, "Diffuse Reflectance Spectroscopy Using a Handheld FTIR."

⁵ Arrizabalaga et al., "Diffuse Reflectance FTIR Database for the Interpretation of the Spectra Obtained with a Handheld Device on Built Heritage Materials."

⁶ Manfredi et al., "Portable Diffuse Reflectance Infrared Fourier Transform (DRIFT) Technique for the Non-Invasive Identification of Canvas Ground: IR Spectra Reference Collection."

⁷ Quye et al., "A Little More Reflection, a Little More Depth: Applications of DRIFTS in Heritage Textile Conservation."

⁸ Forsskåhl et al., "Depth Profiling of a Photochemically Yellowed Paper. Part II: FT-IR Techniques."

In textiles, there is a lot more cellulose present relative to the amount of dye complex, which produces a bulk cellulose signal that may obscure smaller bands from Turkey red components. The complexity of the dyeing process also means there are molecules from a series of treatments present in the finished pieces. This research compares spectra from plain calico that has received no oil treatment, oiled calico, dyed Turkey red calico, and calico dyed with madder and no oil. Preparation of the re-created oiled calico, Turkey red, and madder dyed calico is described in Chapter 4. The 19th c. pieces analysed in this chapter by non-invasive FTIR include Turkey red from a range of dyeing manuals and the United Turkey Red (UTR) sample pattern books at the University of Glasgow, and two pieces of oiled calico from a 19th c. dyeing manual by Persoz.⁹ This makes it possible to compare spectra between replica and historical pieces at two points in the dyeing process. Published data for a variety of techniques is available on the ageing degradation of cellulose,¹⁰ so any resulting differences from this can be identified, although based on the good condition of the textiles, few to none are anticipated.

6.1.1 ATR instrument and acquisition

ATR analysis was done at the CTC on a Perkin Elmer Spectrum One FTIR spectrometer with a diamond/thallium-bromoiodide C/KRS-5 crystal ATR accessory and an infrared source beam that penetrates to a depth of about 2 μ m. The interface operates through specular reflectance, with the incident angle of the radiation at 45° to the crystal. An initial background scan was taken of the uncovered crystal and then the sample spectra were collected as the average of 16 scans taken from 4000-400 cm⁻¹ at 8 cm⁻¹ resolution in absorbance mode. Three spectra were taken from different locations on the sample surface for the textiles.

The ATR interface requires the sample to be pressed against the crystal, which is accomplished using the pressure clamp that registers a degree of force from 0-100 in the instrument software. This degree of force affects the acquisition of spectra, as shown in Figure 6-1.

⁹ Persoz, Traité théorique et pratique de l'impression des tissus, 192.

¹⁰ Chettra, "Microscopy and Surface Chemical Investigations of Dyed Cellulose Textiles," 22.



Figure 6-1 ATR spectra of plain calico taken at clamping forces against the crystal. One scan per sample, spectra not normalised.

When the spectra are normalised by maximum peak height as in Figure 6-2, the spectra become more homogeneous but still show some variance related to the initial clamping force.



Figure 6-2 ATR spectra of plain calico taken with varied clamping force after correction. One scan per sample, normalised to 1.0 at 1029 cm⁻¹.

The effect of the clamping force on spectral acquisition makes it necessary to normalise the ATR spectra by maximum height to eliminate as much of the effect as possible for interpretation. In this chapter, each of the ATR spectra were normalised to a maximum height of 1.0 for the highest peak, around 1030 cm⁻¹. To further control for this affect, all spectra were acquired with the clamp force set around 50 (±5) for consistency. The average and deviation of each set of three scans was calculated using Panorama Pro software (LabCognition). ATR spectra can also be processed using a tool called ATR correction, which adjusts the spectrum to compensate for the refractive index of the crystal (around 2.4 according to manufacturer) and the incident angle of the beam (45°). It was not used in this research to maintain consistency with published reference spectra,

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which were not treated in this manner, excepting in Section 6.7.5 for consistency with the ATR corrected spectrum received from the V&A.

Using the same conditions, spectra were also taken of the oils used to prepare the calico samples in Section 4.2 by placing a drop of oil on the crystal. Since these samples were not clamped, they were not normalised and the replicates were averaged as acquired.

6.1.2 DRIFTS instrument and acquisition

DRIFTS spectra of historical Turkey red were taken in February 2015 at the Centre for Textile Conservation using an Agilent 4300 Handheld FTIR with a diffuse reflectance sample interface. Dr Pik Leung Tang, an Applications Specialist with Agilent Technologies, generously provided access to the instrument, guidance, and support while collecting and analysing the data. The quicker instrument made it possible to take more spectra that were the average of more scans in less time than the ATR. This, and its increased sensitivity toward rough surfaces, means the DRIFTS spectra are generally more detailed than the ATR. The beam from this interface penetrates the sample to a depth of about 7 μ m, producing a greater bulk sample signal than the ATR interface. Each spectrum was the average of 128 scans taken from 5000-650 cm⁻¹ at 8 cm⁻¹ resolution in absorbance mode. A background of the instrument cap was taken every ten minutes. This instrument requires only contact with the sample, a significant difference from the force-dependent ATR instrument that affects how the spectra are processed.



Figure 6-3 DRIFTS spectra of four plain calico samples. One scan per sample, no normalisation.



Figure 6-4 DRIFTS spectra of four plain calico samples after correction. One scan per sample, normalised to 1.0 at 3400 cm⁻¹.

In Figure 6-3, the raw DRIFTS spectra are much more consistent than the unprocessed ATR spectra shown in Figure 6-1. Because of the different sampleinstrument interface the maximum peak is no longer 1030 cm⁻¹ as in the ATR spectra. Normalisation to a maximum peak height of 1.0 in Figure 6-4 does not significantly alter spectra from the same calico, but in a comparison of different weaves (see Figure 6-44) the effect would be much greater. The scaling also affects the response related to the texture of the sample, producing spurious results in the DRIFTS spectra, which are more sensitive than ATR to uneven surfaces.¹¹ For these reasons, the DRIFTS spectra were not normalised. A different type of adjustment may be beneficial for these spectra, however. The effect of scattered radiation and the diffuse reflector, plus the uneven textile surfaces, causes some DRIFTS spectra to have a slightly irregular y-offset (vertical displacement, see Figure 6-5). For quantitative analysis this should be corrected, but for displaying static figures the slight y-offset is helpful because each sample can be more easily distinguished in an overlay. Figure 6-6 shows that after y-offset correction from 22000-2000 cm⁻¹, the Turkey red spectra line up very well in the overlay, but the individual samples are less clearly visible. In general, DRIFTS spectra in this research were not adjusted for y-offset unless otherwise noted, usually when comparing spectra from different weaves of cotton.

¹¹ Tang, "Processing FTIR Spectra."



Figure 6-5 DRIFTS spectra of historical Turkey red with no y-offset correction. The red spectrum is the calico blank. Samples are discussed later in this chapter.



Figure 6-6 DRIFTS spectra of historical Turkey red with the y-offset corrected between 2200-2000 cm⁻¹. The red spectrum is the calico blank.

Replicates of six spectra were taken from different locations on the replica samples and three spectra from different locations on the historical samples due to time constraints. These spectra were averaged as described above. Infrared spectra below 650 cm⁻¹ are difficult to interpret, and above 4000 cm⁻¹ begins to enter the near-infrared range, which the ATR instrument does not collect, so the DRIFTS spectra were analysed from 4000-650 cm⁻¹.

6.2 FTIR spectra of reference materials

6.2.1 ATR and DRIFTS spectra of plain calico

References for FTIR spectroscopy of cellulosic fibres^{12,13,14} provides peak assignments for bands from the cellulose of the cotton fibres. In Table 6-1 and

¹² Schultz, Templeton, and McGinnis, "Rapid Determination of Lignocellulose by Diffuse Reflectance Fourier Transform Infrared Spectrometry."

Table 6-2, the significant peak assignments¹⁵ for plain calico are provided. Especially for the DRIFTS spectra, not all peak assignments are made because the level of detail is beyond the scope of this project. General trends in the spectra are identified and discussed. The figures were generated using EssentialFTIR software with the automatic peak picking threshold set at the lowest peak above the baseline. The feature has an adjustable degree of sensitivity from 1-100. This work found the ATR spectra required a sensitivity of 100 to identify all major bands, while the more detailed DRIFTS had hundreds of small peaks labelled at this level and were better represented at a peak-picking sensitivity of 50.



Figure 6-7 ATR spectrum of plain calico. Average of three replicates normalised to 1.0 at 1029 cm⁻¹.

¹³ Garside and Wyeth, "Identification of Cellulosic Fibres by FTIR Spectroscopy: Thread and Single Fibre Analysis by Attenuated Total Reflectance."

¹⁴ Fan, Dai, and Huang, "Fourier Transform Infrared Spectroscopy for Natural Fibres."

¹⁵ Socrates, Infrared and Raman Characteristic Group Frequencies.
Position (cm ⁻¹)	Assignment
3333	OH stretching
3288	
2897	CH ₂ asymmetrical stretching
1642	Adsorbed water
1427	C-H, O-H in-plane bending
1360	C-H in-plane bending
1334	CH ₂ wagging
1314	CH ₂ rocking at C6
1280	CH ₂ twisting
1248	C-OH out-of-plane
1203	C-O-C symmetric stretching
1160	C-O-C asymmetric bridge oxygen stretching
1107	C-O-C glycosidic stretching
1053	C-OH 2° alcohol
1029	C-OH 1° alcohol
1001	C-C, C-OH, CH ring and side group vibrations
986	C-C, C-OH, CH ring and side group vibrations
898	C-O-C in plane, symmetric
663	C-OH out-of-plane bending

Table 6-1 Peak assignments for ATR spectrum of plain calico.

The carbonyl stretching region (1800-1600 cm⁻¹)¹⁶ is key to identifying FFAs on the fibres. In the spectrum of plain calico, the only peak in this region is for adsorbed water around 1640 cm⁻¹. The same absence of a carbonyl signal is seen in the DRIFTS spectrum for plain calico below. The location of the carbonyl band as well as changes elsewhere in the spectrum will provide more information about the chemistry of the process and how the oil bonds to the cellulose.



Figure 6-8 DRIFTS spectrum of plain calico. Average of three replicates; spectra not normalised.

¹⁶ ibid.

Position (cm ⁻¹)	Assignment	
3459		
3425		
3403	OH stretching	
3388		
3366		
3306		
3247		
2904	CH ₂ asymmetrical stretching	
2743	Combinatorial OH bands	
2542		
1644	Adsorbed water	
1431	C-H, O-H in-plane bending	
1372	C-H in-plane bending	
1338	CH ₂ wagging	
1319	CH ₂ rocking at C6	
1282	CH ₂ twisting	
1237	C-OH out-of-plane	
1204	C-O-C symmetric stretching	
1178	C-O-C asymmetric bridge oxygen stretching	
1129	C-O-C asymmetrical stretching	
1092	C-O-C asymmetrical stretching	
1044	C-OH 2° alcohol	
1020	C-OH 1° alcohol	
1003	C-C, C-OH, CH ring and side group vibrations	
898	C-O-C in plane, symmetric	
678	C-OH out-of-plane bending	

Table 6-2 Peak assignments for DRIFTS spectrum of plain calico.

More definition is visible in the DRIFTS spectra from 3700-3000 cm⁻¹ than in the ATR spectra, showing the DRIFTS instrument is more sensitive toward $v_{str}(-OH)$ signals. Combinatorial bands from -OH stretching and deformation are marked at 2743 cm⁻¹, with the remainder appearing from 2300-1900 cm⁻¹ but not labelled. The ATR technique does not detect these peaks, so for a detailed study of cellulose hydroxyls DRIFTS is clearly the more sensitive apparatus.

6.2.2 ATR spectra of oils

Spectra of the neat oils used for treatment in Figure 6-9 were taken for comparison to spectra of oiled calico as well as differences in the oils. Peaks are marked for oleic acid-1-¹³C. Bands for $v_{asym}(-CH_2-)$ around 2922 cm⁻¹ and $v_{sym}(-CH_2-)$ around 2854 cm⁻¹ are consistent across all samples. The spectra

show varied $v_{str}(-OH)$ for TROs, ricinoleic acid, and castor oil, and virtually none in olive oil/oleic acid.



Figure 6-9 ATR spectra of neat oils. Average of three replicates each; spectra not normalised. Peaks from oleic acid-1-¹³C.

In Figure 6-10, the expanded regions of interest are shown with peaks marked for three samples. The TRO samples have a band from adsorbed water at 1643 cm⁻¹. The peak for v_{asym} (C=O) appears around 1745 cm⁻¹ in oleic acid, olive oil, and castor oil while the two TROs have a less sharp band around 1713 cm⁻¹. Ricinoleic acid carbonyl stretching appears at 1708 cm⁻¹ and the oleic acid spectrum has an additional peak at 1669 cm⁻¹ unique to this sample. The effect of a heavier 1-¹³C isotope causes a downshift in stretching vibrations¹⁷ that has an effect on the rest of the molecule.¹⁸ The introduction of the asymmetry from the isotope causes a downshift in the C=C stretching band which is also more intense relative to the non-isotopic samples since the technique is better at detecting uneven bonds. Aside from the isotope effect, these differences in the carbonyl stretching region are indicative of what complexes are present, discussed further in this chapter. This is consistent with the TRO samples being largely fatty acids, resulting in different v_{asym} (C=O) bands that are discussed further in the next section.

¹⁷ Blume, Huebner, and Messner, "Fourier Transform Infrared Spectroscopy of ¹³C=O-Labeled Phospholipids Hydrogen Bonding to Carbonyl Groups."

¹⁸ Larsen, Isotope Effects in Vibrational Spectroscopy.



Figure 6-10 Region of interest for ATR spectra of neat oils. Average of three replicates each; spectra not normalised. Peaks according to legend.

The band at 1549 cm⁻¹ in some samples is attributed to v_{asym} (COO-Na) of carboxylic acid sodium salts.¹⁹ The Fluka sample is sold as 'Turkey red oil sodium salt' and the replica TRO was made with Na⁺ ions, explaining the presence of the band. The spectra provide a reference for the oil bands in the treatments for comparison against the oiled calico.

6.3 Characterisation of FTIR bands in oiled calico samples

This research is the first modern investigation into the chemistry of the Turkey red oiling process and how the fatty acids adhere to the cellulose. As such, there are no previous investigations in this context that this work could refer to. The proposed chemistry of the oiling process is bonding between cellulose hydroxyls and fatty acid carboxyls, so other analyses of fatty acid and hydroxyl bonding by FTIR spectroscopy were sought.

Oiling cotton for Turkey red dyeing was described earlier as a surface coating process. One advantage of comparison to studies of oleic acid coatings on noncellulose substrates is that band identification and assignment is facilitated

¹⁹ Socrates, Infrared and Raman Characteristic Group Frequencies, 126.

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without the presence of a bulk cellulose signal. An FTIR study by Gong *et al.* of oleate adsorption on apatite, a group of phosphate minerals containing calcium and OH⁻, F⁻, and Cl⁻ ions, found that aqueous oleic acid solutions above pH 8.5 contained RCOOH, RCOO⁻, and dimeric carboxylic acids.²⁰ The conditions are consistent with Turkey red oiling techniques and their findings similar to the range of v_{asym}(C=O) bands seen in the oils in Figure 6-10.

Research by Lee *et al.* on oleic acid-coated soda-lime-silicate (SLS), sodasilicate, and silica glasses particles identifies bands from oleic acid complexes.^{21,22} Silicates have hydroxyl groups, enabling a comparison to cellulose in this case. The particles were coated from an aqueous oleic acid solution, similar to Turkey red oiling, and the FTIR spectra show oil bands in agreement with the results from the oiled calico samples presented in the following section. The research found the coating mechanism depended on the composition of the solvent and the ion content of the substrate; in the case of Turkey red, water or soda ley (aqueous sodium carbonate) and cellulose. Bands for v_{asym} (C=O) were identified at 1711 and 1743 cm⁻¹ for oleic acid dimers and monomers, respectively, in pure oleic acid, and higher concentrations of oleic acid were found to result in more dimers. In coated SLS glass, dimeric oleic acid appears at the same wavenumber while band for the monomeric species appeared as a shoulder around 1731 cm^{-1 23}, a pattern also observed by Gong *et* al.²⁴ According to these values, the spectra in Figure 6-10 indicate that the TRO samples and ricinoleic acid contain more dimers while the oleic acid is monomeric based on the position of $v_{asym}(C=0)$. Coated SLS glass also had $v_{asym}(-CH_2-)$ and $v_{sym}(-CH_2-)$ at 2925 and 2854 cm⁻¹, respectively, again consistent with the oil spectra.

²⁰ Gong et al., "Adsorption of Oleate on Apatite Studied by Diffuse Reflectance Infrared Fourier Transform Spectroscopy."

²¹ Lee and Condrate, "FTIR Spectral Characterization of Thin Film Coatings of Oleic Acid on Glasses: I. Coatings on Glasses From Ethyl Alcohol."

²² Lee, Condrate, and Lacourse, "FTIR Spectral Characterization of Thin Film Coatings of Oleic Acid on Glasses Part II Coatings on Glass From Different Media Such as Water, Alcohol, Benzene and Air."

²³ Lee and Condrate, "FTIR Spectral Characterization of Thin Film Coatings of Oleic Acid on Glasses: I. Coatings on Glasses From Ethyl Alcohol."

²⁴ Gong et al., "Adsorption of Oleate on Apatite Studied by Diffuse Reflectance Infrared Fourier Transform Spectroscopy."

Lee *et al.* determined Na⁺ ions had a role dissociating COOH groups in oleic acid, and that the sodium oleate species would to dissociate in water.^{25,26} FTIR spectra of coated glass particles containing Na⁺ ions had a bands at 1562 cm⁻¹ from v_{asym}(COO-Na). The research found carboxyls (COOH) preferentially formed metal oleates in the presence of ions like Na⁺, Ca²⁺, Mg²⁺, and Al³⁺, but otherwise made hydrogen bonds with surface Si-OH groups, forming a hydrophobic layer of oleic acid on the particle surface. In the glass particles, the signal from hydrogen-bonded carboxyls increased correspondingly with oleic acid concentration. Lee *et al.* found additional oleic acid molecules condense between those that are hydrogen-bonded and the metal carboxylates, strengthening dimeric COOH bonds. Gong *et al.* explain this is via hydrocarbon chain adsorption and that COOH monomers and dimers are adsorbed.²⁷ Decreased v_{str}(-OH) corresponding with increased oleic acid concentration was also identified, attributed to COOH groups forming hydrogen bonds with Si-OH groups.

Band	Approximate wavenumber (cm ⁻¹)
v _{str} (-OH)	3600-2400
v _{asym} (-CH ₂ -)	2925
v _{sym} (-CH ₂ -)	2860
v _{asym} (C=O)	1744-1700
v _{asym} (C=O) monomer (free acid)	1743
v _{asym} (C=O) monomer (adsorbed)	1730
v _{asym} (C=O) dimer	1711
v _{asym} (COO-Na)	1560
v _{sym} (COO-Na)	1425
v _{def} (-CH ₂ -)	1345-1180

Table 6-3 Table of band assignments used to characterise FFA-cellulose bonds for Turkey red oiling.

The similarities in sample preparation and chemistry between Turkey red oiling and oleic acid coatings on mineral and glass particles provide a useful analytical reference to compare FTIR results. The findings from these studies

²⁵ Lee and Condrate, "FTIR Spectral Characterization of Thin Film Coatings of Oleic Acid on Glasses: I. Coatings on Glasses From Ethyl Alcohol."

²⁶ Papageorgiou et al., "Metal-Carboxylate Interactions in Metal-Alginate Complexes Studied with FTIR Spectroscopy."

²⁷ Gong et al., "Adsorption of Oleate on Apatite Studied by Diffuse Reflectance Infrared Fourier Transform Spectroscopy."

presented in this section are applied to the discussion of spectra from the textiles analysed for this project in Sections 6.4 and 6.6.

6.4 FTIR spectra of oiled calico

Analysis of oiled calico samples by both ATR and DRIFTS was done to study the oil on the fibres without the other components of finished Turkey red being present, and to test the usefulness of both interfaces prior to application of the DRIFTS instrument on historical pieces. The sample sets were designed to test various conditions of the oiling process to determine their effect on oil uptake and bonding. Two samples of oiled calico were also obtained from another dyer, Debbie Bamford (DB), and DRIFTS spectra of two samples of historical oiled calico from a dyeing manual were taken for comparison to the replica samples to determine the authenticity of the re-creation. Each sample set is discussed individually and general conclusions drawn at the end of the section.

6.4.1 Sample set A01

The A01 sample set (see Section 4.2.2) was designed to give an overview of the changes from different oil treatments and periods of heat treatment. Calico was prepared with an aqueous solution of Fluka TRO or replica TRO, using water for a control set, and placed in an oven at 60 $^{\circ}$ C for 1,4,10, or 21 days with an additional set each at room temperature for 30 days. One set was steamed, which is also discussed.

6.4.1.1 Comparison of treatments across time points

In this section, spectra of samples prepared with the same treatment are compared across all time points. In Figure 6-11, the calico samples treated with replica TRO show significant differences between the blank and treated samples in the oil band regions identified in Figure 6-10 (3000-2800 cm⁻¹ and 1800-1600 cm⁻¹).



Figure 6-11 ATR spectra for A01 replica TRO samples. Average of three replicates normalised to 1.0 at 1030 cm⁻¹; peaks from 21-day.

A band for dimeric $v_{asym}(C=0)$ is detected 1714 cm⁻¹, but the software fails to identify the shoulder appearing around 1734 cm⁻¹ for monomeric adsorbed $v_{asym}(C=0)$ species (see Table 6-3). Bands for the aliphatic chain $v_{str}(-CH_2-)$ appear clearly at 2925 and 2856 cm⁻¹. Less distinct changes are seen in the $v_{str}(-OH)$ region from 3300-3100 cm⁻¹, though the blank sample is visible above the oiled spectra, which may indicate some differences in the -OH environments between the samples. The fingerprint region (1500-500 cm⁻¹) shows more differentiation between the blank and oiled spectra from 1500-1200 cm⁻¹, especially for the 21-day sample. Although interpretation of this region can be complicated, it also provides useful information on the carboxyl environments as discussed in Section 6.3. The ATR spectra show increased $v_{def}(-CH_2-)$ of aliphatic chains from 1345-1180 cm⁻¹²⁸ in the oiled calico relative to the blank.

The DRIFTS spectra in Figure 6-12 better show differentiation from the blank for $v_{str}(-OH)$ from 3600-3400 cm⁻¹, a region associated with intramolecular hydrogen-bonded O–H and unassociated –OH. In contrast, the effect of the oil treatment is less pronounced for $v_{def}(-CH_2-)$ from 1345-1180 cm⁻¹ than in the ATR spectra (see Figure 6-11), which may indicate that, based on the depth of penetration of ATR (ca. 2 µm) vs DRIFTS (ca. 7µm)²⁹, these vibrations are from groups closer to the textile surface and therefore may give it some hydrophobic properties. This is consistent with the previously discussed oleic acid coating studies that identified the formation of a hydrophobic surface layer.

²⁸ Socrates, Infrared and Raman Characteristic Group Frequencies, 127.

²⁹ Forsskåhl et al., "Depth Profiling of a Photochemically Yellowed Paper. Part II: FT-IR Techniques."



Figure 6-12 DRIFTS spectra for A01 replica TRO samples. Average of six replicates, spectra not normalised. Peaks from 21-day.

The inset in Figure 6-13 shows two peaks are detected at 1715 cm⁻¹ and 1726 cm⁻¹, again consistent with values for v_{asym} (C=O) dimers and monomers. Here, v_{str} (-CH₂-) appears at 2911 and 2863 cm⁻¹, slightly shifted but consistent with previous values. The spectra for the 10- and 21-day samples have a weak band at 1551 cm⁻¹ consistent with v_{asym} (COO-Na) of carboxylic acid sodium salts.



Figure 6-13 Inset of DRIFTS spectra for A01 replica TRO samples. See Figure 6-12 for details.

Figure 6-14 compares the samples treated with Fluka TRO across all time points. Unlike the ATR spectra for the replica TRO samples in Figure 6-11, the spectra for the Fluka TRO samples have a peak around 1560 cm⁻¹ consistent with $v_{asym}(COO-Na)$. A band for $v_{asym}(C=O)$ dimers is detected at 1713 cm⁻¹ with a similar unmarked shoulder appearing as before around 1734 cm⁻¹ as shown in Figure 6-15, consistent with adsorbed monomeric $v_{asym}(C=O)$. Aside from the peaks related to sodium carboxylate salts, the spectra for calico samples treated with Fluka and replica TRO are similar and show bands from the oil not present in the blank at 2925 and 2856 cm⁻¹ that correspond to increased periods of heating.



Figure 6-14 ATR spectra for A01 Fluka TRO samples. Average of three replicates each normalised to 1.0 at 1030 cm⁻¹; peaks from 21-day.



Figure 6-15 Inset of ATR spectra for A01 Fluka TRO samples. See Figure 6-14 for details.

The DRIFTS spectra for the Fluka TRO samples in Figure 6-16 are similar to those for the replica TRO in Figure 6-12, though the 10- and 21-day samples have a strong band around 1560 cm⁻¹ consistent with v_{asym} (COO-Na). A peak for dimeric v_{asym} (C=O) is marked 1711 cm⁻¹ and again appears to overlap monomeric v_{asym} (C=O) around 1726 cm⁻¹. Band assignments for v_{str} (-CH₂-) are consistent with DRIFTS spectra of the A01 replica TRO samples, and decreased v_{str} (-OH) relative to the blank is also visible from 3600-3400 cm⁻¹.



Figure 6-16 DRIFTS spectra for A01 Fluka TRO samples. Average of six replicates each, spectra not normalised. Peaks from 21-day.



Figure 6-17 Inset of DRIFTS spectra for A01 Fluka TRO samples. See Figure 6-16 for details.

The ATR and DRIFTS spectra for the control samples prepared with water (Figure 6-18 and Figure 6-19) show no new bonds form such as those seen in the oiled samples. The spectra are consistent with undegraded cellulose based on the literature and the reference spectra (Figure 6-7 and Figure 6-8) and do not indicate fundamental changes to the polymer structure.



Figure 6-18 ATR spectra for A01 water control samples. Average of three replicates each normalised to 1.0 at 1029 cm⁻¹; peaks for 21-day.



Figure 6-19 DRIFTS spectra for A01 water control samples. Average of six replicates each, spectra not normalised. Peaks from 21-day.

6.4.1.2 Comparison of treatments at same time point

In Figure 6-20, the ATR spectra of A01 1-day samples for all treatments are overlaid to highlight the difference between the oiled, blank, and control samples for $v_{asym}(C=0)$. An inset of the spectra in Figure 6-21 shows bands for $v_{str}(-CH_2-)$ at 2902 and 2858 cm⁻¹ in the oiled samples but not in the blank or control, and a similar situation for dimeric $v_{asym}(C=0)$, marked at 1710 cm⁻¹ in the replica TRO sample but consistent with previous spectra that also have an unmarked overlapping band for the monomer around 1734 cm⁻¹.



Figure 6-20 ATR spectra for A01 1-day samples, all treatments. Average of three replicates each normalised to 1.0 at 1030 cm⁻¹; peaks for replica TRO.



Figure 6-21 Inset of ATR spectra for A01 1-day samples. See Figure 6-20 for details.

The DRIFTS spectra in Figure 6-22 show the same oil bands as the ATR spectra (inset Figure 6-23). Differences between the blank and oiled calico spectra from 3600-3200 cm⁻¹ for v_{str} (-OH) may indicate an interruption of the hydrogen bonds between the cellulose monomers and a decrease in unassociated -OH groups³⁰, which would be in agreement with the uptake of FFAs. A decrease in intramolecular hydrogen bonding reduces the rigidity of the cellulose and allows for more movement of the fibres.



Figure 6-22 DRIFTS spectra of A01 1-day samples, all treatments. Average of six replicates each, spectra not normalised. Peaks from replica TRO.

³⁰ Jandura, Kokta, and Riedl, "Fibrous Long-Chain Organic Acid Cellulose Esters and Their Characterization by Diffuse Reflectance FTIR Spectroscopy, Solid-State CP/MAS."



Figure 6-23 Inset of DRIFTS spectra for A01 1-day samples. See Figure 6-22 for details.

This effect may also explain the usefulness of Turkey red oil to add drape and softness to fabric³¹ if this is the case. This region is less detailed in the ATR spectra, which may be related to the shallower depth of penetration for this interface (ca. 2 μ m) compared to that of the DRIFTS at around 7 μ m. If so, this indicates v_{str}(-OH) from 3600-3200 cm⁻¹ is deeper, based on the DRIFTS response, than v_{def}(-CH₂-) from 1345-1180 cm⁻¹, which is more distinct in the ATR spectra.³² This is consistent with fatty acid carboxyls bonding to cellulose hydroxyls with the aliphatic chain extending away from the fibre, effectively surface-coating the cellulose.

6.4.1.3 Effect of steaming on same time point

Two sets of 4-day samples for all treatments were prepared and one set subjected to an additional steaming treatment in a pressure cooker for one hour to test the effect on the oiling process. Figure 6-24 shows the spectra of the oiled samples versus a calico blank; the water controls (Figure 6-18) did not have any oil peaks.

³¹ Panda, The Complete Book on Textile Processing and Silk Reeling Technology, 448.

³² Forsskåhl et al., "Depth Profiling of a Photochemically Yellowed Paper. Part II: FT-IR Techniques."



Figure 6-24 ATR spectra of A01 4-day samples, steamed and unsteamed. Average of three replicates each normalised to 1.0 at 1030 cm⁻¹; peaks for replica 4-day + steam.

In the inset in Figure 6-25, dimeric $v_{asym}(C=0)$ is marked at 1712 cm⁻¹ with an overlapping peak for monomeric $v_{asym}(C=0)$ around 1730 cm⁻¹. Bands in the replica TRO samples are higher than in the Fluka ones relative to the baseline, and the same applies for the steamed samples versus the unsteamed ones, indicating the replica TRO was more effective at oiling the calico and that steaming increases FFA uptake by the cellulose.



Figure 6-25 Inset of ATR spectra for A01 4-day oiled calico samples. See Figure 6-24 for details.

6.4.1.4 Comparison of oiled calico and oil treatment

Spectra from samples of oiled calico were also overlaid with spectra of the neat TRO oil treatment for comparison. In Figure 6-26, the 21-day replica TRO oiled calico has similar dimeric v_{asym} (C=O) to the peak in the oil sample, at 1713 cm⁻¹ (peaks for this spectrum). The band is broad and indicative overlap with adsorbed v_{asym} (C=O) monomers, as consistently seen in this analysis seen here

around 1735 cm⁻¹. The oil also has a band at 1549 cm⁻¹ consistent with v_{asym} (COO-Na).



Figure 6-26 ATR spectra of replica TRO and A01 replica 21-day calico. Average of three replicates each, calico spectra normalised to 1.0 at 1030 cm⁻¹. Peaks for replica TRO.

In the spectra for 21-day Fluka TRO oiled calico and the Fluka TRO in Figure 6-27, the oil spectrum has a band for v_{asym} (COO-Na) at 1551 cm⁻¹ that matches the spectrum of the oiled calico, though a corresponding v_{sym} (COO-Na) around 1425 cm⁻¹ is less apparent. The values for v_{asym} (C=O) in these spectra indicate similar carboxylate environments in the Turkey red oils and the oiled calico.



Figure 6-27 ATR spectra of Fluka TRO and A01 Fluka 21-day oiled calico. Average of three replicates each, calico spectra normalised to 1.0 at 1030 cm⁻¹. Peaks for Fluka TRO.

6.4.1.5 Summary of A01 sample set

The FTIR spectra for the A01 sample set show FFAs can easily be detected on cotton fibres with ATR and DRIFTS instruments. The discussion of FTIR analyses of oleic acid coatings of hydroxy-rich substrates in Section 6.3 found band assignments for $v_{asym}(C=0)$, $v_{str}(-CH_2-)$, and $v_{str}(COO-Na)$ consistent with the new

peaks seen in the oiled calico spectra of the A01 sample set when compared to the plain calico spectra. The spectra indicate adsorbed dimeric $v_{asym}(C=0)$ around 1711 cm⁻¹ with a shoulder for the monomeric species around 1730 cm⁻¹. Values for v_{asym} (C=O) closer to 1740 cm⁻¹ may be indicative of ester formation or monomeric free fatty acids. FTIR studies of fatty acid cellulose esters (FACE) found this band appears closer to 1750 cm⁻¹ and had distinct changes from 1166-1065 cm⁻¹ proportional to those for $v_{asym}(C=0)$ that are not seen in the oiled calico spectra. The spectra and the sample preparation conditions overall are less in favour of ester formation as an explanation of fatty acid cellulose bonding in Turkey red. Bands for aliphatic v_{str} (-CH₂-) around 2925 and 2860 cm⁻¹ and $v_{def}(-CH_2-)$ from 1345-1180 cm⁻¹ also appear in the oiled samples. As discussed earlier, the work of Lee *et al.*³³ found these bands corresponded to the formation of a hydrophobic surface layer on the glass particles. Fatty acid monomers and dimers may also condense between hydrogen-bonded fatty acids via hydrocarbon chain adsorption as discussed by Gong et al.³⁴ The presence of peaks for v_{str} (COO-Na) around 1560 cm⁻¹ is discussed further in following sections. Less pronounced changes in the v_{str} (-OH) region from 3600-3200 cm⁻¹ are seen, particularly in the DRIFTS spectra when compared to the ATR, which may be connected to the interfaces differing depths of penetration.³⁵ These changes were associated with COOH and Si-OH groups forming hydrogen bonds in the oleic acid coating of SLS glass.

6.4.2 Sample set A02

The A02 sample set studies the effect of oil concentration and of washing the fabric with soda ley (also called salt samples) or plain water. As discussed in the review, the 'old' process required repeated washing in soda ley after oiling, but the 'new' process with Turkey red oil supposedly required only water to wash. Sample preparation is found in Section 4.2.3.

³³ Lee, Condrate, and Lacourse, "FTIR Spectral Characterization of Thin Film Coatings of Oleic Acid on Glasses Part II Coatings on Glass From Different Media Such as Water, Alcohol, Benzene and Air."

³⁴ Gong et al., "Adsorption of Oleate on Apatite Studied by Diffuse Reflectance Infrared Fourier Transform Spectroscopy."

³⁵ ibid.

6.4.2.1 Varied concentration washed with water

The ATR spectra of the A02 water-washed samples in Figure 6-28 have the same oil bands seen in spectra for the A01 samples. The band for $v_{sym}(-CH_2-)$ appears at 2856 and $v_{asym}(-CH_2-)$ at 2924 cm⁻¹. Oil concentration appears to have a corresponding affect on band intensity relative to the blank sample, an effect also seen for $v_{def}(-CH_2-)$ in the ATR spectra from around 1345-1180 cm⁻¹. The inset in Figure 6-29 shows the typical $v_{asym}(C=0)$ with a shoulder for dimers and monomers around 1713 and 1731 cm⁻¹.



Figure 6-28 ATR spectra of A02 water-washed samples prepared with replica TRO. Average of three replicates each normalised to 1.0 at 1030 cm⁻¹; peaks for 50% oil sample.



Figure 6-29 Inset of A02 water-washed samples prepared with replica TRO. See Figure 6-28 for details.

The DRIFTS spectra in Figure 6-30 have peaks for dimeric and monomeric v_{asym} (C=O) marked at 1714 and 1725 cm⁻¹. The 50% oil sample has weak v_{asym} (COO-Na) band around 1560 cm⁻¹. They are less sensitive to v_{def} (-CH₂-) from 1345-1180 cm⁻¹ but show more differentiation between the blank and oiled samples for v_{str} (-OH) between 3600-3400 cm⁻¹, shown better in the inset in Figure 6-31 where the blank and 50% oil spectra are in alignment at the baseline

from 2200-2000 cm⁻¹ and have a different response from 3600-3400 cm⁻¹. The findings are consistent with the research discussed in Section 6.3, but a more systematic investigation is recommended to draw stronger conclusions about the hydroxyl stretching region.



Figure 6-30 DRIFTS spectra of A02 water-washed samples prepared with replica TRO. Average of six replicates each, spectra not normalised. Peaks for 50% oil sample.



Figure 6-31 Inset of DRIFTS spectra for AO2 water-washed samples. See Figure 6-30 for details.

6.4.2.2 Varied concentration washed with soda ley

Turkey red processes caution against the over-washing of oiled fabric, and the use of soda ley seems to remove more oil than water does, so a balance between removing excess oil without removing bonded oil must have been desired. The effect of the washing media also indicates something about the nature of the bonds between FFAs and cellulose, since they can be broken with a fairly mild treatment, supporting the hypothesis that hydrogen bonds are more likely to form than covalent ester bonds. Bands in the ATR spectra (Figure 6-32) of the A02 soda-washed samples are less intense relative to the blank when compared to the water-washed samples.



Figure 6-32 ATR spectra of A02 soda-washed samples prepared with replica TRO. Average of three replicates each normalised to 1.0 at 1030 cm⁻¹; peaks for 50% oil sample.

A peak is marked at 1730 cm⁻¹ in these samples and the inset in Figure 6-33 shows it is a combination of overlapping peak, possibly a different distribution of dimeric and monomeric $v_{asym}(C=0)$ from the soda wash. The peak for $v_{asym}(-CH_2-)$ has shifted slightly to 2902 cm⁻¹ in these samples, but $v_{sym}(-CH_2-)$ around 2857 cm⁻¹ is consistent with the A01 spectra. A band around 1564 cm⁻¹ from $v_{asym}(COO-Na)$ is also detected in these spectra.



Figure 6-33 Inset of ATR spectra for A02 soda-washed samples. See Figure 6-30 for details.

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In Figure 6-34, the DRIFTS spectra of the A02 soda-washed samples are consistent with the samples discussed thus far, though with a band for v_{asym} (COO-Na) at 1566 cm⁻¹ that is more distinct from the blank calico spectrum than detected with ATR instrument. The DRIFTS spectra for v_{str} (-OH) from 3600-3400 cm⁻¹ may also reveal more about how the fatty acid bonding alters the hydroxyl environments and hydrogen-bonding of the cellulose, which would be consistent with the discussion in the literature. These changes are subtler than the obvious appearance of a v_{asym} (C=O) band and not as straightforward to evaluate.



Figure 6-34 DRIFTS spectra of A02 soda-washed samples prepared with replica TRO. Average of six replicates each; spectra not normalised. Peaks for 50% oil sample.

Figure 6-35 shows a comparison of DRIFTS spectra for the 50% oil samples, both washes, and the changes caused by the soda ley. The spectra have similar $v_{str}(-CH_2-)$ bands around 2904 and 2867 cm⁻¹. In the soda sample, adsorbed monomeric $v_{asym}(C=0)$ bands are marked at 1730 cm⁻¹ and in the water sample two peaks appear 1714 and 1725 cm⁻¹, consistent with the soda wash changing the distribution of carboxyl environments. Both calico samples have $v_{asym}(COO-Na)$ around 1566 cm⁻¹, and its increased height relative to the baseline in the salt sample is the result of RCOO-Na forming with Na⁺ ions from the sodium carbonate wash.



Figure 6-35 DRIFTS spectra of A02 50% oil samples prepared with replica TRO, both washes. Average of six replicates each, spectra not normalised. Peaks for carbonate wash sample.



Figure 6-36 Inset of DRIFTS spectra for A02 50% oil samples, both washes. See Figure 6-35 for details.

6.4.2.3 Summary of A02 sample set

The spectra of the A02 samples are consistent with the A01 spectra for both ATR and DRIFTS techniques and show a corresponding increase in FFA uptake with increased oil concentration. In the glass particles studies, the signal from hydrogen-bonded carboxyls increased correspondingly with oleic acid concentration, consistent with the A02 sample set. The position of $v_{str}(-CH_2-)$ is fairly consistent across all samples, with one shifting from 2925-2900 cm⁻¹ and the other consistently around 2860 cm⁻¹. Band intensity relative to the blank increases with oil treatment concentration and is affected by the choice of washing media. These spectra have bands for adsorbed dimeric and monomeric $v_{asym}(C=O)$ from about 1730-1712 cm⁻¹, consistent with previously seen values and assignments in the literature. The findings strengthen the case for further analysis and spectral deconvolution for more precise assignments. The A02 sample set also indicates the appearance in the calico samples of a distinct band from v_{asym} (COO-Na) around 1560 cm⁻¹ corresponds to application of a sodium carbonate wash with the introduction of Na⁺ ions. This value is consistent with the findings of Lee *et al.* that the presence of sodium ions causes sodium oleate to precipitate. Changes to v_{str} (-OH) around 3600-3200 cm⁻¹ identified in the glass particles research corresponded to COOH groups forming hydrogen bonds with Si-OH groups; in these spectra, changes in this region may be indicative of hydrogen bonding to cellulose -OH groups but this is less clear than the evidence of oil uptake based on v_{asym} (C=O) and v_{asym} (COO-Na).

6.4.3 Sample set A05

The A05 sample set (Section 4.2.4) was specifically designed for ssNMR analysis and was prepared in a manner closer to the 'old' process, using oleic acid $(1^{-13}C)$ tagged) in olive oil rather than Turkey red oil. A series of incremental time points was chosen to determine how rapidly bonds formed, which may indicate something about the nature of the bonds. Hydrogen bonds form more rapidly than esters under these conditions; these samples test whether the difference across time points is indicative of bonding. The presence of bands in all samples, including 0 h (treatment applied and washed off immediately), indicates the bonds form quickly. Only ATR spectra were taken of these samples because the DRIFTS instrument was unavailable.

The spectra in Figure 6-37 have oil bands consistent with the A01 and A02 sample sets. Peaks (marked for 72 h sample) from $v_{str}(-CH_2-)$ are at 2920 and 2854 cm⁻¹, consistent with other spectra. The inset in Figure 6-38 shows the oil band regions, where the peak height for $v_{asym}(C=0)$ relative to the baseline does not correspond to the duration of heating, likely the result of residual oil remaining after washing with a weak soda ley.



Figure 6-37 ATR spectra of A05 sample set prepared with isotopic oleic acid and olive oil. Average of three replicates each normalised to 1.0 at 1029 cm⁻¹; peaks for 72 h sample.



Figure 6-38 Inset of ATR spectra for A05 sample set prepared with isotopic oleic acid. See Figure 6-37 for details.

The band for $v_{asym}(C=O)$ appears at 1744 cm⁻¹, a higher value than previously seen in calico samples, but consistent with the spectra for olive oil and oleic acid (Figure 6-9) and values for monomeric carboxylates in the literature.³⁶ This may be the result of the low oleic acid concentration in the treatment relative to the amount of olive oil (ca. 1:3 ratio). Unlike the previous samples prepared with Turkey red oil, $v_{asym}(C=O)$ is symmetric and does not appear to have any dimeric species present. This is consistent with the anticipated homogeneity of the oleic acid-olive oil treatment compared to the Turkey red oils, which are the result of complex sulfuric acid reactions with castor oil. The research by Lee *et al.* found higher concentrations of oleic acid resulted in the presence of more dimers,³⁷ so monomers are reasonable to expect here with lower concentrations

³⁶ Gong et al., "Adsorption of Oleate on Apatite Studied by Diffuse Reflectance Infrared Fourier Transform Spectroscopy."

³⁷ Lee and Condrate, "FTIR Spectral Characterization of Thin Film Coatings of Oleic Acid on Glasses: I. Coatings on Glasses From Ethyl Alcohol."

of acid. The bands for $v_{asym}(C=0)$ around 1730-1711 cm⁻¹ in the A01 and A02 sample sets versus these samples may indicate something about the composition of Turkey red oil since the spectra indicate different $v_{asym}(C=0)$ environments are present.

The spectra of the 72-hour sample and the isotopic oleic acid in Figure 6-39 shows $v_{asym}(C=0)$ is consistently around 1745 cm⁻¹ in both samples. If an ester bond formed, this band should have shifted noticeably between the oleic acid and the oiled calico, and the oiled calico and blank do not reveal any ester peaks forming around 1100 cm⁻¹. The consistency of $v_{asym}(C=0)$ is in favour of physisorbed (i.e. hydrogen bonded) rather than chemisorbed FFAs. There is no corresponding peak at 1669 cm⁻¹ in the 72 h calico sample as appears in the oleic acid-1-¹³C spectrum.



Figure 6-39 ATR spectra of olive oil, oleic acid, and A05 oiled calico. Average of three replicates each, calico spectra normalised to 1.0 at 1032 cm⁻¹. Peaks for oleic acid= $1=^{13}$ C.

It is unclear from these samples whether this is because the isotope effect of the ¹³C atom is less visible in the oiled calico spectra or if the fatty acid reacting with the olive oil released non-isotopic oleic acid that formed more bonds. The changes in the A05 samples are generally consistent with the A01 and A02 sets, though no correlation can be made between the sample heating and signal strength in these samples.

6.4.4 Sample set A06

The A06 sample set was prepared to collect spectra from samples prepared with a wider range of treatments across the same time point. The treatments include three Turkey red oils, ricinoleic acid, and an aqueous solution of dry sodium oleates. Sample preparation is in Section 4.2.5. In general, the spectra are consistent with the previous ATR spectra discussed so far.



Figure 6-40 ATR spectra of A06 sample set. Average of three replicates each from two samples normalised to 1.0 at 1029 cm⁻¹; peaks for ricinoleic acid.



Figure 6-41 Inset of ATR spectra for A06 sample set. See Figure 6-40 for details.

The inset of the $v_{asym}(C=0)$ region in Figure 6-41 has peaks for ricinoleic acid and sodium oleates marked by colour (black is shared). In ricinoleic acid dimeric $v_{asym}(C=0)$ is marked at 1710 cm⁻¹ and a similar band is present in the replica, Fluka, and DB TO samples, though they also have an adsorbed monomer shoulder at 1730 cm⁻¹. Unlike the A05 sample set in Figure 6-37 also prepared with fatty acids, the value for $v_{asym}(C=0)$ is more consistent with dimeric fatty acids. The sample was prepared and washed with a weak soda solution because the water-insoluble compound was difficult to apply and remove from the calico sample, contributing to the peaks for $v_{asym}(COO-Na)$ around 1550 cm⁻¹ from sodium ricinoleate. The results are consistent with fatty acids in the TRO bonding in a similar manner to the ricinoleic acid, however the water-solubility of Turkey red

oil makes it vastly superior to ricinoleic acid in terms of handling which may indicate why pure fatty acids were never adopted.

The spectrum from the sample treated with aqueous sodium oleates has peaks in this area consistent with sodium oleate, but lacks a distinct $v_{asym}(C=O)$ band indicate of fatty acid uptake. It is not clear from these samples whether it was how the oil treatment was applied or if the reconstituted dry sodium oleates were unsuitable for preparing calico according to a Turkey red process.

6.4.5 Debbie Bamford samples

Another set of replica oiled calico samples was kindly proved natural dyer Debbie Bamford (DB) of Sheffield, who also supplied the Turkey red oil in the A06 sample set. The samples were both treated with sheep dung, tannins, and alum, one with rancid olive oil and the other with castor oil soap. The ATR spectra in Figure 6-42 show an increased $v_{str}(-CH_2-)$ bands in the castor oil soap sample than in the olive oil or A01 sample when compared to the baseline around 2200 cm⁻¹





The inset of the $v_{asym}(C=0)$ region in Figure 6-43 has peaks marked by colour and shows the castor oil soap sample has a series of broad, overlapping bands around 1650 cm⁻¹. The A01 sample has dimeric $v_{asym}(C=0)$ at 1710 cm⁻¹ with an overlapping peak for adsorbed monomers around 1730 cm⁻¹; the castor oil soap spectrum is similar but the software had difficulty detecting peaks with the other bands in the area. It should also be noted that the DB samples were prepared with a different type of fabric and that this can affect the spectra. The band appears in the rancid olive oil sample at 1700 cm⁻¹.



Figure 6-43 Inset of ATR spectra for DB and A01 Fluka TRO ambient oiled calico samples. See Figure 6-42 for details.

In Figure 6-44, DRIFTS spectra of the DB samples compared to A01 Fluka ambient and blank have more baseline differentiation. The differences occur in regions associated with $v_{asym}(C=0)$ and $v(COO^-)$ stretching, and for $v_{str}(-OH)$ of tannins and may the result of the additional sheep dung, tannin, and alum treatments and probably the different weave of the calico substrates, which the DRIFTS instrument is more sensitive toward. The y-offset was not corrected due to the different shape of the spectra around 3200-3000 cm⁻¹.



Figure 6-44 DRIFTS spectra of DB and A01 Fluka TRO ambient oiled calico samples. Average of six replicates each, spectra not normalised. Peaks for DB castor soap.

The spectra of the DB samples show the same oil bands seen in previous sample sets indicative of and dimeric and monomeric adsorbed $v_{asym}(C=0)$ from 1730-1710 cm⁻¹ and $v_{str}(-CH_2-)$ from 3000-2800 cm⁻¹, with the aforementioned differences in baseline potentially affecting a complete interpretation of the

spectra. Further investigation of the role of aluminium is discussed later in this chapter.

6.4.6 Historical oiled calico from Persoz

Although unfinished historical textiles are rare, Persoz provides two samples of oiled calico in his 1846 dyeing manual as part of his discourse on Turkey red,³⁸ allowing a comparison between replica and historical oiled calico. Based on the date of publication, the samples were prepared by the 'old' process. The spectra are consistent with the A01 Fluka TRO ambient sample to which they are compared in Figure 6-45. The y-offset was corrected from 2200-2000 cm⁻¹, where the spectra are consistent across all samples, to compensate for the baseline differentiation. Persoz #92 is 'cotton with four white baths'. In Persoz #93, 'cotton oiled and degreased', dimeric $v_{asym}(C=0)$ appears at 1712 cm⁻¹ and $v_{str}(-CH_2-)$ at 2910 and 2860 cm⁻¹. The inset in Figure 6-46 shows that again the shoulder around 1730 cm⁻¹ present for the adsorbed monomeric $v_{asym}(C=0)$.



Figure 6-45 DRIFTS spectra of Persoz and A01 Fluka TRO ambient oiled calico. Replica samples average of six replicates each, Persoz avg. of three. Spectra not normalised, y-offset corrected from 2200-2000 cm⁻¹⁻. Peaks for Persoz #93.

³⁸ Persoz, Traité Théorique Et Pratique De L'impression Des Tissus 192-193.



Figure 6-46 Inset of DRIFTS spectra for Persoz and A01 Fluka TRO ambient oiled calico. See Figure 6-45 for details.

The DRIFTS spectra from the Persoz samples indicate the 'old' oiling process produced textiles for Turkey red dyeing similar to the replica oiled calico samples generated for this research. Since it was not possible to accurately replicate the 'old' rancid olive oil process for this research due to difficulty sourcing materials, the Persoz samples provide a valuable connection between the findings of this research and historical 'old' process Turkey red.

6.4.7 Summary of FTIR analysis of oiled calico

The findings of the ATR and DRIFTS analysis of the A01, A02, A05, A06, DB, and Persoz oiled calico samples identified spectral bands not present in the calico blanks that were consistent with the findings of the oleic acid coating studies by FTIR discussed in Section 6.3. In general, the DRIFTS instrument was more sensitive toward the uneven textile surfaces and had the additional advantage of not compressing the sample and potentially causing damage. The spectra show consistent changes in bands related to the uptake of FFAs for $v_{asym}(-CH_2-)$ around 2925 and $v_{sym}(-CH_2-)$ around 2860 cm⁻¹. The most obvious indicator of fatty acids on calico are bands arising for $v_{asym}(C=0)$ around 1800-1600 cm⁻¹ in the oiled samples when compared to the blank. Their position can also indicate something about the type of carbonyl environment. Bands for $v_{asym}(C=0)$ of saturated aliphatic esters appear around 1750-1725 cm⁻¹ and 1740-1700 cm⁻¹ for aliphatic carboxylic acids.³⁹ Esters have strong bands for $v_{asym}(C-O-C)$ from 1275-1185 cm⁻¹ and $v_{sym}(C-O-C)$ from 1160-1050 cm⁻¹, but no bands are distinguished above the background cellulose signal in these regions and signs of fatty acid

³⁹ Socrates, Infrared and Raman Characteristic Group Frequencies, 125.

cellulose ester formation⁴⁰ are not present. The spectra are more consistent with carboxylic acids and the values for $v_{asym}(C=0)$ around 1712 cm⁻¹ are consistent with dimeric fatty acid carboxyl environments. This band often overlaps one around 1730 cm⁻¹ for adsorbed monomeric $v_{asym}(C=0)$ species, and the A02 sample set indicates soda ley alters the distribution of these peaks (see Figure 6-36).

Additionally, vibrations from $v_{asym}(COO-Na)$ around 1550 cm⁻¹ are consistent with the formation of fatty acid sodium salts. Some samples, especially those washed with soda ley, have a band around 1560 cm⁻¹ consistent with $v_{asym}(COO-Na)$ from precipitated fatty acid sodium salts, though a corresponding $v_{sym}(COO-Na)$ band was not as distinct and may be masked by cellulose signals. Washing with soda ley appears to affect the distribution of overlapping $v_{asym}(C=O)$ peaks (see Figure 6-33), possibly effect of Na⁺ ions reacting with certain carboxyl species. If signal strength is affected by differences in the depth of penetration differences between ATR and DRIFTS, the spectra indicate FFA carboxyls bond to cellulose hydroxyls as monomers and dimers with the aliphatic tails pointed away from the fibre.⁴¹ The effect of soda washing potentially breaking the bonds and the sample preparation conditions being inconsistent with fatty acid cellulose ester formation are in favour of physisorbed, or hydrogen-bonded FFAs and precipitated fatty acid sodium salts from a Turkey red oiling process.

Bands for $v_{def}(-CH_2-)$ from 1345-1180 cm⁻¹ in oiled calico samples are more pronounced relative to the baseline in ATR spectra than in DRIFTS (see Figure 6-11 and Figure 6-12), which based on the depth of penetration for the interfaces (2 µm vs 7 µm, respectively) may be consistent with the formation of a hydrophobic aliphatic layer as identified by Lee *et al.*⁴² in the review. This occurs via hydrocarbon chain adsorption, where the aliphatic fatty acid chains condense onto the substrate via fatty acids hydrogen-bonded to the cellulose hydroxyls. Changes to $v_{str}(-OH)$ from 3600-3200 cm⁻¹ relative to the baseline, as

⁴⁰ Jandura, Kokta, and Riedl, "Fibrous Long-Chain Organic Acid Cellulose Esters and Their Characterization by Diffuse Reflectance FTIR Spectroscopy, Solid-State CP/MAS."

⁴¹ Forsskåhl et al., "Depth Profiling of a Photochemically Yellowed Paper. Part II: FT-IR Techniques."

⁴² Lee and Condrate, "FTIR Spectral Characterization of Thin Film Coatings of Oleic Acid on Glasses: I. Coatings on Glasses From Ethyl Alcohol."

seen in the DRIFTS spectra (Figure 6-31), may be indicative of fatty acid uptake affecting cellulose hydrogen bonding.

In the absence of published studies of oil coating on cotton or cellulose by FTIR, the studies of oleic acid coatings on apatite and SLS glass particles discussed in Section 6.3 provide a useful framework to discuss the ATR and DRIFTS spectra of oiled calico. The similar chemistry of the sample preparations (coating from aq. solution) and substrates (-OH groups) allows for a reasonable comparison of results. Bands and wavenumber assignments from the spectra presented in this section are consistent with the values in the literature and indicate that fatty acid dimers and monomers form hydrogen bonds with cellulose hydroxyl groups. The hydrogen bonding of cellulose hydroxyls is responsible for the adsorption and retention of some dye molecules, and the potential to form bonds is strong in the amorphous region of the fibre.⁴³ Additional fatty acid chains may attach via hydrocarbon chain adsorption and the presence of Na⁺ ions encourages the formation of fatty acid sodium salts. To further investigate whether hydrogen bonding is occurring, ¹³C ssNMR spectra of the A05 sample set are discussed in Section 6.5.

6.5 ¹³C ssNMR spectroscopy of oiled calico

Further analysis of oiled calico was done using ssNMR as an additional *in situ* analytical technique. The sample preparation is not suitable for conservation-based analysis, but for the replica samples it is useful to complement the FTIR data. Sample set A05 (Section 4.2.4) was designed using ¹³C1 isotopic oleic acid to address the low natural abundance of ¹³C in non-tagged oil and the strong bulk cellulose signal relative to the amount of oil in the samples. The details of NMR and ssNMR are discussed in Appendix A.

6.5.1 Instrument and acquisition

The ssNMR spectra of the A05 sample set were taken by the EPSRC ssNMR service at Durham University using a Varian VNMRS spectrometer with a 9.4 T magnet and a MAS probe with a 6 mm rotor. The spectra were recorded at 100 MHz at room temperature with a 5 s recycle delay. The cross-polarisation (CP) contact

⁴³ Shore, "Dye Structure and Application Properties."

time was 1 ms with an external reference of neat tetramethylsilane (TMS). Spectra were taken of the isotope-oiled samples at time points 0 h, 3 h, 12 h, 24 h, and 72 h, and of the water and oil (no isotope) control samples at 0 h and 72 h. The spectra were processed using TopSpin software from Bruker and overlaid with iNMR software, setting the C1 shift to 105.71 ppm. Full spectra are available in Appendix G.

6.5.2 ssNMR spectra of oiled calico

The cellulose signals in the ¹³C ssNMR spectra in Figure 6-47 are consistent with published ssNMR spectra of cellulosic fibres.^{44,45} There are small signals in the oil control 0 h sample around 30 ppm from oleic acid $-CH_2$ - carbons, indicating the sample was not adequately washed of excess oil before analysis, which is consistent with the lack of correspondence to time point in the FTIR spectra discussed earlier (see Figure 6-37). The additional peaks for C4' and C6' are the result of variations between surface and interior cellulose polymers, crystallinity, and hydrogen-bonding patterns.





⁴⁴ Jandura, Kokta, and Riedl, "Fibrous Long-Chain Organic Acid Cellulose Esters and Their Characterization by Diffuse Reflectance FTIR Spectroscopy, Solid-State CP/MAS."

⁴⁵ Focher et al., "Structural Differences Between Non-Wood Plant Celluloses: Evidence From Solid State NMR, Vibrational Spectroscopy and X-Ray Diffractometry."



Figure 6-48 ¹³C ssNMR spectra of A05 isotope samples. Spectra displayed with vertical offset for clarity.

The spectra in Figure 6-48 for the isotope samples all have two non-cellulose C1 signals around 185.2 and 179.4 ppm whose relative strength does not increase correspondingly with progressive time points. This is inconsistent with the carbonyl stretching bands of increasing intensity in the FTIR spectra and may be the result of low isotope natural abundance (ca. 1%) or quantitative limitations of the ssNMR. Mielczsarski et al. identified these signals in a study of calcium oleate precipitated from basic solution by ¹³C NMR;⁴⁶ for these samples sodium oleate is the relevant analyte. They attributed the two signals to two structural forms of the carboxyl group, chemisorbed oleate and precipitated oleate, which can be explained by the soda wash precipitating some sodium oleate. In samples precipitated from acidic solution, oleic acid was also present.⁴⁷ In the A05 samples, the sodium oleate was precipitated during the wash with soda ley. Washing the oiled calico with soda ley as in the 'old' process would therefore precipitate sodium oleate complexes on the fibres.

An ester bond between a fatty acid and cellulose hydroxyl has a C1 shift around 172-173 ppm.^{48,49} No signals are visible in this region for the A05 spectra, which is helpfully distinct from where the carboxylate signals appear. These

⁴⁶ Mielczarski et al., "Nature and Structure of Adsorption Layer on Apatite Contacted with Oleate Solution. 1. Adsorption and Fourier Transform Infrared Reflection Studies."

⁴⁷ Mielczarski et al., "Nature and Structure of Adsorption Layer on Apatite Contacted with Oleate Solutions. 2. in Situ and Ex Situ Fourier Transform Infrared, NMR, and X-Ray Photoelectron Spectroscopy Studies."

⁴⁸ Nagel and Heinze, "Study About the Efficiency of Esterification of Cellulose Under Homogeneous Condition: Dependence on the Chain Length and Solvent."

⁴⁹ Jandura, Kokta, and Riedl, "Fibrous Long-Chain Organic Acid Cellulose Esters and Their Characterization by Diffuse Reflectance FTIR Spectroscopy, Solid-State CP/MAS."

findings support the conclusion from the FTIR analysis that the oiling process imbues the cellulose with sodium carboxylates and hydrogen-bonded fatty acids.

6.6 FTIR identification of aluminium in Turkey red

The conclusion from the analysis of oiled calico sample sets in Section 6.4.7 was that the oiling process imbues the cotton fibres with fatty acids that form hydrogen bonds with cellulose hydroxyl groups. When a metal ion (M) like sodium is present, RCOO-M complexes form. These metal carboxylate compounds are key to identifying how aluminium becomes part of the Turkey red complex when it is applied to oil-prepared cotton and have also been characterised by FTIR spectroscopy.

In their study of oleic acid-coated glass particles, Lee *et al.* found that in aqueous solution, sodium oleate (RCOO-Na) dissociated easily due to the nature of its ionic bond. As discussed in Section 6.3, they also found Na⁺ ions dissociated RCOO-H, so the use of soda leys may have facilitated oil uptake for Turkey red by converting fatty acids into sodium carboxylates. The research also determined that while aluminium ions reacted slowly with isolated COO⁻ ions, Al⁺³ readily precipitated RCOO-Al from RCOO-Na by replacing the sodium ion.⁵⁰ Aluminium carboxylates more covalent, and therefore more stable than the sodium salts, which would decrease the lability of the complex to water, a valuable property for a functional textile.

FTIR spectra of metal carboxylates have bands for $v_{asym}(COO^{-})$ from 1600-1500 cm⁻¹ and $v_{sym}(COO^{-})$ from 1500-1400 cm⁻¹. Sodium oleate appears around 1560 cm⁻¹ for $v_{asym}(COO^{-})$ and 1425 cm⁻¹ for $v_{sym}(COO^{-})$, consistent with results from the oiled calico samples, although the band from symmetric stretching is fairly weak. Aluminium oleate appears around 1585 cm⁻¹ for $v_{asym}(COO^{-})$ and 1465 cm⁻¹

⁵⁰ Lee and Condrate, "FTIR Spectral Characterization of Thin Film Coatings of Oleic Acid on Glasses: I. Coatings on Glasses From Ethyl Alcohol."

for $v_{sym}(COO^{-})$.⁵¹ Studies of aluminium lake pigments in oil paintings also identified similar values.⁵²

The position of $v_{asym}(COO^{-})$ and $v_{sym}(COO^{-})$ for metal carboxylates can be can be used to assign bonding geometry of the complex and is calculated by Δv , $v_{asym}(COO^{-})$ minus $v_{sym}(COO^{-})$.⁵³ This is possible because different ligands have different bond energies and vibrations, which have previously been characterised by FTIR. The peaks in the Turkey red samples are discussed in the following section, and in the conclusions these principles are applied to the data to determine whether the nature of the aluminium-fatty acid-cellulose complex can be characterised from this work.

6.7 FTIR spectra of historical and replica Turkey red

The analysis of finished Turkey red textiles should identify the same oil bands seen in the spectra of oiled calico, plus other bands related to the subsequent treatments of the process. This section discusses the spectra of historical Turkey red from the UTR collection at Glasgow University and pieces in 19th c. dyeing manuals, assorted textiles from the CTC Karen Finch reference collection, and the replica Turkey red dyed in Section 4.3.3. Analysis of a dress in the V&A Textiles and Fashion collection, which may be an unusual example of early 19th c. Turkey red, is also presented. Full images are provided in Appendix H.

6.7.1 DRIFTS analysis of historical Turkey red in dyeing manuals

Dyeing manuals with textile swatches are a useful resource for samples accompanied by the method used to dye them, assuming the author was genuine in the presentation of his work. The analysis of Turkey red from dyeing manuals by Persoz,⁵⁴ Knecht,⁵⁵ and Crookes,⁵⁶ plus a piece in Perkin's article in *Journal of*

⁵¹ Lewis et al., "Multispectroscopic (FTIR, XPS, and TOFMS-TPD) Investigation of the Core-Shell Bonding in Sonochemically Prepared Aluminum Nanoparticles Capped with Oleic Acid."

⁵² Kirby, Spring, and Higgitt, The Technology of Eighteenth- and Nineteenth-Century Red Lake Pigments.

⁵³ Papageorgiou et al., "Metal-Carboxylate Interactions in Metal-Alginate Complexes Studied with FTIR Spectroscopy."

⁵⁴ Persoz, Traité Théorique Et Pratique De L'impression Des Tissus, 195-233.

⁵⁵ Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*.

⁵⁶ Crookes, A Practical Handbook of Dyeing and Calico-Printing, 326.
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*the Chemical Society*⁵⁷ is an opportunity to examine if the included samples really were as advertised by the author. The manuals from Persoz, Knecht, Crookes, and Perkin are held in the University of Glasgow Special Collections, and a second copy of Knecht came from the personal collection of Anita Quye. The origin or dyer of the samples is not always provided; Crookes's madder-dyed sample was produced by Steiner in Accrington,⁵⁸ a rare attribution.



Figure 6-49 DRIFTS spectra of Turkey reds in Persoz, 1846. Average of three replicates each, spectra not normalised. Peaks for Persoz #100.

The DRIFTS spectra from finished Turkey red samples in Persoz (Figure 6-49) are similar. Peak assignments are for Persoz #100, 'calico oiled, dyed, and cleared three times'. The weave of the blank spectrum compared to the Persoz samples causes it to stand out in the region for $v_{str}(-OH)$ from 3600-3200 cm⁻¹. The presence of oil is detected by the peaks for $v_{asym}(-CH_2-)$ at 2911 cm⁻¹ and $v_{sym}(-CH_2-)$ around 2854 cm⁻¹, and $v_{asym}(C=O)$ is detected at 1712 cm⁻¹ again overlapping monomeric $v_{asym}(C=O)$ around 1730 cm⁻¹. The region for $v_{def}(-CH_2-)$ from 1345-1180 cm⁻¹ is more difficult to interpret here due to the baseline differences, but the spectra show that finished Turkey red has more bands from 1650-1400 cm⁻¹, the carboxylate stretching region, than the oiled calico. These bands are the next step in the characterisation of Turkey red, indicating how aluminium complexes to form the basis for the colour complex, and will be discussed further.

⁵⁷ Perkin, "XVI.-on Artificial Alizarin."

⁵⁸ Crookes, A Practical Handbook of Dyeing and Calico-Printing, 327.

A new band appears in the Turkey red spectra around 839 cm⁻¹ from adjacent v_{def} (C-H) out-of-plane on an aromatic ring,⁵⁹ consistent with the addition of hydroxyanthraquinone dyes from madder or synthetic alizarin. The difference is clearer when comparing spectra for Turkey red and discharged Turkey red from Persoz #111 in Figure 6-50, which shows the alkyl chain and carbonyl bands are still present (left box). The band at 839 cm⁻¹ has disappeared, however, along with the colour (right box). There is also a decrease in carboxylate stretching in the white dots compared to the Turkey red spectrum, indicating the bleaching affects some but not all of the complex as well. The spectrum for the red area has a stronger peak around 1640 cm⁻¹ for adsorbed water than the blank calico (note y-offset from 2200-2000 cm⁻¹). This may be the result of by water molecules bound in the lake complex, which is discussed in Section 6.8, but a more systematic investigation is recommended since it is beyond the scope of this work.



Figure 6-50 DRIFTS spectra of Persoz #111, Turkey red ground and discharged white dots. Average of three replicates each, spectra not normalised. Peaks for Persoz #111 red.



Figure 6-51 Textile samples dyed with artificial alizarin from Perkin 'On artificial alizarin', 1870. GU Special Collections (left), GU Chemistry Library (centre), RSC.

⁵⁹ Socrates, Infrared and Raman Characteristic Group Frequencies, 158.

Similar spectra were taken from samples of Turkey red in dyeing manuals from Knecht and Crookes, and from the University of Glasgow Special Collections copy of Perkin's 1870 article 'On artificial alizarin'.⁶⁰ Perkin's samples are not described as Turkey red, but the colours and style are characteristic and it is logical that Perkin would advertise his new dye to the industry. Interestingly, the pieces also have different patterns. A copy held in the Royal Society of Chemistry (RSC) collection (viewed online only) has a third pattern. The DRIFTS spectrum from the Special Collections copy is characteristic of Turkey red and shows the same oil bands, so appears to be the case that all samples are Turkey red. Peaks for Perkin are marked in Figure 6-52.



Figure 6-52 DRIFTS spectra of Turkey red from historical dyeing manuals. Average of three replicates each, spectra not normalised. Peaks for Perkin 1870.

The variety of calico substrates in these samples results in spectra with different baselines that appear more consistent when comparing spectra from the same text. Each spectrum has a band for dimeric v_{asym} (C=O) around 1712 cm⁻¹, consistent with Persoz and the oiled calico spectra, as well as v_{str} (-CH₂-) from 3000-2800 cm⁻¹ and RCOO-M bands from 1600-1400 cm⁻¹. The results show the samples in the dyeing manuals are Turkey red, as advertised, making them a fascinating and valuable resource on the transmission of technology and knowledge in the 19th c. that makes it possible to connect process with product.

The carboxyl region from 1600-1400 cm⁻¹ is of interest in these spectra in order to understand how the aluminium becomes part of the complex. In Figure 6-53 and Figure 6-54, this region is expanded for the Persoz and dyeing manual Turkey red spectra.

⁶⁰ Perkin, "XVI.-on Artificial Alizarin."



Figure 6-53 Inset of DRIFTS spectra for Persoz Turkey red (1846). See Figure 6-49 for details.



Figure 6-54 Inset of DRIFTS spectra for Turkey red from historical dyeing manuals. See Figure 6-52 for details.

In the Persoz samples, each spectrum has a peak a show each sample has bands at 1587 and 1468 cm⁻¹ consistent with published values for aluminium oleate asymmetric and symmetric stretching. The dye manual spectra also have these bands around 1592 and 1463 cm⁻¹, varying slightly more due to the multiple dyers represented by these textiles. Bands for RCOO–Al do not appear in oiled calico samples (see Figure 6-12). They should be visible in the DB oiled calico samples, which received an alum treatment, but they are not easily identified in the (see Figure 6-44), possibly due to the lower quantity of FFAs adsorbed from the non-TRO oils used by that dyer.

6.7.2 DRIFTS analysis of historical Turkey red from UTR collection

The Turkey red in the UTR collection at the Glasgow University Archives was produced by the constituent firms of the company for the market, whereas the dyeing manuals were presumably made for show. Spectra were taken from samples in the books listed in Table 6-4, which were chosen because many of

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the samples have original dates of entry, making it possible to choose a range that encompassed 'old' and 'new' processes. The sample set includes spectra from a pink printed area, a dark red area that was printed over, a black area, and a green area. Overall, the spectra were consistent with those from the dyeing manuals and show the same bands for $v_{asym}(C=0)$ around 1712 cm⁻¹ and and $v_{str}(-CH_2-)$ from 3000-2800 cm⁻¹. The band for adsorbed water around 1640 cm⁻¹ is more intense relative to the blank spectrum, which as mentioned before may be from complexed water in the lake (see Section 6.6 for discussion).

Accession no.	Date of manufacture	No. samples
UGD 13/8/2	1856-1861	3
UGD 13/8/4	1857-1863	3
UGD 13/8/5	After 1867	1 (ATR & DRIFTS)
UGD 13/8/6	1886-1888	3
UGD 13/8/7	1887	3

Table 6-4 UTR sample pattern books from Glasgow University Archives analysed by FTIR.



UGD 13/8/6 #11

UGD 13/8/6 #12

UGD 13/8/6 #13

Figure 6-55 UGD 13/8/6 samples analysed by DRIFTS with sample areas circled. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/6.



Figure 6-56 UGD 13/8/7 samples analysed by DRIFTS with sample areas circled. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/7.





The spectra from UGD 13/8/6 and UGD 13/8/7 in Figure 6-57 (samples shown in Figure 6-55 and Figure 6-56) are consistent with those presented thus far from the dyeing manuals. The spectrum for UGD 13/8/1 #11, taken from a black area that appears to have underlying red colour, the only difference from the red spectra was a small bump around 2100 cm⁻¹, discussed later in this section. For UGD 13/8/7 #11, the spectrum was taken of the pink areas on the print. The spectra show the oil bands indicative of fatty acid bonding to cellulose that are not present in the blank. Bands for v_{str}(RCOO-Al) are present at 1591 and 1466 cm⁻¹, which do not appear in the oiled calico samples. In the inset in Figure 6-58, the band at 838 cm⁻¹ from adjacent aromatic v_{def}(C-H) is lower than in other samples, consistent with pink being a lighter shade of red.



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Figure 6-58 Inset of DRIFTS spectra for UGD 13/8/6 and UGD 13/8/7. See Figure 6-57 for details.



Figure 6-59 UGD 13/8/2 samples analysed by DRIFTS with sample areas circled. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/2.



From top: UGD 13/8/4 #11 UGD 13/8/4 #12 UGD 13/8/4 #13

Figure 6-60 UGD 13/8/4 samples analysed by DRIFTS with sample areas circled. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/4.

The sample UGD 13/8/4 #12, shown in Figure 6-60, has a darker red ground from which the spectra were taken, in contrast to the typical Turkey red hue on the flower details. The spectra from this sample are overlaid in Figure 6-61 with those from UGD 13/8/2; samples from these peaks are shown in Figure 6-59. The spectrum from UGD 13/8/4 #2 has a peak at 2086 cm⁻¹ not seen in the other spectra, otherwise it is characteristic of Turkey red along with the other spectra from UGD 13/8/4 and UGD 13/8/2. Based on the dates in the volume (1857-1863) and the Turkey red printing process, it is very unlikely to be a synthetic dye. The peak is consistent with FTIR identification of inorganic cyanides, which appear around 2250-2000 cm⁻¹.⁶¹ Prussian blue pigment, or ferric ferrocyanide,

⁶¹ Socrates, Infrared and Raman Characteristic Group Frequencies, 85.

was standard in Turkey red printing and its FTIR band was identified by Ghosh at 2080 $\rm cm^{-1}.^{62}$



Figure 6-61 DRIFTS spectra of Turkey red in UGD 13/8/2 and UGD 12/8/4. Average of three replicates each, spectra not normalised. Peaks for UGD 13/8/4 #12.

The band at 2086 cm⁻¹ in UGD 13/8/4 #12 is consistent with this value, indicating most of the red textile ground was overprinted with a thin layer of Prussian blue. Compared spectra from red and green areas of UGD 13/8/6 #12 in Figure 6-62 have a similar band at 2092 cm⁻¹ in the green sample, again consistent with printing practices layering Prussian blue and lead yellow. The presence of lead yellow may also explain why the green spectrum is less defined than other spectra in the fingerprint region. The dyes analysis in Chapter 7 found that a black fibre appears to have been made by printing Prussian blue over Turkey red, which is confirmed by FTIR-ATR and discussed in that chapter.



Figure 6-62 DRIFTS spectra of red and green areas from UGD 13/8/6 #12. Average of three replicates each, spectra not normalised. Peaks for UGD 13/8/6 #12 (green).

⁶² Ghosh, "Infrared Spectra of the Prussian Blue Analogs."



Figure 6-63 DRIFTS spectra of UGD Turkey red compared to black, dark red, and green areas. Average of three replicates each, spectra not normalised. Peaks for UGD 13/8/4 #12.

Curiously, the spectrum from the black area of UGD 13/8/6 #11 in Figure 6-63 shows that although the colour is much darker, the sample has at most a weak band indicative of Prussian blue around 20686 cm⁻¹. This is not consistent with the depth of hue, but the presence of blue detail on the textile (see Figure 6-55) may explain the less intense signal relative to UGD 13/8/6 #12 (green) and UGD 13/8/4 #12 (dark red). Based on this spectrum and the fairly strong band from Prussian blue, it appears to be the case that another dye, potentially logwood, was used to create the black areas.

6.7.3 Comparison of ATR-FTIR and DRIFTS spectra of Turkey red

Most of the UTR textiles were mounted in fragile books, making it impossible to analyse them on an ATR instrument. A brief comparison is made here with a few available pieces of unmounted historical Turkey red to determine whether ATR instruments can be used for identification. A small piece from the UTR collection, UGD 13/8/5 #12, was found stuck in the binding, unmounted, and therefore could be analysed on the ATR instrument.



Figure 6-64 Sample UGD 13/8/5 #12. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/5.

A bi-fold cardboard square with two pieces Turkey red pasted over it was kindly donated to the Centre for Textile Conservation (CTC) by Dr Norman Tennent. The edge of the 'small pattern' side has become slightly unglued, making it possible to position on the ATR device.



Figure 6-65 'Small pattern' (left) and 'large pattern' on historical Turkey red piece from Dr Norman Tennent. Centre for Textile Conservation collection.

Two mid-20th c. textiles from UTR, both in the style of Turkey red, were donated by Judith Townson. Her father, Robert Peel, was a printer at UTR. These pieces are not expected to be Turkey red based on the date of manufacture and the loose, open weave of the textiles, though it is interesting that they imitate the printed style. Townson B has a label affixed that states it was dyed with synthetic alizarin. Their appearance and texture suggests they were treated with a finishing agent, leaving them stiff and shiny, which may affect the spectra through increased reflectance or mask other signals.



Figure 6-66 Mid-20th c. UTR textiles from Judith Townson; Townson A (left) and Townson B. Centre for Textile Conservation collection.

The loose textiles make it possible to compare ATR and DRIFTS analyses on some historical pieces. Bands for are less distinct than in the ATR spectra (Figure 6-67) for replica oiled calico. In Tennent Turkey red (small pattern) (peaks marked for this sample), v_{asym} (C=O) appears at 1709 cm⁻¹. Overall, the ATR spectra were not as useful at distinguishing Turkey red from the Townson textiles as the DRIFTS spectra shown in Figure 6-68. Here, the characteristic strong dimeric v_{asym} (C=O) appears in the two Tennent Turkey red spectra and UGD 13/8/5 #12 around 1713 cm⁻¹, whereas Townson A appears closer to the blank spectrum. The different weave and finishing treatment likely contribute to the raised baseline and altered shape of the spectrum. Chromatography of dyes extracted from the Townson pieces in Chapter 7 reveals more about their manufacture, but based on these spectra and their date of production they appear not to be Turkey red.



Figure 6-67 ATR spectra of Tennent and Townson textiles. Average of three replicates each normalised to 1.0 at 1030 cm⁻¹, peaks for Tennent TR.



Figure 6-68 DRIFTS spectra of Tennent and Townson textiles. Average of three replicates each, spectra not normalised but y-offset corrected from 2200-2000 cm⁻¹. Peaks for Tennent small pattern.

6.7.4 ATR and DRIFTS analysis of replica Turkey red

Samples of replica Turkey red prepared with Fluka TRO and dyed with madder or alizarin were prepared in Section 4.3.3 (See Figure 4-21) and analysed by ATR and DRIFTS. The samples were prepared in triplicate (three for each dye) and compared to spectra from calico dyed with madder but no oil and samples from Debbie Bamford (DB).

DRIFTS spectra from replica Turkey red dyed with madder and alizarin in Figure 6-69 show the textiles are similar to historical Turkey red, validating the usefulness of replicas in the characterisation of the dye complex. Both interfaces distinguish between cotton dyed with madder and no oil (blue lines) and Turkey red (see Figure 6-71), but DRIFTS is more sensitive.



Figure 6-69 DRIFTS spectra of replica Turkey red and madder-dyed calico without oil. Average of three replicates each, spectra not normalised. Peaks for Replica TR alizarin 2.

The dye source of alizarin (green) or madder (purple) appear to produce spectra with slightly different trends, but analysis of a larger sample set is required to determine any cause or significance. The band from aromatic $v_{def}(C-H)$ at 839 cm⁻¹ from the anthraquinones appears in all dyed samples. The inset in Figure 6-70 highlights the carbonyl and carboxyl region for these samples.





The spectra from calico dyed without oil (blue lines) are more consistent with the blank spectrum in the region (black box), where dimeric and monomeric v_{asym} (C=O) are marked at 1713 and 1736 cm⁻¹. In DB Replica TR, v_{asym} (C=O) is around 1744 cm⁻¹. This indicates more free monomeric oleic acid present in the sample, which was prepared with rancid olive oil. Since naturally rancid olive oil is expected to still have a higher glyceride content than Turkey red oil, this is consistent with the sample preparation. Ester formation is unlikely considering the mild and aqueous preparation conditions. The ATR spectra of replica Turkey red in Figure 6-71 are much less easy to interpret than the DRIFTS spectra, showing how the two FTIR techniques 'see' the samples differently. Some samples have bands for adsorbed monomeric $v_{asym}(C=0)$ around 1730 cm⁻¹ and aromatic $v_{def}(C-H)$ around 838 cm⁻¹, but detection is much poorer and the peaks are less intense relative to the baseline than in the DRIFTS spectra. The inset in Figure 6-72 shows the diminished $v_{asym}(C=0)$ band as well as subtle differences consistent with madder or synthetic alizarin as a dye. The cause of these cannot be determined from this research but may be useful in future analyses. All six replica Turkey red spectra have bands around 1591 and 1464 cm⁻¹ consistent with aluminium carboxylate complexes.



Figure 6-71 ATR spectra of replica Turkey red and madder-dyed calico without oil. Average of three replicates each, normalised to 1.0 at 1029 cm⁻¹. Peaks for Replica TR alizarin 2.



Figure 6-72 Inset of ATR spectra for replica Turkey red and madder-dyed calico without oil. See Figure 6-71 for details. Green peaks from Replica TR alizarin 1, pink from DB Replica TR, and black are shared.

6.7.5 ATR-FTIR analysis of V&A dress

A dress in the Textile & Fashion collection at the V&A provided an opportunity to test FTIR as a means of authenticating Turkey red objects. The dress (T.74-1988) dates from 1825-1830, is of British provenance, and is catalogued as having a Turkey red ground. The style and colours of the pattern are atypical when compared to the other Turkey red examined during this project, raising the question of whether it was indeed Turkey red.



Figure 6-73 Fabric of dress T.74-1988. Image courtesy of the V&A.



Figure 6-74 Full image of T.74-1988. © Victoria and Albert Museum

Analysis of a fibre removed from the dress seam was done by the Science Section of the Conservation Department at the V&A. The spectrum was taken using a Nicolet iS10 FTIR spectrometer with a Golden Gate diamond ATR attachment. The spectrum was collected in transmission mode at 4 cm⁻¹ with an average of 32 scans. An ATR correction and baseline correction were performed on the raw spectrum using OMNIC software. The sample was compared to ATR spectra of plain calico, madder-dyed calico, and Tennent Turkey red 'small pattern' taken at the CTC (Figure 6-75). Because the spectrum from the V&A was ATR corrected, the other spectra were as well for this figure.



Figure 6-75 ATR spectra of V&A dress T.74-1988 compared to other samples. Average of three replicates each (T.74-1988 solo) ATR corrected and normalised to 1.0 at 3336 cm⁻¹. Peaks for Tennent Turkey red (small pattern).



Figure 6-76 Inset of ATR spectra for T.74-1988 and comparison. See Figure 6-75 for details. Peaks for T.74-1988.

The overall shape of the spectrum for T.74-1988 has much more in common with the Tennent spectrum than the non-Turkey red calico dyed without oil, as shown in Figure 6-76. T74-1988 has a band for v_{asym} (C=O) marked at 1720 cm⁻¹ and bands around 1461 cm⁻¹ and 1593 cm⁻¹ consistent with v_{str} (COO-Al). Peaks around 1550 cm⁻¹ are consistent with sodium carboxylate v_{asym} (COO-Na).

The ATR spectrum from the T.74-1988 fibre appears to be a spectrum from a piece of Turkey red, though this research also determined ATR is less sensitive than DRIFTS for this analysis. The fabric pattern has a softer, natural palette with a painted appearance created by overlaid greens and blues. The majority of historical Turkey red pieces viewed during this research have sharper lines with bolder, single-toned colours, markedly different from the fabric of the dress. Stylistically, a few pieces in the UTR collection at Glasgow University from the late 1850s are closer to T.74-1988, but still have more in common with typical UTR pieces.



Figure 6-77 Pattern samples in UGD 13/8/4 from the late 1850s. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/4.

There are many potential explanations for the difference in pattern, including manufacturer, era, and intended market, but this is beyond the scope of this project. Further analysis by DRIFTS is recommended for a more conclusive

identification, though from this analysis the dress appears to be a remarkable example of printed Turkey red.

6.7.6 Characterisation of oil-aluminium complex by FTIR

In Section 6.6, the discussion of sodium and aluminium carboxylates from the literature reviewed for this analysis stated that the position of $v_{asym}(COO^{-})$ and $v_{sym}(COO^{-})$ can be used to assign bonding geometry of the complex due to the different bonding energies of possible ligands, which have been characterised by FTIR. The configuration is determined by Δv , or $v_{asym}(COO^{-})$ minus $v_{sym}(COO^{-})$.⁶³ Potential bonding geometries include unidentate coordination, bidentate chelating, and bidentate bridging.⁶⁴



Figure 6-78 Unidentate coordination (left), bidentate chelating (centre), and bidentate bridging complexes of metal carboxylates.

Bronstein *et al.* assign bond geometry using the following Δv values: $\Delta v > 200$ cm⁻¹ for unidentates, $\Delta v < 110$ cm⁻¹ for bidentates, and $140 < \Delta v < 200$ for bridging.⁶⁵ *Papageorgiou et al.* use values relative to the ionic complex of the compound (the sodium carboxylate) and assign $\Delta v(COO^{-})_{complex} << \Delta v(COO^{-})_{Na}$ for bidentate chelation, $\Delta v(COO^{-})_{complex} \approx \Delta v(COO^{-})_{Na}$ for bidentate bridging, and $\Delta v(COO^{-})_{complex} >> \Delta v(COO^{-})_{Na}$ for unidentate coordination.⁶⁶ Lee *et al.* give the

⁶³ Papageorgiou et al., "Metal-Carboxylate Interactions in Metal-Alginate Complexes Studied with FTIR Spectroscopy."

⁶⁴ Socrates, Infrared and Raman Characteristic Group Frequencies, 316.

⁶⁵ Bronstein et al., "Influence of Iron Oleate Complex Structure on Iron Oxide Nanoparticle Formation."

⁶⁶ Papageorgiou et al., "Metal-Carboxylate Interactions in Metal-Alginate Complexes Studied with FTIR Spectroscopy."

value of $\Delta v(COO^{-})_{Na}$ as about 137 cm⁻¹,⁶⁷ which is consistent with the RCOO-Na peaks seen in this work.

In this research, $\Delta v(COO^-)_{complex}$ for RCOO-Al in historical and replica Turkey red samples is around 125 cm⁻¹, a figure not included in the ranges provided by Bronstein *et al.* Other sources attribute values in this range to bidentate chelation, ⁶⁸ bidentate bridging,⁶⁹, or a combination of both.⁷⁰ Neither bidentate bridging or chelation is consistent with the conclusions regarding the oiling process, however, because the hydrogen bond between the FFA carbonyl and cellulose hydroxyl is not taken into account. Papageorgiou *et al.* also discuss a unidentate ligand with smaller Δv values resulting from a carboxylic oxygen not coordinating because it is hydrogen-bonded to another ligand. This complex is described as a 'pseudo bridged unidentate arrangement'.⁷¹



Figure 6-79 Structure of 'pseudo bridged unidentate' ligand. In Turkey red, R^1 is cellulose, R^2 is an aliphatic chain, and M is aluminium.

This proposed structure is consistent with the practices of Turkey red dyeing, where the carbonyl is initially hydrogen-bonded to the cellulose, leaving the other oxygen available to attract aluminium. This also fits the conclusion that more oil attracted more aluminium, and that a method with aluminium in the oil bath is not true Turkey red because the initial hydrogen bonding of the FFAs would not occur before an aluminium carboxylate formed. The stability and low water-solubility of aluminium oleate probably contribute to the fastness of Turkey red when precipitated onto the fibre as practiced in traditional methods.

⁶⁷ Lee and Condrate, "FTIR Spectral Characterization of Thin Film Coatings of Oleic Acid on Glasses: I. Coatings on Glasses From Ethyl Alcohol."

⁶⁸ Mahdavi et al., "Synthesis, Surface Modification and Characterisation of Biocompatible Magnetic Iron Oxide Nanoparticles for Biomedical Applications."

⁶⁹ Lewis et al., "Multispectroscopic (FTIR, XPS, and TOFMS-TPD) Investigation of the Core-Shell Bonding in Sonochemically Prepared Aluminum Nanoparticles Capped with Oleic Acid."

⁷⁰ Roonasi and Holmgren, "A Fourier Transform Infrared (FTIR) and Thermogravimetric Analysis (TGA) Study of Oleate Adsorbed on Magnetite Nano-Particle Surface."

⁷¹ Papageorgiou et al., "Metal-Carboxylate Interactions in Metal-Alginate Complexes Studied with FTIR Spectroscopy."

Lee et al. found metal ions made the alkyl chains to be more rigid and regularly oriented, causing the coating layer to be more ordered and compact. This in turn increased the bonding strength of adsorbed carboxylic acid dimers.⁷² The conclusion from this research is that when cotton oiled for Turkey red dyeing is exposed to Al³⁺ ions, aluminium oleate precipitates on the fibres and the complex is stabilised by hydrogen bonding between the fatty acids and cellulose hydroxyls. Other complexes like bidentate briding and chelates may form to an extent in such a complex process, but the pseudo bridge unidentate complex is proposed as most consistent with the whole of the Turkey red process and the FTIR data from this project.

6.7.7 Summary

This work shows FTIR spectroscopy is a useful, non-invasive tool for the identification and characterisation of dyed and printed Turkey red textiles. The ATR and DRIFTS interfaces were evaluated, and although both are capable of identifying Turkey red, the DRIFTS instrument was more sensitive on the uneven textile surface and overall the better choice. Furthermore, in the case of the fragile UTR sample pattern books that could not be manipulated onto an ATR crystal, the handheld DRIFTS instrument was the only means of analysis. It also required no application of pressure or sample preparation, making it an ideal tool for heritage object research. FTIR bands characteristic of Turkey red textiles identified in this chapter are listed in Table 6-5.

⁷² Lee and Condrate, "FTIR Spectral Characterization of Thin Film Coatings of Oleic Acid on Glasses: I. Coatings on Glasses From Ethyl Alcohol."

Position (cm ⁻¹)	Group	Vibration		
3600-3400	-OH	intramolecular hydrogen-bonded stretching		
2925	-CH ₂ -	asym. stretching		
2850	-CH2-	sym. stretching		
2086	C≡N	asym. stretching (Prussian blue)		
1740	C=0	asym. stretching (free monomeric FA)		
1730	C=0	asym. stretching (adsorbed monomeric FA)		
1712	C=0	asym. stretching (dimeric FA)		
1640	H ₂ O	adsorbed water		
1560	RCOO-Na	asym. stretching		
1585	RCOO-Al	asym. stretching		
1465	RCOO-Al	sym. stretching		
1425	RCOO-Na	sym. stretching		
1345-1100	-CH ₂ -	deformation		
839	C-H	out-of-plane aromatic deformation		

Table 6-5 Approximate position of FTIR bands found in Turkey red textiles.

The spectra for finished Turkey red have the same oil bands identified in the oiled calico samples from hydrogen-bonded FFAs on the cellulose fibres. Spectra for replica and historical Turkey red are similar, indicating a successful recreation. Detection of dyes was not anticipated in this analysis, but the band around 839 cm⁻¹ shows aromatic rings of anthraquinones are also detected. Prussian blue pigment has a distinct band around 2086 cm⁻¹ that was seen in the overprinted Turkey red and the spectrum from the green printed area. The presence of aluminium carboxylates and the peak positions for symmetric and asymmetric stretching reveal information about the metal coordination complex. Based on the data, the literature, and the nature of the Turkey red process, the spectra indicate aluminium ions precipitate aluminium soaps on the cotton by forming a 'pseudo bridged unidentate' ligand with the hydrogen-bonded fatty acids. In the following section, analysis of the aluminium complex by ssNMR is discussed as a complementary analytical technique.

6.8 ²⁷Al ssNMR spectra of *in situ* Turkey red

The review of literature in Section 3.8.1 on the aluminium-calcium-alizarin lake in Turkey red dyeing concluded that the complex proposed by Soubayrol *et al*.

was reasonable for Turkey red based on the conditions of the dyeing process.^{73,74} They used ²⁷Al ssNMR, in which a signal between -10 and +20 ppm indicates a coordination number of six and between +55 and +85 ppm a coordination number of four. They found the complex $[Al_2(\mu-OH)_2Ca_2(C_{14}H_6O_4)_4(H_2O)_4](H_2O)_2$ (Al, Ca, alizarin, and water) had a chemical shift of 24.7 ppm, an atypical value attributed to deformation of the four O-Al bonds proposed in the core of the structure, which they called a 'binuclear closed structure complex' where Ca²⁺ ions are 'sandwiched' between facing benzene rings of alizarin molecules. The study also determined two of the H₂O molecules from each 'dibenzene sandwich' could be replaced with a cellobiose molecule representing cellulose. If, instead of cellobiose, a fatty carboxylate replaces the water, then the model is a reasonable explanation of Turkey red formation. Water molecules in this complex could also explain the stronger band for adsorbed water around 1640 cm⁻¹ in the Turkey red spectra.

For this project, ²⁷Al ssNMR spectra were obtained of plain calico, calico oiled and treated with alum, and finished Turkey red (samples trimmed from Turkey red re-creation in Section 4.3.3. The spectra were taken at the Durham University EPSRC facility on a Varian VNMRS spectrometer with a 9.4 T magnet and a MAS probe with a 6 mm rotor. They were recorded at 104 MHz at room temperature with a 0.2 s recycle delay. Direct excitation (DE) was used with a pulse duration of 1 µs with an external reference of 1 M aq. Al(NO₃)₃. Full spectra are included in Appendix G.

⁷³ Soubayrol, Dana, and Man, "Aluminium-27 Solid-State NMR Study of Aluminium Coordination Complexes of Alizarine."

⁷⁴ Soubayrol, "Préparation et étude structurale des complexes formés entre l'aluminium et l'alizarine: Importance de la nature du solvant et de la base utilisés sur le degré de condensation de l'aluminium et l'agencement moléculaire."



Figure 6-80²⁷Al ssNMR spectra of plain calico, oiled and alumed calico, and replica Turkey red as prepared in Section 4.3.3. -20 ppm progressive offset to display spectra.

The plain calico has a weak signal at 8 ppm, which can be explained by the natural occurrence of aluminium in living organisms. The sample prepared with oil and alum has a signal at -6 ppm, in both samples indicating the Al atoms are in a six-fold coordination complex with oxygen. This could be to -OH, COO⁻, or a mixture of both. The spectrum from Turkey red has a signal at -5 ppm from sixfold coordination and a narrow signal indicating an ordered environment at 26 ppm. This agrees with the data from Soubayrol *et al.* and indicates their structure is present in Turkey red textiles. This complex would be more easily accommodated by the stabilised 'pseudo' bridged unidentate ligand, whereas a bidentate complex would require reconsideration of the lake. Other hydroxyanthraquinone dyes also fit this model provided -OH groups are at the 1 and 2 positions. The two signals in finished Turkey red suggest not all aluminium becomes part of a lake, probably based on whether the atom is oriented in a way to attract alizarin and calcium. If it does not form a lake, it likely remains on the fibre as aluminium carboxylates. The ²⁷Al ssNMR results are consistent with the conclusions from the FTIR analysis of Turkey red and the aluminium complex.

6.9 Summary

The *in situ* analysis of historical and replica Turkey red and oiled calico by FTIR and ssNMR supports the hypothesis that FFAs in the oil treatment form hydrogen bonds with cellulose hydroxyl groups. Studies of oleic acid surface coatings on

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hydroxyl-rich substrates by FTIR provide useful references to characterise the textiles. The FTIR spectra of the textiles show sodium carboxylates also precipitate onto the fibres when sodium ions are present. A strong $v_{asym}(C=0)$ band resulting from the oil treatment, usually around 1711 cm⁻¹ and indicative of dimeric carboxyl complexes, is characteristic of Turkey red and was visible in spectra from samples in dyeing manuals and textiles manufactured by UTR. It was often accompanied by a peak for monomeric adsorbed $v_{asym}(C=0)$. Carboxylic dimers, which adsorb to hydrogen-bonded fatty acids and sodium carboxylates via hydrocarbon chain adsorption, create a hydrophobic barrier around the cellulose fibres that likely contributes to the overall fastness of the textile by slowing the degradative effects of water. The DRIFTS interface and portable instrument were overall much better for non-invasive analysis of uneven textile surfaces, though the results show ATR can be used to identify oil on Turkey red. The ATR spectrum of a dress at the V&A that appears to be a stylistically unusual piece of Turkey red had characteristic peaks, but further investigation with DRIFTS is recommended for confirmation.

Studies on carboxylate complexes show Al³⁺ ions replace Na⁺ in RCOO-M complexes, precipitating aluminium carboxylates. When applied in the Turkey red process, the aluminium chelates with hydrogen-bonded fatty acids in a stabilised 'pseudo' bridged unidentate ligand. The RCOO-Al complex is more covalently bonded and therefore very stable on the fibre, in addition to its low water solubility, a factor that probably also contributes to the fastness of Turkey red. The conclusion from this research shows that while they could not support their hypothesis with in situ analytical data, historical researchers proposing the formation of metal soaps in Turkey red had a sound hypothesis. The celluloseoil-aluminium ligand complex proposed in this chapter accommodates the aluminium-calcium-alizarin lake complex proposed by Soubayrol et al., and in situ ²⁷Al ssNMR analysis of replica Turkey red is consistent with their structure for the lake precipitated from aqueous media. Figure 6-81 shows a proposed model for fatty acid bonding to cellulose with an aluminium-calcium-alizarin lake attached. The lake complex is one half of Soubayrol's proposed alizarincalcium-alizarin complex, keeping the same hexavalent coordination of aluminium with four bonds to the two alizarin carbonyls and two hydroxyls, one to the fatty acid, and one to a water molecule. The calcium is 'sandwiched'

between the rings of two alizarin molecules in the complex, though the bonds are not shown in the diagram. The geometry of the diagram is not precise, but it suggests a reasonable way for the components of the Turkey red complex to bond as suggested by the literature and the analytical results.



Figure 6-81 Proposed model for cellulose-fatty acid-lake complex in Turkey red. Note: Model arranged for optimal component display, geometry not confirmed. Cellulose segment terminates with C atoms in this graphic.

This research and the *in situ* analysis of the textiles discussed in this chapter finally answer the persistent questions regarding the role of the oil in Turkey red and how it becomes part of the complex. The application of two FTIR techniques showed both were effective at non-invasive analysis of heritage objects, and that the re-creation of Turkey red for this project was successful in producing textiles similar to the historical pieces. Spectra for ¹³C and ²⁷Al ssNMR complemented the FTIR data and supported previous conclusions. This technique, which is *in situ* but requires stuffing the sample in a rotor, was only applied to replica pieces since no historical Turkey red of the appropriate dimensions was available. This work concludes answering the question for this project regarding the role of the oil, which serves as a means to attract aluminium for the later formation of the colour lake, and as a hydrophobic coating for the cotton fibres, likely increasing their colour fastness and longevity. Another remaining question, regarding whether it was possible to dye Turkey red following a historical process, was answered by the similarity between spectra from historical and replica textiles. This is to say that the

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Turkey red complex was re-created and characterised, but it is worth noting that much remains to be explored about its fastness properties and that although it was considered a high-quality textile, varying degrees of quality existed within the spectrum of Turkey red. The results of this analysis are consistent with the cotton receiving some hydrophobic properties from the oil treatment, which likely contributes to the wash fastness of the colour. Whether this also contributes to its light fastness is worth investigation for its conservation and display applications.

A proposal for the origins of the oiling process is made here based on its relatively simple chemistry. Historically, soap making involved treating fat (often tallow or olive oil) with sodium hydroxide, producing sodium carboxylates. With repeated washings, these could accumulate on cotton fibres in the same way they do for Turkey red dyeing, very slowly at such a low concentration. Dyers who mordanted and dyed an old, repeatedly washed cotton item may have obtained a much deeper and brighter hue than they obtained from dyeing freshly spun cotton and made the connection to the repeated exposure to soap, eventually developing it into the Turkey red process by increasing the FFA content of the oil baths and adding finishing steps.

7 Analysis of dyes and pigments on 19th c. Turkey red textiles

The identification of colourants on historical textiles by fibre extraction and chromatography can reveal more about how or when an object was made. It is also an important aspect of object conservation, since knowing whether particularly stable or labile compounds are present determines whether an item can be safely displayed or requires extra care. There are a number of studies on the composition of madder dyes and madder extracts, yet there is little research thus far on early synthetic dyes, including alizarin. This chapter discusses the analysis of dyes on historical Turkey red textiles, for which no comprehensive study has been done to date, to determine whether the dye source—madder, garancine, or synthetic alizarin—can be identified. This answers the final question for this project regarding which dyes are present on historical Turkey red and whether they can be used to determine object provenance.

The primary analytical technique used here is ultra high performance liquid chromatography with photodiode array detector (UHPLC-PDA), which is capable of efficiently separating and identifying components of a sample extracted from a small quantity of dyed thread (ca. 0.5-1 cm).^{1,2} Identifications are made based on a combination of retention time (RT), or how long the compound spends on the column before passing through the detector, and UV-Vis absorbance spectra. This requires comparison to known reference compounds to determine which compound corresponds to RT values and UV-Vis spectra. References of modern and historical madder and synthetic alizarin were used for comparison to the textile sample chromatograms. It is worth noting that since UHPLC technology is relatively new to the market³, it has not yet been applied to the analysis and identification of madder dyestuffs on a large scale but may yield even more detailed results than previously possible.

¹ Serrano, van Bommel, and Hallett, "Evaluation Between Ultrahigh Pressure Liquid Chromatography and High-Performance Liquid Chromatography Analytical Methods for Characterizing Natural Dyestuffs."

² Troalen et al., "Historical Textile Dyeing with Genista Tinctoria L.: A Comprehensive Study by UPLC-MS/MS Analysis."

³ Webster, Cullen, and Kott. "Method Transfer Between HPLC and UHPLC Platforms."

The name 'Turkey red' often invokes not only the bright red shade created from the dyeing process, but also the bold printed textiles that comprise the majority of the samples in the United Turkey Red (UTR) sample pattern books examined for this project. The focus of this research is on the characterisation of the red complex, but the significance of the printed textiles merited a brief analysis to determine whether the compounds described in the literature were present. This was done with a combination of FTIR-ATR (Fourier transform infrared spectroscopy attenuated total reflectance) and SEM-EDX (scanning electron microscope with energy dispersive X-ray).

7.1 UHPLC-PDA analysis of anthraquinone dyes

This section outlines the samples analysed and prepared for UHPLC-PDA analysis in this project. Further discussion of the technique in general is provided in Appendix A.

7.1.1 Samples

The sample sets analysed for this research include modern reference compounds, historical reference compounds, and replica and historical textiles. They were classified into four groups based on their origin—collections textiles, dye manual textiles, replica textiles, and reference compounds. All textile samples in this section were red unless otherwise noted. For the collection samples, the sample name is the accession number of the object from which it was taken.

7.1.1.1 References

A variety of madders and anthraquinone dye samples of both modern and historical origin were analysed. All modern madder samples are *Rubia tinctorum* L. except for the *R. cordifolia* sample. All available information for historical samples is included and the supplier listed for modern samples.

ID	Sample	Source	Туре
R1	French madder	Couleur Garance	modern
R2	English madder	Fibrecraft	modern
R3	Iranian madder	Fibrecraft	modern
R4	Turkish madder	Kremer Pigmente	modern
R5	Rubia cordifolia	Jing Han	modern
R6	Dutch madder	TU Dresden H. F.	historical
R7	Russian madder	TU Dresden H. F.	historical
R8	Silesian madder	TU Dresden H. F.	historical
R9	Garancine	Catalyst Science Discovery Centre	historical
R10	Alizarin (97% purity)	Acros Organics	modern
R11	Purpurin (>90% dye)	Sigma-Aldrich	modern
R12	Anthrapurpurin	Pfaltz & Bauer	modern
R13	Alizarin A.1903.37.34	National Museums Scotland	historical
R14	Alizarin Apolda	TU Dresden H. F.	historical
R15	Alizarin from madder	TU Dresden H. F.	historical
R16	Alizarin Merck	TU Dresden H. F.	historical
R17	Alizarin PA Prag	TU Dresden H. F.	historical
R18	Alizarin extra rein für Orange BASF	TU Dresden H. F.	historical
R19	Alizarinrot IG Farben	TU Dresden H. F.	historical
R20	Alizarinrot WG Teig 20% BASF	TU Dresden H. F.	historical
R21	Synthetic alizarin, Zöllner und Morell Chemnitz (purveyor)	TU Dresden H. F.	historical

Table 7-1 Reference samples analysed by UHPLC.

The abbreviation TU Dresden H.F. refers to the Technishes Universität Dresden Historisches Farbstoffsammlung (historical dyes collection), which dates from the mid-19th to early 20th c. The information in Table 7-1 is what was provided with the samples, which were prepared by Dr Horst Hartmann. Zöllner und Morell was a purveyor rather than a manufacturer, and the meaning of 'WG', as discussed in Chapter 3, is unknown. The sample 'Alizarin aus Krapp' translates to 'alizarin from madder', which could describe garancine, but the sample was completely soluble in methanol whereas garancine contains woody material like madder. German texts also call it *Garancin*, so the name is more likely an indicator that it could be used like madder.



Figure 7-1 Samples of Russian (R7 left), Silesian (R8 centre), and Dutch madder (R6) from the TU Dresden H.F.



Figure 7-2 Historical synthetic alizarin samples from TU Dresden H.F. Samples prepared by Dr Horst Hartmann. From left: R14, R18, R16, R19, R17, R21, R20, R15.

The garancine sample from the Catalyst Science Discovery Centre (Widnes, England, UK) was originally from the University of Leeds (Leeds, England, UK) Food Science department and accessioned into their collection in 1985. Previous garancine analyses discussed in Chapter 3 were from another department at the University of Leeds, so they may be connected.





7.1.1.2 Dyeing manuals

The publication date and texts of the dyeing manuals provide information about which dye was used on the textile, which is not always known with collection samples. These manuals were used to communicate dyeing processes and promote new products, e.g. Perkin's articles on synthetic alizarin. Following ethical sampling procedures, a segment of thread ca. 0.5-1 cm long was taken from an already frayed edge of the textile. All available information is included in the table and full titles can be found in the bibliography.

ID	Sample	Book	Provenance
M1	Turkey red (madder, dyed by Steiner & Co.)	Crookes (1874), page 326.	GU Special Collections
M2	Turkey red (alizarin, supplied by Perkin)	Crookes (1874), page 326.	GU Special Collections
M3	Turkey red (alizarin, supplied by Perkin)	Perkin (1870), "XVI on Artificial Alizarin" opp. page 133.	GU Chemistry Library
M4	Turkey red (alizarin, supplied by Perkin)	Perkin (1870), "XVI on Artificial Alizarin." opp. page 133.	GU Special Collections
M5	Turkey red (alizarin, supplied by Perkin)	Perkin (1873), "XV on Anthrapurpurin." opp. page 425.	GU Chemistry Library
M6	Turkey red (anthrapurpurin, supplied by Perkin)	Perkin (1873), "XV on Anthrapurpurin." opp. page 425.	GU Chemistry Library
M7	Rouge d'anthrapurpurine avivé no. 231	Dépierre (1892), page 96.	Susan-Kay Williams private collection



Out of the above samples, only the ones from Crookes are specifically labelled as Turkey red in the source text. The 1870 sample from Perkin (GU Special Collections copy) was analysed by DRIFTS in Chapter 5 (Figure 6-52) and found to be Turkey red, which is logical of Perkin since the industry would be his biggest buyer. The 1873 Perkin samples are also unlabeled but are very likely to be Turkey red as well, again given the intended market and the characteristic bright red hue of the cotton. The Dépierre sample 'anthrapurpurin red, brightened' (cleared) is not labelled as Turkey red but appears to be so as well, though it was not analysed by FTIR.

7.1.1.3 Collections

Fibre samples of historical Turkey red were obtained as described above following ethical sampling practices from objects in the Glasgow University Archives UTR collection, the Victoria and Albert Museum (V&A) Textiles & Fashion collection, and the Centre for Textile Conservation (CTC) Karen Finch Reference collection. The majority are red threads; those labelled in *bold & italic* text were printed black but also contained red dye.

ID	Sample	Date	Source	Provenance
C1	UGD 13/8/1 #1	unknown	GU Archives	UTR
C2	UGD 13/8/1 #3	unknown	GU Archives	UTR
C3	UGD 13/8/1 #4	unknown	GU Archives	UTR
C4	UGD 13/8/2 #1	1858	GU Archives	UTR
C5	UGD 13/8/2 #2	1858	GU Archives	UTR
C6	UGD 13/8/2 #4	1859	GU Archives	UTR
C7	UGD 13/8/3 #1	1857	GU Archives	UTR
C8	UGD 13/8/3 #2	1857	GU Archives	UTR
C9	UGD 13/8/3 #3	1857	GU Archives	UTR
C10	UGD 13/8/3 #6	1857	GU Archives	UTR
C11	UGD 13/8/3 #7	1857	GU Archives	UTR
C12	UGD 13/8/3 #9	1857	GU Archives	UTR
C13	UGD 13/8/3 #10	1858	GU Archives	UTR
C14	UGD 13/8/3 #11	1858	GU Archives	UTR
C15	UGD 13/8/4 #1	unknown	GU Archives	UTR
C16	UGD 13/8/4 #2	unknown	GU Archives	UTR
C17	UGD 13/8/4 #4	1863	GU Archives	UTR
C18	UGD 13/8/5 #1	1867 or later	GU Archives	UTR
C19	UGD 13/8/5 #3	1867 or later	GU Archives	UTR
C20	UGD 13/8/5 #4	1867 or later	GU Archives	UTR

ID	Sample	Date	Source	Provenance
C21	UGD 13/8/5 #7	1867 or later	GU Archives	UTR
C22	UGD 13/8/5 #8	1867 or later	GU Archives	UTR
C23	UGD 13/8/5 #9	1867 or later	GU Archives	UTR
C24	UGD 13/8/5 #10	1867 or later	GU Archives	UTR
C25	UGD 13/8/5 #11	1867 or later	GU Archives	UTR
C26	UGD 13/8/5 #12	1867 or later	GU Archives	UTR
C27	UGD 13/8/6 #1	1887	GU Archives	UTR
C28	UGD 13/8/6 #2	1887	GU Archives	UTR
C29	UGD 13/8/6 #3	1887	GU Archives	UTR
C30	UGD 13/8/6 #4	1888	GU Archives	UTR
C31	UGD 13/8/7 #1	1887	GU Archives	UTR
C32	UGD 13/8/7 #2	1887	GU Archives	UTR
C33	UGD 13/8/7 #3	1887	GU Archives	UTR
C34	UGD 13/8/7 #4	1887	GU Archives	UTR
C35	UGD 13/8/7 #5	1887	GU Archives	UTR
C36	UGD 13/8/8 #1	1878	GU Archives	UTR
C37	UGD 13/8/8 #2	1878	GU Archives	UTR
C38	UGD 13/8/8 #4	1878	GU Archives	UTR
C39	UGD 13/8/8 #5	1878	GU Archives	UTR
C40	UGD 13/8/8 #6	1878	GU Archives	UTR
C41	UGD 13/8/8 #7	1878	GU Archives	UTR
C42	UGD 13/8/8 #8	1878	GU Archives	UTR
C43	UGD 13/8/9 #1	1899	GU Archives	UTR
C44	UGD 13/8/9 #2	ca. 1900	GU Archives	UTR
C45	UGD 13/8/9 #3	1901	GU Archives	UTR
C46	UGD 13/8/9 #4	ca. 1901	GU Archives	UTR
C47	UGD 13/8/9 #5	ca. 1901	GU Archives	UTR
C48	1797-1899	ca. 1890	V&A	Switzerland
C49	1798-1899	ca. 1890	V&A	Switzerland
C50	1799-1899	1890-1899	V&A	Germany
C51	1800-1899	1840-1899	V&A	Germany
C52	1801-1899	1898	V&A	Germany
C53	1802-1899	1880-1899	V&A	Germany
C54	1803-1899	1880-1899	V&A	Germany
C55	1804-1899	1880-1899	V&A	Germany
C56	1805-1899	1887-1899	V&A	Italy
C57	1807-1899	1888-1899	V&A	Germany
C58	T 4-1992	1871	VA	Berberich &
C70	1.4-1772	1071	Y U.A	Co., Germany
C59	T.5-1992	1871 1830-1840	V&A V&A	J. Winkel, Bad
				Sackingen,
				Germany
C60	1.0-17/0 (0.07 Dattorn 10			Printworks
C61	T 8-1978 n 89	1840-1840	V&A	Foxhill Rank
	Turkey red			Printworks

ID	Sample	Date	Source	Provenance
C62	T.344-1919	1820-1850	V&A	Marseilles, France
C63	T.74-1988 (dress)	1825-1830	V&A	Great Britain
C64	T.74-1988 (lining)	1825-1830	V&A	Great Britain
C65	T.12B-1984	1830-1890	V&A	England
C66	T.133-1976	1860-1880	V&A	UTR
C67	T.133(1)-1976	1860-1880	V&A	UTR
C68	T.133(2)-1976	1860-1880	V&A	UTR
C69	T.133(3)-1976	1860-1880	V&A	UTR
C70	T.133(4)-1976a	1860-1880	V&A	UTR
C71	T.133(5)-1976	1860-1880	V&A	UTR
C72	T.133(6)-1976	1860-1880	V&A	UTR
C73	T.133(7)-1976	1860-1880	V&A	UTR
C74	T.133(8)-1976	1860-1880	V&A	UTR
C75	T.133(9)-1976	1860-1880	V&A	UTR
C76	T.133(10)-1976	1860-1880	V&A	UTR
C77	T.133(11)-1976	1860-1880	V&A	UTR
C78	T.133(12)-1976	1860-1880	V&A	UTR
C79	T.133(13)-1976	1860-1880	V&A	UTR
C80	T.133(14)-1976	1860-1880	V&A	UTR
C81	T.133(15)-1976	1860-1880	V&A	UTR
C82	T.133(16)-1976	1860-1880	V&A	UTR
C83	T.133(17)-1976	1860-1880	V&A	UTR
C84	T.133(18)-1976	1860-1880	V&A	UTR
C85	T.133(19)-1976	1860-1880	V&A	UTR
C86	T.133(20)-1976	1860-1880	V&A	UTR
C87	T.133(21)-1976	1860-1880	V&A	UTR
C88	T.133(22)-1976	1860-1880	V&A	UTR
C89	T.133(23)-1976	1860-1880	V&A	UTR
C90	T.133(24)-1976	1860-1880	V&A	UTR
C91	T.133(25)-1976	1860-1880	V&A	UTR
C92	T.133(26)-1976	1860-1880	V&A	UTR
C93	T.133(27)-1976	1860-1880	V&A	UTR
C94	T.133(28)-1976	1860-1880	V&A	UTR
C95	T.133(29)-1976	1860-1880	V&A	UTR
C96	T.133(30)-1976	1860-1880	V&A	UTR
C97	T.133(31)-1976	1860-1880	V&A	UTR
C98	Tennent small	ca. late 19th	СТС	UTR
C99	Judith Townson A	mid-20th c	СТС	UTR
C100	Judith Townson B	mid-20th c.	СТС	UTR

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Table 7-3 Collection historical textiles analysed by UHPLC.

Samples from the GU Archives UTR pattern books were selected based on availability and to include a wide range of dates. As with the dyeing manuals, a segment of fibre was cut from a previously frayed edge, avoiding any further damage to the textile pieces. Some pattern books were missing many pieces that were removed before the collection was accessioned, leaving fewer to sample. Some samples were carefully pasted to pages, binding the edges with glue and preventing unravelling, while others were less carefully pasted and offered more sampling opportunities. The dates for the GU Archives samples are given when the information is directly related to the sample (i.e. on the same page) written in original hand. Books UGD 13/8/1 and UGD 13/8/5 do not contain any original dates, though 13/8/5 has 'Mr Ewing' and '4/6/67' written on the stationer's label in what appears to be original script. Both volumes were sold by Kerr & Richardson, a wholesale stationer located at 89 Queen Street in Glasgow when the volumes were purchased.



Figure 7-4 Stationer's labels from Kerr & Richardson in UGD 13/8/1 and 13/8/5. Pencilled notes "Mr Ewing" and "4/6/67" marked with red circles. © University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248.

UGD 13/8/1 has a large script 'D.H.' written under the label, which is in a different style from 13/8/5. Kerr & Richardson first appears at this address in the 1864-1865 Glasgow Post Office directory⁴, supporting the possible 1867 date of book 13/8/5 and that the samples were probably dyed no earlier than the mid-1860s.

The pieces from UTR in the V&A collection appear to have been collected with a different purpose than the samples in the GU Archives books. The loose

⁴ Post-Office Annual Glasgow Directory 1864-1865, 172.
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(not pasted in a volume) pieces, some stamped with labels like 'HB 626' or 'FB 554' are generally larger (approx. A4 size) and were cut so that all or a majority of the motif is included. Out of the 32 pieces, peacocks feature on 24, paisley designs on 5, and one a heraldic design, and one a picnic basket and flowers (Figure 7-5). The final piece, T.133(10)-1976 in Figure 7-6 has an Indian provenance and is distinctly not Turkey red. See Appendix H for all images.



Figure 7-5 Object T.133(15)-1976 (C81) in the V&A collection. Image courtesy of the V&A.



Figure 7-6 Object T.133(10)-1976 (C76) in the V&A collection. Image courtesy of the V&A.

The V&A also has a set of Turkey red handkerchiefs, mostly German in origin, though some are Swiss and one Italian. These are a valuable example of a common Turkey red product not found in the GU Archives and would have been familiar to the 19th c. European consumer.⁵ The motifs include commemorations of events, the new German Reichstag building, the adoption of new military equipment, fantasy scenes, human figures, and the Strasbourg Cathedral. Figure 7-7 shows German handkerchiefs depicting a woman riding a velocipede and late-19th c. members of the German Reichstag. In Figure 7-8, a Swiss handkerchief shows an Ottoman soldier on horseback and firearms used by the Italian military from 1871-1887.



Figure 7-7 Objects 1799-1899 (C50) and 1801-1899 (C52) in the V&A collection. Images courtesy of the V&A.

⁵ Nenadic and Tuckett, Colouring the Nation: the Turkey Red Printed Cotton Industry in Scotland C. 1840-1940.



Figure 7-8 Swiss handkerchief 1798-1899 (C49) and Italian handkerchief 1805-1899 (C56). Images courtesy of the V&A.

The book of dyeing recipes from Foxhill Bank contains two samples of printed Turkey red, and the V&A collection also has two miscellaneous pieces of loose Turkey red. Finally, samples were taken from the outer fabric and lining of dress T.74-1988, the unusual dress analysed by FTIR in Section 6.7.5. The date and provenance information for these samples was taken as-is from the records of the V&A.



Figure 7-9 Item T.344-1919 (C62) in the V&A collection. Image courtesy of the V&A.

The CTC pieces from UTR comprise the mid-20th c. Townson pieces and the late-19th c. Tennent Turkey red also analysed by FTIR. The piece Townson B has an original label affixed stating it was dyed with synthetic alizarin, while

Townson A has a pattern and palette characteristic of Turkey red. The weave and texture of the fabric is also very like T.133(10)-1976, though the Townson pieces are of Scottish and not Indian origin.

7.1.1.4 Replicas

For references of dyes extracted from fibres (as opposed to pure reference compounds), samples were taken from the replica Turkey red dyed with madder, synthetic alizarin, and synthetic purpurin for this project. A sample was also taken from the Turkey red dyed by Debbie Bamford. Wool and silk dyed with madder by Gwen Fereday, a natural dyer, were also included to observe any differences in dye uptake by the fibre.

ID	Replica	Dyer
D1	Turkey red, alizarin #1	Wertz
D2	Turkey red, alizarin #2	Wertz
D3	Turkey red, alizarin #3	Wertz
D4	Turkey red, madder	Bamford
D5	Turkey red, madder #1	Wertz
D6	Turkey red, madder #2	Wertz
D7	Turkey red, madder #3	Wertz
D8	Turkey red, purpurin #1	Wertz
D9	Turkey red, purpurin #2	Wertz
D10	Turkey red, purpurin #3	Wertz
D11	Wool with alum and madder	Fereday
D12	Silk with madder	Fereday

Table 7-4 Replica samples analysed by UHPLC.

7.1.2 Chemicals

The following chemicals were used in the preparation of samples and mobile phases: dimethyl sulfoxide (DMSO, HPLC grade), hydrochloric acid (HCl, 36% aq., analytical grade), formic acid (analytical grade 98-100%), and methanol (MeOH, HPLC gradient grade) were purchased from Fisher Scientific; oxalic acid dihydrate (99+%) from Acros Organics; acetone (ACS grade, \geq 99%) from Sigma-Aldrich. Ultrapure water was supplied by a Millipore Direct-Q 3 UV water purifier (18.2 M Ω resistivity).

7.1.3 Madder and garancine extraction

A review of madder extraction techniques found many variations on the process using Soxhlet extraction,⁶ sonication,⁷ refluxing,⁸ and soaking at room temperature.⁹ Specific techniques can preserve glycosides, which often hydrolyse during extraction.¹⁰ Ethanol solvent can form undesired ethoxy derivatives of compounds.¹¹ A method from Mouri and Laursen used water/MeOH (1:1) at 65 °C for one hour¹² and was chosen as the extraction technique for this research because the heating conditions are similar to a Turkey red dye bath. As a madder derivative with a similar content of woody matter, the garancine sample was treated as madder for sample preparation.

Approximately 10 mg of each sample of dried, ground madder root was weighed and placed in an individual 2-mL amber glass vial with a cap. 500 μ L each ultrapure water and MeOH were added with a micropipette and the vials were swirled to mix the solvents. They were placed in a Talboys dry block heater set to 65 °C with the caps loosely on to reduce evaporation and shaken lightly every 20 minutes. After one hour, they were removed and left to cool to room temperature, then a portion of the solvent was filtered through a 0.2 μ m PTFE syringe filter to remove particulates. No further dilution was made before analysis.

7.1.4 References and historical alizarin

The reference and historical alizarin samples were prepared at a concentration of about 0.01 mg sample/mL. This was done by weighing a few milligrams into a

- ¹⁰ Derksen et al., "Two Validated HPLC Methods for the Quantification of Alizarin and Other Anthraquinones in Rubia Tinctorum Cultivars," 398.
- ¹¹ Henderson, Rayner, and Blackburn, "Isolation and Extraction of Lucidin Primeveroside From *Rubia Tinctorum* L. and Crystal Structure Elucidation," 105.
- ¹² Mouri and Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC."

⁶ Burnett and Thomson, "Naturally Occurring Quinones. Part XV. Biogenesis of the Anthraquinones in Rubia Tinctorum L. (Madder)."

⁷ Bányai et al., "HPLC Analysis of Alizarin and Purpurin Produced by Rubia Tinctorum L. Hairy Root Cultures" 112.

⁸ Derksen et al., "High-Performance Liquid Chromatographic Method for the Analysis of Anthraquinone Glycosides and Aglycones in Madder Root (Rubia Tinctorum L.)," 279.

⁹ Wouters, "High Performance Liquid Chromatography of Anthraquinones: Analysis of Plant and Insect Extracts and Dyed Textiles," 121.

volumetric flask and dissolving the sample with methanol; some samples required sonication to break up persistent lumps. An aliquot of the stock solution, based on the initial sample weight, was taken and diluted in a smaller volumetric flask with DMSO to obtain ca. 0.01 mg/mL. This figure corresponds only to the initial sample weight, which is not 100% dye molecules. This analysis is qualitative and does not attempt to make any quantitative conclusions in terms of the colorant concentration of historical samples.

7.1.5 Textile samples

There are a variety of extraction methods for dyes from historical textiles in the literature.^{13,14,15,16} Harsh extraction conditions, which may be necessary to remove all the dyes, may also hydrolyse or alter some compounds, though anthraquinones are fairly stable.¹⁷ Recently, 'soft' extraction techniques using DMSO and oxalic acid have been explored to attempt a better recovery of minor components.^{18,19,20} Formic acid was found to be most efficient at extraction from madder-dyed textiles compared to HCl and EDTA.²¹ Research by Han at the CTC on the analysis of historical Chinese textile dyes uses a two-step soft extraction

¹³ Wouters, "High Performance Liquid Chromatography of Anthraquinones: Analysis of Plant and Insect Extracts and Dyed Textiles," 121.

¹⁴ Hofmann-de Keijzer and van Bommel, "TLC and HPLC Analysis of Red and Violet Cotton Yarns of Indonesian Textiles," 74.

¹⁵ van Bommel et al., "High-Performance Liquid Chromatography and Non-Destructive Three-Dimensional Fluorescence Analysis of Early Synthetic Dyes," 262.

¹⁶ Valianou, Karapanagiotis, and Chryssoulakis, "Comparison of Extraction Methods for the Analysis of Natural Dyes in Historical Textiles by High-Performance Liquid Chromatography," 2176.

¹⁷ Zhang and Laursen, "Development of Mild Extraction Methods for the Analysis of Natural Dyes in Textiles of Historical Interest Using LC-Diode Array Detector-MS," 2022.

¹⁸ Lech and Jarosz, "Novel Methodology for the Extraction and Identification of Natural Dyestuffs in Historical Textiles by HPLC-UV-Vis-ESI MS. Case Study: Chasubles From the Wawel Cathedral Collection."

¹⁹ Wouters, Grzywacz, and Claro, "A Comparative Investigation of Hydrolysis Methods to Analyze Natural Organic Dyes by HPLC-PDA - Nine Methods, Twelve Biological Sources, Ten Dye Classes, Dyed Yarns, Pigments and Paints."

²⁰ Mouri and Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC."

²¹ Zhang and Laursen, "Application of LC-MS to the Analysis of Dyes in Objects of Historical Interest," 2023.

technique suitable for historical textiles and a broad range of dyes,²² and this method is used in this research.

The fibre sample was placed in a 1.0 mL flat-bottomed glass vial, 50 μ L DMSO added, and the open vials were placed in a Talboys dry block heater at 80 °C for 10 minutes. The DMSO was then extracted with a micropipette and retained in a second vial. The fibre is extracted a second time with 75 μ L oxalic acid solution made of 0.5 M oxalic acid/acetone/water/MeOH (1:30:40:30 v/v/v/v). The vials were returned to the block heater and left for 15 minutes at the same temperature. The oxalic acid extract was then vacuum evaporated to dryness using a BUCHI R-215 Rotavapor at 40 °C and 16 mbar for 30 minutes. The DMSO portion was returned with a micropipette to the fibre vial and the residue reconstituted to combine the extracts. This was filtered through a 0.2 μ m PTFE syringe filter to remove particulates and collected in a vial insert.



Figure 7-10 Different colours of extracted dyes based on varied composition of alizarin, anthrapurpurin, and flavopurpurin. From left: UGD 13/8/9 #2 (C44), UGD 13/8/9 #3 (C45), UGD 13/8/9 #4 (C46).

7.1.6 Chromatography

Sample analysis was performed on a Waters ACQUITY UPLC H-Class system at the Centre for Textile Conservation. The system is comprised of a sample manager with a flow through needle, a quaternary solvent manager, a column with thermostat ability, and a PDA detector. The system was operated using Waters

²² Han, "The Historical and Chemical Investigation of Dyes for High Status Chinese Costume and Textiles of the Ming and Qing Dynasties," 205.

ACQUITY UPLC Console software and acquisition made with Waters Empower 3 software. Separation was done using a Waters C18 Ethylene Bridged Hybrid (BEH) Shield column (150 mm x 2.1 mm i.d., particle size 1.7 μ m) with a Waters C18 BEH Shield VanGuard pre-column (5 mm x 2.1 mm i.d., particle size 1.7 μ m) to protect the column from potential textile particulates. More information about UHPLC is found in Appendix A.

A gradient elution method was used with the following solvents and parameters listed in Table 7-5: 10% (v/v) aqueous methanol (A), 100% methanol (B), and 1% (v/v) aqueous formic acid (C). All gradients are linear and the flow rate was set at 0.2 mL/min.

Time (min)	% Solvent A	% Solvent B	% Solvent C
0	80	10	10
1.33	80	10	10
2.33	74	16	10
5.33	55	35	10
9	55	35	10
14	30	60	10
25	5	85	10
26	0	100	0
30	0	100	0
32	80	10	10
40	80	10	10

Table 7-5 Gradient programme for UHPLC elution.



Figure 7-11 Graphic layout of gradient programme.

The sample chamber was left at room temperature and the column heater set to 40 $^{\circ}$ C. Sample injection volume was 4 μ L and the detector was set to acquire data from 210-800 nm at a resolution of 1.2 nm.

For a general dyes analysis, 254 nm is a useful wavelength to extract a chromatogram that will show coloured compounds from yellow to blue. Since this analysis focuses on anthraquinone dyes, the chromatograms were extracted at 430 nm, which is good for detecting orange and red compounds.^{23,24} The Empower 3 software offers ApexTrack integration, improving peak detection by evaluating the second derivative of the chromatogram. Due to a previously undiagnosed internal seal failure, the retention time (R_t) values shift between some sample sets, in a range of about 0.35 min with alizarin appearing from 20.49 to 20.83 minutes as a reference. The R_t ratios relative to alizarin ($R_{t(peak)}$ - $R_{t(alizarin)}$ for compounds eluting after alizarin; $R_{t(alizarin)}$ - $R_{t(peak)}$ for compounds eluting before alizarin) are consistent across all samples, which is how this data is interpreted. A combination of R_t/R_t ratio, UV-Vis absorbance spectra, and known references were used to identify components. The purity threshold of peaks was set to auto-detect and co-eluting components were identified when the purity angle of a peak was greater than the purity threshold. The similarity of the components means many elute close together, affecting the purity from peak to peak and sample to sample. The samples were not re-run after the diagnosis of the seal failure because conservation of the remaining sample was prioritised for future analysis with an optimised UHPLC method for these compounds and robust equipment.

7.2 Discussion of UHPLC results

This section discusses the results of the UHPLC analysis, how the data was interpreted to identify compounds present on historical textiles, and whether the information can be used to determine anything about the provenance or date of manufacture. In the textile and synthetic alizarin sample chromatograms, peaks generally appeared between 18 and 26 minutes when

²³ Serrano, van Bommel, and Hallett, "Evaluation Between Ultrahigh Pressure Liquid Chromatography and High-Performance Liquid Chromatography Analytical Methods for Characterizing Natural Dyestuffs," 105.

²⁴ Derksen, Niederländer, and van Beek, "Analysis of Anthraquinones in Rubia Tinctorum L. by Liquid Chromatography Coupled with Diode-Array UV and Mass Spectrometric Detection," 126.

extracted at 430 nm. Madder extracts have peaks from 13 to 26 minutes, and more minor peaks are present. Tentative identifications of ruberythric acid and lucidin primeveroside were made based on RT and UV-Vis spectra, but since most of the madder compounds do not act as dyes in Turkey red based on their absence in textile extracts, identification was not a priority for this work.

There are four major compounds identified in the samples that are discussed in this research-alizarin, purpurin, anthrapurpurin, and flavopurpurin. Recent research by Liu et al. using HPLC-PDA-MS with UV-Vis identified alizarin, anthrapurpurin, and flavopurpurin on a red cotton textile that includes UV-Vis spectra²⁵ consistent with those seen in this project. In addition to the known compounds, there are around ten unidentified peaks that appear more than once, while some samples contain a single unidentified peak. Most of the unknown peak areas are less than 1% of the total integrated area and two pairs of unknowns have very similar R_t values, necessitating distinction by UV-Vis spectrum. A few of these unknowns, including 'false anthrapurpurin', may also be indicators of a synthetic or natural dye source, but further investigation is required. It was not possible to fully characterise the unknowns during this analysis due to a lack of references and mass spectrometry (MS) equipment. Although they are present in relatively small amounts, the light fastness of these unknowns is potentially significant to the conservation of Turkey red. Based on these findings, further research on the separation and identification of these orange-red dyes by UHPLC-MS is recommended.

²⁵ Liu et al., "Identification of Early Synthetic Dyes in Historical Chinese Textiles of the Late Nineteenth Century by High-Performance Liquid Chromatography Coupled with Diode Array Detection and Mass Spectrometry."



Figure 7-12 Structure and UV-Vis absorbance spectra for alizarin, purpurin, anthrapurpurin, and flavopurpurin.

Alizarin appears in every sample except the purpurin reference standard R11 and comprises a small percentage of the dye extracted from replica Turkey red dyed with purpurin D8-D10. In general, the integrated area of the textile sample chromatograms was much higher than for the dye reference samples, indicating these were prepared at a lower concentration than yielded through the fibre extraction. As such, a more concentrated **R11** should show an alizarin peak like the textile samples do. Because there were no further identifications to be made from the reference standards, they were not re-run at higher concentration.

The results presented in this chapter are semi-quantitative, comparing the integrated areas of the four compounds of interest plus the sum area of unknown peaks. The approximate R_t of each compound and R_t ratio to alizarin is given in Table 7-6.

Compound	RT (min)	RT ratio to alizarin
Anthrapurpurin	19.9	0.96
Alizarin	20.7	-
Flavopurpurin	20.8	1.01
Purpurin	24.4	1.18

Table 7-6 Anthraquinone dyes R_v values and R_t ratios.

Fully quantitative results were not possible because flavopurpurin and alizarin were not resolved under the analytical conditions used (see Figure 7-13). A trial injection of 1807-1899 **C57** using a Phenomenex Gemini C18 HPLC column (150 mm x 2 mm i.d., particle size 5 μ m) on the same UHPLC with the same mobile phases, temperature and gradient (flow rate adjusted for column dimensions to 0.05 mL/min) changed the elution order and separated alizarin and flavopurpurin.



Figure 7-13 Comparison of chromatograms for 1807-1899 (C57) on two columns at 430 nm wavelength. Method for Waters in Section 7.1.6, adjustments for Phenomenex above.

Further experimental injections were made with slight adjustments to the gradient, but the resolution was not significantly improved between anthrapurpurin and flavopurpurin. The integrated areas of peaks in both

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chromatograms show the areas for the co-eluting peaks with the BEH Shield column are different from the resolved peaks of the Phenomenex chromatogram. Resolution is most complete for anthrapurpurin in both methods, but Table 7-7 shows there is around a difference of 2% in the integrated areas between alizarin and flavopurpurin depending on how they are resolved by the column, or difference of about 6-8% in the individual peak areas. The conclusions from this research do not depend on the quantification of alizarin and flavopurpurin or their relative amounts, because the flavopurpurin is taken to be a consistent indicator of synthetic alizarin, whereas the results show the relative amount of anthrapurpurin is significant to the determination of a dye source, discussed further in this chapter. Nevertheless, the incomplete resolution of the components in these samples shows a need for a more tailored, anthraquinonespecific UHPLC method for the separation and identification of these compounds. All samples analysed in this chapter used the Waters BEH Shield column because it was the only one available at the time the analysis was done.

Peak % area	Waters BEH Shield	Phenomenex Gemini
Anthrapurpurin	39.5	39.5
Alizarin	25.0*	27.0
Flavopurpurin	35.4*	33.4

Table 7-7 Comparison of integrated areas for 1807-1899 on two columns. *Deconvoluted by Empower 3 ApexTrack integration.

The results of this analysis indicate it is unlikely a chromatographic profile of dye extracted from Turkey red can be used to determine the source of synthetic alizarin because there are too few distinguishing components amongst the many manufacturers and blends. As discussed in the review, many late-19th c. firms produced alizarin and sold multiple varieties based on the mixture of colorants. Most synthetic alizarin contains three major components (alizarin, anthrapurpurin, and flavopurpurin), though the results of the textile fibre analyses indicate there are a few unknown compounds that might also serve as chemical markers. The lack of concrete understanding of the dye uptake mechanism is also a factor to consider, as shown by the lighter and less level replica Turkey red dyed with purpurin compared to the alizarin samples, despite using the same prepared cotton. It is unknown whether the colorant ratio in the dye is reflected in a fibre analysis based on this uptake. For these reasons, plus the limited quantity of sample available from historical materials, the samples

were not re-run with the Phenomenex column to resolve alizarin and flavopurpurin. The remaining samples have been reserved for possible future analysis with an improved separation technique.

חו	Sample	%	%	%	%	% Unk
שו	Sample	Anthra.	Alizarin*	Flavo.*	Purpurin	% UIIK.
R1	French madder	0.0	22.4	0.0	0.0	77.6
R2	English madder	0.0	46.0	0.0	11.1	42.8
R3	Iranian madder	0.0	6.8	0.0	0.7	92.6
R4	Turkish madder	0.0	36.1	0.0	3.0	60.9
R5	Rubia cordifolia	0.0	4.2	0.0	0.0	95.8
R6	Dutch madder	0.0	28.7	0.0	3.3	68.1
R7	Russian madder	0.0	60.9	0.0	7.1	32.0
R8	Silesian madder	0.0	14.0	0.0	5.2	80.8
R9	Garancine	0.3	67.1	0.0	14.2	18.5
R10	Alizarin (97% purity)	1.2	98.9	0.0	0.0	0.0
R11	Purpurin (>90% dye)	0.0	0.0	0.0	100.0	0.0
R12	Anthrapurpurin	14.3	38.3	45.9	0.0	1.5
R13	Alizarin (NMS)	1.3	98.7	0.0	0.0	0.0
R14	Alizarin Apolda	1.8	95.4	2.8	0.0	0.0
R15	Alizarin aus Krapp	15.7	78.7	5.6	0.0	0.0
R16	Alizarin Merck	0.0	100.0	0.0	0.0	0.0
R17	Alizarin PA Prag	0.0	100.0	0.0	0.0	0.0
R18	Alizarin extra rein für Orange BASF	0.0	100.0	0.0	0.0	0.0
R19	Alizarinrot IG Farben	1.6	98.4	0.0	0.0	0.0
R20	Alizarinrot WG Teig 20% BASF	65.4	18.4	16.2	0.0	0.0
R21	Synthetic alizarin, Zöllner und Morell Chemnitz (purveyor)	22.8	61.7	15.5	0.0	0.0

7.2.1 Composition of references

Table 7-8 UHPLC chromatogram integrated peak areas for reference samples at 430 nm. *Deconvoluted by Empower 3 ApexTrack integration.

The discussion on dyes in Chapter 3 did not identify any reliable publications on naturally occurring anthrapurpurin and flavopurpurin, flagging them as useful markers for synthetic alizarin as the dye source. The UHPLC profiles of the reference samples show neither compound appears in any of the madder samples analysed, but the garancine sample **R9** shows that to conclude they are exclusive to synthetic alizarin is not entirely correct. The sample contains 0.3% anthrapurpurin, which was not expected in a madder-derived product. The manufacture of both synthetic alizarin and garancine use hot sulfuric acid, so

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perhaps some of the same reactions may occur to the anthraquinone side groups. Every madder sample contains a quantity of the unknown "false anthrapurpurin" (see Appendix G), so-called because it has an R_t very close to anthrapurpurin (Figure 7-14) and a similar, though distinct, UV-Vis spectrum (Figure 7-15). When present in the same sample, anthrapurpurin and false anthrapurpurin co-elute. It may be the case that the two are structurally similar and trace amounts of false anthrapurpurin are converted to anthrapurpurin by sulfuric acid. It is slightly less hydrophobic than anthrapurpurin since it elutes earlier, so perhaps it still has a sulfate group, although this explanation does not immediately fit with its appearance in madder samples.



Figure 7-14 Segment of garancine (R9) chromatogram showing co-eluting anthrapurpurin and false anthrapurpurin at 430 nm.



Figure 7-15 UV-Vis spectra for anthrapurpurin and false anthrapurpurin.

The presence of anthrapurpurin in the garancine sample means the compound cannot be an exclusive indicator of a synthetic source, though the significantly lower relative amount compared to the 19th c. alizarin samples means some conclusions can be reasonably drawn when taking the entire chromatogram into consideration. Since only one sample of garancine was available and there is not much data available on its composition, in this research no attempt is made to distinguish between the 'natural' sources of madder and garancine. The role of anthrapurpurin as a marker is discussed further with the results from the collection samples analysis.

The presence or absence of purpurin is a useful tool to distinguish madder from synthetic alizarin—it is not a major component of synthetic alizarin (trace amounts appear at higher concentration, see Section 7.2.4), but it appears in most of the madder samples. It is worth noting that the madder used by Turkey red dyers in the 19th c. had been cultivated for hundreds of years, but with the collapse of the market in the early 1870s the cultivars were abandoned for other crops, so whether their dyeing capacity is comparable is unknown. An analysis of historical madders by Cuoco et al. found some samples have a higher content of purpurin relative to alizarin than seen in these results.²⁶



Figure 7-16 Chromatogram of Silesian madder sample R8 at 430 nm.

The age of the TU Dresden madder samples **R6-R8** is unknown, so no strong comparisons can be made from this research because the varietals of madder may have changed with shifts in cultivation. The quantity of purpurin detected on textile fibres may be augmented by pseudopurpurin (purpurin with a carboxyl at position 3) since it decarboxylates to purpurin during extraction and heating.²⁷

²⁶ Cuoco et al., "Characterization of Madder and Garancine in Historic French Red Materials by Liquid Chromatography-Photodiode Array Detection."

²⁷ Mouri and Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC."

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In general, the amount of purpurin detected on the textile samples was noticeably more than in the madder extracts. The discussion of purpurin as a chemical marker is continued later.

The synthetic alizarin samples **R10-R21** are the only references that have flavopurpurin, and with the exception of the purpurin reference **R11** they have no peak for purpurin. The low concentration of the references relative to the textile fibre extracts means some samples, like **R16-R18**, may contain other colorants in quantities below the detection limit, but the occurrence of unknowns and purpurin in the textile samples dyed with synthetic alizarin indicate these are unlikely, or minimal and not within the scope of this work. The anthrapurpurin reference **R12** contains two unknowns with different RT values and UV-Vis spectra that do not appear in any textile chromatograms or other samples and are not thought to be dyes because they are not taken up by the fibres.



Figure 7-17 Chromatogram of anthrapurpurin reference (R12) extracted at 254 nm.



Figure 7-18 UV-Vis absorbance spectra of unknowns in anthrapurpurin reference.

Surprisingly, anthrapurpurin was the third most abundant compound in reference **R12** after flavopurpurin and alizarin, but the mixture of dyes is consistent with the earlier discussion on 19^{th} c. alizarin.

The sample Alizarinrot WG Teig 20% BASF **R20** (20% conc. alizarin) in Figure 7-19 and Figure 7-20 from the TU Dresden H.F. is unusual for having a labelled concentration. The value is consistent with the concentration of synthetic alizarin product available in the late 19th c., and whereas the rest of the samples are dry powders, **R20** was received as a thick paste, which is how the product was sold to dyers.



Figure 7-19 Alizarinrot WG Teig 20% BASF (R20) from TU Dresden H.F.





The analysis of modern and historical anthraquinone dyes, including madders, synthetic alizarins and anthraquinone references, and garancine, generally supports the conclusions from the review on dyes in Turkey red that the presence of anthrapurpurin and flavopurpurin can be used as chemical markers to indicate a synthetic alizarin dye source. In some synthetic alizarin samples, these dyes comprise a fairly large proportion of the colorants, which is consistent with descriptions of the 19th-c. product and synthetic process. The madder samples contain many more compounds, not all of which act as dyes in Turkey red based on the analysis of the fibre samples. The garancine sample indicates anthrapurpurin does not occur exclusively in synthetic alizarin and may form in small quantities in madder-derived products, though at lower relative amount (0.3%) than the synthetic alizarin samples contain. This may be connected to the unknown called false anthrapurpurin, but further analysis and identification is recommended.

7.2.2 Composition of dye manual samples

The analysis of the dye manual samples reveals more than previously seen in the reference compounds. The only sample dyed with madder (M1), from Crookes, in Figure 7-21 contains alizarin and purpurin, consistent with the madder extracts. His synthetic alizarin sample M2 contains all four analytes (anthrapurpurin, alizarin, flavopurpurin, and purpurin), a combination not seen in any of the reference samples. Crookes used alizarin supplied by Perkin, which was also used in samples M3-M5. The review did not find purpurin was a significant product of alizarin synthesis, and it was more expensive to produce. It is unclear whether the relatively low amount of purpurin is the result of a side-reaction or if Perkin incorporated it when mixing a blended product. Samples M3-M4 are from different copies of the same publication and have similar quantities of each colorant, so they appear to be from the same source. The M5 sample was dyed with a different blend containing no purpurin and a much higher proportion of alizarin.

ID	Sample	% Anthra.	% Alizarin*	% Flavo.*	% Purpurin	% Unk.
M1	Turkey red (madder, dyed by Steiner & Co.)	0.0	92.4	0.0	7.6	0.0
M2	Turkey red (alizarin, supplied by Perkin)	18.9	58.9	10.3	11.9	0.0
M3	Turkey red (alizarin, supplied by Perkin)	36.7	39.8	16.8	3.8	2.8
M4	Turkey red (alizarin, supplied by Perkin)	39.1	41.2	15.4	2.1	2.1
M5	Turkey red (alizarin, supplied by Perkin)	3.3	93.1	3.6	0.0	0.0
M6	Turkey red (anthrapurpurin, supplied by Perkin)	68.1	26.8	5.2	0.0	0.0
M7	Rouge d'anthrapurpurine avivé no. 231	65.9	16.6	17.4	0.0	0.0

Table 7-9 UHPLC chromatogram integrated peak areas for dye manual samples at 430 nm. *Deconvoluted by Empower 3 ApexTrack integration.

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Figure 7-21 Chromatogram of Turkey red dyed with madder from Crookes sample M1 at 430 $\,\rm nm.$



Figure 7-22 Samples from two copies of the same article from Perkin.

Glasgow University Chemistry Library (M3, left) and Glasgow University Special Collections (M4). Images courtesy of GU Chemistry Library and GU Special Collections.



Figure 7-23 Samples in the 1873 *Journal of the Chemical Society* article by Perkin. Alizarin (M5, top left) and anthrapurpurin (M6, bottom right). Image courtesy of the GU Chemistry Library.

Samples **M6** and **M7**, dyed with anthrapurpurin, also have alizarin and flavopurpurin in varying relative amounts (for M7 see Figure 7-24 and Figure

7-25, Table 7-9). In the dyeing manual samples, anthrapurpurin and flavopurpurin account for varying proportions of pieces dyed with synthetic alizarin, whereas the madder-dyed sample has only alizarin and purpurin.



Figure 7-24 Chromatogram of sample dyed with anthrapurpurin from Dépierre (M7) at 430 nm.



Figure 7-25 Sample no. 231 in Dépierre (M7).

7.2.3 Results from collection samples

The set of samples from historical textiles in museum and archive collections is the largest analysed in this project. One of the questions for this research is whether the chromatographic profile of dye extracted from historical Turkey red reveals anything about the dye source, determined by the literature review to be madder, garancine, or synthetic alizarin. Identifying anthrapurpurin or flavopurpurin, compounds characteristic of synthetic alizarin, automatically places the date of production for a piece of Turkey red after 1869, when synthetic alizarin became commercially available, which helps determine object provenance. The set contains 100 samples with known and unknown dates of manufacture, some within a range of dates (e.g. the T.133 samples from the V&A collection) that means they could have been dyed with natural or synthetic

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dye. There is no indication in the literature that dyers used both in the same batch, although there is also no statement against the practice. Based on the differences in oiling and clearing required for madder or alizarin and the general collapse of the madder industry, this is not expected to have occurred.

To simplify the discussion of so many samples and help identify any trends, the results are discussed in sub-sets. A date of manufacture 1869 or later means the textile *could* be dyed with synthetic alizarin, but the AOE ledger shows UTR continued using natural sources until the late 1870s.²⁸ Samples made after the mid-1870s were probably dyed with synthetic alizarin, but without records from the dyer the date of manufacture can only be used to identify pieces that must have a natural dye (pre-1869). *Bold and italic* samples were printed black with red underneath.

ID	Sample	% Anthra.	% Alizarin*	% Flavo.*	% Purpurin	% Unk.
C4	UGD 13/8/2 #1	0.0	85.3	0.0	11.6	3.1
C5	UGD 13/8/2 #2	0.2	85.3	0.0	8.5	6.1
C6	UGD 13/8/2 #4	0.0	87.3	0.0	7.0	5.7
C7	UGD 13/8/3 #1	0.4	74.2	0.0	24.6	0.8
C8	UGD 13/8/3 #2	0.0	85.8	0.0	13.4	0.8
C9	UGD 13/8/3 #3	0.0	82.0	0.0	14.5	3.5
C10	UGD 13/8/3 #6	0.0	86.5	0.0	11.1	2.4
C11	UGD 13/8/3 #7	0.0	88.9	0.0	8.7	2.4
C12	UGD 13/8/3 #9	0.4	77.7	0.0	16.9	5.0
C13	UGD 13/8/3 #10	0.0	85.6	0.0	13.2	1.3
C14	UGD 13/8/3 #11	0.5	72.2	0.0	26.5	0.8
C17	UGD 13/8/4 #4	0.0	68.2	0.0	30.7	1.0
C60	T.8-1978 p.87 Pattern 40	0.0	95.6	0.0	2.2	2.3
C61	T.8-1978 p.89 Turkey red	0.0	96.3	0.0	1.6	2.1
C62	T.344-1919	0.0	92.8	0.0	4.9	2.4
C63	T.74-1988 (dress)	0.0	85.6	0.0	1.8	12.6
C64	T.74-1988 (lining)	0.0	91.5	0.0	3.8	4.7

Table 7-10 UHPLC chromatogram integrated areas for collection samples dyed prior to 1869 at 430 nm.

*Deconvoluted by Empower 3 ApexTrack integration. *Bold and italic* samples were printed black.

²⁸ Turkey Red Dyeing Calculation Book AOE Lennoxbank. UGD 13/4/1.

The results show that no sample contains flavopurpurin, though four have traces of anthrapurpurin (**C5**, **C7**, **C12**, **C14**) in a relative amount from 0.2-0.5%, consistent with the results from garancine **R9**. None of these samples contain false anthrapurpurin (see Appendix I). By far the major components are alizarin and purpurin, a combination that appears to indicate a natural dye source.



Figure 7-26 Chromatogram of sample C63 from V&A dress T.74-1988.

The samples of unknown date and those dyed after 1869 were grouped based on the chromatographic profile and identified a natural or synthetic dye source. Samples containing 0-1% anthrapurpurin and no flavopurpurin were classed as natural, meaning they were dyed with madder or garancine. The samples in Table 7-11 contain no flavopurpurin and have a relative amount of purpurin around 20%. Samples containing anthrapurpurin also have purpurin, more consistent with garancine than synthetic alizarin.

ID	Sample	% Anthra.	% Alizarin	% Flavo.	% Purpurin	% Unk.
C18	UGD 13/8/5 #1	0.3	76.0	0.0	22.0	1.7
C21	UGD 13/8/5 #7	0.0	72.8	0.0	27.2	0.0
C22	UGD 13/8/5 #8	0.0	73.3	0.0	26.7	0.0
C50	1799-1899	0.0	83.9	0.0	14.0	2.1
C58	T.4-1992	0.0	60.6	0.0	25.0	14.4
C59	T.5-1992	0.0	55.3	0.0	30.6	14.1
C65	T.12B-1984	0.3	89.4	0.0	5.5	4.9
C66	T.133-1976	0.0	73.2	0.0	25.9	0.9
C67	T.133(1)-1976	0.2	83.2	0.0	15.7	1.0
C68	T.133(2)-1976	0.2	68.2	0.0	30.8	0.8
C69	T.133(3)-1976	0.2	74.7	0.0	24.0	1.1
C70	T.133(4)-1976a	0.0	77.7	0.0	22.3	0.0
C71	T.133(5)-1976	0.2	69.7	0.0	29.3	0.8
C72	T.133(6)-1976	0.0	75.3	0.0	23.6	1.2
C73	T.133(7)-1976	0.2	77.3	0.0	22.1	0.5
C74	T.133(8)-1976	0.0	81.4	0.0	16.0	2.6
C75	T.133(9)-1976	0.0	76.7	0.0	22.1	1.2

	Samplo	%	%	%	%	%
טו	Sample	Anthra.	Alizarin	Flavo.	Purpurin	Unk.
C77	T.133(11)-1976	0.0	76.6	0.0	22.2	1.2
C78	T.133(12)-1976	0.3	72.1	0.0	26.6	1.0
C79	T.133(13)-1976	0.0	80.1	0.0	17.6	2.3
C80	T.133(14)-1976	0.0	70.9	0.0	29.1	0.0
C82	T.133(16)-1976	0.2	65.6	0.0	33.4	0.8
C83	T.133(17)-1976	0.0	80.5	0.0	18.8	0.8
C84	T.133(18)-1976	0.0	76.2	0.0	22.7	1.1
C86	T.133(20)-1976	0.0	76.4	0.0	22.2	1.5
C87	T.133(21)-1976	0.0	77.8	0.0	21.6	0.6
C89	T.133(23)-1976	0.2	70.7	0.0	27.8	1.3
C90	T.133(24)-1976	0.0	74.9	0.0	23.6	1.4
C91	T.133(25)-1976	0.1	72.1	0.0	26.1	1.7
C92	T.133(26)-1976	0.0	72.9	0.0	25.8	1.4
C93	T.133(27)-1976	0.0	78.1	0.0	21.0	0.8
C94	T.133(28)-1976	0.2	74.7	0.0	23.8	1.4
C95	T.133(29)-1976	0.2	74.8	0.0	23.2	1.8
C96	T.133(30)-1976	0.4	66.4	0.0	32.0	1.3
C97	T.133(31)-1976	0.3	68.9	0.0	29.9	0.9

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Table 7-11 UHPLC chromatogram integrated areas of collection samples dyed with madder or garancine at 430nm.



Figure 7-27 Chromatogram of sample C58 from V&A handkerchief T.4-1992.



Figure 7-28 Chromatogram of sample C92 from V&A object T.133(26)-1976.

The remaining samples contain anthrapurpurin in a relative amount $\ge 1\%$. With five exceptions, they also contain flavopurpurin, supporting the conclusion that the dye source was synthetic. The samples without flavopurpurin (**C2**, **C3**, **C32**, **C34**, **C35**) have 3.0-7.7% anthrapurpurin and no purpurin, still more consistent with a synthetic source than a natural one.

		%	%	%	%	%
ID	Sample	Anthra.	Alizarin	Flavo.	Purpurin	Unk.
C1	UGD 13/8/1 #1	2.9	85.2	7.1	0.0	4.9
C2	UGD 13/8/1 #3	3.6	96.4	0.0	0.0	0.0
C3	UGD 13/8/1 #4	3.0	92.3	0.0	0.0	4.7
C15	UGD 13/8/4 #1	7.1	78.8	7.9	0.0	6.2
C16	UGD 13/8/4 #2	5.5	84.9	7.2	0.0	2.4
C19	UGD 13/8/5 #3	24.8	56.1	8.2	7.4	3.5
C20	UGD 13/8/5 #4	13.8	63.8	4.3	14.1	4.0
C23	UGD 13/8/5 #9	11.2	80.1	7.7	0.0	1.1
C24	UGD 13/8/5 #10	9.3	68.4	5.3	13.4	3.7
C25	UGD 13/8/5 #11	17.7	65.4	5.9	7.6	3.3
C26	UGD 13/8/5 #12	20.1	61.9	5.9	9.0	3.1
C27	UGD 13/8/6 #1	3.5	88.4	6.0	0.0	2.1
C28	UGD 13/8/6 #2	10.0	78.1	9.0	0.0	2.9
C29	UGD 13/8/6 #3	6.4	83.1	8.1	0.0	2.4
C30	UGD 13/8/6 #4	13.0	79.2	5.5	0.0	2.3
C31	UGD 13/8/7 #1	26.1	65.1	8.0	0.0	0.9
C32	UGD 13/8/7 #2	4.8	94.8	0.0	0.0	0.4
C33	UGD 13/8/7 #3	22.6	62.4	12.6	0.0	2.4
C34	UGD 13/8/7 #4	5.7	91.5	0.0	0.0	2.8
C35	UGD 13/8/7 #5	7.7	92.1	0.0	0.0	0.3
C36	UGD 13/8/8 #1	4.5	86.2	7.8	0.0	1.6
C37	UGD 13/8/8 #2	4.2	85.3	8.5	0.0	2.0
C38	UGD 13/8/8 #4	6.4	82.7	8.6	0.0	2.3
C39	UGD 13/8/8 #5	9.2	78.2	10.1	0.0	2.5
C40	UGD 13/8/8 #6	11.9	70.7	13.7	0.0	3.8
C41	UGD 13/8/8 #7	8.0	80.7	8.5	0.0	2.8
C42	UGD 13/8/8 #8	4.5	85.0	9.3	0.0	1.2
C43	UGD 13/8/9 #1	18.7	64.1	6.4	0.0	10.8
C44	UGD 13/8/9 #2	74.7	11.1	13.8	0.0	0.3
C45	UGD 13/8/9 #3	3.4	89.9	6.7	0.0	0.0
C46	UGD 13/8/9 #4	11.1	80.6	8.3	0.0	0.0
C47	UGD 13/8/9 #5	9.2	84.3	6.5	0.0	0.0
C48	1797-1899	37.5	41.3	11.5	0.0	9.7
C49	1798-1899	36.7	41.0	11.7	0.0	10.6
C51	1800-1899	37.5	43.6	19.0	0.0	0.0
C52	1801-1899	25.3	31.6	43.0	0.0	0.1
C53	1802-1899	35.3	25.1	39.4	0.0	0.2
C54	1803-1899	38.4	29.7	31.9	0.0	0.0
C55	1804-1899	40.3	18.7	41.0	0.0	0.0
C56	1805-1899	45.4	18.3	36.3	0.0	0.0
C57	1807-1899	39.5	25.1	35.4	0.0	0.0

ID	Sample	% Anthra.	% Alizarin	% Flavo.	% Purpurin	% Unk.
C81	T.133(15)-1976	11.1	75.1	11.7	0.0	2.1
C85	T.133(19)-1976	8.9	77.3	10.6	0.0	3.2
C88	T.133(22)-1976	13.0	66.9	12.2	4.6	3.3
C98	Tennent small	14.0	66.0	9.6	6.5	3.9
C100	Judith Townson B	17.1	64.0	14.7	0.0	4.2

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Table 7-12 UHPLC chromatogram integrated areas of collection samples dyed with synthetic alizarin at 430nm.



Figure 7-29 Chromatogram of sample C55 from V&A handkerchief 1804-1899.



Figure 7-30 Chromatogram of sample C23 from UGD 13/8/5 #9.

The results confirm that some of the pages in UGD 13/8/4 are not original to the volume. The book, whose binding and page edges are in poor condition, has a set of pages at the front not attached to the rest of the binding (the front cover is also detached). Many pages in the book have entries dated from 1857-1863, but this set of pages is undated. Sample C17, from an entry dated 1863, is comprised of alizarin and purpurin with a small percentage of unknown (see Table 7-10). Two other samples from this book (C15 and C16), taken from the unbound front pages with no dates, have relative amounts of anthrapurpurin and flavopurpurin consistent with synthetic alizarin as the dye source. Some of the samples on these pages have black and white "OFF" stickers not used on the bound pages, which can also be found in UGD 13/8/5. It is the conclusion from this research that these pages are from a different book, the samples were dyed

with synthetic alizarin, and they were inserted into UGD 13/8/4 at some point before it was accessioned.



Figure 7-31 Page in UGD 13/8/4 with "OFF" stickers; top left textile sampled for C15.

The results from the collection samples indicate UGD 13/8/5 contains pieces dyed with natural and synthetic sources, which is consistent with the proposed date of the book (ca. late 1860s) and the transition to synthetic alizarin. The results from 13/8/1 are more indicative of synthetic alizarin, possibly giving it a later date of manufacture than 13/8/5. Out of the V&A UTR pieces, most appear to have a natural dye source since only three contain flavopurpurin and a larger quantity of anthrapurpurin. Three handkerchiefs, including the one depicting a woman riding a velocipede, (C50, C58, C59) appear to be naturally dyed, while the rest certainly have a synthetic source.

Of the 100 fibres analysed, two (**C76** and **C99**) were not expected to be Turkey red and the results show they were dyed with unidentified synthetic, non-anthraquinone dyes.





Figure 7-32 Chromatogram and UV-Vis spectra for C76 from T.133(10)-1976.



Figure 7-33 Chromatogram and UV-Vis spectra for C99 from Judith Townson A.

These results confirm the Townson A textile is not Turkey red. The FTIR spectrum for Townson B was inconclusive due to the finishing agent on the fibres, but the presence of alizarin (C100) and the bright red colour are both in favour of Turkey red, though the date of manufacture is not. It may be an example of the cheaper Alizarin Red dyeing process, but further research is recommended.

7.2.4 Composition of replica samples

The results from the replica samples are less consistent than those already discussed. The wool and silk samples, **D11-D12**, have only alizarin and purpurin

as expected, plus a larger quantity of unknowns probably resulting from the different chemistry of protein fibres. The sample from Debbie Bamford (**D4**) has a similar profile to the other madder-dyed Turkey red in Table 7-10 and Table 7-11. The replica samples **D5-D7** dyed with madder, however, show a relative amount of anthrapurpurin similar to the garancine samples.

	Deplies	%	%	%	%	%
טו	Replica	Anthra.	Alizarin	Flavo.	Purpurin	Unk.
D1	Turkey red, alizarin #1	1.1	98.6	0.0	0.0	0.3
D2	Turkey red, alizarin #2	1.0	98.9	0.0	0.0	0.1
D3	Turkey red, alizarin #3	1.0	95.3	3.3	0.1	0.3
D4	Turkey red, madder	0.0	80.9	0.0	13.0	6.1
D5	Turkey red, madder #1	0.4	82.1	0.0	15.7	1.9
D6	Turkey red, madder #2	0.3	72.0	0.0	22.7	5.0
D7	Turkey red, madder #3	0.2	86.5	0.0	12.4	0.9
D8	Turkey red, purpurin #1	0.0	0.7	0.0	99.0	0.3
D9	Turkey red, purpurin #2	0.0	0.8	0.0	98.7	0.5
D10	Turkey red, purpurin #3	0.0	1.8	0.0	98.2	0.0
D11	Wool with alum and madder	0.0	46.0	0.0	11.1	42.8
D12	Silk with madder	0.0	44.4	0.0	9.3	46.4

Table 7-13 UHPLC chromatogram integrated areas of replica samples at 430nm.



Figure 7-34 Chromatogram of D6, replica Turkey red madder #2.

The irregularity of this occurrence and the fairly low amount, coupled with the unlikeliness of it forming, make a doubtful case that anthrapurpurin is actually present but certainly underscores the importance of further analysis by mass spectrometry. The madder used to dye the samples (**R1**) contains false anthrapurpurin, which does not appear on textile samples and is not thought to act as a dye. These results muddle the distinction between madder and garancine as a dye source, another reason they are grouped as natural in these conclusions.

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Figure 7-35 Chromatogram of D3, replica Turkey red alizarin #3.

The sample **D3** dyed with synthetic alizarin contains all four analytes, as seen in some of the samples dyed with Perkin's alizarin, so the chromatogram for modern alizarin reference **R10** has trace amounts of purpurin and flavopurpurin below the detection limit. The profile is consistent with a synthetic dye source. The samples dyed with purpurin have trace amounts of alizarin and no anthrapurpurin or flavopurpurin.

7.2.5 Summary

The UHPLC analysis of historical Turkey red, replica dyed textiles, dye manual samples, and historical and modern reference dyes found a variety of known and unknown anthraquinones. This analysis focuses on four major components that were identified as potential marker compounds for whether the textile was dyed with a natural (madder/garancine) or synthetic source. Over the course of the 19th c., Turkey red dyers used madder, garancine, and synthetic alizarin to colour their cotton. Dyes from a broad sampling of historical Turkey red of known and unknown dates of manufacture were extracted and analysed by UHPLC. These results were compared to chromatographic profiles of a range of modern and historical madder extracts and synthetic dyes. This research does not attempt to identify the unknown components that appear in various samples, but further investigation is recommended.

This analysis identified two chromatographic profiles characteristic of a natural or synthetic dye source. The data on garancine is insufficient to distinguish it from madder, but the profile of garancine is similar to madder-dyed samples. Natural samples have alizarin and purpurin as major components, contain no flavopurpurin, and may have trace amounts of anthrapurpurin (ca. \leq 1%). Anthrapurpurin may be present in garancine and in the replica Turkey red

dyed with madder based on the PDA spectra, but confirmation with mass spectrometry is required for any strong conclusions given the low relative amount and unlikely synthesis. Synthetic samples contain alizarin, a greater quantity of anthrapurpurin, and flavopurpurin. Purpurin is sometimes present, though much less often. Some synthetic samples contain more anthrapurpurin than alizarin; the quantity of flavopurpurin is generally less and under these analytical conditions co-elutes with alizarin.

The results of this analysis show alizarin, anthrapurpurin, flavopurpurin, and purpurin are the primary dyes found on historical Turkey red and can be used with reasonable confidence to identify the type of dye source. Synthetic markers indicate a piece was not produced before 1869, though this analysis also shows some dyers still used madder after this date (see T.4-1992). Modern synthetic alizarin contains significantly less anthrapurpurin and flavopurpurin than its historic counterparts, so comparison to samples from the TU Dresden Historisches Farbstoffsammlung was vital to this research. Anthraquinone dyes have good lightfastness properties,²⁹ which likely contributes to the reputed fastness of Turkey red, though no systematic fastness study of Turkey red or textiles dyed with synthetic alizarin has yet been undertaken. Understanding these properties and the fastness of anthrapurpurin and flavopurpurin is the next step in improving conservation and display practices for historical Turkey red.

7.3 Analysis of non-red fibres

This section discusses the analysis of non-red fibres from Turkey red prints for the identification of compounds anticipated from the literature. A number of black threads were analysed as part of the dyes analysis since they also contained red dye, and pigments were characterised on a blue, a yellow, and a green fibre by FTIR-ATR and SEM-EDX.

²⁹ Cristea and Vilarem, "Improving Light Fastness of Natural Dyes on Cotton Yarn."

ID	Sample	Date	Source	Provenance
C12	UGD 13/8/3 #9	1857	GU Archives	UTR
C16	UGD 13/8/4 #2	unknown	GU Archives	UTR
C19	UGD 13/8/5 #3	1867 or later	GU Archives	UTR
C23	UGD 13/8/5 #9	1867 or later	GU Archives	UTR
C32	UGD 13/8/7 #2	1887	GU Archives	UTR
C35	UGD 13/8/7 #5	1887	GU Archives	UTR
C36	UGD 13/8/8 #1	1878	GU Archives	UTR
C39	UGD 13/8/8 #5	1878	GU Archives	UTR

7.3.1 UHPLC analysis of black fibres

Table 7-14 Collection samples of black thread containing red dye.

The reason black fibres in printed Turkey red contain red dye is because black was obtained by printing over red areas with logwood or Prussian blue.^{30,31}



Figure 7-36 Magnified (ca. 200x) image of sample UGD 13/8/7 #2 (C32). The sample appears black to the eye but under magnification red fibres show under the black printing.

The identification of non-red dyes on the samples in Table 7-14 was not conclusive for most samples. Logwood dye (*Haematoxylum campechianum* L.) is identified on textiles by haematoxylin or haematein (oxidised haematoxylin). Mantzouris et al. found in an analysis of monastic textiles that samples had to be treated with HCl to release the dyes.³² The softer oxalic acid extraction technique used here may not have released enough dye to be detected, and it is

³⁰ Duerr and Turnbull, *Bleaching and Calico-Printing* : a *Practical Manual*.

³¹ Storey, "Turkey Red Prints."

³² Mantzouris et al., "HPLC-DAD-MS Analysis of Dyes Identified in Textiles From Mount Athos."

also worth noting that since the black was printed rather than dyed onto the fibre the quantity present was also likely low to begin with. Examining the fibres after extraction yielded some interesting results. Sample UGD 13/8/5 #9 (C23), originally a black thread, was blue after extraction, whereas most samples were yellowish white. This research did not identify any components indicative of logwood, though by process of elimination it is likely to be the case for fibres did not have residual Prussian blue after extraction. A less general extraction technique more suited for logwood dyes is recommended for future analysis.



Figure 7-37 Sample UGD 13/8/5 #9 (C23) was taken from the black thread at the bottom edge of the textile.

© University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/5.



Figure 7-38 Magnified (ca. 200x) image of UGD 13/8/5 #9 (C23) before extraction.



Figure 7-39 UGD 13/8/5 #9 (C23) was blue after extracting the dye.

This indicates the black colour was obtained by printing Prussian blue over Turkey red and that the pigment was not susceptible to the extraction process. The DRIFTS analysis of green printed Turkey red in Section 6.7.2 identified bands characteristic of cyano groups in Prussian blue, a technique applied as well to this fibre in the next section.

7.3.2 FTIR identification of Prussian blue

The DRIFTS spectrum of a green area on printed Turkey red in Section 6.7.2 identified bands for cyano groups characteristic of Prussian blue pigment (ferric ferrocyanide). This is consistent with descriptions of the printing process, where Prussian blue was layered with lead chromate to make green.³³ To confirm the pigment was layered with red to make black, after extraction sample **C23** was gently rinsed with ultrapure water and blotted to remove solvent residues, then left to air dry. A spectrum was taken using the FTIR-ATR at the CTC under the same parameters as described in Section 6.1.1 and compared to spectra of a fibre that was originally blue (sample UGD 13/8/4 #3), and one of plain calico.

³³ Crookes, Dyeing and Tissue Printing, 252.



Figure 7-40 Sample UGD 13/8/4 #3 was taken from the edge of this textile, an unusual piece with a blue ground.

© University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/4.



Figure 7-41 Magnified (ca. 200x) image of sample UGD 13/8/4 #3.




Figure 7-42 ATR spectra of plain calico, UGD 13/8/4 #3, and UGD 13/8/5 #9.

The spectra for both samples have a band around 2080 cm⁻¹ consistent with Ghosh's study of Prussian blue pigments by FTIR³⁴ and the earlier DRIFTS analysis, indicating it was layered to make the black on **C23**. An ATR spectrum was also taken of green fibre sample UGD 13/8/3 #5, from a piece of printed Turkey red with a blue-tinted medium green ground and a red pattern. This was done to confirm the presence of Prussian blue on the sample, but FTIR does not detect an inorganic pigment like lead chromate. This is identified by SEM-EDX in the next section.

³⁴ Ghosh, "Infrared Spectra of the Prussian Blue Analogs."



Figure 7-43 Sample UGD 13/8/3 #5 was taken from the bottom swatch of printed Turkey red. © University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/3.



Figure 7-44 Full view of sample UGD 13/8/3 #5, green with red segments from printed pattern.



Figure 7-45 Magnified images of UGD 13/8/3 #5.

Two magnified images of the sample show that at close range the green colour is actually the result of a stippled effect between blue and yellow, consistent with descriptions of the printing technique. The ATR spectrum has a band around 2080 cm⁻¹characteristic of the pigment cyano groups.



Figure 7-46 ATR spectrum of UGD 13/8/3 #5.

These results from confirm Prussian blue was used to print green, blue, and sometimes black, and its light fastness³⁵ likely contributed to the overall durability of the textiles (black printed with logwood being an exception). Lead chromate, on the other hand, can exhibit a darkening effect over time with light exposure,³⁶ which may affect the integrity of some historical pieces.

7.3.3 SEM-EDX identification of lead chromate

Elemental analysis techniques like SEM-EDX are useful to identify a pigment like lead chromate because the lead and chromium atoms are easily detected and identified. The technique is non-destructive in that the sample is recovered, but for analysis it must be placed in a vacuum chamber, so it most likely has to be removed from the object. Further details of SEM-EDX are discussed in Appendix A. Analysis was performed by Peter Chung of the Imaging Spectroscopy and Analysis Centre (ISAAC), School of Geographical and Earth Sciences, University of Glasgow. The instrument is a Carl Zeiss Sigma Variable Pressure Analytical SEM

³⁵ Kirby and Saunders, "Fading and Colour Change of Prussian Blue: Methods of Manufacture and the Influence of Extenders."

³⁶ Easthaugh et al., *The Pigment Compendium: a Dictionary of Historical Pigments*, 225.

with Oxford Microanalysis software. The samples were situated on a carbon tab and placed in the sample chamber at 45 Pa. Detectors for secondary electron (SE), electron backscatter diffraction, and energy dispersive X-ray (EDX) were used to investigate the sample surfaces, elemental distribution, and composition. The secondary electron and electron backscatter used an acceleration voltage of 20 kV and the EDX used 0-20 kV depending on the required intensity of the signal. The secondary electron identified concentrated areas of pigment on the sample, the electron backscatter diffraction investigated elemental distribution, and the EDX detected X-ray emission at the targeted location to identify the elemental composition. The green sample UGD 13/8/3 #5 was analysed along with yellow sample UGD 13/8/1 #2.

The secondary electron scan of the yellow sample at 2.5k magnification shows the particles of pigment on the cellulose strands.



Figure 7-47 Secondary electron image of yellow fibre UGD 13/8/1 #2.

The electron backscatter image detected the heaviest elements (white areas) were concentrated where the pigment is on the SE image.

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Figure 7-48 Electron backscatter diffraction image of yellow fibre UGD 13/8/1 #2.



Figure 7-49 EDX spectra taken from three spots on the yellow fibre.

Spectrum 3 (Figure 7-50), taken of the white area in Figure 7-49, shows high quantities of lead and chromium. This confirms the presence of lead chromate is the pigment in the yellow prints. The spectrum also shows the presence of aluminium from the discharged red complex. Chlorine, sodium, and potassium are probably from the various salts used in the dyeing process; this may also explain the silicon peak since silicates were used in the printing process.³⁷ It is not immediately clear why sulfur is present, but it may be the result of impurities in the lead compounds.

³⁷ O'Neill, Chemistry of Calico Printing, Dyeing, and Bleaching, 73.



Figure 7-50 EDX spectrum of pigment on yellow fibre.

The electron backscatter diffraction image of the green fibre in Figure 7-51 identified a pigment area containing heavier elements for analysis. Spectra were taken from two areas on the sample, one white and one grey.



Figure 7-51 Electron backscatter diffraction image of green fibre UGD 13/8/3 #5.



Figure 7-52 EDX spectra taken from two spots on the green fibre.

Spectrum 13, from the grey area, has the same elements as spectrum 14, but in a different distribution. More aluminium and silicon are detected in 13, and more lead and chromium in 14, consistent with the increased intensity of the latter indicating more pigment. Iron from Prussian blue is present, though weak. Calcium may be residual from the discharge process or the red complex, and the source of the copper is uncertain; it may be from a vessel used in the dyeing process, the print roller, or a regent impurity.



Figure 7-53 EDX spectrum of pigment on green fibre.

7.3.4 Summary

The analysis of black, blue, yellow, and green fibres from printed Turkey red textiles shows results consistent with the techniques described in the literature. Extraction of the dyes from black fibre UGD 13/8/5 #9 left a blue, rather white or yellow fibre, which was confirmed to be Prussian blue by FTIR-ATR. A fibre

Electron Image 7

from a blue textile UGD 13/8/4 #3 had a similar spectrum. The cyano band around 2080 cm⁻¹ was also seen for green fibre UGD 13/8/3 #5, so Prussian blue was involved in three colours of Turkey red prints. This pigment has good light fastness properties, though according to the literature some black was also printed with the less-fast logwood, which must be taken into account. This research did not identify any logwood due to the extraction technique used, but a more specific extraction method could offer different results, or else DRIFTS identification of logwood by the absence of Prussian blue on black areas would be a useful, non-invasive screening technique.

Lead chromate was identified on the green and yellow fibres by SEM-EDX analysis, which also showed aluminium mordant and various residual salts. This identification has implications for the integrity of historical Turkey red printed with yellow and green, since lead chromate is known to darken with light exposure. The confirmation of these pigments on printed Turkey red is useful for the conservation of these textiles since their particular fastnesses and properties can be taken into account for cleaning and display.

7.4 Summary

The research in this chapter investigated the chromatographic profile of a range of historical Turkey red samples, replica textiles, and historical and modern reference compounds by UHPLC-PDA analysis to answer the question for this project about which dyes are found on Turkey red, for which there has been no previous comprehensive analysis. Furthermore, the work aimed to determine whether a chromatogram could indicate whether madder, garancine, or synthetic alizarin was used. The results show it is possible to distinguish between pieces dyed with madder or garancine (natural) and those dyed with synthetic alizarin. About ten unknown compounds in low relative amounts were also seen in the chromatograms but could not be used to draw conclusions without further analysis by MS. The analysis of dyes on historical Turkey red answers the questions for this project regarding which dyes are present in the objects, and whether this information can be used to determine dye source or historical provenance.

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Synthetic alizarin dye produced in the 19th c. contained varying proportions of anthrapurpurin and flavopurpurin in addition to alizarin, compounds that have not been identified in madder and are used here as markers to identify synthetic dye. This research found that garancine contains a small quantity of anthrapurpurin and the extraction process may produce some from madder, but historical synthetic alizarin generally had a much larger amount and a quantity of flavopurpurin as well. This research was able to use these compounds to predict a natural or synthetic dye source for Turkey red of unknown provenance with reasonable confidence. The robustness of historical Turkey red to light exposure depends on the fastness of its dye components, and although anthraquinones are fairly stable, their identification, including the unknowns seen in this analysis, is an important part of the continued preservation of these objects.

Dyes analysis also found a black fibre that was made by printing Prussian blue over Turkey red. No conclusive results were obtained on whether other black fibres were printed with logwood due to the extraction technique used. Textiles printed with logwood may be less light fast, but these can be distinguished by the absence of a cyano band in an FTIR spectrum of a black area. FTIR-ATR analysis of a blue and a green fibre identified bands from the cyano groups in Prussian blue pigment. Lead chromate was identified on a green and a yellow fibre by SEM-EDX. Prussian blue has good light fastness properties, but darkening of lead chromate may be a conservation issue for display. This research was not able to address the fastness or fading properties of Turkey red or the hydroxyanthraquinone dyes on the red fibres, but the identification of the primary components alizarin, anthrapurpurin, flavopurpurin, and purpurin is a step toward being able to do so, further improving our understanding and preservation of these remarkable textiles.

Conclusions

This thesis researched historical Turkey red dyeing methods in the larger context of the British textile industry and, specifically, the Turkey red industry of 19th c. Scotland. Throughout the 19th c., dyed and printed Scottish Turkey red was exported globally and recognised as an exceptional textile product. The industry was one of the main employers in the Glasgow area and a significant part of the regional economy. Turkey red production ended in the 1930s and with it jobs disappeared and works were closed, leaving as its only tangible legacy the brilliant red textiles preserved in museum and archive collections. The intricate and unique Turkey red dyeing technique produced the brightest, fastest shade of red possible on cotton fibres. Another significant aspect of Turkey red is that it was the first natural dyeing process to adopt a synthetic dye, seen through the transition from madder to garancine to synthetic alizarin. Despite intense interest from 19th c. dyers and chemists in how the colour formed, they were never fully able to answer their questions regarding the nature of the complex, questions which still persist today. The historical significance of the industry, the transition from natural to synthetic dye, and the professed remarkable fastness of historical Turkey red all merit an investigation and characterisation of these unique textiles. A better understanding of their chemistry improves display and conservation practices, extending their life for the appreciation of future generations and contributing to the field of conservation science. This interdisciplinary project incorporates history, textile conservation, and chemistry, using a process-based approach with primary source historical documentation to identify key features of a Turkey red process. This review is used to test the information available in the literature through a re-creation of the process, producing replica samples for material analysis. The re-creation is necessary because the Turkey red dyeing process is so lengthy and involved that a good understanding of it requires practical experience. The conservation science-based analytical methods are also applied to historical textiles to characterise the complex and confirm a valid re-creation. Other material analyses in this research include the re-creation and characterisation of Turkey red oil and the analysis of dyes on historical textiles.

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Novel topics in this research include:

•An extensive review and comparison of English and French of Turkey red materials and methods, evaluating them with particular consideration toward the chemistry of each step, and incorporating archival material from the 19th c. British Turkey red industry to determine how historical pieces were dyed in Scotland (Chapter 1).

•Development of conservation-based *in situ* analysis of replica Turkey red by Fourier transform infrared spectroscopy (FTIR), comparing attenuated total reflectance (ATR-FTIR) and diffuse (DRIFTS) interfaces, to characterise the oil complex on the cotton and how aluminium is adsorbed. Supporting analysis was done by ¹³C ssNMR spectroscopy. The non-invasive DRIFTS technique confirms the complex on historical Turkey red pieces and provides a valuable screening technique for unidentified Turkey red in collections (Chapter 6). The presence of the oil is expected to have a role in the fastness of the textiles, so characterising it is a step toward being able to measure the fastness of Turkey red in modern terms significant to conservators and curators.

• First comprehensive analysis of dyes on historical Turkey red, taking advantage of new UHPLC-PDA technology to improve detection and analysis with minimal sample required (Chapter 7). The Turkey red industry is an unusual case for being such a large consumer of a single dyestuff, and for being the first instance where a natural dye was replaced with its synthetic analogue. Extensive research on madder and madder-dyed textiles has been published, but to date there has been little investigation into late-19th c. synthetic alizarin or garancine, a 'semi-synthetic' concentrated madder product frequently referenced in the literature. This research begins to redress these analytical gaps by studying the chromatographic profiles of these dyes from references and textiles, which can be improved upon with further investigation by UHPLC-MS.

Re-creation of Turkey red and materials used in the process following historical methods (Chapter 4). This produced reference samples for testing analytical techniques prior to their application on historical objects.
 Characterisation of Turkey red oil by ¹H and ¹³C NMR and HPLC-MS (Chapter 5) was used to form a hypothesis about the role of the oil and its chemistry in the

overall process. This information improved the re-creation of dyed Turkey red and the *in situ* analysis of historical textiles.

The primary conclusions of this research are:

Definition of the European Turkey red process

The review of Turkey red methods published in English and French, dating from 1765 to 1911, found that while individual methods contain some variation in terms of handling and ingredients, a definition of the process is possible based on overarching characteristics. The process can be defined as one for dyeing cotton fibres prepared with fatty acids (oil) using aluminium, calcium, and madder, garancine, or synthetic alizarin. The focus of this research is on late 19th c. Scottish Turkey red, which the methods from the period show was dyed in this manner. The order of steps is significant since the fatty acids must be applied first, followed by the aluminium, and then dyeing with calcium in the dye bath. Auxiliary ingredients like tannins, dung, and blood were used to improve the quality of the dyeing, but are not part of the Turkey red complex.

In situ characterisation of cellulose-fatty acid and cellulose-fatty acidaluminium complex

Characterisation of oil on the cotton fibres of Turkey red required *in situ*, or non-extractive, analysis, because the colour is effectively 'built' onto the fibre. This was accomplished using a combination of ATR and DRIFTS spectroscopy on replica oiled calico and Turkey red, and on historical Turkey red. A secondary analysis by ¹³C ssNMR on re-created samples supported the conclusions from the FTIR analysis; sample preparation for ¹³C ssNMR was unsuitable for the historical textiles. Both FTIR instruments identified bands consistent with adsorbed fatty acids, primarily through the presence of a strong carbonyl band and one for an aliphatic chain. The DRIFTS interface was more sensitive toward the uneven textile surface, and the handheld instrument was more suitable for analysing historical Turkey red in the fragile pattern books. Bands in the FTIR spectra show the fatty acid carbonyls form hydrogen bonds with cellulose hydroxyls, mostly in the form of carboxylic dimers. Further fatty acids are bonded by hydrocarbon chain adsorption. Differences in how the ATR and DRIFTS interfaces 'see' the

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sample, related to individual depths of penetration, gives some indication that the fatty acids are bonded by the carboxyl to the cellulose hydroxyl while the aliphatic chain extends away from the fibre, making it more superficial and more clearly detected by the ATR interface, which 'sees' around 2 µm into the sample as opposed to the 7 μ m by DRIFTS. This surface coating would provide a level of hydrophobicity that probably contributes to the fastness of Turkey red. When metal ions like sodium or aluminium are applied, they form metal soaps with the fatty acids on the fibres. The low water solubility of aluminium soaps makes them less likely to be removed from the fibres by washing, another factor that improves wash fastness. Because the oil is a key feature of Turkey red and characteristic of the process, identifying it through non-invasive conservationbased analysis like FTIR makes it possible to identify previously unknown Turkey red artefacts in collections. Knowledge of the complex also improves our understanding of what Turkey red is, allowing for better-informed conservation practices and making a contribution toward measuring its fastness. The surface complexing between the fatty acids of the oil treatment and the cellulose hydroxyls may have some parallel chemistry with similar, naturally occurring fatfibre combinations. The initial coating of fats and waxes on cotton fibres, and of lanolin on wool-bearing animals, likely has some parallels to Turkey red oiling, however these coatings are also significantly more complicated mixtures than the Turkey red oil and presumably not suitable for a dyeing process or scouring would not be necessary.

Chromatographic profiles and identification of dyes in historical Turkey red

During the 19th c., Turkey red dyers used madder, garancine, and synthetic alizarin as sources of red dye. The late 19th c. was a significant period of technological advancement in dyeing as synthetic dyes entered the market. This research aimed to identify whether chromatographic profiles of historical Turkey red could indicate which dye was used, and therefore the potential age of an object (synthetic alizarin was commercially available from 1869). Chromatograms were obtained of modern madder and anthraquinone reference compounds, and historical references of madder, garancine and 19th c. synthetic alizarin from the TU Dresden Historisches Farbstoffsammlung (Historical Dyes Collection) and the Catalyst Science Discovery Centre. This research focused on the four major components identified in reference and on historical Turkey red: anthrapurpurin, alizarin, flavopurpurin, and purpurin.

The review identified the dyes anthrapurpurin and flavopurpurin as molecules that appear in synthetic alizarin, but do not occur in madder. They form as side reactions during synthesis, and are less abundant in modern synthetic alizarin due to more precise control of the process than was possible in the 19th c. There is very little research available on early synthetic alizarin, so the light fastness of these compounds is not well known, but it is significant to object conservation given their relative abundance in some pieces. The madder samples contain a multitude of coloured compounds, many of them yellow to orange according to their UV spectra and most without tinctorial properties based on their absence in textile chromatograms. The major components in madder were usually alizarin and purpurin. Unexpectedly for a madder product, garancine also contained a small amount (<1%) of anthrapurpurin, though no flavopurpurin. Garancine and synthetic alizarin were both made with sulfuric acid as a reagent, so it may be that some madder compounds are converted to anthrapurpurin in trace amounts. Chromatograms from replica Turkey red dyed with madder contained trace quantities of anthrapurpurin similar to the garancine profile, which may have formed in the extraction process. Only one sample of historical garancine was located, limited the available data, and re-creation was not possible due to the hazardous nature of the process requiring special equipment. Flavopurpurin does not appear when anthrapurpurin is present in trace amounts, making it a more confident indicator of a synthetic source. The results from this research cannot distinguish between natural dye sources madder and garancine, but a natural or synthetic source can be identified due to the difference in relative amount of anthrapurpurin and presence of flavopurpurin in synthetic alizarin.

Around 100 fibre samples from historical Turkey red, dating from ca. 1850s-1900s, were analysed by UHPLC-PDA. Most were of Scottish manufacture from the United Turkey Red firm, but a few samples were obtained from objects of German, Swiss, French, Italian, and English provenance as well. The AOE dyestuffs ledger records the use of synthetic alizarin from the early 1870s when the ledger begins and madder is quickly phased out, which is consistent with the chromatograms of samples known to be dyed during this period. Some ledger

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entries contain madder/garancine and synthetic alizarin, but because entries are averages over a six-month period it is unclear whether they were used in the same batches. The literature does not indicate combining natural and synthetic dyes in one dye bath was common practice, A few chromatograms contain alizarin, anthrapurpurin, flavopurpurin, and purpurin, which may indicate a mixture of natural and synthetic dye sources. Samples of known provenance from the V&A collection dyed after this date (1871) appear to have been dyed naturally, so the transition occurred over a period of years and not all dyers immediately adopted synthetic alizarin. Across the textile samples, around ten unknown compounds were detected as minor components. Two pairs had similar retention times and had to be distinguished by UV-Vis spectra. A few unknowns may also be indicators for a natural or synthetic dye source, but further identification and an improved anthraquinone-specific separation technique is recommended. The light fastness of these unknowns, and of anthrapurpurin and flavopurpurin, has an impact on object conservation and display, meriting further investigation.

Identification of pigments on printed Turkey red

Pigments on historical printed Turkey red consistent with descriptions of the printing process in the literature were also identified by in situ analysis using FTIR spectroscopy and SEM-EDX. Both techniques are non-destructive and conservation-based, though fibre sampling is typically required for SEM-EDX since the analysis operates in a vacuum. Infrared spectra of a blue and a green fibre showed a band from cyano groups, indicating Prussian blue was used for both colours. The SEM-EDX analysis of a yellow and a green fibre confirmed the presence of lead chromate, a yellow pigment that was overlaid with Prussian blue to make green. Extraction of dyes from a black fibre yielded a chromatogram of red dyes with a residual blue fibre, confirming black was sometimes produced by printing Prussian blue over Turkey red without discharging the underlying red. The analysis of other black fibres did not confirm the presence of logwood, another dye used to make black, but logwood components are difficult to extract and require special techniques not used in this research. The absence of Prussian blue on black areas of Turkey red, determined by FTIR, may be a way to identify textiles printed with logwood. Identifying these compounds has significance for conservation of historical

textiles depending on their light fastness. Prussian blue has generally good light fastness, but black made with logwood would be more susceptible to fading. Lead chromate has a tendency to darken with light exposure, though this has been studied primarily in the context of paints rather than printed textiles and further investigation is recommended.

Original contributions

The original contributions of this research include characterising how the oil bonds to cellulose fibres and becomes part of Turkey red, how aluminium becomes part of this complex, distinguishing natural and synthetic anthraquinone dye sources in historical Turkey red, and identifying pigments on printed Turkey red textiles. This work makes significant contributions to our understanding of Turkey red and which compounds and dyes are present on the fibre, which can be used to improve care and display practices for their continued conservation and appreciation.

The comprehensive review of historical Turkey red recipes and the juxtaposition with archival material from dyeing works reveals that although the process was jealously guarded by dyers, information was available and the methods were largely similar. This research defines what a Turkey red process is and identifies the variations dyers used over 150 years to improve the quality of their product. The literature states that dyeing Turkey red depended on being shown the process, and that it could not be learned from a book. The successful re-creation of Turkey red following Hummel's recipe shows it is possible to dye from reading a method rather than by demonstration or experience, although with the caveat that many methods were evaluated for this research, making it possible to fill in perceived gaps in any one method. Historically, this level of access to texts would have been unlikely and the limited transmission of information probably necessitated demonstration or firsthand knowledge. The results from this re-creation and analysis show Turkey red can be re-created from a book, though it does not entirely contradict the earlier assertion since it was re-created from many books with the advantages of modern chemical understanding.

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The re-creation of ingredients like Turkey red oil and synthetic alizarin also tested how valuable industrial processes were recorded and communicated. For the unsuccessful re-creation of synthetic alizarin, numerous challenges were presented in terms of how the reaction should proceed and under what conditions, which shows that acquiring knowledge of a process does not always guarantee successful execution. The re-creation of Turkey red oil faced similar challenges, but the outcome was positive in this instance and yielded a product consistent with other samples of Turkey red oil. It remains unknown whether authors and inventors were intentionally concealing pieces of information to discourage competition or if documentation practices in the 19th century were simply less refined than today-both explanations may apply. While patents offered some level of protection for chemical manufacturers, the prevalence of dyeing manuals implies that this group relied more on an individual's skill to make a desirable product than on secrecy. In addition to exploring how historical methods can be interpreted by a modern reader, re-creating ingredients and the Turkey red process gives a fuller appreciation of how these pioneering chemists worked. The sights, smells, and surprises not documented in the texts can only be experienced by practical re-creation, giving a fuller appreciation of how incredible the early synthetic dye and Turkey red industries must have been in the 19th century. In a world of increasingly strained resources, it may be worthwhile to look back toward processes from an earlier time and explore whether some aspects could be adapted for modern use. Finally, re-creations provide samples on which to test analytical procedures, especially valuable in heritage research when samples for characterisation may be limited or inaccessible.

A combination of analytical techniques was essential in the characterisation of historical Turkey red. Analysis by *in situ* FTIR was a significant step in the understanding of these unique textiles, making it possible to identify unknown Turkey red in collections through non-invasive means. The characterisation of the cellulose-fatty acid complex explains how oil acts in a dyeing process and may explain some of the notable fastness properties Turkey red was said to have. Fading is a serious concern for historical textiles, so its continued preservation depends on further understanding and measurement of its fastness. The identification anthraquinone dyes by UHPLC-PDA from madder, garancine, and synthetic alizarin is also an important factor in the preservation of these textiles, because knowing which dyes are present, and whether they are labile, affects the integrity of the object when put on display. The same applies for pigments on printed Turkey red. Anthraquinone dyes are fairly robust to light exposure, but this does not except them from being at risk of fading and identifying which dyes are present assists future fastness studies for these objects. Certain compounds in the dye profile are also useful to indicate a possible date of manufacture, improving object records.

The outcomes from this research elucidates the chemistry of the entire Turkey red complex in more detail than has previously been possible. Understanding this complex is an essential step toward quantifying its fastness in modern terms and preserving the remaining heritage textiles in collections. The richness of its history and its obscure origins, its desirability as an industrial process, the complexity and peculiar nature of the methods to make it, and the legendary, fiery brilliance of its colour have made Turkey red a topic of fascination for centuries. This research benefits conservators by providing more information about the chemistry of the colour, enabling better-informed decisions about display, cleaning, and care conditions. It also initiates an investigation and comparison of natural and synthetic dye sources and the potential ramifications for robustness to light exposure if certain compounds are more or less sensitive. The work connects early synthetic dyes and the developing chemical industry of the 19th c. with Scotland's rich textile history and provides curators with a non-invasive, conservation-based means to identify Turkey red in collections.

Future research

This extensive study of the chemistry of Turkey red dyeing answered many questions about the nature of the complex and identified a few more:

1. Separation and identification of madder components by UHPLC and mass spectrometry with an anthraquinone-specific method for more detailed understanding than previously possible with HPLC analysis. Further identification of unknown dyes on textile fibres by MS.

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2. Study of the effect of extraction method on hydroxyanthraquinone dyes and how solvent choices improve or affect the results.

3. Systematic fastness study of textiles prepared with oil in the manner of Turkey red to determine its contributions to the overall fastness of the piece.

4. Fastness study of hydroxyanthraquinone dyes identified on Turkey red, especially for synthetic components anthrapurpurin and flavopurpurin and unknowns. Fastness study of printed Turkey red with Prussian blue, logwood, and lead yellow.

5. Research on how auxiliary ingredients used in a variety of dyeing processes (tannins, ruminant dung, blood, and substitutes) affected the chemistry of the process and the outcome of the final product.

Beginning in March 2017, "LightFasTR", an EU-funded Marie Skłodowska-Curie Fellowship at the Centre for Textile Conservation, University of Glasgow, will continue the investigation of Turkey red with an emphasis on light fastness in order to create light exposure guidelines for sustainable collections display. This project will draw heavily on the conclusions from this thesis and continue the material investigation of historical objects using modern chemistry.

Appendix A Instrumental

This appendix provides more detail about the instrumental analyses used in this research and their suitability and limitations with regards to the research.

A.1 NMR and ssNMR spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is a useful tool for the characterisation of organic compounds. It provides information about molecular structure and can be adjusted to detect different atoms, hydrogen (¹H) and carbon (¹³C) being the most commonly analysed. In traditional solvent-based NMR, the analysis can be non-destructive if the sample can be recovered from the solvent, though because it requires very little sample it still has conservation applications. NMR acquires information about molecular structure by taking advantage of an atom's nuclear spin (I), a value that varies based on its 'environment', meaning its location within the molecule. In this research, NMR is applied in the analysis of Turkey red oils and for intermediate analysis in the experimental synthesis of alizarin. The technique cannot distinguish mixtures, which may produce overlapping signals, as was the case with the samples analysed here, but the similarity of the compounds (fatty acids or anthracenes) means the results are still useful.



Figure A-1 Diagram of NMR sample tube in instrument. In ssNMR, the solvent would not be present and the sample rotor is angled.

By exposing the sample to magnetic pulses, the atoms align with the field and then relax, releasing energy that is detected and processed as a spectrum.¹ The signal strength is dependent on the abundance of atoms in a particular environment. This means ¹H spectra, as the most abundant isotope, are easier to obtain than ¹³C, with a natural abundance of about 1%. The sample must be solvated, where the abundance of ¹H becomes a problem. In order to obtain a spectrum where the sample can be 'seen' over the solvent, a deuterated (¹H replaced with D, deuterium) must be used so the solvent is not seen. This is not as much of an issue with ¹³C NMR, where the solvent also contains few ¹³C atoms. The solvent signals in an NMR spectrum provide a useful reference signal in the comparison of spectra when comparing across the same solvent. Around 0.7 mL of solvent is suitable for preparing an NMR sample, which is loaded in a special glass tube.

In ¹H NMR, the area of an integrated peak corresponds to the number of ¹H atoms in that environment relative the numbers in other environments. For a pure compound, these could be scaled to whole numbers, but for mixtures the information can be difficult to interpret. In order to obtain a quality ¹H spectrum, a sample must be dry. Water molecules interact with the solvent via hydrogen bonding, which produces a broad peak with a solvent-specific shift that can mask sample signals. If a sample contains water, there are techniques available to remove the water without altering the sample before putting it on the instrument. Hydrogen bonding also occurs between the sample and the solvent, which affects the shift values. To account for this, compared spectra may be from different instruments but need to be from the same solvent. The integral areas in ¹³C NMR do not correspond to the number of atoms producing a peak due to variations in relaxation rates. The solvent will have a signal if it contains carbon, so chloroform-d (CDCl₃) would be visible but water-d (D₂O) would not.

Solid-state NMR (ssNMR), a variation in which the analyte is not solvated, was used here for *in situ* analysis of oiled calico. The same principle of applying a magnetic field and a radio frequency pulse is used, but the sample is not in solvent. The absence of the solvent signal affects the process in a few ways.

¹ Harwood and Claridge, *Introduction to Organic Spectroscopy*, 33.

Solvent in traditional NMR often serves as a reference signal for the spectrum. Putting an internal reference, most of which are liquids, in an ssNMR sample is usually not an option because the sample would be inhomogeneous, so external referencing is used. ssNMR spectra are not affected by the solvent, so an external reference is reliable.² Analysis requires stuffing the sample (about 400 mg) in a sample rotor. Samples in ssNMR are spun to average out anisotropic nuclear spin interactions. Although the samples in this ssNMR analysis are completely recoverable, since the dimensions are fairly specific it is more easily applied to replica textiles, which can be cut to suit, than a historical piece.

A.2 Chromatography

A.2.1 TLC, HPLC, and UHPLC

In the simplest terms, chromatography separates a mixed analyte into constituent molecules based on based on different physical interactions between the compounds and the system. A system is a solid substrate, called the stationary phase, combined with a fluid phase immiscible with the stationary phased, called the mobile phase. There are a variety of chromatographic techniques available based on the analytes and equipment available. In this research, liquid chromatography in the form of thin-layer chromatography (TLC), high performance liquid chromatography (HPLC), and ultra high performance liquid chromatography (UHPLC) are used. These techniques follow the same principles but have differing efficiencies, separating capacity, and associated costs.

The separation of mixtures in liquid chromatography takes advantages of differences in hydrophobicity, hydrophilicity, and polarity. A system with a hydrophilic stationary phase and a non-polar mobile phase is called 'normal phase' chromatography, since this was the initial setup, whereas the 'reverse phase' uses a hydrophobic stationary phase with a polar mobile phase. The varied interactions between the individual compounds in the sample and the two phases cause them to separate, and resolution is improved by manipulating the polarity of the mobile phase with additives like acids and other solvents.

² Apperley, Harris, and Hodgkinson, Solid-State NMR: Basic Principles and Practice.

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TLC is an open system where the sample is spotted, often with references, on a metal or glass plate coated with the stationary phase. The plate is placed in a covered vessel with mobile phase in the bottom, and as it climbs the plate it interacts with the analytes. Column chromatography is similar, but the sample components can be eluted rather than left on the plate, and the stationary phase is already saturated with mobile phase before the analyte is loaded on the system. HPLC is a closed version of column chromatography, where the sample is injected into a controlled, high-pressure system operating around 1,000-4,000 psi, with the mobile phase constantly flowing through the column.³ The flow rate and mode, either isocratic or gradient, can be manipulated, enabling the separation of μ -scale samples, high reproducibility, and more precise separation of similar compounds. These instruments can be used for preparatory work and quantitative analysis. UHPLC is an improvement upon HPLC technology, operating at higher pressure (5,000-15,000 psi) for increased efficiency, separation, and detection.

In HPLC and UHPLC, the stationary phase is packed in a steel column whose dimensions affect its separating capacity. This is seen in peak resolution, or how much baseline there is between two peaks, which can be manipulated by altering the mobile phase composition and flow rate.



Figure A-2 Peaks 1 and 2 have good resolution, but 2 and 3 are co-eluting.

³ The LC Handbook: Guide to LC Columns and Method Development.

Closed systems also require a detector, as opposed to visual identification in TLC and column chromatography. After travelling through the column, the mobile phase and analytes flow through a detector, often a photodiode array (PDA) or mass spectrometer (MS), which records how long the compound took to exit the column, a figure called the retention time (R_t). PDA detection uses a UV-Vis light source to detect the absorbance maxima of a compound, helping to make identifications based on similarities and reference chromatograms.

The number of variables in an HPLC/UHPLC analysis and the nature of the technique means chromatograms often differ slightly between two systems, and that two chromatograms from the same system can also vary. Care must be taken by the analyst to ensure reproducible mobile phases are used each time, especially for pH adjustment, which can significantly affect R_t values. Method development involves considering many available parameters in order to tailor a method best-suited for that analysis. The techniques have good conservation applications due to the large amount of information available from fairly small samples (for dyes, ca. 0.5-1 cm thread). In terms of sample recovery, the amount of mobile phase added during analysis makes this difficult, but this is usually unnecessary due to the small sample volume.

In MS, which can be used as a secondary detector to a PDA, known and unknown compounds are identified by detecting the mass of the compound and possible fragments, depending on the ionisation technique used.⁴ The ionised analytes are carried through a tunnel by an electrical current on an oscillating path. The ionised molecules are measured in m/z, which is the ratio of mass to charge. Ions with a stable m/z ratio pass through to the detector, while others are deflected and hit the side of the tunnel. The highest m/z ratio corresponds to the charged intact molecule and is called the molecular ion. This technique also has conservation science applications, but the samples are non-recoverable.

A.3 Infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a useful analytical technique for organic materials that has excellent conservation applications

⁴ Harwood and Claridge, *Introduction to Organic Spectroscopy*.

since it requires small samples or no sample preparation at all. Infrared spectroscopy operates in a similar manner to UV-Vis spectroscopy, by the absorption and emission of radiation, here through the vibrational excitation of covalent bonds using infrared radiation.⁵ The emitted radiation can be detected by transmittance, how much light is transmitted by the sample, or absorbance, how much light is absorbed by the sample. In this research, the opaque textile samples are analysed in absorbance. The detector, a thermocouple, records the difference in intensity between the sample and the background, taken prior to sample analysis. The addition of a Fourier transform to IR spectroscopy increased its usefulness as an analytical tool by increasing the speed at which a spectrum can be acquired.

IR spectra are displayed in the number of waves per cm, expressed in units of cm⁻¹ and called wavenumbers (v). They typically cover a range of 4000-400 cm⁻¹. Spectral bands can be correlated to specific types of bond, but for robust interpretation they should not be considered separately from the rest of the molecule. Bonds oscillating in the molecule affect the absorption of radiation, creating overtones and harmonics that contribute to the spectrum, especially in the 'fingerprint' region from 1500-600 cm⁻¹. The resolution of the sample is also expressed in cm⁻¹.⁶ The surface of the sample affects the beam scatter, making some samples more difficult to analyse because of scattered radiation. Usually, multiple spectra are taken from a sample by the instrument and averaged; the number depends on the depth of analysis and the instrument, with newer models capable of taking more spectra in a shorter time. FTIR is a useful diagnostic tool for organic compounds and requires minimal to no sample preparation, with most spectra collected in less than a minute.

There are two FTIR techniques applied in this research, attenuated total reflectance (ATR) and diffuse reflectance (DRIFTS, Diffuse Reflectance Infrared Fourier Transform Spectroscopy). ATR has long been used in conservation and heritage research, for fibre identification and in the identification of pigments, to name some examples. Analysis by ATR requires the sample to be pressed against a crystal, which involves clamping the sample with a small amount of

⁵ ibid.

⁶ Åmand and Tullin, *The Theory Behind FTIR Analysis*.

force. Because the sample must be manipulated onto the instrument and held in place with the clamp, analysis of large or fragile objects is difficult and the clamp can leave small indentations. The book shown in Figure A-5, which is both unwieldy and fragile, does not fit beneath the clamp at all and would be damaged by manipulating it onto the plate.



Figure A-3 FTIR-ATR The space between the crystal in the centre of the plate and the clamp is too small to accommodate large objects like the Turkey red sample books.



Figure A-4 Diagram of ATR instrument and sample interface. The sample would be held against the crystal with the clamp pictured in the figure above.

The infrared beam passes through a crystal with a high refractive index that works at a fixed grazing angle. ATR works by scattered specular reflectance, the same kind of reflectance produced by mirrors. This is better suited to flat surfaces, where most of the incident reflection will have the same direction. For uneven surfaces like textile fibres, the signal is scattered and not all radiation will reach the detector, making the technique less suitable for this particular research and the samples involved. Nevertheless, the availability of these instruments means their potential applications for surface analysis of Turkey red is still worth exploring for objects that can be analysed by ATR.



Figure A-5 Sample pattern book from United Turkey Red, 1856-1861. University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD13/8/2.

DRIFTS has also been used to a degree in heritage science, but until recently required the sample to be ground and pressed into a cup, unsuitable in the case of Turkey red. In contrast to ATR, the DRIFTS detects diffuse energy, so it obtains more information from an uneven textile surface. New, handheld instruments with diffuse accessories allow spectra to be taken with no sample preparation. The portability means the instrument can be taken to the object, especially useful for the large and fragile UTR pattern books. As shown in Figure A-6, the instrument needs only to be in contact with the sample, no pressure required, and the instrument compensates for slight shifts in placement or contact because it was designed to be handheld.



Figure A-6 DRIFTS analysis of UTR sample book Turkey red textile.

These instruments have not been used widely in the surface analysis of historical textiles, making this research an ideal opportunity to test their potential applications.



Figure A-7 Diagram of DRIFTS instrument and sample interface. The diffuse reflectance radiation is collected by a detector.

A.4 SEM-EDX

To identify the presence of lead chromate pigment on printed Turkey red, energy dispersive x-ray with a scanning electron microscope (SEM-EDX) was used as a tool for elemental analysis. The technique uses a beam to excite electrons in individual atoms. The excitation causes electrons in inner shells to be ejected, leaving a hole that is filled by an electron from a higher-energy shell. This energy is detected and processed into an image or spectrum depending on the type of analysis.⁷

The samples were first raster scanned with a low-energy beam to emit secondary electrons (SE), which are emitted from the outermost electron shell and detected by a photomultiplier. The output can be displayed as a digital image where the brightness corresponds to the number of secondary electrons reaching the detector. After this, a beam of high-energy electrons was used to measure the backscatter from the elements present on the sample, also recorded as an image. The brightness in this image is determined by atomic number, so heavier elements appear white and lighter ones grey. In this research, it helps identify concentrated areas of pigment on the fibres. Finally, the EDX beam excites inner-shell electrons, which are ejected from the shell, leaving a hole. When a higher-energy electron from an outer shell shifts to fill the hole, the X-ray energy shift is detected and converted to a signal. The unique atomic structure of each element makes it possible to assign the energy to a particular atom, enabling the identification of individual elements present.



Figure A-8 Diagram of SEM-EDX instrument and sample interface.

⁷ Goldstein et al., Scanning Electron Microscopy and X-Ray Microanalysis.

Appendix B Turkey red methods and archive material

Published methods in chronological order

1765. Mémoire contenant le procédé de la teinture du coton rouge-incarnat d'Andrinople sur le coton filé. Paris: l'Imprimerie Royale. http://gallica.bnf.fr/ark:/12148/bpt6k6359837w.

First widely available published method for dyeing Turkey red, from the government of France. Dyes 100 lbs. cotton yarn and uses huile tournante, sheep droppings, gall nuts, alum, madder, and blood in a typical 'old' process. The leys are made by pouring water through a series of buckets containing soda ash.

Henry, Thomas. 1790. "Considerations Relative to the Nature of Wool, Silk, and Cotton, as Objects of the Art of Dying; on the Various Preparations, and Mordants, Requisite for These Different Substances; and on the Nature and Properties of Colouring Matter. Together with Some Observations on the Theory of Dying in General, and Particularly the Turkey Red." In Memoirs of the Literary and Philosophical Society of Manchester, 3:343-408. London: Warrington.

Section of a dyeing manual by Thomas Henry, a chemist and member of the Manchester Philosophical Society. Henry provides the 'old' process the Borelles presented for the Parliamentary award in 1785, another characteristic 'old' method. The method recommends the freshest sheep's blood possible as well as fresh dung that has not been rained on. Henry also discusses the chemistry of compounds and cites research from contemporaries.

Berthollet, Claude-Louis. 1791b. Éléments de l'art de la teinture. Vol. 2. Paris: F. Didot. http://www.archive.org/details/lmentsdelart02bert.

Section of a dyeing manual by eminent French chemist Berthollet, who provides a 17-step 'old' process for dyeing Turkey red and a detailed discussion of the chemistry of various reagents and processes. In French.

Berthollet, Claude-Louis. 1791a. Elements of the Art of Dyeing. Translated by William Hamilton. London: Stephen Couchman.

English translation of above text.

Pallas, Simon Peter. 1798. "II. the Genuine Oriental Process for Giving to Cotton Yarn or Stuff the Fast or Ingrained Colour, Known by the Name of Turkey Red, as Practised at Astracan." Philosophical Magazine Series 1 1 (1): 4-11. doi:10.1080/14786447808676783.

Pallas, a German zoologist and botanist, mentions a small publication on Turkey red by a Profession Oettinger at Tübingen in 1764, though no further evidence of it was found. The text describes Turkey red dyeing at Astrakhan, on the northern Black Sea coast, as recounted to him by a friend, the proprietor of a dye house. This article, the first of two (see 1806), describes the dyeing broadly as well as how madder and sumac are acquired. The dyers use fish oil, likely the most abundant source for the region, an unusual diversion from the olive oil typically seen.

Le Pileur d'Apligny. 1798. L'art de la teinture des fils et étoffes de coton. Paris: Servière.

French text for 'old' Turkey red process. Includes some discussion of ingredients, preparations, and technique.

Haussmann, Jean-Michel. 1802b. "XXXII. Observations on Maddering; Together with a Simple and Certain Process for Obtaining, with Great Beauty and Fixity, That Colour Known Under the Name of the Turkey or Adrianople Red."
Philosophical Magazine Series 1 12 (46): 170-75. doi:10.1080/14786440208676046.

In the first of two texts, Haussmann, an apothecary and dyer, claims to have discovered the addition of chalk to compensate for soft water in Turkey red dyeing some time in the 1770s. Ure (reference below, p. 791) says this was precipitated by a move from Rouen, where the water was calciferous, to Logelbach near Mulhouse, where the water was soft. He discusses techniques for improving madder colours and the dyeing process in broad terms, which is published in the following article.

Haussmann, Jean-Michel. 1802a. "XLIII. Observations on Maddering; Together with a Simple and Certain Process for Obtaining, with Great Beauty and Fixity, That Colour Known Under the Name of the Turkey or Adrianople Red." Philosophical Magazine Series 1 12 (47): 260-66. doi:10.1080/14786440208676058.

Haussmann's second text describes his dyeing process for Turkey red, which unusually recommends an oil bath made with linseed oil containing both aluminium (alum) and calcium (quicklime), a practice generally condemned by his peers in the literature. The clearing step involves a boil with wheat bran and he discusses the polygenetic qualities of madder dyeing and some matters of ingredient quality. 1804. "V. Account of the Process Followed by M. Pierre Jacques Papillon for Dyeing Turkey Red." Philosophical Magazine Series 1 18 (69): 43-47. doi:10.1080/14786440408676443.

This is the process Papillon disclosed to Dr Joseph Black as part of his agreement with the Board of Manufactures in Edinburgh. It includes the irregular use of sal ammoniac and sulfuric acid, but otherwise is a typical 'old' Turkey red method using huile tournante, sheep dung, blood, and madder. As in other methods, the leys are made by running water through a series of buckets containing soda ash.

Pallas, Simon Peter. 1806. "II. Process for Dyeing the Adrianople or Turkey Red, as Practised at Astracan: Being a Supplement to His Former Publications on That Art." Philosophical Magazine Series 1 25 (97): 8-9. doi:10.1080/14786440608563401.

Pallas states that the process was communicated to him by a friend who owned a dye house in Astrakhan. The 'old' process, using fish oil, is dyed outdoors and takes less than a week.

Chaptal, Jean-Antoine-Claude. 1807. L'art de la teinture du coton en rouge. Paris: l'Imprimerie de Crapelet. http://books.google.co.uk/books?id=FU0UAAAAQAAJ&dq=chaptal+l%27art+de+ la+teinture&source=gbs_navlinks_s.

In 'The art of dyeing cotton red', Chaptal, a pioneering French chemist and polymath, describes how to set up a dyeing facility, source appropriate ingredients, and the dyeing process. He discusses the effect of various ingredients and says Turkey red dyeing takes around thirty days.

Cooper, Thomas. 1815. A Practical Treatise on Dyeing, and Callicoe Printing: Exhibiting the Processes in the French, German, English, and American Practice of Fixing Colours on Woollen, Cotton, Silk, and Linen. Philadelphia: Thomas Dobson. https://archive.org/details/practicaltreatis00coop.

Cooper, an American professor of chemistry at Dickenson College in Pennsylvania, had extensive practical experience as a dyer and printer but admits he is writing his book many decades afterward. He cites Berthollet and D'Apligny and provides the Borelle method for Turkey red dyeing from Henry and D'Apligny. Cooper thoroughly disapproves of Papillon and his process and considers it necessary for any potential dyer to have a knowledge of chemistry.

Vitalis, Jean Baptiste. 1823. Cours élémentaire de teinture sur laine, soie, lin, chanvre et coton, et sur l'art d'imprimer les toiles. Paris: Galerie Bossange Père.

Vitalis was a French professor of chemistry and Rouennais dyer provides two routes for his 'old' Turkey red process, the shorter 'marche en gris' and the longer 'marche en jaune' that produced a higher-quality textile. He discusses ingredients and many aspects of the chemistry of dyeing and solution preparation. Printing Prussian blue is also mentioned. Berthollet, Claude-Louis, and A B Berthollet. 1841. Elements of the Art of Dyeing and Bleaching. Translated by Andrew Ure. New edition. London: Thomas Tegg.

Translation of Berthollet's second edition by Scottish chemist Dr Andrew Ure. The Turkey red process is not significantly altered from the earlier text.

Ure, Andrew. 1844. A Dictionary of Arts, Manufactures, and Mines. 3rd ed. Vol. 2. New York: D. Appleton & Company.

http://books.google.co.uk/books?id=6zEKAAAAIAAJ&printsec=frontcover&sour ce=gbs_ge_summary_r&cad=0#v=onepage&q&f=false.

Ure discusses Turkey red dyeing in broad terms in this Dictionary, which attempts to encompass most technological advances of the Industrial Revolution that to date, as well as phenomena of the natural world. He describes Turkey red dyeing in a production environment and comments on various processes from other dyers, naming Haussmann and Koechlin.

Persoz provides an 'old' method for Turkey red dyeing in French in his series on textile printing, as well as numerous calico samples that were analysed as part of this thesis. He also discusses the roles and chemistry of various ingredients, although some parts relevant to Turkey red are found in other volumes.

Jenny, M. 1868. "Mémoire sur la fabrication du rouge d'Andrinople." Bulletin de la Société Industrielle de Mulhouse 38.

Jenny, again writing in French, describes an 'old' Turkey red process and discusses the quality and roles of ingredients, conditions for dyeing, etc.

Sansone, Antonio. 1885. "Alizarin-Red and Turkey-Red Dyeing and Printing on Cotton." Journal of the Society of Dyers and Colourists 1 (8): 203-11.

Sansone describes the present state of Turkey red dyeing, which at that time had recently adjusted to the 'new' process. He also proposes potential structures for the colour complex, discusses dye sources, and hypothesises about the chemistry of the process.

Chateau, Theodore. 1876. "Critical and Historical Notes Concerning the Production of Adrianople or Turkey Red, and the Theory of This Colour." Ed. Charles O'Neill. *The Textile Colourist* 2 (4-6). Manchester: 262-272.

In a serialised text, Chateau describes Turkey red dyeing methods from sources like Haussmann, Chaptal, Vitalis, and Koechlin, underscoring the avid interest in Turkey red process that persisted through the 19th c.

Hummel provides 'old' and 'new' methods for Turkey red dyeing as well as a Steiner process, including detailed technical drawings of specialist equipment that are likely his own work. The 'new' process was taken as the basis for the re-creations following historical processes and is discussed in Chapter 1.

Persoz, Jean-François. 1846. Traité théorique et pratique de l'impression des tissus. Vol. 3. Paris: Victor Masson.

Hummel, John James. 1886. The Dyeing of Textile Fabrics. 2nd ed. London: Cassell & Company, Limited.

Dépierre, Joseph. 1892. Traité de la teinture et de l'impression des matières colorantes artificielles. 2^{me} partie, l'alizarine artificielle et ses dérivés. Vol. 2. Paris: Baudry et Cie.

Dépierre provides a 'new' process for Turkey red, but the text is on synthetic alizarin rather than Turkey red dyeing. The method is from Braun & Cordier, dated 1868, and uses blood and garancine. Dépierre also provides a Steiner process with more information than Hummel, though the oiling directions are still sparse compared to the other techniques. A number of calico samples are also included in this book, as in Persoz, including a piece dyed with anthrapurpurin that was sampled from the personal copy of Susan Kay-Williams.

Knecht, Edmund, Christopher Rawson, and Richard Loewenthal. 1893. A Manual of Dyeing. Vol. 2. London: Charles Griffin & Company, Limited.

Much of the 'old', Steiner, and 'new' processes from Knecht are essentially reprints of Hummel's texts. Knecht provides more information on ingredients like Turkey red oil, alum, and printing elsewhere in his work. A volume of sample swatches includes two pieces of Turkey red before and after steaming, but the edges are too well attached to sample. Analysis by in situ infrared spectroscopy was done on two copies in Chapter 6.

Carruthers, W S. 1911. "A New Process of Dyeing Turkey Red." Journal of the Society of Dyers and Colourists 27 (5): 123-26. doi:10.1111/j.1478-4408.1911.tb00557.x.

Toward the end of an era, the forced economies facing the Turkey red industry yielded truncated dyeing processes that attempted to shift toward a 'one bath' approach. The quality was lower than Turkey red but considered to be good enough for the circumstances. Approaches like this likely share a good deal of chemistry with Turkey red, perhaps technically making them such, though certainly not top-quality Turkey red.

Archive material

- n.d. Book of Dye Recipes and Samples of Printed Cotton Made by Foxhill Bank Printworks England 1830-1840s. London: Victoria & Albert Museum, Textiles & Fashion Collection. T.8-1978.
- n.d. Turkey Red Dyeing Calculation Book AOE Lennoxbank. Glasgow: University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248. UGD 13/4/1.
- Collin, Dr. n.d. Turkey Red Process for Cotton Yarn. Paisley: Paisley Central Library, Records of J&P Coats, Limited. 1/9/3.
- Tannahill, Mr. 1906. Turkey Red Dyeing. Paisley: Paisley Central Library, Records of J&P Coats, Limited. 1/9/3.
- Straugh, Mr. 1908. Recipe From Mr Straugh. Paisley: Paisley Central Library, Records of J&P Coats, Limited. 1/9/3.
- Brennan, Louis N, John Tannahill, and James P Percy. 1943. Turkey Red Process for Cotton Yarn. Paisley: Paisley Central Library, Records of J&P Coats, Limited. 1/9/3.

Appendix C Hummel's Turkey red processes

Text in the public domain.
THE DYEING

OF

TEXTILE FABRICS.

BY

J. J. HUMMEL, F.C.S.,

PROFESSOR AND DIRECTOR OF THE DYEING DEPARTMENT OF THE YORKSHIRE COLLEGE, LEEDS.

WITH 97 DIAGRAMS.

SECOND EDITION.

CASSELL & COMPANY, LIMITED:

LONDON, PARIS, NEW YORK & MELBOURNE.

1886.

[ALL RIGHTS RESERVED.]

MARE BOOKCASE

ANTHRACENE COLOURS.

it is liable to rub off; it also withstands the action of light fairly well.

The following equation represents the formation of Xylidine Red in this way :---

 $\begin{array}{l} C_{6}H_{3}(CH_{3})_{2}\cdot N = N \cdot Cl + C_{10}H_{7} \cdot ONa = \\ Diazo-xylene-chloride. & Sodium-\alpha-naphthol. \\ = C_{6}H_{3}(CH_{3})_{2}\cdot N = N \cdot C_{10}H_{6} \cdot OH + NaCl. \\ & Xylidine \ red. \end{array}$

Application to Wool.—Dye with 1—2 per cent. of colouring matter, with the addition of 2—4 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1.84), and 15—30 per cent. of sodium sulphate. Enter the wool at 40° — 50° C., raise the temperature gradually, in the course of an hour, to 100° C., and boil a quarter of an hour.

Several of the colouring matters give brighter colours if the sulphuric acid is replaced by 5—10 per cent. of alum, or 5—10 per cent. of stannic chloride, 120° Tw. (Sp. Gr. 1.6). Care must always be taken to have the bath sufficiently acid to develop the full colouring power; and if there is any tendency to uneven dyeing, the temperature should be raised very gradually.

Application to Silk.—Dye in a bath containing "boiled-off" liquor, slightly acidified with sulphuric acid.

The above modes of application do not, of course, apply to Azarin S, Azo Blue, and Chrysamin.

CHAPTER XX.

ANTHRACENE COLOURING MATTERS.

399. Alizarin $[C_{14}H_6O_2(OH)_2]$.—This valuable colouring matter, formerly only known as a substance obtainable from madder root, is now made in large quantities from the coal-tar product, anthracene.

Alizarin is the best type of those colouring matters

DYEING OF TEXTILE FABRICS.

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which dye only with the aid of a mordant, and which yield various colours according to the mordant employed (polygenetic colouring matters). In itself it has little or no colouring power, having no affinity for the vegetable fibres, and merely imparting a comparatively fugitive orange-brown colour to the animal fibres. It possesses, however, the valuable property of forming variouslycoloured insoluble precipitates or lakes when combined with many of the metallic oxides, and it is on this property that its use in dyeing depends. Its compound with alumina is red, with stannous oxide orange, with chronic oxide claret-brown, and with ferric oxide violet. All the colours produced on the textile fibres by means of these mordants are extremely fast to light, boiling with soap solutions, milling, &c.

Very closely allied to Alizarin are the colouring matters: *Isopurpurin* or *Anthrapurpurin*, *Flavopurpurin*, and *Purpurin* $C_{14}H_5O_2$ (OH)₃. Their method of application is so similar to that employed for Alizarin, that only special reference will be made to each, where points of difference arise. They are sold separately or mixed together in various proportions, each manufacturer giving his own brand to the different qualities and mixtures. It is customary, for the sake of simplicity, to sell them, whether separate or mixed, under the common name, "Alizarin."

Those which consist entirely, or most largely, of alizarin are called the *btue shades of alizarin*, while those in which Flavo-purpurin, or Isopurpurin predominate, constitute the *yellow shades of alizarin*. These designations have arisen because the former dye alumina mordanted cotton, a crimson or *bluish* shade of red, while the latter give a scarlet or *yellow* shade of red.

Application to Cotton.—Alizarin serves principally for the production of the brilliant Turkey-red dye, already referred to under the head of Madder. For this purpose it has entirely supplanted Madder and its commercial preparation Garancin, because the colours it yields are far more brilliant, quite as fast, and less expensive.

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ALIZARIN.

Turkey-red dyeing probably had its origin in India. At an early date it was introduced into Turkey (hence its name), and about the middle of the eighteenth century it began to be practised in France.

Since the publication of the process in the year 1765 by the French Government, it has been carried on largely in Switzerland, Germany, and Britain. At the present time, the chief seats of this important industry are the Vale of Leven, near Glasgow, and Elberfeld in Germany.

Numerous alterations and improvements have been gradually introduced, until it has now reached a very high state of perfection indeed. All the details of the process now employed have been empirically determined throughout a long period, and the successful production of the best Turkey-red depends upon their careful execution.

Cotton is dyed Turkey-red in the form of yarn and cloth. The process for *yarn*-dyeing seems to have experienced little change since the time when Madder was the dyestuff employed, and may serve as a type of the older methods of Turkey-red dyeing. It may be distinguished as the *Emulsion process*.

The present method of Turkey-red *cloth*-dyeing differs considerably in the earlier stages from that in vogue for yarn, and is known as *Steiner's process* (from the name of its inventor). Practical difficulties have prevented the adoption of this improved process for yarndyeing.

There is, however, a third process of Turkey-red dyeing applicable to both cloth and yarn, which represents the method most recently introduced. This may be termed the *Sulphated-oil process*. It is not impossible that this last process, or some modification of it, may gradually entirely displace the others; one cannot, however, speak with absolute certainty on this point, and at present all three are in use.

400. Emulsion Process for Dyeing 500 kilos. of Turkey-red Yarn.—The grey yarn is first "laced," *i.e.* the



Fig. 86.-Turkey-red Yarn-Wringing Machine.

knotted, once or several times, for the purpose of subsequently recognising the various lots.

1st Operation: Boiling. — Boil the yarn 6—8 hours with a solution of carbonate of soda, 1° Tw. (Sp. Gr. 1.005), then wash well with water, squeeze and dry in a stove at 55° —60° C.

2nd Operation: First green liquor.—This liquor is an emulsion (see p. 234) made up with 75 kilos. of olive oil, 8 kilos. of sheep-dung, about 1,000 litres of water,

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and a sufficiency of a concentrated solution of carbonate of soda to make the whole to 2° Tw. (Sp. Gr. 1.01).

Work the hanks of yarn separately in this emulsion at a temperature of 30° — 40° C., till thoroughly saturated (about half a minute), and wring out as evenly as possible. This process is usually called "tramping" (Fr., *tremper*, to steep).

Fig. 86 represents the taking-off end of an excellent wringing machine made by Messrs. Duncan Stewart and Co., Glasgow, and used in some Turkey-red works in this country.

It consists of two large discs revolving on a common shaft. On the periphery of each, and directly opposite each other, are several large iron hooks connected with springs, cog-wheels, and rackwork, in such a manner that those on one of the discs are capable of twisting, while at the same time both sets of hooks yield inwards as the two discs revolve. The hanks of yarn are properly steeped in the emulsion by hand, and at once placed on a pair of the hooks ; as the discs make a quarter of a revolution, the hooks twist and squeeze out the excess of liquor ; during the next quarter of the revolution the hooks untwist themselves, and at the opposite side of the machine the hanks are thrown or pushed off by a pair of strong upright arms.

Fig. 87 represents a tramping machine of A. Weser, Elberfeld, and used in Germany, which performs the steeping as well as the wringing, hand-labour being required only for putting on and taking off the hanks of yarn. It consists essentially of the liquor trough E, above which are situated the fixed revolving roller B, and loose roller A, on which the hanks are suspended. D is an L-shaped arm, the horizontal portion of which passes within the loop of the hank and depresses it into the liquor. c is an iron cylinder pressing against B, and serves to impregnate the yarn with the solution.

The various movements of the machine are regular and automatic. The hank of yarn is placed on the rollers A



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and B when the arm D is in the horizontal position; the arm D at once falls and steeps the yarn in the liquid, and the rollers revolve for a short period; the arm D now again takes the horizontal position, the roller B ceases to revolve, and the roller A first twists then untwists the hank, and it is ready to be removed by the attendant.

Whichever of the above machines is used, the work of "tramping" the yarn is practically continuous.

The prepared hanks are allowed to remain piled together over-night (12-20 hours), and are then dried in the stove. In this operation (*stoving*) the temperature is raised gradually to $55^{\circ}-60^{\circ}$ C., which is maintained for two hours. Care must be taken to allow the escape of the steam which is given off during the first stages of drying, otherwise the yarn is apt to be tendered.

3rd and 4th Operations: Second and third green liquors.—These are almost exact repetitions of the second operation, the liquor employed being made up separately and with the same proportions of the several ingredients as given above. The sole difference is that it is not necessary to let the prepared yarn lie in pile over-night; instead of this, if it is not raining, it is suspended on tin rods, and exposed to the open air for about 2—4 hours previous to stoving.

It is evident that, after stoving, the dry yarn is charged with sodium carbonate, and since it is very important that all the liquors should be maintained regularly at the same specific gravity, it is customary not to allow the liquor expressed during the wringing of the hanks to flow back into the "tramping" box, except in the case of the "first green liquor," but to collect it separately, and then, if necessary, to dilute it with water before using again.

The total amount of oil used is about thirty per cent. of the weight of yarn, but only a portion of this becomes fixed on the fibre.

5th, 6th, 7th, and 8th Operations: First, second,

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third, and fourth white liquors.—The solution here used is simply carbonate of soda, at 2° Tw. (Sp. Gr. 1.01), but after working the yarn in it a short time, it necessarily becomes an oil emulsion from the oil stripped off the cotton, apart from the fact that it is always mixed with the surplus and expressed liquor from the similar operations with previous lots of yarn.

The yarn is "tramped" in the liquor, wrung out, exposed in the open air, and dried in the stove, as in the previous operations.

9th Operation: Steeping.—Steep the yarn during 20—24 hours in water heated to 55° C., wash well, and dry in the stove at about 60° C. If the yarn contains much unmodified oil, a solution of carbonate of soda at $\frac{1}{2}$ ° Tw. (Sp. Gr. 1.0025) may be used; in this case a second steeping for two hours in tepid water is requisite before washing, &c.

10th Operation: Sumaching. — A decoction of Sumach is made by boiling 60 kilos. of best leaf Sumach for about half an hour, with sufficient water to make the cold filtered solution stand at $1\frac{1}{2}$ ° Tw. (Sp. Gr. 1.0075). The stoved yarn, while still warm, is steeped in large vats in this decoction as hot (40°—50° C.) as it can be borne by the boys who usually tramp it with bare feet beneath the surface of the solution. After steeping about 4—6 hours, the solution is drained off, and the excess is removed by a hydro-extractor.

11th Operation: Mordanting or Aluming.—A basic solution of alum is made by dissolving ordinary rockalum in hot water, and when nearly cold, adding gradually a cold solution of one-fourth its weight of carbonate of soda crystals. The solution is made to stand at 8° Tw. (Sp. Gr. 1.04). Sometimes, though this is not essential, a further addition is made of about 150—200 cubic centimetres of "red liquor," 16° Tw. (Sp. Gr. 1.08), and 5—7 grams of tin-crystals (SnCl₂) per kilo. of alum. The sumached yarn while still damp is tramped in the alum solution at a temperature of 40° —50° C., and left

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to steep for twenty-four hours. It is then thoroughly washed and hydro-extracted.

12th Operation : Dyeing.—Dye with 150—180 grams of Alizarin (10 per cent.), 30 grams of ground Sumach,



Fig. 88.-Clearing Boiler.

and about 300 grams of bullock's blood, per kilo. of cotton yarn. If the water contains little or no lime, add also ground chalk in the proportion of 1 per cent. of the weight of Alizarin (10 per cent.) employed. The yarn is introduced into the cold solution of the dye-vessel, the temperature is gradually raised to 100° C., in the course

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of one hour, and the boiling is continued for $\frac{1}{2}$ —1 hour. After dyeing, the yarn is washed, although this is not absolutely necessary.

13th Operation: First Clearing.—Boil the yarn for four hours at 3—4 pounds' pressure with about 30 grams of carbonate of soda crystals, and 30 grams of palm-oil soap, dissolved in a sufficiency of water, per kilo. of yarn. Wash afterwards. The "clearing boiler" used, and



Fig. 89.—Plan of Fig. 88.

shown in Fig. 88, and in plan in Fig. 89, is similar in construction to an ordinary low-pressure bleaching kier; it is, however, made of copper instead of iron. A represents the yarn; B the lid provided with safety valve and blow-off pipe; c the perforated false bottom; D the pufferpipe; E the bonnet for distributing the liquor over the yarn;

F the draw-off pipe. During the boiling, the liquor which collects below the false bottom is forced by the steam up to the top of the puffer-pipe, there to be ejected and spread over the goods. This action is of an intermittent character, since, after each ejection of the liquor, the pressure of the steam must accumulate below the false bottom until it is again able to overcome the weight of the column of water in the puffer-pipe.

14th Operation: Second Clearing.—Boil the yarn for 1—2 hours at 3—4 pounds' pressure with a solution containing 25 grams of palm-oil soap and $1\frac{1}{2}$ grams of tincrystals per kilo. of yarn. Wash well and dry in an openair shed. Previous to drying, the large excess of water

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is removed by means of the hydraulic press represented in Fig. 90. It consists of a strong iron framework D D, with a strong, fixed, but adjustable head A above, and



Fig. 90.-Hydraulic Press.

a similar one B below, attached to the hydraulic piston C, and thus capable of being moved up or down. By means of this machine a very large quantity of wet yarn may be rapidly and efficiently squeezed.

The above fairly represents the "Emulsion process"

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of Turkey-red yarn-dyeing as practised at the present time. It consists, therefore, of a somewhat numerous series of operations, occupying usually about three weeks' time, and although, hitherto, no absolutely satisfactory scientific explanation has been given of the exact nature of the chemical changes effected by every detail of the whole process, still their general character is tolerably well understood. The object of the frequent steeping in oilemulsion, drying in the open air, and stoving, is to impregnate the fibre evenly and thoroughly with oil, and to modify it in such a manner that it is not affected or removed by weak alkaline solutions, and that it will attract alumina from its solutions.

Many kinds of oil have been employed, but long experience has proved that olive oil gives the best and most certain results. The particular quality of oil most suitable for the purpose is that obtained by a second pressing of the olives after they have somewhat fermented and been steeped in boiling water. (Fr., huile tournante). It contains nitrogenous and extractive matters, which cause it gradually to become rancid, particularly when exposed to the air, *i.e.*, it decomposes, and a portion of the glycerine and fatty acids (margaric and oleic acids) is liberated. One of the chief characteristics of a good olive oil suitable for Turkey-red, is, that when one measure of it is shaken up with about 16 measures of sodium or potassium carbonate solution at 3° Tw. (Sp. Gr. 1.015), it forms a white milky liquid or emulsion, from which the oil does not readily separate even after standing for 12-18 hours. The oil which forms the most perfect and permanent emulsion with the least quantity of potash or soda is the best. This property of emulsifying, however, can be readily imparted to any oil by mixing it with 5-15 per cent. of oleïc acid.

The exact nature of the chemical changes which the oil undergoes during exposure to the air and stoving is unknown. It is probable, however, that under the influence of the alkaline carbonate and heat, the oil

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is decomposed and oxidised in such a manner that there remains on the fibre essentially an insoluble oxyoleic acid. Whatever may be the exact chemical composition of the modified oil, it has the property of fixing or combining with alumina, and the compound thus produced can further combine with Alizarin to form a red-lake. The effect which it has of giving brilliancy and fastness to the ultimate colour is probably, in part at least, due to its physical action of enveloping the coloured lake with a transparent oily varnish, which protects it more or less from external influences. All unchanged oil must be removed before mordanting (see Operation 9).

The impregnation of the cotton with tannin matter fixes an additional amount of alumina on the fibre, and tends to give deeper and fuller shades. Its use is, however, by no means absolutely essential, as seemed to be the case when Garancin or Madder was used, and by some dyers it is not used.

During the steeping in alum solution an insoluble basic aluminium compound is formed with the modified oil and also with the tannic acid if present. The complex mordant thus fixed on the cloth at this stage combines with Alizarin in the subsequent dye-bath to form the Turkey-red lake. The bullock's blood used is said to prevent, by reason of the coagulation of its albumen, certain impurities accompanying the Alizarin from being fixed on the cotton, but some practical Turkey-red dyers say that blood-albumen, glue, and other substitutes which have been tried, cannot entirely replace it. It certainly adds brilliancy and purity to the colour.

The "First Clearing" operation is for the purpose of removing any remaining impurities which the mordant may have attracted in the dye-bath, but for which its affinity is far less than for Alizarin.

The "Second Clearing" is said by some to introduce into the already extremely complex coloured lake a small portion of stannous oxide. Others allege that there is simply a tin-oleate produced, which is melted and

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spread over the fibre, as it were, without entering into chemical combination with the red-lake. Liechti has proved analytically that as much as 60 per cent. of the fatty acid of the soap employed, may disappear and become fixed in this manner upon the fibre.

The practical object of this operation is to give the colour the maximum purity and brilliancy of which it is capable.

401. Steiner's Process for Dyeing 500 kilos. of Turkey-red Cloth.—The main difference between this and the "emulsion process" already described, resides in the mode of applying the oil. In the process now to be described the cloth is impregnated with the requisite amount of oil at *one* operation, namely, by padding it in clear hot oil instead of in an oil-emulsion, after which it receives several passages through weak solutions of alkaline carbonate.

This method is capable of yielding a Turkey-red dye of exceptional brilliancy and intensity—better, indeed, than it is possible to obtain by the "emulsion process."

1st Operation. Bleaching. — The pieces are well washed and boiled during 2—3 hours, with water only; then boiled for 10—12 hours with 22 litres of caustic soda, 70° Tw. (Sp. Gr. 1.35), and washed: then boiled a second time for 10 hours with 16 litres of caustic soda, 70° Tw., and washed; and finally steeped for two hours in sulphuric acid, 2° Tw. (Sp. Gr. 1.01), well washed and dried.

In order to avoid tendering the fibre in the next operation by reason of traces of acid left in the cloth, it is padded with carbonate of soda solution at 4° Tw. (Sp. Gr. 1.02), and then dried.

2nd Operation. Oiling.—The cloth is padded in the open width in olive oil maintained at a constant temperature of 110° C.

Fig. 91 represents a section of the oil-padding

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machine of Messrs. Duncan Stewart and Co. It consists of a double-jacketed tank B (inside copper, outside iron) for containing the oil. It is heated by means of steam, and is provided with a series of rollers at the top and bottom. Above is a pair of heavy squeezing rollers c. The cloth is passed through as indicated in the figure,



Fig. 91.-Oil-padding Machine.

being well opened out and made free from creases before entering the oil, by means of the straining bars AAA, and afterwards loosely plaited down by the folder D.

After padding, the cloth is detached in ten-piece lengths, and hung in the drying stove, the temperature of which is raised as rapidly as possible to 70° C., and this is maintained for two hours.

3rd to 9th Operation. Liquoring.—Pad the cloth seven times in the open width through a solution of carbonate of soda at 4° Tw., and hang in the stove

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after each padding operation, maintaining the temperature in each case for two hours at 75° — 77° C.

In winter the padding liquors are made warm $(35^{\circ}-40^{\circ} \text{ C.})$, but in summer they are always cold, since if too hot, oil is stripped off the piece to an excessive and injurious degree. In the course of regular working, the liquors soon become veritable oil-emulsions, and constant



Fig. 92.-Section of Liquor-padding Machine.

oversight is necessary in order to maintain their specific gravity as constant as possible, and thus ensure ultimately a regular and satisfactory colour.

A section of the liquor-padding machine of Messrs. Duncan Stewart and Co. is shown in Fig. 92. It consists of a wooden box or tank A to hold the liquor, provided with rollers above and below. Over this are supported two pairs of heavy squeezing rollers B c and D E. At F a few straining bars serve to open out and stretch the cloth; G is the folder. The mode of passing the pieces through the machine is readily understood from the diagram.

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With regard to the stoving, it is well to bear in mind that during the first stages of drying much vapour is given off, and special attention must be given to ensure adequate ventilation. Fig. 93 is the ground plan, showing heating flues, and sectional elevation of a modern four-storeyed Turkeyred stove. A A represent ordinary coal fires situated in the basement; the hot fluegases pass first through channels made of firebrick, then through iron pipes, and finally make their exit to the chimney at B. The upper part of the stove is divided, by floors of iron-grating, into several storeys C, D, E, F, each of which is furnished with wooden framework, supporting, one above the other, two pairs of horizontal rails provided with short, upright, wooden pegs. Over these pegs one selvedge of the





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cloth is firmly hooked alternately from right to left, while the other is allowed to hang down; thus, when the stove is filled, each storey is closely packed with two tiers of cloth suspended in such a manner that the heated air from below can readily pass between each fold.

A yarn stove is similarly constructed, but in this case the ends of the rods holding the yarn are supported on horizontal rails free from pegs.

Another mode of hanging cloth, but one which is not so economical of space, is to have only one storey in the stove. Above, near the roof, are fixed a number of strong, smooth, wooden rails, on which the cloth is suspended in long folds, reaching down to within one or two feet of the iron-grating immediately above the hot flues.

In all cases efficient ventilation is secured by means of numerous side windows, which can be readily opened and closed at will.

10th Operation. Steeping.—Run the cloth in the open width through a machine consisting of a large vat divided into several compartments fitted with rollers above and below. The first compartments are filled with a solution of carbonate of soda at $\frac{1}{2}^{\circ}$ Tw. (Sp. Gr. 1.0025), and heated to 40° C. The last is filled with water only.

The cloth is then well washed, and dried in the stove at about 65° C.

11th to 14th Operation. — These operations, consisting of mordanting, dyeing, and clearing, are precisely similar to those already described for yarn-dyeing.

It may be well to state that the number of paddings in dilute soda solution (liquoring) varies according to the quantity of oil which it is desired to fix upon the cloth. Good Turkey-red contains about 10 per cent. of modified oil on the fibre.

402. "Sulphated Oil Process" for Dyeing 500 kilos. of Yarn or Cloth.—In this process the frequent repetitions of passing the fabric through oil-emulsions or

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sodium carbonate and then stoving are not used. The olive oil is replaced by an alkaline solution of sulphated olive or castor oil (see p. 234) with which only a single impregnation is necessary, followed by a steaming or stoving process.

1st Operation. Bleaching or Boiling.—This is identical with that already given in describing the previous processes for yarn and cloth.

2nd Operation. Preparing. — The dry cotton is thoroughly impregnated by "tramping" or "padding" with a cold or tepid solution of 10—15 kilos. of neutralised sulphated-oil (50 per cent.) per 100 litres of water. The excess is removed, and the cotton is merely dried in the stove, or it may be heated for 1—2 hours to 75° C.

3rd Operation. Steaming.—The prepared and dried cotton is submitted to the action of steam, 2—5 lb. pressure, during $1-1\frac{1}{2}$ hour.

4th Operation. Mordanting.—The cotton is worked and steeped for 2—4 hours in a tepid solution of commercial aluminium acetate (tin-red-liquor), or more economically in basic aluminium sulphate, $Al_2(SO_4)_2(OH)_2$, at 8° Tw. (Sp. Gr. 1.04).

After mordanting, the excess of aluminium solution is removed by wringing or hydro-extracting, the cotton is dried and then either simply well washed in cold water, or first worked for half an hour at 40°—50° C. in a chalk bath containing 20—30 grams of ground chalk per litre. A solution of sodium phosphate may replace the chalk water. Alkaline fixing-agents like ammonia and sodium carbonate are best avoided in case any of the oil-preparation should be stripped off.

5th Operation. Dyeing. — Dye with 15—20 per cent. of Alizarin (10 per cent.), with the addition of 1 per cent. of its weight, of chalk or acetate of lime. The cotton is dyed in the cold for half an hour to ensure regularity of colour, the temperature is then gradually raised to 70° C. in the course of an hour, and the dyeing is continued at this temperature till the bath is exhausted.

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The cotton is then well washed (although with highly calcareous water this is best omitted), hydro-extracted, and dried.

6th Operation. Second Preparing.—The dyed and dried cotton is again impregnated with a dilute solution of neutralised sulphated oil (namely, 50—60 grams of sulphated oil [50 per cent.] per litre), and then dried. This second preparing may also take place after the mordanting, the oil being then fixed by means of a second mordanting with a weak solution of basic aluminium sulphate, &c.

7th Operation. Second Steaming.—The dried cotton is steamed as before, for one hour.

8th and 9th Operations. First and Second Clearing. —These may be identical with operations 13 and 14, described in the "Emulsion process," although many chemists think that soap alone should be used here, and consider that the addition of stannous chloride is altogether unnecessary if not irrational.

The "sulphated-oil process" is comparatively so new, that numerous slight modifications of the process as here given are naturally tried and adopted by various dyers, and to some of these reference will now be made.

The sulphated - oil used is invariably carefully neutralised, either with caustic soda or ammonia. As a rule, ammonia is preferred, since even the addition of an excess of ammonia would have little or no injurious effect, owing to its volatility; and further, the ammonia compound of sulphated-oil is more readily decomposed on steaming than the sodium compound, and a more complete fixing of the oil results. Either sulphated castor oil or olive oil may be used. Very good results are even obtained by the simple use of a carefully made castor oil soap, which, being excessively soluble, and giving thin solutions, is well fitted to impregnate the fibre thoroughly.

In the "preparing" process, the cotton does not attract or fix any of the oil. It simply absorbs a definite



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amount of the solution, and supposing sulphated olive oil to have been used, the prepared cotton contains the sodium or ammonium compounds of oxyoleïc acid and of the glycerine-sulphuric-ethers of oxyoleïc and oxystearic acids, these being its constituent elements. It is very important to know the exact percentage of sulphated-oil contained in the solution, since it is this which determines the amount of oil and alumina ultimately fixed on the cotton, and consequently the beauty, brilliancy, and fastness of the colour.

According to Liechti and Suida, the action of the *first* steaming process is, to decompose the ammonium or sodium compounds of the ether constituent of sulphated-oil into ammonium or sodium sulphate, glycerine, oxyoleïc and oxystearic or trioxyoleïc acid, according as olive or castor oil has been employed. The other constituent (oxyoleïc or trioxyoleïc acid) remains unchanged. At the same time the steaming causes a better penetration of the fibre by these oxidised fatty acids. Sometimes the steaming at this stage is altogether omitted. The decomposition of the compound ether referred to may also be effected by heating the dye-bath to the boiling point instead of only to 70° C., the bath becomes acid, and the brilliancy of the colour is developed suddenly.

Fig. 94 represents a steaming-chest for yarn made by Messrs. Tulpin Frères, of Rouen. The hanks of cotton are suspended on square wooden rods resting on an iron skeleton-carriage or framework, and are capable of being turned during the steaming process to ensure every portion being efficiently steamed. The iron carriage is supported on wheels, so that it can be filled with yarn and then run into the chest. The steaming-chest itself consists of a wrought-iron horizontal boiler, with a movable door at one end provided with clamps. For the prevention of drops there is fixed internally and at the top a cover of sheet-copper, in such a manner as to leave a space between it and the boiler-plate. The chest is provided with a steam-gauge, safety-valve, and blow-off

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pipe. The steam enters by a perforated pipe running along the bottom of the boiler, and which is usually covered with a perforated iron plate.

Cotton cloth may be reeled and suspended on rods in a similar way, or it may be steamed in the continuous steaming-chest of Messrs. Duncan Stewart and Co., Glasgow, represented in Fig. 95. It consists of an annularshaped iron cylinder or chamber AB, in the upper part of which a series of brass radial rods c are caused to circulate slowly by means of the endless screw E driven by the engine D. The cloth (in the open width) enters the annular space through a pair of squeezing rollers at F. By an ingenious arrangement the cloth is suspended in long, loosely-hanging folds on the radial rods, is carried round the annular space, and makes it exit by a second pair of squeezing rollers at G. The chamber is constructed of boiler-plate, so that the goods can be submitted to high-pressure steam. Another form of continuous steaming-machine is that in which loose rods, supporting the cloth in a similar manner, are passed continuously by means of endless chains through a large rectangular brick chamber filled with very low-pressure steam.

If in the mordanting process the cotton was merely dried after the preparing with sulphated-oil, there are produced upon the fibre the aluminium compounds both of the ether and of the oxy- or trioxy-oleïc acid; but if it was also steamed, there is then fixed on the fibre essentially the normal aluminium compound of oxy- or trioxy-oleïc acid (Liechti & Suida).

A brighter colour is obtained by adding a small proportion of stannous chloride to the aluminium solution, or stannate of soda to the oil solution.

After mordanting and washing, a slightly basic aluminium salt remains on the fibre, its basic character being generally caused by the calcareous condition of the water. Traces of lime are also present. If, previous to washing, a warm chalk bath is used, a much more

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basic and more calcareous aluminium compound is formed.

During the dyeing process there is probably formed the Alizarin compound of the basic oxy- or trioxy-oleate of aluminium and calcium just referred to.

If there is a deficiency of oil on the fibre, the brightest shades are always obtained by dyeing at the low temperature indicated (70° C.), but otherwise the temperature may be raised to the boiling point, although there is then a tendency of a portion of the oily mordant being softened and boiled out, especially if it is in slight excess.

With the use of pure Alizarin—*i.e.*, the "blue shade of Alizarin," as it is generally called—a fiery brilliant red is not obtained; hence such as contains Isopurpurin (Anthrapurpurin)—*i.e.*, the "yellow shade of Alizarin"—is generally preferred.

The second preparing and steaming operations have for their object the neutralising of the basic compound present on the fibre at this stage. This operation of steaming after dyeing has a most remarkable effect in giving brilliancy and fastness to the colour, especially if the dyeing has been conducted at a low temperature. If 100° C. was employed, then the brightening effect has taken place to a considerable extent, if not entirely, already in the dye-bath, as above mentioned. Sometimes the second preparing is omitted, and a small quantity of neutralised sulphated-oil is added to the dye-bath instead.

The method of "clearing" described (see p. 434), in which the cotton remains stationary while the liquor circulates through it, gives very much better results than if the cotton were worked vigorously in the solution, since in this latter case much of the red-lake would be mechanically removed by friction; and the colour would look poor and weak.

403. The Action of Lime-salts in the Dye-bath. --One of the most interesting facts connected with the

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Appendix D Alizarin synthesis patent from Caro, Graebe, and Liebermann

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424 Appendix D • Alizarin synthesis patent from Caro, Graebe, and Liebermann



A.D. 1869, 25th JUNE, Nº 1936.

Preparing Coloring Matters,

- LETTERS PATENT to Heinrich Caro, of Mannheim, Grand Duchy of Bade, Chemist, Charles Graebe, of Berlin, Kingdom of Prussia, Chemist, and Charles Liebermann, of Berlin, Chemist, for the Invention of "Improvements in Preparing Coloring Matters."
- Sealed the 11th January 1870, in pursuance of an Order of the Lord Chancellor, and dated the 25th June 1869.
- **PROVISIONAL SPECIFICATION** left by the said Heinrich Caro, Charles Graebe, and Charles Liebermann at the Office of the Commissioners of Patents, with their Petition, on the 25th June 1869.
- We, HEINRICH CARO, of Mannheim, Grand Duchy of Bade, Chemist, 5 CHARLES GRAEBE, of Berlin, Kingdom of Prussia, Chemist, and CHARLES LIEBERMANN, of Berlin, Chemist, do hereby declare the nature of the said Invention for "IMPROVEMENTS IN PREPARING COLORING MATTERS," to be as follows :---

This Invention relates to improvements on an Invention for which 10 Letters Patent were granted to Charles Liebermann and Charles Graebe,

A.D. 1869.—N° 1936.

Provisional Specification.

Caro, Graebe, & Liebermann's Impts. in Preparing Coloring Matters.

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for "Improvements in Preparing Coloring Matters," dated the 18th day of December 1868, No. 3850, in which the preparation of artificial alizarine is based upon the action of caustic alkalies upon bibromanthrakinon or bichloranthrakinon. We have now discovered that a similar result may be obtained by substituting sulphuric acid for bromine 5 or chlorine in the above process. We thus obtain the sulpho-acids of anthrakinon, which by being dissolved in and heated with an excess of caustic alkali are converted into alizarine.

SPECIFICATION filed in pursuance of the conditions of the Letters Patent, and of an Order of the Lord Chancellor, by the said 10, Heinrich Caro, Charles Graebe, and Charles Liebermann in the Great Seal Patent Office on the 13th January 1870.

TO ALL TO WHOM THESE PRESENTS SHALL COME, we, HEINRICH CARO, of Mannheim, Grand Duchy of Bade, Chemist, CHARLES GRAEBE, of Berlin, in the Kingdom of Prussia, Chemist, and CHARLES 15, LIEBERMANN, of Berlin, Chemist, send greeting.

WHEREAS Her most Excellent Majesty Queen Victoria, by Her Letters Patent, bearing date the Twenty-fifth day of June, in the year of our Lord One thousand eight hundred and sixty-nine, in the thirty-third year of Her reign, did, for Herself, Her heirs and successors, give and 20, grant unto us, the said Heinrich Caro, Charles Gruebe, and Charles Liebermann, Her special license that we, the said Heinrich Caro, Charles Graebe, and Charles Liebermann, our executors, administrators, and assigns, or such others as we, the said Heinrich Caro, Charles Graebe, and Charles Liebermann, our executors, administrators, or assigns, should at 25. any time agree with, and no others, from time to time and at all times thereafter during the term therein expressed, should and lawfully might make, use, exercise, and vend, within the United Kingdom of Great Britain and Ireland, the Channel Islands, and Isle of Man, an Invention for "IMPROVEMENTS IN PREPARING COLORING MATTERS," upon the condition 30 (amongst others) that we, the said Heinrich Caro, Charles Graebe, and Charles Liebermann, our executors or administrators, by an instrument in writing under our hands and seals, or under the hand and seal of one of us, should particularly describe and ascertain the nature of the said Invention, and in what manner the same was to be performed, and 35 Specification.

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cause the same to be filed in the Great Seal Patent Office on or before the Thirteenth day of January One thousand eight hundred and seventy.

NOW KNOW YE, that we, the said Heinrich Caro, Charles Graebe, 5 and Charles Liebermann, do hereby declare the nature of our said Invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement, that is to say :---

This Invention relates to improvements on an Invention granted to 10 Charles Liebermann and Charles Graebe for improvements in preparing coloring matters, dated the Eighteenth day of November One thousand eight hundred and sixty-eight, No. 3850, in which the preparation of artificial alizarine is based upon the action of caustic alkalies upon bibromanthrakinon or bichloranthrakinon. We have now discovered that a

15 similar result may be obtained by substituting sulphuric acid for bromine or chlorine in the above process. We thus obtain the sulphoacids of anthrakinon, which by being dissolved in and heated with an excess of caustic alkali are converted into alizarine.

This Invention relates to improvements in the production of coloring 20 matters, and more especially to improvements in the method of producing what is known as artificial alizarine from anthracene, a method of producing which was described in Letters Patent granted to Charles Liebermann and Charles Graebe, dated Eighteenth December One thousand eight hundred and sixty-eight, and consisted in the 25 production of artificial alizarine by converting anthracene into either bibromanthrakinon or bichloranthrakinon, and then acting upon the same by means of an alkali and precipitating the alizarine contained in the alkaline solution by means of an acid.

In the Complete Specification of the aforesaid Letters Patent granted 30 to Charles Liebermann and Charles Graebe two different series of processes are described for obtaining the brominated or chlorinated derivatives of anthrakinon.

In the first of these processes the anthracene is submitted to the action of oxidising agents, as is well understood, and the oxidised anthracene 35 or anthrakinon is then treated with bromine or chlorine.

In the second of these processes the anthracene is first treated with bromine or chlorine, and subsequently submitted to an oxydising process

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in order that the desired compounds, videlicet, bibrom or bichlor anthrakinon, may be obtained.

In an analogous manner we now employ sulphuric acid as a substitute for the bromine or chlorine employed in the processes above referred to, and we thus obtain the sulphuric acid derivatives of 5 anthrakinon, which we call the sulpho-acids of anthrakinon.

Our Invention is carried into effect by means of either of the two processes, which we will proceed to describe.

In the one process we proceed as follows :---We take about one part by weight of anthrakinon and about three parts by weight of sulphuric 10. acid of about the specific gravity of 1.848, and introduce the same into a retort, which may be made of glass or of porcelain or of other material not easily acted upon by sulphuric acid, and the contents are then to be heated up to about two hundred and sixty degrees centigrade, and the 15 temperature is maintained until the mixture is found no longer to contain any appreciable quantity of unaltered anthrakinon. The completion of this desired operation may be ascertained or tested by withdrawing a small portion of the product from time to time and continuing the operation at the high temperature until such product upon being diluted with water is found to form a substantially perfect solution, thereby indicating 20that the anthrakinon has become either entirely or in greater part converted into the desired product. The results of this operation are then allowed to cool and are diluted with water; we then add carbonate of lime in order to neutralize and remove the excess of sulphuric acid contained in the solution; the mixture is then filtered, and to the 25 filtrate carbonate of potash or carbonate of soda, by preference in solution, is to be added until carbonate of lime is no longer precipitated; the mixture is then filtered and the clear solution is evaporated to dryness, by which means the potash or soda salts of what we call the sulpho-acids of anthrakinon are obtained and which are to be treated in the following 30 manner :--- We take about one part by weight of this product and form two to three parts by weight of solid caustic soda or potash; water may be added or not, but by preference we add as much water as is necessary to dissolve the alkali after admixture; we heat the whole in a suitable vessel, and the heating operation is continued at a temperature of 35 from about one hundred and eighty degrees to about two hundred and sixty degrees centigrade for about one hour or until a portion of the mixture is found upon withdrawing and testing it to give a solution in

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water, which being acidulated with an acid, for example sulphuric acid, will give a copious precipitate of the coloring matters. The heating operation having been found to have been continued for a sufficient time the resulting products are then dissolved in water, and
5 we either filter or decant the solution of the same, from which we precipitate the coloring matters or artificial alizarine by means of a mineral or organic acid, such, for example, as sulphuric or acetic acid. The precipitated coloring matters thus obtained are collected in a filter or otherwise, and after having been washed may be employed
10 for the purposes of dyeing and printing either in the same way as preparations of madder are now used or otherwise.

In carrying out our other process we proceed as follows :--We take about one part by weight of anthracene and about four parts by weight of sulphuric acid of specific gravity of about 1.848, and the mixture 15 being contained in a suitable vessel is heated to a temperature of about one hundred degrees centigrade, at which temperature it is to be maintained for the space of about three hours; the temperature is then to be raised to about one hundred and fifty degrees centigrade, which temperature is to be maintained for about one hour or until a small 20-portion of the product when submitted to the subsequent processes herein-after described is found to produce the desired colouring matters; we then allow the result obtained by this operation to cool, and dilute it with water, by preference in the proportion of about three times its weight. To the solution thus obtained we add for every part of an-25 thracene by weight which had been employed in the previous operation

about from two to three parts by weight of peroxide of manganese, preferring to employ an excess, and we boil the whole strongly for some time, and in order fully to ensure the desired degree of oxidation the mixture may be subsequently concentrated and by preference be

30 evaporated to dryness and the heat be continued until a small portion of the oxidised product when submitted to the subsequent processes herein-after described will produce the desired coloring matters. We then neutralise and remove the sulphuric acid contained in this mixture, and at the same time precipitate any oxides of manganese which may

35 be held in solution by adding an excess of caustic lime, which we use by preference in the form of milk of lime, and we add the same until the mixture has an alkaline reaction. We then filter and add to the filtrate carbonate of potash or soda until there is no further precipitation of carbonate of lime. The solution is then filtered and

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evaporated to dryness, and we thus obtain the potash or soda salts of what we call the sulpho-aeids of anthrakinon.

In effecting the conversion of the oxydised products thus obtained into coloring matters or into what we call artificial alizarine, we proceed as follows :---We take one part by weight of this product and from 5 two to three parts by weight of solid caustic soda or potash, and water may be added or not, but by preference we add as much water as is necessary to dissolve the alkali. After admixture we heat the whole in a suitable vessel and continue the heating operation at a temperature from about one hundred and eighty degrees to about two 10 hundred and sixty degrees centigrade for about one hour, or until a portion of the mixture is found to give solution in water which upon acidulation with an acid, for example sulphuric acid, is found to give a copious precipitate of the coloring matters. The heating operation having been found to have been continued for a sufficient time 15 then dissolve the product in water, and either filter or decant the solution of the same, from which we precipitate the coloring matters or artificial alizarine by means of a mineral or organic acid, such, for example, as sulphuric or acetic acid. The precipitated coloring matters thus obtained are collected on a filter or otherwise, and after having 20 been washed may be employed for the purposes of dyeing and printing either in the same way as preparations of madder are now used or otherwise. Instead of acting upon anthracene by means of sulphuric acid of the density before mentioned fuming sulphuric acid may be employed. but we prefer to use the ordinary acid, as before described. 25

In order to effect the process of oxidation before referred to other oxidising agents may be used in place of the peroxide of manganese before mentioned, such, for example, as peroxide of lead, or chromic, nitric, or other acids capable of effecting the desired oxidation may be employed. If the oxidising agent be a soluble one, such, for instance, 30 as chromic acid, any excess of the oxidising agent that may have been employed should be removed or reduced before proceeding with the subsequent operation. Thus, for example, had chromic acid been used in excess, sulphurous acid may be passed through the product before adding the lime. In the case of the employment of nitric acid 35 the oxidised mixture should be heated until the greater proportion of the nitric acid has been evaporated, and until the sulphuric acid has become so concentrated that it commences to volatilise.

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Caro, Graebe	& Liebermann's Imp	ots. in Preparing Cold	oring Matters.
Although w and of caustic sulphuric acid treatment of an it will be under and which will processes may	e have mentioned the lime for the purpose of existing in the solution thrakinon and from a erstood that other back l not in any way be be substituted for the	e employment of car of effecting the neutra on of the products obtanthracene, as herein-b uses which will neut injurious in any of same.	bonate of lime lization of the ained from the efore described, ralize the acid the subsequent
Having now	described our Inve	ntion, and methods	we employ in
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Secondly. The thracene to the obtained, heating precipitating the	e manufacture of c action of sulphuric and ag such oxydised prod ne coloring matters t	oloring matters by a acid, oxydising the p luct with an alkali, an herefrom by means	submitting an- roduct thereby d subsequently of an acid as
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Appendix F Oil analysis report from University of Pisa



GC/MS analysis of free fatty acids and HPLC/MS profiling of triglycerides

Dr. Ilaria Degano, Dr. Jacopo La Nasa

SCIBEC Dipartimento di Chimica e Chimica Industriale Università di Pisa http://www.dcci.unipi.it/scibec/





Materials and methods

Gas chromatography/mass spectrometry

Instrumentation

GC/MS instrumentation consisted of an Agilent Technologies 6890N Gas Chromatograph coupled with a 5973 Mass Selective Detector single-quadrupole mass spectrometer.

Samples were injected in splitless mode at 280 °C. GC separation was performed on a fused silica capillary column HP-5MS (J&W Scientific, Agilent Technologies, US, stationary phase 5% diphenyl-95% dimethyl-polysiloxane, 30 m lenght, 0.25 mm i.d., 0.25 µm film thickness). Chromatographic conditions were: initial temperature 80°C, 2 min isothermal, 10 °C/min up to 200°C, 4 min isothermal for the separation of unsaturated C18 fatty acids and their isomers, 6 °C/min up to 280°C, 40 minutes isothermal. The helium (purity 99.9995%) gas flow was set in constant flow mode at 1.2 mL/min. MS parameters: electron impact ionization (EI, 70 eV) in positive mode; ion source temperature 230°C; scan range 50-700 m/z; interface temperature 280°C. The injection volume was 2 µL. Peak assignment was based on a comparison with library mass spectra (NIST 1.7, WILEY275).

Sample pretreatment

For the analysis 1-3 mg of sample were added with 1 mL of distilled water and acidified with HCl 6 M. Thus, the free fatty acids are solubilized. In order to maximize the extraction yield, two solvents were used: the possibly present neutral compounds were extracted with n-hexane; the residual solution was acidified with hydrochloric acid (6 M) and then carboxylic acids were extracted with diethyl ether (400 μ L, three times). The two extracts (neutral + acid fraction) were combined for GC/MS analysis in order to analyze them in a single chromatographic run, evaporated to dryness under nitrogen stream and subjected to derivatization with 20 μ L of *N*,*O*-bistrimethylsilyltrifluoroacetamide (BSTFA), 150 μ L of iso-octane and 5 μ L of tridecanoic acid (standard for derivatization) solution at 60 °C for 30 min. 5 μ L of hexadecane (standard for injection) solution were added just before injection.



A C

Quantitative analysis

The GC/MS quantitative analysis for all the samples was performed using calibration curves calculated on the basis of the extract ion chromatograms and corrected with the derivatization standard (tridecanoic acid). The selected ions for the SIM acquisition were: lauric acid m/z 117;257, suberic acid m/z 169;303, azelaic acid m/z 149;317, myristic acid m/z 117;285, sebacic acid m/z 149;331, palmitic acid m/z 117;3131, oleic acid m/z 117;339, m/z stearic acid 117;341. The quantitative analysis for ricinoleic acid was performed on the basis of the stearic acid calibration curve, using as selected ions m/z 187 and 328.

High performance liquid chromatography/mass spectrometry

HPLC-ESI-Q-ToF analyses were carried out using a 1200 Infinity HPLC, coupled with a Quadrupole-Time of Flight tandem mass spectrometer 6530 Infinity Q-ToF detector by a Jet Stream ESI interface (Agilent Technologies, U.S.A.).

The HPLC conditions were: Poroshell 120 EC-C18 column (3.0 mm x 5.0 mm, 2.7 μ m particle size) with a Zorbax eclipse plus C-18 guard column (4.6 mm x 12.5 mm, 5 micron μ m particle size); a flow rate of 0.3 mL/min, an injection volume of 1 μ L and a column temperature of 45 °C. Separation was achieved using a gradient of methanol (eluent A) and iso-propanol (eluent B). The elution gradient was programmed as follows: 90% A for 5 minutes, followed by a linear gradient to 90% B in 25 min, then held for 5 min. Re-equilibration time for each analysis was 10 min.

The ESI operating conditions were: drying gas (N2, purity >98%): 350 °C and 10 L/min; capillary voltage 4.5 KV; nebulizer gas 35 psig; sheath gas (N2, purity >98%): 375 °C and 11 L/min.

High resolution MS and MS/MS spectra were acquired in positive mode in the range 100-1700 m/z. The fragmentor was kept at 200 V, nozzle voltage 1000 V, skimmer 65 V, octapole RF 750 V, and the collision energy for the MS/MS experiments was set at 50 V. The collision gas was nitrogen (purity 99.999%). The data were collected by auto MS/MS acquisition with an MS scan rate of 1.03 spectra/sec and an MS/MS scan rate of 1.05 spectra/sec; only one precursor was acquired per cycle (relative threshold 0.010%).



Results and discussion

Gas Chromatography/Mass Spectrometry

In the following table the fatty acid % profiles and the total amount of free fatty acids with respect to the sample weight for each analyzed sample are reported:

	TRO-DB	TRO- Sigma	Sulfated castor	Castor oil	Sulfated oleates	Sodium oleates	Olive oil	SDC
Lauric acid	9.0	14.1	1.3	0.0	2.5	0.0	13.7	21.8
Suberic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Azelaic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	24.5
Myristic acid	7.4	12.4	1.5	0.0	9.1	0.0	6.8	0.0
Sebacic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Palmitic acid	20.2	1.2	30.2	31.5	65.0	0.0	46.8	16.4
Oleic acid	14.5	25.0	39.1	0.0	4.7	100.0	19.3	0.0
Stearic acid	24.1	1.6	27.8	27.7	18.8	0.0	13.4	7.3
Ricinoleic acid	24.8	45.7	0.0	40.8	0.0	0.0	0.0	29.9
Free Fatty acid % (W/W)	6.4	4.1	42.6	1.5	54.9	48.3	3.4	1.9



As an example, the chromatogram obtained for sample TRO-DB is reported in Figure 1:



derivates

Summarizing:

The Turkish Red Oils (Sigma and DB) were characterized by the presence of free fatty acids in the range 4.1-6.4%. Both samples showed the presence of free ricinoleic acid in the free fatty acid fraction of the material. This results confirm that this material was originally prepared from castor oil, according to the traditional recipe.



Sulfated castor oil was characterized by the presence of an high amount of free fatty acids (42.6%). The analytical results suggested that the castor oil treated with sulphuric acid undergoes hydrolysis and dehydration processes, leading to the formation of oleic acid from ricinoleic acid.

Castor and olive oils were characterized by the presence of free fatty acids in the range 1.5-3.4%, which is typical of fresh oils. Their TAGs profiles are consistent with those reported in the literature.

"Sulfated oleates" sample was characterized by the presence of an high amount of free fatty acids (54.9%). The main peak observed in the chromatogram is due to palmitic acid, while oleic acid represents less than 5% of the whole mixture. The fatty acid profile of this sample is extremely aspecific and thus its interpretation does not allow us to unambiguously identify the origin of the lipid material used for its production.

"Sodium oleates" sample was characterized by the presence of oleic acid only. If calculated as percentage of the free fatty acid on the sample weight, it corresponds to less than the 50% of the sample weight. If we calculate it as equivalent moles of sodium carboxylate, it accounts for the 52% of the sample. This low percentage can derive either from a lack of purity of the original sample or a low extraction yield due to a not efficient conversion of the sodium salts to the free fatty acids using hydrochloric acid in the adopted conditions.

The sample from the Society of Dyers and Colourists was characterized by a chemical composition similar to those obtained for the Turkish Red Oils. Moreover, the sample was characterized by the presence of azelaic acid. Dicarboxylic acids generally derive from the oxidation processes undergone by the unsaturated fatty acids originally present in the samples. Thus, this finding is consistent with the age of the sample, which may have undergone oxidation processes.



High performance liquid chromatography/mass spectrometry

In the following table the triglycerides profiles for the analyzed samples are reported:

	TRO-DB	TRO-Sigma	SDC	Sulfated	Castor oil	Olive oil
RnC _{18.0H} C _{18.0H}	2.6	24.7	4.4	15.8	-	-
РС _{18:1.0Н} С _{18:1.0Н}	2.2	-	-	-	-	-
OxTAGs (m/Z 881.7)	15.7	-	-	-	-	-
RnRnRn	50.5	9.2	50.9	59.9	74.6	-
RnRnL	13.5	12.1	11.1	12.1	8.2	-
RnRnO	5.8	16.3	13.0	4.3	8.5	-
RnRnS	2.2	13.2	16.0	4.2	7.5	-
RnLL	6.0	9.0	1.3	1.1	0.4	-
RnLO	0.8	6.8	1.1	1.6	0.4	-
RnLS	0.5	4.9	1.1	1.1	0.3	-
С _{18:20Н} ОР	-	2.9	-	-	-	-
С _{18:10Н} ОР	-	0.9	-	-	-	-
LLP	-	-	-	-	-	2.5
LLO	-	-	-	-	-	4.6
PLP	-	-	-	-	-	2.8
LOP	-	-	-	-	-	12.1
OOL	-	-	-	-	-	11.2
РОР	-	-	-	-	-	5.2
ООР	-	-	-	-	-	19.9
000	-	-	-	-	-	30.0
OSP	-	-	-	-	-	3.5
oos	-	-	-	-	-	8.2

Figure 2 reports the amount of extracted triglycerides in the analyzed samples: the results were obtained by normalization of the sum of the areas of all the species towards the weight sample and the dilution factor of the solution injected in the HPLC system.

As expected, the total amounts of triglycerides identified in the oils is higher than those obtained for the historical sample and for the oils treated with sulfuric acid.





Figure 2 – Amount of soluble triglycerides in the analyzed samples



Conclusions

The combination of the analytical results obtained with GC/MS and HPLC/MS allowed us to evaluate the hydrolysis degree of the different samples, in particular:

- comparing the Castor oil and the sulfated castor oil, a drastic decrease in the amount of triglycerides and an increase in the amount of fatty acids in the soluble fraction of the sample can be observed (Figure 3);
- the "olive oil" sample has free fatty acids and TAGs profiles consistent with a fresh olive oil;
- the TRO-DB, TRO-Sigma and the historical sample SDC contain a low amount of both soluble triglycerides and free fatty acids, suggesting that these materials were characterized by an higher polymerization degree than the untreated oils.



Figure 3 – Normalized amount (%) of soluble triglycerides and free fatty acids in the analyzed samples



References

M. P. Colombini, A. Andreotti, I. Bonaduce, F. Modugno, E. Ribechini. Analytical strategies for characterizing organic paint media using gas chromatography/mass spectrometry. Accounts of Chemical Research 2010 (43) 715-727

J. La Nasa, I. Degano, E. Ghelardi, F. Modugno, M.P. Colombini, "Core shell stationary phases for a novel separation of triglycerides in plant oils by high performance liquid chromatography with electrospray-quadrupole-time of flight mass spectrometer", Journal of Chromatography A, 2013, vol.1308, p 114-124












A05













Appendix H Historical Turkey red samples



Persoz #92: Cotton oiled four times.

Persoz, Jean-François. 1846. *Traité théorique et pratique de l'impression des tissus*. Vol. 3, p. 192. Paris: Victor Masson. University of Glasgow Special Collections.



Persoz #93: Cotton oiled and degreased.

Persoz, Jean-François. 1846. *Traité théorique et pratique de l'impression des tissus*. Vol. 3, p. 193. Paris: Victor Masson. University of Glasgow Special Collections.



Persoz #95: Cotton oiled, mordanted, and dyed once with madder.

Persoz, Jean-François. 1846. *Traité théorique et pratique de l'impression des tissus*. Vol. 3, p. 195. Paris: Victor Masson. University of Glasgow Special Collections.



Persoz #96: Cotton oiled, mordanted, dyed once with madder and mordanted for a second time. Original tissue cover shown in this sample.

Persoz, Jean-François. 1846. *Traité théorique et pratique de l'impression des tissus*. Vol. 3, p. 195. Paris: Victor Masson. University of Glasgow Special Collections.



Persoz #97: Cotton oiled, mordanted twice, and dyed twice with madder.

Persoz, Jean-François. 1846. *Traité théorique et pratique de l'impression des tissus*. Vol. 3, p.196. Paris: Victor Masson. University of Glasgow Special Collections.

Persoz #98: Cotton oiled and dyed with madder, then cleared once.

Persoz, Jean-François. 1846. Traité théorique et pratique de l'impression des tissus. Vol.
3, p. 196. Paris: Victor Masson. University of Glasgow Special Collections.





Persoz, Jean-François. 1846. *Traité théorique et pratique de l'impression des tissus*. Vol. 3, p. 197. Paris: Victor Masson. University of Glasgow Special Collections.



Persoz #101: Cotton oiled, dyed with madder, cleared, and boiled with bran.

Persoz, Jean-François. 1846. Traité théorique et pratique de l'impression des tissus. Vol.
3, p. 198. Paris: Victor Masson. University of Glasgow Special Collections.



Turkey red dyed with madder.

Crookes, William. 1874. A Practical Handbook of Dyeing and Calico-Printing. p. 326. London: Longmans, Green, and Co. University of Glasgow Special Collections. M1



Turkey red dyed with synthetic alizarin from Perkin.

Crookes, William. 1874. A Practical Handbook of Dyeing and Calico-Printing. p. 326. London: Longmans, Green, and Co. University of Glasgow Special Collections. M2



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Turkey red, #37 'before steaming' and #38 'after steaming'.

Knecht, Edmund, Christopher Rawson, and Richard Loewenthal. 1893. *A Manual of Dyeing*. Vol. 3. London: Charles Griffin & Company, Limited. Anita Quye private collection.



Turkey red, #37 'before steaming' and #38 'after steaming'.

Knecht, Edmund, Christopher Rawson, and Richard Loewenthal. 1893. *A Manual of Dyeing*. Vol. 3. London: Charles Griffin University of Glasgow Special Collections.



Turkey red, 'large pattern', late 19th c.

Centre for Textile Conservation Karen Finch Reference Collection. Gift from Dr Norman Tennent.

Below: Turkey red, 'small pattern', late 19th c.

Centre for Textile Conservation Karen Finch Reference Collection. Gift from Dr Norman Tennent. C98





Turkey red dyed with synthetic alizarin.

Perkin, William Henry. 1870. "XVI.-on Artificial Alizarin." Journal of the Chemical Society 23: 133-43. University of Glasgow Chemistry Library. M3

Turkey red dyed with synthetic alizarin.

Perkin, William Henry. 1870. "XVI.-on Artificial Alizarin." Journal of the Chemical Society 23: 133-43. University of Glasgow Special Collections. M4





Above: Turkey red dyed with synthetic alizarin.

Perkin, William Henry. 1873. "XV.on Anthrapurpurin." Journal of the Chemical Society 26: 425-433. University of Glasgow Chemistry Library. M5



Above: Turkey red dyed with synthetic anthrapurpurin.

Perkin, William Henry. 1873. "XV.on Anthrapurpurin." Journal of the Chemical Society 26: 425-433. University of Glasgow Chemistry Library. M6



'No. 231 Rouge d'anthrapurpurine avivé'

Dépierre, Joseph. 1892. Traité de la teinture et de l'impression des matières colorantes artificielles. 2^{me} partie, l'alizarine artificielle et ses dérivés. Vol. 2. Paris: Baudry et Cie. Susan Kay-Williams private collection. M7 UGD 13/8/2 #11, 1856-1861.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/2.



UGD 13/8/2 #12, 1856-1861.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/2.



UGD 13/8/2 #13 '349', 1856.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/2.



UGD 13/8/4 #11 '3213', 1857-1863.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/4.



UGD 13/8/4 #12, 1857-1863.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/4.





UGD 13/8/4 #13, 1857-1863.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/4.



UGD 13/8/6 #11, 1886-1888.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/6.



UGD 13/8/6 #12, 1886-1888.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/6.



UGD 13/8/6 #13, 1886-1888.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/6.



Townson Textile B, mid-20th c.

Centre for Textile Conservation Karen Finch Reference Collection C100



UGD 13/8/7 #11, 1887.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/7.



UGD 13/8/7 #13, 1887.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/7.



UGD 13/8/7 #12, 1887.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/7.



Townson Textile A, mid-20th c.

Centre for Textile Conservation Karen Finch Reference Collection C99



UGD 13/8/1 #1 "Order 484", mid-19th c.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UG 13/8/1. C1



UGD 13/8/1 #4 "Order 506", mid-19th c.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/1. C3



UGD 13/8/1 #3 "Order 502", mid-19th c.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/1. C2



UGD 13/8/2 #1 "Order 313", 1858.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/2. C4 UGD 13/8/2 #2 "Order 347", 1856.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/2. C5



UGD 13/8/2 #4 "Order 401", 1859.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/2. C6



UGD 13/8/3 #1 "Order 19", 1857.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/3. C7



UGD 13/8/3 #2 "Order 115", 1857.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/3. C8



UGD 13/8/3 #3 "Order 117", 1857.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/3. C9





UGD 13/8/3 #6 "Order 417", 1857.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/3. C10



UGD 13/8/3 #7 "Order 480", 1857.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/3. C11



UGD 13/8/3 #9 "Order 604", 1857.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/3. C12



UGD 13/8/3 #10 "Order 6", 1858.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/3. C13



UGD 13/8/3 #11 "Order 366", 1858.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/3. C14



UGD 13/8/4 #1 "Order 3202", 1857-1863.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/4. C15

UGD 13/8/4 #2, 1857-1863.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/4. C16



UGD 13/8/4 #4 , 1857-1863.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/4. C17



UGD 13/8/5 #7 "Order 2459", mid-19th c.





UGD 13/8/5 #8 "Order 2489", mid-19th c.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/5. C22



UGD 13/8/5 #1 "Order 2217", mid-19th c.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/5. C18



UGD 13/8/5 #4 "Order 2255", mid-19th c.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/5. C20



UGD 13/8/5 #3 "Order 2237", mid-19th c.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/5. C19



UGD 13/8/5 #9 "Order 2647", mid-19th c.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/5. C23 UGD 13/8/5 #10 "Order 2765", mid-19th c.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/5. C24



UGD 13/8/6 #1, 1887.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/6. C27





UGD 13/8/6 #3, 1887.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/6. C29



UGD 13/8/7 #1 "202", 1887.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/7. C31



UGD 13/8/5 #11 "Order 2872", mid-19th c.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/5. C25



UGD 13/8/5 #12, mid-19th c.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/5. C26



UGD 13/8/6 #2, 1887.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/6. C28



UGD 13/8/6 #4, 1888.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/6. C30



UGD 13/8/7 #2 "256", 1887.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/7. C32



UGD 13/8/7 #4 "714", 1887.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/7. C34



UGD 13/8/7 #3 "283", 1887.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/7. C33



UGD 13/8/7 #5 "811", 1887.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/7. C35



UGD 13/8/8 #1 "Order 969", 1878.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/8. C36



UGD 13/8/8 #2 "Order 997", 1878.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/8. C37



UGD 13/8/8 #4 "Order 1056", 1878.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/8. C38



UGD 13/8/8 #5 "Order 297", 1878.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/8. C39

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UGD 13/8/8 #6 "Order 927", 1878

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/8. C40



UGD 13/8/8 #8 "Order 350", 1878

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/8. C42



UGD 13/8/8 #7 "Order 904", 1878

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/8. C41



UGD 13/8/9 #4, ca.1900.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/9. C46

UGD 13/8/9 #1, 1899



University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/9. C43



UGD 13/8/9 #2, ca. 1900.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/9. C44



UGD 13/8/9 #3, ca. 1900.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/9. C45



UGD 13/8/9 #5, ca. 1900.

University of Glasgow Archive Services, Records of United Turkey Red Co Ltd, GB248 UGD 13/8/9. C47



T.133(1)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C67



T.133-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C66



T.133(4)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C70



T.133(5)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C71



T.133(3)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C69



T.133(2)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C68



T.133(6)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C72



T.133(10)-1978, 1850-1870. Chhotalal Ravicarandas & Co Image coutesy of the V&A. C76



T.133(7)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C73



T.133(8)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C74



T.133(9)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C75



T.133(13)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C79



T.133(15)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C81



T.133(18)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C84





T.133(17)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C83



Left: T.133(11)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C77



T.133(12)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C78



T.133(16)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C82

T.133(19)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C85

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T.133(14)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C80



T.133(21)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C87



T.133(23)-1978, 1860-1880. United Turkey Red. Image coutesy of the V&A. C89



T.133(22)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C88



T.133(20)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C86



T.133(24)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C90



T.133(25)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C91



T.133(26)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C92

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T.133(27)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C93



T.133(28)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C94



T.133(29)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C95



T.133(30)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C96



T.133(31)-1978, 1860-1880. United Turkey Red Image coutesy of the V&A. C97



T.74-1988, 1825-1830. England Image coutesy of the V&A. C63/C64



T.344-1919, 1820-1850. Marseilles, France Image coutesy of the V&A. C62



T.12B-1984, 1830-1890. Image coutesy of the V&A. C65


T.8-1978 Pattern 40 p.87, 1830-1840. Foxhill Bank Printworks, England Image coutesy of the V&A. C60



T.8-1978 Turkey red p. 89, 1830-1840 Foxhill Bank Printworks, England Image coutesy of the V&A. C61



1797-1899, ca. 1890. Switzerland Image coutesy of the V&A. C48



1798-1899, ca. 1890. Switzerland Image coutesy of the V&A. C49



1799-1899, ca. 1890. Switzerland Image coutesy of the V&A. C50



1800-1899, ca. 1844-1899. Germany Image coutesy of the V&A. C51



1801-1899, ca. 1898. Germany Image coutesy of the V&A. C52



1803-1899, ca. 1880-1899. Germany Image coutesy of the V&A. C54



1802-1899, ca. 1880-1900. Germany Image coutesy of the V&A. C53



1804-1899, ca. 1880-1899. Germany Image coutesy of the V&A. C55



1805-1899, ca. 1887-1899. Italy (?) Image coutesy of the V&A. C56

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1807-1899, ca. 1888-1899. Germany Image coutesy of the V&A. C57



T.4-1994, ca. 1871 Germany Image coutesy of the V&A. C58



T.5-1994, ca. 1871 Germany Image coutesy of the V&A. C59

Appendix I Tables of unknown relative amounts from UHPLC analysis

This section provides tables of relative amounts for the main unknowns recurring in the UHPLC analysis in Chapter 7. The analytical conditions and samples are described in Section 7.1. The unknowns described in this table are called false anthrapurpurin, Unk. 1, Unk. 2 248 nm, Unk. 2 277 nm, Unk 3., Unk. 4 258 nm, Unk. 4 277 nm, Unk. 5, Unk. 6, Unk. 7. Unknowns 2 and 4 are so named because the pairs have similar retention time (R_t) values but different UV-Vis spectra. The order of numbering was based on when a pattern of occurrence was identified and does not correspond to significance or order of elution. All tables include values for anthrapurpurin, alizarin, flavopurpurin, and purpurin, unless there is none in any of the samples.

The undiagnosed internal seal leak discussed in Chapter 7 caused shifting R_t values for peaks that complicated identification. All unknowns in this work are tentatively identified by the R_t window and UV-Vis spectrum; confirmation by further analysis with more precise chromatography and mass spectrometry is required to draw stronger conclusions. The occurrence of unknowns is not discussed in detail here since it is speculative at this point in the analysis.

False anthrapurpurin - Rt ca. 19.8 minutes

False anthrapurpurin appears primarily in madder samples and the garancine (R9), with two samples from V&A Turkey red (C58 and C59) as the only textiles with the compound. Based on its co-elution with anthrapurpurin, it may be related.



Figure I-1 UV-Vis spectrum of false anthrapurpurin from analysis in Chapter 7.



Figure I-2 UV-Vis spectrum of anthrapurpurin from analysis in Chapter 7.



Figure I-3 Chromatogram of garancine (R9) at 430 nm. Note co-eluting false anthrapurpurin and purpurin peaks.

ID	Sample	% False anthrapurp.	% Anthrap.	% Alizarin	% Purp.
C58	T.4-1992	1.18	0	60.64	24.95
C59	T.5-1992	0.6	0	55.33	30.55
D4	Turkey red, madder	0.23	0	80.9	13.04
D12	Silk with madder	1.01	0	44.35	9.28
R1	French madder	5.91	0	22.36	0
R2	English madder	3.28	0	46.04	11.13
R3	Iranian madder	1.39	0	6.78	0.65
R4	Turkish madder	11.45	0	36.06	3.04
R5	Rubia cordifolia	1.25	0	4.21	0
R6	Dutch madder	2.81	0	28.65	3.25
R7	Russian madder	2.41	0	60.92	7.05
R8	Silesian madder	1.86	0	13.96	5.22
R9	Garancine	3.17*	0.33*	67.06	14.16

Table 15 Relative amounts of components in samples containing 'false anthrapurpurin' at 430 nm.

*Deconvoluted by Empower 3 ApexTrack integration. No values for flavopurpurin.

Unknown 7 - Rt ca. 19.2 minutes



Figure I-4 UV-Vis spectrum for Unknown 7 from analysis in Chapter 7.



Figure I-5 Chromatogram of UGD 13/8/5 #7 (C21) at 430 nm.

	Sample	%	%	%	%	%
U	Sample	Unk 7	Anthrap.	Alizarin	Flavop.	Purp.
C4	UGD 13/8/2 #1	0.29	0	85.32	0	11.61
C5	UGD 13/8/2 #2	0.33	0.17	85.25	0	8.49
C7	UGD 13/8/3 #1	0.38	0.39	74.17	0	24.61
C9	UGD 13/8/3 #3	0.53	0	88.91	0	8.65
C10	UGD 13/8/3 #6	0.42	0.42	77.71	0	16.89
C11	UGD 13/8/3 #7	0.58	0	85.59	0	13.16
C12	UGD 13/8/3 #9	0.77	0.49	72.23	0	26.51
C13	UGD 13/8/3 #10	0.75	0	85.83	0	13.42
C16	UGD 13/8/4 #2	0.1	5.51	84.86*	7.22*	0
C17	UGD 13/8/4 #4	0.41	0	68.23	0	30.73
C18	UGD 13/8/5 #1	0.46	0.34	76.01	0	21.96
C21	UGD 13/8/5 #7	0.2	9.26	68.37*	5.28*	13.37
C32	UGD 13/8/7 #2	0.11	4.79	94.84	0	0
C62	T.344-1919	0.54	0	92.75	0	4.86
C64	T.74-1988 (lining)	0.51	0	91.47	0	3.81
C65	T.12B-1984	0.32	0.28	89.35	0	5.45
C66	T.133-1976	0.33	0	73.22	0	25.88
C67	T.133(1)-1976	0.39	0.16	83.15	0	15.73
C68	T.133(2)-1976	0.47	0.2	68.15	0	30.83
C69	T.133(3)-1976	0.48	0.22	74.65	0	24.01
C71	T.133(5)-1976	0.5	0.2	69.66	0	29.32
C72	T.133(6)-1976	0.43	0	75.28	0	23.55
C73	T.133(7)-1976	0.29	0.19	77.27	0	22.06
C74	T.133(8)-1976	0.53	0	81.4	0	15.96
C75	T.133(9)-1976	0.52	0	76.67	0	22.09
C77	T.133(11)-1976	0.68	0	76.61	0	22.17
C78	T.133(12)-1976	0.41	0.26	72.13	0	26.61
C79	T.133(13)-1976	0.32	0	80.06	0	17.63
C82	T.133(16)-1976	0.54	0.21	65.59	0	33.43
C83	T.133(17)-1976	0.3	0	80.45	0	18.77
C84	T.133(18)-1976	0.47	0	76.2	0	22.71
C85	T.133(19)-1976	0.07	8.94	77.28*	10.62*	0
C86	T.133(20)-1976	0.58	0	76.38	0	22.17
C87	T.133(21)-1976	0.37	0	77.84	0	21.56
C88	T.133(22)-1976	0.11	13.01	66.86*	12.2*	4.62

	Samplo	%	%	%	%	%
	Sample	Unk 7	Anthrap.	Alizarin	Flavop.	Purp.
C89	T.133(23)-1976	0.28	0.19	70.7	0	27.82
C91	T.133(25)-1976	0.57	0.13	72.1	0	26.09
C92	T.133(26)-1976	0.61	0	72.86	0	25.77
C93	T.133(27)-1976	0.41	0	78.12	0	21.04
C94	T.133(28)-1976	0.42	0.19	74.67	0	23.75
C95	T.133(29)-1976	0.48	0.24	74.8	0	23.15
C96	T.133(30)-1976	0.36	0.37	66.35	0	31.95
C97	T.133(31)-1976	0.34	0.26	68.9	0	29.92
D4	Turkey red,					
	madder	3.86	0	80.9	0	13.04
D5	Turkey red,				-	
	madder #1	0.82	0.37	82.09	0	15.67
D6	Turkey red,					
	madder #2	1.81	0.29	/2.03	0	22.7
D7	Turkey red,					
07	madder #3	0.57	0.24	86.48	0	12.38
D12	Silk with madder	1.17	0	44.35	0	9.28
R2	English madder	0.6	0	46.04	0	11.13
R6	Dutch madder	0.93	0	28.65	0	3.25
R7	Russian madder	1.02	0	60.92	0	7.05
R8	Silesian madder	0.43	0	13.96	0	5.22
R9	Garancine	3.53	0.33	67.06	0	14.16

Table 16 Relative amounts of components in samples containing Unknown 7 at 430 nm. *Deconvoluted by Empower 3 ApexTrack integration.



Unknown 1 248 nm - Rt ca. 21.5 minutes

Figure I-6 UV-Vis spectrum of Unknown 1 248 nm from analysis in Chapter 7.



Figure I-7 Chromatogram of T.133(19)-1976 (C85) at 430 nm.

ID	Sample	% Unk 1 248 nm	% Anthrap.	% Alizarin	% Flavop.	% Purp.
C8	UGD 13/8/3 #2	0.6	0	86.52	0	11.13
С9	UGD 13/8/3 #3	1.06	0	88.91	0	8.65
C16	UGD 13/8/4 #2	0.18	5.51	84.86*	7.22*	0
C17	UGD 13/8/4 #4	0.62	0	68.23	0	30.73
C50	1799-1899	0.29	0	83.9	0	13.98
C60	T.8-1978 p.87 Pattern 40	1.09	0	95.56	0	2.19
C61	T.8-1978 p.89 Turkey red	1.2	0	96.3	0	1.63
C62	T.344-1919	1.85	0	92.75	0	4.86
C63	T.74-1988 (dress)	1.99	0	85.64	0	1.79
C64	T.74-1988 (lining)	2.69	0	91.47	0	3.81
C65	T.12B-1984	0.83	0.28	89.35	0	5.45
C67	T.133(1)-1976	0.17	0.16	83.15	0	15.73
C82	T.133(16)-1976	0.09	0.21	65.59	0	33.43
C84	T.133(18)-1976	0.18	0	76.2	0	22.71
C85	T.133(19)-1976	2.56	8.94	77.28*	10.62*	0
C86	T.133(20)-1976	0.46	0	76.38	0	22.17
C89	T.133(23)-1976	0.34	0.19	70.7	0	27.82
C90	T.133(24)-1976	1.01	0	74.93	0	23.62
C95	T.133(29)-1976	0.87	0.24	74.8	0	23.15
C96	T.133(30)-1976	0.48	0.37	66.35	0	31.95
R2	English madder	2.05	0	46.04	0	11.13
R4	Turkish madder	18.23	0	36.06	0	3.04
R9	Garancine	3.12	0.33	67.06	0	14.16

Table 17 Relative amounts of components in samples containing Unknown 1 with UV-Vis absorbance maxima at 248 and 430 nm at 430 nm.

*Deconvoluted by Empower 3 ApexTrack integration.





Figure I-8 UV-Vis spectrum of Unknown 1 274 nm from analysis in Chapter 7.



Figure I-9 Chromatogram of UGD 13/8/5 #10 (C24) at 430 nm.

п	Cample	% Unk 1	%	%	%	%
טו	Sample	274 nm	Anthrap.	Alizarin	Flavop.	Purp.
C15	UGD 13/8/4 #1	0.91	7.14	78.82*	7.88*	0
C21	UGD 13/8/5 #7	1.1	9.26	68.37*	5.28*	13.37
C22	UGD 13/8/5 #8	2.75	17.71	65.43*	5.90*	7.62
C23	UGD 13/8/5 #9	2.41	20.07	61.94*	5.87*	9.03
C24	UGD 13/8/5 #10	3.49	24.81	56.07*	8.21*	7.43
C25	UGD 13/8/5 #11	2.11	13.79	63.78*	4.29*	14.14
C27	UGD 13/8/6 #1	0.65	3.53	88.39*	6.01*	0
C28	UGD 13/8/6 #2	1.8	10	78.11*	8.99*	0
C29	UGD 13/8/6 #3	1.83	6.42	83.08*	8.06*	0
C30	UGD 13/8/6 #4	1.6	13	79.20*	5.54*	0
C31	UGD 13/8/7 #1	0.88	26.05	65.06*	8.01*	0
C33	UGD 13/8/7 #3	1.88	22.62	62.4*	12.57*	0
C34	UGD 13/8/7 #4	0.7	5.68	91.49	0	0
C35	UGD 13/8/7 #5	0.26	7.69	92.05	0	0
C36	UGD 13/8/8 #1	0.46	4.45	86.18*	7.75*	0
C37	UGD 13/8/8 #2	1.99	4.17	85.30*	8.54*	0

п	Sample	% Unk 1	%	%	%	%
שו	Sample	274 nm	Anthrap.	Alizarin	Flavop.	Purp.
C38	UGD 13/8/8 #4	2.32	6.4	82.74*	8.55*	0
C39	UGD 13/8/8 #5	0.76	9.21	78.21*	10.11*	0
C40	UGD 13/8/8 #6	2.19	11.87	70.67*	13.71*	0
C41	UGD 13/8/8 #7	2.43	7.97	80.69*	8.53*	0
C42	UGD 13/8/8 #8	1.16	4.5	85.03*	9.31*	0
C43	UGD 13/8/9 #1	2.12	18.73	64.08*	6.41*	0
C48	1797-1899	5.43	37.51	41.32*	11.51*	0
C49	1798-1899	6.54	36.7	40.96*	11.70*	0
C81	T.133(15)-1976	2.11	11.08	75.08*	11.73*	0
C88	T.133(22)-1976	2.02	13.01	66.86*	12.20*	4.62
C98	Tennent small pattern	2.81	14.04	65.98*	9.64*	6.47
C100	Judith Townson B	1.95	17.13	64.00*	14.70*	0
M3	Turkey red (alizarin, supplied by Perkin)	2.85	36.69	39.82*	16.81*	3.84
M4	Turkey red (alizarin, supplied by Perkin)	2.14	39.11	41.23*	15.40*	2.12

Table 18 Relative amounts of components in samples containing Unknown 1 with UV-Vis absorbance maxima at 274 and 430 nm at 430 nm. *Deconvoluted by Empower 3 ApexTrack integration.

Unknown 3 - Rt ca. 24.8 minutes



Figure I-10 UV-Vis spectrum of Unknown 3 from analysis in Chapter 7.

See Figure I-5 for example chromatogram.

		%	%	%	%	%
ID	Sample	Unk 3	Anthrap.	Alizarin	Flavop.	Purp.
C1	UGD 13/8/1 #1	4.92	2.86	85.17*	7.05*	0
C3	UGD 13/8/1 #4	4.72	2.97	92.30	0	0
C4	UGD 13/8/2 #1	2.78	0	85.32	0	11.61
C5	UGD 13/8/2 #2	5.77	0.17	85.25	0	8.49
C6	UGD 13/8/2 #4	5.71	0	87.28	0	7.01
C7	UGD 13/8/3 #1	0.45	0.39	74.17	0	24.61
C8	UGD 13/8/3 #2	1.75	0	86.52	0	11.13
C9	UGD 13/8/3 #3	0.84	0	88.91	0	8.65
C10	UGD 13/8/3 #6	4.56	0.42	77.71	0	16.89
C11	UGD 13/8/3 #7	0.67	0	85.59	0	13.16
C14	UGD 13/8/3 #11	3.54	0	81.96	0	14.5
C15	UGD 13/8/4 #1	4.95	7.14	78.82*	7.88*	0
C16	UGD 13/8/4 #2	1.05	5.51	84.86*	7.22*	0
C18	UGD 13/8/5 #1	1.23	0.34	76.01	0	21.96
C21	UGD 13/8/5 #7	1.87	9.26	68.37*	5.28*	13.37
C22	UGD 13/8/5 #8	0.35	17.71	65.43*	5.90*	7.62
C23	UGD 13/8/5 #9	0.35	20.07	61.94*	5.87*	9.03
C25	UGD 13/8/5 #11	1.04	13.79	63.78*	4.29*	14.14
C27	UGD 13/8/6 #1	1.42	3.53	88.39*	6.01*	0
C28	UGD 13/8/6 #2	1.1	10	78.11*	8.99*	0
C29	UGD 13/8/6 #3	0.2	6.42	83.08*	8.06*	0
C30	UGD 13/8/6 #4	0.67	13	79.20*	5.54*	0
C32	UGD 13/8/7 #2	0.26	4.79	94.84	0	0
C33	UGD 13/8/7 #3	0.52	22.62	62.40*	12.57*	0
C34	UGD 13/8/7 #4	2.13	5.68	91.49	0	0
C36	UGD 13/8/8 #1	1.15	4.45	86.18*	7.75*	0
C39	UGD 13/8/8 #5	1.08	9.21	78.21*	10.11*	0
C40	UGD 13/8/8 #6	0.7	11.87	70.67*	13.71*	0
C43	UGD 13/8/9 #1	5.9	18.73	64.08*	6.41*	0
C48	1797-1899	0.65	37.51	41.32*	11.51*	0
C49	1798-1899	0.45	36.7	40.96*	11.70*	0
C50	1799-1899	1.61	0	83.90	0	13.98
C60	T.8-1978 p.87 Pattern 40	1.15	0	95.56	0	2.19
C61	T.8-1978 p.89 Turkey red	0.87	0	96.30	0	1.63
C63	T.74-1988 (dress)	10.57	0	85.64	0	1.79
C64	T.74-1988 (lining)	1.53	0	91.47	0	3.81
C65	T.12B-1984	3.77	0.28	89.35	0	5.45
C66	T.133-1976	0.57	0	73.22	0	25.88
C67	T.133(1)-1976	0.4	0.16	83.15	0	15.73
C68	T.133(2)-1976	0.35	0.2	68.15	0	30.83
C69	T.133(3)-1976	0.64	0.22	74.65	0	24.01
C71	T.133(5)-1976	0.32	0.2	69.66	0	29.32

	Comple	%	%	%	%	%
טו	Sample	Unk 3	Anthrap.	Alizarin	Flavop.	Purp.
C72	T.133(6)-1976	0.73	0	75.28	0	23.55
C73	T.133(7)-1976	0.18	0.19	77.27	0	22.06
C74	T.133(8)-1976	2.11	0	81.4	0	15.96
C75	T.133(9)-1976	0.72	0	76.67	0	22.09
C77	T.133(11)-1976	0.54	0	76.61	0	22.17
C78	T.133(12)-1976	0.59	0.26	72.13	0	26.61
C79	T.133(13)-1976	1.99	0	80.06	0	17.63
C82	T.133(16)-1976	0.14	0.21	65.59	0	33.43
C83	T.133(17)-1976	0.48	0	80.45	0	18.77
C84	T.133(18)-1976	0.44	0	76.2	0	22.71
C86	T.133(20)-1976	0.41	0	76.38	0	22.17
C87	T.133(21)-1976	0.23	0	77.84	0	21.56
C88	T.133(22)-1976	0.32	13.01	66.86*	12.20*	4.62
C89	T.133(23)-1976	0.66	0.19	70.7	0	27.82
C90	T.133(24)-1976	0.44	0	74.93	0	23.62
C91	T.133(25)-1976	1.11	0.13	72.1	0	26.09
C92	T.133(26)-1976	0.75	0	72.86	0	25.77
C93	T.133(27)-1976	0.43	0	78.12	0	21.04
C94	T.133(28)-1976	0.97	0.19	74.67	0	23.75
C95	T.133(29)-1976	0.46	0.24	74.8	0	23.15
C96	T.133(30)-1976	0.49	0.37	66.35	0	31.95
C97	T.133(31)-1976	0.59	0.26	68.9	0	29.92
C98	Tennent small pattern	1.06	14.04	65.98*	9.64*	6.47
C100	Judith Townson B	0.94	17.13	64.00*	14.70*	0
D1	Turkey red, alizarin #1	0.26	1.1	98.64	0	0
D2	Turkey red, alizarin #2	0.12	0.99	98.89	0	0
D3	Turkey red, alizarin #3	0.2	0.95	95.32*	3.33*	0.1
M7	Rouge d'anthrapurpurin e avivé no. 231	5.92	0	87.44	0	6.64

Table 19 Relative amounts of components in samples containing Unknown 3 430 nm. *Deconvoluted by Empower 3 ApexTrack integration.





Figure I-11 UV-Vis spectrum of Unknown 4 258 nm from analysis in Chapter 7.



Figure I-12 Chromatogram of Replica Turkey red madder #2 (D6) at 430 nm.

ID	Sample	% Unk 4 258 nm	% Anthrap.	% Alizarin	% Purp.
D4	Turkey red, madder	1.96	0	80.9	13.04
D5	Turkey red, madder #1	0.95	0.37	82.09	15.67
D6	Turkey red, madder #2	3.17	0.29	72.03	22.7
D11	Wool with alum and madder	22.79	0	28.15	44.15
D12	Silk with madder	44.19	0	44.35	9.28
R1	French madder	12.92	0	22.36	0
R2	English madder	29.97	0	46.04	11.13
R3	Iranian madder	1.72	0	6.78	0.65
R4	Turkish madder	14.51	0	36.06	3.04

ID	Sample	% Unk 4 258 nm	% Anthrap.	% Alizarin	% Purp.
R5	Rubia cordifolia	1.63	0	4.21	0
R6	Dutch madder	1.92	0	28.65	3.25
R7	Russian madder	14.84	0	60.92	7.05
R8	Silesian madder	3.28	0	13.96	5.22

518 Appendix I • Tables of unknown relative amounts from UHPLC analysis

Table 20 Relative amounts of components in samples containing Unknown 4 with UV-Vis absorbance maxima at 258 and 425 nm at 430 nm.

No values for flavopurpurin.

Unknown 4 277 nm - Rt ca. 25.5 minutes



Figure I-13 UV-Vis spectrum for Unknown 4 277 nm from analysis in Chapter 7.



Figure I-14 Chromatogram of UGD 13/8/9 #1 (C43) at 430 nm.

ID	Sample	% Unk 4 277 nm	% Anthrap.	% Alizarin	% Flavop.	% Purp.
C21	UGD 13/8/5 #7	0.44	9.26	68.37*	5.28*	13.37
C22	UGD 13/8/5 #8	0.24	17.71	65.43*	5.90*	7.62
C25	UGD 13/8/5 #11	0.85	13.79	63.78*	4.29*	14.14
C40	UGD 13/8/8 #6	0.38	11.87	70.67*	13.71*	0
C43	UGD 13/8/9 #1	1.47	18.73	64.08*	6.41*	0
C48	1797-1899	1.06	37.51	41.32*	11.51*	0
C49	1798-1899	1.04	36.7	40.96*	11.70*	0
C88	T.133(22)-1976	0.23	13.01	66.86*	12.20*	4.62
C100	Judith Townson B	0.58	17.13	64.00*	14.70*	0

Table 21 Relative amounts of components in samples containing Unknown 4 with UV-Vis absorbance maxima at 277 and 425 nm at 430 nm. *Deconvoluted by Empower 3 ApexTrack integration.

Unknown 2 - Rt ca. 20.7 minutes

Unknown 2 as poor resolution from alizarin/flavopurpurin peak(s).



Figure I-15 UV-Vis spectrum for Unknown 2 from analysis in Chapter 7.





Figure I-16 Chromatogram of 1797-1899 (C48) at 430 nm.

ID	Sample	% Unk 2	% Anthran	% Alizarin	% Flavon	% Purp
			Antinup.	AllZum	riavop.	i di p.
C29	UGD 13/8/6 #3	0.4	6.42	83.08*	8.06*	0
C40	UGD 13/8/8 #6	0.48	11.87	70.67*	13.71*	0
C41	UGD 13/8/8 #7	0.38	7.97	80.69*	8.53*	0
C48	1797-1899	0.77	37.51	41.32*	11.51*	0
C49	1798-1899	0.72	36.7	40.96*	11.70*	0
C53	1802-1899	0.04	35.27	25.14*	39.41*	0
C85	T.133(19)-1976	0.52	8.94	77.28*	10.62*	0
C88	T.133(22)-1976	0.43	13.01	66.86*	12.20*	4.62

Table 22 Relative amounts of components in samples containing Unknown 2 at 430 nm. *Deconvoluted by Empower 3 ApexTrack integration.

Unknowns 5 and 6 - Rt ca.



250.00 300.00 350.00 400.00 450.00 500.00 550.00 600.00 650.00 700.00 750.00 800.00

Figure I-17 UV=Vis spectrum of Unknown 5 from analysis in Chapter 7.



Figure I-18 UV-Vis spectrum of Unknown 6 from analysis in Chapter 7.

ID	Sample	% Unk 5	% Unk 6	% Anthrap.	% Alizarin	% Flavop.
C43	UGD 13/8/9 #1	0	0.92	18.73	64.08*	6.41*
C48	1797-1899	0.63	0.54	37.51	41.32*	11.51*
C49	1798-1899	0.76	0.42	36.7	40.96*	11.70*

See Figure I-16 for example chromatogram.

Table 23 Relative amounts of components in samples containing Unknowns 5 and 6 at 430 $\,$ nm.

*Deconvoluted by Empower 3 ApexTrack integration. No values for purpurin.

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Research activity

Conference presentations

- Dyes in History and Archaeology (DHA) 32, La Rochelle, France (Oct 2013) "Resurrecting Turkey red: Adapting an historic process for modern recreation and analysis"
- Scottish Business and Industrial History, Stirling, Scotland (April 2015) "Turkey Red Textile Dyeing in Glasgow: A Cross-Disciplinary Investigation into Scotland's Bygone Industry"
- GDCh-Wissenschaftsforum Chemie 2015, Dresden, Germany (Sep 2015) "Taking historical chemistry to the bench: A new perspective for modern chemists through the re-creation and analysis of 19th-century Scottish Turkey red dyed textiles"
- Dyes in History and Archaeology (DHA) 34, Thessaloniki, Greece (Oct 2015) "Shining a light on Turkey red: Applying FTIR for non-invasive identification of heritage textiles"
- SEAHA 2nd International Conference, Oxford, England (Jun 2016) "Unravelling 19th c. Turkey red textiles: approaches for heritage science through historical re-creation and chemical analysis"
- Dyes in History and Archaeology (DHA) 35, Pisa, Italy (Oct 2016) "Natural or synthetic? The identification of anthraquinone dyes on historical Turkey red by UHPLC-PDA anaylsis"

Conference posters

- 9th Annual International Conference for the History of Chemistry, Uppsala, Sweden (Aug 2013) "Textile dyeing in late-nineteenth-century Glasgow: Interpreting and re-creating the dye chemists' experiments from lab to manufacture"
- Historic Scotland Heritage Research Showcase, Edinburgh, Scotland (Feb 2014) "Textile dyeing in late-nineteenth-century Glasgow: Interpreting and re-creating the dye chemists' experiments from lab to manufacture"
- Dyes in History and Archaeology (DHA) 33, Glasgow, Scotland (Oct 2014) "Creation and analysis of synthetic alizarin and replicating Turkey red"
- SEAHA 1st International Conference, London, England (July 2015) "A little more reflection, a little more depth: applications of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) in heritage textile conservation."

Talks and Public engagement

- 3-Minute Thesis, College of Arts, Glasgow University (March 2013)
- ReINVENT workshop, Glasgow University (April 2013)
- 3-Minute Thesis presentation at College of Arts Industry Day, Glasgow University (May 2013)
- Talk at Encounters with Livingstone event, Blantyre (Sept 2013)
- Historical Perspectives group, Glasgow University (Dec 2013)
- Hunterian Associate (2013-2014)
- Friends of the Glasgow University Library (April 2014)
- Hunterian Insight Talk, Glasgow University (June 2014)
- Glasgow Science Festival Natural Dyeing and Printing Workshop (June 2014)
- Interview in The Independent graduate feature about project (July 2014)

- Glasgow Science Festival Harvest Festival at the Concrete Gardens display (Sept 2014)
- Archi've Opened poster with Archives & Records Association (Fall 2014)
- ReCREATE workshop, National Museums Scotland (Dec 2014)
- Arts in the Archive: Scottish Graduate School for the Arts and Humanities— Scottish Universities Special Collections and Archives Group, Stirling University (Feb 2015)
- Glasgow University Archive Services Training Session (Feb 2015)
- RSC Twitter Poster Conference (Feb 2015)
- 3-Minute Thesis, College of Arts, Glasgow University (Mar 2015)
- 3-Minute Thesis, University of Glasgow (Mar 2015)
- Informal talk to German high school students about applied chemistry and research at Integrierte Gesamtschule Franzsches Feld, Braunschweig, Germany (April 2015)
- Jacob Bronowski Award Lecture for Science and Art, British Science Festival, Bradford, England (Sept 2015)
- Talk for Airdrie Embroiderers Guild (Sept 2015)
- Talk for Glasgow Embroiderers Guild (Jan 2016)
- Talk at Winchester Science Festival (Aug 2016)

Academic and research activities

- Member of organizing committee for DHA 33 conference **Oct. 2014**
- Historical dyeing and printing workshop for 3rd year students
 Jun.
 2014
- Member of ReCREATE research network 2014-2015
- Hunterian Associates Program, University of Glasgow 2013-2014
- Three Minute Thesis, University of Glasgow 2013, 2015
- Beginning German (2013-2014)
- Member of ReINVENT research network 2013-2014
- Student representative, School of Culture and Creative Arts **2012-2014**
- Student representative, College of Arts Graduate School Board 2012-2014
- Student representative, Staff-Student Liaison Committee 2012-2014
- Lead Editor, eSharp Issue 20
- eSharp editorial board 2012-2013

Funding

• £400 from New Initiative Fund for Glasgow Science Festival workshop

Awards

- Annual Lord Kelvin Adam Smith Scholarship Event Best Poster winner (2013)
- Annual Lord Kelvin Adam Smith Scholarship Event Pecha Kucha Runner Up (2014)
- British Science Association Jacob Bronowski Award Lecture for Science and the Arts (Sep 2015)

Publications

• 'Turkey Red Textile Dyeing in Glasgow: A Cross-Disciplinary Investigation into Scotland's Bygone Industry', *Scottish Business and Industrial History*, November 2014.