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THE HISTORICAL AND CHEMICAL INVESTIGATION OF DYES IN HIGH STATUS CHINESE COSTUME AND TEXTILES OF THE MING AND QING DYNASTIES (1368-1911)

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Abstract

Costume colour held special significance in Chinese history. This thesis pioneers the multi-perspective exploration of dyes in high-status costume and textiles of the Ming and Qing Dynasties using the dual approach of history and chemistry.

Through the examination and comparison of four important historical manuscripts of dye recipes (Chapter 1) and dyes in high-status historical and archaeological textiles (Chapter 4), dyes and dyeing techniques used during the Ming and Qing Dynasties are revealed. Results show that nine natural dyes were commonly used, and synthetic dyes were used from the late 19th century. Dyes were used according to specific rules to obtain various shades. Further research improves the understanding of some of the textiles including better knowledge of ownership and more accurate dating, as well as the role of dyeing in the social and global contexts (Chapter 4).

Meanwhile, the botanical provenance, names and preferences for the significant dyes in Chinese textile history are clarified for the first time (Chapter 2). A database for the chemical composition of 22 reference Chinese dyes using Ultra high performance liquid chromatography coupled with Photodiode array detector and Mass spectrometer (UHPLC-PDA-MS) and UHPLC-PDA is first established, and the understanding of the chemical constituents of several dyes is improved. The investigation of dyes and dyeing techniques of the Li minority group in Hainan Province marks the start of the chemical research of ethnographic dyeing in China (Chapter 3). The accelerated light ageing study of reference dyes improves the knowledge of the lightfastness of the dyes. Suggestions on the conservation, preservation and exhibition of the dyes are provided (Chapter 5).

This research contributes significantly to dyeing history, textile history and colour history both of China and the world.

Maps of the Ming and Qing Dynasties

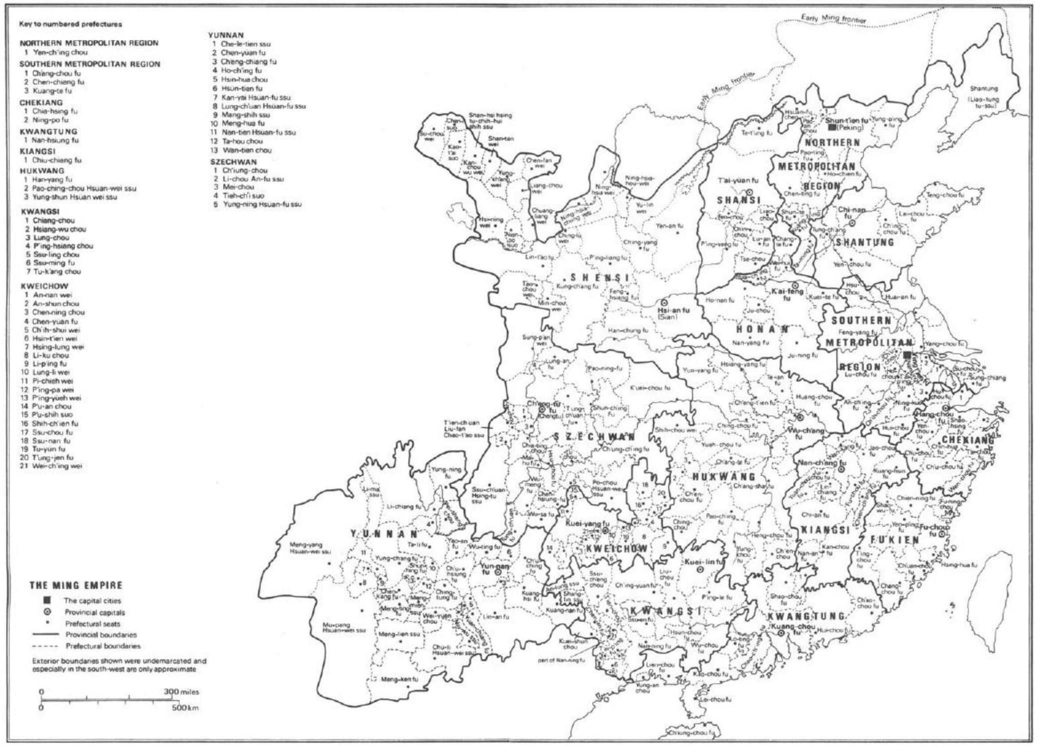

Figure I Map of the Ming Dynasty[1]

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[1] © Denis Crispin Twitchett and Frederick W. Mote, *The Cambridge History of China*, vol. 8. Part 2 (Cambridge: Cambridge University Press, 2008).

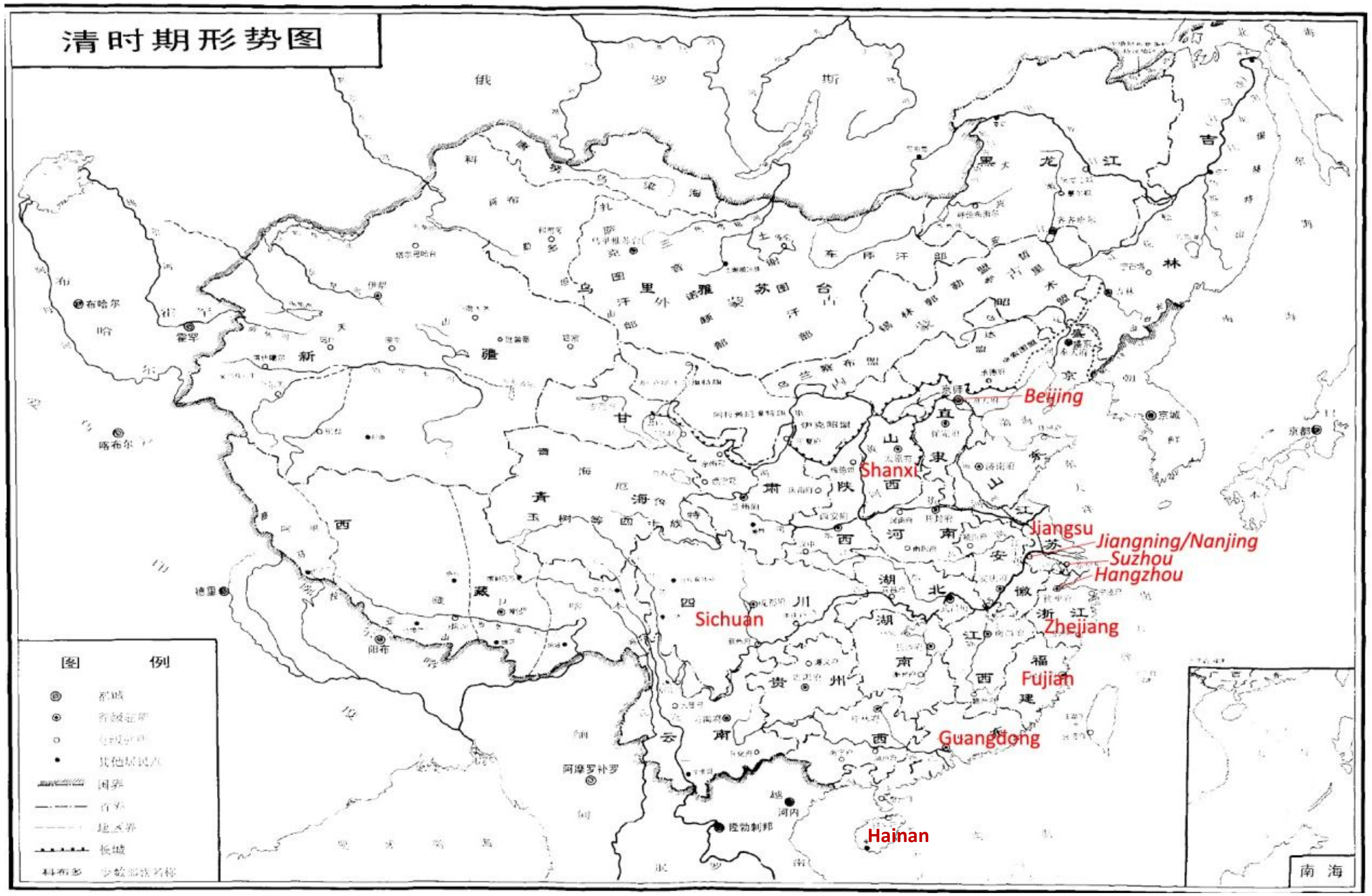

Figure II Map of the Qing Dynasty (1820)[2]

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[2] © Zhiting Li, *Qing Shi* [History of Qing] (Shanghai: Shanghai renmin chubanshe, 2002).

Table of Contents

List of Tables

List of Figures

Preface

Colour held special significance in Chinese history. It had a close relationship with the principle ideological theory 'Five Elements' and its derived theory 'Five Virtues'.[3] Five Elements theory explained the nature by the five elements, water, fire, wood, metal and earth, and their generating and overcoming interactions. The corresponding five colours, black, red, *qing* (a conflation of green and blue), white and yellow, were regarded as the most important colours in ancient China. Five Virtues theory applied Five Elements theory to the explanation of dynasties in the history of mankind by attributing each dynasty with a virtue, which corresponds to an element, and thus linking dynasties with the overcoming interaction of the five elements.[4] In this way, each dynasty advocated a certain colour.

With such significance, colour became an indispensable element of official decrees on dress in imperial China (from the Qin Dynasty, 221-207 BC, to the Qing Dynasty, 1644-1911) to distinguish ranks and contribute to the stability of social hierarchy and bureaucratic systems.[5] The official decrees of dress were mainly recorded in *Yu fu zhi* 輿服志 (Record of the Proper Carriage and Attire) of each dynasty. They regulated pattern, colour, material and the number of patterns and accessories used for coronets, costumes for various occasions and accessories that people of different ranks could wear.[6] As early as the Qin Dynasty, the colour of ribbons on clothes was used to indicate rank. During the Sui

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[3] Wenjuan Wang, "The Five Elements and the Five Colours," *Art Observation*, no.3 (2005): 81-87.

[4] Yu'e Ma, "Gudai Fushi Yanse Dengjizhi De Xingcheng Ji Qi Yuanyin," [The Formation and Causes of the Dress Color Ranking System in Ancient Times], *Journal of Luoyang Teachers College* 11, no.1 (2005): 98-99.

[5] Michael Loewe, *Imperial China: The Historical Background to the Modern Age* (New York: Praeger, 1966), 42-69. In imperial China, the imperial family of every dynasty, civil officials and military officials were at the top of the social hierarchy. During the Ming and Qing Dynasties there were strict grading systems to regulate ranks. Details are available in Bingwen Nan and Gang Tang, *Ming Shi* [History of Ming] (Shanghai: Shanghai renmin chubanshe, 1985), 76-102, 544-631; Z. Li, 463-474.

[6] Jun Zhao and Yumin Li, "Zhongguo Lidai Fushi De Dengji Zhidu," [Costume hierarchy in ancient China], *Northwest Institute of Textile Journal* 11, no.1 (1997): 60-70; Nengfu Huang and Juanjuan Chen, *Zhongguo Fuzhuang Shi* [History of Chinese costumes] (Beijing: Zhongguo lvyou chubanshe, 1995); Verity Wilson, *Chinese Dress* (London: Bamboo Publishing Ltd. in association with the Victoria and Albert Museum, 1986, reprinted in 1990); George W. Digby, "Chinese Costume in the Light of an Illustrated Manuscript Catalogue from the Summer Palace," *Gazette des beaux-arts* 41, no.6 (1953): 37-50.

and Tang Dynasties (581 - 907), a strict hierarchical system of colour on costume called '*pin se fu* 品色服 (Colour Grading Clothing)' was formed, and this system was further strengthened in the following dynasties.[7] In each dynasty official decrees were issued on the ranking by colour for costume and textiles.[8] The colour of various types of clothes and related accessories were regulated for people of different ranks. Bans on some special colours among officials and common people were issued.

During the Ming (1368-1644) and Qing (1644-1911) Dynasties, the flourish of commodity economy and the prosperity of world trade affected various aspects of the society.[9] The colour grading system of the Ming and Qing Dynasties involved more grades and colours than those of previous dynasties. According to *yu fu*, the Ming Dynasty advocated the colour red, which corresponded with the element fire, inheriting the advocation of red in the Zhou (1123-256BC), Han (202BC-220AD), Tang (618-907) and Song (960-1279) Dynasties. The colour of official dress was graded from high to low into *fei* 緋 (red), *qing* 青 (dark blue) and *lv* 綠 (green). Three colours, *xuan* 玄 (reddish black), *huang* 黃 (yellow) and *zi* 紫 (purple), were regarded as imperial colours and their use were prohibited amongst officials and common people.[10] The Qing Dynasty inherited the general tradition of the emperor wearing yellow in Chinese history.[11] On the one hand, it was thought that the emperor was located in the centre of the five directions and the centre was represented by the element earth and the colour yellow. On the other hand, yellow was considered as the colour of the sun: just as there cannot be two suns in the sky, there cannot

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[7] Ma, "Gudai Fushi Yanse Dengjizhi De Xingcheng Ji Qi Yuanyin," 98-99.

[8] Jing Zhao, "Analysis on the Inheritance and Development of Costume Patterns from Han by the Qing Dynasty from 'Examples of Clothing Colours and Carriages' in the Early Qing Dynasty," *Modern Decoration(Theory)*, no.5 (2011): 63-64; Xiuli Zhao, "Influence of Ming Emperors on the Social Fashion," *Journal of Hubei Normal University (Philosophy and Social Sciences)*, no.6 (2007): 75-79; Fulin Gau, "Official Dress Code and Violations in the Ming Dynasty (A.D.1368-1644)" (Master's dissertation, Fu Jen Catholic University, 1995).

[9] Xing Fang *et al.*, *Zhongguo Jingji Tongshi, Qingdai Jingji Juan* [General history of Chinese economy, Qing economy volume] (Beijing: Jingji ribao chubanshe, 2000), 845; Peng Zhu, "Mingdai Yu Qingdai Qianqi Guangdong De Haishang Sichou Maoyi" (Master's dissertation, Jinan University, 2003); Jinmin Fan and Wen Jin, *Jiangnan Sichoushi Yanjiu* [Studies in the history of silk in Jiangnan] (Beijing: Nongye chubanshe, 1993), 235; Jane Burbank and Frederick Cooper, *Empires in World History: Power and the Politics of Difference* (Princeton, N.J.: Princeton University Press, 2010), 152.

[10] Tingyu Zhang, "Yu Fu," in *Jing Yin Wenyuange Sikuquanshu* (Taipei: Taiwan shang wu yin shu guan, 1986).

[11] Fei Liu, "Qing Qianqi Huangshi Ji Guizu Fushi Yanjiu [The Research of Clothing of Royal and Noble in the Early Qing Dynasty]" (PhD thesis, Shandong University, 2014).

be two emperors in a nation.[12] In the official regulation of the Qing Dynasty *Huangchao liqi tushi* 皇朝禮器圖示 (Illustrations of Imperial Ritual Paraphernalia), subtle shades were used to distinguish close ranks: it was regulated that *minghuang* 明黃 (bright yellow) was only for the court robes and dragon robes of the emperor and empress, the court robe and *mang* robes for crowned princes should be *xinghuang* 杏黃 (apricot yellow), other princes be *jinhuang* 金黃 (golden yellow), while those for imperial family members of lower ranks be *qing* 青 (dark blue) and *shiqing* 石青 (azurite blue).[13]

The knowledge of Chinese costume and textiles has been growing, including not only official decrees and evolving designs of various kinds of dress and textiles for different uses, but also their production, trading and collection.[14] In terms of the costume and textiles of the Ming and Qing Dynasties, research was also focussed on the illustrations of official decrees on costume and the accurate dating of the textiles especially dragon robes.[15] It was also found that during this time period handicrafts underwent both quantitative and qualitative advancements in such aspects as production technology and production structure.[16] However, how the colours on the costume and textiles were achieved and how textile dyeing techniques interacted with various aspects of the concurrent society remain unclear.

The research presented in this thesis aims to improve the knowledge of Chinese dyeing

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[12] Xueyan Li, "Zunbei Guijian, Wang Er Zhi Zhi - Mingdai Caomu Ranse Yu Dengji Zhiyue," [Hierarchy Appearances—Vegetable Dyeing and the Hierarchy in the Ming Dynasty], *Journal of Nanjing Arts Institute (Fine Arts & Design)*, no.3 (2012): 56-60.

[13] Lu Yun, "Huangchao Liqi Tushi," in *Jingyin Wenyuange Siku Quanshu* [Jing Yin Wenyuan Collection House Sikuquanshu] (Taibei: Taiwan Shangwu Yinshuguan, 1976), 5-212.

[14] Wilson, "Chinese Dress"; Verity Wilson, *Chinese Textiles* (London: V & A Publications, 2005); Huang and Chen; Feng Zhao, *Zhongguo Sichou Tongshi* [The general history of Chinese silk] (Suzhou: Suzhou daxue chubanshe, 2005); Rose Kerr, Verity Wilson, and Craig Clunas, *Chinese Art and Design: The T.T. Tsui Gallery of Chinese Art* (London: Victoria and Albert Museum, 1991).

[15] Digby, "Chinese Costume in the Light of an Illustrated Manuscript Catalogue from the Summer Palace," 37-50; Alan Priest, *Costumes from the Forbidden City* (New York: the Metropolitan Museum of Art, 1945), 12; Alan Priest and Pauline Simmons, *Chinese Textiles; an Introduction to the Study of Their History, Sources, Technique, Symbolism, and Use* (New York: The Metropolitan Museum of Art, 1934); Helen Elizabeth Fernald, *Chinese Court Costumes* (Toronto: The University of Toronto Press, 1946); Schuyler Cammann, *China's Dragon Robes* (New York: Ronald Press Co., 1952).

[16] Bozhong Li, *Jiangnan De Zaoqi Gongyehua (1550-1850 Nian)* [The Early Industrialization in Jiangnan: 1550-1850] (Beijing: Shehui kexue wenxian chubanshe, 2000), 37-38; Shengnian Ding, "Aesthetic Cultural Research on Porcelain’s Color of Yuyaochang in Ming Dynasty" (Master's dissertation, Jiangnan University, 2012); Yingxia Lv, "A Research on the Cultural Idea and Cultural Expression of Traditional Chinese Architecture Color" (Master's dissertation, Harbin Institute of Technology, 2008).

history by answering the following questions:

1. What indigenous and/or imported dye sources and dyeing methods were used in China for high status costumes during the Ming and Qing Dynasties, as revealed by literature research and chemical analysis?

2. What are the chemical characteristics of indigenous dyes in China that can be used for their identification in historical and archaeological textiles?

3. What can be learnt from the dyes to interpret, date and preserve the colours of historical and archaeological Chinese textiles?

To answer these questions, this research pioneers the application of the combined approach of history and chemistry to the systematic exploration of dyes and dyeing techniques in the Ming and Qing Dynasties. Both historical literature, especially historical dye recipes, and dyes on historical and archaeological textiles of the period of interest are investigated. Specifically, the approaches taken in this thesis include:

1. Archival research of important dye recipes of the Ming and Qing Dynasties.

2. Archival research, together with the methodologies of botany and chemistry for the provenance of historical dye plants.

3. Chemical analysis of historical and archaeological dyes of the Ming and Qing Dynasties based on the study of reference Chinese dyes and their ageing.

4. Art history research of dyes on historical and archaeological costume and textiles and of dyeing handicraft during the Ming and Qing Dynasties.

The thesis is structured as follows:

Chapter 1 presents the archival research of historical dye recipes of the Ming and Qing Dynasties. The dyes and dyeing methodologies recorded in four important historical manuscripts of dye recipes are examined. Issues such as the reliability of historical dyeing resources, the combination of raw materials, factors affecting the choices of dyes and dyeing methods and the advancement of dyeing are discussed. Lastly, to better illustrate the colour and dyeing properties of the dyes, the chemical structures of their main dye components are also discussed.

Chapter 2 acts as a complement for the research in Chapter 1 on the historical dye recipes by investigating the botanical provenance of common dye plants used in ancient China in order to promote a more accurate understanding of the raw materials of dyeing. The dyeing properties of relevant dyes are compared and research outcomes from the field of herbal medicine are introduced. Reasons for the ambiguity of their botanical provenance are explored as well.

Chapter 3 lays a foundation for the chemical analysis of historical and archaeological dyes. The analytical characterisation the chemical composition of reference dyes by ultra performance liquid chromatography with photo diode array detection with mass spectrometric detection (UHPLC-PDA-MS) and UHPLC-PDA is carried out and a database of the results created. Reference dyes characterised include twelve common dyes, ten less common dyes, and dyes from Ethnic Minority Li in Hainan Province. The chemical analysis protocol used for common Chinese dyes is evaluated and the certainty of dye identification based on characteristic components is discussed.

Chapter 4 undertakes the chemical and historical research of historical and archaeological dyes from costume and textiles of the Ming and Qing Dynasties. Chemical analysis methods applied include UHPLC-PDA and Scanning electron microscopy (SEM) analysis. Dye sources identified are used to better interpret the costume and textiles. The analytical results are compared with historical records (Chapters 1 and 2) in order to obtain an overall view of dyes and dyeing methods used in the Ming and Qing Dynasties. Issues on indigenous dyes in China and communication about dyeing between China and Europe are then discussed. The relationship between dyeing handicraft and other aspects of the concurrent society is explored as well.

Chapter 5 improves the understanding of the chemistry of Chinese dyes obtained in Chapter 3 and Chapter 4 by undertaking the accelerated light ageing study of reference dyes. The lightfastness of the dyes and the change of their chemical profiles during ageing are investigated and the results are applied to interpret the preservation state of historical and archaeological dyes. Implications for the conservation, preservation and exhibition of historical dyes are discussed.

This research improves the knowledge of Chinese dyeing history in terms of the raw materials and dyeing methods used and how dyeing developed over time. It also contributes to a better understanding of dyeing handicraft in the Ming and Qing Dynasties and helps with the interpretation, dating and preservation of dyes on historical and archaeological textiles.

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Abbreviations

BSE image	Backscatter electron image
DMSO	Dimethyl sulfoxide
ESI	Electrospray ionization
HPLC	High performance liquid chromatography
LC	Liquid chromatography
MS	Mass spectrometry
PDA	Photodiode array
UHPLC	Ultra high performance liquid chromatography
UV-vis	Ultraviolet–visible

1 Preliminary Evidence of Dyes and Dyeing Methods Based on Primary Documentary Sources

1.1 Introduction

There has been growing interest in dyeing in ancient China over the past decades. Research was carried out since the 1980s on historical Chinese dyes and dyeing techniques based on both historical records on dyeing and current knowledge in the fields of modern chemistry and textile production.[17] The work by Chen revealed the usage of dyes in different time periods and laid a solid foundation for research on Chinese dyeing history.[18] After that, dye recipes in several historical manuscripts were investigated independently and issues including raw materials and dyeing processes were discussed.[19] Further research was carried out on the use and chemistry of historical dyes and on dyeing techniques including scouring, dyeing, mordanting and finishing.[20] Moreover, the spatial and temporal variation of dyes and dyeing in

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[17] J. Griffiths, *Colour and Constitution of Organic Molecules* (London: Academic Press, 1976); Heinrich Zollinger, *Color Chemistry: Syntheses, Properties, and Applications of Organic Dyes and Pigments* (Weinheim: Wiley-VCH, 2003).

[18] Weiji Chen, *Zhongguo Fangzhi Kexue Jishushi, Gudai Bufen* [History of the science and technology of Chinese textile, the ancient part] (Beijing: Kexue chubanshe, 1984).

[19] Feng Zhao, "*Duoneng Bishi* Ransefa Chutan," [A preliminary study on dyeing in *Duoneng bishi*], *Southeast Culture* 7, no.1 (1991): 72-78; Feng Zhao, "*Tiangong Kaiwu* Zhangshipian Zhongde Ranliao He Ranse," [Dyes and dyeing in the chapter 'colouring' in *Tiangong kaiwu*], *Agricultural Archaeology* 7, no.1 (1987): 354-358; Bin Li, "Qingdai Ranzhi Zhuanzhu *Bu Jing* Kao," [A study on a monograph of dyeing *Bu jing* of the Qing Dynasty], *Southeast Culture* 7, no.1 (1991): 79-86; Yehong Wang, Jian Liu, and Yongji Tong, "Qingdai Zhiranju Ranse Fangfa Ji Secai," [Dyeing methods and colours in the Weaving and Dyeing Bureau of the Qing Dynasty], *Historical Archives* 31, no.2 (2011): 125-127.

[20] Feng Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," in *Zhongguo Sichoushi, Zhuanlun*, ed. Xinyu Zhu (Beijing: Zhongguo fangzhi chubanshe, 1997), 209-248; Kuanghua Zhao and Jiahua Zhou, *Zhongguo Kexue Jishushi, Huaxuejuan* [History of Chinese science and technology, chemistry volume] (Beijing: Kexue chubanshe, 1998); Dominique Cardon, *Natural Dyes: Sources, Tradition, Technology and Science* (London: Archetype, 2007), 482, 696. Zhao and Zhou; Kuanghua Zhao, "Zhongguo Gudai Yan, Xiao, Fan De Huaxue," in *Zhongguo Kexue Jishushi, Huaxuejuan*, ed. Kuanghua Zhao and Jiahua Zhou (Beijing: Kexue chubanshe, 1998), 506-518; Bing Zhu, "Ranzheng Jishu," in *Zhongguo Kexue Jishushi, Fangzhi Juan*, ed. Jiaxi Lu and Chengze Zhao (Beijing: Kexue chubanshe, 2002), 263-294; Xiaoping Qian, *Zhongguo Chuantong Gongyi Quanji, Sichou Zhiran* [Complete works of Chinese traditional craft, silk weaving and dyeing] (Zhengzhou: Daxiang chubanshe, 2005), 77-82; Shyhbao Chiang,

ancient China was explored and the development of dyeing as affected by exchange between dyeing regions was studied.[21] In addition, research on contemporary traditional dyeing and natural dyes promoted the understanding of historical dyeing. Field records and investigation into these aspects by researchers in textile handicrafts and ethnobotany complemented records in historical manuscripts on such issues as raw materials for dyeing, facilities, detailed dyeing procedures, *etc*.[22] For the further application of traditional dyeing, the colouring properties and the fastness of the dyes were also explored in-depth.[23]

So far, the overall framework of Chinese dyeing history is established and the knowledge of raw materials for dyeing, dyeing techniques and chemistry involved in dyeing has been obtained. Nevertheless, the Chinese dyeing history of each period is not very clear. For the specific time period of the Ming and Qing Dynasties, when natural dyeing reached its peak of production, what dyes and dyeing techniques were used and how dyeing advanced during this historical period remain to be investigated. To answer these questions, this chapter attempts a comparative analysis of several historical Chinese documents of dyeing to understand its practice. Archival research is undertaken to search for and investigate historical dye manuscripts. The research makes use of statistical analysis based on the frequency that different dye sources and dyeing methods are mentioned within each of the historical texts examined, a methodology used already in some studies of historical dyeing,[24] and further investigates data obtained on dyeing for the comprehensive analysis

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"Zhongguo Chuantong Tianran Ransecai Zhi Xianse Guanxi Yanjiu - Yi Zhiwu Ranse Zhi Hongsexi Weili" (PhD thesis, National Yunlin University of Science and Technology, 2002).

[21] Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 244-246.

[22] Junping Wang and Bin Wang, "Shujin Chuantong Gongyi Ranse - Tianran Zhiwu Sesu Ranse," [The traditional dyeing process of Shu Brocade- natural plant dyes dyeing], *Sichuan Textile Technology* 23, no.2 (2001): 47-51; Gong Jixian and Li Huiqin, "Woguo Chuantong De Dianlan Ranse Gongyi," [Traditional Dyeing Technology of Natural Indigo in China], *Beijing Textile Journal* 24, no.5 (2002): 25-27; Guoxue Zhang, Shengji Pei, and Bingjun Li, "The Use of Ethnobotany Methods in the Research of Ethnic Folk Dyeing Plants," *Acta Botanica Yunnanica* 25, no.14 (2003): 115-122.

[23] Lihua Lv, "Tianran Zhiwu Ranliao Yongyu Xianweisu Xianwei Zhiwu Ranse Xingneng Yanjiu" (Master's dissertation, Dalian Polytechnic University, 2005); Sung Hee Kim, *Ranzuo Jiangnan Chunshui Se* [The classical colors of China] (Kunming: Yunnan renmin chubanshe, 2006); Wei Wang, "Chuantong Caomu Ranliao De Wuse Sesu Cuiqu Ji Yingyong Yanjiu" (Master's dissertation, Southwest Jiaotong University, 2006); Caiyun Shi, "Tianran Ranliao De Yiyufa Pingse Ranse Jishu Yanjiu" (Master's dissertation, Suzhou University, 2012).

[24] Dominique Cardon, "Yellow Dyes of Historical Importance: Beginnings of a Long-Term Multi-Disciplinary Study; Part 1" in *Dyes in History and Archaeology 13*, ed. P Walton Rogers, 59-73 (York: Textile Research Associates, 1994); Judith H. Hofenk de Graaff, "Textile Dyeing in Leiden:

of dye recipes in four detailed historical manuscripts. Both the overall status and the similarities and differences among various documents in terms of the use of raw materials and dyeing sequence are discussed. Such issues as the reliability and recording styles of historical documents on dyeing, the way raw materials for dyeing were combined, factors affecting the choices of dyes and dyeing methods and the advancement of dyeing are explored in-depth, filling the gaps in these aspects of existing research. Lastly, to better illustrate the colour and dyeing properties of the commonly recorded dyes, the chemical structures of their major dye components are discussed. This chapter contributes to the understanding of dyeing techniques in the Ming and Qing Dynasties and is helpful for the identification of dyes on historical and archaeological Chinese textiles.

1.2 Resources and Methodologies

Historical documents from the Ming and Qing Dynasties including original documents, copies of the original documents and transcribed versions were searched for in primary resources of dye recipes from both books of handicrafts and compilation of literature. Catalogues in Ancient Books Reading Room of Peking University Library and Shanghai Library and several electronic databases of historical manuscripts in Peking University Library, especially *Zhongguo jiben guji ku* 中國基本古籍庫 (Chinese Classic Ancient Books Database), were searched. Published contents of historical dye recipes were also accessed. From the found documents, manuscripts with numerous dye recipes were selected for further systematic investigation because these dye recipes tended to be more systematic and therefore more suitable for comparative and comprehensive analysis.

The historical dye recipes were analysed in a general context first. To enable more accurate interpretation of these records, some methodologies of historical literature research in

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Changes in the Use of Dyestuffs from the 16th to the 17th Century," in *The Colourful Past : Origins, Chemistry and Identification of Natural Dyestuffs*, ed. Judith H Hofenk de Graaff, Wilma G Th Roelofs, and Maarten R van Bommel, 324-333 (London: Archetype Publications, 2004).

chemistry history and technical art history were consulted.[25] The overviews of manuscripts containing these dye recipes were examined in terms of authorship, purpose, content, and readership to judge their extents of reliability as historical sources. Then the dye recipes were summarised in terms of their content and style. It is to be mentioned that the languages of these texts are slightly different from modern Chinese mainly in terms of the usage of words, grammar and punctuation. Particularly, some words are rarely used in modern times and some have changed slightly in meaning. Therefore the texts were studied closely by consulting classical Chinese dictionaries and some historical literature such as *Ben cao gang mu* 本草綱目 (*Compendium of Materia Medica*, 1578) and by textual comparison to reveal their exact meanings. Most texts were interpreted clearly but several rarely-used dyeing additives are still unclear due to the lack of relevant evidences. The examination of dye names and the botanical provenance of these dye plants are undertaken in Chapter 2.

Based on the above knowledge, detailed statistical analysis was carried out on dye recipes in the aspects of dyes and dyeing techniques respectively: 1) For dyes, the frequency of occurrence of dyes recorded was counted to see what dyes were commonly used and what dyes were eliminated, with comparison to the choice of dyes in earlier periods.[26] Factors affecting people’s choice of dyes were studied with reference to current knowledge of the dyeing properties, colouring effects, fastness, *etc.* of these dyes. Similarities and differences in the use of dyes among these manuscripts were investigated. 2) For dyeing techniques, the frequencies of the use of dyes in single dyeing and the combination of dyes in multi dyeing were counted to find out how the dyes were used and what colours were obtained. The use of minerals in dyeing (called mordants) was studied as well. Dyeing sequences, that is, the timing of using dyes and mordants, was also investigated. To study the differences in dyeing among these manuscripts and know about how dyeing advanced, dye recipes were further analysed statistically in terms of the combinations of dyes and mordants and variations in the quantity of raw materials for dyeing.

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[25] Zhao, "Xvlun," 6-11; Mark Clarke, *The Art of All Colours: Mediaeval Recipe Books for Painters and Illuminators* (London: Archetype, 2001), 26-39.

[26] W. Chen; Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 209-248; Zhu, "Ranzheng Jishu," 263-294.

1.3 Results and discussion

1.3.1 Historical records

1.3.1.1 Main historical sources recording dyeing

Table 1. 1 Historical manuscripts with numerous dye recipes

Original title with pinyin pronunciation	**Date**	**Author**	**District**[27]	**Overview**
多能鄙事 Duoneng bishi	early Ming Dynasty	(shown as) Liu Ji (1311-1375)	probably southeast China	An integrated work of crafts in everyday life.
天工開物 Tiangong kaiwu[28]	late Ming Dynasty (first published in 1637)	Song Yingxing (1587-1666)	across China	An integrated work on agriculture and handicrafts.
中國第一歷史檔案館藏內務府全宗檔案,織染局簿冊 Neiwufu quanzong dang'an, Zhiranju buce[29]	Qing Dynasty (1754)	Probably someone in the Weaving and Dyeing Bureau.	Official weaving and dyeing bureau located in the Jiangnan area or in Beijing	Official record of the central weaving and dyeing bureau.
布經 Bu jing	Qing Dynasty (Jiaqing period to Daoguang period, 1795-1850)	Craftsmen who have extensive experience in dyeing and weaving.	Songjiang (currently in southwest Shanghai)	A work on the handicraft of cotton cloth.

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[27] See Figures I and II for the maps of China in the Ming and Qing Dynasties.

[28] *Tiangong kaiwu* has been translated into English by E-Tu Zen Sun and Shiou-Chuan Sun in 1966 with the title *Chinese Technology in the Seventeenth Century.*

[29] *Neiwufu quanzong dang'an, Zhiranju buce* was inaccessible in the First Historical Archives of China at the time of research, therefore all the analysis on this document in this research was undertaken on published content: Wang, Liu, and Tong, "Qingdai Zhiranju Ranse Fangfa Ji Secai," 125-127.

Four historical manuscripts with numerous dye recipes were found,[30] as shown in Table 1. 1. The authorship, purpose, content, and readership of the four manuscripts are discussed in detail as follows.

The two manuscripts of the Ming Dynasty, *Duoneng bishi* 多能鄙事 (Various arts in everyday life) and *Tiangong kaiwu* 天工開物 (Chinese Technology in the Seventeenth Century), are both integrated works on various crafts and they were published to the general public. Their difference is that the former was compiled as a popular book while the latter was a more rigorous manuscript recording and discussing contemporary science and technology. To be specific, *Duoneng bishi* is a *ri yong lei shu* 日用類書, a kind of book on daily crafts of various aspects arranged according to categories. *Ri yong lei shu*, which originated in the Southern Song Dynasty (1127-1279) and became popular in the Ming Dynasty, were usually compiled from various sources by low rank literati or bookstore owners. These books were produced for commercial purpose mainly for low rank literati or the squire class.[31] The records probably originated from the practical experience of craftsman or the investigation of low rank literati, because most craftsmen were not able to read or write at that time.[32] Liu Ji, a very famous military strategist, politician and thinker in the early Ming Dynasty, was regarded as the author of the book but it might not be the case because sometimes the names of celebrities were printed as authors to attract readers.[33] As to the place of origin, since most book workshops and stores were located in southeast China and it was more convenient to use local resources,

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[30] "Jujia Biyong Shilei Quanji: Quan Shi Juan," in *Beijing Tushuguan Guji Zhenben Congkan*, ed. Beijing tushuguan guji chuban bianjizu (Beijing: Shumu wenxian chubanshe, Yuan Dynasty, republished in 1988), 286-288; "Duoneng Bishi," in *Xuxiu Siku Quanshu*, ed. *Xuxiu Siku quanshu* bianzuan weiyuanhui (Shanghai: Shanghai guji chubanshe, 1995), 49,50; Yingxing Song and Jixing Pan (ed.), *Tiangong Kaiwu Yizhu* [Chinese Technology in the Seventeenth Century, translated and annotated] (Shanghai: Shanghai guji chubanshe, 1992), 261-263; *Bu Jing*, [The Cloth Classic] (Hefei: Anhui Library, Qing Dynasty); *Neiwufu Quanzong Dang'an, Zhiranju Buce* [Complete File of the Imperial Household, Volume of the Weaving and Dyeing Bureau] (Beijing: The First Historical Archives of China, Qing Dynasty).

[31] Yi Zhao, "Mingdai Tongsu Riyong Leishu Yu Shumin Shehui Shenghuo Guanxi De Zaitantao," [Further Study of the relationship between popular daily encyclopedias and the social life of common people], *Gudian Wenxian Yanjiu* 16, (2013): 41-59.

[32] Zhao, "Xvlun," 7,8.

[33] Zhenghua Wang, "Shenghuo, Zhishi Yu Wenhua Shangpin - Wanming Fujian Ban 'Riyong Leishu' Yu Qi Shuhuamen," [Life, knowledge and cultural goods - 'ri yong lei shu'of Fujian version, its calligraphy and painting in the Late Ming Dynasty], *Bulletin of the Institute of Modern History, Academia Sinica*, no.41 (2003): 1-85.

this area may also be the origin of the activities recorded.[34] In terms of time period, since some contents on dyeing also appeared in another *ri yong lei shu* of the Yuan Dynasty (1271-1368) called *Jujia biyong shilei quanji* 居家必用事類全集 (Guide to domestic operations), it can surmised that these records on dyeing probably reflect dyeing activities in the Yuan Dynasty or in the early Ming Dynasty.

The other manuscript with numerous dye recipes of the Ming Dynasty, *Tiangong kaiwu*, was written by Song Yingxing, a literati in the late Ming Dynasty. Influenced by pragmatism that started during the mid Ming Dynasty, he believed that science and techniques made the largest contribution to the country and people in comparison to other fields.[35] *Tiangong kaiwu* was written based on Song Yingxing's investigation into agriculture and handicrafts all across China, which guaranteed the high credibility of the records.[36] The book was an unprecedented initiative in that it systematically described large amounts of techniques, including some advanced scientific and technological achievements that had rarely been recorded.[37]

Contrary to the two manuscripts of the Ming Dynasty, the two manuscripts of the Qing Dynasty, *Neiwufu quanzong dang'an, Zhiranju buce* 內務府全宗檔案，織染局簿冊 (Complete File of the Imperial Household, Volume of the Weaving and Dyeing Bureau, abbreviated as *Zhiranju buce* in the following text) and *Bu jing* 布經 (The cloth classic) are both specialised books on textile handicrafts, probably written mostly for internal circulation within the dyeing institutes. It is very likely that the two manuscripts were written by experts in the field or recorded by literati based on interviews and investigation. Therefore these records reflected practical dyeing activities to a large extent. To be specific, *Zhiranju buce*, as one of various documents produced by the Imperial Household Agency, which served the imperial family, recorded the materials used for textiles in the court. The

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[34] Liangxiong Xu, "Shilun Mingdai Shufang Chubanye De Fazhan Ji Qi Gongguo," *Tian Yi Ge Wencong*, no.2 (2006), http://www.tianyige.com.cn/tygwc_detail.asp?ID=1251.

[35] Jixing Pan, *Song Yingxing Pingzhuan* [The biography of and comments on Song Yingxing] (Nanjing: Nanjing daxue chubanshe, 1990).

[36] Ibid.

[37] Ibid.

other manuscript, *Bu jing*, is a professional manuscript on textile handicrafts that originated in Songjiang (currently in the southeast of Shanghai) and it was probably written by a senior craftsman with a certain extent of literacy.[38] This manuscript, used as teaching materials, records practical experience and tricks in aspects of cotton production such as choosing raw materials, dyeing and finishing.

Overall, these manuscripts were based either on investigation into dyeing practice or on practical dyeing experience. Judging from their places of origin, *Duoneng bishi* and *Bu jing* originated from southeast China, where the most important centres for weaving and dyeing with both silk and cotton were located.[39] *Zhiranju buce* originated from an official weaving and dyeing bureau in the Jiangnan area (approximately the lower valley of Yangtze River) or in the capital Beijing. *Tiangong kaiwu* originated from the investigation across China. Therefore records in these four manuscripts stand for actual dyeing practice at that time to a large extent. To be specific, *Duoneng bishi* and *Tiangong kaiwu* were written for general use, thus the records might be incomplete and there might be some errors, to which extra attention needs to be paid in research. In contrast, *Zhiranju buce* and *Bu jing* were written by experts in the field for professional use and thus they are relatively more reliable.

1.3.1.2 Dye recipes recorded in these historical sources

Table 1. 2 presents the contents and documentation styles of dyeing recipes recorded in these four manuscripts. The differences in the purpose of writing and in the authors' degrees of knowledge resulted in different contents and recording styles of dye recipes. Details are discussed as follows.

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[38] Li, "Qingdai Ranzhi Zhuanzhu *Bu Jing* Kao," 79-86.
[39] Fan and Jin, 114,138.

Table 1. 2 An overview of dyeing recipes recorded in the four manuscripts

Title	**Materials and type of Fabric**	**Number of colours with dye recipes**	**Number of dyes used**	**Recipes with given measurements**	**Sequence**
Jujia biyong shilei quanji	silk cloth	7	9	√ (for most of the recipes)	√
Duoneng bishi	silk cloth	13	14	√ (for most of the recipes)	√
Tiangong kaiwu	Both silk and cotton cloth were mentioned.	27	13	× (Sometimes the quantity are indicated by 'deep' or 'lightly' dyeing.	√
Neiwufu quanzong dang'an, Zhiranju buce	silk yarn	40	11	√	×
Bu jing	cotton cloth	66	18	√	×

Firstly, in the aspect of content, the dye recipes in these manuscripts more or less vary, especially in terms of fabric type and colours obtained. In terms of fabric type, silk and cotton are the two kinds of fabrics used in these dye recipes. Cotton replaced hemp and ramie and became a major clothing material during the Ming and Qing Dynasties, while most high-status clothes were still made of silk.[40] However, no distinction in the use of

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[40] Zhu, "Ranzheng Jishu," 132-135, 146-150; Huang and Chen, 304.

dyes and dyeing methods between the recipes for silk and cotton has been found yet. This is interesting because the fibres are chemically different: silk is proteinaceous and cotton is cellulosic. The difference leads to different chemical processes of the fibers and dyes binding.[41] In terms of fabric structures, cloth was mostly used but in *Zhiranju buce* yarn was used, which suggests a change from cloth dyeing to yarn dyeing, a method that is more difficult but produces textiles of a better quality. Research showed that this change took place in the mid Ming Dynasty, after which yarn dyeing became a main technique in the Jiangnan area.[42] Moreover, in terms of colour range, *Jujia biyong shilei quanji* 居家必用事類全集 (Guide to domestic operations) and *Duoneng bishi* 多能鄙事 (Various arts in everyday life) are mainly for the brown series, that is, a mixture of black with red or yellow, while all the other manuscripts cover the entire colour range. Brown was a popular colour among common people in the Yuan Dynasty because common people were banned from wearing some bright colours and dark colours were more practical in showing less dirt.[43] Therefore the workshops that these two dye recipes originated from were most likely for common people. The number of colours obtained and the dyes used in these dye recipes are discussed further in sections 1.3.2 to 1.3.4.

Secondly, in terms of recording styles, there are both records with measurements and detailed instruction on dyeing sequences and relatively brief records only presenting raw materials for dyeing. In the two documents of the Qing Dynasty, the quantity of raw materials is described clearly but the dyeing sequence is not recorded. The reason might be that these dye recipes were used only for the preparation of raw materials, or that there were some fixed regulations for dyeing sequence that the craftsmen learned by heart, and so consequently there was no need to record them.

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[41] Judith H Hofenk de Graaff, Wilma G Th Roelofs, and Maarten R van Bommel, *The Colourful Past: Origins, Chemistry and Identification of Natural Dyestuffs* (London: Archetype Publications, 2004).

[42] Bozhong Li, 37-85.

[43] Huang and Chen, 246.

1.3.1.3 Other historical sources recording dyes and dye recipes

In addition to the above four manuscripts containing numerous dye recipes, sporadic records of dyes and dye recipes have also been found. Dye recipes were found in a manuscript of central government and two specialised manuscripts including *Zhusi zhizhang* 诸司执掌 (Responsibilities of All the Ministries, 1393), *Gujin yitong daquan* 古今醫統大全 (The Complete Works of Medical, 1557) and *Yecan lu* 野蠶録 (Record on Wild Silkworm, 1902). Dyes were recorded in local chronicles and warehousing inventories such as *Huizhou fuzhi* 徽州府志 (Chronicle of Huizhou Prefecture, Hongzhi 1487-1505) and *Daming huidian* 大明會典 (Collected Statutes of the Ming Dynasty, Ming Dynasty). In addition, in *Wuli xiaoshi* 物理小識 (Small knowledge of the principle of things, late Ming Dynasty),[44] dyes for certain colours were enumerated with some criteria for choosing dyes.

1.3.2 Dyes

Before the invention of synthetic dyes in 1856, people used natural materials for dyeing. The parts of plants containing most colourants were used, mostly roots, barks, wood, fruits and flowers. The use of dyes changed over time, and the choice and preference of dyes reflects requirements for dyes.

1.3.2.1 Commonly used dyes

Table 1.3 summarises the use of dyes in the four historical manuscripts. It can be seen that altogether eight dyes were frequently recorded: sappanwood, safflower, smoketree, Amur

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[44] Yizhi Fang, "Wu Li Xiao Shi," in *Siku Quanshu Zhenben 11 Ji* (Taipei: Shangwu yinshuguan, 1981), 41-42.

cork tree, pagoda bud, indigo, Chinese gallnut and acorn cup. The botanical sources (investigated further in Chapter 2) and parts for dyeing of these dyes are also listed in Table 1. 3 and photographic images presented in Figure 1. 1. The juice of dark plum (smoked plum) is used with safflower because it contains quite a lot of fruit acids that usefully act as an acid assistant in safflower dyeing.[45] It should be noted that compared with the full colour range, there are no single direct natural sources for lightfast green dyes (the green colourant from chlorophyll molecules is unstable under light).[46]

Figure 1. 1 Photographic images of eight common dyes recorded in the dye recipes

From left to right, top to bottom: safflower, sappanwood, smoketree, pagoda bud, Amur cork tree, indigo, acorn cup and Chinese gallnut.

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[45] Nanjing University of Traditional Chinese Medicine, *Zhongyao Dacidian* [Dictionary of Chinese medicine], 2nd ed., (Shanghai: Shanghai kexue jishu chubanshe, 2006), 2563. Safflower contains both red and yellow components: most yellow components are water soluble while most red components are insoluble in water or acid but soluble in alkalis. Therefore, ancient people discard yellow components by soaking safflowers in water and then in soured millet solution or rice juice solution, as was recorded in *Tiangong kaiwu*. In *Wuli xiaoshi*, it was recorded that after the extraction with alkali, dark plum juice is added to precipitate (the red components) for dyeing fabrics. Since no other sources of acid were recorded in the recipes, dark plum juice may also have been used in the extraction step.

[46] John C Kephart, "Chlorophyll Derivatives —Their Chemistry, Commercial Preparation and Uses," *Economic Botany* 9, no.1 (1955): 3-38.

Table 1. 3 The choice of common dyes in these dye recipes[47]

Name of dyes	**Most likely botanic species**	**Part for dyeing**	***Duoneng bishi***	***Tian-gong kaiwu***	***Bu jing***	***Zhiranju buce***
sappanwood	*Caesalpinia sappan* L.	heart-wood	√	√	√	√
pagoda bud	*Styphnolobium japonicum* L.	bud	√	√	√	√
smoketree	*Cotinus coggygria* var. *cinerea* Engl.	heart-wood	√	√	√	√
Amur cork tree	*Phellodendron chinense* var. *glabriusculum* C.K. Schneid. and *Phellodendron chinense* Schneid.	bark without cork		√	√	√
safflower & dark plum	*Carthamus tinctorius* L. and *Prunus mume* (Siebold) Siebold & Zucc.	flower, fruit		√	√	√
Chinese gallnut	Caused by the parasitism of insects *Melaphis chinensis* Bell or *M. paitan* Tsai & Tang	gallnut	√	√	√	√
acorn cup	*Quercus acutissima* Carr. and *Quercus wutaishanica* Mayr.	acorn cup	√		√	√
indigo	Mainly *Strobilanthes cusia* (Nees) Kuntze, *Persicaria tinctoria* (Aiton) H.Gross, *Indigofera tinctoria* L. and *Isatis tinctoria* L.	leaf		√	√	√

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[47] To simplify the analysis, uncommonly recorded dyes are not included in this table, nor are they included in the following analysis of single dyeing or multi dyeing.

The use of each of these eight dyes began in different periods of Chinese history, from the Zhou Dynasty (1123-256 BC) to the North Song Dynasty (960-1127). In the Ming and Qing Dynasties these dyes had already been used for dyeing in China for long. Acorn cup, smoketree, indigo and safflower were used for dyeing as early as the Zhou Dynasty and the Han (202BC-220AD) Dynasty: acorn cup was the earliest tannin dye used in ancient China, recorded in documents of the Zhou Dynasty.[48] Smoketree and indigo were used for dyeing from no later than the Han Dynasty.[49] Safflower was introduced to China and began to be used as a dye in the Western Han Dynasty (202 BC-9 AD).[50] The use of sappanwood originated in south Asia and southeast Asia and was extensively introduced to the Central Plain of China for dyeing around the Wei to Tang Dynasties (3rd-10th century).[51] Amur cork tree and pagoda bud were recorded earlier for other uses long before they were recorded to be used as textile dyes: Amur cork tree was recorded in *Qimin yaoshu* 齊民要術 (Main techniques for the welfare of the people) of the Northern Wei Dynasty (AD 386 - 534) to dye paper and in manuscripts of the Southern and Northern Dynasties (420-589) to dye silk.[52] Because of its insecticidal properties, Amur cork tree was used to dye official and religious documents.[53] Pagoda bud was recorded in documents of the Zhou Dynasty (1123-256 BC) and the earliest record on its use for dyeing is in *Bencao yanyi* 本草衍義 (Augmented Materia Medica) of the North Song Dynasty (960-1127).[54] The earliest record of Chinese gallnut for dyeing is also in *Bencao yanyi*.[55]

There are some similarities and differences in the use of dyes among the four historical

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[48] Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 224; Shanghai Textile Research Institute and Huadong Institute of Textile (currently Donghua University), "Lian Ran Yin Zheng Gongyi Jishu De Wanshan," in *Zhongguo Fangzhi Kexue Jishushi*, *Gudai Bufen*, ed. Weiji Chen (Beijing: Kexue chubanshe, 1984), 265.

[49] Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 222; Shanghai Textile Research Institute and Cultural Heritage Research Group, Shanghai Silk Industry Company, "Changsha Mawangdui Yihao Hanmu Chutu Fangzhipinde Yanjiu," (Beijing: Wenwu chubanshe, 1980), 81-100; Shanghai Textile Research Institute and Huadong Institute of Textile, 78-79.

[50] The institute for the history of natural sciences and Beijing textile research institute, "Lianran Gongyi Jishude Xingcheng," in *Zhongguo Fangzhi Kexue Jishushi, Gudai Bufen,* ed. Weiji Chen (Beijing: Kexue chubanshe, 1984), 79.

[51] Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 211.

[52] Zhao, "Zhongguo Gudai Ranse Huaxueshi," 640-641.

[53] Peter J Gibbs and Kenneth R Seddon, "Berberine and Huangbo: Ancient Colorants and Dyes," (British Library London, 1998), 18-21.

[54] Zhao, "Zhongguo Gudai Ranse Huaxueshi," 640.

[55] Ibid.

manuscripts. For common dyes, sappanwood, pagoda bud, smoketree and Chinese gallnut were recorded in all the four manuscripts, while safflower, Amur cork tree and indigo were recorded in all of them except for *Duoneng bishi*. The focussed range of colours of *Duoneng bishi* probably explains why these three dyes are not used. In *Duoneng bishi* there are up to eight dyes that are exclusively used because some dye recipes in this manuscript are for special purposes, *e.g.* to make stronger cloth (not clarified in detail in the manuscript).

Although most of the dyes are easy to use, it is difficult to dye safflower and indigo. For safflower dyeing, large amounts of safflower are needed because safflower florets yield only 0.3 to 0.6% of red components.[56] According to *Zhiranju buce*, the weight of safflower needed for pure red dyeing is ten times the weight of the fabric. The process of separating its red colourants from its yellow colourants using water is complex and time-consuming but necessary for a good quality red. In ancient China, when safflower had just been introduced to the Central Plain along the silk route from the northern Egypt and the Near East around 3th century AD,[57] the dyeing technique was not good enough and dyed fabrics tended to be orange.[58] From around the Tang Dynasty (618-907), safflower dyeing technique developed and a crimson colour called *da hong* 大紅 (pure red) or *zhen hong* 真紅 (true red) was achieved, which became an important and popular colour in the court of the Ming Dynasty because the colour purity was advocated in the authoritative theory *Wu Xing* (the Five Elements).[59] Likewise, indigo dyeing is complex but it was popular in ancient China as well. Unlike other dyes, indigo was obtained by vat fermentation from the leaves of several plants. Since indigo is not water-soluble, indigo dyeing involves the chemical processes of reduction and oxidation.[60] The processes of making indigo and dyeing with it were so complex that it was recorded in detail in many manuscripts including *Qimin yaoshu* 齊民要術 (Main techniques for the welfare of the

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[56] Zhaomu Wang, Yuehua Chen, and Youqiang Chen, *Honghua* [Safflower] (Beijing: Zhongguo zhongyiyao chubanshe, 2001), 108.

[57] Feng Zhao, "Honghua Zai Gudai Zhongguo De Chuanbo, Zaipei He Yingyong," [The spread, cultivation and application of safflower in ancient China], *China Agricultural History* 7, no.3 (1987): 61-71.

[58] Ibid.

[59] Zhang, "Yu Fu," 68-103.

[60] Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 213; Cardon, 335-336.

people, 533-544) and *Tiangong kaiwu*.[61] Despite these complexities, indigo remained a popular dye because it was not only the best source for blue,[62] but also an important dye to be used with other dyes to create purples and greens. From the above two cases, it can be seen that in ancient China dyers were willing to carry out complex dyeing procedures to achieve a colour if it was regarded as important enough, like others worldwide.

Furthermore, these dye recipes record quite a few dyes containing relatively large amounts of tannin. According to modern theories in chemistry, tannin dyes produce light brown colours, and the shades darken when combined with ferrous sulphate. In cotton dyeing tannin also enhances chemical bonding interaction between cotton and dyes; and in silk dyeing it adds weight to silk and improves some of its physical properties.[63] Among the dyes containing tannin, Chinese gallnut is the most frequent dye recorded in the four manuscripts, followed by acorn cup. Acorn cup began to be used in the Zhou Dynasty (1046-256 BC) and it was later replaced by Chinese gallnut to a large extent, which contains tannin up to 60-70% of its weight. Additionally, some other dyes containing tannin, mainly barks, leaves and nutshells, are also recorded, suggesting a wide range of easily accessible sources for tannins.[64] It was found by visible chromatography that different sources of tannin used as black dyes create slightly different shades, depending on the types of tannin and other colourants contained in the dye sources.[65] Dyes containing tannin were used extensively probably because common people were not allowed to wear bright colours and tannin could be obtained easily and cheaply to dye dark colours.[66]

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[61] Sixie Jia and Qiyv Miao, *Qimin Yaoshu Jiaoshi* [Main techniques for the welfare of the people], 2nd ed., (Beijing: Zhongguo nongye chubanshe, 1998), 374-375.

[62] Cardon, 335-336.

[63] Juan Wu and Weixian Li, "Danning Zai Ranzheng Zhong De Yingyong," [Application of tannin in the dyeing industry], *Textile Auxiliaries* 25, no.2 (2008): 1-4.

[64] Shanghai Textile Research Institute and Huadong Institute of Textile (currently Donghua University), "Lian Ran Yin Zheng Gongyi Jishude Wanshan," 265-266; Qishou Lin, "Zhongcaoyao Chengfen Huaxue," (Beijing: Kexue chubanshe, 1977), 168; Cardon, 409-484.

[65] Rangi Te Kanawa *et al.*, "Traditional Maori Dyes" in *Dyes in History and Archaeology 18*, ed. Jo Kirby, 47-50 (London: Archetype publications, 2002).

[66] Zhao, "Zhongguo Gudai Ranse Huaxueshi," 643; Liliane Masschelein-Kleiner, J Lefebvre, and M Geulette, "The Use of Tannins in Ancient Textiles" in *Icom Committee for Conservation 6th Triennial Meeting 1981 Preprints*, 7-1 to 7-7.

1.3.2.2 Eliminated dyes

Some dyes that had been frequently recorded in earlier periods,[67] rarely appear in these dye recipes: gardenia (mainly *Gardenia jasminoindes* f. *longicarpa* Z. W. Xie & M. Okada, fruit) and turmeric (*Curcuma longa* L., rhizome) are only mentioned in one of the documents, while munjeet (also known as Indian madder, mainly *Rubia cordifolia* L., root) and gromwell (mainly *Lithospermum erythrorhizon* Siebold & Zucc., root) are not recorded at all (Figure 1. 2). The reasons that the four dyes do not appear often in these dye recipes are discussed respectively as follows: 1) Gardenia and turmeric. It was recorded that the cultivation of gardenia and its use for dyeing had been very common since the Qin and Han Dynasties (221BC–220AD), but it was replaced by pagoda bud because of the former's poor lightfastness.[68] Turmeric was recorded as a yellow dye in historical documents such as *Bencao gangmu* 本草綱目 (*Compendium of Materia Medica*, 1578). Its poor lightfastness probably resulted in its being eliminated.[69] 2) Munjeet. Munjeet was the earliest red plant dye used in ancient China and was a major dye source from the Zhou Dynasty.[70] It was largely replaced by safflower in the Western Han Dynasty (202BC-9AD) when safflower was introduced and cultivated because of the beautiful colour safflower dyeing achieves as discussed above.[71] Though munjeet has far better fastness than safflower, it was still eliminated.[72] 3) Gromwell. The earliest record found on the use of gromwell for dyeing is of the Eastern Zhou Dynasty (1046-771 BC).[73] The use of gromwell for purple was probably a regional feature: the popularity occurred in the state Qi (currently in Shandong Province) in the Spring and Autumn and Warring States Period

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[67] W. Chen; Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 209-248; Zhu, "Ranzheng Jishu," 263-294.

[68] Shanghai Textile Research Institute and Huadong Institute of Textile, 260; Gabriel J. Lauro and F. J. Francis, *Natural Food Colorants: Science and Technology* (New York: Marcel Dekker, 2000), 93.

[69] Tim Padfield and Sheila Landi, "The Light-Fastness of the Natural Dyes," *Studies in Conservation* 11, no.4 (1966): 181-196.

[70] Shanghai Textile Research Institute and Huadong Institute of Textile, 257.

[71] The institute for the history of natural sciences and Beijing textile research institute, "Lianran Gongyi Jishude Xingcheng," 79; Shanghai Textile Research Institute and Huadong Institute of Textile, 256-257; Qijun Wu, *Zhiwu Mingshi Tukao* [Illustrated Research on Reality and Titles of Plants], vol. 22 (Shanghai: Shangwu yinshuguan, 1957), 535.

[72] Padfield and Landi, "The Light-Fastness of the Natural Dyes," 181-196; William Gawan Sewell *et al.*, "The Natural Dyes of Szechwan, West China," *Journal of the Society of Dyers and Colourists* 55, no.8 (1939): 412-415.

[73] Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 222.

(770-221 BC) and lasts till modern times.[74] Though gromwell is one of the few purple dye plants and it was available for the Ming Court,[75] it was not recorded in these dye recipes, probably because the main dye component of gromwell, shikonin, has poor water-solubility and needs special methods for extraction, dyeing and post-processing.[76] Also, temperatures above 75℃ affect its dye components and dulls the colour.[77] Instead, in these four manuscripts, purple is achieved by dyeing sappanwood with a mordant, which is ferrous sulphate in *Tiangong kaiwu* and alum in *Bu jing*, or by the combination of red and blue dyes, allowing dyers to better control the purple shades.

Figure 1. 2 Photographic images of four dyes commonly used in previous periods

From left to right: gardenia, turmeric, munjeet and gromwell.

1.3.2.3 The criteria for choosing dyes

In *Wuli xiaoshi*, some properties of dyes were criticised including their colouring effects, fastness and damage to the textile (as mentioned for Chinese gallnut and ferrous sulphate, *e.g.* the use of ferrous sulphate and gallnut damages the fabric. It was also recorded that a special function of cloth dyed with *Dioscorea cirrhosa* Lour. and *Diospyros oleifera* Cheng is that it cools the wearer: this is due to a rigid hydrophobic film formed within the fabric

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[74] The institute for the history of natural sciences and Beijing textile research institute, "Lianran Gongyi Jishude Xingcheng," 81; Zhu, "Ranzheng Jishu," 280.

[75] Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 222-225; Tinglong Gu, "Daming Huidian," in *Xuxiu Sikuquanshu* (Shanghai: Shanghai guji chubanshe, 1995), 541-542.

[76] Cardon, 69.

[77] Qiubao Zhou, Zhicheng Yv, and Ying Chen, "Zicao Ranliao Dui Zhensi Zhiwu Ranse Xingneng De Yanjiu," [Study on the Dyeing Performance of Zicao to Silk Fabrics], *Silk Monthly* 47, no.5 (2002): 22-24.

and on its surface by the rich condensed tannin of the dyes, keeping clothes away from skin and allowing air circulation in the microenvironment between the two.[78] Together with the above analysis, it can be seen that colouring effect, fastness and availability are the main factors affecting dyers' choice of dyes. Colour is primarily a symbol of social status or ideals, and it is an element of aesthetics and fashion. The light and wash fastness of dyes is an important indicator of the lifespan of dyed textiles. Availability is an essential factor, but once dyes and dyeing skills are available and affordable, the difficulty of dyeing and prices is not as decisive as the aesthetic effect for people's choice, as in the cases of safflower and indigo. Sometimes this effect weighs more favourably than fastness, as in the cases of safflower, while sometimes it is the opposite, as in the cases of turmeric and gardenia. Moreover, some dyes were chosen for special functions, such as the cooling effect mentioned above. These results are generally in accordance with the current understanding of the choices of European dyes.[79]

1.3.3 Dyeing techniques

Dyeing techniques mainly involve the use of a single dye or the combination of dyes, the use of additives and dyeing sequence. Additives sometimes are used to help with dyeing processes, to enhance the shade or to fix dyes with fabrics. The most important additive for dyeing is mordant, usually a mineral salt, to help achieve a certain colour shade and to improve the fastness of the dye. The sequence of adding and combining dyes, additives and fabrics in the dye bath also affects the final colour. The dyeing order was recorded in some of the dye recipes examined. The dyeing techniques are discussed as follows.

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[78] Nanjing University of Traditional Chinese Medicine, 3722-3723.

[79] Su Grierson, "The Colour Cauldron," (Perth: S. Grierson, 1986), 40; Cardon, "Yellow Dyes of Historical Importance: Beginnings of a Long-Term Multi-Disciplinary Study; Part 1," 59-73; Dominique Cardon and Claude Andary, "Yellow Dyes of Historical Importance. III: New Historical / Chemical Evidence on a Wild Mediterranean Dye-Plant, *Daphne Gnidium*" in *Dyes in History and Archaeology 16/17, 1997/1998*, ed. Jo Kirby, 5-9 (London: Archetype publications, 2001); Hofenk de Graaff, "Textile Dyeing in Leiden: Changes in the Use of Dyestuffs from the 16th to the 17th Century," 324-333.

1.3.3.1 Raw materials and how they are combined

Single dyeing

Table 1. 4 summarises the frequency of single dyeing, that is, dyeing with a single dye, recorded in the four dye manuscripts.

Table 1. 4 The frequency of the records of dyes for single dyeing and detailed dyeing methods

Dye plant	Frequency of single dyeing	Main additives	Main type of dyeing	General colours achieved
sappanwood	3	alum or ferrous sulphate	mordant dyeing	brown and purple
safflower	10	dark plum and alkali	acidic dyeing	various shades of red
smoketree	5	alum or ferrous sulphate	direct dyeing (sometimes alkali such as plant ash solution and lye is used to adjust colour) and mordant dyeing	yellow
pagoda bud	5	alum or ferrous sulphate	mordant dyeing	yellow and green
Amur cork tree	5	sometimes with 'gang zhi' (unidentified)	direct dyeing	yellow
turmeric	1	none	direct dyeing	yellow
Chinese gallnut	6	ferrous sulphate	mordant dyeing	black or grey
acorn cup	2	ferrous sulphate	mordant dyeing	black
indigo	4	none	vat dyeing	blue

All the eight commonly recorded dyes can be used for single dyeing, which is consistent with their good colouring effects. These dyes are used for single dyeing in various ways depending on their chemical properties.[80] To be specific, safflower is used by acidic dyeing, sappanwood, pagoda bud, Chinese gallnut and acorn cup are used with mordants, Amur cork tree and smoketree are both direct dyes, smoketree is also used with a mordant in some cases to enhance its yellow shades, and indigo is used by vat dyeing.

Multi dyeing

Different dyes are combined together to obtain more colours. Usually two dyes are used in a multi–dyeing recipe, occasionally three dyes are used. Table 1. 5 lists the statistical analysis results of the combination of two dyes in these dye recipes. In the table, the first row and the first column are dyes used as raw materials, and the numbers and colours in the main part of the table respectively represent the frequency of the combination of the two corresponding dyes and the colour obtained by this combination.

Table 1. 5 The frequency of the records of the combination of two dyes and the colours they obtain

Dye\Dye	smoketree	Amur cork tree	pagoda bud	turmeric	gardenia	indigo	Chinese gallnut	acorn cup
sappan-wood	1, red		1, red	1, orange		8, purple and pinkish grey	8, red and brown	1, brown
safflower	3, red			3, red	1, cream	1, purple	2, grey and black	
pagoda bud	1, yellow	1, yellow					4, green and yellowish grey	
smoketree								1, brown
Indigo		5, green	6, green				1, black	

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[80] Zhao, "Zhongguo Gudai Ranse Huaxueshi," 635-648.

There are several regulations in the combination of dyes. First, red and yellow dyes were used together to dye red shades. In one case, apricot yellow was obtained by multi dyeing with sappanwood and turmeric. The combination of dyes enriches the number and range of colours achieved, which is proved by the abundance of colour names of multi dyeing. Sometimes it saved cost: in *Tiangong kaiwu* 天工開物 (*Chinese Technology in the Seventeenth Century*), it was recorded that smoketree is used to dye the ground colour before using safflower. Moreover, occasionally two yellow dyes are used together to obtain various yellow shades, but the two red dyes, sappanwood and safflower are never used together, probably because safflower dyeing is too precious to use for colours other than crimson.

Second, indigo is often used with sappanwood to make such colours as purple, and with yellow dyes including Amur cork tree and pagoda tree to dye greens. Indigo was used frequently in multi dyeing for these colours because few dyes create satisfactory and stable purple or green colours alone.[81] However, indigo is used with safflower only once, probably for the same reason of maintaining the pure colour of safflower mentioned above. Another reason might be that the red colourants of safflower dissolve easily in the alkaline reduction dyeing process of indigo.[82]

Third, dyes containing tannin such as Chinese gallnut and acorn cup are usually combined with ferrous sulphate in order to darken the shade of other colours in multi dyeing processes.[83] This combination is often used together with sappanwood, and less often with other dyes, probably because red makes beautiful dark brown colours with tannin and ferrous sulphate.

Moreover, dye recipes that involve three dyes or more are mostly in *Zhiranju buce* and *Bu jing*. For brown shades, usually ferrous sulphate with either sappanwood or Chinese gallnut is included, ensuring a dark colour. Pagoda bud and Amor cork tree are used to adjust the

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[81] Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 222-225.
[82] Ibid.
[83] Zhao, "Zhongguo Gudai Ranse Huaxueshi," 651-652.

shades. On the other hand, to obtain green shades, dark blue and black, usually the combination of indigo, a yellow dye and a dye containing tannin are used. Sometimes ferrous sulphate is also added with tannin dyes to darken the green (blue and yellow). In this way, dark shades with rich tones are achieved.

Mordanting

In these documents, alum and ferrous sulphate are frequently used as mordants. In the three documents (except for *Duoneng bishi*), alum is mainly used with sappanwood and pagoda bud, while ferrous sulphate is mainly used with Chinese gallnut and other dyes containing tannin such as lotus shell and chestnut shell. This is consistent with current knowledge that alum helps the colourants of sappanwood and pagoda bud to be fixed to the fibres and the combination of ferrous sulphate and tannin darkens the colour.[84]

In *Duoneng bishi*, alum and ferrous sulphate are used together in single dye recipes using sappanwood, smoketree or *Vitex negundo* leaves, both with and without acorn cup Table 1.6 below). In the cases where acorn cup is added, the shade darkens, judging from the colour names in the recipes. The use of a single dye with mordants of both alum and ferrous sulphate is unique. The entry ‘Method of using ferrous sulphate’ in this document that ferrous sulphate should be added little by little to achieve an ideal shade more or less explains this combination of two mordants. This method is not recorded in the other three documents; instead, to achieve a dark shade, a dye containing tannin is usually used with ferrous sulphate. This method was abandoned probably because the use of a dye containing tannin decreases the amount of ferrous sulphate needed, preventing fabrics from being damaged in the dyeing process and being fugitive afterwards.[85] In addition, some rare mordants and additives such as acids and alkalis used require further investigation.

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[84] Ibid.

[85] Paul Garside, Sophia Lahlil, and Paul Wyeth, "Characterization of Historic Silk by Polarized Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy for Informed Conservation," *Applied spectroscopy* 59, no.10 (2005): 1242-1247; Cardon, 410.

1.3.3.2 Dyeing sequences

The dye recipes usually involve several dyes and mordants to obtain a certain colour. Dyeing sequences are described in *Duoneng bishi* and *Tiangong kaiwu*, the two dye recipes of the Ming Dynasty. Since these records are not always specific or articulate, efforts were made to find out actual dyeing sequences by investigating into some key words, integrated understanding and the consideration of the operability of these dyeing processes. The dyeing sequences recorded in these two manuscripts are shown in Table 1.6.

Table 1. 6 Dyeing sequence

Colour	**Pre-mordanting**	**Dyeing/ Simultaneous mordanting**	**Over-dyeing**	**Post-mordanting**	**Not mentioned when to add**	**Dyes used together or separately**	**Mordanting**
Duoneng bishi							
zao he 棗褐 (jujube brown)	sappanwood (second decoction) and alum	sappanwood (first decoction)		ferrous sulphate added to dye bath		— (Only one dye is used.)	pre-mordanting (with dyes present) and post-mordanting
jiao he 椒褐 (pepper brown)	sappanwood (second decoction) and alum	sappanwood (first decoction)		ferrous sulphate	acorn cup	unclear	pre-mordanting (with dyes present) and post-mordanting
ming cha he 明茶褐 (light tea brown)	alum	smoketree		ferrous sulphate added to dye bath		—	pre-mordanting and post-mordanting (with dyes present)
an cha he 暗茶褐 (dark tea brown)	alum	smoketree		ferrous sulphate added to dye bath	acorn cup	unclear	pre-mordanting and post-mordanting (with dyes present)

Table 1. 6 Dyeing sequence (continued)

jing he 荊褐 (jing brown)	alum	leaf of *Vitex negundo* variants[86]		ferrous sulphate		—	pre-mordanting
ai he 艾褐 (wormwood brown)	alum	leaf of *Vitex negundo* variants		ferrous sulphate	acorn cup	unclear	pre-mordanting
xiao hong 小紅 (light red)	pagoda bud then alum	sappanwood (second decoction) and lead oxide	sappanwood (first decoction)			dyed separately	post-mordanting and pre-mordanting (with dyes present)
xiao hong 小紅 (light red) (2)		pegoda bud and sappanwood				two dyes in the same dye bath	not mentioned
zhuan he 磚褐 (brick brown)		*jiang cha* 江茶 (probably *Camellia sinensis* (L.) O. Ktze.)		ferric oxide[87]		—	post-mordanting
qing zao 青皂 (black)		Chinese gallnut, ferrous sulphate, leavened Chinese gallnut (fermented Chinese gallnut and other materials) and *Fraxinus chinensis* Roxb.[88]				three dyes in the same dye bath	one bath-mordanting

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[86] Shizhen Li, *Bencao Gangmu: Jiaodianben* [Compendium of Materia Medica, rev. and punctuated] (Beijing: Renmin weisheng chubanshe, 1975), 968.

[87] Guojia zhongyiyao guanlijv zhonghua bencao bianweihui, "Zhonghua Bencao," (Shanghai: Shanghai kexue jishu chubanshe, 1999), 2602.

[88] Jialin Wu and Zongwan Xie, "Zhongyao Qinpi De Bencao Kaozheng," [Herbal medicine research on Cinese medicine Qinpi], *Acta Chinese Medicine and Pharmacology* 11, no.5 (1983): 64-70.

Table 1. 6 Dyeing sequence (continued)

bai meng si bu 白蒙絲布 (white)		oyster and clam shell ash				two dyes in the same dye bath	none
tie li bu 鐵驪布 (black) (2)		mulberry bark and lotus leaf				two dyes in the same dye bath	none
zao jin sha 皂巾紗 (black) (3)	with acorn cup in iron pot	black bean and pomegranate peel				three dyes in two dye baths	one bath-mordanting
jiu zao pi se 舊皂皮色 (black) (4)		*ni fan* 泥矾 ('mud mordant', unidentified), *bai yao jian* 百藥煎 (leavened Chinese gallnut as its main component) and *ji shui* 虀水 (mixed liquid)				—	one bath-mordanting
Tiangong kaiwu							
cha he se 茶褐色 (tea brown)		lotus shell		ferrous sulphate		—	post-mordanting
zi se 紫色 (purple)		sappanwood		ferrous sulphate		—	post-mordanting
jin huang se 金黃色 (golden yellow)		smoketree		plant ash, then alkali		—	none
ou he se 藕褐色 (lotus root brown)		sappanwood		lotus shell and ferrous sulphate		dyed separately	one bath-mordanting
mu hong se 木紅色 (wood red)		sappanwood		alum and Chinese gallnut		dyed separately	one bath-mordanting

Table 1. 6 Dyeing sequence (continued)

bao tou qing se 包頭青色 (black)		chestnut shell or lotus shell		iron ore and ferrous sulphate		—	post-mordanting
you lv se 油綠色 (light green)		pagoda bud		ferrous sulphate		—	post-mordanting
xuan se 玄色 (black) (2)		indigo		Chinese gallnut and ferrous sulphate		dyed separately	one bath-mordanting
da hong se 大紅色 (pure red)		smoketree (optional)	safflower			dyed separately	none
tian qing se 天青色 (deep-sky blue) and *pu tao qing* 葡萄青 (grape blue)		indigo	sappanwood			dyed separately	none
xuan se 玄色 (black)		indigo	smoketree, strawberry bark, *etc*. separately			dyed separately	none
da hong guan lv se 大紅官綠色 (official green)		pagoda bud	indigo		alum	dyed separately	not sure, probably post-mordanting for pagoda bud
dan qing se 蛋青色 (egg-shell blue), *e huang se* 鵝黃色 (goose yellow) and *dou lv se* 豆綠色 (bean green)		Amur cork tree	indigo			dyed separately	none

There are both similarities and differences in the timing of using dyes and mordants between the dye recipes of the two historical manuscripts.

The first issue is the timing of using two or more dyes. In *Duoneng bishi* some dyes were used together in the same dye bath, especially dyes with similar dye components, *e.g.* oyster and clam shell ash containing calcium carbonate and mulberry bark and lotus leaf containing tannin.[89] In contrast, in *Tiangong kaiwu*, dyes are always used in separate dye baths. One possible reason is that dyes with similar components are not used in the same dye recipe any longer. Another reason might be to prevent the competition of different dyes during dyeing processes. Dyeing all the dyes at once is much simpler and saves time and labour, but it is less controllable for colour production. As to dye sequence, usually lighter dyes are used first followed by darker dyes, *e.g.* dyeing Amur cork tree or pagoda bud followed by indigo, and dyeing indigo followed by sappanwood. This helps control the shade by preventing the darker shades from saturating the lighter ones. Multi dyeing processes using indigo in *Bu jing* are the opposite: a blue background, probably achieved by indigo, is prepared before other dyes are used to create green and purple colours. This is probably because the dyers used ready blue cloth instead of practicing vat dyeing with indigo by themselves.

The second issue to be discussed is the timing of adding mordants. On one hand, in *Duoneng bishi*, all the dye methods of pre-mordanting, post-mordanting and one-bath mordanting are used. Usually alum is used as a pre-mordant to prepare fabrics for taking colourants and ferrous sulphate as a post-mordant for ‘saddening’ dyed fabrics.[90] The method of one-bath mordanting, that is to use the dye and mordant in the same bath, is used in three dye recipes for black respectively using three dyes. This method of one-bath mordanting saves time, labour and expense but needs high requirements on the quantity of dyes and mordants and the resulting colour stays more superficially.[91] This may suggest that with one-bath method good black shades are easier to achieve than other shades. Moreover, in *Duoneng bishi*, sometimes dyes are also present in a pre-mordanting bath

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[89] Qian, 162; Peter J Hernes and John I Hedges, "Tannin Signatures of Barks, Needles, Leaves, Cones, and Wood at the Molecular Level," *Geochimica et Cosmochimica Acta* 68, no.6 (2004): 1293-1307.

[90] Cardon, 12-15.

[91] J. J. Hummel, "The Dyeing of Textile Fabrics," (London: Cassell, 1885), 271-272.

(usually the second decoction of a dye) or in a post-mordanting bath (the mordant added directly to the dye bath). This always happens in one of the mordanting processes when both pre-mordanting and post-mordanting are used, probably to further enhance the bind among the mordant, dyes and fabrics. On the other hand, in *Tiangong kaiwu*, the use of mordants is relatively simple. In single-dye recipes, usually the method of post-mordanting is used to adjust shades and achieve better fastness. In dye recipes with two or more dyes wherein one of them is Chinese gallnut, Chinese gallnut is used in the second dye-bath together with a mordant in order to sadden the fabrics. This method is used to simplify the dyeing process, probably on the basis that it does not have great influence on colour effects when compared to using the dye and the mordant separately.

In summary, the dyeing sequence depends largely on the combination of dyes and mordants and their dyeing properties, which decide their performance in dyeing as well as their colouring effects. Generally speaking, one-bath method (either for dyes or for mordanting) saves time, labour and expense but it is more demanding in terms of the quantity of raw materials and there is a risk of poor performance of dyeing.

1.3.4 The enrichment of colours

In addition to improvements in shades and fastness, enrichment of colours was an advancement of dyeing in China in the periods studied. As discussed above, the former was mainly achieved by the adoption and abandonment of dyes and some dyeing techniques. In this part how ancient dyers enriched colours is investigated.

Table 1. 7 shows the combination of raw materials for dyeing in the four manuscripts. A sharp increase in the numbers of shades can be found, from 13 in *Duoneng bishi* to 66 in *Bu jing*, over about 500 years, resulting from an increase mainly by variations in the combination and quantity of dyes and mordants rather than the fluctuated amount of dyes

used. First, variation in the combination of raw materials raised the amount of colours dramatically. The numbers of combination of raw materials recorded in *Tiangong kaiwu* and in *Bu jing* increased greatly (*Duoneng bishi* were not included in this comparison because of the limited colour range). This is realised by increased variation in single-dye recipes, combinations of two dyes, combinations of three or more dyes and variation in the use of mordants. All these factors nearly double and contribute greatly to the increased amount of shades achieved. Second, variations in the quantity of raw materials also greatly accounts for the abundance of colours.

Table 1. 7 Statistical results of the combination of raw materials[92]

	Number of dyes used	**Number of variations of single-dye recipes**	**Number of combinations of two dyes**	**Number of combinations of three or more dyes**	**Number of variations with mordants**	**Total number of dye recipes of different combinations**
Tiangong kaiwu	13	7	7	1	2	17
Bu jing	18	12	14	3	4	33
Difference	5	5	7	2	2	16

Table 1. 8 shows the statistical results of dye recipes with the same dyes and mordants but of different quantities. Variations in the same combination group achieve shades of the same series but of slightly different shades and hues. The number of dye recipe groups with the same combination of raw materials rises from 0 to 13 and the number of these dye recipes increases from 0 to 46. Accordingly, the percentage of dye recipes with different combinations of dyes and mordants decreased by half from 100% to 50%. The above analytical results show that dyers became more capable of controlling colouring effects by varying the combinations of dyes and mordants and changing quantities, which resulted in the enrichment of colours. Additionally, according to Fan, the technique of refining yellow

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[92] Variations in additives were not counted because their effects on shades are not as significant as dyes or mordants and some of the additives have not been identified yet. But the case of pouring alkali to smoketree dyed fabric is counted because in this special case alkali helps change the colour of the dyed fabric.

silk in the Ming Dynasty probably also contributed to the abundance of colours because it made dyeing light colours possible.[93]

Table 1. 8 Statistical results of variations in quantity in the dye recipes

\Items Manuscripts	Number of colours with dye recipes	Number of dye recipe groups with the same dyes and mordants	Number of dye recipes with the same dyes and mordants	Number of dye recipes in a group	Number and percentage of dye recipes with combinations of raw materials different from each other
Duoneng bishi	13	0	0	0	13 (100%)
Tiangong kaiwu	27	4	14	2~5	17 (63%)
Bu jing	66	13	46	2~6	33 (50%)

1.3.5 Discussion on the chemistry of dyes

This section is to illustrate why dyes have certain colours and are dyed in certain ways by modern chemistry.[94] The classification of dyes according to the chemical structure of their dye components also functions as a foundation of discussion on dye components from the next chapter.

1.3.5.1 Colour

Dye components are coloured chemicals and their dyeing properties in terms of colour and method of dyeing depend on their molecular structures. Dyes show colour largely because their dye components absorb certain portions of the visible light spectrum and the

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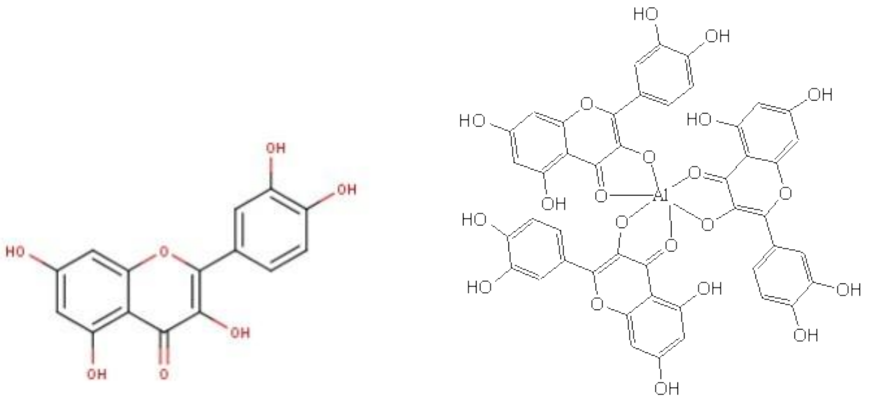
[93] Fan and Jin, 386.

[94] In ancient China, people developed their own theoretical system for understanding natural phenomena and using laws of nature. This is beyond the scope of this research, but research in this aspect can be referenced from, for example, Zhao and Zhou.

unabsorbed spectral wavelengths are reflected and perceived by us.[95] The visible light spectrum that dyes absorb is determined by their chemical structures. When a mordant is used, the metal ions of the mordant and surrounding dye molecules form new chemical bonds and thus a new structure, called complex. The complexes formed absorb different visible light spectrum from the original dye molecules, resulting in the change of colour.[96] Figure 1. 3 shows an example of a complex formed when dyeing pagoda bud with alum, which involves quercetin, a dye component of pagoda bud, and aluminium ion, the metal ion alum contains.



a quercetin molecule a quercetin-aluminium complex[97]

Figure 1. 3 An example of a dye-mordant complex

1.3.5.2 Dyeing property

In dyeing, the two key properties for dyes are water-solubility and affinity to fabrics, both determined by the chemical structure of dye components and the latter also by the type of

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[95] Asim Kumar Roy Choudhury and Textile Institute, *Principles of Colour Appearance and Measurement. Volume 1, Object Appearance, Colour Perception and Instrumental Measurement* (Amsterdam: The Textile Institute in association with Elsevier/Woodhead Publishing, 2014), 53-55.

[96] James House, *Inorganic Chemistry*, 2nd ed., (Waltham, MA: Academic Press, 2013), 553.

[97] Liuyun Jiang and Yuming Liu, "Preparation, Biological Activity and Quantum Chemistry Calculation of Quercetin-Aluminium Complex," *Chemistrymag* 6, no.12 (2004): 87.

fabric. In terms of water-solubility, most dye components have good solubilities in water and thus can be easily extracted from dye sources with water. Dye components of poor water-solubility are extracted by other means, such as using alkali to dissolve the red colourants in safflower and using a reducing agent in indigo dyeing. In terms of affinity to fabrics, dyes connecting well with fabrics are used as direct dyes. If not, mordants are added to enhance the connection between the dyes and fibres by forming complexes among the three.

1.3.5.3 Dye classes according to chemical structure

Dyes of similar chemical structures share similar physical and chemical properties and thus they are of similar colours and are used with similar dyeing methods. The dye components of the dyes discussed in this chapter are of flavonoid, chalconoid, carotenoid, diarylheptanoid, alkaloid quinone, indigoid and tannin classes (Table 1. 9).

Table 1. 9 The classification of dyes by chemical structure

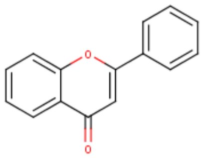
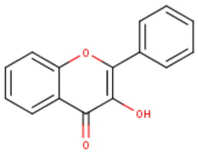
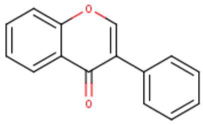
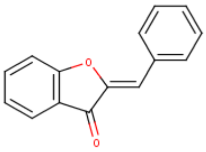
Classification	Chemical structure(s)	Main dye components	Dye Source(s)
flavonoid	  flavone flavonol   isoflavone aurone	rutin, quercetin, sulfuretin, brasilein	pagoda bud, smoketree, sapppanwood

Table 1. 9 The classification of dyes by chemical structure (continued)

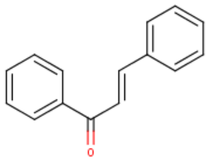
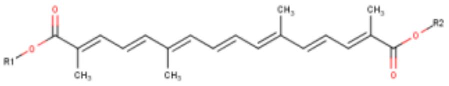
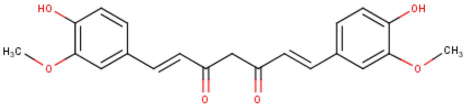
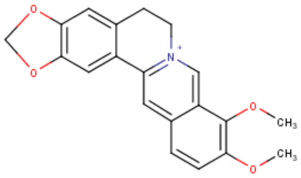
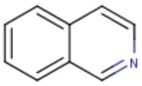
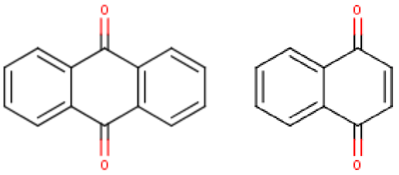
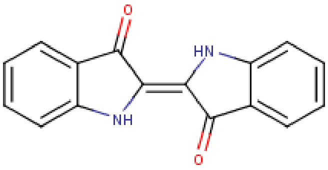
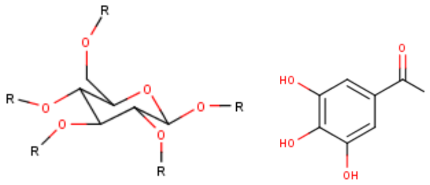
chalconoid		carthamin	safflower
carotenoid	 crocetin as an example	crocetin, crocin	gardenia
diarylheptanoid / enone/ diketone	 curcumin as an example	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin	turmeric
alkaloid	 berberine as an example  isoquinoline	berberine	Amur cork tree
quinone	 anthraquinone and naphthoquinone	6-hydroxyrubiadin, purpurin, shikonin	munjeet, gromwell
indigoid	 indigo as an example	indigotin and indirubin	indigo

Table 1. 9 The classification of dyes by chemical structure (continued)

tannin	 a gallotannin (left) as an example, R= galloyl groups (right)	gallic acid, gallotannin, ellagic acid, ellagitannin	Chinese gallnut, acorn cup

These dye classes are described in detail as following.

Flavonoid dyes

Flavonoid dyes, present extensively in nature, are the largest group of dyes in ancient China, showing a variety of red and yellow colours. Flavonoid refers to 2-phenyl-chromone formed by two phenyl rings with phenolic hydroxyl group bonded to each other through three carbon atoms in the middle.[98] Natural flavonoid compounds generally exist in the form of glycosides in such tissues as flower, leaf and fruit and in the form of free aglycones in wood.[99] Flavonoid dyes can be further classified: rutin and quercetin in pagoda bud are flavonols, brasilein in sappanwood is isoflavone, carthamin in safflower is chalcone and sulfuretin in smoketree is aurone. In terms of solubility, most flavonoid aglycones are sparingly soluble or insoluble in water, except for such aglycones as aurone and chalcone which have relatively stronger polarity. In contrast, flavonoid glycosides are usually soluble in water.[100] Some of the flavonoids are used as direct dyes and some are used as mordant dyes, depending on their affinity to fibres and requirement for colour.

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[98] Lijun Wu, *Tianran Yaowu Huaxue* [Natural Medicinal Chemistry], 6th ed., (Beijing: Renmin weisheng chubanshe, 2012), 183.

[99] L. Wu, 198.

[100] L. Wu, 194-5.

Chalconoid dyes

Chalconoid is also known as chalcone. In natural synthesis, chalcones are precursors of flavonoids. They usually have a central core formed by an aromatic ketone and an enone. Chalcones have poor water solubility.[101] Carthamin in safflower is a quinochalcone.

Carotenoid dyes

The basic structure of carotenoids is poly-isoprenoid. An carotenoid is composed of a long chain with alternative single and double bonds in the centre with two end groups, forming an almost symmetry structure. The conjugated structure makes carotenoids yellow, orange, or red.[102] Though carotenoids are extremely hydrophobic,[103] attached sugar bonds increase their water solubilities. The crocetin and various crocins gardenia contains are carotenoids.

Diarylheptanoid dyes

The main dye components of turmeric, curcumin, desmethoxycurcumin and bisdesmethoxycurcumin are diarylheptanoids, composed of two aromatic rings connected by a seven carbons chain.[104] Diarylheptanoid has poor aqueous solubility.

Alkaloid dyes

Alkaloids are a group of compounds mostly containing cation nitrogen atoms. Alkaloids of quaternary ammonium are usually water soluble and thus being used as direct dyes.[105] Berberine is an alkaloid with quaternary ammonium.

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[101] Ibid.

[102] George Britton, "Structure and Properties of Carotenoids in Relation to Function," *The FASEB Journal* 9, no.15 (1995): 1551-1558.

[103] Ibid.

[104] Goutam Brahmachari, *Chemistry and Pharmacology of Naturally Occurring Bioactive Compounds* (CRC Press, 2013), 285.

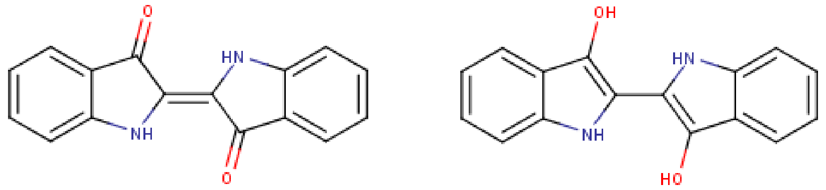
[105] L. Wu, 394.

Quinone dyes

Quinones either are unsaturated cyclic diones or compounds that convert easily to this kind of structure.[106] Further classified by the parent structure of quinones, munjeet is an anthraquinone dye and gromwell is a naphthoquinone dye. Substituents like phenolic hydroxyls on the parent structure act as auxochromes and make colours ranging from yellow, orange to purple.[107] Quinones containing phenolic hydroxyls are acidic and are soluble in alkali.[108] In general, anthraquinones are present in plants in the form of glycosides while naphthoquinons in the form of aglycones.[109] The aglycones of quinone are of low polarity and are almost insoluble in water, but the corresponding glycosides are of much higher polarity and are easily dissolved in hot water.[110] Because of the poor affinity of quinone dyes to fabrics, these dyes are usually used with mordants for dyeing.

Indigoid dyes

Indigoids are a group of compounds having a structure related to indigotin, the principle dye compound in indigo. Indigotin is not water-soluble but its reduced form, leuco-indigotin (Figure 1. 4), is soluble. Therefore indigo is used by means of reduction dyeing.



indigotin   leuco-indigotin

Figure 1. 4 Indigotin and its reduced form

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[106] L. Wu, 156.
[107] L. Wu, 163.
[108] L. Wu, 164.
[109] L. Wu, 163.
[110] Ibid.

Tannin dyes

Tannins are polyphenolic compounds. They can be divided into two classes: hydrolysable tannin, including gallotannins and ellagitannins, and condensed tannin (also known as proanthocyanidins).[111] Tannin is used in silk dyeing to produce dark shades by complexes formed with ferrous sulphate.

1.4 Conclusions

This chapter made a comprehensive comparative analysis on dyes and dyeing methods in four historical manuscripts to know about dyes and dyeing techniques in the Ming and Qing Dynasties.

Results showed that *Duoneng bishi* and *Tiangong kaiwu* were written for general use, while *Zhiranju buce* and *Bu jing* were written by experts in the field for professional use. The records in these four manuscripts stand for actual dyeing practice at that time to a large extent. The dye recipes in these four manuscripts vary with each other in both content and recording styles. The dye recipes in *Duoneng bishi* are for ordinary people and they are unique in terms of colour range, the use of dyes and some dyeing methods compared to those of high-status textiles.

With respect to dyes, it was found that sappanwood, safflower, smoketree, Amur cork tree, pagoda bud, indigo, Chinese gallnut and acorn cup are most commonly recorded. With respect to dyeing, it was found that all the commonly recorded dyes can be used for single dyeing. The method of multi dyeing is applied to enrich the colour and sometimes to save expense. In terms of the combination of dyes, red and yellow dyes or two yellow dyes can be used together, but red dyes are never used in this way to avoid the overlap of colours.

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[111] Cardon, 409-484.

Indigo is often used with sappanwood, Amur cork tree and pagoda tree to achieve such shades as purple and green. Dyes containing tannin are extensively used. They are usually used with ferrous sulphate to make dark shades. In the aspect of mordants, alum and ferrous sulphate are often used, where alum is mainly used with sappanwood and pagoda bud to help the bind with fabrics, and ferrous sulphate is mainly used with such dyes as Chinese gallnut to darken the colours.

Moreover, dyeing sequences vary between *Duoneng bishi* and *Tiangong kaiwu*. In the aspect of dyes, in *Duoneng bishi*, some dyes are used together in a dye bath, especially those with similar dye components, while in *Tiangong kaiwu*, dyes are always used in separate dye baths. Usually lighter dyes are used first followed by darker dyes, helping control the shade by preventing the darker colour from saturating the light colour. In the aspect of dyeing methods, in *Duoneng bishi*, usually alum is used as a pre-mordant to prepare fabrics for taking colours and ferrous sulphate as a post-mordant for saddening dyed fabrics. The method of one-bath mordanting is applied when using dyes with similar dye components. In *Tiangong kaiwu*, usually post-mordanting is used in single-dye recipes to adjust shades and achieve better fastness. When Chinese gallnut is used with another dye, it is usually added in the second dye-bath with a mordant to sadden the fabrics to simplify the dyeing process.

Altogether, the choice of dyes largely depends on colouring effects, fastness, availability and sometimes special functions. Based on a certain combination of raw materials, the choice of dyeing methods depends on their dyeing properties, which decide their performance in dyeing and their colouring effects. Though the dye recipes studied are isolated pieces and are of different extents of completeness and reliability, the comprehensive study on them still revealed that the advancement of dyeing is mainly achieved by the improvement of colours and fastness and the enrichment of colours. The former is achieved by the adoption and abandonment of dyes and dyeing skills, and the latter by variations in the combination and quantity of raw materials.

Additionally, by examining the chemical structures of the common dyes, it was found that the dye components of the major dyes discussed in this chapter are of flavonoid, chalconoid, carotenoid, diarylheptanoid, alkaloid quinone, indigoid and tannin groups. Their special chemical structures contribute to their colours and dyeing properties.

Through this chapter, a framework of the use of dyes and dyeing techniques in the Ming and Qing Dynasties was built up. Such important issues in dyeing as the liability of historical documents on dyeing, the combination of raw materials, factors affecting the choices of dyes and dyeing methods and the advancement of dyeing were explored in depth. The next chapter focusses on the botanical provenance of dyes recorded in the historical recipes.

2 Botanical Provenance Research of Historical Chinese Dye Plants[112]

2.1 Introduction

Dye plants are an essential part of textile dyeing. Tracing the botanical provenance of dye plants recorded in historical dye recipes ensures correct knowledge of raw materials for dyeing. This is of great importance not only to the recreation of historical dyeing activities but also to the chemical identification of dyes.[113] It would also contribute to art history and socioeconomic studies of people's choices of raw materials for textiles, and the cultivation and trade of dyes.[114] Historical records of plants in historical manuscripts of botany, herbal medicine, agriculture and local chronicles provide rich information on various aspects of plants including provenance, morphology, cultivation and functions. Among them, *Bencao gangmu* 本草綱目 (*Compendium of Materia Medica*, 1578) by Li Shizhen is widely recognised and regarded as the most complete and comprehensive book of herbal medicine in ancient China. The introduction of the Linnaean taxonomy to China in 1858 resulted in updated directories for national and local floras and herbal medicine.[115] The methodologies of textual research on herbal medicine plants and theories of herbal

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[112] This Chapter was mostly adapted from a published article: J. Han, Botanical provenance research of historical Chinese dye plants. *Economic Botany*, 2015, 69 (3) 230-239. Permission of adaption has been granted by *Economic Botany*.

[113] David A Peggie *et al.*, "Towards the Identification of Characteristic Minor Components from Textiles Dyed with Weld (Reseda Luteola L.) and Those Dyed with Mexican Cochineal (Dactylopius Coccus Costa)," *Microchimica Acta* 162, no.3 (2008): 371-380; Chika Mouri and Richard Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC," *Microchimica Acta* 179, no.1-2 (2012): 105-113.

[114] Anita Quye *et al.*, "An Historical and Analytical Study of Red, Pink, Green and Yellow Colours in Quality 18th-and Early 19th-Century Scottish Tartans" in *Dyes in History and Archaeology 19*, 2000, ed. Jo Kirby, 1-12 (London: Archetype publications, 2003).

[115] Chinese Academy of Sciences 'Flora Republicae Popularis Sinicae' Editorial, Zhongguo Zhiwu Zhi, (Beijing: Kexue chubanshe, 1959-2004), http://frps.eflora.cn/; Ruichao Lin, Ji Zhang, and Jian Zheng, *Zhongguo Yaocai Biaozhun Minglu* [Standard Directory of Chinese Herbs] (Beijing: Kexue chubanshe, 2011); Guojia zhongyiyao guanlijv zhonghua bencao bianweihui, *Zhonghua Bencao* [Chinese herbal medicine] (Shanghai: Shanghai kexue jishu chubanshe, 1999); Peigen Xiao, Dapeng Li, and Shilin Yang, *Xin Bian Zhong Yao Zhi* [Modern Chinese materia medica] (Beijing Shi: Hua xue gong ye chubanshe, 2002).

medicine varieties were also established, addressing issues of the relationship among herbal medicine varieties, their properties and medical effects, the continuity and change of varieties and genuine (道地 *dao di*) herbal plants.[116] In addition, through ethnobotanical investigations on Chinese dye plants, sources and corresponding dyeing methods used by minority groups in China were identified.[117]

However, the clarification of the names and botanical provenance of historical Chinese dye plants is still very limited.[118] By integrating research from botany and Chinese herbal medicine with research into the dye plants and dyeing history of China, a better understanding of the botanical provenance of dye plants recorded in historical documents could be gained. This is the approach taken for the research presented in this chapter, where a systematic investigation into dye plants recorded in the four extensive historical manuscripts of dye recipes from the Ming and Qing Dynasties is approached by comparing their names and dyeing properties with historical and current knowledge of dye plants and by applying research from the fields of herbal medicine and botany to help provenance the dye plants in the historical dye recipes.[119]

2.2 Materials and methods

The research in this chapter focussed on the four important historical Chinese dye manuscripts of the Ming and Qing Dynasties studied in Chapter 1. These dye recipes were

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[116] Zongwan Xie, "Zhongyaocai Pinzhong Bencao Kaozheng De Silu Yu Fangfa (1)," [Ideas and methods of herbal medicine research on Chinese herbal medicines (1)], *Journal of Chinese Medicinal Materials* 7, no.3 (1984): 37-39.

[117] Zhang, Pei, and Li, "The Use of Ethnobotany Methods in the Research of Ethnic Folk Dyeing Plants," 115-122; GuoXue Zhang, "Xishuangbanna Chuantong Ranse Zhiwu Zhi Minzu Zhiwuxue Yanjiu" (PhD thesis, Kunming Institute of Botany, Chinese Academy of Sciences, 2007); Guoxue Zhang *et al.*, "A Study on Edible Pigment-Plant Resources in Xishuangbanna, Yunnan Province of China," *Acta Botanica Yunnanica* 26, no.15 (2004): 61-69.

[118] Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 209-248; Hansheng Zhao, "Songdai Yi Shanfan Ranse Zhi Shishi He Gongyi De Chubu Tantao," [A preliminary discussion on the history and technology of Symplocos Caudata in Song Dynasty], *Studies in the History of Natural Sciences* 42, no.1 (1999): 87-94.

[119] Qian, 152-158; W. Chen; Nanjing University of Traditional Chinese Medicine; Guojia zhongyiyao guanlijv zhonghua bencao bianweihui.

all considered relative systematic and reliable resources for plant names, dyeing properties and typical desired colouring effects for the dyes of interest. More sporadic records of dyes and dyeing were also consulted to complement the above historical records.[120] Research on Chinese dyeing history was also referenced in terms of common dye plants of earlier historical periods from around the 11th century BC as well as their dyeing properties.[121]

The botanical and medical records of dye plants in *Bencao gangmu* were investigated especially the entries of name explanation (釋名 *shi ming*), the summary of earlier records (集解 *ji jie*) and processing (修治 *xiu zhi*), which provide information on plant names, origin, distribution, morphology, dyeing effects, processing, *etc*. Some plants were further studied by comparing historical and modern records on both specific dyeing properties and general properties such as morphology and distribution.[122] Relevant research outcomes in the fields of Chinese medicine plants and botany on the botanical provenance of these plants were introduced.

2.3 Results and discussion

2.3.1 A general view of common dye plants

Table 2. 1 presents the major botanical provenance of common historical dyes plants, including eight plants frequently mentioned as dyes in the four historical dyeing manuscripts of the Ming and Qing Dynasties, one additional plant as dyeing additive (dark plum) and an additional four dye plants commonly used in earlier historical periods from around the 11th century BC.

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[120] Tinglong Gu; Shenyin Wu, "Ran Jing," [The Dyeing Classic], *Zhongguo fangzhi kejishi ziliao*, no.12 (Republic of China); Yuanlong Chen, *Gezhi Jingyuan* [Mirror Origins of Investigating Things and Extending Knowledge], vol. 65 (1735), 11.

[121] W. Chen; Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 209-248; Qian, 152-158.

[122] Chinese Academy of Sciences 'Flora Republicae Popularis Sinicae' Editorial.

Table 2. 1 Major botanical provenance of common historical Chinese dyes

Chinese name as a dye	**English name**	**Major species**[123]	**Parts for dyeing**	**Typical desired colouring effect**
紅花 *hong hua* or 川紅花 *chuan hong hua*	safflower	*Carthamus tinctorius* L. (Compositae)[124]	floret[125]	various shades of red
蘇木 *su mu*	sappan-wood	*Caesalpinia sappan* L. (Leguminosae)[126]	heartwood and larger branch[127]	brown and purple (mordanted with alum or ferrous sulphate)
黃櫨木 *huang lu mu*, 黃蘆 *huang lu* or 蘆/櫨木 *lu mu*	smoketree	Mainly *Cotinus coggygria* var. *cinerea* Engl. (Anacardiaceae). The two variants var. *pubescens* Engl. and var. *glaucophylla* C. Y. Wu were possibly used as well.[128]	wood[129]	yellow

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[123] The species names are used according to The Plant List http://www.theplantlist.org. In cases where species names used in original research are not consistent with those in The Plant List, the species names in original research are in square brackets.

[124] Nanjing University of Traditional Chinese Medicine, 1376-1377.

[125] Song and Pan, 261-263.

[126] Guojia zhongyiyao guanlijv zhonghua bencao bianweihui, vol. 4, 376.

[127] Ibid.

[128] Zhensheng Qi and Chungao Li, "Wei Chuantong Mingyao 'Huangbo' He 'Huanglu' Zhengming," [Name correction for traditional herbs of 'Huangbo' and 'Huanglu'], *Hebei Journal of Forestry and Orchard Research* 27, no.2 (2012): 189-193.

[129] Shizhen Li.

Table 2. 1 Major botanical provenance of common historical Chinese dyes (continued)

槐花 *huai hua*, 槐米 *huai mi* or 槐子 *huai zi*	pagoda bud	*Styphnolobium japonicum* (L.) Schott (Leguminosae) [*Sophora japonica* L.][130]	bud (discussed below)	yellow (with alum) or green (with ferrous sulphate)
黃檗 *huang bo* or 黃柏 *huang bai*	Amur cork tree	*Phellodendron chinense* var. *glabriusculum* C.K. Schneid. (Rutaceae) and *Phellodendron chinense* Schneid.[131]	bark without cork[132]	yellow
靛 *dian* or 靛青 *dian qing*	indigo	Mainly *Strobilanthes cusia* (Nees) Kuntze [*Baphicacanthus cusia* Bremek.] (Acanthaceae), *Persicaria tinctoria* (Aiton) H.Gross [*Polygonum tinctorium* Ait.] (Polygonaceae), *Indigofera tinctoria* L. (Leguminosae) and *Isatis tinctoria* L. [*Isatis indigotica* Fort.] (Cruciferae)[133]	leaf	blue
五倍/棓子 *wu bei zi* or 川棓 *chuan bei*	Chinese gallnut	Gallnuts caused by the parasitism of insect *Melaphis chinensis* Bell or *M. paitan* Tsai & Tang on trees *Rhus chinensis* Mill., *R. potaninii* Maxim., *R. punjabensis* var. *sinica* (Diels) Rehder & E.H. Wilson (Anacardiaceae), *etc*.[134]	gallnut	black or grey (with ferrous sulphate)

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[130] Nanjing University of Traditional Chinese Medicine, 3439.

[131] Shenghuang Chen, Tasi Liu, and Kuanyu Liu, *Huangbai* [Amur cork tree] (Beijing: Zhongguo zhongyiyao chubanshe, 2001), 8; Qi and Li, "Wei Chuantong Mingyao 'Huangbo' He 'Huanglu' Zhengming," 189-193.

[132] Chen, Liu, and Liu, 8.

[133] Nanjing University of Traditional Chinese Medicine, 3403.

[134] Nanjing University of Traditional Chinese Medicine, 523-526.

Table 2. 1 Major botanical provenance of common historical Chinese dyes (continued)

皂鬥 *zao dou*， 象/橡鬥 *xiang dou* or 橡椀子 *xiang wan zi*	acorn	*Quercus acutissima* Carr. and *Quercus wutaishanica* Mayr. [*Q. liaotungensis* Koidz.] (Fagaceae)[135]	acorn cup[136]	black (with ferrous sulphate)
烏梅 *wu mei*	dark plum	*Prunus mume* (Siebold) Siebold & Zucc. (Rosaceae)[137]	fruit (smoked)	an additive in safflower dyeing
茜草 *qian cao*	munjeet (Indian madder)	Mainly *Rubia cordifolia* L. (Rubiaceae), Some other species of genus *Rubia* were also used.[138]	root	red (with alum)
紫草 *zi cao*	gromwell	It is mainly *Lithospermum erythrorhizon* Siebold & Zucc. (Boraginaceae) that was recorded in historical documents. *Onosma paniculatum* Bureau & Franch of the same family was also recorded.[139]	root	purple (with alum)
薑黃 *jiang huang*	turmeric	*Curcuma longa* L. (Zingiberaceae) (discussed below)	rhizome	yellow
梔子 *zhi zi*	gardenia	*Gardenia jasminoindes* f. *longicarpa* Z. W. Xie & M. Okada (Rubiaceae)	fruit	yellow (with or without a mordant)

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[135] Nanjing University of Traditional Chinese Medicine, 3656-3658.

[136] Ibid.

[137] Nanjing University of Traditional Chinese Medicine, 657.

[138] Guojia zhongyiyao guanlijv zhonghua bencao bianweihui, vol. 6, 470, 475; Sibao Chen *et al.*, "Qiancaoshu Yaoyong Zhiwu De Yanjiu - I. Zhongyao Qiancao De Yuanzhiwu Yu Guonei Ziyuan," [A study on the medicinal plants of genus rubia. I. Botanical origins and resource of chinese traditional medicine munjeet], *Natural Product Research and Development* 3, no.4 (1991): 7-15; Xiao, Li, and Yang, 639-643.

[139] Di Wu and Chengyi Li, "Zicao De Bencao Kaozheng," [Textual Research on Arnebia], *Lishizhen Medicine and Materia Medica Research* 19, no.8 (2008): 2042-2043.

As can be seen, one plant name referred to plants of several species or varieties, although most belonged to one or two major species or variants. Dyes from plants with close genetic relationship, for example of the same genus or species, are usually similar in their chemical composition and dyeing properties. For gromwell and indigo, a wider range of plant sources are available. Gromwell stands for two species of different genera in Trib. *Lithospermeae*. Indigo stands for four species of different orders in class *Dicotyledoneae*. Though the four plant species differ from each other to a larger extent, they still share similar property of producing the chemical colourant indigotin.

Sometimes the places of production were indicated by the dye plant names, *e.g.* 川紅花 *chuan hong hua* ('Sichuan safflower') and 川棓 *chuan bei* ('Sichuan gallnut') recorded in *Bu jing*. Quality rankings for dye plants from different production places were also evident for the dyes sappanwood, pagoda bud, Amur cork tree and safflower in *Bu jing*. In addition, in ancient China, plant quality was evaluated within the concept of genuine herbal plants: if the quality of a certain kind of plant produced in a place was better than this kind of plant produced elsewhere, the plants of this place were called genuine herbal plants, which were classified as good genetic stock, environment and cultivation techniques.[140]

Dye plants with relatively complicated issues on botanical provenance and names are discussed in detail as follows.

2.3.2 *Hong hua* 紅花 (safflower) and *fan hong hua* 番紅花 (saffron)

Saffron (*Crocus sativus* L.) and safflower (*Carthamus tinctorius* L.) were valued by ancient dyers for the red and yellow colourants that both plants yield (Table 2. 2). The shades of red and yellow were distinctly different for each plant because of differences in

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[140] Zongwan Xie, "Zhongyao Pinzhong Lilun Yanjiu," (Beijing: Zhongguo zhongyiyao chubanshe: Xinhua shudian keji faxingsuo faxing, 1991), 92-93.

the chemical composition of their colourants.[141] However, saffron was sometimes confused as safflower by herbalists of the past, *e.g. Bencao gangmu* records that saffron is safflower in western regions.[142] This is not only because of their similarity in colour but also because of the similarities in origin and name between these two plants. On one hand, safflower was introduced to the Central Plains of China from western regions along the silk route around the 3rd century AD and was called *hong hua* 紅花, meaning red flowers.[143] On the other hand, saffron was imported to China in relatively small amounts by Mohammedan during the Mongol period (1260-1367) and was unfamiliar to most Chinese.[144] Saffron was named as *fan hong hua* (western red flowers), similar to the name *hong hua* (safflower), and therefore it is not surprising that saffron was confused with safflower.

Table 2. 2 The major colourants and colouring effects of safflower and saffron

Plant name	**Major colourants**	**Colouring effects**
safflower	Safflower contains red and yellow components such as carthamin and precarthamin.[145]	red and yellow
saffron	The yellow dye components are mainly crocin and crocetin (water soluble). The red and orange dye components include lycopene, α-carotene, β-carotene and zeaxanthin (fat soluble).[146]	yellow only

In addition, the historical dye receipts show that safflower was used intensively for dyeing red despite the low content of the red components in its florets (0.3% to 0.6% per

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[141] For ease of use, the chemical structures of the characteristic components of all the common dyes are presented together in Figure 3. 29 at the end of section 3.4.1.

[142] Shizhen Li, 968.

[143] Zhao, "Honghua Zai Gudai Zhongguo De Chuanbo, Zaipei He Yingyong," 61-71.

[144] Berthold Laufer, *Sino-Iranica: Chinese Contributions to the History of Civilization in Ancient Iran: With Special Reference to the History of Cultivated Plants and Products* (Chicago: Field Museum of Natural History, 1919).

[145] Cardon, 55.

[146] SR Sampathu *et al.*, "Saffron (Crocus Sativus Linn.) - Cultivation, Processing, Chemistry and Standardization," *Critical Reviews in Food Science & Nutrition* 20, no.2 (1984): 123-157.

weight).[147] This is because of the pure red colour safflower dyes can achieve (section 1.3.2.2). Though the yellow components of safflower are in higher concentration (25% to 36%), they were usually discarded probably because of their poor lightfastness.[148] Only one documents, from north China of the Jin Dynasty (265-420), mentions using safflower for dyeing yellow.[149]

2.3.3 *Su mu* 蘇木 (sappanwood)

The main species of *su mu* is *Caesalpinia sappan* L.[150] It was also recorded as *su fang* 蘇方/枋 and *su fang mu* 蘇方/枋木. Though today this plant grows in south China,[151] in ancient times it was mainly imported from foreign countries and not produced domestically. Only one record has been found on the local production of *su mu*, whereas many documents record its import from southeast Asian countries to Guangzhou, the country's overseas trade centre.[152]

Apart from *Caesalpinia sappan* L. (sappanwood), it is likely that these names also referred to foreign redwoods. In *Ben cao gang mu*, the entry of *su fang mu* records a country *su fang* named after its indigenous plant *su fang*.[153] According to *Kun yu wan guo quan tu* 坤輿萬國全圖 (A Map of the Myriad Countries of the World, Ming Dynasty), this country is

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[147] Wang, Chen, and Chen, 108.

[148] Liping Zhang and Lina Zeng, "Si Zhong Tianran Ranliao Dui Yangmao Zhiwu De Ransexing Bijiao," [Comparison of the wool dyeing properties of four natural dyes], *Wool Textile Journal* 34, no.7 (2006): 17-22.

[149] Zaochi Xi, "Yu Yan Wang Shu," [A letter to the emperor of Yan], in *Shiji Jinzhu* [Historical Records], ed. Maqian Si (Nanjing: Fenghuang chubanshe, 2013), 1471.

[150] Guojia zhongyiyao guanlijv zhonghua bencao bianweihui, vol. 4, 376.

[151] Chinese Academy of Sciences 'Flora Republicae Popularis Sinicae' Editorial.

[152] Jun Zhang, Dinglun Xing, and Yiqian Zhao, *Yazhou Zhi* [Records of Yazhou] (Guangzhou: Guangdong renmin chubanshe, 1983), 77; Yanwu Gu, "Tianxia Junguo Libing Shu," in *Gu Yanwu Quanji*, ed. Huadongshifandaxue Gujisuo (Shanghai: Shanghai guji chubanshe, 2011), 3934; Dajun Qu, "Guangdong Xinyu," in *Xuxiu Sikuquanshu*, ed. Xuxiu Sikuquanshu Bianweihui (Shanghai: Shanghai guji chubanshe, 1995), 676-678.

[153] Shizhen Li, 968.

Brazil.[154] Therefore, the plant *su fang* here referred to redwoods abroad, including several species of the two genera *Caesalpinia* and *Haematoxylum*.[155] Whether these redwoods were imported to China in the Ming and Qing Dynasties for dyeing is not clear, but further investigation by literature research especially on trading records and by the chemical analysis of historical dyes may help answer this question.

2.3.4 *Huang lu mu* 黃櫨木, *huang lu* 黃蘆, *lu mu* 蘆/櫨木 and *lu mi* 蘆米 (smoketree)

All these names appear in the historical dye recipes. The two Chinese characters 櫨 *lu* and 蘆 *lu* share a similar structural part and pronounce the same, however, according to current knowledge, they stand for different plants, respectively some variants of *Cotinus coggygria* Scop. and the species *Berberis amurensis* Rupr.,[156] both suitable for dyeing. Table 2. 3 lists the historical records and botanical provenance of them in current knowledge. Further investigation shows that 櫨 and 蘆 in the dye recipes stand for the same plant. The first reason is that there are some similarities between 蘆木 *lu mu* and 黃櫨木 *huang lu mu* in the usage of dyeing: in *Tiangong kaiwu* and *Zhiranju buce,* they are both used for multi dyeing with safflower; in *Bu jing* and *Zhiranju buce*, they are both used for dyeing with pagoda bud and Chinese gallnut. The second reason is that 黃蘆 *huang lu* recorded in *Jujia biyong shilei quanji* where some contents of *Duoneng bishi* originated, changed to 黃櫨木 *huang lu mu* in *Duoneng bishi*, indicating they probably stand for the same plant. Judged by the great similarity in dyeing and the change of character in the two versions of

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[154] Matteo Ricci, *Matteo Ricci's World-Map in Chinese, 1602* (Beijing: Beiping yvgong xuehui, 1935), 2.

[155] Witold Nowik, "The Possibility of Differentiation and Identification of Red and Blue 'Soluble' Dyewoods: Determination of Species Used in Dyeing and Chemistry of Their Dyestuffs" in *Dyes in History and Archaeology 16/17,* 2001, ed. Jo Kirby, 129-144 (London: Archetype publications, 2001); Cardon, 274-289.

[156] Chinese Academy of Sciences 'Flora Republicae Popularis Sinicae' Editorial.

dye recipes, 櫨 and 蘆 refer to the same dye plant.

Table 2. 3 Current knowledge of *huang lu mu* 黃櫨木, *huang lu* 黃蘆 and *lu mu* 蘆/櫨木

Chinese character (simplified and unsimplified)	**Chinese name**	**Historical record**	**Latin name**	**English name**	**Major colourant**
栌，櫨	*Huang lu mu* 黄櫨木	Recorded in *Duoneng bishi* and in *Zhiranju buce* as 黄栌木.	Mainly *Cotinus coggygria* var. *cinerea* Engl. Other two variants of *Cotinus coggygria* Scop. may also have been used.	smoketree	sulfuretin[157]
芦，蘆	*huang lu* 黄蘆 or *lu mu* 蘆木)	Recorded in *Tian gong kai wu* (蘆木), *Bu jing* (芦木), and *Jujia biyong shilei quanji* (黄蘆).	*Berberis amurensis* Rupr.	Chinese goldthread	alkaloids[158]

Further investigation into historical records on both dyeing properties and plant distribution shows the recorded dye plants refer to the variants of *Cotinus coggygria* Scop. Firstly, both *Tiangong kaiwu* and *Bu jing* describe that golden yellow shade is achieved by the coordination of *lu mu* and an alkali. In some dye recipes in *Jujia biyong shilei quanji* and *Duoneng bishi*, the plant is used for dyeing with alum and ferrous sulphate. Both properties of changing golden yellow in alkali and mordant dyeing fit well with the dye

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[157] Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 209-248.

[158] Nanjing University of Traditional Chinese Medicine, 2873-2874.

component sulfuretin of *Cotinus coggygria* variants.[159] In contrast, alkaloids, the main dye components of *Berberis Amurensis* Rupr., do not have these properties: alkali does not affect much the acidity of the solution because alkaloids are strong bases, and they are direct dyes which need no mordants.[160] Secondly, in terms of plant distribution, *Cotinus coggygria* variants grow in hillside forests in the Central Plain, Jiangnan, south China, *etc*., while *Berberis Amurensis* Rupr. grows in a variety of terrain in Central Area, northwest, north and northeast of China.[161] The facts that some of the dye recipes recording this plant are of the Jiangnan area and it is recorded that *huang lu* grows in hillside forests in Shangluo (in Shanxi Province) and in Sichuan Province and can be used for dyeing confirms that the plant refers to *Cotinus coggygria* variants.[162] Additionally, only *Cotinus coggygria* variants grow in Jiangnan and south China, indicating the two names 櫨 and 蘆 were possibly regarded as the same plant in these areas in ancient times.

Apart from these names, the dye name *lu mi* 蘆米 is also recorded in *Bu jing*. It may have been wrongly written from the word *lu mu* 蘆木 because there is no historical or modern records found regarding *lu mi*, and the dye recipes of *lu mu* and *lu mi* are similar to each other. Specifically, the dye recipe for golden yellow by *lu mi* is similar to that in *Tiangong kaiwu:* alkali was used in both dye recipes with respectively *lu mi* and *lu mu*. Another evidence is that the recipes for the colours cinnamon (古銅 *gu tong*) and brown (紅捫 *hong men*) in *Bu jing* using multi-dyes including respectively *lu mu* and *lu mi* are similar: both Chinese gallnut, pagoda bud and ferrous sulphate are used in these two dye recipes. Consequently, judged from the above evidences, these dye plant names all stand for *Cotinus coggygria* variants.

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[159] TA Geissman and Leonard J, "Anthochlor Pigments. IX. The Structure of the Aurone Pigment of Cosmos Sulfureus, “Orange Flare” and “Yellow Flare”," *Journal of the American Chemical Society* 76, no.17 (1954): 4475-4476.

[160] Qian, 152-158.

[161] Chinese Academy of Sciences 'Flora Republicae Popularis Sinicae' Editorial.

[162] Shizhen Li, 968.

2.3.5 *Huai hua* 槐花*, huai mi* 槐米*, huai hua mi* 槐花米 and *huai zi* 槐子 (pagoda bud)

These four dye names are all recorded in historical dye recipes, literally referring to pagoda flower, pagoda bud and pagoda fruit in current understanding (Table 2. 4). These parts of pagoda tree all contain dye components such as rutin and quercetin,[163] but literature and experimental evidences in both the fields of dyeing and herbal medicine show that probably only pagoda bud was used in ancient times for dyeing and medicine. On one hand, the bud of pagoda was clearly stated to be used as a dye: In *Ge zhi jing yuan* 格致鏡原 (Mirror Origins of Investigating Things and Extending Knowledge, 1896) and *Tian gong kai wu*, pagoda buds are respectively used for dyeing yellow and green.[164] By the chemical analysis of historical dyes, it was confirmed the idea that pagoda bud was used for dyeing and found that pagoda bud contains a large amount of rutin, a yellowish green dye component more light-stable than quercetin, the main dye component of pagoda flower.[165] Pagoda bud changes from yellowish green to dark yellow gradually after picking because of its loss of rutin.[166] On the other hand, some clear historical records were found in herbal medicine of using pagoda buds, *e.g.* in the entry *huai hua* of *Ben cao gang mu*, it is described to collect (pagoda buds) before they blossom.[167] Additionally, it was found that these names all refer to the same part, judging from the facts that in all the manuscripts on herbal medicine and historical prescriptions *huai hua* is mostly recorded while *huai hua mi* and *huai mi* are only occasionally mentioned, and no difference is found among their usages.[168]

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[163] Nanjing University of Traditional Chinese Medicine, 3439-3440.

[164] Yuanlong Chen, 11; Song and Pan, 261-263.

[165] X. Zhang *et al.*, "The Role of Glycosides in the Light-Stabilization of 3-Hydroxyflavone (Flavonol) Dyes as Revealed by HPLC," *Microchimica Acta* 169, no.3 (2010): 327-334.

[166] Ningfei Lei *et al.*, "Huaihua Zhong Luding De Tiqu Gongyi Yanjiu," [Study on the Extraction Technology of Rutin from Sophora japonica L.], *Lishizhen Medicine and Materia Medica Research* 19, no.4 (2008): 860-861.

[167] Shizhen Li, 968.

[168] Qi Wang, "Huaihua Yv Huaimi Bingcun Zhide Shangque," [The coexist of huaihua and huaimi is debatable], *Information on Traditional Chinese Medicine* 4, no.3 (1986): 45.

Table 2. 4 Records for dyeing and current understanding of pagoda bud/flower/fruit

Name	**Current understanding**[169]	**Historical records**
槐花 *huai hua*	pagoda flower	*Duoneng bishi*, *Tian gong kai wu*, local records and warehouse list used in this research
槐米 *huai mi*	pagoda bud	*Bu jing*, *Ge zhi jing yuan*
槐花米 *huai hua mi*	pagoda bud	*Ran jing* 染經 (The dyeing classic, 20th century)[170]
槐子 *huai zi*	pagoda bud or pagoda fruit	*Zhiranju buce*

2.3.6 *Jiang huang* 薑黃 and *yv jin* 郁金 (turmeric)

Jiang huang and *yv jin* were both recorded as dyes in historical manuscripts,[171] but they cannot be allocated according to current understanding because their meanings have changed over time. In ancient China, *jiang huang* referred to some plants of genus *Curcuma* and *yv jin* was regarded as the rhizome of *Curcuma longa* L., but during late Ming and early Qing, the meaning of *yv jin* changed to the tuber of some plants in genus *Curcuma* and *jiang huang* became the rhizome of *C. longa* L. (Table 2. 5).[172] Judged from the time periods of the records of using *yv jin* and *jiang huang* for dyeing, both of them refer to the rhizome of *C. longa* L. Additionally, chemical analysis revealed that in the plants of genus *Curcuma*, the rhizome of *C. longa* L. contains an abundance of dyes (1.8-5.4%) but other parts of this plant or other plants in this genus contain few dyes.[173]

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[169] Nanjing University of Traditional Chinese Medicine, 3439-3440.

[170] Shenyin Wu, "Ran Jing."

[171] Shizhen Li, 968; Qijun Wu, "Zhiwu Mingshi Tukao," 634.

[172] Xianen Hao, Nan Li, and Siping Wang, "Jianghuang De Bencao Yanjiu," [Herbal research of turmeric], *Journal of Hebei traditional Chinese medicine and pharmacology* 15, no.2 (2000): 29-30; Guojia yaodian weiyuanhui, *Zhonghua Renmin Gongheguo Yao Dian* [Pharmacopoeia of the People's Republic of China] (Beijing: Zhongguo yiyao keji chubanshe, 2010); Lin, Zhang, and Zheng.

[173] Hao, Li, and Wang, "Jianghuang De Bencao Yanjiu," 29-30.

Therefore, the correct allocation of historical records and evidences for their suitability for dyeing both lead to the conclusion that it is the rhizome of *C. longa* L. that was used for dyeing in ancient China.

Table 2. 5 The change of meanings of *jiang huang* and *yv jin*

Name in records	**Ancient meaning**	**Current meaning (since the turn of the Ming and Qing Dynasties)**
薑黃 *jiang huang*	some plants in the genus *Curcuma*	the rhizome of *Curcuma longa* L., suitable for dyeing
郁金 *yv jin*	the rhizome of *Curcuma longa* L., suitable for dyeing	the tuber of some plants in the genus *Curcuma*

2.3.7 *Zhi zi* 梔子, *shan zhi zi* 山梔子, *huang zhi zi* 黃梔子, *shui zhi zi* 水梔子 and *fu shi zhi zi* 伏屍梔子 (gardenia)

Historical documents recorded that various kinds of *zhi zi* (gardenia) were for different usages. The difference of *zhi zi* for medicine and dyeing was recorded in the Northern and Southern Dynasties (420-589) and later in the Song Dynasty (960-1279), the fruits and flowers of different types of *zhi zi* were for medicine, dyeing and ornament.[174] Some historical documents recorded the morphology of *zhi zi* for different purposes, for example, *Tu jing ben cao* 圖經本草 (Illustrated Classic of the Materia Medica) says that round and small *zhi zi* are for medicine while long and big *zhi zi* are for dyeing.[175] The round and small ones are called *shan zhi zi* (‘mountain gardenia’), referring to *Gardenia jasminoindes* Ellis.[176] They are also called *zhi zi* or *huang zhi zi* (‘yellow gardenia’).[177] On the contrary,

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[174] Yinglan Shu, "Gudai Zhizi Jiqi Zaipei Yu Liyong," [Ancient gardenia and its cultivation and utilization], *Agricultural History of China* 12, no.3 (1992): 78-84.

[175] Song Su and Zhijun Shang (ed.), *Bencao Tujing* [Illustrated Classic of the Materia Medica] (Hefei Shi: Anhui kexue jishu chubanshe, 1994), 372.

[176] Nanjing University of Traditional Chinese Medicine, 2240-2241.

[177] Ibid.

the bigger and longer ones used for dyeing are called *fu shi zhi zi* ('lying bodies gardenia'), which are also called *shui zhi zi* ('river gardenia') and are classified as *Gardenia jasminoides* f. *longicarpa* Z. W. Xie & M. Okada.[178] In the aspect dye components, this variant contains more of the dyeing component crocin than the original variant.[179] Table 2. 6 presents the names, botanical species and main usages of various *zhi zi*. Though different *zhi zi* can be used for different purposes, it is still questionable whether this difference was widely recognised or practised because all these historical dye recipes and the contribution and storage lists in the Ming and Qing Dynasties studied only recorded the name *zhi zi*.[180] Additionally, whether the different heading characters in these names refer to the colours and growing environment of these *zhi zi* still needs further investigation.

Table 2. 6 Various names and uses of *zhi zi*

Chinese name	**Latin name**	**Main usage**
zhi zi 梔子	Mainly *Gardenia jasminoindes* Ellis. Its variants may be used as well.	medicine, dyeing and ornament
shan zhi zi 山梔子 and *huang zhi zi* 黃梔子	*Gardenia jasminoindes* Ellis	medicine
fu shi zhi zi 伏尸梔子 and *shui zhi zi* 水梔子	*Gardenia jasminoindes* f. *longicarpa* Z. W. Xie & M. Okada	dyeing

2.3.8 Further discussion

The confusion of plant names is a major factor resulting in the difficulty of provenancing

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[178] Rie Bu, "Meng Yaocai Zhizi De Bencao Kaozheng," [Herbal medicine research of the Mongolian medicine gardenia], *Journal of Chinese Medicinal Materials* 27, no.9 (2004): 692-694; Zongwan Xie, "Suizhizi De Pinzhong Kaozheng Ji Pinzhi Pingjia Chuyi," [Discussion on the variety and quality evaluation of water gardenia (shui zhizi)], *Journal of Chinese Medicinal Materials* 14, no.7 (1991): 45-47.

[179] Xie, "Suizhizi De Pinzhong Kaozheng Ji Pinzhi Pingjia Chuyi," 45-47.

[180] Ze Peng, "Hongzhi Huizhou Fuzhi," in Siku Quanshu Cunmu Congshu, Shibu (Jinan: Qilu shushe, 1997), 679; Shi Li, *Xvzuan Chun'an Xianzhi* [The Sequel to the records of Chun'an], vol. 5 (1884), 10; Li and Shen.

dyes in historical literature. This probably resulted from the facts that people from different regions or of different ethnic groups named plants in different ways and there was no uniform regulation on address either in pronunciation or in writing.[181] Besides, the change of plant name over time and wrongly written characters also contributed to the variety of plant names.[182] Whether these characters in plant names indicating origin, colour or other characteristics stand for different plant varieties needs detailed case-based investigation.

It is to be noted that plant species is only a particular level of classification rather than the utmost level or the exact extent the information that chemical and historical investigation can reveal to. Even if a dye plant is of certain genus, there may still be different assortments, whose chemical compositions are not necessarily the same.[183] For example, safflower (*Carthamus tinctorius*) has several assortments in current Chinese markets and they are named after places of origin such as Huai (Henan Province), Chuan (Sichuan Province) and Yun (Yunnan Province).[184]

2.4 Conclusions

This chapter approached the identification of the botanical provenance of common historical Chinese dye plants by studying historical and current records mainly on dyeing properties and introducing relevant outcomes on the botanical provenance of plants. Through investigation, the botanical provenance of common dye plants was identified. For some complicated cases, the following results were obtained:

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[181] Zongwan Xie, "Jiu Dangqian Zhiwu Zhongwen Mingcheng Zhong Chuxian De Yixie Wenti, Tan Zuohao Zhongyao Yuanzhiwu Zhongming Quming Gongzuo De Guanjian," [Some opinions on how to name well the original plants of Chinese herbal medicines, faced with current issues appearing in Chinese plant names], *Journal of Chinese Medicinal Materials* 10, no.3 (1987): 42-43.

[182] Ping Liu *et al.*, "Guanshang Zhiwu (20 Zhong) Guhanming Chubu Kaozheng," [The Tentative Criticisim on the Ancient Chinese Names of 20 Ornamental Plants], *Journal of Henan Normal University (Natural Science)* 40, no.2 (1999): 58-63.

[183] Yi Sun, Tao Guo and Famei Li., "Butong Chandi Honghua Yaocai De Gaoxiao Maoxiguan Dianyong Zhiwen Tupu Yanjiu," [Study on the fingerprints of Flos Carthami from different sources by HPCE], *Chinese Pharmaceutical Journal*, no.3 (2003): 16-18.

[184] Mansuer Maibula and Xiaoguang Jia, "The Historical Origins and Role of Xinjiang Safflower," *Journal of Chinese Medicinal Materials* 19, no.11 (1996): 580-583.

a) Saffron was confused with safflower in Ming Dynasty herbal plants instructions. They were mainly used to dye respectively yellow and red.

b) *Su mu* 蘇木 was in most cases *Caesalpinia sappan* L, but it also referred to foreign redwoods from genera *Caesalpinia* and *Haematoxylum* occasionally.

c) *Huang lu mu* 黃櫨木, *huang lu* 黃蘆, *lu mu* 蘆/櫨木 and *lu mi* 蘆米 in historical dye recipes all referred to the same plant, the variants of *Cotinus coggygria* Scop.

d) *Huai hua* 槐花, *huai mi* 槐米, *huai hua mi* 槐花米 and *huai zi* 槐子 used for dyeing all standed for pagoda bud.

e) *Jiang huang* 薑黃 and *yv jin* 郁金 recorded for dyeing both referred to the rhizome of *Curcuma longa* L.

f) Various *zhi zi* 梔子 were used for different purposes and the kind of *zhi zi* used for dyeing was *Gardenia jasminoindes* f. *longicarpa* Z. W. Xie & M. Okada, however, it is not clear whether this preference was widely recognised or practised in ancient times.

Generally speaking, most dye plants referred to one or two major species or variants, mainly depending on their dyeing properties and the availability of plant species. Nearly half of the dye plants were addressed by two or more names in the historical dye recipes. Investigation into records of dyeing properties was vital for the botanical provenance of historical dye plants. Existing methodologies, theories and results in the field of botany and herbal medicines also contributed greatly. Confusion about plants mostly resulted from the lack of uniform naming conventions and conversion between different taxonomies.

This chapter promoted a correct understanding of historical Chinese dye plants. The research outcomes also complemented existing outcomes of herbal medicine research in terms of dyeing. In the next chapter, the chemical analysis of reference dyes is carried out and a database for the chemical composition of dyes used in ancient China by UHPLC-PDA-MS is created.

3 Analytical Characterisation of Chemical Components for Identifying Historical and Archaeological Chinese Textile Dyes by UHPLC-PDA-MS

3.1 Introduction

There has been extensive chemical research on historical and archaeological dyes since the 19th century.[185] At first the main chemical analysis method used for historical dye identification was thin layer chromatography.[186] Then, more advanced micro-chemical techniques were introduced for historical dyes research including high performance liquid chromatography (HPLC),[187] fluorescence analysis,[188] mass spectrometry,[189] reflectance spectroscopy[190] and surface-enhanced Raman spectroscopy.[191] These analytical methods have their own advantages in terms of the amount of sample needed and the level of information about dyes revealed, and some were used together to investigate historical and archaeological dyes.[192] Other techniques like nuclear magnetic resonance have been used

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[185] Cardon.

[186] Helmut Schweppe, "Identification of Red Madder and Insect Dyes by Thin-Layer Chromatography" in *Historic Textile and Paper Materials II: Conservation and Characterization*, ed. S. Haig Zeronian and Howard L. Needles, 188-219 (Washington, D.C: American Chemical Society, 1989).

[187] Jan Wouters and André Verhecken, "The Coccid Insect Dyes: HPLC and Computerized Diode-Array Analysis of Dyed Yarns," *Studies in Conservation* 34, no.4 (1989): 189-200.

[188] Maarten R van Bommel, "The Analysis of Dyes with HPLC Coupled to Photodiode Array and Fluorescence Detection" in *Dyes in History and Archaeology 20*, 2001, ed. Jo Kirby, 30-38 (London: Archetype publications, 2005); Yasuko Noda and Susumu Shimoyama, "Non Destructive Analysis of Ukiyo-E, Traditional Japanese Woodblock Prints, Using a Portable X-Ray Fluorescence Spectrometer" in *Dyes in History and Archaeology 18*, 2002, ed. Jo Kirby, 73-86 (London: Archetype publications, 2002).

[189] Ester Simões Baptista Ferreira, "New Approaches Towards the Identification of Yellow Dyes in Ancient Textiles" (PhD thesis, University of Edinburgh, 2002).

[190] Gianluca Poldi, "Re-Thinking to Reflectance Spectrometry as a Tool to Identify Some Classes of Dyes in Old Textiles and Paintings in Situ with Examples" (paper presented at *Dyes in History and Archaeology 31*, Antwerp, 2012).

[191] A.V. Whitney, R.P. Van Duyne, and F. Casadio, "An Innovative Surface‐Enhanced Raman Spectroscopy (Sers) Method for the Identification of Six Historical Red Lakes and Dyestuffs," *Journal of Raman Spectroscopy* 37, no.10 (2006): 993-1002.

[192] Jing Han, "Zhongguo Gudai Tianran Ranliao Fenxi Fangfa Bijiao Yanjiu" (Master's dissertation, Peking University, 2012); André Verhecken, "A Concise History of Dye Analysis" in *Dyes in History and Archaeology 20*, 2001, ed. Jo Kirby, 1-22 (London: Archetype publications, 2005); Jan Wouters, "Possible Future Developments in the Analysis of Organic Dyes" in *Dyes in History and Archaeology 20*, 2001, ed. Jo Kirby, 23-29 (London: Archetype publications, 2005); Sophia Sotiropoulou, "Analytical Investigation

for more specific questions about dye structures.[193]

The method of HPLC was used widely in the research of historical and archaeological dyes since the late 1980s and became the most commonly used technique in this field.[194] This method reveals much detailed information from a small amount of sample (usually a thread end of less than 1 cm) by separating different components of the sample and identifying them respectively. This is especially important for dyes, which are chemical mixtures and their chemical fingerprint of major and minor components is the distinguishing criteria. In addition, HPLC analysis not only allows the identification of dyes but also reveals information on the provenance, pre-processing, dyeing and ageing of dyes by detecting characteristic components and tracing changes in the relative amount of the components, based on known references.[195] Ultra high performance liquid chromatography (UHPLC) is an advancement of HPLC, and its advantages include smaller sample size and better separation effects for dye components of similar chemical structures as well as using less solvent during analysis.[196] The techniques of HPLC and UHPLC are described in more detail in section 3.2

In terms of the chemical analysis of historical and archaeological Chinese dyes, research was first published in 1980 for dyes from Mawangdui Han Tomb (2nd century BC), and in

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Strategies on Organic Materials in Cultural Heritage Objects. Focus on Analytical Strategies for Natural Dyestuffs Investigations: Intercomparison of Methodologies and Evaluation of Results" (paper presented at *Dyes in History and Archaeology 24*, Liverpool, 2005); Yulin Xie *et al.*, "Identification of the Main Component of Red Dyes on Wool Textiles of the Zhou and Han Dynasties," *Sciences of Conservation and Archaeology* 13, no.1 (2001): 1-7; Cecily M. Grzywacz *et al.*, "GCI's Asian Organic Colorants Project: A Study of Gardenia Augusta Colorants by HPLC-PDA-MS, Raman, SERS and MicroSPEX " (paper presented at *Dyes in History and Archaeology 27*, Istanbul, 2008).

[193] Gundula Voss, "NMR Spectroscopy of Leucoindigotins and Formation of Deuterated Indigotins" in *Dyes in History and Archaeology 18*, 1999, ed. Jo Kirby, 21-29 (London: Archetype publications, 2002).

[194] Jan Wouters, "High Performance Liquid Chromatography of Anthraquinones: Analysis of Plant and Insect Extracts and Dyed Textiles," *Studies in Conservation* 30, no.3 (1985): 119-128.

[195] Zhang *et al.*, "The Role of Glycosides in the Light-Stabilization of 3-Hydroxyflavone (Flavonol) Dyes as Revealed by HPLC," 327-334; David A Peggie, "The Development and Application of Analytical Methods for the Identification of Dyes on Historical Textiles" (PhD thesis, University of Edinburgh, 2006); Jo Kirby *et al.*, "From Botanical Source to Analytical Result: The Influence of Recipe and Plant Source on Appearance and Composition of Anthraquinone and Flavonoid Dyes and Pigments" (paper presented at *Dyes in History and Archaeology 32*, La Rochelle, 2013).

[196] Ana Serrano, Maarten van Bommel, and Jessica Hallett, "A New Method for Characterizing Dyestuffs with Ultra-Performance Liquid Chromatography" (paper presented at *Dyes in History and Archaeology 31*, Antwerp, 2012); Lore Gertrud Troalen, "Historic Dye Analysis: Method Development and New Applications in Cultural Heritage" (PhD thesis, University of Edinburgh, 2013).

the 1990s for dyes on Dunhuang Diamond Sutra, dated to 868 AD.[197] More research was undertaken to identify historical and archaeological Chinese dyes during the last decade.[198] Research on the characteristic components of specific groups of historical Asian dye sources such as flavonoids, protoberberines and *Rubia* species promoted the precise identification of relevant dye sources.[199] There was growing knowledge of the chemical composition of Chinese dyes, both in the field of historical and archaeological dyes and in other fields such as medicine and biochemistry. However, knowledge on historical Chinese dyes in these aspects was still limited.

The research described in this chapter aims to establish an analytical methodology for historical Chinese textile dyes by UHPLC coupled with photodiode array detector (PDA) and to improve the understanding of the chemical composition of these dyes. The chemical

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[197] Shanghai Textile Research Institute and Cultural Heritage Research Group, Shanghai Silk Industry Company, "Changsha Mawangdui Yihao Hanmu Chutu Fangzhipinde Yanjiu," (Beijing: Wenwu chubanshe, 1980), 81-100; Peter J Gibbs *et al.*, "Analysis of Ancient Dyed Chinese Papers by High-Performance Liquid Chromatography," *Analytical chemistry* 69, no.10 (1997): 1965-1969.

[198] Bing Zhu *et al.*, "Analysis of Dyed Silk Excavated from Yongxing Tomb of the Han Dynasty, Sichuan," *The Chinese Journal for the History of Science and Technology* 24, no.2 (2003): 59-63; Xuelian Zhang *et al.*, "Analysis of Ancient Textile Dyes," *Sciences of Conservation and Archaeology* 5, no.1 (1996): 1-8; Xie *et al.*, "Identification of the Main Component of Red Dyes on Wool Textiles of the Zhou and Han Dynasties," 1-7; Wang, Liu, and Tong, "Qingdai Zhiranju Ranse Fangfa Ji Secai [Dyeing methods and colours in the Weaving and Dyeing Bureau of the Qing Dynasty]," 125-127; Xian Zhang *et al.*, "Characterization of Yellow Dyes in Nineteenth-Century Chinese Textiles," *Studies in Conservation* 52, no.3 (2007): 211-220; Jan Wouters, Cecily Grzywacz, and Ana 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," *Studies in Conservation* 56, no.3 (2011): 231-249; Estrella Sanz Rodr ́guez *et al.*, "Characterization of Natural and Synthetic Dyes Employed in the Manufacture of Chinese Garment Pieces by LC-DAD and LC-DAD-QTOF," *E-conservation Magazine* 5, no. 21 (2011), http://www.acrro.ro/pdf/biblioteca-virtuala/surse/reviste/e-conservation%20the%20online%20Magazine%2021,%20sept%202011.pdf; Regina Hofmann-de Keijzer *et al.*, "Yellow Silk for Buddha – Dye Analysis on Tang Dynasty Textiles from the Famen Temple near Xi'an, Shaanxi Province, China" (paper presented at *Dyes in History and Archaeology 33*, Glasgow, 2014); Jing Han and Anita Quye, "Dyeing Practice and the Society: A Study of Historical Chinese Dyes of the Ming and Qing Dynasties (1368-1911) by Chemical Analysis and History of Art" (paper presented at *Dyes in History and Archaeology 33*, Glasgow, 2014); Han, "Zhongguo Gudai Tianran Ranliao Fenxi Fangfa Bijiao Yanjiu."

[199] Chika Mouri and Richard Laursen, "Identification and Partial Characterization of *C*-Glycosylflavone Markers in Asian Plant Dyes Using Liquid Chromatography–Tandem Mass Spectrometry," *Journal of Chromatography A* 1218, no.41 (2011): 7325-7330; X. Zhang *et al.*, "Preliminary Studies toward Identification of Sources of Protoberberine Alkaloids Used as Yellow Dyes in Asian Objects of Historical Interest," *Studies in Conservation* 55, no.3 (2010): 177-185; Yoshiko Sasaki and Ken Sasaki, "Analysis of Protoberberines in Historical Textiles_ Determining the Provenance of Easy Asian Textiles by Analysis of Phellodendron," *e-Preservation Science* 10, no. 10 (2013), http://www.morana-rtd.com/e-preservationscience/2013/Sasaki-20-01-2013.pdf; Jan Wouters, Cecily Grzywacz, and Ana Claro, "Markers for Identification of Faded Safflower (Carthamus Tinctorius L.) Colorants by HPLC-PDA-MS Ancient Fibres, Pigments, Paints and Cosmetics Derived from Antique Recipes," *Studies in Conservation* 55, no.3 (2010): 186-203; Mouri and Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC," 105-113.

profiling of silk samples dyed by common dyes and less common dyes, and dyes and dyed cotton of the Li ethnic minority is carried out for the following:

a) Common dyes.

UHPLC-PDA analysis of silk samples dyed by reference common dyes is undertaken. To characterise new components, an additional detection method is used, called Electrospray Ionisation Mass Spectrometry (ESI-MS), which is described in detail in section 3.2 below. This technique is applied for the first time to the chemical characterisation of the twelve common dyes in ancient China (Chapter 1).

b) Less common dyes.

The chemical profiling of less common dyes used in ancient China listed in existing research results by UHPLC-PDA is carried out and the analytical results are compared with those of the common dyes and are used to complement the UHPLC-PDA library of Chinese dyes.[200] Though there has been research on the chemical composition of these plants in the fields of Chinese plant medicine and biochemistry, this is the first time to chemically characterise the dye components of dyed reference with these less common dyes, except for carpet grass and Chinese goldthread.[201]

c) Dyes of the Li ethnic minority.

Furthermore, this chapter also explores the cotton dyeing techniques of the Li ethnic minority in Hainan, which developed continually from past to present, shedding light on dyeing techniques in ancient China. The Li group was the first group in Chinese history to use cotton textiles. Relevant written records of as early as 1st century BC show that Li

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[200] Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 222-225.

[201] Xian Zhang and Richard Laursen, "Application of LC–MS to the Analysis of Dyes in Objects of Historical Interest," *International Journal of Mass Spectrometry* 284, no.1 (2009): 108-114; Zhang *et al.*, "Preliminary Studies toward Identification of Sources of Protoberberine Alkaloids Used as Yellow Dyes in Asian Objects of Historical Interest," 177-185.

cotton products were used to contribute to court since the Tang Dynasty (618-907).[202] It was from the Li group that Huang Daopo (c.1245-1330), an important Figure in Chinese textile history, learned advanced cotton handicrafts, and then spread and improved the techniques in her hometown, Songjiang, which greatly promoted cotton handicrafts in Jiangnan area and led to its dominance in cotton handicrafts in China for hundreds of years.[203] Because of the important place of the cotton handicrafts of the Li group in Chinese textile history and its endangered situation faced with the challenges of modern industry today, 'traditional Li textile techniques: spinning, dyeing, weaving and embroidering' was listed as national intangible cultural heritage in 2006 and was inscribed on the List of Intangible Heritage in Need of Urgent Safeguarding by UNESCO in 2009.[204] Though there was increasing research on the dyes and dyeing techniques of the Li group in recent years,[205] so far there has been no research on the chemical analysis of dyes and dyed fabrics of the Li group. In fact, despite the increasing research investigating dye sources and dyeing techniques used by ethnic minorities across China in recent decades, no chemical analysis of the dyes and dyed samples of ethnic minorities has been undertaken.[206] This part of the research pioneers the chemical analysis of dyes of Chinese ethnic minorities by exploring the chemical composition of dyed samples and dyes of the Li group. This not only improves the understanding of historical Chinese dyeing techniques but also contributes to the further understanding and the preservation of the precious textile handicrafts of the Li group.

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[202] Zhichao Xing, *Lizu Wenhua Suyuan* [Origin of Li culture] (Guangzhou: Zhongshan daxue chubanshe, 1993), 112-113.

[203] Hengxian Tu, "Huangdaopo Dui Jiangnan Mian Fangzhi Fazhan De Gongxian" in Annual Conference for History of Science and Technology, 2006, 72-74.

[204] UNESCO, "Traditional Li Textile Techniques: Spinning, Dyeing, Weaving and Embroidering. Inscribed in 2009 (4.COM) on the List of Intangible Cultural Heritage in Need of Urgent Safeguarding," http://www.unesco.org/culture/ich/index.php?lg=en&pg=00011&USL=00302.

[205] Wei Wang, "Li Jin - Xiumian Long Bei Yanjiu Chutan" (Master's dissertation, Minzu University of China, 2012); Zhebo Wang and Dadong Zhan, "Shixi Tianran Ranliao Zai Xiandai Lizu Zhijin Zhong De Diwei," [Analysis of the status of natural dyes in modern Li brocade], *Journal of Qiongzhou University* 19, no.4 (2013): 59-63; Qingxin Zhang, "Lun Lizu Zhijin Zhiwuran Jiyi Zai Xiandai Fuzhuang Sheji Zhong De Yunyong," [The application of plant dyeing techniques in Li brocade to modern fashion design], *Textile Science Research* 28, no.11 (2014): 100-102.

[206] Zhang, "Xishuangbanna Chuantong Ranse Zhiwu Zhi Minzu Zhiwuxue Yanjiu"; Wang and Wang, "Shujin Chuantong Gongyi Ranse - Tianran Zhiwu Sesu Ranse," 47-51; Ru Long *et al.*, "Hebei Yesheng Ranliao Zhiwu De Diaocha Yanjiu," [Investigation of wild dyeing plants in Hebei Province], *Journal of Anhui Agricultural Sciences* 36, no.7 (2008): 2895- 2897.

Lastly, the chemical analysis protocol used in this chapter is evaluated and the certainty of dye identification based on characteristic components is discussed.

The characterisation of the less common dyes and Li dyes was undertaken by UHPLC-PDA analysis at the Centre for Textile Conservation (CTC) while the characterisation of the common dyes was undertaken at the Cultural Heritage Agency of the Netherlands (RCE) with Maarten van Bommel and Jantien Wanrooij, where UHPLC-PDA-ESI MS was available. The UHPLC-PDA-ESI MS system was operated by Wanrooij.

The characterisation of reference Chinese dyes is of great importance for understanding the dye composition of historical and archaeological objects, not only in China but also in other areas worldwide using similar dyes.

3.2 General principles of UHPLC-PDA-MS

3.2.1 HPLC and UHPLC: principle and instrumental structure

Chromatography is a chemical analysis technique that separates different constituents of a mixture and identifies them respectively. Generally speaking, chromatography involves a stationary phase and a mobile phase. When a mixture passes the stationary phase with the mobile phase, its constituents interact with the two phases and come out at different times. In this way these constituents are separated from each other. When the mobile phase is liquid, the technique is called liquid chromatography.

High performance liquid chromatography generally involves a column packed with porous polymer particles, called the stationary phase, and solvents that are pumped by high pressure through the column, called the mobile phase or eluents. Samples of dye dissolved in a solvent are injected into the column and the separation of different dye constituents takes place as samples pass through the column with the mobile phase (Figure 3. 1). In addition, because of the chemical nature of dyes, a non-polar (hydrophobic) stationary phase is typically used, and the method is termed 'reversed phase chromatography'.[207] In reversed phase chromatography, the hydrophobic stationary phase attracts the more hydrophobic components in the sample, while the more polar (hydrophilic) molecules in the sample are attracted to the hydrophilic mobile phase. During the analysis, a more hydrophobic solvent is gradually added to the mobile phase, which attracts the hydrophobic molecules on the stationary phase. With the right mixture of solvents, all the sample components pass through the column (elute) as individual separated components.

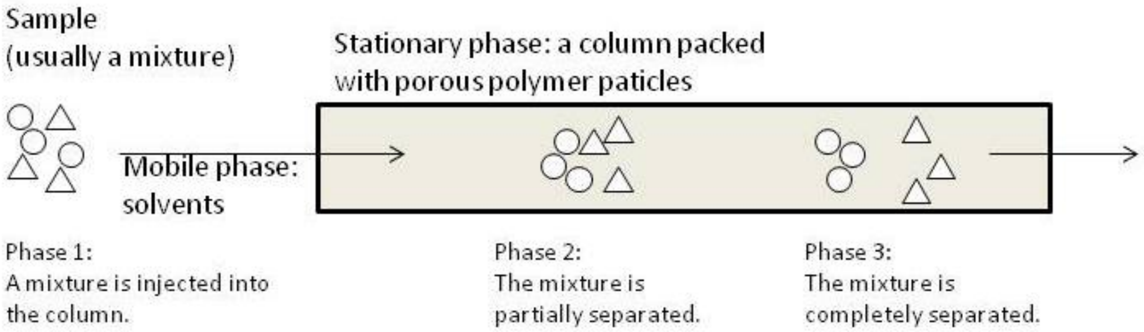

Figure 3. 1 The separation of a mixture when passing through an (U)HPLC column

Figure 3. 2 shows the overall structure of an HPLC system. It mainly consists of solvents, a pump, a sample injector, a column and a detector. Solvents are pumped into the column and a sample is injected. In the column, the different constituents of the sample are separated. Then these constituents come out of the column separately, called elute, and are detected by the detector.

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[207] Serban Moldoveanu and David Victor, *Essentials in Modern HPLC Separations* (Waltham, MA: Elsevier, 2013), 9-10.

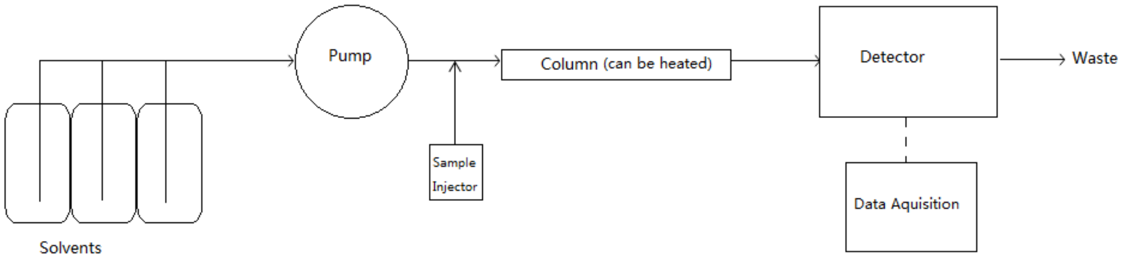

Figure 3. 2 Diagram of an (U)HPLC system

In the latest decade, the technique of HPLC was developed rapidly and an advanced technique, UHPLC, came into existence. The core advances of UHPLC compared to HPLC are that the polymer particle size in the column is decreased significantly, from around 5 µm to sub-2 µm, and the pressure the system can withstand is increased accordingly to up to 1,000 bar, enabling better resolution and sensitivity, and smaller amount of sample besides other benefits.[208] These advantages fostered the application of UHPLC to cultural heritage objects because of strong interests in advanced techniques to reduce the size of samples taken from the precious cultural heritage objects. The advances in UHPLC necessitated advances in the chemistry of the stationary phase. For this research, Ethylene Bridged Hybrid (BEH) was selected (ACQUITY BEH Shield RP18, Waters Ltd) based on existing research results comparing different UHPLC columns used for the identification of historical dyes.[209]

3.2.2 (U)HPLC coupled with PDA

(U)HPLC can be couple with various detectors such as ultra violet-visible (UV-vis)

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[208] Quanyun A. Xu, *Ultra-High Performance Liquid Chromatography and Its Applications* (Hoboken, N.J.: Wiley, 2013), vii.

[209] Serrano, Bommel, and Hallett, "A New Method for Characterizing Dyestuffs with Ultra-Performance Liquid Chromatography."

detector, mass spectrometry detector and fluorescent detector. The UV-vis detector and mass spectrometry (MS) detector (section 3.2.3) are the two most common detector incorporated with HPLC to analyse historical and archaeological dyes. The UV-vis detector records UV-vis spectral information of coloured and non-coloured components. Nowadays the use of PDA allows to record the spectral information by multi-wavelength.

The analytical result of (U)HPLC-PDA is presented by the form of a graph called a chromatogram. Figure 3. 3a presents a chromatogram of a pure chemical berberine (the main dye component of Amur cork tree) as an example. In a chromatogram, each peak relates to an individual component. The horizontal axis shows the retention time of the component, which refers to the time duration from sample injection till the component is detected by the PDA detector. The vertical axis shows the absorbance intensity of the component at a certain wavelength, which relates to the amount of this component in the sample injected into the column and its absorption intensity at this wavelength. In this example, the major peak, standing for berberine, has retention time of 8.39 min. In another word, this component elutes at 8.39 min. It has an absorbance intensity of 1 at 254 nanometers (nm). The number of separated components and their relative peaks are characteristic for different dyes, and each dye's chemical chromatographic 'fingerprint' enables the dye to be identified. Another characteristic property of the individual separated components that can be measured to characterise the dye is the ultra-violet and visible (UV-vis) light that the individual component absorbs, which is presented in the form of an UV-vis spectrum. This information is gained from the PDA detector, which measures the full UV-visible spectrum of each separated component from 190 to 800 nm. Figure 3. 3b shows the UV-vis spectrum of berberine detected in the above example. It has maximum absorption at 229.3, 264.8, 346.5 and 424.7 nm. The analyst uses the information from the chromatogram and the component spectra to differentiate and identify dyes by matching the result to known compounds and dyes. For example, if the analytical result of extracts from an unknown historical Chinese dye by UHPLC-PDA using the same system condition with that for reference samples shows that the main component of the unknown dye elutes at the same time with berberine and has the same UV-vis spectrum as that of berberine, this dye component can be identified as berberine. The dye source can tentatively be identified as Amur cork tree (further discussed in section 3.4.5).

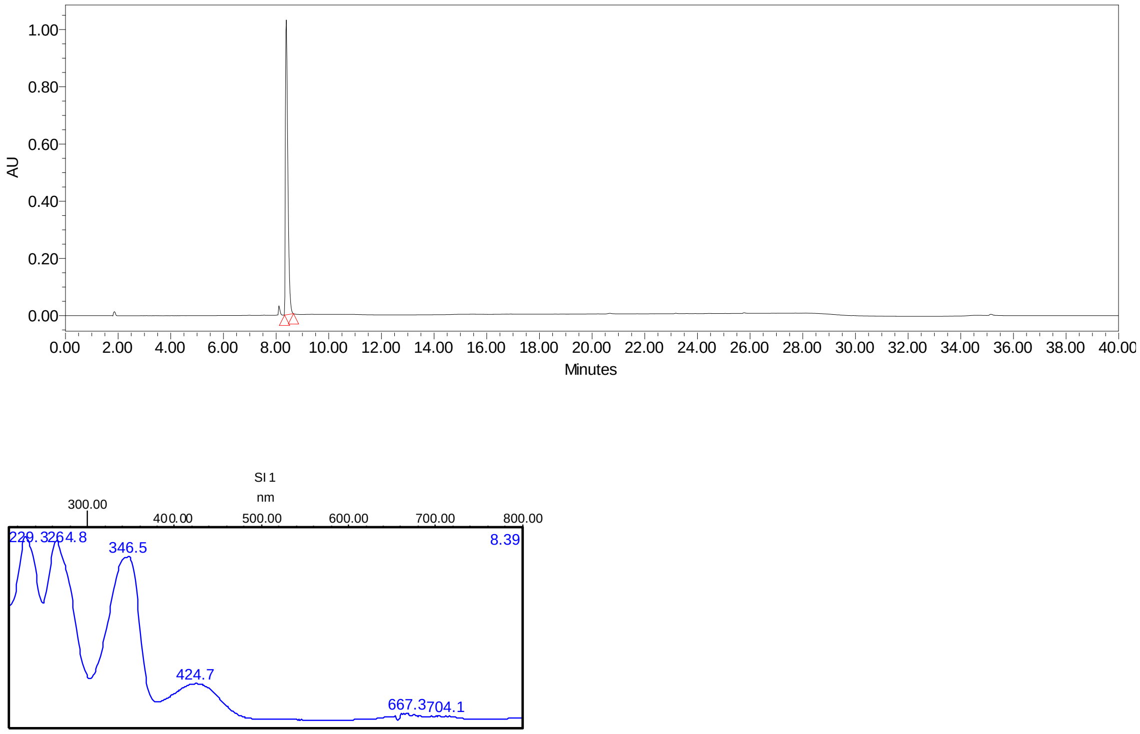

Figure 3. 3 An analytical result of UHPLC-PDA including a chromatogram (monitored at 254 nm) and a corresponding UV-vis spectrum

3.2.3 (U)HPLC coupled with MS and MS/MS

A mass spectrometer detector provides information on molecular weight and structure. This is especially helpful in dye analysis in cases where dye components have similar UV-vis absorption, reference components are not available, or information on the molecular structure of dye components is needed.[210]

When the components separated by (U)HPLC enter a MS detector, the MS ionises these

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[210] Mouri and Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC," 105-113; Ferreira, "New Approaches Towards the Identification of Yellow Dyes in Ancient Textiles."

components, separates the ions by their mass-to-charge ratio (m/z) values and then detects the ions by their m/z and abundance.[211] ESI (Electrospray Ionisation) is an ionisation technique that produces ion sources by generating an electrospray: sample solution is sprayed intro a strong electric field from a charged syringe and forms a spray of highly charged droplets which are attracted to an MS inlet. Then the solvent evaporates and the repulsion within the charged droplets forces out gaseous ion fragments which are measured in the spectrometer.[212] ESI-MS causes little fragmentation for the molecules and thus is suitable to detect the molecular weight of the analytes.[213] Furthermore, if more detailed information on molecular structure is needed, the method of MS/MS (also called tandem MS) is applied, by which selected ions are further fragmented by MS to obtain the m/z values of the fragments of the selected ions.[214]

Similar to the analytical result of (U)HPLC-PDA, the analytical result of (U)HPLC-MS is also presented as a chromatogram. The difference is that the vertical axis of an (U)HPLC-MS chromatogram shows the intensity of ion production, which refers to either the overall intensity of ion production in a total ion current (TIC) chromatogram (see Figure 3. 4a as an example) or the intensity of an selected ion in a selected ion monitoring (SIM) chromatogram (see Figure 3. 14). Figure 3. 4b shows the mass spectrum of a component eluting at 9.7 min. The m/z of its molecular ion $[M - H]^-$ is 787, and thus the molecular weight is 788, which helps identify the component as tetragalloyl glucose ($C_{34}H_{28}O_{22}$).

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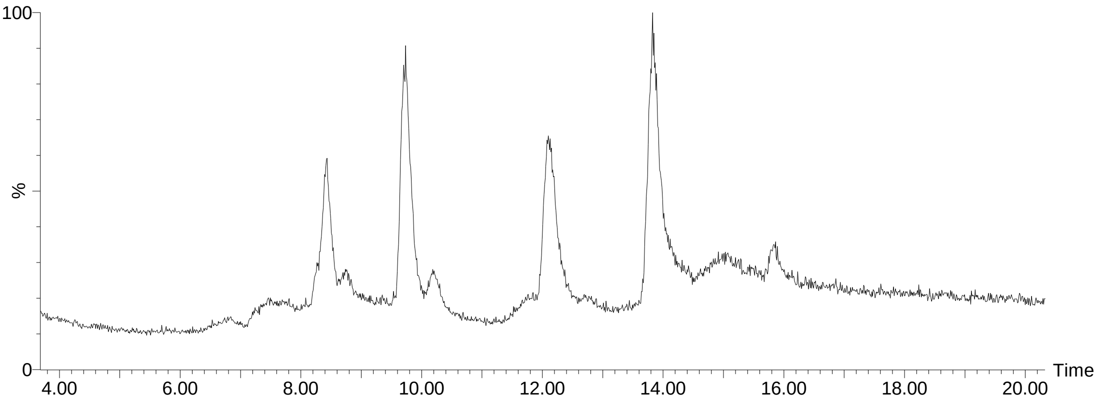
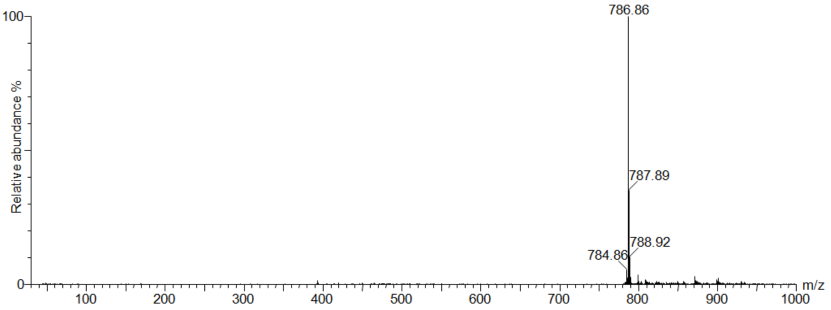
[211] Jürgen H. Gross, *Mass Spectrometry*, 2nd ed., (Berlin: Springer, 2011), 415-416.
[212] Gary Siuzdak, *Mass Spectrometry for Biotechnology* (San Diego, Calif.: Academic Press, 1996), 14.
[213] Gross, 415-416.
[214] Ibid.



(a)



(b)

Figure 3. 4 UHPLC-MS total ion current chromatogram of the extract of a gallnut dyed silk (a) and mass spectrum of tetragalloyl glucose (b)

3.3 Materials and methods

3.3.1 Materials

3.3.1.1 Silk samples dyed by common dyes and less common dyes

Dyeing was undertaken according to historical dye recipes to prepare for reference samples.

Dyes

Silk samples dyed with the twelve common dyes in ancient China, as determined from the historical research in Chapter 1, were used to first evaluate the UHPLC-PDA analytical methodology at the Centre for Textile Conservation (CTC), and then the dye components in these samples were characterised by the optimised method. The common dyes included safflower, sappanwood, munjeet (also known as Indian madder), gromwell, smoketree, Amur cork tree, turmeric, pagoda bud, gardenia, indigo, Chinese gallnut and acorn cup. Following this investigation with common dyes, the chemical profiles of ten less common dyes was undertaken. The less common dyes obtained included small carpetgrass, safflower (to dye yellow), lotus leaf, lotus seed shell, pomegranate, silkworm thorn (also known as cudrang and mandarin melon berry), Chinese goldthread (also known as cudrang and mandarin melon berry), saffron, Japanese knotweed and rhubarb (Figure 3. 5). Most of the dyes are of reliable botanical provenance in China. Nine common dyes and all the less common dyes were purchased in Chinese medicine shops in Anguo, Beijing and Shanghai. Acorn cup was collected at Peking University. There are several common species of munjeet and smoketree in China. To ensure correct plant species, reference plants were collected respectively from a hill in Beijing and in the botanical garden of Institute of Medicinal Plant Development, Beijing. A list of dye sources and their corresponding species is presented in Table 3. 1 and Table 3. 2.

Figure 3. 5 Photos of the nine less common dyes used in ancient China

From left to right, top to bottom: small carpetgrass, lotus leaf, lotus seed shell, pomegranate, silkworm thorn, Chinese goldthread, saffron, Japanese knotweed and rhubarb. A photo for safflower is presented in Figure 1. 1.

Table 3. 1 General information on reference common dyes

English name	**Latin name**	**Parts used for dyeing**
safflower	*Carthamus tinctorius* L.	flower
sappanwood	*Caesalpinia sp.* (most likely *Caesalpinia sappan* L.)	heartwood and larger branches
munjeet (also known as Indian madder)	*Rubia cordifolia* L.	root
gromwell	Most likely *Lithospermum sp.*	root
smoketree	*Cotinus coggygria* var. *cinerea* Engl.	wood
Amur cork tree	*Phellodendron chinense* Schneid.	bark without cork
turmeric	*Curcuma longa* L.	rhizome
pagoda bud	*Styphnolobium japonicum* L.	bud
gardenia	*Gardenia jasminoindes* f. *longicarpa* Z. W. Xie & M. Okada	fruit
indigo	*Strobilanthes cusia* (Nees) Kuntze, *Persicaria tinctoria* (Aiton) H.Gross, *Indigofera tinctoria* L. or *Isatis tinctoria* L.	leaf
Chinese gallnut	produced by the insect *Melaphis chinensis* Bell or *M. paitan* Tsai & Tang	gallnut
acorn	*Quercus acutissima* Carr. or *Quercus wutaishanica* Mayr.	cup

Table 3. 2 General information on reference less common dyes

English name	**Chinese name**	**Latin name**	**Family**	**Parts used for dyeing**[215]	**Dye class**[216]
small carpetgrass	藎草 *jin cao*	*Arthraxon hispidus* (Thunb.) Makino	Gramineae	all aerial parts	flavonoid
safflower (to dye yellow)	紅花 *hong hua*	*Carthamus tinctorius L.*	Asteraceae	floret	flavonoid
lotus leaf	荷葉 *he ye*	*Nelumbo nucifera* Gaertn.	Nymphaeaceae	leaf	flavonoid
lotus seed shell	蓮子殼 *lian zi ke*	*Nelumbo nucifera* Gaertn.	Nymphaeaceae	shell	flavonoid
pomegranate	石榴 *shi liu*	*Punica granatum* L.	Punicaceae	rind	flavonoid & tannin
silkworm thorn	柘 *zhe*	*Maclura tricuspidata* Carri ère	Moraceae	wood	flavonoid & tannin
Chinese goldthread	黃連 *huang lian*	*Coptis chinensis* Franch.	Ranunculaceae	rhizome	alkaloids
saffron	番紅花 *fan hong hua*	*Crocus sativus* L.	Iridaceae	stigma	carotenoid
Japanese knotweed	虎杖 *hu zhang*	*Reynoutria japonica* Houtt.	Polygonaceae	rhizome and root	anthraquinones
rhubarb	大黃 *da huang*	*Rheum spp.*	Polygonaceae	rhizome	anthraquinones & tannin

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[215] Cardon.

[216] Summarised from literature and analytical results presented in section 3.4.2.

Fabrics

Silk (Habotai Silk Medium White B1) was used as substrate material for dyeing because silk was the most common material for high-status costume and textiles. When mass dyeing with common dyes a piece of silk of about 1.3 g (20 cm × 20 cm) was used for each dye recipe. When dyeing with less common dyes a stipe of silk of about 0.1 g (4 × 10 cm) was used for each dye recipe.

Chemicals

Pure chemicals were used as additives for dyeing to enable the identification of the key components of the reference dyes before the chemical analysis of the more chemically complex historical dye samples. Chemicals used for dyeing included aluminium potassium sulphate dodecahydrate (ACS, >=98%) and sodium carbonate (>=99.0%) from Sigma-Aldrich (Dorset, UK), iron (II) sulphate (>=99.0%), potassium carbonate (ACS, 99+%), sodium hydroxide (analytical grade) and citric acid monohydrate (analytical grade, 99.5%) from Acros organics (Geel, Belgium), acetic acid (ACS, >=99.7%) and ethanol (analytical grade) from Fisher Scientific (Loughborough, UK) and thiourea dioxide (>=98%) from Fibrecrafts (Guildford, UK).

Dyeing processes

The detailed processes of souring, extracting dye components, dyeing and mordanting are presented as follows. Parameters for dyeing experiments such as temperature and time duration were rarely recorded and therefore modern dyeing practices were also consulted.[217]

Souring. Before dyeing, silk was scoured with soda (bath ratio 1:50, pH 9) at simmer for 15 mins to remove impurities.

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[217] Wang, "Chuantong Caomu Ranliao De Wuse Sesu Cuiqu Ji Yingyong Yanjiu"; Yunsong Sun, "Zhiwu Ranse Jishu," [Plant dyeing techniques], *Silk* 45, no.10 (2000): 24-27.

Extracting dye components from dyes. Dyes were cut into small pieces or grinded to powders, soaked in 250 ml deionised water (180 ml for less common dyes) for 20 mins, brought to boil and then simmered at 90 ℃ for 30 mins. The solution was filtered by a piece of wet cotton. This procedure was repeated once to let more colourants in the plants come out. Around 250-300 ml decoction was obtained for dyeing. Pagoda buds and gromwell were used for dyeing in slightly different ways: pagoda buds were fried with mild heat before boiling according to historical records such as those in *Duoneng bishi*. For the extraction of gromwell dyes, water was adjusted to pH 10 to help the dissolution of the dyes and then adjusted to pH 5 during dyeing. Extraction and dyeing was carried out at 50-60 ℃ for 40 mins to prevent possible decomposition of its dye components.

Dyeing. A piece of silk was wetted, soaked in 40 ℃ dye bath, the dye bath heated slowly to 60-70 ℃ and remained for 1 hr, with regular stirring. The fabric was then rinsed and left to dry, protected from light.

Safflower was used for dyeing by acidic dyeing and indigo by reduction dyeing because of their special chemical properties. Details for dyeing with these two dyes are as follows.

Acidic dyeing with safflower. In the process of safflower dyeing, the yellow colourants of safflower were extracted to dye yellow before the extraction of red colourants. According to the different solubilities of the colourants, water and alkaline were used successively to extract these colourants. Safflower florets were soaked in 1,000 ml water, pounded, and the yellow leaching solution wrung away with a piece of cotton. 1,000 ml more water was added to the safflower florets and the yellow leaching solution wrung away. This soaking-wringing process was repeated altogether for five times and then the safflower florets was soaked in an acidic solution (adjusted by acetic acid to pH 5-6, to prevent the red colourants from dissolving in water) and left overnight to allow most of the yellow colourants left to be dissolved in water. The next day, the yellow leaching solution was wrung away and this process using acid was repeated for another two times. In this way, almost all the yellow colourants were removed. After that, the florets were soaked in an alkaline solution (adjusted by sodium carbonate to pH 10 when the florets were in the solution) and the solution was heated to 60 ℃ and remained for 1 h to dissolve the red colourants. Then the solution was filtered with another piece of cotton and the filtered solution was used for dyeing. When dyeing, the dye bath was adjusted to pH 5-6 by citric acid. A piece of silk was soaked in the dye bath and kept at room temperature for 2 hrs, with constant stiring. Then the silk was taken out and soaked in citric acid solution (pH 5) and remained for 10 mins to fix the red colourants on the silk and to dissolve potential yellow colourants. Last the dyed silk was rinsed and allowed to dry in air.[218]

Reduction dyeing with indigo. In ancient times indigo dyeing involves a time-consuming natural reduction procedure.[219] To simplify this procedure and to better control the analytical results of indigo dyed samples, modern reducing agents were used instead. Since indigo is not water-soluble, it is reduced to its soluble form for dyeing and then oxidised back to indigo. Indigo vat was prepared with dissolving 5.5 g thiourea dioxide and 1.6 g sodium hydroxide in deionised water. 2/3 vat was diluted to 75 ml and transferred to a beaker with 1 g indigo, pre-mixed with ethanol. The vat was heated at 60 ℃ for 15 mins and then cooled to 40 ℃. A yellowish green vat was obtained, indicating the reduction of indigo. Then the rest of the vat was diluted to 125 ml and transferred to the beaker with reduced indigo to keep the solution reductive. Vat dyeing was carried out at 30℃. A piece of silk was soaked in the vat for 1 min, spin dried and oxidised in air for 3 min. This process was repeated for 4 to 6 times till a dark blue shade was achieved. Last, indigo dyed silk was rinsed and allowed to dry in air.[220]

Mordanting. Mordants used for dyeing included alum (2 g/L) and ferrous sulphate (0. 05 g/L). Mordanting with alum was usually undertaken before dyeing and mordanting with ferrous sulphate after dyeing. First, mordants were dissolved in water or in the dye bath

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[218] Wouters, Grzywacz, and Claro, "Markers for Identification of Faded Safflower (Carthamus Tinctorius L.) Colorants by HPLC-PDA-MS Ancient Fibres, Pigments, Paints and Cosmetics Derived from Antique Recipes," 186-203.

[219] Zhao, "Zhiwu Ranliao Zai Gudai Zhongguo De Yingyong," 229.

[220] Jianguo Wu *et al.*, "Tigao Zhuma Zhiwu Dianlan Ranse Deseliang Gongyi Tantao," [An investigation into improving the colour yield of indigo dyeing on ramie fabrics], *Textile Dyeing and Finishing Journal* 26, no.1 (2004): 17-19.

and heated slowly to 40 ℃. Then the wet silk was soaked in the mordant solution, the bath heated slowly to 60-70 ℃, kept for 15-30 mins and allowed to cool. Surplus mordants were rinsed away. Silk pre-mordanted with alum was kept wet till dyeing. Silk post-mordanted with ferrous sulphate was dried in air.

Dye recipes and dyed samples

Dye recipes in the four manuscripts of the Ming and Qing Dynasties, especially those using a single dye and for a deeper shade, were replicated to dye reference samples. For the dyes with which historical dye recipes were not available, direct-dyeing was undertaken to prepare reference dyed samples, and, if the colour obtained was too light, pre-mordanting with alum and post-mordanting with ferrous sulphate were carried out in the dyeing process. Detailed dye recipes for common dyes and less common dyes and the photos of dyed samples are presented respectively in Table 3. 3 and Table 3. 4.

Table 3. 3 Dye recipes for dyeing with common dyes and colours obtained

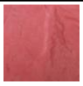
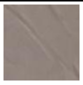
Dye	Amount (g)	Main additive(s)	Dyeing method	Colour achieved	Photo
safflower	30	acetic acid, citric acid and alkali	acidic dyeing	red	
sappanwood	1	alum	post-mordanting	brown	
	1	ferrous sulphate	post-mordanting	purple	
munjeet	1	alum	pre-mordanting	red	
gromwell	1.5	alum	pre-mordanting	purple	
smoketree	0.5	alum	post-mordanting	yellow	
Amur cork tree	0.5	none	direct dyeing	yellow	
turmeric	5	none	direct dyeing	yellow	
pagoda bud	1	alum	post-mordanting	yellow	
	1	ferrous sulphate	post-mordanting	green	
gardenia	1	none	direct dyeing	yellow	
indigo	1	none	vat dyeing	blue	
Chinese gallnut	0.3	ferrous sulphate	post-mordanting	black	
acorn cup	0.5	ferrous sulphate	post-mordanting	black	

Table 3. 4 Dye recipes for dyeing with less common dyes and colours obtained

English name	Amount (g)	Dyeing method	Colour achieved	Photo
small carpetgrass	1	direct dyeing	yellow	
safflower (to dye yellow)	1	direct dyeing	yellow	
lotus leaf	0.4	direct dyeing	brown	
lotus seed shell	0.5	post-mordanting with ferrous sulphate	brown	
pomegranate	2	pre-mordanting with alum	yellow	
silkworm thorn	3	pre-mordanting with alum	yellow	
Chinese goldthread	0.2	direct dyeing	yellow	
saffron	0.01	direct dyeing	yellow	
Japanese knotweed	1	pre-mordanting with alum	yellow	
rhubarb	1	direct dyeing	yellow	

3.3.1.2 Dyed cotton samples and dyes from the Li group

In the aspect of Li dyeing, dyed cotton threads were collected from Li dyers by textile curator Yu Ying at the Shanghai Museum during fieldwork on the traditional textile handicrafts of the Li group in Baisha Li Autonomous County and Ledong Li Autonomous County of Hainan Province in 2014 and information on their dye sources and dyeing methods was provided. Altogether eight dyed cotton samples were collected. The dyes for the cotton samples include sappanwood, turmeric, chestnut bark, chestnut shell, and two indigo dyes, *lan dian* and *jia lan dian* (details in Table 3. 3). The two samples dyed with turmeric were respectively dyed with and without plant ash. In addition, a piece of jambul bark and a piece of tree bark used to fix dyes (plant source unclear) were collected (Figure 3. 6).

Table 3. 5 General information on the dye sources used by the Li group

Chinese name	**English name**	**Latin name**	**Family**	**Parts used for dyeing**
紅心蘇木 *hong xin su mu*	sappanwood	*Caesalpinia sappan* Linn.	Leguminosae	heartwood
黃薑 *huang jiang*	turmeric	*Curcuma longa* L.	Zingiberaceae	rhizome
藍靛 *lan dian*	literally means 'indigo'	probably *Indigofera tinctoria* L. (commonly known as 木藍 *mu lan*)	Papilionaceae	leaf
假藍靛 *jia lan dian*	literally means 'fake indigo'	*Indigofera suffruticosa* Mill. (also known as 野青樹 *ye qing shu*)	Papilionaceae	leaf
板栗 *ban li*	chestnut	*Castanea mollissima* Blume	Fagaceae	bark and shell
烏墨樹 *wu mo shu*	jambul	*Syzygium cumini* (L.) Skeels	Myrtaceae	bark

Figure 3. 6 A piece of jambul bark (left) and a piece of tree bark (right) used to fix dyes used by the Li group

3.3.1.3 Chemicals

At the CTC, DMSO (HPLC grade), 36% hydrochloric acid (analytical reagent grade) and methanol (HPLC gradient grade) from Fisher Scientific (Loughborough, UK), oxalic acid dihydrate (99+%) from Acros organics (Geel, Belgium) and acetone (ACS reagent, >=99.5%) from Sigma-Aldrich (Dorset, UK) were used for sample preparation. Methanol (HPLC gradient grade) and formic acid (analytical grade 98/100%) from Fisher Scientific (Loughborough, UK) and deionised water (18.2 MΩ·cm) purified by Millipore Direct-Q 3 UV Water purifier (Darmstadt, Germany) were used for the preparation of elution solutions for UHPLC analysis. At the RCE, chemicals of similar grades were used, including DMSO, oxalic acid dihydrate and 37% hydrochloric acid from Merck-Schuchardt (Hohenbrunn, Germany), and methanol from Sigma-Aldrich (Munich, Germany) used for sample preparation; and methanol and formic acid from Sigma-Aldrich (Munich, Germany) and deionised water (Millipore Simplicity TM Simpak® 2, R = 18.2 MΩ·cm, Ettenleur, The Netherlands) used for the preparation of elution solutions for all analyses.

3.3.2 Analytical Methods

3.3.2.1 Extraction

In sample preparation, four different methods were used to extract dye components from the samples. They included a two-step extraction method, dimethyl sulfoxide (DMSO) followed by oxalic acid solution (OA), and three one-step extraction methods respectively using hydrochloric acid (HCl) solution, DMSO and deionised water. DMSO is especially suitable for the dyes which bind to the textile fibres via hydrophobic interaction, i.e. vat dyes and direct dyes, while oxalic acid solution and hydrochloric acid solution are used to break the metal-dye bond of the mordant dyes. Dyes and additives were extracted by water to mimic actual dyeing process. The combination of these extraction methods could enable further understanding of the dye composition. Details for the four different extraction methods used for the reference samples are as follows.

Extraction method 1

DMSO-OA for all the reference dyed samples, including silk samples dyed by the common dyes and the less common dye and dyed cotton samples of the Li group. Samples were extracted individually with a two-step extraction method using DMSO and oxalic acid. A sample of dyed silk of approximately 1 cm^2 (3 mg) or dyed cotton of approximately 1 cm (1 mg) was taken and transferred into a 1 ml flat-bottom glass vial. 100 µl of DMSO was added to the sample with a micropipette and the vial heated at 80 ℃ for 10 mins in a Talboys block heater. By this step all vat and direct dyes are extracted. Next, the DMSO extract was transferred by a micropipette with a disposable tip into a plastic vial and this extract retained. An aliquot of 100 µl of oxalic acid solution, composed of a mixture of 0.5M oxalic acid / acetone / water / methanol (1:30:40:30 (v/v/v/v)) was added to the fibre sample remaining in the vial. The sample was heated for a further 15 mins at 80 ℃ in the block heater to extract the mordant dyes and the extract was then evaporated to dryness using a BUCHI R-215 Rotavapor. Subsequently, this dried extract was reconstituted using the first DMSO fraction, thereby combining the extracts from the two steps together.

Extraction method 2

HCl for munjeet dyed silk. A munjeet dyed silk sample was extracted with a one-step method using 100 µl methanolic hydrochloric acid solution (6 N hydrochloric acid / water / methanol, 1:1:2 (v/v/v)) at 100 ℃ for 10 mins in a 1 ml flat-bottom glass vial. The sample was then evaporated to dryness and dissolved in 100 µl DMSO.

Extraction method 3

DMSO for gromwell plant. The dye components of gromwell were extracted directly from the plant by 100 µl DMSO, heated at 80 ℃ for 10 mins.

In the final stage, all the hydrolysates were filtered through 0.2 µm Agilent premium syringe filters into full recovery vials with top spring vial inserts. 2-4 µl was injected for analysis. At the RCE, a water bath was used for heating and a gentle nitrogen flow for the evaporation of extracts. The (combined) extracts were centrifuged for 10 mins at 2000 rpm, and then the solvent was transferred into a new micro-insert vial, with great care to avoid transferring any precipitates, and were centrifuged again for 10 mins at 2000 rpm to avoid the injection of any particles which would block the UHPLC column.

Extraction method 4

Deionised water for the jambul bark and the tree bark for stabilising shades of the Li group. Approximately 0.5 g sample was taken and put into a flat-bottom vial, 0.5 ml deionised water added, the sample heated at 100 ℃ for 10 mins and filtered through a 0.2 µm syringe filter. 10ul was injected for UPLC-PDA analysis.

3.3.2.2 UHPLC-PDA analysis

The extracts were analysed by Waters® ACQUITY UPLC® H-Class system at both the CTC and the RCE. The UHPLC system is composed of a quaternary solvent manager, a sample manager Flow Through Needle (FTN), a column manager and a PDA detector. The system is controlled by ACQUITY UPLC Console and Empower 3 software. Prepared samples were placed in a vial support located in the sample manager chamber. A volume of 4 µl was injected by an auto-sampler for each analysis (2 µl at the RCE). A Waters C18 Ethylene Bridged Hybrid (BEH) shield column (150 × 2.1 mm I.D., particle size 1.7 µm) was used for separation. At the CTC, a C18 BEH shield VanGuard pre-column (5 × 2.1 mm I.D., particle size 1.7 µm) was installed in front of the C18 BEH shield column to prevent the column from being blocked by potential particles in samples. A gradient elution programme involving water, methanol and formic acid was used. The mobile phase was composed of 10% aqueous methanol (v/v) (solvent A), pure methanol (solvent B) and 1%

aqueous formic acid (v/v) (solvent C) and a 40-min gradient elution programme was set for each analysis. Column temperature was set at 40 ℃ and the flow rate was 0.2ml/min. The initial eluent composition was 80% A : 10% B : 10% C and held till 1.33 min; this ratio changed linearly to 74% A : 16% B : 10% C from 1.33 to 2.33 min, then to 55% A : 35% B : 10% C from 2.33 to 5.33 min. This composition was held till 9 min, changed linearly to 30% A : 60% B : 10% C from 9 to 14 min, to 5% A : 85% B : 10% C from 14 to 25 min, and then to 100% B from 25 to 26 min. The ratio remained till 30 min, returned linearly to the initial ratio of 80% A : 10% B : 10% C from 30 to 32 min and held for 8 minutes till 40 min (Figure 3. 7). UV-Vis data was collected in the range of 190 to 800 nm with the resolution of 1.2 nm and was monitored at 254 nm.

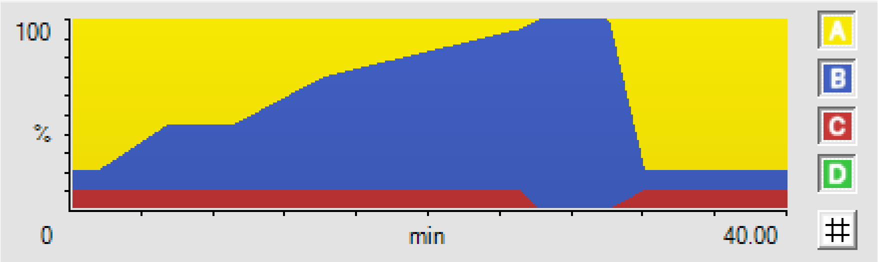


Figure 3. 7 Gradient elution programme used. Solvent A: 10% aqueous methanol; solvent B: pure methanol; solvent C: 1% aqueous formic acid.

In terms of data processing, the chromatogram obtained was extracted at one or two wavelengths that allowed the best detection of all the characteristic peaks of the dye. ApexTrack integration method in the Empower software, a method detecting peaks by their 2nd derivative and thus allowing for better integration, was applied. A chromatogram of the time range 2.5 minutes (min) to 28 min was integrated, which included all the characteristic peaks of the dyes and excluded a solvent peak eluting at the beginning. The co-elution of some components, showing as partly overlapped peaks, disturbs their identification. The co-elution of components is detected by peak purity test. The standard purity threshold was set at 5, which is the largest purity angle obtained from the analytical results of pure chemicals of dye components that have absorbance units less than 1. Co-eluting peaks were detected when the purity angle of the peak is larger than its purity threshold. These co-eluting peaks were separated by adjusting the extraction wavelength.

The extracted characteristic components were identified by means of their UV-vis spectra obtained with the PDA detector together with their retention time. At the RCE, a UHPLC-PDA software library is available containing more than 100 spectra of reference materials extracted and analysed under exactly the same conditions. If all main components in a sample are detected, there was no need for additional MS analysis. However, those components which could not be identified by their UV-vis spectra due to lack of appropriate reference materials were further characterised using MS. The UV-vis spectra of unknown components were also compared with those published in the field of cultural heritage and in the fields of medicine, food chemistry and forestry science. All the characteristic components detected were added to a UHPLC-PDA software library at the CTC to establish a database for Chinese dyes.

3.3.2.3 UHPLC-ESI-MS analysis

An MS system was coupled with UHPLC to further characterise the separated dye components. The MS system was a Micromass QTOF-2 system with an electrospray ionisation ion source inlet. The system was controlled by MassLynx NT software. A split was used in such a way that 20% of the effluent was transported to the MS detector while 80% of the effluent was guided through the PDA detector. A negative ionisation mode was used. The collision energy was 8-10 eV for single MS mode. Source conditions included a capillary voltage of 3.0 kV, a cone voltage of 40 V, a source temperature of 80 ℃ and a desolvation gas temperature of 150 ℃. The nitrogen gas flow rate was set at 120 L/h for cone gas, 90 L/h for nebulizer gas and 120 L/h for desolvation gas. The scan range for m/z was usually 0-800. For the analysis of gallnut it was adjusted to 0-1100 to detect dye components of higher molecular weight. For MS/MS analysis the collision energy was set at 80 eV and increased to 160 eV when necessary. Acquired data of unknown dye components was compared with published data of relevant components for identification.

3.4 Results and discussion

3.4.1 Characterisation of the dye components of common dyes[221]

3.4.1.1 Gallnut

A UHPLC-PDA chromatogram was obtained from the extract of the silk sample dyed with gallnut (Figure 3. 8). Spectral information shows that there are a series of constituents with similar UV-vis absorption profiles, with characteristic maximum absorptions around 219 and 277 nm. The components were identified by comparing their retention time and spectral information to the in-house UHPLC-PDA library of standard dye compounds. As a result, two tannin components, gallic acid (eluting at 3.0 min) and ellagic acid (co-eluting with another component at 13.5min), were identified.

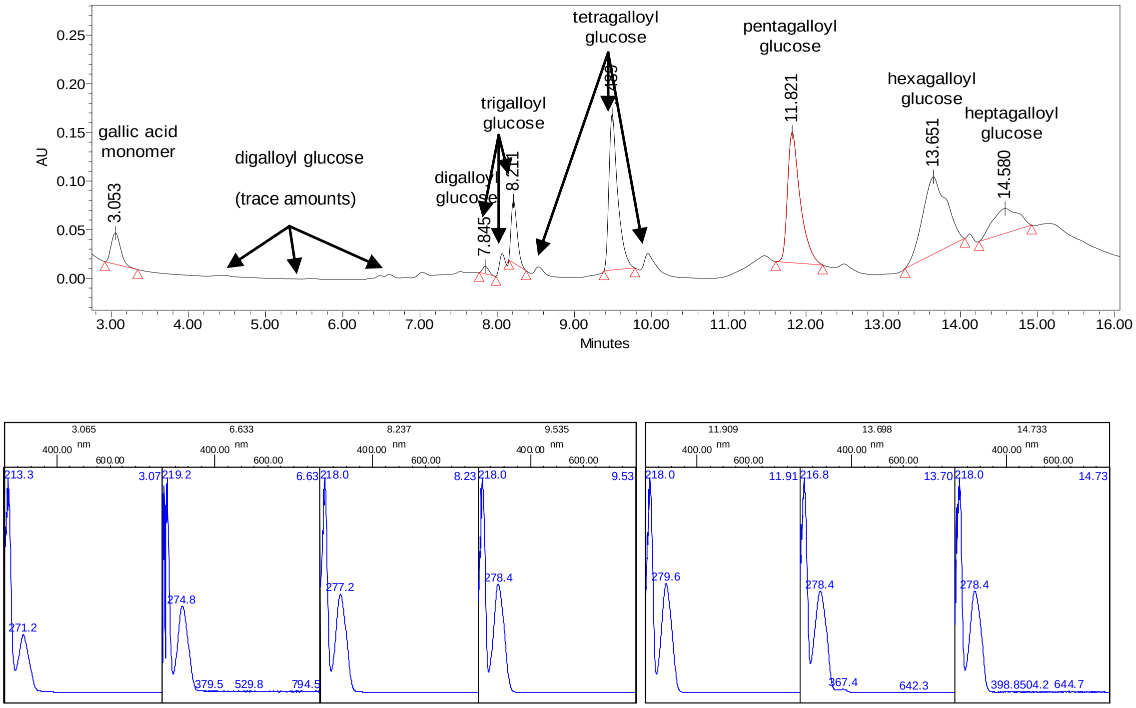


Figure 3. 8 UHPLC-PDA chromatogram (monitored at 254 nm) of the gallnut dyed silk extract and the UV-Vis spectra of its main constituents

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[221] For ease of use, the chemical structures of the characteristic components of all the common dyes are presented together in Figure 3. 29 at the end of this section.

UHPLC-ESI-MS analysis of the extract of the gallnut dyed silk sample helped the further identification of the unknown components (Figure 3. 9). The analytical results are summarised in Table 3. 6. It can be seen that the parent ions $[M - H]^-$ of these components with similar UV-vis absorption increased continually from 169 to 1243 Da, with a difference of 152 Da in between.

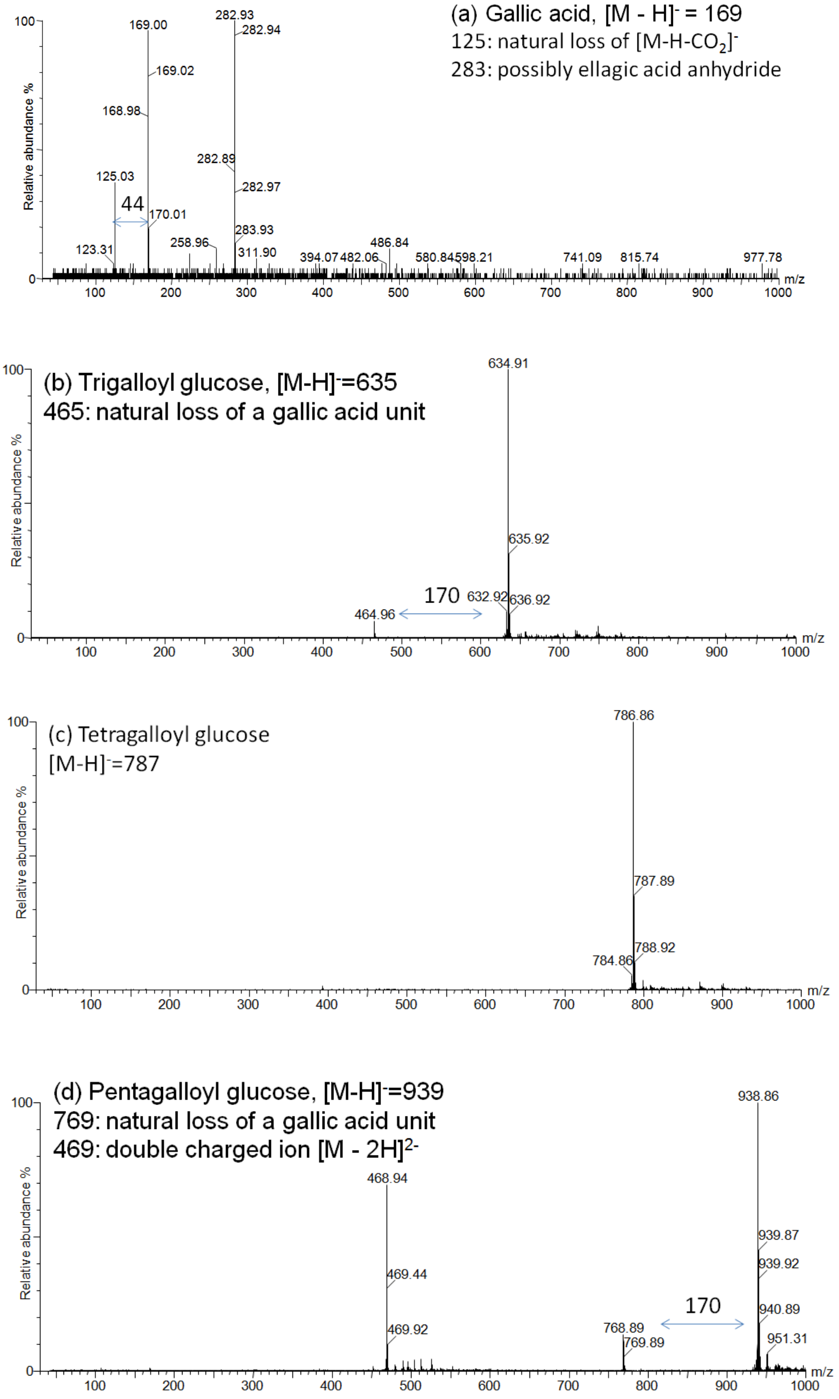

Figure 3. 9 Mass spectra of the main constituents of gallnut

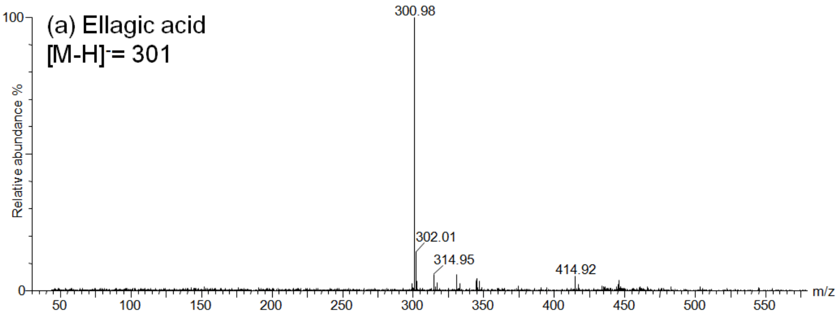

Figure 3. 10 Mass spectrum of ellagic acid

Table 3. 6 Retention times and MS fragmentation of the main components of the gallnut dyed silk extract

Retention time (min)	**$[M - H]^-$ (m/z)**	**Molecular weight of parent ion (Da)**	**Component identified**	**Daughter ions and other ions (m/z)**
3.0	169, 125, 283	170	gallic acid monomer	125: natural loss of $[M\text{-}H\text{-}CO_2]^-$ (44) 283: possibly ellagic acid anhydride
6.6	483	484=170×2+180-18×2	digalloyl glucose	
8.2	635, 465	636=170×3+180-18×3	trigalloyl glucose	465: natural loss of a gallic acid unit (170)
9.5	787	788=170×4+180-18×4	tetragalloyl glucose	
11.8	939, 769, 469	940=170×5+180-18×5	pentagalloyl glucose	769: natural loss of a gallic acid unit (170) 469: double charged ion $[M - 2H]^{2-}$
13.7	1091	1092=170×6+180-18×6	hexagalloyl glucose	302: probably ellagic acid coeluting
14.6	1243, 621	1244=170×7+180-18×7	heptagalloyl glucose	621: double charged ion $[M - 2H]^{2-}$

Literature investigation showed that the main constituents of gallnut are gallotannins. They are polyphenol molecules formed by the esterification of a central β-D-glucose with surrounding gallic acid units.[222] Compared with published data on the molecular weight of gallotannins of different levels of esterification from tannic acid and gallnut extracts,[223] the main constituents were respectively identified as gallic acid isomer, trigalloyl glucose, tetragalloyl glucose, pentagalloyl glucose, hexagalloyl glucose and heptagalloyl glucose (Table 3. 6). A trace amount of dimer was also detected. It is to be noted that the degree of esterification of gallotannins may change by hydrolysation during processing processes like extraction, therefore rigorous comparison of gallotannins from different sources needs to be carried out under the same processing condition. Moreover, a close examination of the MS data revealed the widespread phenomenon of isomerisation of these gallotannins, resulting from the attachment of galloyl groups with the central β-D-glucose at different positions. For example, the three components eluting at 4.5, 5.5 and 6.6 min were of the same molecular mass 484, indicating that they are digalloyl glucose with different structures. Likewise, three components were found to be trigalloyl glucose isomers (respectively eluting at 7.9, 8.1 and 8.2 min) and three were tetragalloyl glucose isomers (eluting at 8.5 min, 9.5 and 9.9 min). For pentagalloyl glucose, no isomer was found, probably because the attachment of one galloyl group with each of the five hydroxyl groups of the central β-D-glucose ensures the most stable structure. The mass of hexagalloyl glucose and heptagalloyl glucose were detected only once, but the broadening of the peaks for these two components in the UHPLC-PDA chromatogram indicates possible coelution of isomers.[224] In addition, some changes in molecular structure during MS analysis process were detected through detailed examination of ion fragmentation data (Table 3. 6), including the presence of double charged ions for pentagalloyl glucose and

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[222] Irene Mueller-Harvey, "Analysis of Hydrolysable Tannins," *Animal Feed Science and Technology* 91, no.1 (2001): 3-20; Xiuping Li *et al.*, "Wubeizi De Yanjiu Gaikuang," [Overview of research on gallnut], *Acta Chinese Medicine and Pharmacology* 28, no.3 (2002): 72-74.

[223] Makoto Nishizawa *et al.*, "Tannins and Related Compounds. Part 5. Isolation and Characterization of Polygalloylglucoses from Chinese Gallotannin," *Journal of the Chemical Society, Perkin Transactions 1* (1982): 2963-2968; Katarzyna Lech and Maciej 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," *Analytical and Bioanalytical Chemistry* 399, no.9 (2011): 3241-3251; K. Pawlak *et al.*, "Blue Natural Organic Dyestuffs—from Textile Dyeing to Mural Painting. Separation and Characterization of Coloring Matters Present in Elderberry, Logwood and Indigo," *Journal of Mass Spectrometry* 41, no.5 (2006): 613-622.

[224] Nanjing University of Traditional Chinese Medicine, 523-524.

heptagalloyl glucose, dehydrated galloyl glucose for trigalloyl glucose and pentagalloyl glucose, decarboxylated gallic acid monomer and ellagic acid anhydride.[225] In addition, it is worth noting that among the large amounts of natural plants containing gallotannins, hexagalloyl glucose was only present in gallnut and therefore this component could be used as a marker component for gallnut.[226]

The presence of gallotannins of different degrees of esterification and the phenomenon of isomerisation in samples dyed by natural dyes have never been clarified before. The knowledge of specific gallotannins gallnut dyed samples contains will be a good starting point for the identification of the sources of gallotannins in historical textiles, leading to further understanding of the production of dark shades from galls.

3.4.1.2 Acorn cup

The UHPLC-PDA chromatogram obtained from the extract of the silk sample dyed with acorn cup and the UV-vis spectra of its main constituents are present in Figure 3. 11 (monitored at 280 nm). Compared to the spectral information and the retention time of standard chemicals in the in-house UHPLC library, the two main constituents of acorn cup eluting respectively at 7.5 and 13.6 min were both identified as tannins: one is ellagic acid and the other is its equivalent. The term ‘equivalent’ indicates unidentified components with UV-vis spectra similar to the identified components but of different retention time. It is expected that the chemical structure of an equivalent is close to that of this component, usually due to connected sugar moieties, polymerisation of different extents or

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[225] J-P Salminen *et al.*, "Characterisation of Hydrolysable Tannins from Leaves of *Betula Pubescens* by High-Performance Liquid Chromatography–Mass Spectrometry," *Journal of Chromatography A* 864, no.2 (1999): 283-291; Pirjo Mämmelä *et al.*, "Analysis of Oak Tannins by Liquid Chromatography-Electrospray Ionisation Mass Spectrometry," *Journal of Chromatography A* 891, no.1 (2000): 75-83; Yean Yean Soong and Philip John Barlow, "Isolation and Structure Elucidation of Phenolic Compounds from Longan (*Dimocarpus Longan* Lour.) Seed by High-Performance Liquid Chromatography–Electrospray Ionization Mass Spectrometry," *Journal of Chromatography A* 1085, no.2 (2005): 270-277.

[226] Guojia zhongyiyao guanlijv zhonghua bencao bianweihui, vol. 10, 638.

isomerisation.

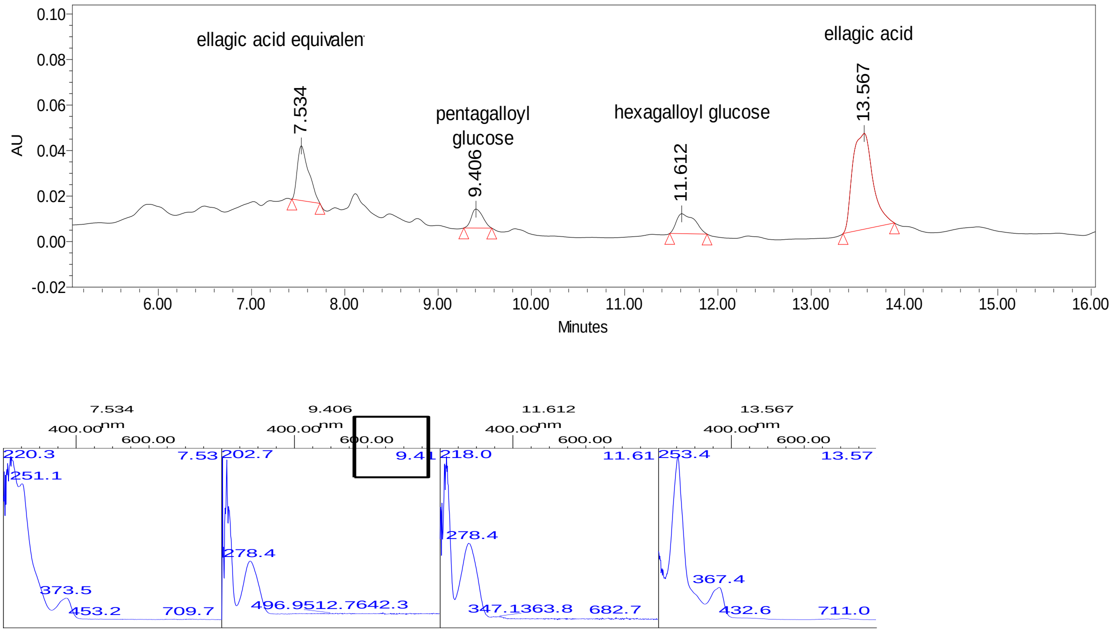

Figure 3. 11 UHPLC-PDA chromatogram (monitored at 280 nm) of the acorn cup dyed silk extract and the UV-Vis spectra of its main constituents

Table 3. 7 Retention times and UV maxima of the main components of the acorn cup dyed silk extract

Retention time (min)	**UV-vis absorption (nm)**	**Component identified**
7.5	220, 251, 374	ellagic acid equivalent
9.4	203, 214, 278	pentagalloyl glucose
11.6	218, 278	hexagalloyl glucose
13.6	253, 367	ellagic acid

The main constituents of acorn cup are ellagitannins. Their basic structure is pentagalloyl glucose, with pairs of gallic acid units connected by oxidation (Fig. 4).[227] Many isomers can be formed relating to different oxidation pathways of the gallic acid units, different

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[227] Mueller-Harvey, "Analysis of Hydrolysable Tannins," 3-20.

binding positions of the units with the central glucose, *etc*.[228] Only one published report elucidates various ellagitannins in acorn cup, in which isovalolaginic acid, vescalin, valolaginic acid, vescalagin, vescvaloninine acid, castalagin and castavaloninic acid were identified.[229] More investigation is needed to identify the ellagitannin eluting at 7.5min in the sample analysed.

Besides ellagitannins, gallotannins are also present in the extract of the acorn cup dyed sample. With reference to the analytical results of the gallnut dyed sample in section 3.4.1.1, the constituents eluting at 9.4 and 11.6 min were identified respectively as pentagalloyl glucose and hexagalloyl glucose. In addition, the UV-vis spectrum obtained at 7.5 min indicates possible co-elution of a gallotannin dimer.

This is the first time that the dye composition of acorn cup has been characterised. This analytical result complements existing knowledge to identify specific dye sources containing ellagitannins. This characterisation will help the detection of acorn cup as a dye source for historical textiles, which has not been possible before.

3.4.1.3 Gardenia

A UHPLC-PDA chromatogram was obtained from the extract of the silk sample dyed with gardenia (Figure 3.12). Spectral information shows that all the major constituents have two adjacent maximum absorptions at around 426 and 464 nm. Compared with the data in the UHPLC library, the component eluting at 26.3 was identified as crocetin.

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[228] Stéphane Quideau and Ken S Feldman, "Ellagitannin Chemistry," *Chemical Reviews* 96, no.1 (1996): 475-504.

[229] Wende Zhang, "Xiangwan Rouzhi De Huaxue Xingzhi Ji Rouge Xingneng," [The chemical aspects and tanning properties of valonia tannin], *Scientia Silvae Sinicae* 16, no.2 (1980): 115-123.

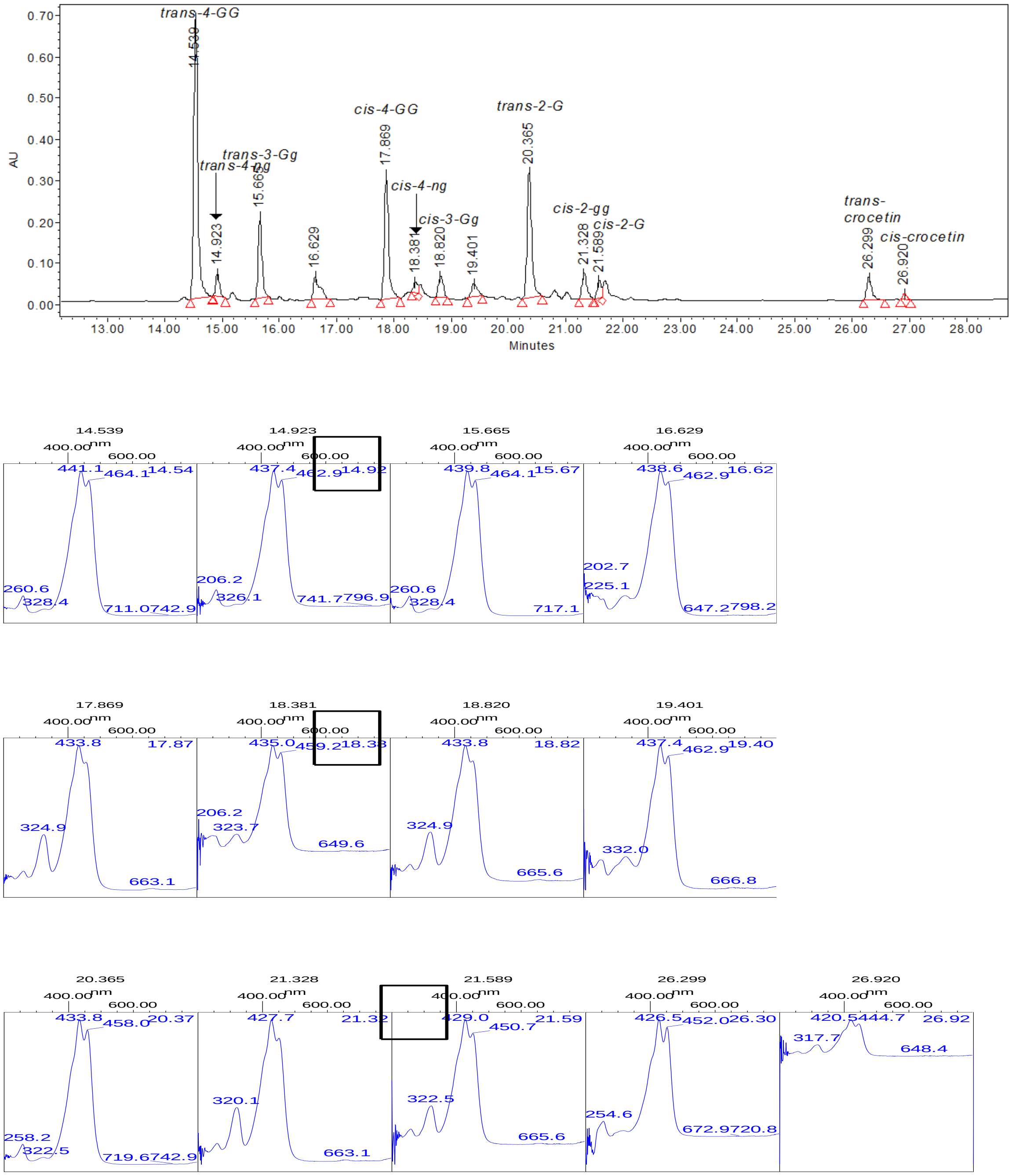

Figure 3. 12 UHPLC-PDA chromatogram (monitored at 425 nm) of the gardenia dyed silk extract and the UV-Vis spectra of its main constituents. g: glucoside; G: gentibioside; N: neapolitanoside. They contain respectively one, two and tree glucosyls.

Gardenia contains crocetin and also many crocins, the esters of crocetin. Previous research in the field of medicine on the commercial extract of *Gardenia jasminoides* Ellis fruits by HPLC-MS with similar LC conditions identified individual chemical structures of these crocins.[230] It was found that crocins are usually composed of a central crocetin and several attached glucoses at the two ends. The difference in the distributions of glycosides on both ends of crocetin and *cis-trans* isomerisation results in the complex isomerisation phenomenon of crocins.

MS analysis enabled the identification of the crocins (Figure 3. 13). The ion fragmentation patterns of the main components of the extract from gardenia dyed silk are presented in Table 3. 8. With reference to published data in the above mentioned article in terms of m/z, UV-vis absorption profiles, eluting sequence and relative amounts, the main components of gardenia dyed samples were tentatively identified (Table 3. 8). The repetitive appearance of ions with m/z at 327, 489, 651, 813 and 975 Da, with differences of 162 Da in between (Figure 3. 14) results from both isomerisation and the natural loss of glucoses from molecules with more glucoses attached.

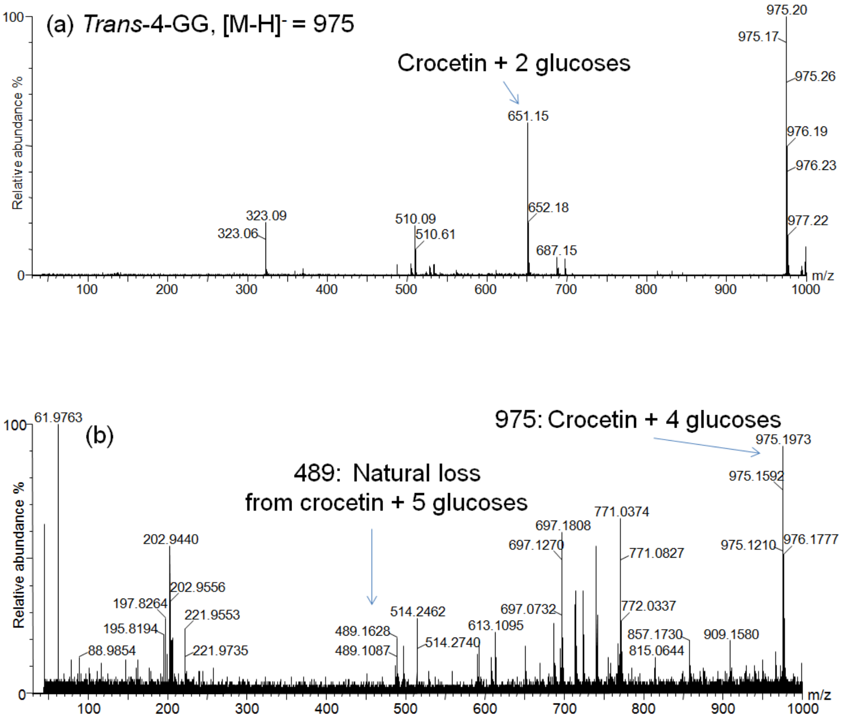

Figure 3. 13 Mass spectra of the main constituents of gardenia

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[230] Manuel Carmona *et al.*, "Crocetin Esters, Picrocrocin and Its Related Compounds Present in Crocus Sativus Stigmas and Gardenia Jasminoides Fruits. Tentative Identification of Seven New Compounds by LC-ESI-MS," *Journal of Agricultural and Food Chemistry* 54, no.3 (2006): 973-979.

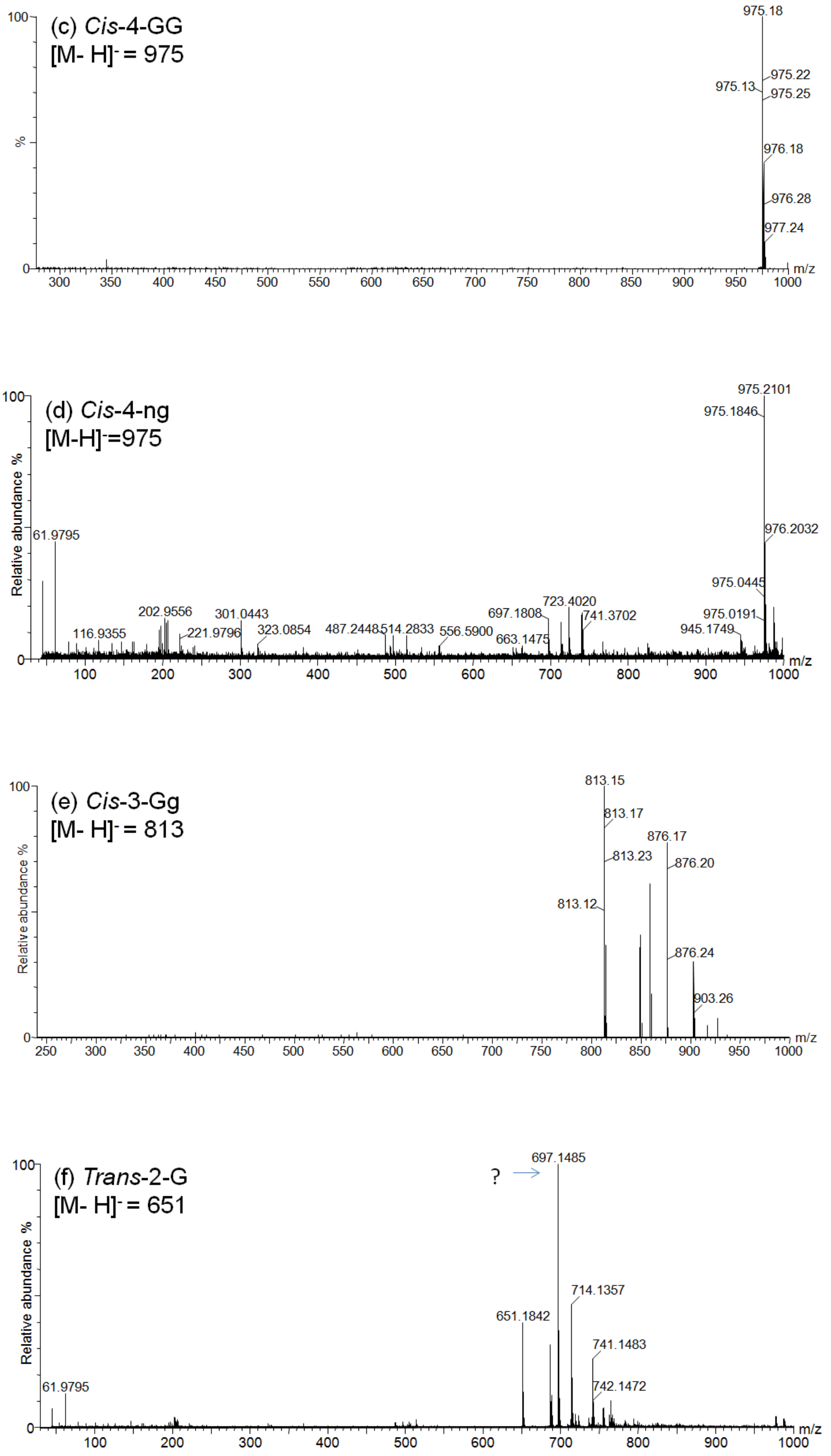

Figure 3. 13 Mass spectra of the main constituents of gardenia (continued)

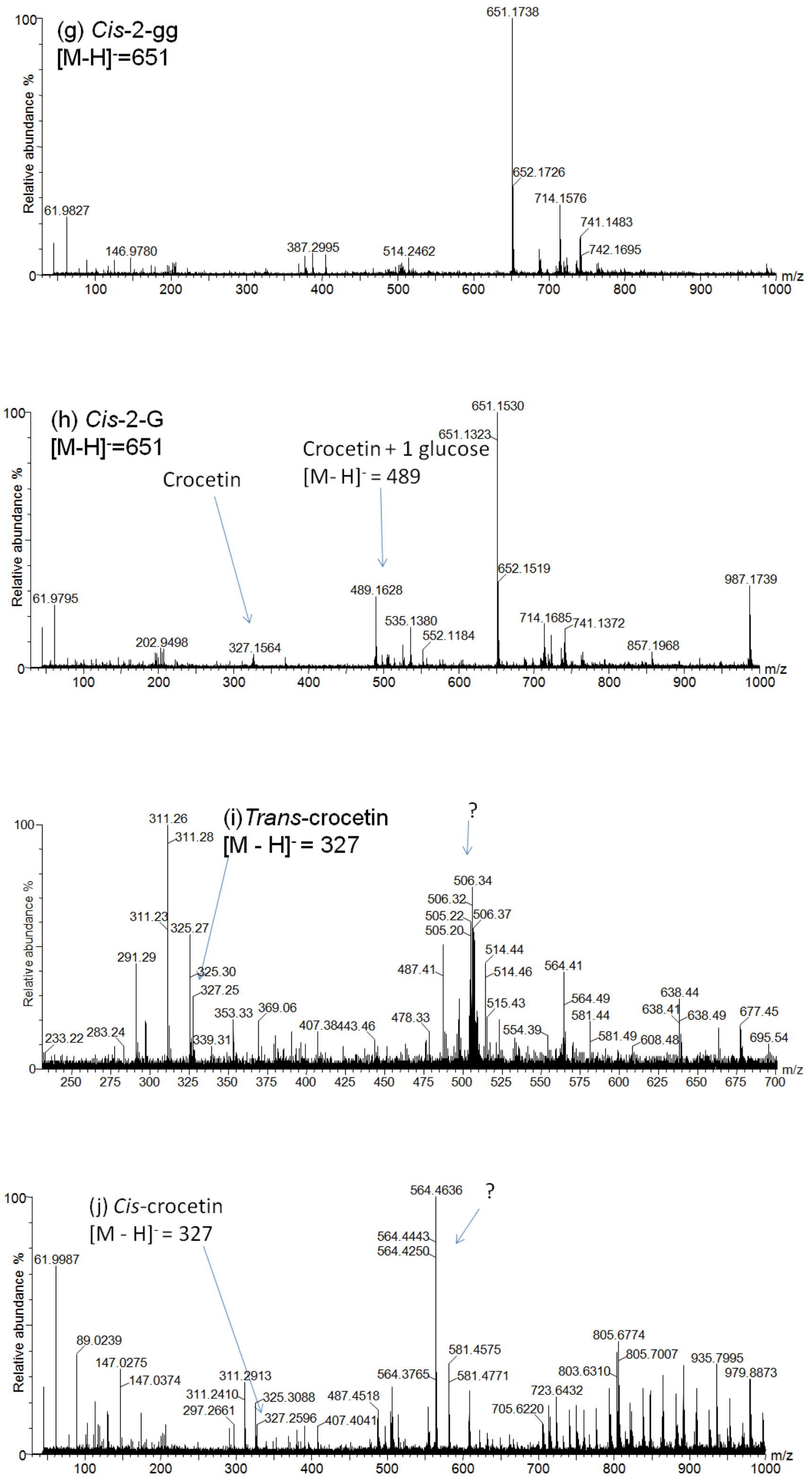

Figure 3. 13 Mass spectra of the main constituents of gardenia (continued)

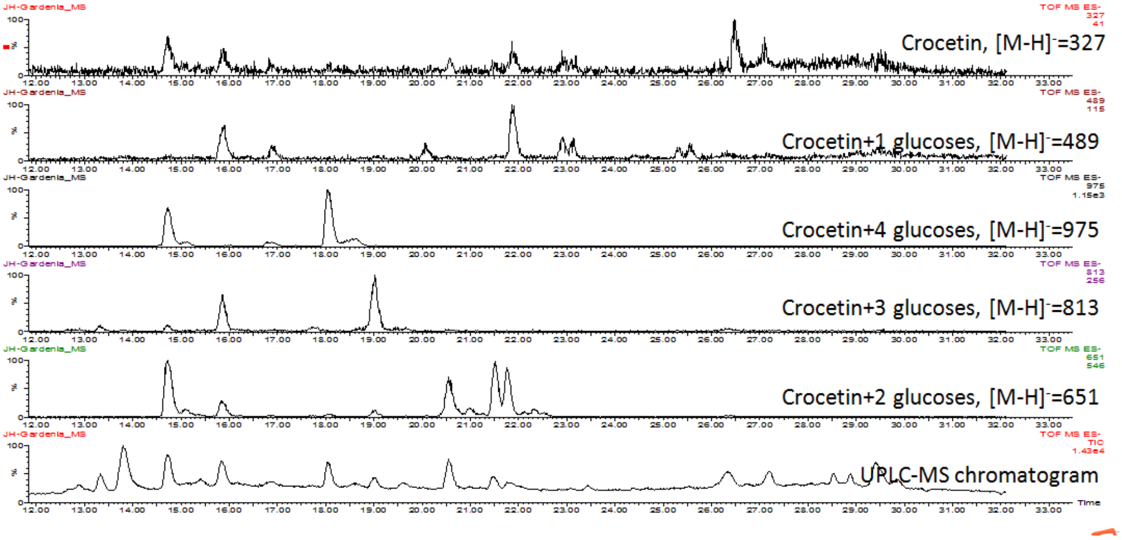

Figure 3. 14 UHPLC-MS selected-ion monitoring chromatograms of the gardenia dyed silk extract

Table 3. 8 Retention times and MS fragmentation of the main components of the gardenia dyed silk extract

Retention time (min)	**Fragmentation patterns [M - H]⁻ (m/z)**[231]	**Number of glycosides**	**Chemical structure**[232]
14.5	975 (813) 651 327	4 3 2 0	*trans*-4-GG
14.9	(975) (651)	4 2	*trans*-4-ng
15.7	813 489 (651) 327	3 1 2 0	*trans*-3-Gg
16.6	(975) (489) (327)	4 1 0	natural loss from 5-crocin
17.9	975 (651)	4 2	*cis*-4-GG
18.4	(975)	4	*cis*-4-ng
18.8	813 (651)	3 2	*cis*-3-Gg
19.4	(813)	3	unknown crocin equivalent
20.4	651 (327)	2 0	*trans*-2-G
21.4	651	2	*cis*-2-gg
21.6	651 489 327	2 1 0	*cis*-2-G
26.3	327	0	*trans*-crocetin
27.0	327	0	*cis*-crocetin

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[231] The components with peak areas less than 1/3 of the largest amount of component of the same mass present are in brackets.

[232] N: neapolitanoside; G: gentibioside; g: glucoside

Moreover, three chromatographic trends were found on the eluting sequence of various crocins. Firstly, for crocins of the same type of steric configuration (*cis* or *trans*), those with more glycosides attached elute earlier. This is because glucose moieties improve the hydrophilicity of the molecule. Secondly, for crocins with the same number of glucoses attached, *trans*-crocins elute earlier than *cis*-crocins. Thirdly, for crocins with the same steric configuration (*cis* or *trans*) and number of glucoses attached, those with glucoses equally distributed on both sides elute earlier than unequally distributed ones, *e.g. cis*-2gg crocin elutes earlier than 2G crocin. These two last trends probably result from the different steric hindrance of the molecules: the less the steric hindrance, the earlier the crocin elute. In addition, differences in UV-vis absorption of *cis*- and *trans*-crocins stated earlier were confirmed:[233] *cis*-crocins contain extra characteristic absorption at around 320-325 nm. The maximum absorption of *trans*-crocins shifts to longer wavelength by around 5 nm compared to the maximum absorption of *cis*-crocins.[234]

The various structures of crocins present in gardenia dyed silk are reported here for the first time, complementing existing knowledge of the dye constituents of gardenia.[235] The understanding of different crocetin esters is essential for differentiating plant sources with similar dye composition to gardenia, like saffron, a precious yellow dye used in Europe and Asia in ancient times.[236] Analysis showed the main dye components of saffron include *trans*-4-GG, *trans*-4-ng, *trans*-3-Gg and *cis*-4-GG (section 3.4.2.7 below). These components characterise this source and differ from the main constituents of gardenia. Therefore, detailed knowledge of crocins contributes to more accurate identification of historical dye sources. Further work on how crocetin and crocins are affected by dyeing processes and ageing will contribute to both better understanding of dye production processes, and the preservation of gardenia and saffron dyes on historical textiles.

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[233] Carmona *et al.*, "Crocetin Esters, Picrocrocin and Its Related Compounds Present in Crocus Sativus Stigmas and Gardenia Jasminoides Fruits. Tentative Identification of Seven New Compounds by LC-ESI-MS," 973-979.

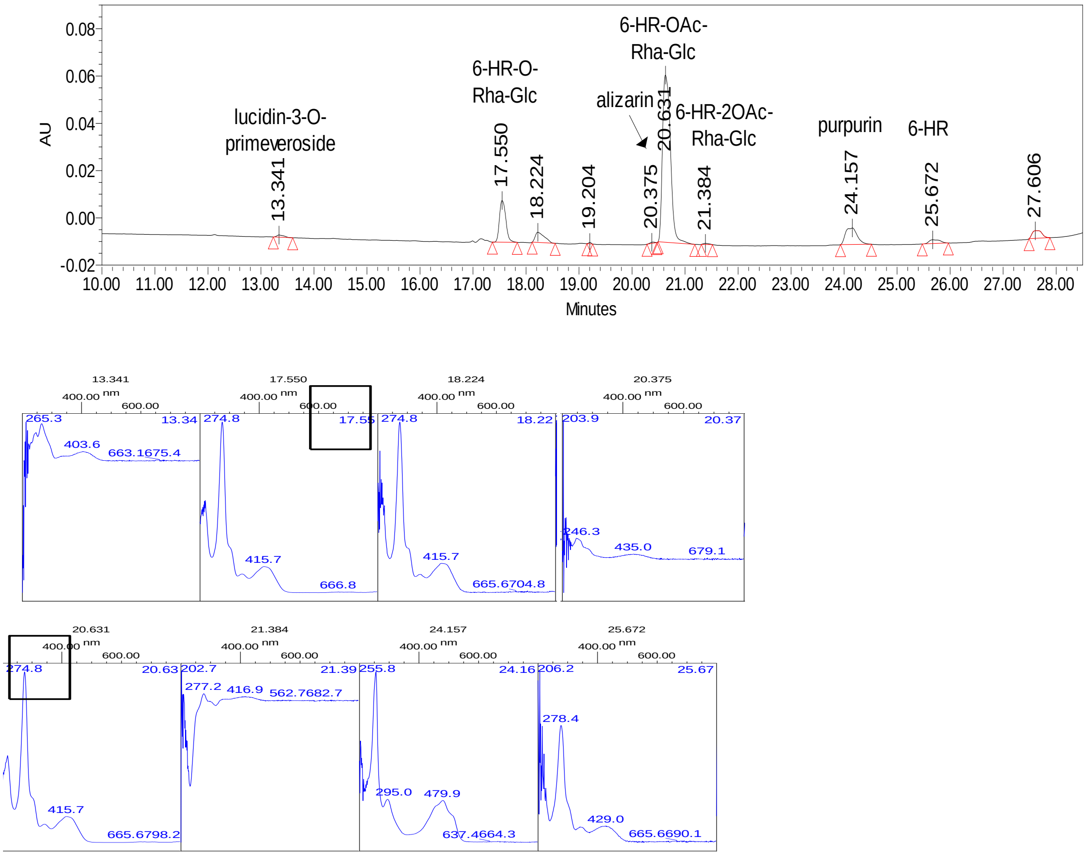
[234] Ibid.

[235] 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," 231-249.

[236] Cardon, 302-307.

3.4.1.4 Munjeet

The roots of *Rubia* species mainly contain a wide range of anthraquinone dyes, both aglycones and glycosides: the dyes are synthesized originally as glycosides and then changed to aglycones by hydrolysation during natural fermentation and dyeing.[237] A UHPLC-PDA spectrum of the DMSO-OA extract of munjeet (*Rubia cordifolia*) dyed silk is presented in Figure 3. 15a. Compared to information in the UHPLC library, two anthraquinones, lucidin-3-O-primeveroside and purpurin were identified. Among the unknown components, five of them share a similar UV-vis maximum absorption, four components at 275 and 416 nm, and one at 278 and 429 nm, indicating the presence of equivalents, probably glycosides.



(a)

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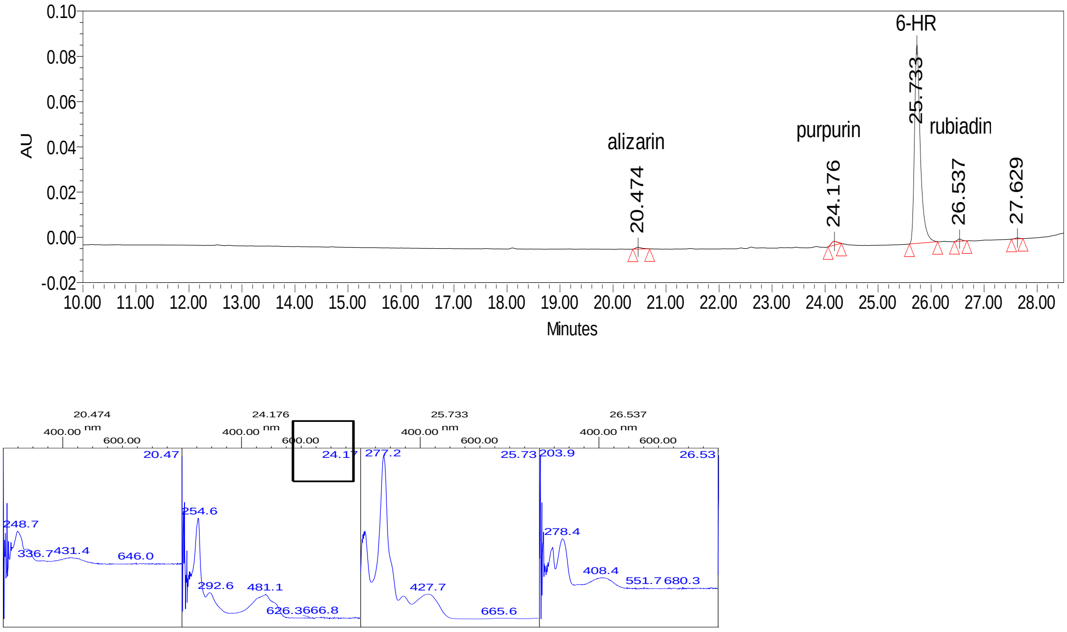
[237] X. Zhang, I. Good, and R. Laursen, "Characterization of Dyestuffs in Ancient Textiles from Xinjiang," *Journal of Archaeological Science* 35, no.4 (2008): 1095-1103; Mouri and Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC," 105-113.



(b)

Figure 3. 15 UHPLC-PDA chromatogram (monitored at 430 nm) of the munjeet dyed silk extracts by (a) DMSO-OA and (b) HCl, and the UV-Vis spectra of their main constituents. 6-HR: 6-hydroxyrubiadin; Glc: glucose; Rha: rhamnose; Ac: Acetyl.

To further confirm the presence of glycosides and identify these components, hydrochloric acid solution was applied to sample preparation and the UHPLC-PDA spectrum of the extract was presented in Figure 3. 15b. In this extract, lucidin-3-O-primeveroside and five of the major components in the DMSO-OA extract disappear. Instead, the amount of the component eluting at 25.7 min increases dramatically, indicating that this may be an aglycone and those disappearing in the hydrochloric acid extract may be its glycosides.

MS/MS analysis was carried out to identify this component eluting at 25.7 min (Figure 3. 16). Its m/z is 269 and literature investigation showed that there are at least four anthraquinones with molecular weight 270 Da. [238] They are respectively lucidin, 6-hydroxyrubiadin, anthragallol 3-methyl ether and 1,4-dihydroxy-2-hydroxymethyl-anthraquinone. MS/MS analysis shows the presence of a fragment at m/z 239. Compared to spectral information and eluting sequence generally

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[238] Ibid.

provided by Mouri and Laursen, this component was identified as 6-hydroxyrubiadin. The loss of 39 Da is most likely the combined loss of one methoxyl group and one hydroxyl group. The identification of this component was further confirmed by the report of the presence of 6-hydroxyrubiadin and its sugars in *Rubia cordifolia* from China.[239]

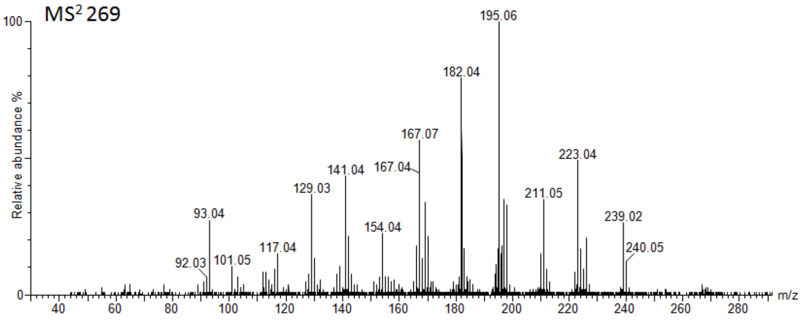

Figure 3. 16 MS/MS spectrum of a component of munjeet eluting at 25.7 min

Based on the identification of this aglycone, the other main components were identified by comparing the m/z of the ions (Figure 3. 17), UV-vis spectra and retention time with information in the UHPLC-PDA library at the RCE, Mouri and Laursen's library and other published data. As a result, four 6-hydroxyrubiadin sugars and esters were identified (Table 3. 9). It must be noted that in the current UHPLC system with the gradient elution of water, methanol and formic acid, two main components of munjeet, namely munjistin and pseudopurpurin, both acids, are partly ionised, partly neutral, and therefore these peaks do not resolve completely, resulting in broad peaks in the chromatogram.

Dye components extracted from fabrics dyed with *Rubia cordifolia* from China have never been examined in detail before. The presence of 6-hydroxyrubiadin and its derivatives were reported to be characteristic components for *R. cordifolia*, *R. cordifolia* var. *pratensis* (now regarded as a synonom of *R. cordifolia*), *R. akane and R. oncotricha.*[240] However, *R.*

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[239] Hideji Itokawa, Kazuhiko Mihara, and Koichi Takeya, "Studies on a Novel Anthraquinone and Its Glycosides Isolated from Rubia Cordifolia and R. Akane," *Chemical & Pharmaceutical Bulletin* 31, no.7 (1983): 2353-2358.

[240] Hideji Itokawa, Yafang Qiao, and Koichi Takeya, "Anthraquinones and Naphthohydroquinones from *Rubia Cordifolia*," *Phytochemistry* 28, no.12 (1989): 3465-3468; Suxian Wang *et al.*, "Qiancao Zhong Enkunlei Chengfen De Yanjiu," [Studies on anthraquinones in munjeet], *Acta Pharmaceutica Sinica* 27,

cordifolia distributes over a large range of areas including Africa, tropical Asia, China, Japan and Australia.[241] The chemical analysis of the dye components of *R. cordifolia* from Bhutan, Tanakanao (uncertain in the original report) and Nepal did not show the presence of the above characteristic components.[242] Therefore the finding of 6-hydroxyrubiadin and its derivatives in *R. cordifolia* from China highlights a potential difference in chemical composition among *R. cordifolia* from various regions. This enables better identification of *Rubia* species and their places of origin for historical dye sources. Further work is needed to find out the distribution areas of 6-hydroxyrubiadin and its derivatives among *R. cordifolia*, *R. akane* and other main *Rubia* species from different regions to ensure correct identification of plant species and places of origin.

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no.10 (1992): 743-747; Hideji Itokawa, Yafang Qiao, and Koichi Takeya, "Anthraquinones, Naphthoquinones and Naphthohydroquinones from Rubia Oncotricha," *Phytochemistry* 30, no.2 (1991): 637-640.

[241] Cardon, 130.

[242] Mouri and Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC," 105-113.

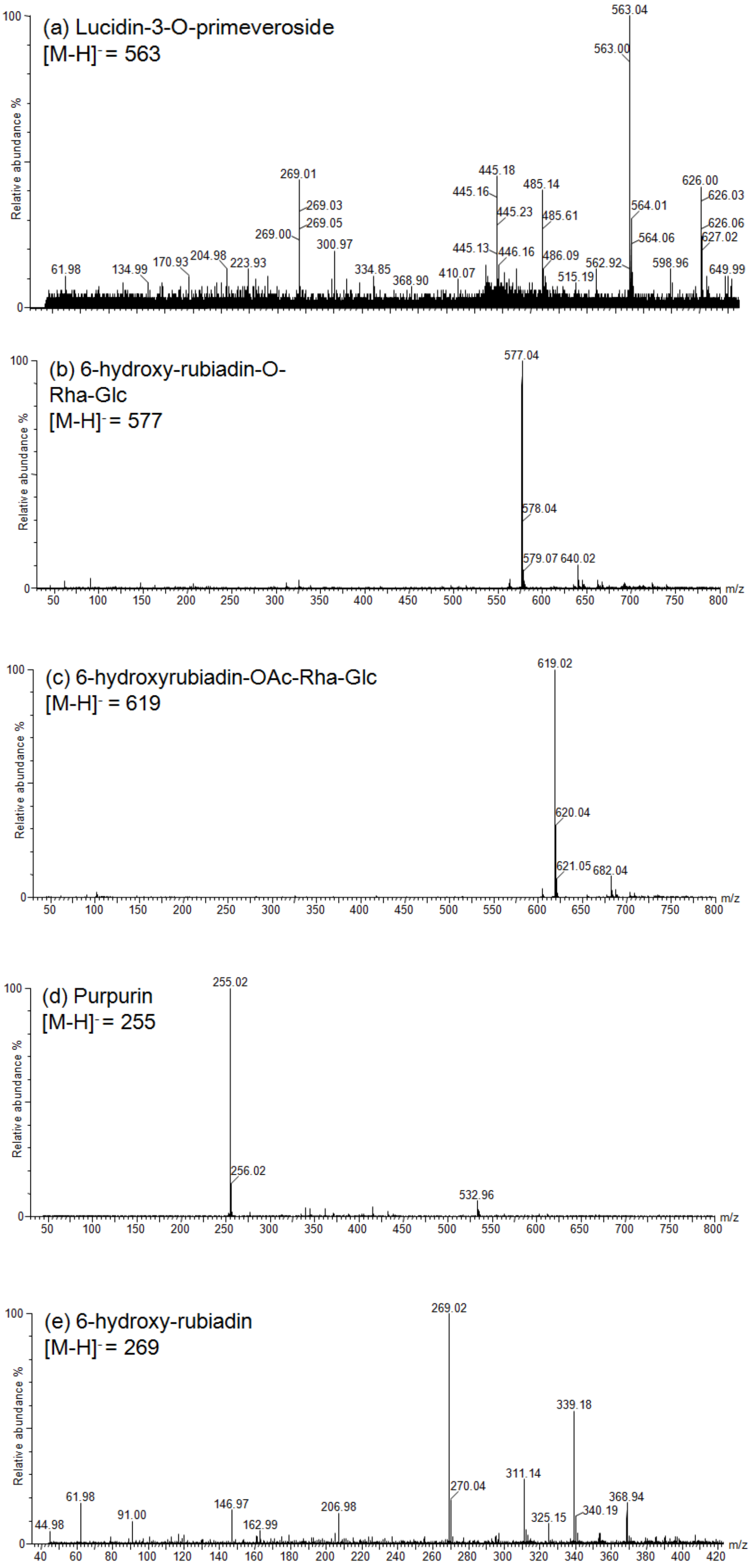

Figure 3. 17 Mass spectra of the main constituents of munjeet

Table 3. 9 Retention times, UV maxima and MS fragmentation of the main components of the *Rubia cordifolia* dyed silk extract[243]

Retention time (min)	**UV-vis absorption (nm)**	**$[M - H]^-$ (m/z)**	**Molecular weight (Da)**	**Component identified**	**Presence**
13.3	265 404	563	564=270+294	lucidin-3-O-primeveroside	DMSO-OA
17.6	275 416	577	578=270+162+146	6-hydroxyrubiadin -O-Rha-Glc	DMSO-OA
18.2	275 416	619	620=270+162+146+42	6-hydroxyrubiadin -O-Rha-Glc (an isomer of a small amount)	DMSO-OA
20.5	249 280 431	The MS response was below the limit of detection (LOD).	240	alizarin	DMSO-OA, HCl
20.6	275 416	619	620=270+162+146+42	6-hydroxyrubiadin -OAc-Rha-Glc	DMSO-OA
21.4	277 417	below LOD		6-hydroxyrubiadin isomer	DMSO-OA
24.2	256 295 480	255	256	purpurin	DMSO-OA, HCl
25.7	278 344 429	269	270	6-hydroxyrubiadin	DMSO-OA, HCl (much higher)
26.5	204 244 278 408	253	254	rubiadin	HCl

3.4.1.5 Turmeric

For the turmeric dyed silk, the improved methodology used enabled better chromatographic resolution of its major components. The UHPLC-PDA chromatogram for the extract of the turmeric shows the presence of three curcuminoids sharing similar UV-vis absorption profiles with some bathochromic shift (7 to 15 nm for the main

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[243] The underlined components show similar UV-vis absorption patterns.

absorptions) (Figure 3. 18).

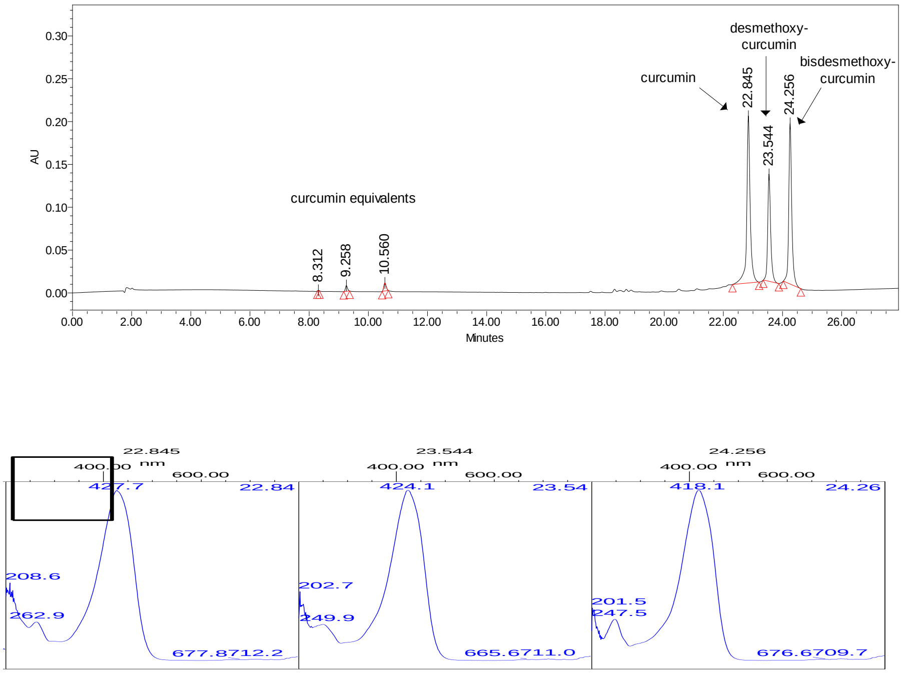

Figure 3. 18 UHPLC-PDA chromatogram (monitored at 425 nm) of the turmeric dyed silk extract and the UV-Vis spectra of its main constituents

MS analysis helped determine the chemical structure of these curcuminoids that belong to the enone group. The m/z of the molecular ions were respectively 367, 337 and 307 Da, with continual decrease of 30 Da, indicating the loss of a methoxy group. Therefore, the three main components of turmeric were identified as curcumin, desmethoxycurcumin and bisdesmethoxycurcumin, as is consistent with current knowledge.[244] These three components usually coelute in HPLC system because of their similar chemical structures.[245] The use of UHPLC and different column technology enhances the separation, and thus the identification, of these three components.

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[244] Wei Li *et al.*, "Gaoxiao Yexiang Sepu Chuanlian Zhipu Fa Fenxi Jianghuang Zhong Weiliang De Jianghuangsulei Huahewu," [Analysis of minor curcuminoids in *Curcuma longa* L. by high performance liquid chromatography tandem mass spectrometry], *Chinese Journal of Chromatography* 26, no.3 (2009): 264-269.

[245] Zhang *et al.*, "Characterization of Yellow Dyes in Nineteenth-Century Chinese Textiles," 211-220.

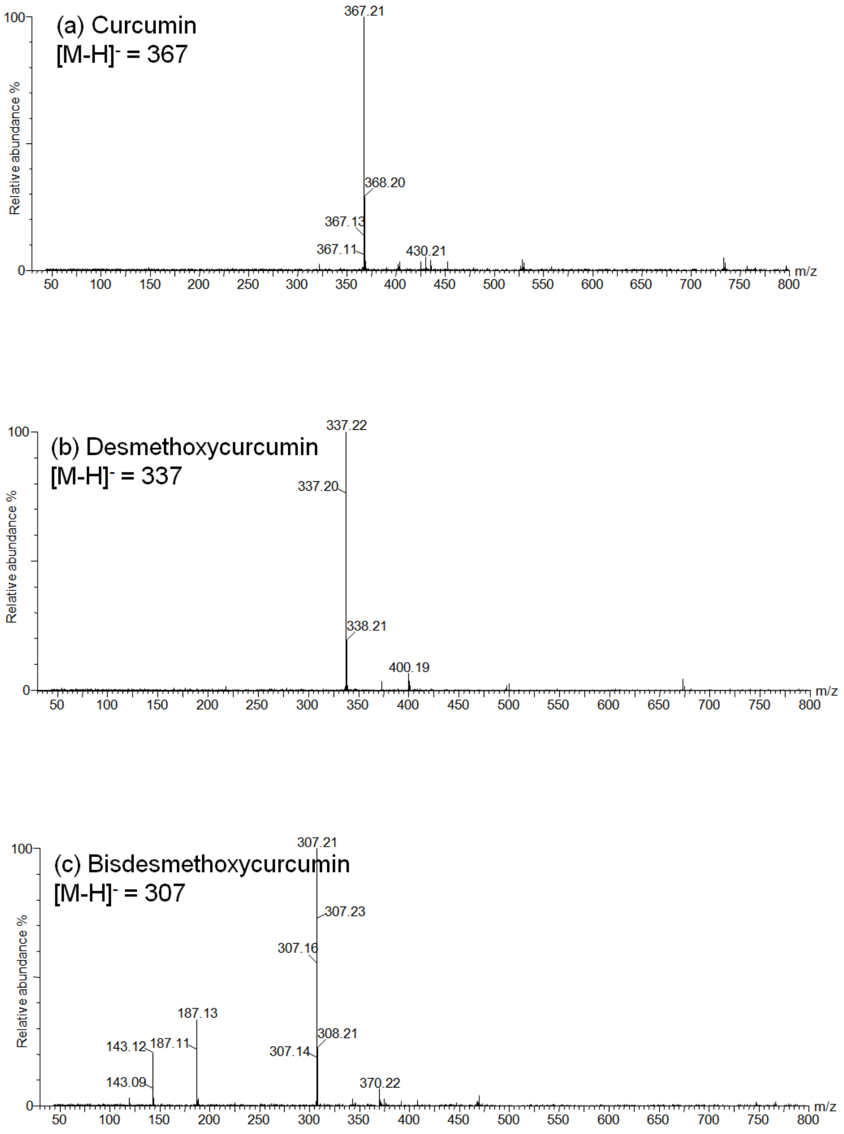

Figure 3. 19 Mass spectra of the main constituents of turmeric

Table 3. 10 Retention times, UV maxima and MS fragmentation of the main components of the turmeric dyed silk extract

Retention time (min)	**UV-vis absorption (nm)**	**$[M - H]^-$ (m/z)**	**Component identified**
22.8	263 428	367	curcumin
23.5	250 424	337	desmethoxycurcumin
24.3	248 418	307	bisdesmethoxycurcumin

3.4.1.6 Pagoda bud

Figure 3. 20 shows the UHPLC-PDA chromatogram of the extract from the silk sample dyed with pagoda bud. There are six main flavonoid components with similar UV-vis absorption peaks at around 255 nm and 351-370 nm. Compared with reference data in the UHPLC library, rutin, quercetin, isorhamnetin and kaempferol were identified.

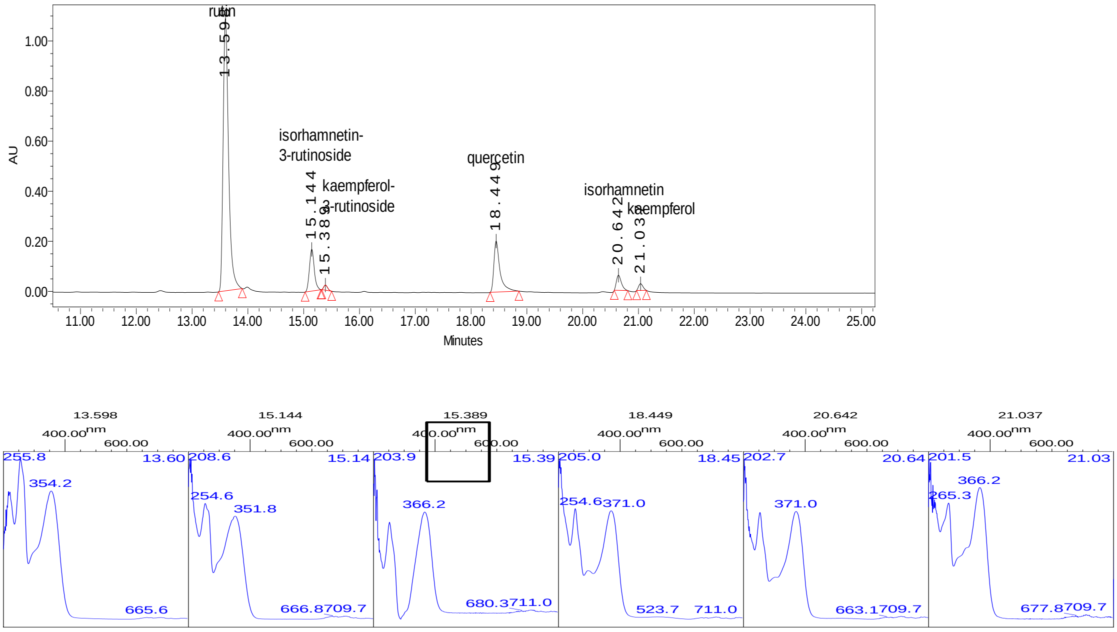

Figure 3. 20 UHPLC-PDA chromatogram (monitored at 350 nm) of the pagoda bud dyed silk extract and the UV-Vis spectra of its main constituents

MS analysis enabled the identification of the other two main dye components. Their m/z were found to be respectively 623 and 593 Da, 308 Da more than isorhamnetin and kaempferol (Figure 3. 21). This indicates that they are the rutinosides (with additional mass of 308) of the two aglycones, with the same relationship as between rutin (quercetin rutinoside) and quercetin. The rutinosides elute earlier because they are more hydrophilic. In addition, close examination of the UV-vis spectra of the main components reveals that rutinosides shift the UV-vis absorption maxima to shorter wavelength. It was reported that in HPLC systems various rutinosides of pagoda bud usually co-elute, and kaempferol and isorhamnetin also co-elute.[246] This is the first successful separation of these dye components by LC method, offering an analytical methodology for better understanding of pagoda bud on historical textiles.

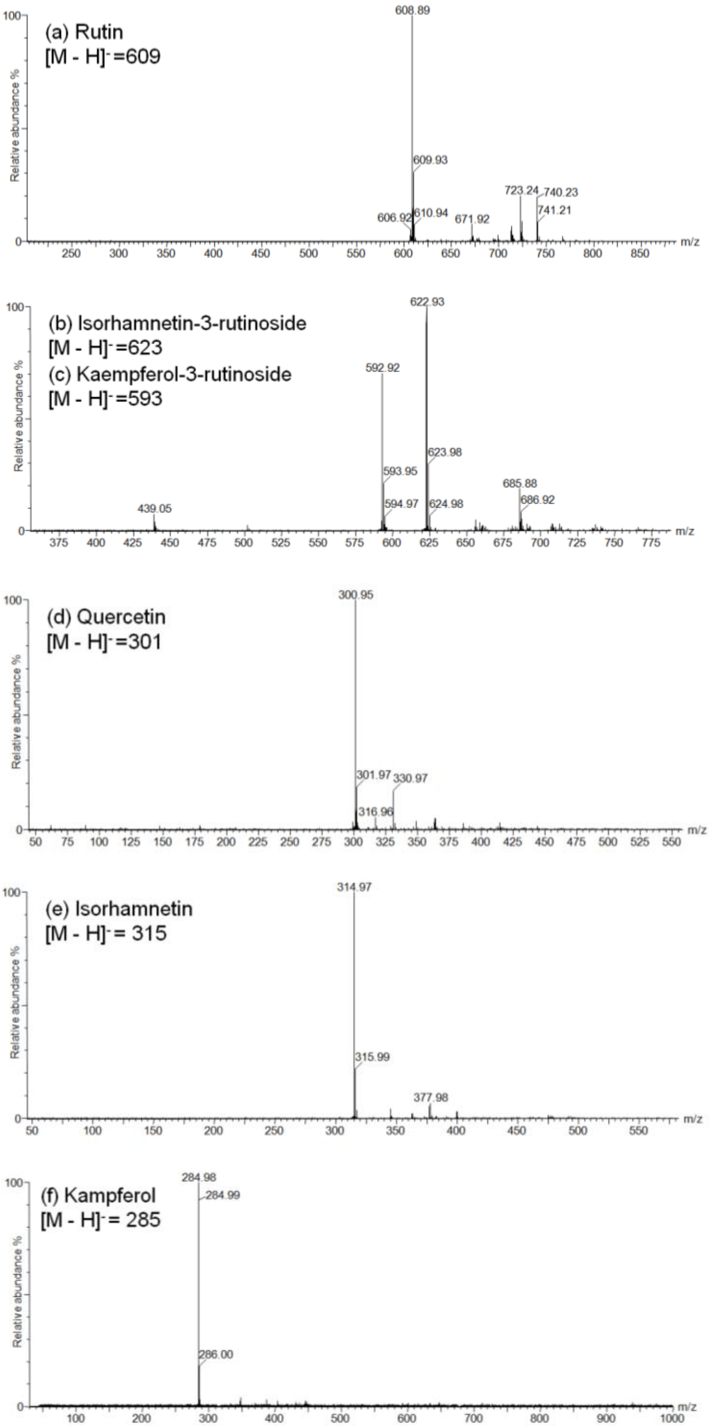

Figure 3. 21 Mass spectra of the main constituents of pagoda bud

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[246] Ibid; Zhang *et al.*, "Preliminary Studies toward Identification of Sources of Protoberberine Alkaloids Used as Yellow Dyes in Asian Objects of Historical Interest," 177-185.

Table 3. 11 Retention times, UV maxima and MS fragmentation of the main components of the pagoda bud dyed silk extract

Retention time (min)	**UV-vis absorption (nm)**	**$[M - H]^-$ (m/z)**	**Component identified**
13.6	256 354	609=301+308	rutin
15.1	255 352	623=315+308	isorhamnetin-3-rutinoside
15.4	253 366	593=285+308	kaempferol-3-rutinoside
18.4	255 371	301	quercetin
20.6	253 371	315	isorhamnetin
21.0	265 366	285	kaempferol

3.4.1.7 Indigo

The UHPLC-PDA chromatogram of the extract from an indigo dyed sample and the UV-vis spectra and Mass spectra of the main constituents are shown in Figure 3. 22. Isatin, indigotin and indirubin were identified. Indigotin and indirubin are the main dye components of indigo. The ratio between the amounts of indigotin and indirubin may indicate different dyeing method or plant sources, though more investigation is needed to confirm this.[247] Characteristic constituents in different plant sources for indigo may be used as marker components to differentiate these plant sources.[248] For example, ‘pseudoindirubin’ was recently found in dyed samples and may lead to being a marker component for woad (*Isatis tinctoria* L.), although additional research is required to confirm this hypothesis as well.[249]

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[247] Estrella Sanz Rodríguez *et al.*, "Characterization of Natural and Synthetic Dyes Employed in the Manufacture of Chinese Garment Pieces by LC-DAD and LC-DAD-QTOF".

[248] Guojia zhongyiyao guanlijv zhonghua bencao bianweihui, vol. 8, 2548; vol. 4, 535; Nanjing University of Traditional Chinese Medicine, 486.

[249] Richard Laursen and Chika Mouri, "Pseudoindirubin: A Marker for Woad-Dyed Textiles?" (paper presented at *Dyes in History and Archaeology 33*, Glasgow, 2014).

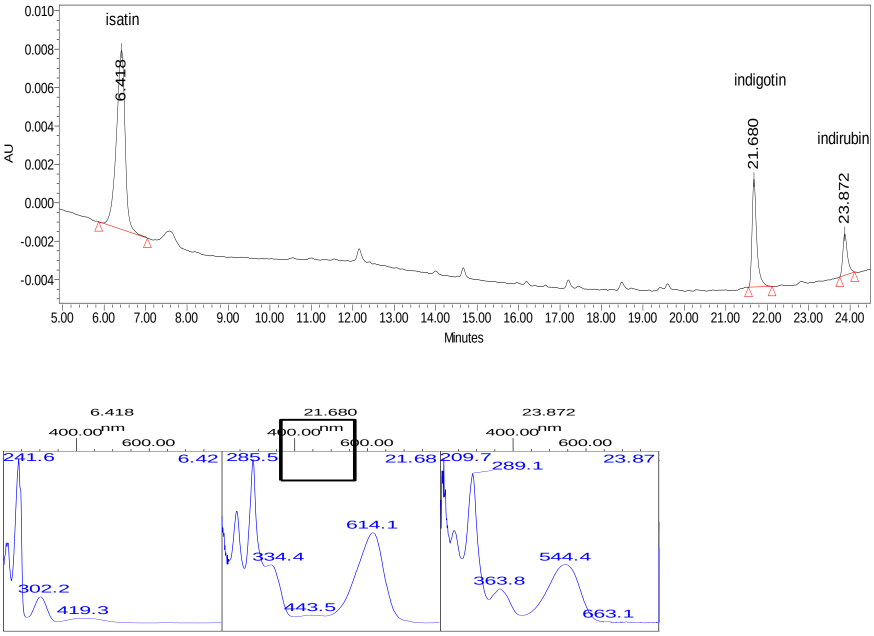

Figure 3. 22 UHPLC-PDA chromatogram (monitored at 425 nm) of the indigo dyed silk extract and the UV-Vis spectra of its main constituents

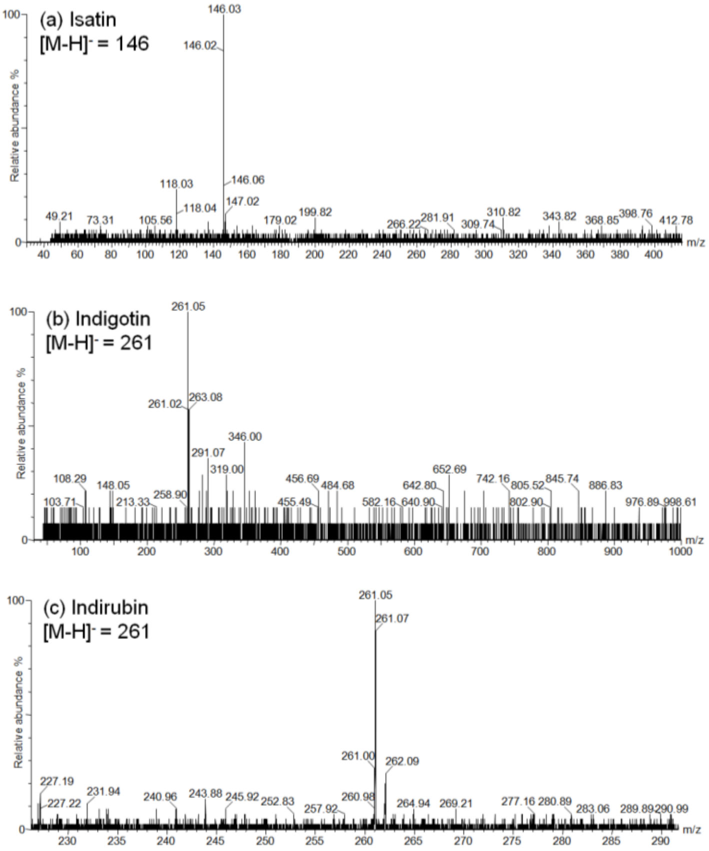

Figure 3. 23 Mass spectra of the main constituents of indigo

Table 3. 12 Retention times, UV maxima and MS fragmentation of the main components of the indigo dyed silk extract

Retention time (min)	**UV-vis absorption (nm)**	**[M - H]$^-$ (m/z)**	**Component identified**
6.4	242 302 419	146	isatin
21.7	240 286 334 614	261	indigotin
23.9	210 238 289 364 544	261	indirubin

3.4.1.8 Amur cork tree

Figure 3.24 presents the UHPLC-PDA chromatogram of the extract from the silk sample dyed with Amur cork tree. The main component was identified as berberine, an alkaloid. Equivalents of berberine in small amounts are also present including magnoflorine, phellodedrine, palmatine and jatrorrhizine.[250] The alkaloid constituents of several species of Asian dyes were compared by Zhang *et al.* using HPLC-MS and it was found that their characteristic components and relative amounts are distinguishing enough to differentiate the dye sources.[251]

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[250] Guojia zhongyiyao guanlijv zhonghua bencao bianweihui, vol. 4, 951.

[251] Zhang *et al.*, "Preliminary studies toward identification of sources of protoberberine alkaloids used as yellow dyes in Asian objects of historical interest."

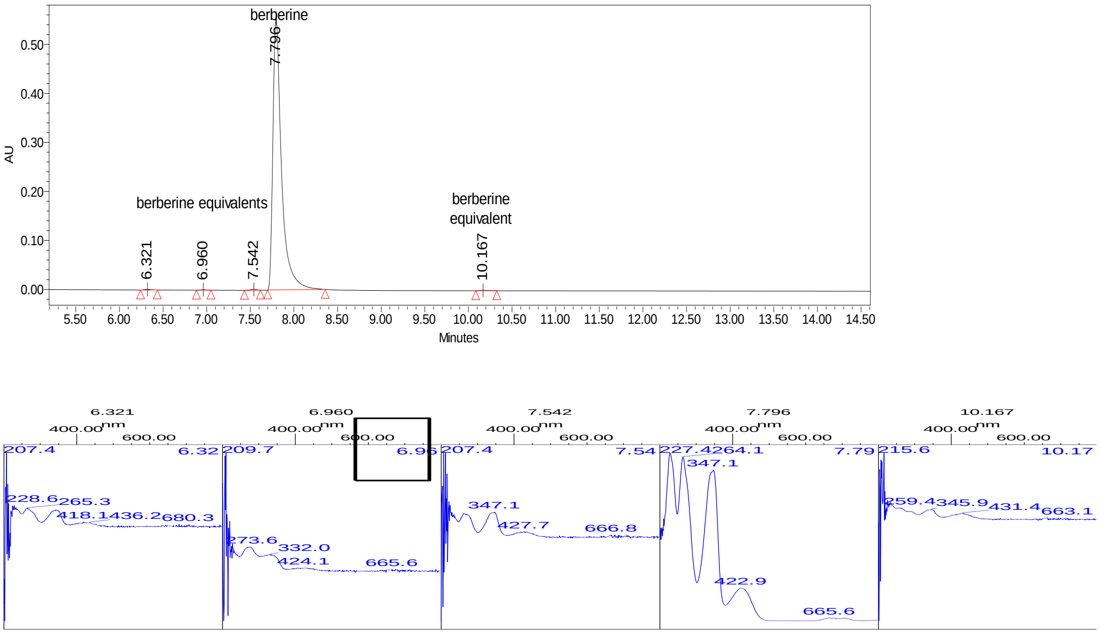

Figure 3. 24 UHPLC-PDA chromatogram (monitored at 350 nm) of the Amur cork tree dyed silk extract and the UV-Vis spectra of its main constituents of Amur cork tree

Table 3. 13 Retention times and UV maxima of the main components of the Amur cork tree dyed silk extract

Retention time (min)	**UV-vis absorption (nm)**	**Component identified**
7.8	227 264 347 423	berberine

3.4.1.9 Smoketree

The UHPLC-PDA chromatogram obtained from the extract of the silk sample dyed with smoketree is shown in Figure 3. 25. The two main dye components were identified as sulfuretin and fisetin, belonging respectively to flavonoid and flavonol groups (Table 3. 14). Smoketree contains several additional compounds including sulfuretin and disulfuretin.[252]

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[252] Nanjing University of Traditional Chinese Medicine, 2860; Lemonia Valianou *et al.*, "Phytochemical Analysis of Young Fustic (Cotinus Coggygria Heartwood) and Identification of Isolated Colourants in Historical Textiles," *Analytical and Bioanalytical Chemistry* 394, no.3 (2009): 871-882; Shuxiang Shan *et al.*, "Zhiwu Huaxue Chengfen Yanjiu - Yesheng Zhiwu Huanglu Huaxue Chengfen Yanjiu [Research on the Chemical Constituents of Plants - Research on the Chemical Constituents of Wild Smoketree]," *Journal of Sichuan Forestry Science and Technology* 19, no.1 (1990): 16-22.

The extreme low ratio of fisetin to sulfuretin (less than 0.1 in this research) in smoketree dyed samples may be a characteristic marker to differentiate it from young fustic (*Cotinus coggygria*), which contains a much higher ratio of the two components (approximately 0.5-1.5).[253]

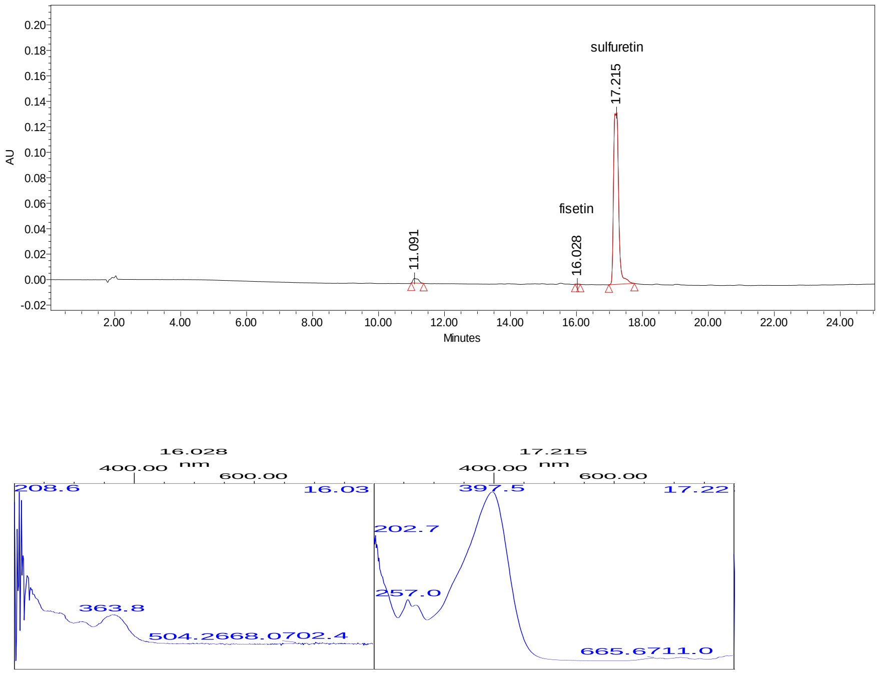

Figure 3. 25 UHPLC-PDA chromatogram (monitored at 425 nm) of the smoketree dyed silk extract and the UV-Vis spectra of its main constituents

Table 3. 14 Retention times and UV maxima of the main components of the smoketree dyed silk extract

Retention time (min)	**UV-vis absorption (nm)**	**Component identified**
16.0	209 364	fisetin
17.2	203 257 398	sulfuretin

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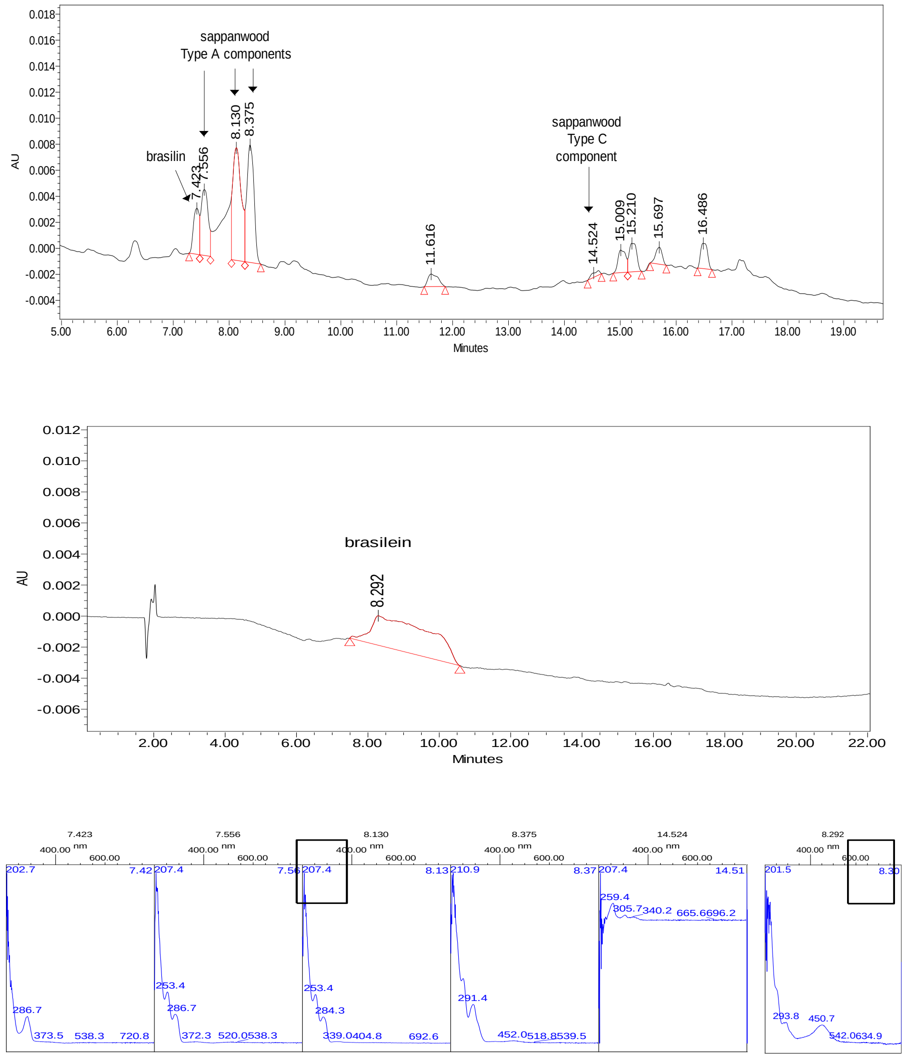
[253] Valianou *et al.*, "Phytochemical analysis of young fustic (Cotinus coggygria heartwood) and identification of isolated colourants in historical textiles."

3.4.1.10 Sappanwood

A UHPLC-PDA chromatogram was obtained from the extract of the silk sample dyed with sappanwood (Figure 3. 26). The main dye component of sappanwood, brasilein, and its precursor, brasilin, are present. Several colourless but characteristic components were found, namely the Nowik type A and Nowik type C components reported earlier.[254] Although these components do not affect the overall colour, they are relatively lightfast and therefore often present in aged samples even when the main dye component is completely degraded.



(a)

(b)

Figure 3. 26 UHPLC-PDA chromatogram (monitored at 295 (a) and 450 (b) nm) of the sappanwood dyed silk extract and the UV-Vis spectra of its main constituents

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[254] Nowik, "The Possibility of Differentiation and Identification of Red and Blue 'Soluble' Dyewoods: Determination of Species Used in Dyeing and Chemistry of Their Dyestuffs," 129-144.

Brasilein does not show good chromatographic behaviour using the current gradient elution programme. As a result, the peak observed from brasilein is rather broad and tailing. Some other brasilin derivatives and flavonoids identified in previous research may be present as well.[255]

Table 3. 15 Retention times and UV maxima of the main components of the sappanwood dyed silk extract

Retention time (min)	**UV absorption (nm)**	**Component identified**
7.4	203 287	brasilin
7.6	207 253 287	Nowik type A component
8.1	207 253 284	Nowik type A component
8.3	202 294 451	brasilein
8.4	211 253 291	Nowik type A component
14.5	259 306 340	Nowik type C component

3.4.1.11 Safflower

In the extract of the silk sample dyed with safflower, the main dye component, carthamin was identified (Figure 3.27). Carthamin is produced by the oxidative decarboxylation of yellow precarthamin when safflower matures. Four other unknown colourless components named as Ct1-Ct4 in previous research were found. These four components can be used as markers for safflower because of their stability during hydrolysis in extraction and during light-ageing.[256] The yellow components of safflower, including water-soluble C-glucosyl quinochalcones and flavonol derivative are usually discarded before dyeing but small

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[255] Guojia zhongyiyao guanlijv zhonghua bencao bianweihui, vol. 4, 377; Xiaojian Bai, "Chaoshi Muzang Huanjing Zhong Chutu Sizhipin De Zhiwu Ranliao Jianding Jishu Yanjiu" (PhD thesis, University of Science and Technology of China, 2014); Yuping Chen *et al.*, "Chemical Constituents from Sappan Lignum," *Journal of Chinese Pharmaceutical Sciences* 17(2008): 82-86; Cardon, 274-289.

[256] Wouters, Grzywacz, and Claro, "Markers for Identification of Faded Safflower (Carthamus Tinctorius L.) Colorants by HPLC-PDA-MS Ancient Fibres, Pigments, Paints and Cosmetics Derived from Antique Recipes," 186-203.

amounts of them may be still present, depending on the quality of dyeing.[257]

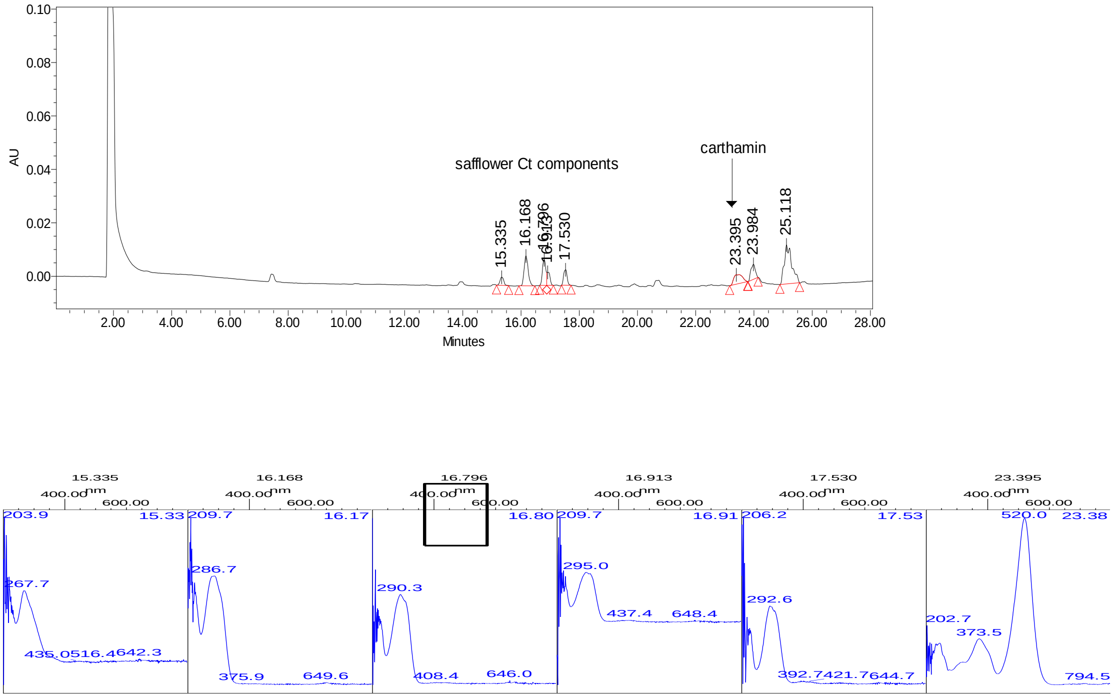

Figure 3. 27 UHPLC-PDA chromatogram (monitored at 295 nm) of the safflower dyed silk extract and the UV-Vis spectra of its main constituents

Table 3. 16 Retention times and UV maxima of the main components of the safflower dyed silk extract

Retention time (min)	**UV absorption (nm)**	**Component identified**
15.3	204 268	Ct1
16.2	210 287	Ct2
16.8	291	Ct3
16.9	210 295	Ct4
17.5	206 293	another Ct component
23.4	244 374 520	carthamin

---

[257] Cardon, 55.

3.4.1.12 Gromwell

Figure 3. 28 shows the UHPLC-PDA chromatogram of the extract from the silk dyed with gromwell. Its main colourant, shikonin, and its equivalent were identified.[258] Gromwell varieties produced in different places vary in main dye components.[259]

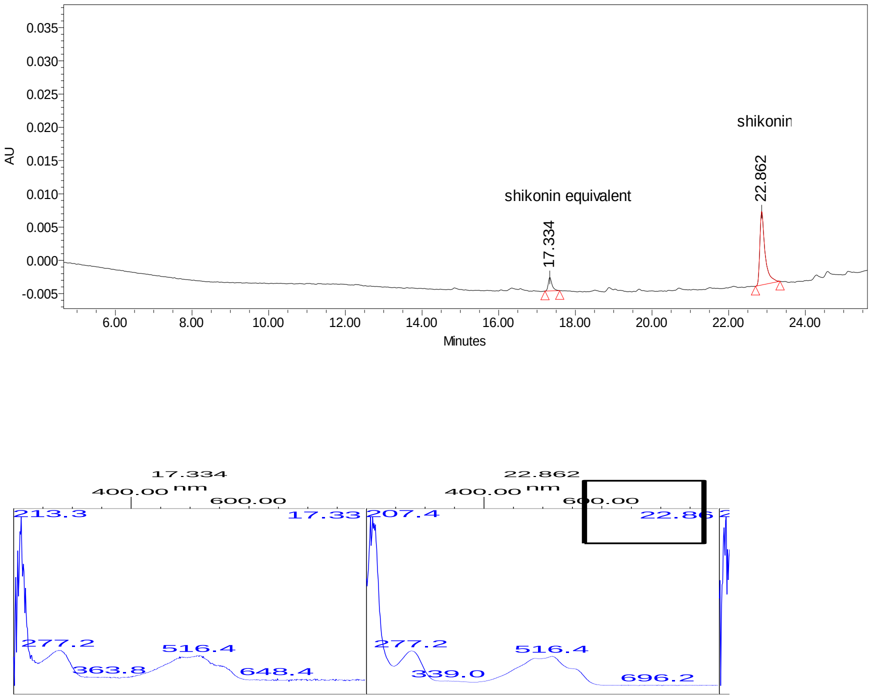

Figure 3. 28 UHPLC-PDA chromatogram (monitored at 515 nm) of the gromwell dyed silk extract and the UV-Vis spectra of its main constituents

Table 3. 17 Retention times and UV maxima of the main components of the gromwell dyed silk extract

Retention time (min)	**UV-vis absorption (nm)**	**Component identified**
17.3	277 516	shikonin equivalent
22.9	277 516	shikonin

---

[258] DMSO was applied to directly extract dye components from the raw plant of gromwell to improve the extraction yield but without success. No characteristic peaks were identified. The reason for this is still under investigation.

[259] Muzou Wang, "Changyong Zhongcaoyao Gaoxiaoyexiangsepu Fenxi," (Beijing: Kexue chubanshe, 1999).

It should be noted that these main dye components in the roots of gromwell are S- and R-enantiomers (namely shikonin and alkannin).[260] It is impossible to distinguish this pair of enantiomers by UHPLC-PDA-MS because they co-elute and there is no spectral difference between them.[261] Other analytical techniques like Nuclear magnetic resonance have been applied to identify various shikonin and alkannin.[262]

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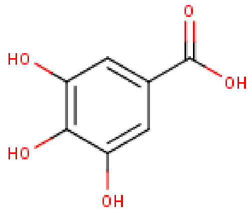
[260] Wenwen Feng *et al.*, "Ruanzicai Yu Yingzicao Naikunlei Huaxue Chengfen De Yanjiu," [A study on the chemical compositions of naphthoquinones in ruanzicao and yingzicao], *Modern Chinese Medicine* 12, no.7 (2010): 15-18.

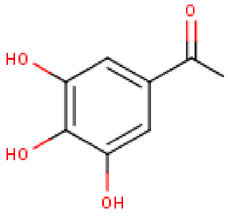
[261] Hofenk de Graaff, Roelofs, and van Bommel, 46.

[262] Lulu Chen *et al.*, "Zicao Zhong Naikunlei Huahewu De Zhipu Jianbie Ji 3 Zhong Chengfen De UPLC Tongshi Ceding," [Mass-spectrum Identification of Naphthoquinone Derivatives and Simultaneous Determination of Shikonin, Acetylshikonin and β,β'-dimethylacrylshikonin in Radix Arnebiae], *Traditional Chinese Drug Research and Clinical Pharmacology* 13, no.1 (2012): 77-80; Jie Han, Xinchu Weng, and Kaishun Bi, "Antioxidants from a Chinese Medicinal Herb–*Lithospermum Erythrorhizon*," *Food Chemistry* 106, no.1 (2008): 2-10; Nanjing University of Traditional Chinese Medicine, 5892-5893; Feng *et al.*, "Ruanzicai Yu Yingzicao Naikunlei Huaxue Chengfen De Yanjiu," 15-18.

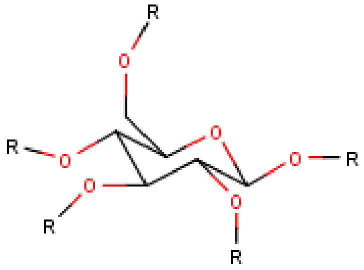
3.4.1.12 Chemical structures of the characteristic components of the common dyes



gallic acid

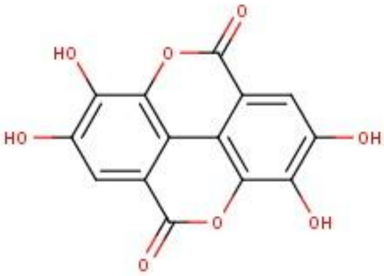


galloyl group

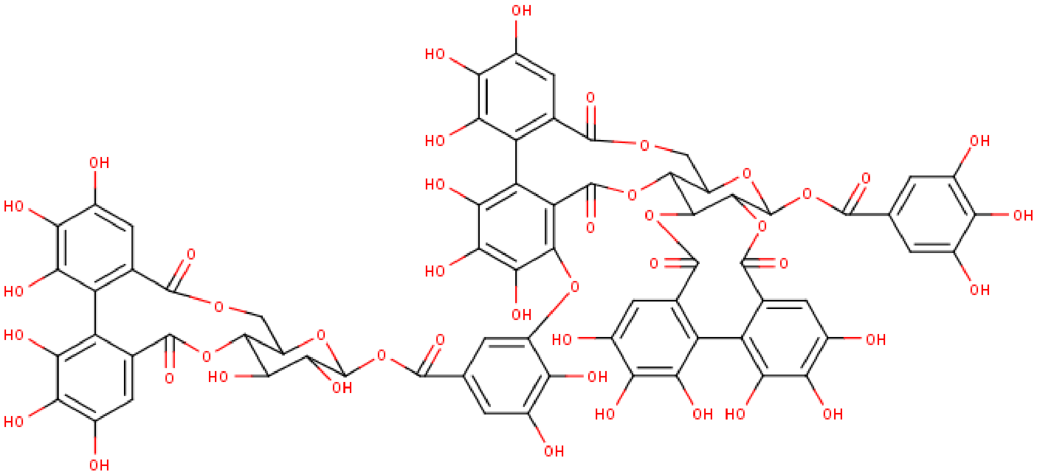


gallotannin (R= galloyl groups)

(a) The characteristic components of gallnut



ellagic acid



an example of ellagitannin (Sanguiin H-10)[263]

(b) The characteristic component of acorn cup and an example of ellagitannin

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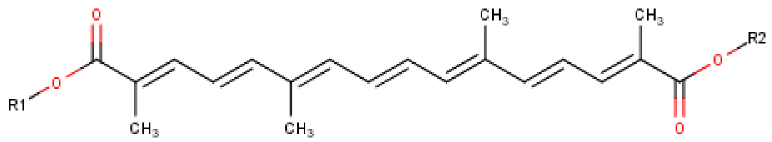
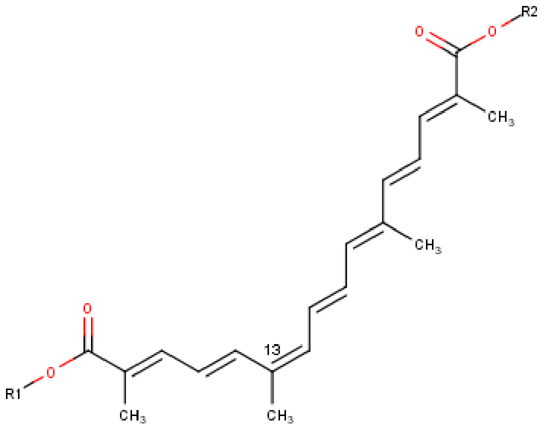
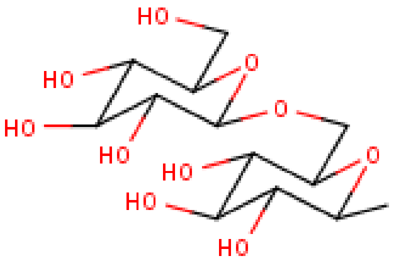
[263] William Mullen *et al.*, "Analysis of Ellagitannins and Conjugates of Ellagic Acid and Quercetin in Raspberry Fruits by LC–MS," *Phytochemistry* 64, no.2 (2003): 617-624.

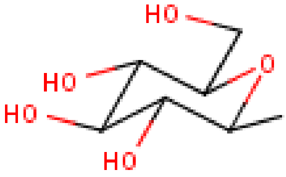


all-*trans*-crocetin



13-*cis*-crocetin





β-D-gentiobiosyl

β-D-glucosyl

(c) The characteristic components of gardenia[264]

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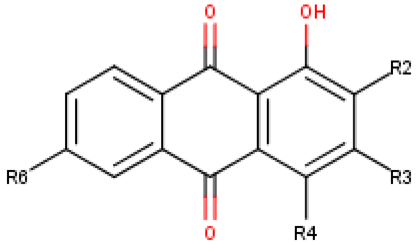
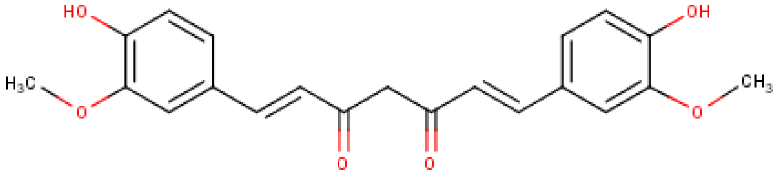
[264] Marie-Rose Van Calsteren *et al.*, "Spectroscopic Characterization of Crocetin Derivatives from Crocus Sativus and Gardenia Jasminoides," *Journal of Agricultural and Food Chemistry* 45, no.4 (1997): 1055-1061.

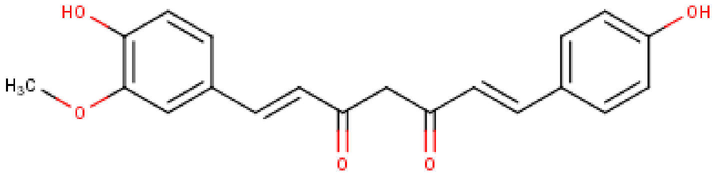


Common name	**R_2**	**R_3**	**R_4**	**R_6**
alizarin	OH	H	H	H
6-hydroxyrubiadin	CH_3	OH	H	OH
lucidin	OH	COOH	OH	H
munjistin	COOH	OH	H	H
pseudopurpurin	OH	H	OH	H
purpurin	CH_3	OH	H	H
rubiadin	CH_2OH	OH	H	H

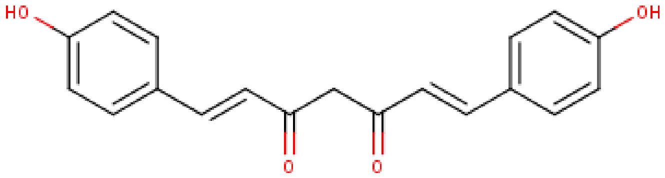
(d) The characteristic components of munjeet[265]



curcumin



desmethoxycurcumin



bisdesmethoxycurcumin

(e) The characteristic components of turmeric

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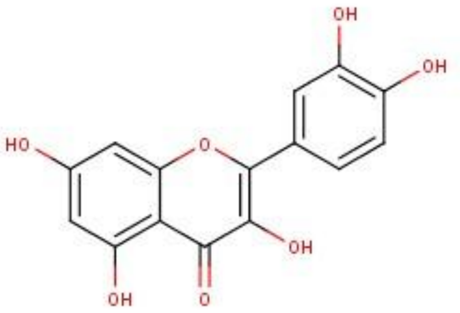
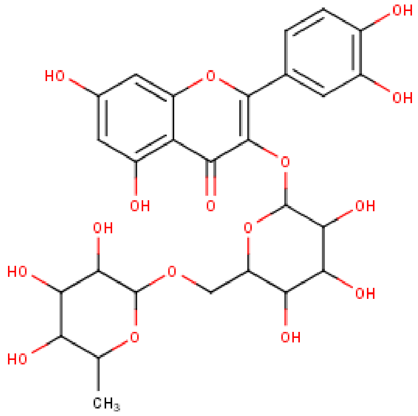
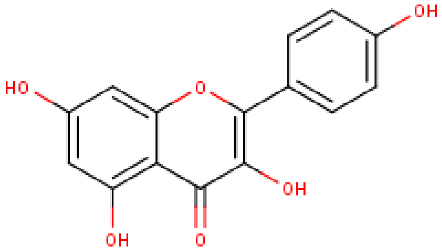
[265] Ram Singh and SMS Chauhan, "9, 10‐Anthraquinones and Other Biologically Active Compounds from the Genus Rubia," *Chemistry & Biodiversity* 1, no.9 (2004): 1241-1264.



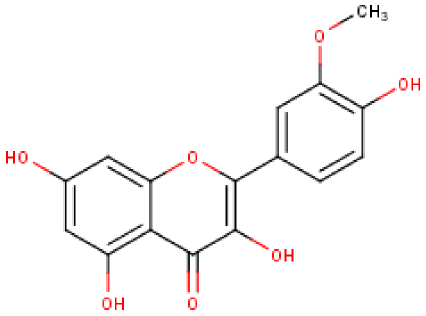
quercetin



rutin

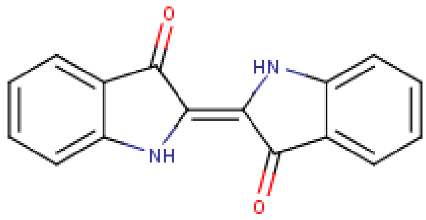


kaempferol

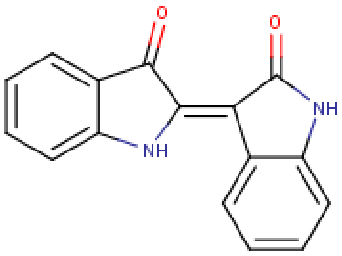


isorhamnetin

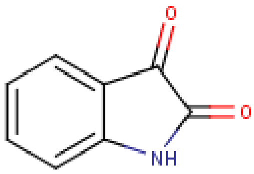
(f) The characteristic components of pagoda bud



indigotin

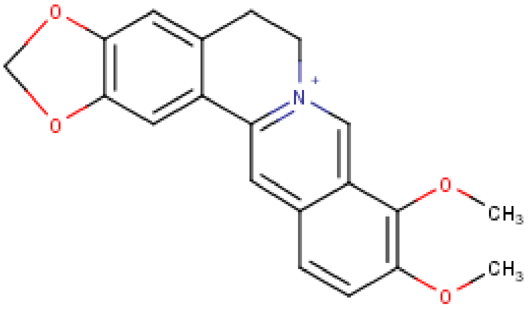


indirubin

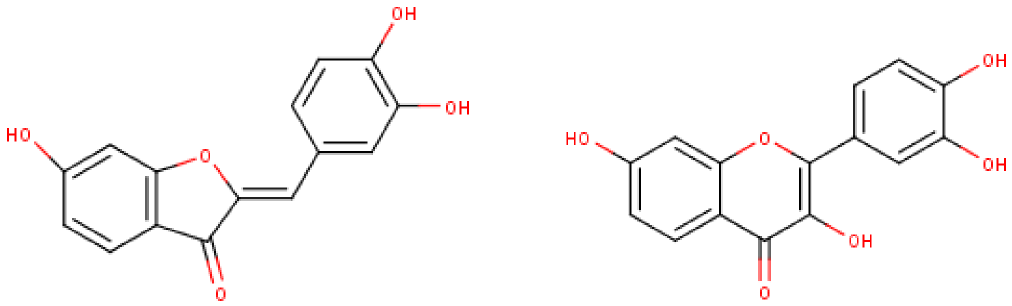


isatin

(g) The characteristic components of indigo

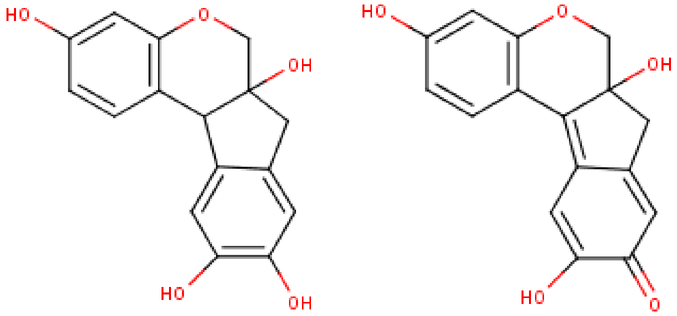


(h) Berberine, the characteristic component of Amur cork tree



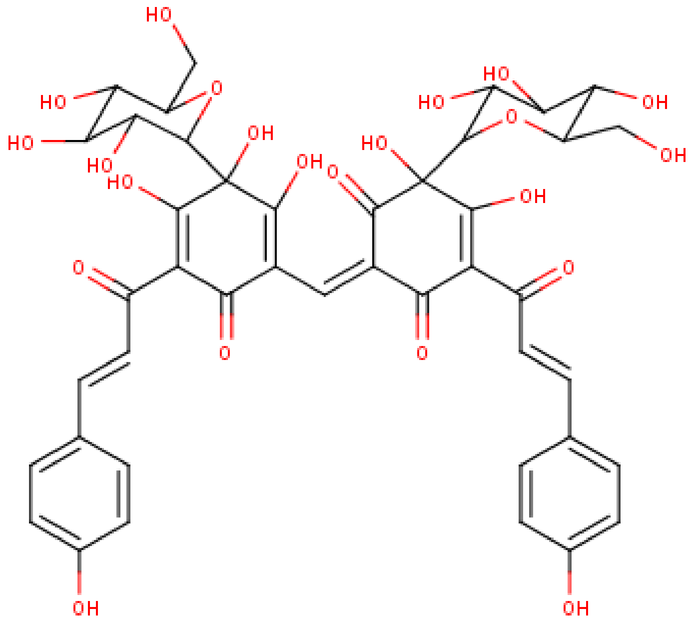
sulfuretin fisetin

(i) The characteristic components of smoketree

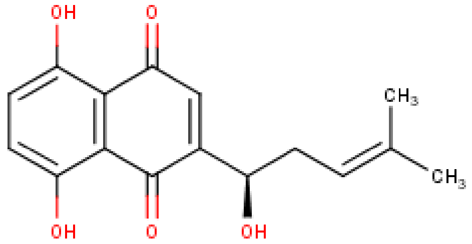


brasilin brasilein

(j) The characteristic components of sappanwood



(k) Carthamin, the characteristic component of safflower



(l) Shikonin, the characteristic component of gromwell

Figure 3. 29 Chemical structures of the characteristic components of the common dyes

3.4.2 Characterisation of the dye components of less common dyes

The basic chemical structures of these less common dyes are similar to those of the common dyes. Flavonoid dyes include small carpetgrass, pomegranate, silkworm thorn, lotus seed shell and lotus leaf. Safflower is a chalcone dye. Chinese goldthread is an alkaloid dye. Saffron is a carotenoid dye. Japanese knotweed and rhubarb are both anthraquinone dyes. Pomegranate, silkworm thorn and rhubarb contain both coloured dye components and tannin. The detailed analytical results of the chemical composition of these dyes are as follows. The dyes are discussed in the sequence of their chemical groups. The two dyes that were analysed by existing research, Chinese goldthread and small carpetgrass, are discussed first. Research outcomes in the fields of Chinese plant medicine and biochemistry were referenced to help interpret the dye compositions of the other less common dyes.

3.4.2.1 Chinese goldthread

The extract of the Chinese goldthread dyed sample contains a series of alkaloids with similar UV-vis spectra (Figure 3. 30). The main alkaloids in Chinese goldthread include jatrorrhizine, palmatine, berberine, epiberberine and coptisine.[266] Structural analysis would help determine the attribution of the main peaks obtained in the chromatogram.

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[266] Guojia zhongyiyao guanlijv zhonghua bencao bianweihui, vol. 3, 293; Zhang *et al.*, "Preliminary Studies toward Identification of Sources of Protoberberine Alkaloids Used as Yellow Dyes in Asian Objects of Historical Interest," 177-185.

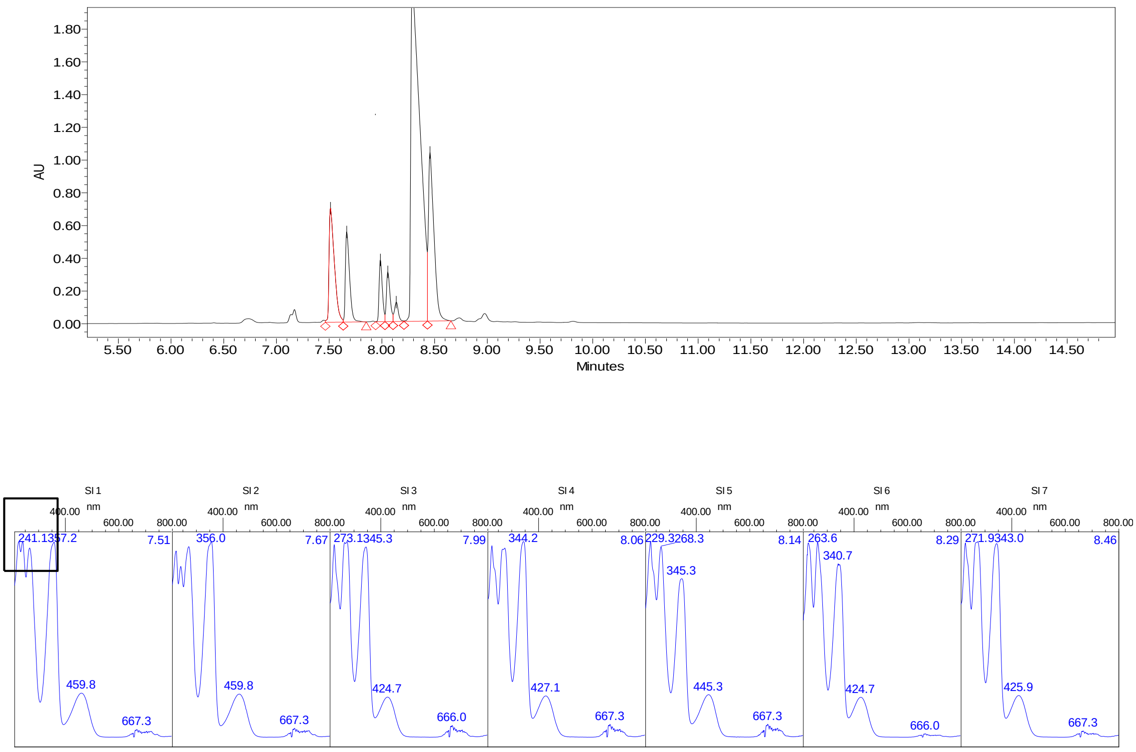

Figure 3. 30 UHPLC-PDA chromatogram (monitored at 254 nm) of the Chinese goldthread dyed silk extract and the UV-vis spectra of its main constituents

3.4.2.2 Small carpetgrass

In the extract of the small carpetgrass dyed sample flavonoids and other components were detected as its major colourants (Figure 3. 31). Compared with published LC chromatogram of a small carpetgrass dyed sample extract, the three major components are probably luteolin, luteolin 8-C-rhamnoside (or isomer) and tricin.[267] These could be used as markers for identifying small carpetgrass.

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[267] Mouri and Laursen, "Identification and Partial Characterization of *C*-Glycosylflavone Markers in Asian Plant Dyes Using Liquid Chromatography–Tandem Mass Spectrometry," 7325-7330.

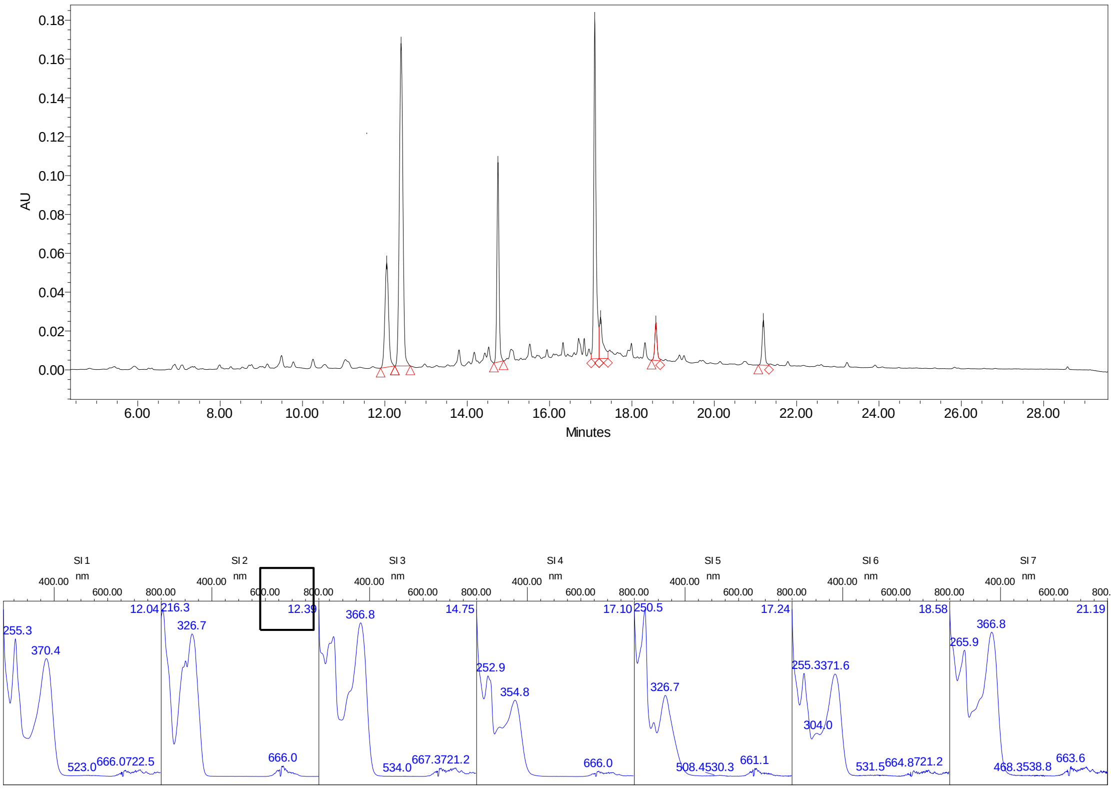

Figure 3. 31 UHPLC-PDA chromatogram (monitored at 350 nm) of the small carpetgrass dyed silk extract and the UV-vis spectra of its main constituents including a flavonoid at 17.10 min, quercetin at 18.58 min and kaempferol at 21.19 min.

3.4.2.3 Pomegranate

In the extract of the pomegranate dyed sample (Figure 3. 32) a series of yellow components with maximum absorption at 258.8 and 380 nm eluting from 3 to 6 min were detected. Based on their UV-vis spectra, they appear to be flavonoids.[268] This extract also contains abundant ellagitannins: characterised by UV-vis spectra, two ellagitannins eluting at 9.1 and 13.8 min were detected, which are probably punicalin and punicalagin.[269]

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[268] Nanjing University of Traditional Chinese Medicine, 858-859.

[269] Cardon, 482.

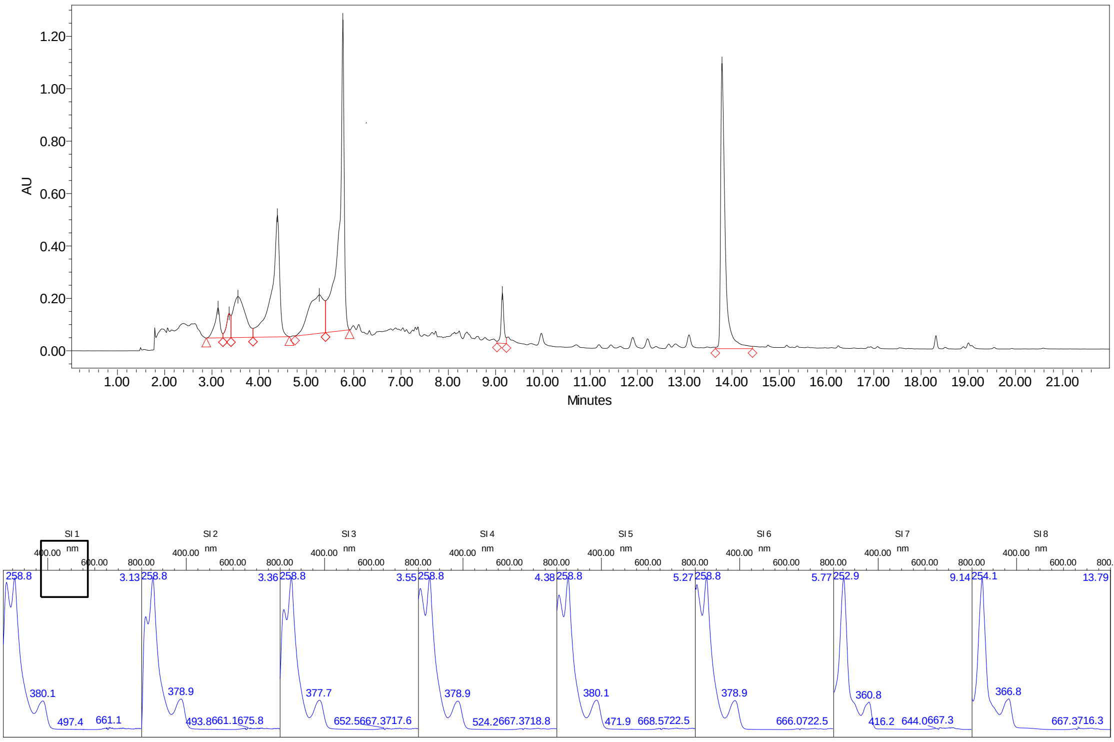

Figure 3. 32 UHPLC-PDA chromatogram (monitored at 254 nm) of the pomegranate dyed silk extract and the UV-vis spectra of its main constituents

3.4.2.4 Silkworm thorn

Similar to pomegranate, in the extract of the silkworm thorn dyed sample flavonoids and ellagitannin were detected (Figure 3. 33).[270]

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[270] Guojia zhongyiyao guanlijv zhonghua bencao bianweihui, vol. 2, 519.

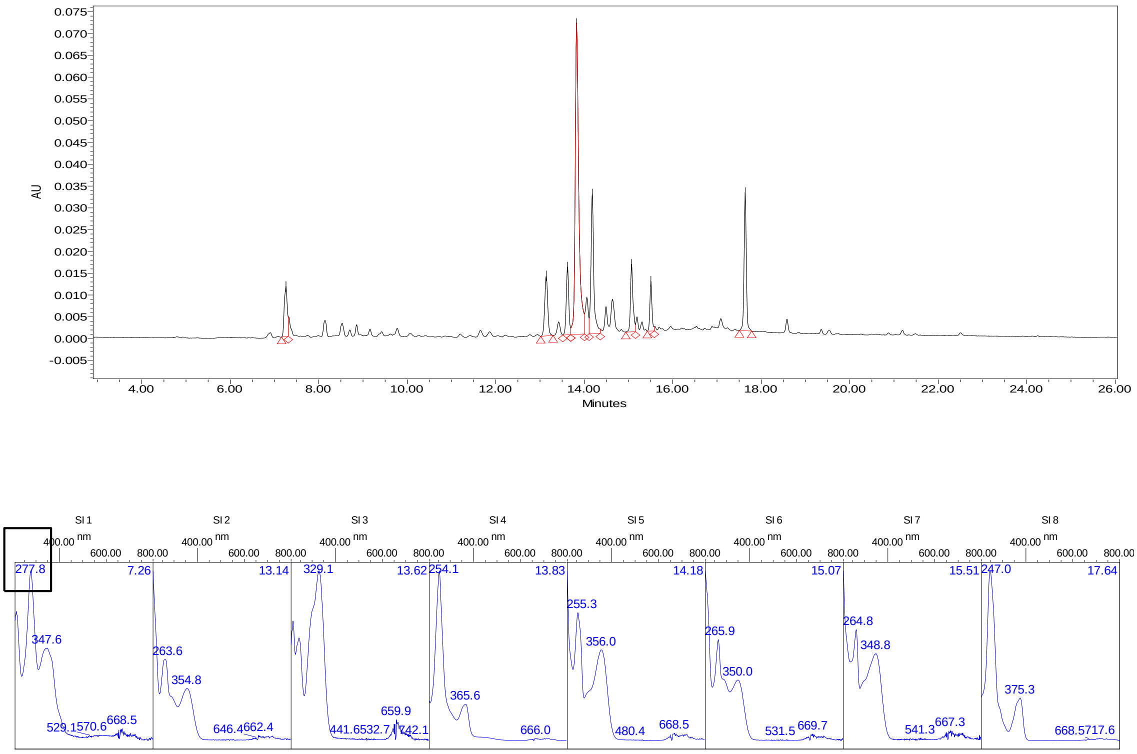

Figure 3. 33 UHPLC-PDA chromatogram (monitored at 350 nm) of the silkworm thorn dyed silk extract and the UV-vis spectra of its main constituents including flavonoids at 13.14, 14.18 (similar to rutin), 15.01 and 15.51 min, ellagic acid at 13.83 min and a component with similar UV-vis spectra at 17.64 min.

3.4.2.5 Lotus seed shell and lotus leaf

Judged from UV-vis spectra, the extracts of lotus seed shell and lotus leaf dyed samples both mainly consist of four flavonoids eluting at 14.1, 14.2, 14.6 and 18.6 min (Figure 3. 34 and Figure 3. 35). The fourth component was identified as quercetin based on both its retention time and UV-vis spectrum. The chemical structures of the first three of these components are similar to rutin, judged by their similar UV-vis spectra to that of rutin. It is known that apart from quercetin, lotus leaf contains flavonoids including isoquercitrin, leucocyanidin and leucodelphinidin, which the first three components detected may be attributed to.[271]

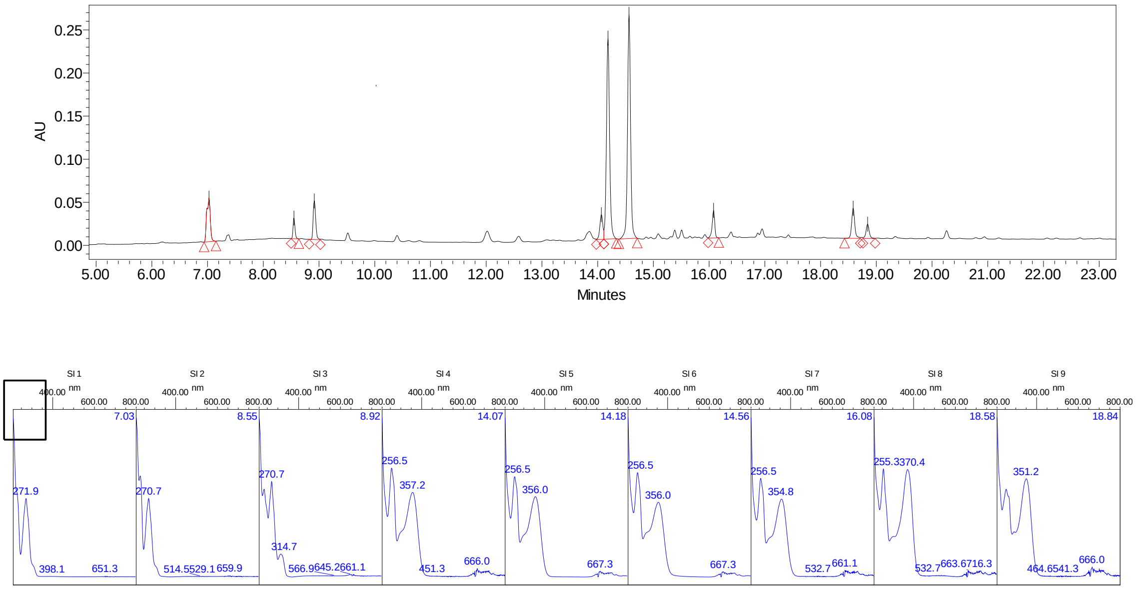

Figure 3. 34 UHPLC-PDA chromatogram (monitored at 254 nm) of the lotus seed shell dyed silk extract and the UV-vis spectra of its main constituents

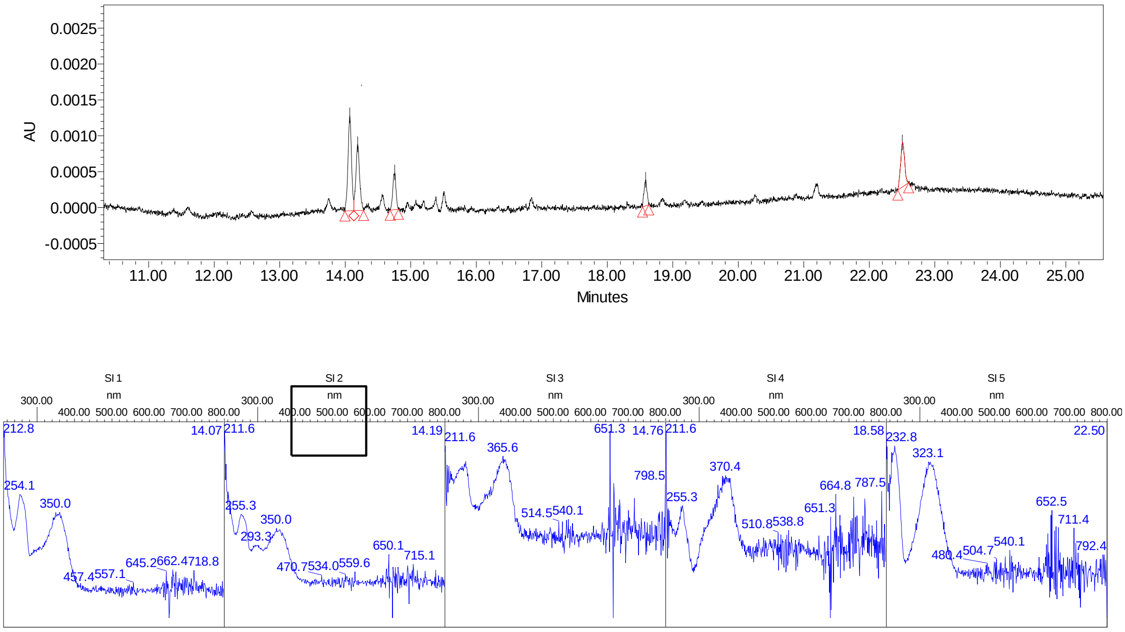

Figure 3. 35 UHPLC-PDA chromatogram (monitored at 350 nm) of the lotus leaf dyed silk extract and the UV-vis spectra of its main constituents

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[271] Nanjing University of Traditional Chinese Medicine, 2489-2499, 2510.

3.4.2.6 Safflower for yellow

The extract of the safflower dyed yellow sample contains both yellow and colourless components (Figure 3. 36). The two major yellow components elute respectively at 14.1 and 15.3 min. Analytical results in biochemistry show that the yellow components of safflower include quinochalcones, flavonol derivatives and other phenolic compounds.[272] One group of colourless components is safflower Ct components eluting at 15.5-17.6 min. The other group of colourless components is a series of compounds eluting at 20.0-26.0 min with multi maximum UV-vis absorption. The chemical structure with this kind of multi maximum UV-vis absorption remains unclear. Small amounts of all these colourless components are also present in the safflower dyed red reference sample (section 3.4.1.11).

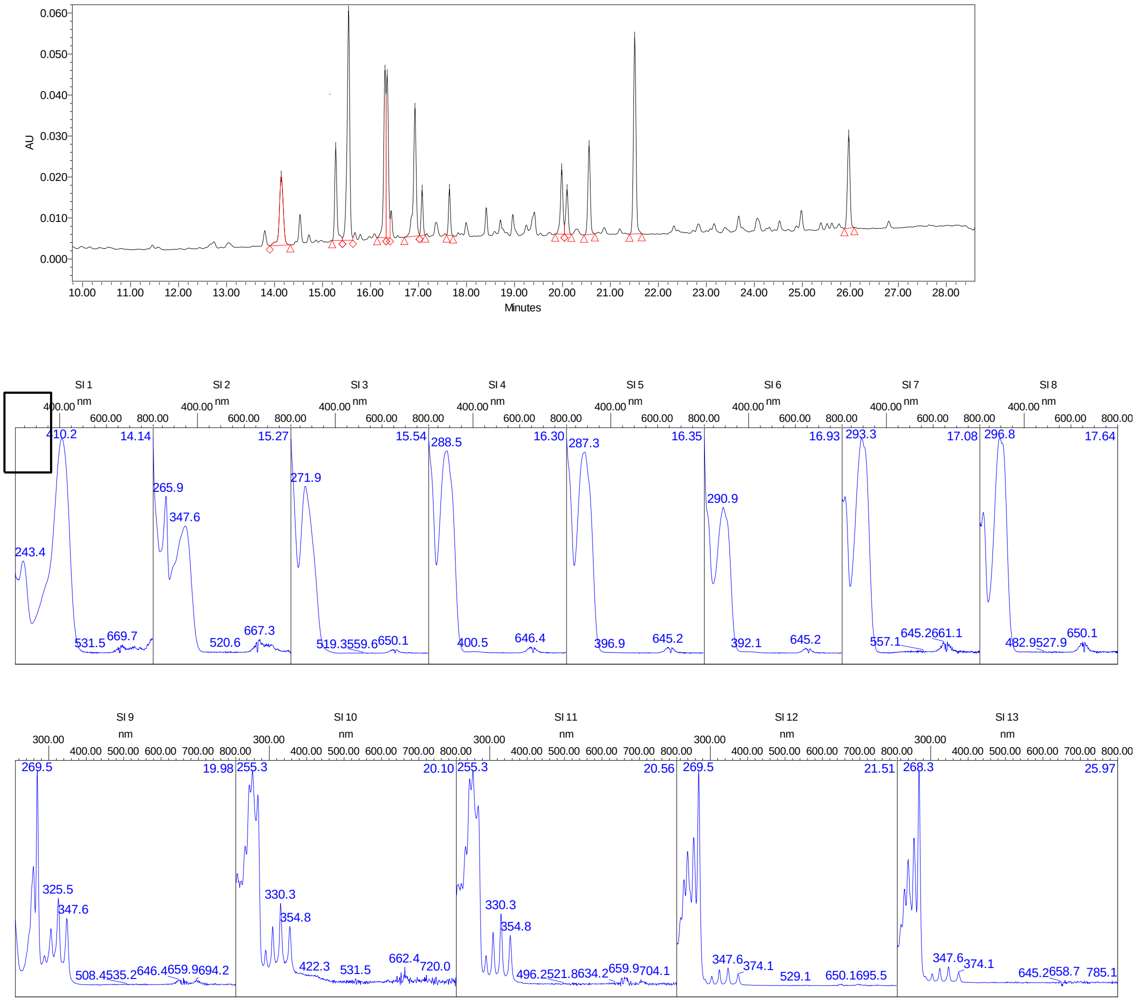

Figure 3. 36 UHPLC-PDA chromatogram (monitored at 254 nm) of the safflower yellow dyed silk extract and the UV-vis spectra of its main constituents

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[272] Cardon, 55.

3.4.2.7 Saffron

In the extract of the saffron dyed sample crocetin and various crocins were detected (Figure 3.37). This combination is similar to that of gardenia, but the crocetin and crocins that the two dyes contain are of different relative amounts,[273] and the relative amounts remain relatively stable during ageing (section 5.4.3.3). Therefore the relative amounts of crocetin and crocins is helpful for distinguishing the two dyes from dyed samples.

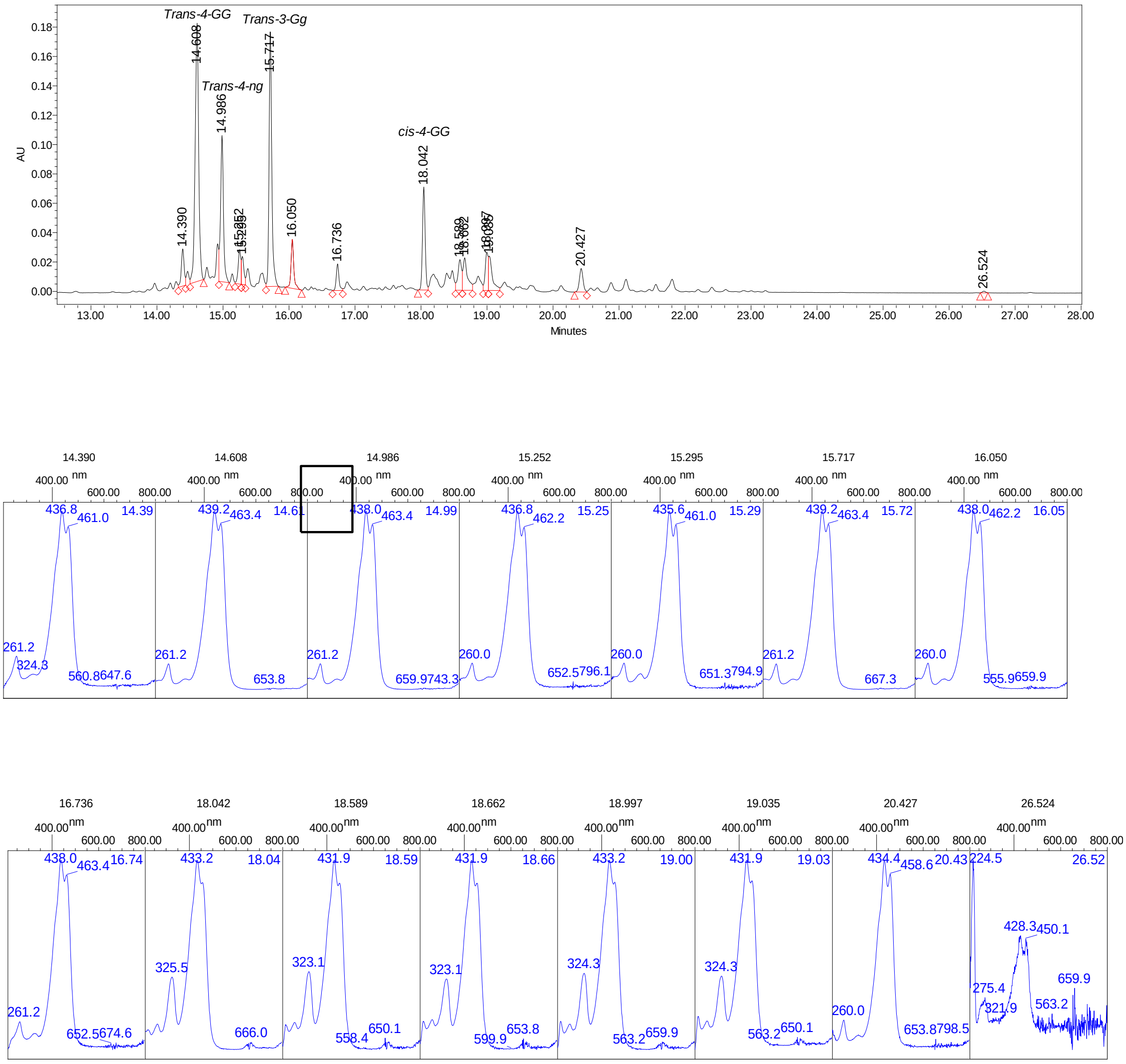

Figure 3. 37 UHPLC-PDA chromatogram (monitored at 450 nm) of the saffron dyed silk extract and the UV-vis spectra of its main constituents

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[273] Carmona *et al.*, "Crocetin Esters, Picrocrocin and Its Related Compounds Present in Crocus Sativus Stigmas and Gardenia Jasminoides Fruits. Tentative Identification of Seven New Compounds by LC-ESI-MS," 973-979.

3.4.2.8 Japanese knotweed

In the extract of the Japanese knotweed dyed sample a serious of coloured anthraquinones components with maximum UV-vis absorption at 222, 280 and 430 nm were detected (Figure 3. 38). It is known that Japanese knotweed contains anthraquinones and anthraglycosides including emodin, physcion and chrysophanol.[274] The two components eluting at 27.9 and 28.9 min are also present in the extract of the rhubarb dyed sample. Additionally, two major colourless components eluting at 10.5 and 15.5 min were also detected.

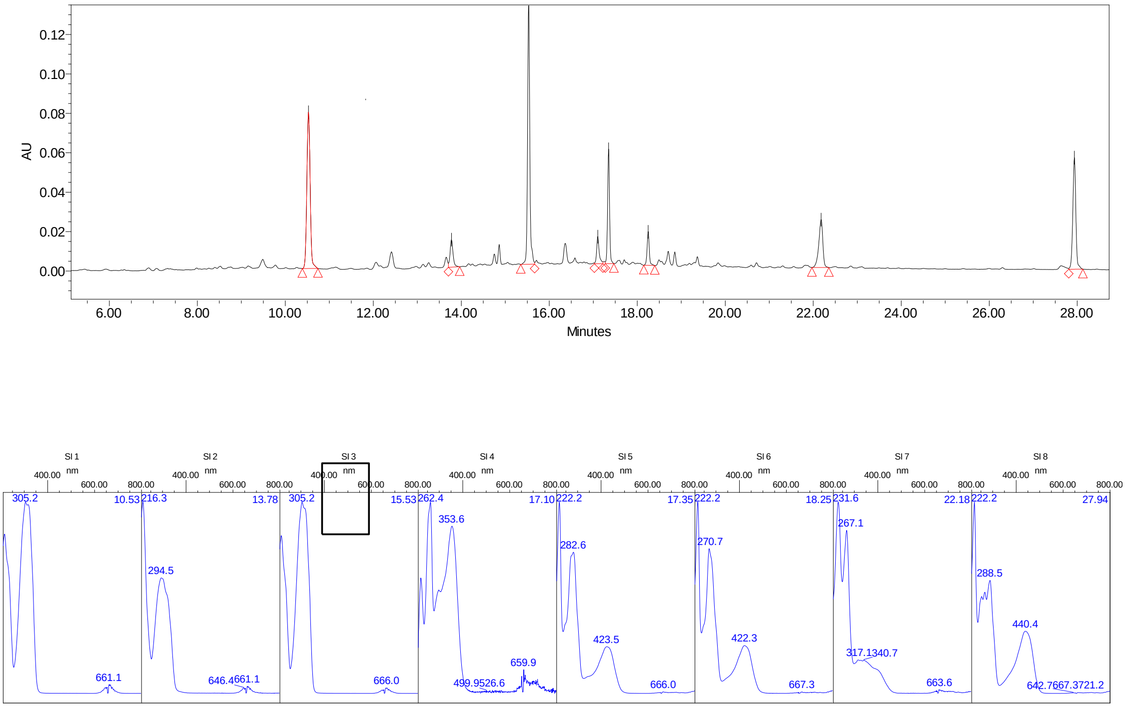

Figure 3. 38 UHPLC-PDA chromatogram (monitored at 350 nm) of the Japanese knotweed dyed silk extract and the UV-vis spectra of its main constituents

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[274] Nanjing University of Traditional Chinese Medicine, 1869-1870.

3.4.2.9 Rhubarb

In the extract of the rhubarb dyed sample two groups of components were detected (Figure 3. 39). The components eluting from 9.5 to 15.4 min show maximum UV-vis absorption at around 280 nm, indicating they may be gallotannins and condensed tannins. The components eluting from 16 to 29 min show UV-vis spectra similar to anthraquinones, probably including chrysophanol, emodin, aloe-emodin, physcion and rhein and their glycosides that survive dyeing, as well as related dianthrones.[275]

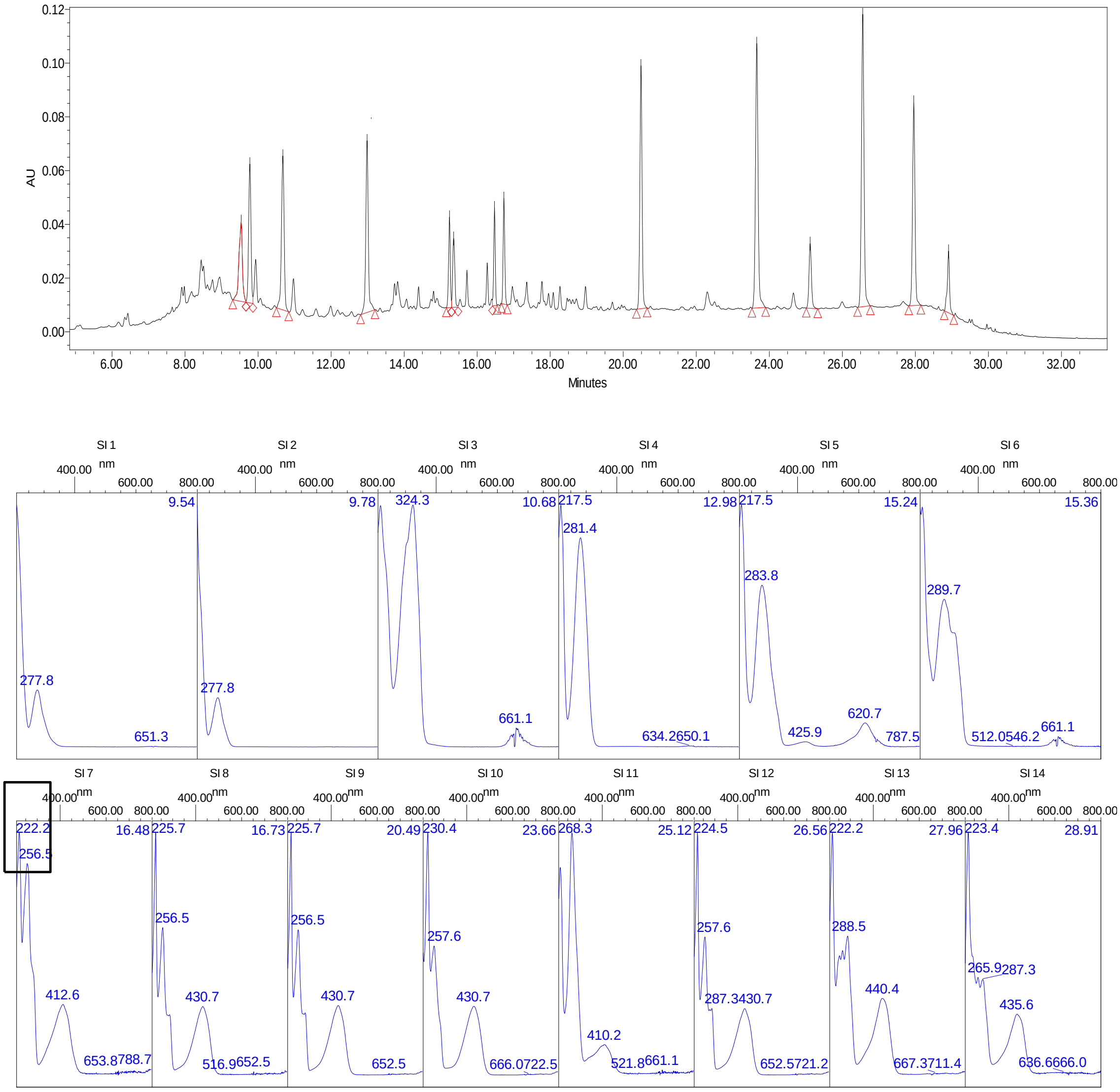

Figure 3. 39 UHPLC-PDA chromatogram (monitored at 254 nm) of the rhubarb dyed silk extract and the UV-vis spectra of its main constituents

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[275] Cardon, 88.

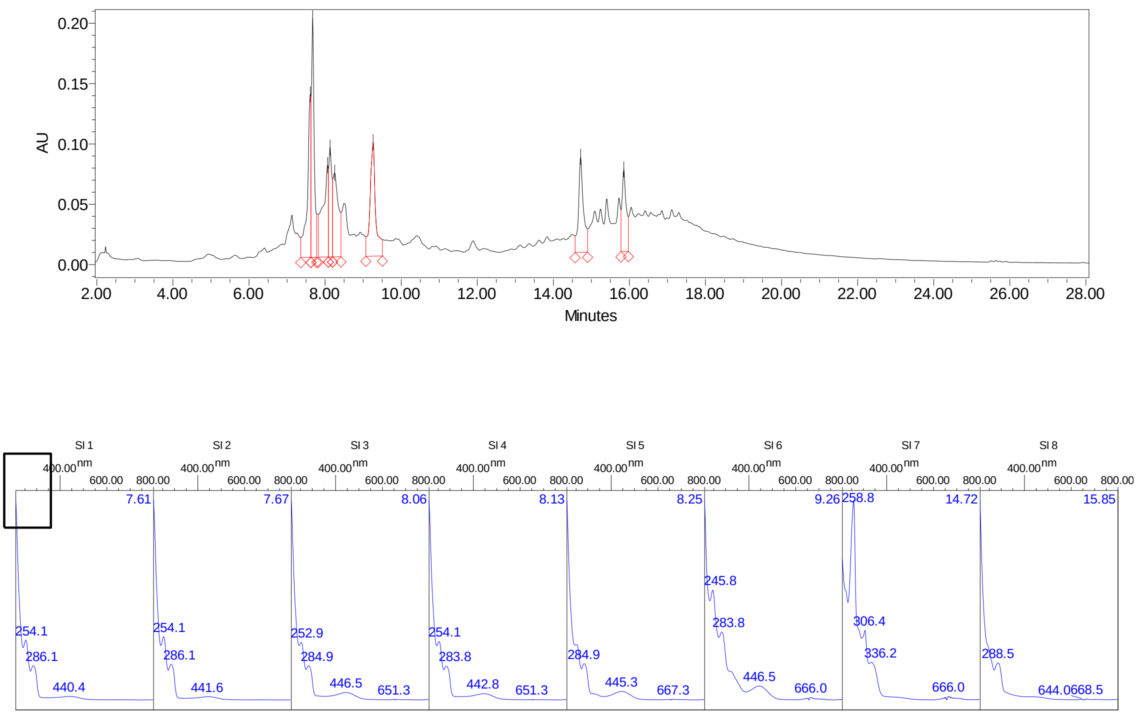
3.4.2.10 Summary of the chemical characterisation of less common dyes

In this section the chemical profiles of ten less common dyes were obtained, though further research utilising the chromatographic conditions is needed for better separation and identification of their characteristic components, such as silkworm thorn and Chinese goldthread. It can be seen that the ten less common dyes share the same groups of dye components with the common dyes: flavonoids, chalconoids, alkaloids, carotenoids, anthraquinones and tannins. Nevertheless, these dyes were not as popular as the common dyes in ancient China. The amount of dye components contained in the dyes, their availability and lightfastness are possible factors affecting their popularities, which needs further investigation. A special group of dyes including pomegranate, silkworm thorn, and rhubarb contains coloured dye components as well as tannins. When used with iron salts, these dyes could make dark shades.

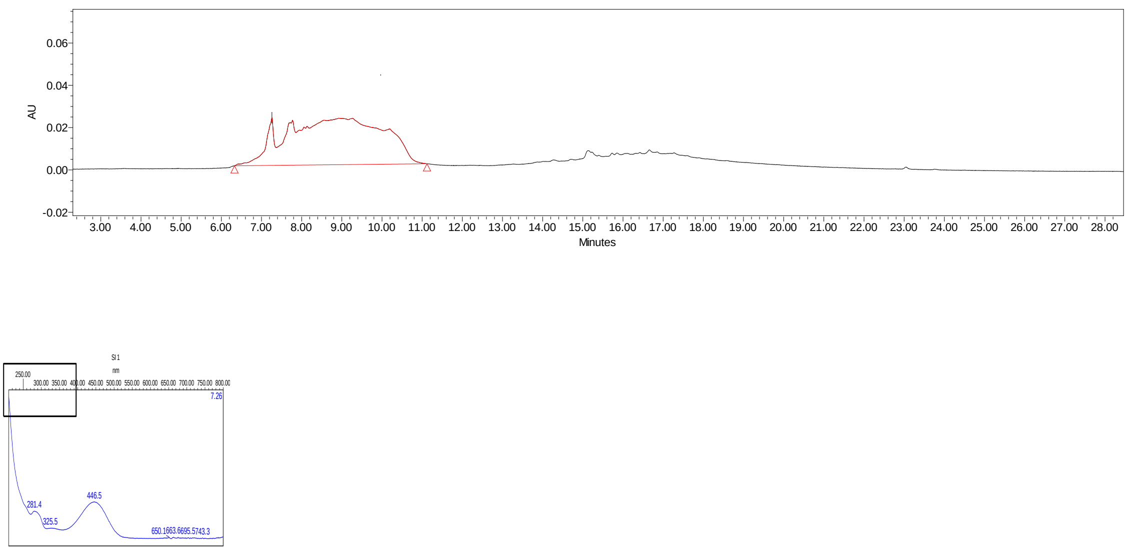
3.4.3 Dyes and dyed cotton from the Li ethnic minority

3.4.3.1 Sappanwood

Figure 3. 40 presents two UHPLC-PDA chromatograms from the extract of the cotton sample dyed with sappanwood extracted respectively at 295 and 450 nm. Spectral information shows the presence of brasilein, Nowik type A components and Nowik type C component, the first being the major colourant of sappanwood and the following components being characteristic colourless components of sappanwood. This analytical result is the same as that of the extract of the silk sample dyed with sappanwood reference (section 3.4.1.10), confirming the suitability of the analytical protocol of dyes for dyed cotton fabrics.



(a) Nowik type A components at 7.61-9.26 min and Nowik type C component at 14.72 min were identified.



(b) Brasilein elutes as a broad peak from 6 to 11 min, coeluting with Nowik type A components.

Figure 3. 40 UHPLC-PDA chromatograms of the sappanwood dyed silk extract, monitored at 295 nm (a) and 450 nm (b), and the UV-Vis spectra of its main constituents.

3.4.3.2 Turmeric

Figure 3. 41a and b show the UHPLC-PDA chromatograms from the extracts of the cotton samples dyed with turmeric, one with plant ash one without. In both extracts, curcumin, demethoxycurcumin and bisdesmethoxycurcumin, three main colourants of turmeric, were detected. This is similar to the analytical results of the extract of turmeric reference dyed silk sample (section 3.4.1.5). Three additional minor yellow components were detected at 17.5, 18.7 and 19.0 min. No significant differences in chemical composition or in shade were found between the sample using plant ash and not using plant ash. The use of plant ash in dyeing does not affect the analytical results of dyed samples by UHPLC-PDA.

Two special dyeing methods were used when dyeing turmeric. First, plant ash is added during dyeing. The alkaline of plant ash helps the dyeing process. Potassium carbonate, the main component of plant ash, hydrolyses in water and generates hydroxide ions, which let the fibres swell and thus making it easier for the dyes to penetrate in between the fibres.[276] Second, when dyeing, turmeric rhizomes are pounded into paste in a container and then cotton is soaked in the paste for dyeing. This method solves the poor water-solubility of turmeric colourants and allows the turmeric particles to precipitate directly on the fibres. By comparing the analytical results of these two turmeric dyed samples with the reference turmeric sample (section 3.4.1.5), it can be seen that they differ in the relative ratio of the three main dye components and the presence of three minor dye components from 17 to 19 min in these two samples. Whether these differences result from different turmeric sources or from the paste-dyeing method remains further investigation.

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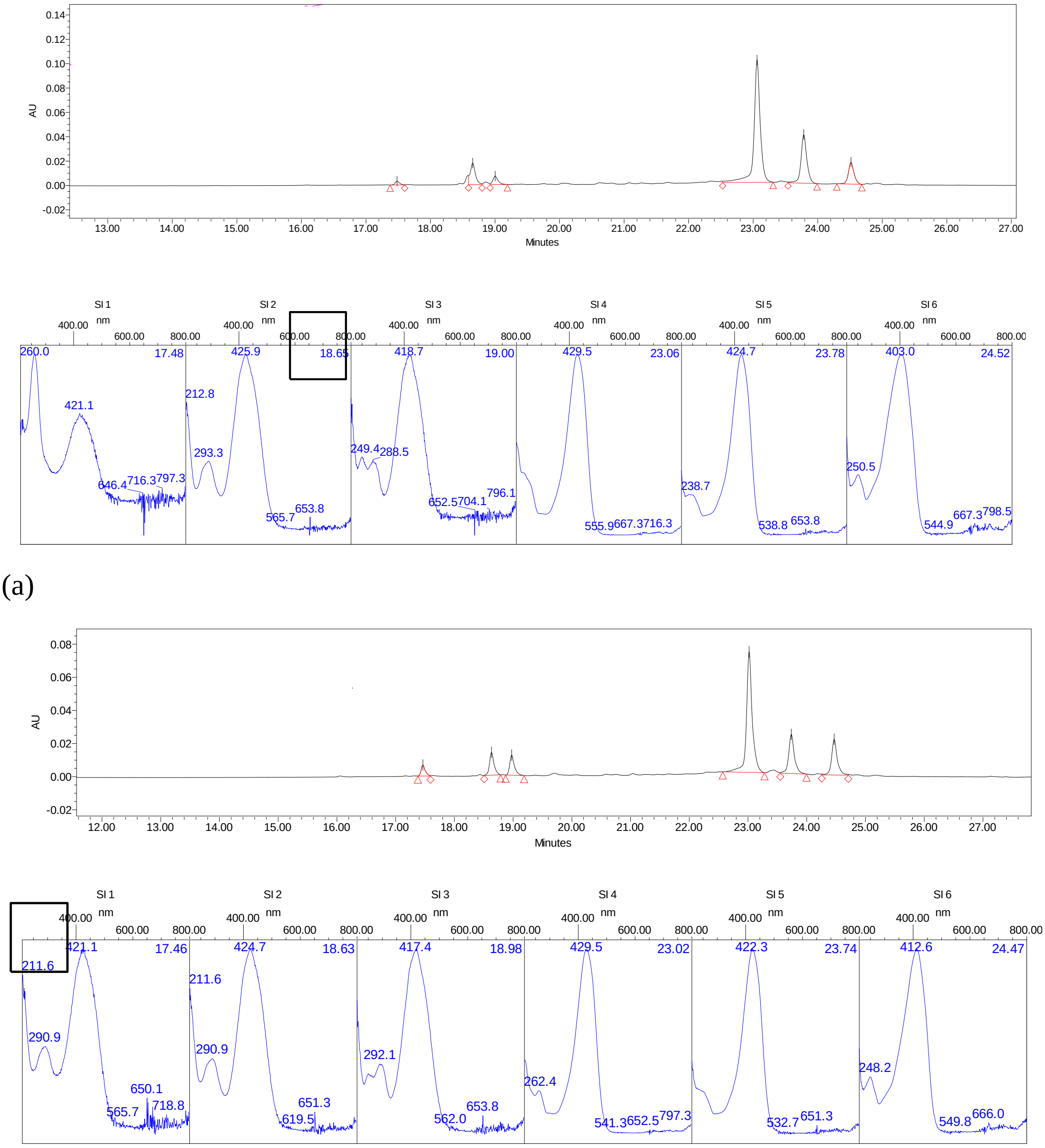
[276] NPCS Board of Consultants & Engineers and National Institute of Industrial Research (India), *Handbook on Textile Auxiliaries, Dyes and Dye Intermediates Technology* (Delhi: Asia Pacific Business Press, 2009), 129-130.



(a)

(b)

Figure 3. 41 UHPLC-PDA chromatograms (monitored at 430 nm) of the turmeric dyed silk extracts with plant ash (a) and without plant ash (b), and the UV-Vis spectra of their main constituents

3.4.3.3 Indigo dyes

Figure 3. 42 shows the UHPLC-PDA chromatogram from the extract of the cotton sample

dyed with *lan dian*. Isatin, indigotin and indirubin were detected, all generated in the process of indigo formation, same as the analytical result of the extract of the indigo reference dyed sample (section 3.4.1.7).[277] Apart from these, a component eluting at 24.4 min, minor yellow components eluting at 4.5 and 17.4 min and a minor colourless component eluting at 7.7 min were detected. The plant source of *lan dian* is probably *Indigofera tinctoria L.*, which grows widely in this area and contains indican glucoside as a precursor for indigo as well as some flavonoids.[278]

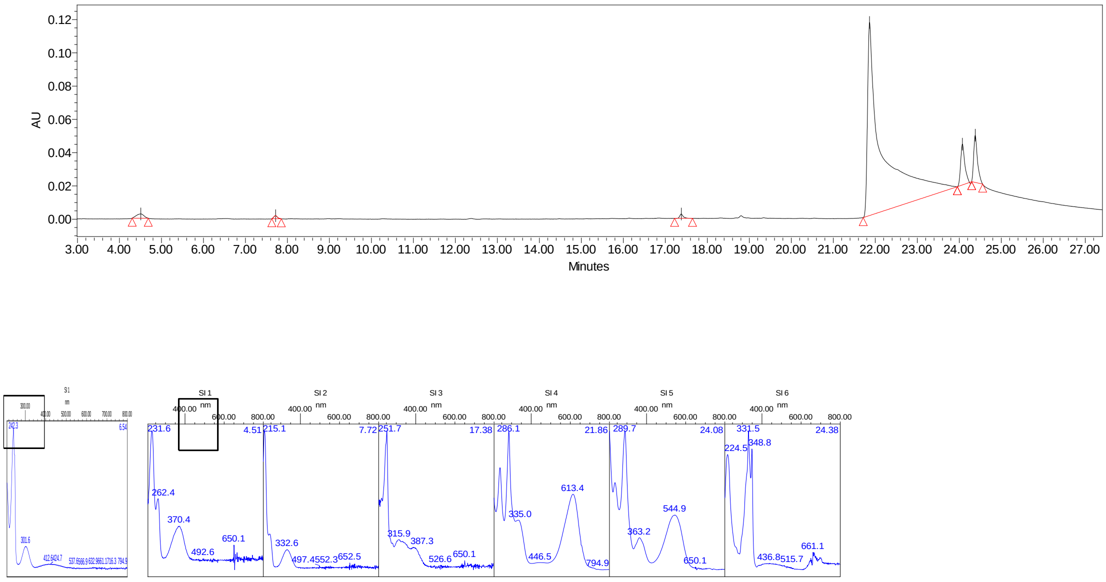


Figure 3. 42 UHPLC-PDA chromatogram (monitored at 425 nm) of the *lan dian* dyed silk extract and the UV-Vis spectra of its main constituents. Isatin at 6.54 min, indigotin at 21.86 min and indirubin at 24.08 min were identified.

Figure 3. 43 shows the UHPLC-PDA chromatogram from the extract of the cotton sample dyed with *jia lan dian*. Indigotin and indirubin were detected as its main dye components. A small amount of isatin is probably present as well. In addition, tannins were detected including gallic acid, ellagic acid and its equivalents. A flavonoid, rutin, is also present, which explains why the sample shows a greenish shade. The plant source for *Jia lan dian* is *Indigofera suffruticosa* Mill. Analytical results by methods like nuclear magnetic

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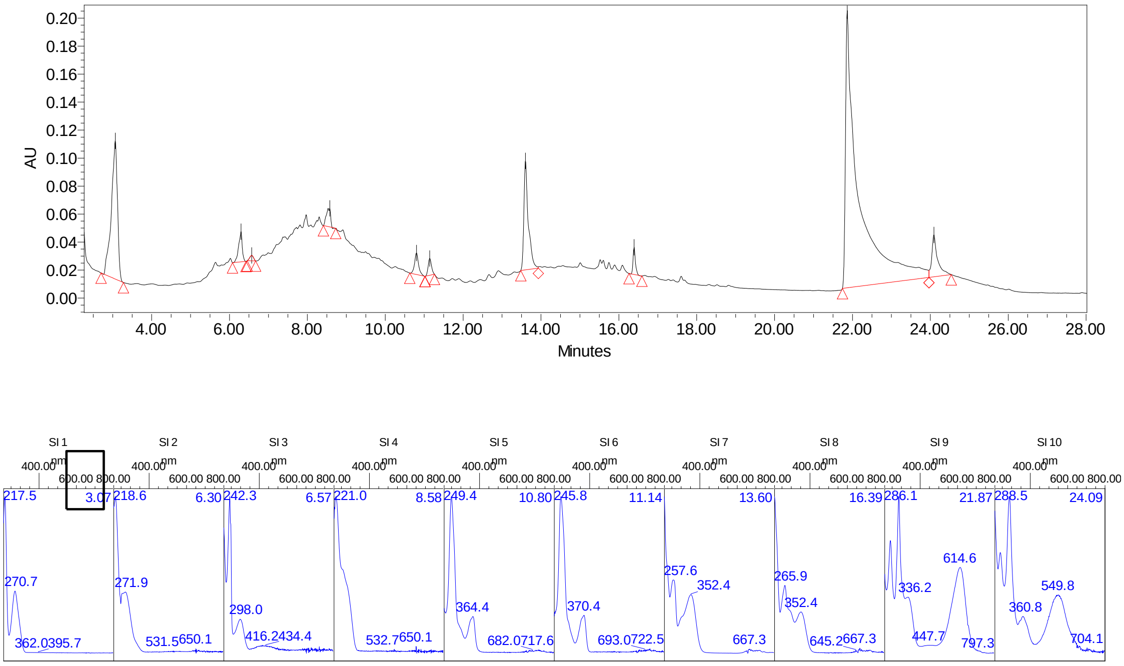
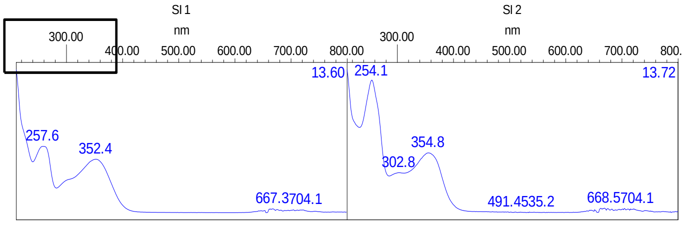
[277] Cardon, 337-339.

[278] Zhang, "Lun Lizu Zhijin Zhiwuran Jiyi Zai Xiandai Fuzhuang Sheji Zhong De Yunyong"; Nanjing University of Traditional Chinese Medicine, 486.

resonance show that the extracts of the whole plant by organic solvents contain D-pinitol, β-sitosterol, louisfieserone, nitropropanoyl-α-glucopyranose, *etc*, which may also be present in this analytical result.[279] The minor characteristic components of the two indigo dyed samples may be characteristic for the identification of particular plant sources for indigo.



(a) Gallic acid at 3.07 min, isatin at 6.54 min, ellagic acid equivalents at 10.80 and11.14 min, rutin and ellagic acid coeluting at 13.60 min, indigotin at 21.86 min and indirubin at 24.09 min were identified.



(b) The coelution of rutin and ellagic acid.

Figure 3. 43 UHPLC-PDA chromatogram (monitored at 280 nm) of the *jia lan dian* dyed silk extract and the UV-Vis spectra of its main constituents.

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[279] Walmir S Garcez *et al.*, "A Nitropropanoyl-Glucopyranoside from Indigofera Suffruticosa," *Phytochemistry* 28, no.4 (1989): 1251-1252.

3.4.3.4 Chestnut shell and chestnut bark

Figure 3. 44 and Figure 3. 45 show the UHPLC-PDA chromatograms from the extracts of the cotton samples dyed with chestnut shell and chestnut bark. The chestnut shell dyed sample contains abundant ellagitannins: ellagic acid was detected at 13.7 min and its two equivalents respectively at 13.3 and 15.9 min. Existing knowledge that various tannins are present in chestnut shell is in accordance with this analytical result.[280] In the chestnut bark dyed sample, three flavonoids were detected including kaempferol eluting at 21.1 min and two other flavonoids eluting at 16.4 and 17.0 min. Ellagitannin was not detected in the chestnut bark dyed sample, showing significant difference in chemical composition from the chestnut shell dyed sample.

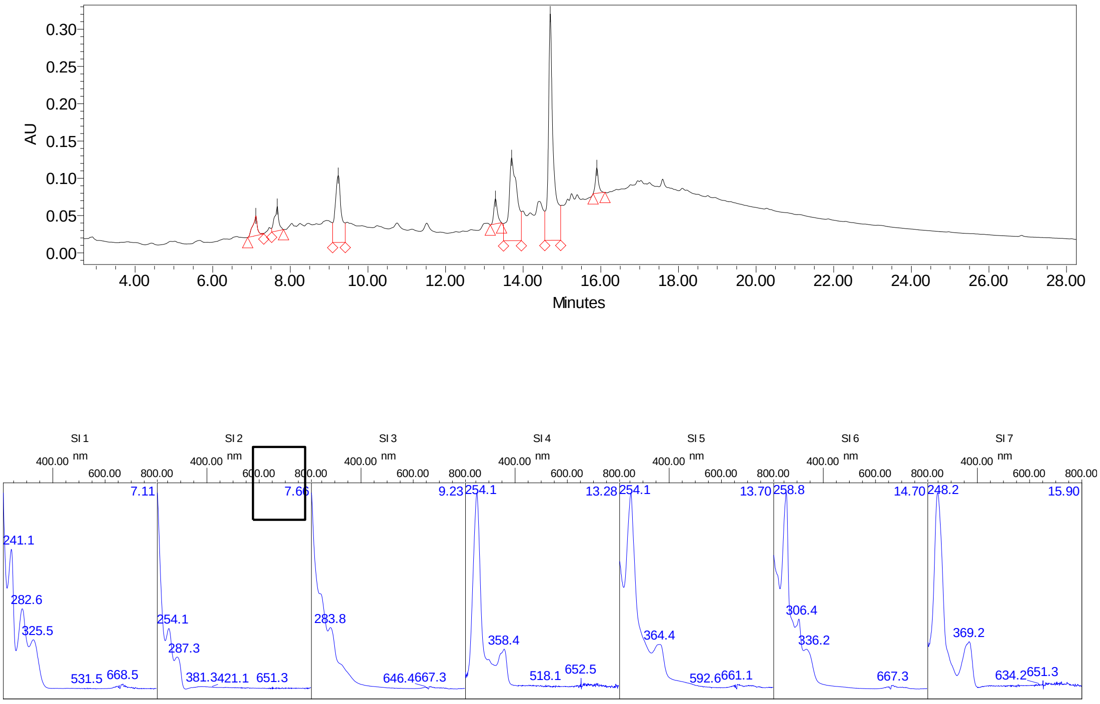

Figure 3. 44 UHPLC-PDA chromatogram (monitored at 254 nm) of the chestnut shell dyed silk extract and the UV-Vis spectra of its main constituents.

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[280] Nanjing University of Traditional Chinese Medicine, 2555-2556; G Vázquez *et al.*, "Evaluation of Potential Applications for Chestnut (Castanea Sativa) Shell and Eucalyptus (Eucalyptus Globulus) Bark Extracts," *Industrial Crops and Products* 29, no.2 (2009): 364-370.

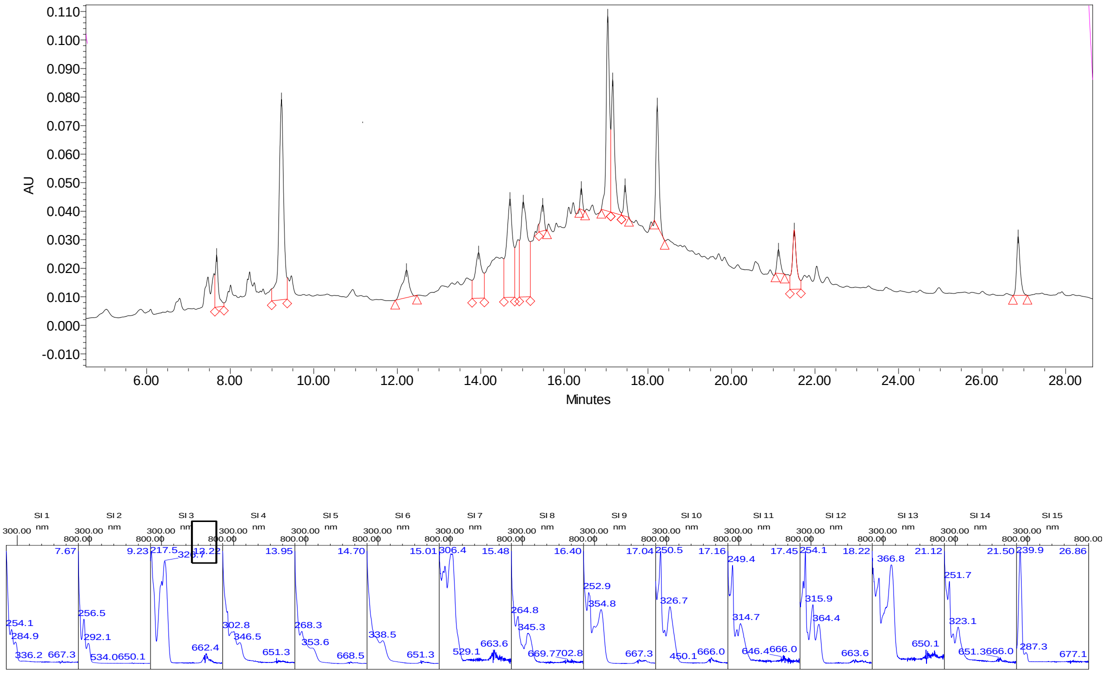

Figure 3. 45 UHPLC-PDA chromatogram (monitored at 254 nm) of the chestnut bark dyed silk extract and the UV-Vis spectra of its main constituents.

3.4.3.5 Jambul

The UHPLC-PDA chromatograms from the water extract of jambul bark is shown in Figure 3. 46. Some colourless components are present. Jambul is usually used with mango kernel and black mud.[281] The ellagitannin jambul bark contains could form complex with iron ions in black mud and make black shades.[282] Mango kernel contains gallic acid, quercetin and genistein,[283] the former functions in a way similar to ellagic acid while the

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[281] Zhang, "Lun Lizu Zhijin Zhiwuran Jiyi Zai Xiandai Fuzhuang Sheji Zhong De Yunyong."

[282] IS Bhatia and KL Bajaj, "Chemical Constituents of the Seeds and Bark of Syzygium Cumini," *Planta Medica* 28, no.4 (1976): 346-352.

[283] Xiaojuan Dong, "Mangguohe Huaxue Chengfen Yanjiu" (Master's dissertation, Luzhou Medical College, 2013); Shihao Huang, "Mangguohe Huaxue Chengfen Ji Yingyong Gongyi Yanjiu" (Master's dissertation, Guangxi Normal University, 2012).

latter two flavonoids contribute to a yellowish shade. Besides, carbon particles in black mud may also attach to the fabric and add to the dark shade.[284]

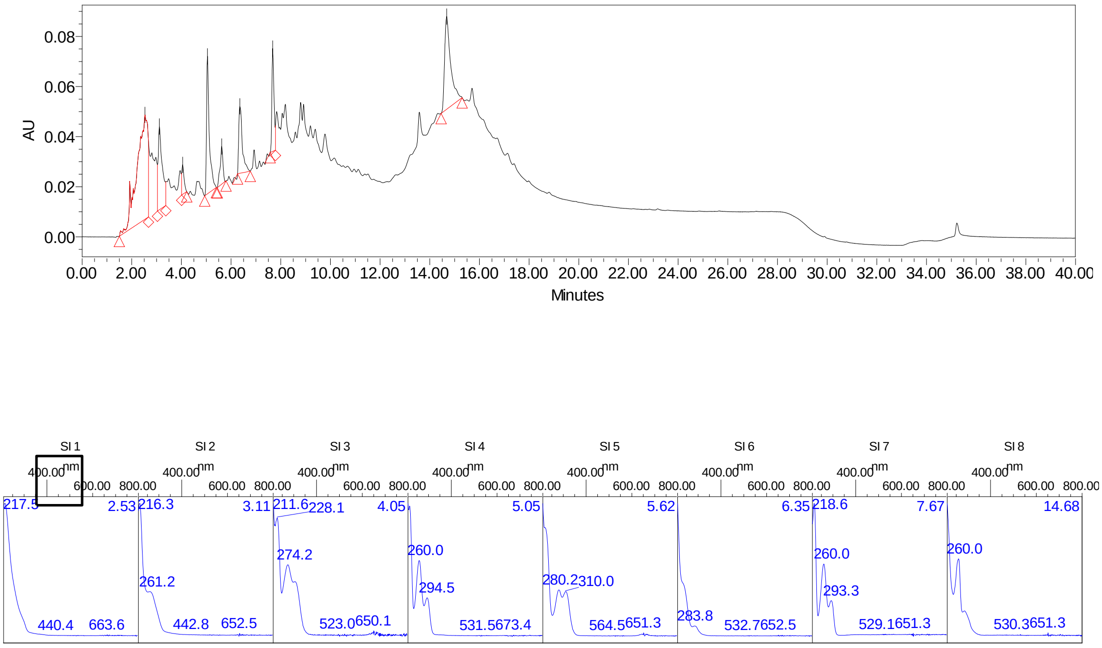

Figure 3. 46 UHPLC-PDA chromatograms (monitored at 254 nm) of the jambul water extract, and the UV-Vis spectra of its main constituents.

3.4.3.6 Tree bark to fix dyes

Analytical results show that the tree bark is mainly composed of ellagitannins: ellagic acid eluting at 13.6 min and its equivalents eluting from 9.5 to 15.1 min were detected in the water extract of the tree bark (Figure 3. 47). The ellagitannins improve cotton dyeing through connecting cotton fibres and dye molecules by the large amounts phenolic hydroxyl groups of ellagitannins. In addition, large tannin molecules help fix colour by wrapping around fibres and dyes.

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[284] Jianbang Chen, "Heise Niantu Zhong Youjizhi Zufen De Chare Yanjiu," [Differential thermal analysis of organic constituents in black clay], *China Ceramics* 20, no.3 (1984): 4-7.

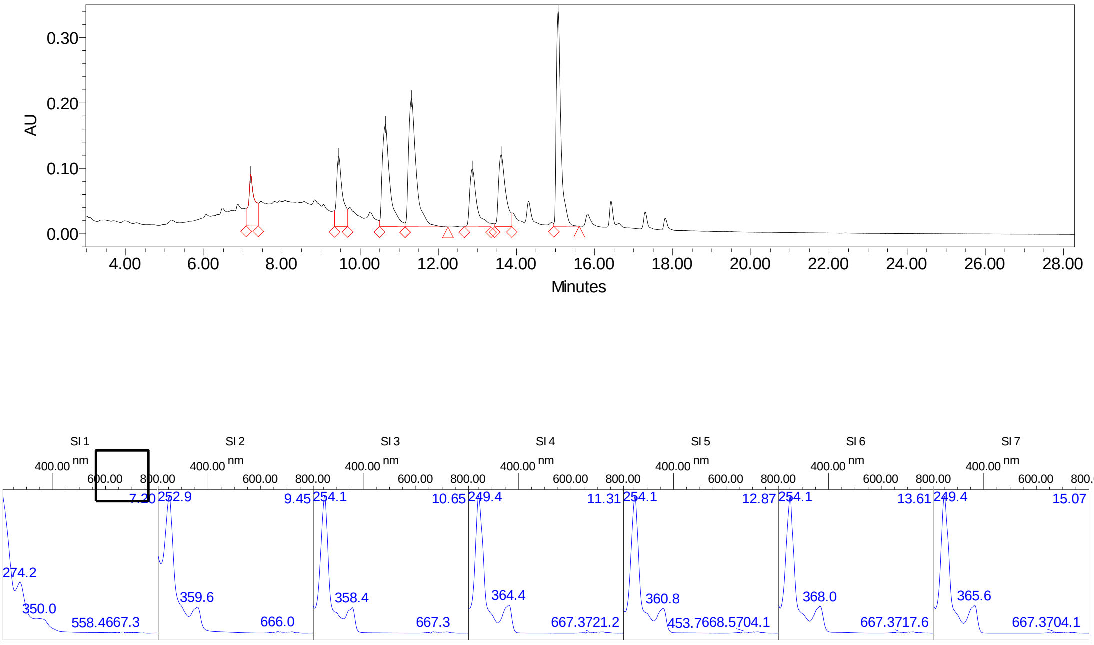


Figure 3. 47 UHPLC-PDA chromatogram (monitored at 350 nm) of the colour fixing tree bark water extract and the UV-Vis spectra of its main constituents.

3.4.3.7 Discussion

The plant dyes used by the Li group are similar to the dyes used in the main textile centres of China during the Ming and Qing Dynasties, sharing dyes such as sappanwood, turmeric and *Indigofera tinctoria*. The great similarity between the analytical results from dyed samples prepared using reference dyes and pure chemicals in the lab and the results from samples prepared by local dye plants in traditional ways justifies the preparation of reference dyed samples to study dyed samples produced in textile workshops. Besides, the analytical result demonstrates the suitability of the current analytical protocol for dyed cotton samples. Distinctive dyes used by Li include *jia lan dian*, chestnut bark, chestnut shell and jambul, which probably depend on the local availability. The detection of these dyes on historical textiles would help the identification their production places.

Since the fabrics of the Li group are mainly cotton, special dyeing methods are used. Unlike silk and wool, which are composed of proteins and have acidic and alkaline groups that easily connect with dyes, cotton fibres are cellulose. The hydroxyl groups of cellulose mainly connect with dyes by hydrogen bonds. The dye fixing tree bark helps cotton dyeing by enhancing the connection between cotton fibres and dyes with the abundant tannin it contains. The paste-dyeing method of turmeric is suitable for cotton dyeing because cotton fibres are usually more coarse and stronger than silk, the main fibre used for high-status textiles in ancient China. In addition, the method of jambul dyeing for black with black mud and mango kernels makes good use of local materials.

3.4.3.8 Summary of the study of dyes and dyed cotton from the Li group

This section unprecedentedly explored dyes and dyeing techniques of the Li group in Hainan Province. Some dyes used by Li are similar to dyes used in the textile centres in China during the Ming and Qing Dynasties and some are different, depending on local availability. The chemical compositions of the shared dyes are similar to those of standard dyes to a large extent, which justifies the preparation of reference dyed samples to study dyed samples produced in textile workshops and demonstrates the suitability of the current analytical protocol for dyed cotton samples (further discussed in section 3.4.4). Some special dyeing methods are used for cotton dyeing and they also depend on local availability.

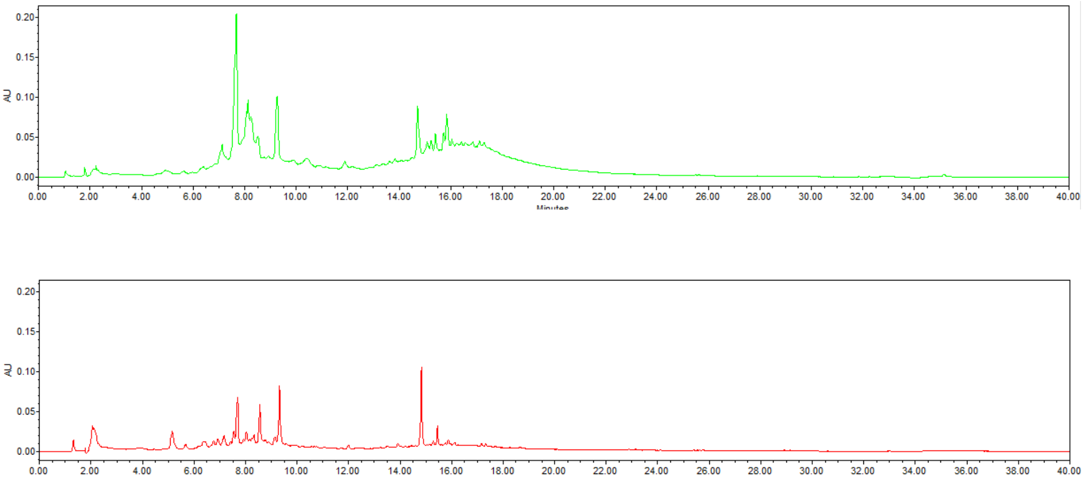
3.4.4 Evaluation of the chemical analytical protocol

The analytical protocol including the extraction method and the gradient elution system used in this chapter proves to be suitable for the analysis of the dyes commonly used in ancient China.

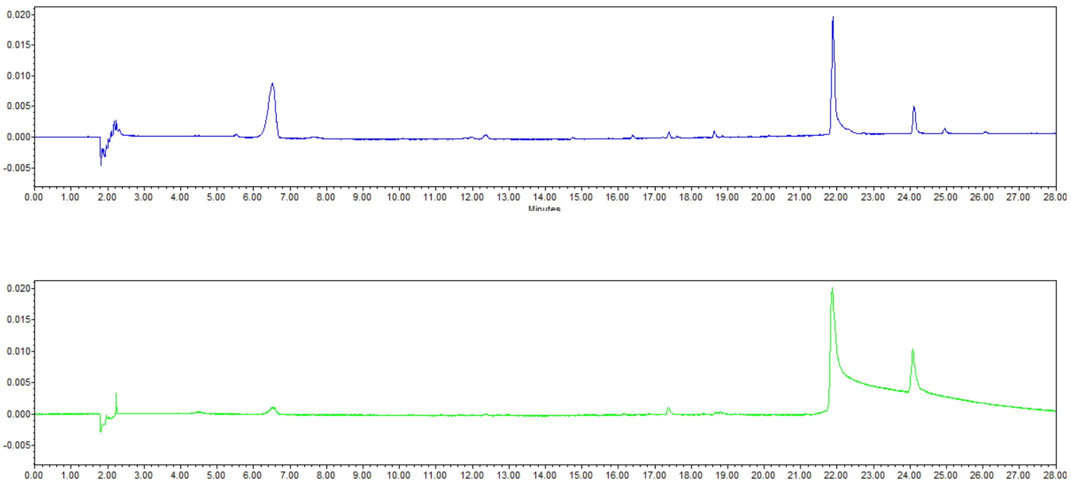
Extraction method

The two-step extraction protocol using DMSO-OA functions well with all the dyes analysed in this chapter in successfully extracting the major dye components of these dyes. This is a universal extraction method for all types of natural dyes: DMSO dissolves all the direct dyes and vat dyes (like indigo), and oxalic acid help dissolve mordant dyes by destructing the complexes formed among the dye components, mordants and fabrics. Sugar bonds are preserved, which may be helpful for further investigation into the dyes.

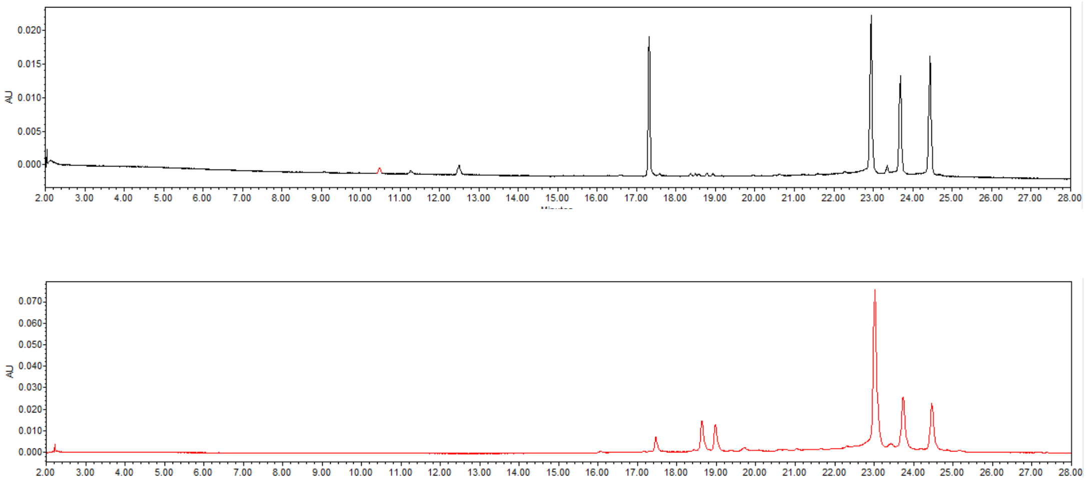
Besides, the successful application of this extraction method to dyed samples of the Li group proves its suitability for not only dyed silk samples but also dyed cotton samples. By comparing the analytical results of sappanwood extracts sourced respectively from reference dyed silk and dyed cotton of the Li group (Figure 3. 48a), it can be seen that they share main characteristic peaks, though minor peaks may vary. Similar results were obtained when comparing the analytical results of indigo and turmeric from the two different sources (Figure 3. 48b and c).



(a) sappanwood 295nm



(b) indigo 425nm



(c) turmeric: reference, cotton without plant ash, 425nm

Figure 3. 48 Comparison of the UHPLC-PDA chromatograms of the same dyes sourced respectively from reference dyed silk and dyed cotton of the Li group

Gradient elution system

The identification of dye sources depends on the detection of individual dye components. Therefore dye components need to elute well and be well separated, which is determined by the gradient program used, the acidity of the mobile phase and the choice of basic elution solvents.

First, most of the dye components elute well in the current system involving methanol/water/formic acid as mobile phase and sharp peaks are obtained, except for brasilein, munjistin, pseudopurpurin, indigotin and berberine. Braselein shows as a broad peak from 6.5 to 10.5 min in the chromatogram of the sappanwood extract. Munjistin and pseudopurpurin, both acids, were not found in the chromatogram of the munjeet extract. The reason may be the acidity of the mobile phase is very close to the pKa, an acid-ionisation constant, of these components. In this way the components are present in both forms of ion and non-ionised molecule and an ion-molecule equilibrium is obtained. This dynamic equilibrium affects the elution of the components. It is recommended that the acidity of the mobile phase should be at least 2 units away from the pKa of the analytes, but it is very difficult to decide the acidity of the mobile phase that suits all the dye components because the pKa of the multitude of dye components are not available and they vary from each other. The problem could be solved by using other characteristic components to identify the dyes such as 6-hydroxyrubiadin and its equivalents for munjeet and colourless Nowik type A components and type C component for the identification of sappanwood. In addition, indigotin and berberine, the main dye component for indigo and Amur cork tree respectively, show peak tailing, resulting from the strong interaction of the components with ionised residual silanol groups on the silica matrix through polar interactions, but the peak shapes do not affect the identification of the dyes. Overall, the current system conditions are relatively suitable for the detection of the dye compositions of the common dyes.

Second, all the characteristic components of the twelve common dyes are separated well in the current system. The only exception is that ellagic acid and rutin co-eluted at around 13.6 min and they have similar UV-vis spectra, but this can be overcome by careful integration of the pair of co-eluting peaks. Some components of the less common dyes are not well separated. Adjustments to gradient elution system are needed if further investigation on their chemical compositions is carried out. Additionally, as presented above, UHPLC shows significant advantage over HPLC in that several sets of similar components not separated well by HPLC are well separated in the current system.

3.4.5 Evaluation of the certainty of dye identification based on characteristic components

The research above revealed the chemical profiles of various Chinese dyes, especially their characteristic dye components. This section further discusses these characteristic dye components and the confidence level of the identification of dye sources.

First, both coloured and colourless components carry information on dyes. Apart from colourants, dye sources are composed of a series of components including cell constituents and metabolites, such as polysaccharide, protein, enzyme, starches, sugars, gums, mucilage and resin[285]. In the process of dyeing, dyes are extracted from dye sources and then attracted to the polymers in the fabric fibres. Usually it is the identification of markers of dye components that enables the knowledge of dye sources. Sometimes other components are also extracted from the dye source and then dyed on fabrics and in some cases these colourless components can be used as markers as well, such as safflower Ct components in safflower and Nowik type Components in sappanwood.[286]

Second, dye composition depends not only on the original composition but also on processing conditions. On the one hand, the original dye composition can be affected by the species, varieties, production place, environment, collection time, *etc*. On the other hand, dye components in a sample change in processing processes including pre-processing for dyeing, dye extraction, dyeing, preservation, and sample preparation for chemical analysis, which can all result in differences between dye components detected in analytical results and those present in original dye sources. Usually the variation in composition of a certain dye is relatively small and does not affect the identification of the dye source. Additionally, it is possible to make use of this variation to investigate further into the dye, such as on the production place of munjeet and the pre-processing method of

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[285] Guojun Xu, *Zhongguo Yaocaixue* [Chinese medicine study] (Beijing: Zhongguo yiyao keji chubanshe, 1996), 12.

[286] Wouters, Grzywacz, and Claro, "Markers for Identification of Faded Safflower (Carthamus Tinctorius L.) Colorants by HPLC-PDA-MS Ancient Fibres, Pigments, Paints and Cosmetics Derived from Antique Recipes," 186-203.

pagoda bud.[287]

Third, the numbers and compositions of the major characteristic components of the reference dyes vary. Most dyes contain a series of similar components – usually of the same group, with slight differences in attached moieties. Sometimes the amounts of the main components of the dye are similar, such as anthraquinones in munjeet, flavonoids in pagoda bud, cucuminoids in turmeric, crocins in gardenia and gallo-tannins in gallnut; sometimes the amount of one component is dominant, like berberine in Amur cork tree. For some dyes, only one component is detected as the major component and small amounts of other components are present, like sulfuretin as the main component of smoketree and indigotin as the main component of indigo.

Fourth, it is necessary to confirm what range of plants the identified group of characteristic components indicates because most characteristic components are present in more than one plant species. An extensive search was undertaken from an encyclopaedia of Chinese medicine *Zhonghua bencao* (Chinese herbal medicine) for the plants containing the characteristic components of reference dyes and the results are presented in Table 3. 18.

Table 3. 18 Dye components of the common dyes and their corresponding plant sources

Dye	**Main dye component(s)**	**Dye sources containing the dye component(s)**
safflower	carthamin	safflower only
sappanwood	brasilein	sappanwood only
smoketree	sulfuretin and fisetin	Only smoketree contains both the components.
gardenia	crocetin and crocins	gardenia and saffron
turmeric	curcumin, desmethoxycurcumin and bisdesmethoxycurcumin	all present in several *Curcuma* species

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[287] Sujing Wang and Shiqing Chang, *Zhongyao Sepu Zhiwen Tupu Jishu Yu Yingyong* [the Technology and Applications for the HPLC Fingerprint of Chinese Medicines] (Zhengzhou: Zhengzhou daxue chubanshe, 2008), 59; Zhang *et al.*, "The Role of Glycosides in the Light-Stabilization of 3-Hydroxyflavone (Flavonol) Dyes as Revealed by HPLC," 327-334.

Table 3. 18 Dye components of the common dyes and their corresponding plant sources (continued)

munjeet	6-hydroxyrubiadin and its derivatives, purpurin, lucidin-3-O-primeveroside, rubiadin	6-hydroxyrubiadin has been only reported to be present in *Rubia cordifolia* and *Rubia akane.*[288]
gromwell	shikonin and its derivatives	Shikonin and its enantiomer alkannin are present in *Lithospermum spp.,Arnebia spp., Onosma spp. and Lappula myosotis V. Wolf*, all of Boraginaceae.
pagoda bud	rutin, isorhamnetin-3-rutinoside, quercetin, isorhamnetin and kaempferol	These flavonoids are present in hundreds of plants of different families.
Amur cork tree	berberine	Berberine is present in dozens of plants from several different families, mainly *Berberidaceae, Menispermaceae* and *Papaveraceae.*
indigo	indigotin, indirubin and isatin	present in plant sources to prepare indigo
gallnut	gallic acid monomer, digalloyl glucose, trigalloyl glucose, tetragalloyl glucose, pentagalloyl glucose, hexagalloyl glucose and heptagalloyl glucose	Gallic acid monomer is present in about a hundred plants from several different families. Specific gallotannins are present in limited dye plants, *e.g.* hexagalloyl glucose is recorded to be only found in gallnut.
acorn cup	ellagic acid	Ellagic acid is present in dozens of plants from several different families. Specific ellagitannins are present in limited dye plants.

It can be seen that the presence of particular dye components may not necessarily indicate

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[288] Itokawa, Mihara, and Takeya, "Studies on a novel anthraquinone and its glycosides isolated from Rubia cordifolia and R. akane."

specific dye sources and further evidence is needed to confirm dye sources.

- For **safflower, sappanwood and smoketree**, the identification of their main components is enough to provenance the original dye source.

- **Gardenia and saffron** contain crocetin and crocins as main colourants but the different relative amounts of these components may help identify the dye sources.

- The main components of **turmeric, munjeet and gromwell** are present in several species of the same family:

    - **Turmeric**: although several *Curcuma species* contain curcumin, desmethoxycurcumin and bisdesmethoxycurcumin, only turmeric (*Curcuma longa*) contains large amounts of these colourants (section 2.3.6), therefore confirming the use of turmeric for dyeing among these species.

    - **Munjeet**, 6-hydroxyrubiadin has been reported to be present in *Rubia cordifolia* and *Rubia akane* therefore further evidence of other characteristic components or relative amounts is needed for more specific identification.[289]

    - **Gromwell**: by botanical provenance (cross reference section 2.3.1) it was found that *Lithospermum spp.* and *Onosma spp.* of *Boraginaceae* are the main source and research of characteristic minor components or ratio between certain components would help more accurate identification of the dye source.

- The main components of **Amur cork tree and pagoda bud**, respectively of the groups of alkaloid and flavonoid, are present in a large amount of plants of different families, but the frequent records of Amur cork tree and pagoda bud as dye sources in historical

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[289] Mouri and Laursen, "Identification of anthraquinone markers for distinguishing Rubia species in madder-dyed textiles by HPLC"; Itokawa, Mihara, and Takeya, "Studies on a novel anthraquinone and its glycosides isolated from Rubia cordifolia and R. akane."

dye recipes help confirm these two dye sources. The relative amounts of the components are also helpful.[290]

- **Indigo**: indigotin, indirubin and isatin are usually present in indigo made from several plant sources because of the fermentation process of indigo.[291] Further evidence on minor components is needed to identify specific dye sources of indigo.

- **Gallic acid and ellagic acid** are present in large amounts of plant and insect sources, but specific gallotannin and ellagitannin exist in limited sources, whose detection helps confirm detailed dye source. Likewise, whether it is sufficient to identify dye source by some colourless characteristic components when dye components degrade needs further investigation on the distribution of these characteristic components among plants.

Moreover, for the less common dyes, though their dye components are similar or the same with those of the common dyes, it is still possible to distinguish the dyes in their unaged conditions by accurate identification of the main components and the comparison of the relative amounts of dye components. For example, berberine is present in both Amur cork tree and in Chinese goldthread, but in Amur cork tree it is the only main component while in Chinese goldthread several other major alkaloids are also present. Another pair of example is gardenia and in saffron: the main dye components of gardenia include *trans*-4-GG, *trans*-3-Gg, *cis*-4-GG and *trans*-2-G, while the main dye components of saffron include *trans*-4-GG, *trans*-4-ng, *trans*-3-Gg and *cis*-4-GG. Therefore *trans*-2-G as a major component could be a marker for gardenia and *trans*-4-ng as a major component could be a marker for saffron. It is recommended to identify dye sources by both characteristic components and the overall composition of dyes.

In short, for some dyes the identification of one or several characteristic components and

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[290] Zhang *et al.*, "Preliminary studies toward identification of sources of protoberberine alkaloids used as yellow dyes in Asian objects of historical interest."

[291] Cardon, 337-339.

knowledge of their relative amounts are enough to confirm the dye sources, but for the other dyes this information indicates a group of dye sources or more. Nevertheless, the main dyes should be those frequently recorded in historical manuscripts. Some plants containing certain dye components are not necessarily used as dyes because the amount of dyes is relatively low or the plants are for other uses like for medicine use. Therefore, in historical and archaeological samples, if the main dye component is detected but the minor components are not detected because of small amount of samples or the degradation of the dye, like only the dye component sulfuretin is detected in a yellow sample, there is a fair possibility that the dye source is smoketree, judged from historical dye recipes.

In summary, the provenance of specific dye sources needs not only the detection of characteristic components but also further evidence of relative amounts of the components, records of dyes in historical manuscripts and the botanical provenance of the historical dyes.

3.5 Conclusions

This chapter applied UHPLC-PDA and UHPLC-PDA-MS for the first time to analyse the chemical composition of historical Chinese dyes. Characteristic components of these dyes were identified by UHPLC-PDA-ESI-MS analysis. The polymerisation pattern of gallic acids, the isomerisation of gallotannins in gallnut dye, the chemical composition of acorn cup on dyed silk and the esterification of crocin in gardenia dye were clarified for the first time. 6-hydroxyrubiadin and its glycosides were first reported to be present in *Rubia cordifolia* dyed sample extracts. UHPLC showed great advantage in enhancing the separation effect of similar components and in increasing detection limit, allowing better identification of these components, such as the main dye components of pagoda bud and turmeric, and the trace amount of crocetin esters present in gardenia dyed sample extracts. Ten less common dyes were characterised and their dye component groups were found to be similar to those of the common dyes, but their main components and the relative amounts of the main components vary. Lastly, the study of dyes of the Li group showed that dyes of the same kind share similar chemical profiles with the reference samples. Some special dyes and dyeing methods are used by the Li group for cotton dyeing and they also depend on local availability.

The analytical protocol including the extraction method DMSO-OA and the gradient elution programme applied enabled most of the significant dye components for identification to be extracted (from both silk and cotton samples), well-eluted and separated. Further investigation on the identification of dye sources by characteristic component showed that the presence of particular dye components may not necessarily indicate specific dye sources and further evidence of relative amounts of the components, records of dyes in historical manuscripts and the botanical provenance of the historical dyes would help confirm the dye sources.

Through the research in this chapter, a database for the chemical composition of reference Chinese dyes was established and the understanding of the chemical composition of Chinese dyes was improved. The next chapter describes and discusses the application of the results to the chemical and historical investigations in the context of dyes used for Chinese historical and archaeological textiles.

4 Chemical and Historical Analysis of Historical and Archaeological Dyes

4.1 Introduction

Over the past decade or so, increasing research on historical and archaeological Chinese textiles by chemical analysis has been undertaken on the identification of historical dyes, the distinction of dye plant species and the pre-processing of dyes.[292] However, the significance of the finding was disjointed and unclear because there was no comprehensive research of the dyes used for Chinese textiles and no broad picture of dyeing in ancient China. A significant factor impeding this had been that the relationship between dyes identified so far on a relatively small sample set of historical and archaeological textiles had neither been placed in the context of Chinese dye history nor unpinned by a systematic study of characteristic chemical profiles for robust identification by scientific investigation. By undertaking the research described and discussed in Chapters 1 to 3, evidence-based historically relevant analytical references were created to enable the necessary systematic scientific analysis investigation of ancient Chinese dyed textiles to provide primary material evidence for the dyes that really were used and to interpret the results within a framework of historical and cultural significance. This chapter undertakes the identification of dye sources and proposed dyeing methods of 216 historical and archaeological samples from 63 pieces of provenanced costume and textiles of the Ming and Qing Dynasties, mostly of high-status, from 11 collections and archaeological institutes by ultra-high performance liquid chromatography with photodiode array

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[292] Estrella Sanz Rodríguez *et al.*, "Characterization of Natural and Synthetic Dyes Employed in the Manufacture of Chinese Garment Pieces by LC-DAD and LC-DAD-QTOF"; Bai, "Chaoshi Muzang Huanjing Zhong Chutu Sizhipin De Zhiwu Ranliao Jianding Jishu Yanjiu"; Jian Liu *et al.*, "Identification of Ancient Textiles from Yingpan, Xinjiang, by Multiple Analytical Techniques," *Journal of Archaeological Science* 38, no.7 (2011): 1763-1770; Mouri and Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC," 105-113; Zhang *et al.*, "The Role of Glycosides in the Light-Stabilization of 3-Hydroxyflavone (Flavonol) Dyes as Revealed by HPLC," 327-334.

detection (UHPLC-PDA) and Scanning Electron Microscopy (SEM) analysis. A semi-quantitative analysis is undertaken[293] and the analytical results are compared with research results on historical dye recipes (Chapter 1). The combined results are used to improve the understanding of the costume and textiles. The exchange of dyeing techniques between China and Europe during this time period is explored.

4.2 Materials and methods

4.2.1 Samples

Altogether 216 historical and archaeological samples from 63 pieces of provenanced costume and textiles of the Ming and Qing Dynasties were collected from 11 collections mainly in the UK, China and Ireland (Figure 4. 1).

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[293] A semi-quantitative method was applied to the analysis of dye identification results obtained in this chapter to investigate which dyes and dyeing methods are relatively dominant and to compare with corresponding research results from historical dye recipes presented in Chapter 1. In this research it was hardly possible to conduct quantitative research because it was difficult to completely ensure the representativeness and average distribution of the historical and archaeological samples in terms of shade, time period, rank of owner *etc.*, though these variants were major factors taken into consideration for sampling. For example, nearly half of the textiles as the sources of historical samples were dragon robes, or court robes with dragons, which could result from the interests of collectors. This proportion is probably significantly higher than the proportion of these kinds of robes among the high-status costume and textiles actually used.

(a)

(b)

Figure 4. 1 A map of China (a) and a map of the UK and Ireland showing the collections and institutes from where the sampes were taken.

Images courtesy of Google Maps.

Historical samples

Table 4. 1 presents details and images for the 39 pieces of historical costume and textiles for sampling. They cover all periods of the Qing Dynasty (8 pieces from the early Qing Dynasty, 10 from the mid Qing Dynasty, 18 from the late Qing Dynasty and a lantern with unknown exact date). In contrast, a limited 2 items from the Ming Dynasty were accessed due to the small number of textiles that have survived. Most of these textiles are likely to have belonged to imperial family members or officials of different grades. Among these textiles, 23 pieces are dragon robes or court robes with dragon patterns. Some other pieces of costume and textiles are also of good quality, indicating high-status. Three pieces are not of high-status, including a dancer's skirt, a robe for a Buddha sculpture and a theatre costume.

Table 4. 1 List of collections (arranged in alphabetical order) and historical costume and textiles for sampling (arranged in the order of sampling)

Reference code	**Title of textile**	**Accession number**	**Date**	**Description**	**Photo**	**Number of samples**
Burrell Collection/Glasgow Museums (abbreviated as BC for sample codes) Altogether 9 samples were taken from 1 piece of silk panel of the Ming Dynasty. The total amount of samples counted included duplicates and undyed reference samples, same as below.						
BC	Panel of silk	BC: 30.2	Ming Dynasty	Silk panel woven with a dragon and cloud pattern against a golden yellow ground.		9

Table 4.1 List of collections and historical costume and textiles for sampling (continued)

Chester Beatty Library (CBL) Altogether 2 samples were taken from 1 piece of dragon robe of the Qing Dynasty.						
CBL	Imperial yellow dragon robe	CBL. 1051	mid-Qing Dynasty	Silk embroidered dragon robe with a yellow ground.		2
Jacqueline Simcox Ltd (JSL) Altogether 27 samples were taken from 6 pieces of textiles, among which 1 piece is of the Ming Dynasty and the other 5 pieces are of the Qing Dynasty.						
JSL-1	Dragon robe	—	Yongzheng period, 1723-1735	Silk brocade imperial robe. (Yellow sleeve inserts were added later.)		4
JSL-2	Dragon robe	—	mid Qianlong period , 1736-1795	Silk embroidered 12-symbol emperor's robe. (sleeve ends and neck edging altered for wear in Tibet)		5
JSL-3	Brown costume cloth	—	late Qing. Guangxu period, 1871-1908	Embroidered silk 'Empress Dowager' pattern birthday robe.		4
JSL-4	Blue court robe	—	late Qing. Tongzhi period, 1862-1874	Embroidered blue court robe with five-clawed dragons.		6

Table 4.1 List of collections and historical costume and textiles for sampling (continued)

JSL-5	Sleeve band	—	late Guangxu period, 1871-1908	A pair of embroidered silk sleeve bands (edges of sleeves from a short jacket) with woven stripes and embroidered patterns.		2
JSL-6	*Dou niu* court robe	—	late Ming. Wanli period, 1573-1619	Embroidered, front opening court robe for high-ranking court official. Four clawed dragons. Altered from two pieces of textiles.		3
National Museums Scotland (NMS) Altogether 53 samples were taken from 13 pieces of costumes of the Qing Dynasty.						
NMS-1	Dragon robe	A.1971.675	late 18th century	Man's embroidered silk dragon robe with a brown background for official court use.		6
NMS-2	Official robe panels	A.1954.338	late 18th century	Trapezoidal shaped part of official robe woven showing different symbols and a five-clawed dragon in pursuit of the magic jewel.		7
NMS-3	Dragon robe	A.1921.1192	19th century	Three-quarter length satin robe with short wide sleeves.		2

Table 4.1 List of collections and historical costume and textiles for sampling (continued)

NMS-4	Dragon robe	K.2001.16	early 19th century	Silk dragon robe with a brown background.		1
NMS-5	Woman's skirt	A.1982.822	late 19th - early 20th century	Woman's skirt of light yellow silk satin woven in a floral pattern and embroidered in white and blue silks with panels of peonies, butterflies and narcissus.		5
NMS-6	Cloak	A.212.94.J	19th century	Magistrate's cloak of red woollen cloth embroidered in coloured silks and gold thread with dragon roundels.	 ©National Museums Scotland	1
NMS-7	Dancer's skirt	A.1929.70	19th century	Dancer's skirt consisting of nine claret-coloured silk strips with embroidered silk strips and bells attached.		5
NMS-8	Women's jacket	A.1979.201	1896	Women's silk jacket embroidered in silks and showing a design of butterflies and bats among flowers with a blue silk lining.		8

Table 4.1 List of collections and historical costume and textiles for sampling (continued)

NMS-9	Robe	A.1954.336	19th century	Yellow satin damask robe showing a design of five-clawed dragons pursuing a magic jewel, possibly an imperial chang fu or informal coat.		2
NMS-10	Women's skirt	A.1966.511	19th century	Woman's red silk damask skirt with ribbon applique and gold couching with designs showing Taoist motifs and butterflies.		3
NMS-11	Women's skirt	A.1964.567	late 19th century	Women's gold satin skirt embroidered in coloured silks.		4
NMS-12	Women's robe	A.1959.607	late 19th - 20th century	Short blue silk satin robe embroidered with coloured silks with yellow damask embroidered sleeve bands.		5
NMS-13	Women's robe	A.1961.545	19th - 20th century	Women's red gauze robe with brocaded roundels of silver and gold lotus flowers and leaves with black gauze brocaded borders.		4

Table 4.1 List of collections and historical costume and textiles for sampling (continued)

Private collection (PC) Altogether 9 samples were taken from 3 pieces of dragon badges of the Qing Dynasty.						
PC-1	Dragon badge	—	early Kangxi period (Kangxi period: 1661-1722)	Multi-coloured dragon badge with a yellow background.		3
PC-2	Dragon badge	—	Kangxi period 1661-1722	Multi-coloured dragon badge with a blue background.		1
PC-3	Dragon badge	—	late Qianlong period 1736-1795	Multi-coloured dragon badge with a brown background.		5
The Palace Museum (TPM) Altogether 8 samples were taken from 4 pieces of court costume and textiles of the Qing Dynasty.						
TPM -1	Dragon robe for a Buddha sculpture		late Qing Dynasty	Dragon robe for a Buddha sculpture.		3
TPM -2	Plaque		1679	Plaque as a gift of Kangxi to the empress dowager with the characters *wan shou wu jiang* (long life).		2

Table 4.1 List of collections and historical costume and textiles for sampling (continued)

TPM-3	*Mian chang* scroll		Qianlong period, 1736-1795	Scroll with the character *mian* (long).		2
TPM-4	Palace lantern		Qing Dynasty	Yellow hanging ear of palace lanterns.		2
Victoria and Albert Museum (V&A) Altogether 53 samples were taken from 11 pieces of costumes of the Qing Dynasty.						
V&A-1	Robe	T.91-1928	1650-1700	Embroidered robe made for use in Daoist religious ceremonies.		1
V&A-2	Robe of red silk damask	T.751-1950	17th century	Robe of red silk damask with short brocade sleeves and collar.		7
V&A-3	Sleeveless jacket for an emperor's military robe	T.185-1948	1662-1722	Sleeveless jacket for an emperor's military robe.		5
V&A-4	Robe	T.190-1948	possibly 1662-1722	Twelve-symbol dragon robe of silk tapestry (*kesi*).		3

Table 4.1 List of collections and historical costume and textiles for sampling (continued)

V&A-5	Robe	T.184-1948	late 17th century-18th century	Red embroidered women's robe, the earliest non-ecclesiastical Chinese garment for a woman in the Museum.		5
V&A-6	Woman's jacket of silk tapestry	T.210-1948	1736-1795	Woman's jacket of silk tapestry (*kesi*).		9
V&A-7	Jacket	T.9-1923	19th century	Child's dragon robe of red silk satin, embroidered with coloured silks and gold thread.		4
V&A-8	Robe	T.45-1933	1880-1930	Theatre costume with a red background.		1
V&A-9	Robe	T.43-1952	1770-1820 (embroidered) 1900-1911 (tailored)	Embroidered female robe as Empress's *chaopao* (ceremonial robe) or *jifu* (formal robe).		3
V&A-10	Robe	T.187-1948	early 18th century	Front-fastening women's robe of weft-pattern woven silk.		12
V&A-11	Emperor's court robe	T.753-1950	1875-1908	Formal court robe for an emperor known as *chaopao*.		3

Images in this table respectively ©Burrell Collection/Glasgow Museums, ©Chester Beatty Library, ©Jacqueline Simcox Ltd, ©Private collection ©The Palace Museum, and ©The Victoria and Albert Museum. Permission to reproduce the images of the textiles collected at the National Museums Scotland has been granted by National Museums Scotland.

Archaeological textile samples

In addition to historical dye samples, archaeological dye samples were collected and analysed. Archaeological textiles in tombs are sometimes better provenanced in terms of owners and dates when accompanied epitaphs are present or there are historical manuscripts recording such information. There are altogether 54 archaeological samples from 24 pieces and groups of costume and textiles from four tombs of imperial members and officials of the Ming and Qing Dynasties (details presented in Table 4. 2). The archaeological textiles where the samples were taken are also of a variety of types. Besides official robes of the same and similar kind of the history costumes, there are also underpants, accessories such as a hat, purse and boots, and other types of textiles like quilt bags. Detailed information on the archaeological sites and the archaeological textiles for sampling are presented in section 4.3.4 for archaeological dyes.

Table 4. 2 Collections and institutes for archaeological samples

Full name of collection or archaeological institute	**Archaeological site**	**Abbreviation for textile and sample reference code**	**Number of pieces**	**Number of samples**
Cultural Heritage Institute of Shijingshan District	Tomb of a first grade military official of the mid-Qing Dynasty.	SJS	9	18
Yinan County Museum	Tomb of a sixth grade civil official of the mid-Qing Dynasty. Located in Heyang, Yinan County.	HY	2	2
Shandong Museum	The tomb of Zhu Tan (朱檀) (1370-1390).	ZT	1	5
Shaanxi Provincial Institute of Archaeology	The clan tomb of Zhu Bingju (朱秉橘), 16th century.	ZBJ	12 groups of textiles	29

4.2.2 Sampling

Historical and archaeological dyed samples were carefully selected and taken based on primary investigations into the colour of the textiles and with the agreement of the textile conservator and the curator, or the owner in the case of private collections. Samples from the clan tomb of Zhu Bingju were taken and provided by textile conservators Karen Horton and Lu Zhiyong. Major factors taken into consideration included the time period, type of the textile, and the colour and use of the thread (*e.g.* threads from ground, lining, patterns, metal thread cores and stitching threads).[294] Faded samples were also collected to compare

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[294] In terms of production place, though there were distinct geographical differences in handicrafts, the production place of textiles is usually not clear. Most of the textiles studied are from the 'central plain area', judged from their styles, corresponding with the origin of the historical dye recipes studied in

with corresponding unfaded samples from the same textile artefact to study the change of chemical composition from fading (presented in Chapter 5). Samples were taken from areas where there were loose ends of threads, such as the reverse side, edges or damaged areas, but usually not from obvious areas of recent repair, which were visually assessed together with the curator and the textile conservator. Sampling for dye analysis involved removing a 5 – 10 mm length of loose thread per colour of interest. The sample was cut with fine springbow scissors and removed with fine-point tweezers for minimal invasion of the textile. The position from which each sample was taken was recorded by photography, and by measurement if possible, following an established research protocol.[295] Samples were wrapped individually in a piece of acid-free paper that was labelled in pencil with a unique sample code, then placed in a polythene laboratory sample bag and stored in a sample box, away from light. Relevant information about the samples including accession number, colour, use of threads, and sample location is recorded in a notebook when sampling and then afterwards entered into Excel and Access databases (Microsoft Inc.) of sample information.

4.2.3 Microscope and SEM analyses

All the samples were carefully observed under a Dino-Lite Premier Digital Microscope at approximately 200 × magnification and a digital image captured before chemical analysis. This was to detect any signs of degradation, contamination and any other special phenomenon like uneven dyeing. Contamination of fibres of other colours was removed.

Based on observation by microscope, SEM analysis was undertaken on selected samples to identify some unknown constituents of the samples, especially contaminations and different materials involved for metal threads, and to provide guidance for sample

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Chapter 1. Jonathan Hay, *Sensuous Surfaces: The Decorative Object in Early Modern China* (London: Reaktion Books, 2010), 42-51; Fan and Jin, 235.

[295] Anita Quye *et al.*, *'Wrought in Gold and Silk' : Preserving the Art of Historic Tapestries* (Edinburgh: NMS Enterprises Limited, 2009).

preparation. Altogether four samples were analysed by SEM including two historical samples (samples V&A-5-3 and V&A-2-1) and two archaeological samples (samples ZBJ-1-7 and ZBJ-1-10). Representative spots of contamination and metal threads were chosen for analysis. SEM analysis was undertaken by Peter Chung at The Imaging Spectroscopy and Analysis Centre (ISAAC) in the School of Geographical and Earth Sciences at the University of Glasgow. A Carl Zeiss Sigma Variable Pressure Analytical SEM with Oxford Microanalysis was used. Samples were stuck on carbon tabs and placed in a sample chamber. The chamber was at 45 Pascal. Three different detectors were applied for the investigations of surface morphology and elemental distribution and composition, including secondary electron, electron backscatter diffraction and energy dispersive X-ray emission. An acceleration voltage of 20 kV was used for the secondary electron and electron backscatter diffraction detectors. The acceleration voltage of the dispersive X-ray detector was 0-20 kV depending on the intensity of signal needed. Usually secondary electron analysis was undertaken on a chosen area to learn about its surface morphology first, followed by the electron backscatter diffraction analysis of this area to investigate its elemental distribution. After that, X-ray emission analysis was carried out on individual spots or small areas of interest to detect their elemental compositions.

4.2.4 UHPLC-PDA analysis

Three extraction methods were applied for sample preparation for UHPLC-PDA analysis.

<u>Extraction method 1</u>

Compared with archaeological samples, dyes from historical samples are relatively better preserved and are of higher concentration. The sample preparation protocol using DMSO-OA as previously described in section 3.3.2.1 was applied to all the historical samples.

Extraction method 2

For most of the archaeological samples, a two-step extraction method of DMSO-HCl was used to aggregate the dye components. Its difference from the DMSO-OA method is that in the second step an aliquot of 75 µl of hydrochloric acid solution, composed of a mixture of 37% hydrochloric acid/methanol/water (2:1:1 v/v/v), was added to the residual and heated at 100 ℃ for 10 mins. The hydrolate was evaporated to dryness and then reconstituted using the first DMSO fraction. The reconstituted hydrolate was transferred back to the vial storing the first DMSO fraction, centrifuged by an Eppendorf Minispin microcentrifuge at 14300 rpm for 15 mins and the supernatant was filtered.

Extraction method 3

Faced with low detection rate for the archaeological samples from the clan tomb of Zhu Bingju compared with the detection rate of samples from the other three archaeological sites, samples ZBJ-2-8 to 19 were extracted by hydrochloric acid solution directly to further aggregate the dye components. An aliquot of 75 µl of hydrochloric acid solution, composed of a mixture of 37% hydrochloric acid/methanol/water (2:1:1 v/v/v) was added to the sample. The sample was heated for 10 mins at 100 ℃, evaporated to dryness, reconstituted using 50 µl DMSO, centrifuged as above and then the supernatant filtered for analysis.

In terms of data analysis, the protocol for reference samples established in Chapter 3 was further developed to ensure that all major dye components were detected. For each sample, the UHPLC-PDA chromatogram was extracted respectively at 254, 350, 430 and 515 nm and all the peaks of no less than 5 times the height of the noise, which was determined by the amplitude of the baseline, were highlighted, though only the wavelength that best highlights all major dye components was used to present final results. Identifications were made predominantly by comparison of the results to the chromatographic and spectral library for reference dyed yarn, fabrics and pure dye components analysed with the

Centre's UHPLC-PDA instrument and associated software. The references of natural dyes for the library came from two main sources. One was dyed silk prepared in the Centre's laboratory with known species of natural dyes for common and less common Chinese dyes, acquired from medicine shops and botanical gardens (Chapter 3), and the other was dyed wool with significant Western dyes of the same period, sourced from commercial suppliers (Kremer), botanical gardens and experienced researchers of historical dyes: madder (*Rubia tinctorum* L.), brazilwood (*Caesalpinia echinata* Lam.), red sandalwood (*Pterocarpus santalinus* L.), logwood (*Haematoxylum campechianum* L.), dyer's greenweed (*Genista tinctoria* L.), weld (*Reseda luteola* L.), old fustic (*Maclura tinctoria* (L.) D.Don ex Steud.), and three insect dyes, lac (*Kerria lacca* (Kerr, 1782)), American cochineal (*Dactylopius coccus* (O. Costa 1835)) and kermes (*Kermes vermilio* (Planchon, 1864)).[296] Meanwhile, published data of early synthetic dyes by HPLC-PDA-MS analysis from the Smithsonian's Helmut Schweppe Collection and an analytical library for synthetic dye reference samples were used for the identification of synthetic dyes.[297] The reference sources for early synthetic dyes in the analytical library were yarns dyed with named synthetic dyes and published in a British dyeing manual from 1882 and 1893.[298] Reference data for early synthetic dyes included a library of the analytical results of dyes from *The English dyer, with instructions on how to dye* - a book of dye samples published in 1882. In addition, *Colour Index* (CI) Volumes 4 and 5 were consulted, where manufactured early synthetic dyes are recorded with information on their physical forms, dates of first synthesis, manufacturers, products available on the market and commercial names.[299]

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[296] Hofenk de Graaff, Roelofs, and van Bommel.

[297] Cátia Susana da Costa Nogueira Souto, "Analysis of Early Synthetic Dyes with HPLC-DAD-MS: An Important Database for Analysis of Colorants Used in Cultural Heritage" (Master's dissertation, Universidade Nova de Lisboa, 2010); Maarten R van Bommel *et al.*, "High-Performance Liquid Chromatography and Non-Destructive Three-Dimensional Fluorescence Analysis of Early Synthetic Dyes," *Journal of Chromatography A* 1157, no.1 (2007): 260-272.

[298] David Smith, *The English Dyer: With Instructions Showing How to Dye* (Manchester: Palmer and Howe, 1882); Edmund Knecht, Christopher Rawson, and Richard Loewenthal, *A Manual of Dyeing: For the Use of Practical Dyers, Manufacturers, Students, and All Interested in the Art of Dyeing* (London: C. Griffin & Co., 1893).

[299] Society of Dyers and Colourists and American Association of Textile Chemists and Colorists, *Colour Index. Volume 4. Chemical Constitutions. Intermediate Compounds*, 3rd ed., (Bradford, 1971), 4380; Society of Dyers and Colourists and American Association of Textile Chemists and Colorists, *Colour Index. Volume 5. Chemical Names - Generic Index, Alphabetic Index* (Bradford, 1976), 5082.

4.3 Results

In the 154 dyed historical samples from 39 pieces of historical textiles analysed, both natural dyes and synthetic dyes were identified. The dye sources of 137 samples were identified with confidence and the overall success rate was 89%. Inconclusive results for the identification of dyes in the rest 17 historical samples included the following four aspects: unidentified dyes, no dye components undetected, missing dyes and possible contaminations. To be specific, dyes in 7 samples were detected but not identified, most of which are potentially synthetic dyes. In 5 coloured samples, dye-related components were not detected probably because their amounts were below the detection limit of the instrument, or dye components were detected but of too small amounts to be identified accurately. In 3 samples, the identified dyes and dyeing methods are not consistent with the shade of the samples, *e.g.* from an orange sample NMS-2-7 only sappanwood, a dye for red, was detected, and thus there may be a yellow dye present but not detected. In another 2 samples it is uncertain whether the dye components detected are present on the fibre originally or contaminations.[300]

Among the archaeological samples, dye components were detected from most of the samples of Shijingshan tomb and Heyang tombs, while fewer dye components were detected from the samples of the tomb of Zhu Tan and the clan tomb of Zhu Bingju. The limited dyes identified and dyeing methods proposed are consistent with those identified in historical samples.

The results are presented in four sections: natural dyes in historical textile samples; synthetic dyes in historical textile samples; metal threads in historical textile samples, and natural dyes in archaeological textile samples. Representative analytical date of identified

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[300] Contamination may happen when the textile was in use by the 'bleeding' of dye components of surrounding parts. This may also happen if small amounts of fibres of other colours were taken together with the sample and were not completely removed when observing by microscope. Contaminations can usually be determined when the colour that the dye obtains is obviously not consistent with the colour of the sample, *e.g.* the presence of indigotin, the main component of indigo for blue, in a yellow sample, and especially when the dye components are of much smaller amounts than those detected in samples (of similar sample size and colour depth) dyed with the dye for certain.

historical and archaeological dyes and characteristic components are presented in each section. Full analytical data is accessible through the Centre's database.

4.3.1 Natural dyes in historical textile samples

4.3.1.1 Chemical analysis results

Figure 4. 2 is an example of a typical analytical result of a historical dye (a green thread sample from BC-3) by UHPLC-PDA analysis, including a chromatogram and UV-vis spectra for the significant dye components. The dye components identified are berberine and its equivalents, along with indigotin and indirubin. These components indicate that the dye sources for this sample are Amur cork tree and indigo.

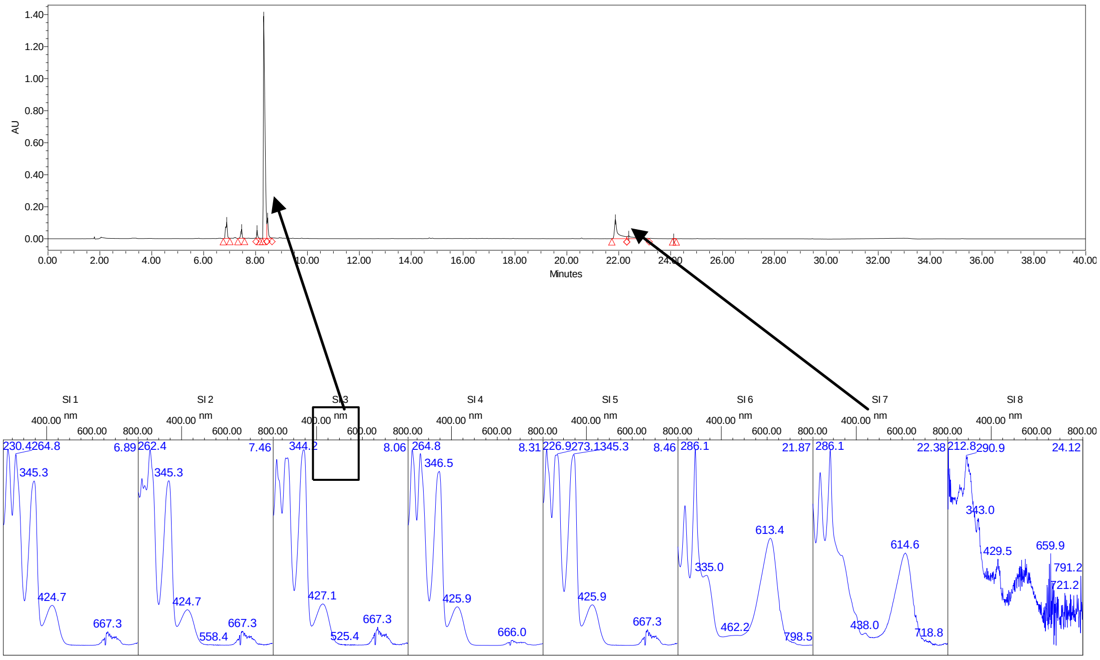

Figure 4. 2 UHPLC-PDA chromatogram (monitored at 350 nm) of the sample BC-3 and UV-Vis spectra of the main constituents detected. The two major dye components identified are respectively berberine (8.1 min) and indigotin (22.4 min).

Table 4. 3 presents the chemical analysis results of the historical samples including major dye components detected and dyes identified. The dyes identified and dyeing methods proposed are discussed first, followed by dyes used in relation to the type of textile they were identified in, to historical dye recipes and to relevant regulations.

Table 4. 3 Identification results of natural dyes in historical samples

Textile reference code	**Sample code**	**Colour**	**Use of thread**	**Major dye components identified**[301]	**Proposed dye source(s)**[302]
BC-1	1	yellow	pattern	berberine and its equivalents	Amur cork tree
	2	blue	pattern	isatin, indigotin and indirubin	indigo
	3	green	pattern	berberine and its equivalents, indigotin, and indirubin	Amur cork tree + indigo
	4	white	ground-warp	—	
	5	apricot yellow[303]	ground-warp	Nowik type A & C components, turmeric component,[304] curcumin, desmethoxycurcumin, bisdesmethoxycurcumin	sappanwood + turmeric
	6	apricot yellow (faded)	ground-warp	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin turmeric component, Nowik type A & C components	sappanwood + turmeric
	7	black	pattern inside to light up silver thread	ellagic acid and a minor unknown yellow component (possibly from the same dye source as that of ellagic acid)	acorn cup

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[301] The colour of the unidentified components were roughly described based on their UV-vis spectra: dye components with maximum absorption of around 400-450 nm are classified yellow, 450-500 nm orange, 500-550 nm red, 550-600 nm purple, and 600-650 nm blue. No major components detected have maximum absorption in the visible light range of 650-800 nm.

[302] Question marks are used in this column in cases where there may be a dye present but not detected, or where it is uncertain whether the dye components of a certain dye are contaminations or not.

[303] In this table apricot yellow and golden yellow refer to general colour shades. They do not correspond to the yellow shades in the official decrees of the Qing Dynasty.

[304] 'Turmeric components' in this Table means proposed characteristic components present in turmeric dyed reference. The same for the other dyes.

Table 4. 3 Identification results of natural dyes in historical samples (continued)

	8	apricot yellow	ground-weft	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin, Nowik type A & C components, sappanwood component	sappanwood + turmeric
	9	apricot yellow	stitching thread	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin, Nowik type A & C components	sappanwood + turmeric
CBL	1	apricot yellow	metal thread core	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin	turmeric + ?
JSL-1	1	yellow	ground	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	2-1	red	pattern	berberine and its equivalents, safflower Ct components, carthamin	safflower + Amur cork tree
	2-2	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	2-3	pale pink	pattern	carthamin, safflower components, rutin and isorhamnetin-rutinoside of small amounts	safflower + pagoda bud ?
	2-4	pink	pattern	carthamin, safflower components, safflower Ct components, berberine and rutin of small amounts	safflower + pagoda bud ? + Amur cork tree ?
JSL-2	1	light purple	pattern	Nowik type A & C components, sappanwood components, indigotin, indirubin	sappanwood + indigo
	2	light pink	pattern	carthamin, safflower components, unknown red and orange components	safflower
	4-1	apricot yellow-deepest	pattern	berberine and its equivalents, carthamin, safflower Ct components, safflower components	safflower + Amur cork tree

Table 4. 3 Identification results of natural dyes in historical samples (continued)

	4-2	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	4-3	apricot yellow-2nd deepest	pattern	safflower components, safflower Ct components, carthamin, trace amount of berberine	safflower + Amur cork tree
	4-4	white	pattern	—	
	4-5	apricot yellow-3rd deepest	pattern	carthamin, safflower components, berberine	safflower + Amur cork tree
	4-6	apricot yellow-4th deepest	pattern	carthamin, safflower components, berberine	safflower + Amur cork tree
	5	red	pattern	berberine and its equivalents, carthamin, safflower yellow components, safflower components	safflower + Amur cork tree
	6	dark yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
JSL-3	1	reddish brown	ground	brasilein, sappanwood components, Nowik type A & C components	sappanwood
JSL-4	1	light yellow-ish brown	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, quercetin, berberine	pagoda bud + Amur cork tree
	2	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	3	yellow-ish brown	pattern	berberine, rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, quercetin	pagoda bud + Amur cork tree
	4	red	pattern	carthamin, safflower yellow components, berberine and its equivalents	safflower + Amur cork tree

Table 4. 3 Identification results of natural dyes in historical samples (continued)

	5	red	pattern	safflower components, safflower Ct components, carthamin, berberine and its equivalents	safflower + Amur cork tree
	6	dark purple	pattern	indigotin, indirubin, isatin, potentially synthetic red colourants	indigo + potentially a synthetic dye
JSL-5	1	dark purple	ground	potentially synthetic purple colourants	potentially a synthetic dye
	2	light purple	ground	potentially synthetic red colourants	potentially a synthetic dye
JSL-6	1	pink	pattern	carthamin, safflower components	safflower
	2	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, sulfuretin, smoketree components	pagoda bud + smoketree
	3	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, quercetin	pagoda bud
NMS-1	1	reddish brown	ground-warp	Nowik type A & C components, sappanwood components	sappanwood
	2	red	pattern	berberine and its equivalents, safflower Ct components, safflower components, carthamin	safflower + Amur cork tree
	3	yellow	stitching thread	potentially synthetic yellow colourants	potentially a synthetic dye
	4	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	5	reddish brown	pattern	Nowik type A & C components	sappanwood
	6	yellow	metal thread core	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin	turmeric
NMS-2	1	purple	pattern	Nowik type A & C components, indigotin, indirubin	sappanwood + indigo

Table 4. 3 Identification results of natural dyes in historical samples (continued)

	2	green	pattern	berberine and its equivalents, indigotin, indirubin	Amur cork tree + indigo
	3	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, quercetin	pagoda bud
	4	red	pattern	berberine and its equivalents, carthamin and safflower Ct components	safflower + Amur cork tree
	5	deeper green	pattern	berberine and its equivalents, indigotin, indirubin	Amur cork tree + indigo
	6	deepest green	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside quercetin, indigotin, indirubin	pagoda bud + indigo
	7	apricot yellow	metal thread core & ground-weft	Nowik type A & C components	sappanwood + ?
NMS-3	1	yellowish brown	ground-weft	Nowik type A & C components, rutin	sappanwood + pagoda bud
	2	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
NMS-4	1	—	metal thread core	core missing	
NMS-5	1	black	ground-warp	isatin, indigotin, indirubin, Nowik type A & C components	sappanwood + indigo
	2	yellow	ground-warp	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin	turmeric
	3	black	stitching thread	isatin, indigotin, indirubin, Nowik type A & C components	sappanwood + indigo
	4	red	lining	berberine, carthamin, safflower component	safflower + Amur cork tree
	5	red (faded)	lining	berberine, carthamin, safflower component	safflower + Amur cork tree

Table 4. 3 Identification results of natural dyes in historical samples (continued)

NMS-6	1	red	ground (bottom of front and back)	laccaic acid A and its equivalents	lac
NMS-7	1	yellow	lining	berberine	Amur cork tree
	2	brown	ground	carminic acid, dc II, dcIV, dcVII,[305] flavokermesic acid, kermesic acid, ellagic acid and potentially synthetic red colourants	cochineal + acorn cup + potentially a synthetic dye
	3	apricot yellow	metal thread core	Nowik type C component	sappanwood + ?
	4	green	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, indigotin, indirubin	pagoda bud + indigo
	5	purple	stitching thread	potentially synthetic red colourants, curcumin, desmethoxycurcumin, bisdesmethoxycurcumin, turmeric component	potentially a synthetic dye for purple and turmeric for yellow
NMS-8	1	white	pattern	—	
	2	yellow	pattern	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin	turmeric
	3	green	pattern	potentially synthetic yellow and green colourants	potentially a synthetic dyes
	4	purple	pattern	potentially synthetic red colourants	potentially a synthetic dye
	5	yellow	pattern	potentially synthetic yellow colourants, curcumin, desmethoxycurcumin, bisdesmethoxycurcumin	potentially a synthetic dye + turmeric
	6	green	pattern for lace	potentially synthetic yellow and green colourants	potentially a synthetic dye

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[305] The dc components are spectral characteristic components of cochineal insects. Details can be found in Wouters and Verhecken, "The Coccid Insect Dyes: HPLC and Computerized Diode-Array Analysis of Dyed Yarns," 189-200; Peggie *et al.*, "Towards the Identification of Characteristic Minor Components from Textiles Dyed with Weld (Reseda Luteola L.) and Those Dyed with Mexican Cochineal (Dactylopius Coccus Costa)," 371-380.

Table 4. 3 Identification results of natural dyes in historical samples (continued)

	7	pink	ground	potentially synthetic red components	potentially a synthetic dye
	8	blue	ground	potentially synthetic purple and blue colourants	potentially a synthetic dye
NMS-9	1	yellow	ground-thin thread	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	2	yellow	stitching thread	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin, turmeric component	turmeric
NMS -10	1	purple	stitching thread	potentially synthetic red and purple colourants	potentially a synthetic dye
	2	green	lining	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, indigotin, indirubin	pagoda bud + indigo
	3	red	ground	berberine, carthamin	safflower + Amur cork tree
NMS -11	1	purple	pattern	Nowik type A & C components, indigotin, indirubin	sappanwood + indigo
	2	yellow	ground	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin, turmeric component	turmeric
	3	yellow	stitching thread	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin, turmeric component	turmeric
	4	black	pattern-lace pattern	ellagic acid, a flavonoid	acorn cup + ?
NMS -12	1	apricot yellow	pattern-lace pattern	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin, carthamin	safflower + turmeric
	2	black	ground-lace ground	ellagic acid	acorn cup

Table 4. 3 Identification results of natural dyes in historical samples (continued)

	3	—	silver thread for lace pattern	core missing	
	4	red	pattern	berberine, carthamin	safflower + Amur cork tree
	5	yellow	pattern	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin, turmeric component	turmeric
NMS -13	1	red	ground	berberine, carthamin	safflower + Amur cork tree
	2	black	ground	ellagic acid	acorn cup
	3	yellow	stitching thread	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, quercetin, curcumin, desmethoxycurcumin, bisdesmethoxycurcumin, turmeric component	turmeric + pagoda bud
	4	red	stitching thread	potentially synthetic red colourants	potentially a synthetic dye
PC-1	1	yellow	ground	rutin, isorhamnetin-rutinoside	pagoda bud
	2	pink	pattern	carthamin	safflower
	3	red	pattern	safflower yellow components, safflower Ct components,[306] carthamin, berberine and its equivalents	safflower + Amur cork tree
PC-2	1	red	pattern	safflower components, safflower Ct components, carthamin, berberine and its equivalents	safflower + Amur cork tree
PC-3	1	yellow	pattern	berberine and its equivalents	Amur cork tree
	2	reddish brown	pattern	rutin, isorhamnetin-rutinoside, Nowik type A & C components, sappanwood components, trace brasilein	sappanwood + pagoda bud

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[306] Safflower Ct components are colourless but stable characteristic components that helps the identification of safflower in faded samples. This was first proposed in Wouters, Grzywacz, and Claro, "Markers for Identification of Faded Safflower (Carthamus Tinctorius L.) Colorants by HPLC-PDA-MS Ancient Fibres, Pigments, Paints and Cosmetics Derived from Antique Recipes," 186-203.

Table 4. 3 Identification results of natural dyes in historical samples (continued)

	3	red	pattern	berberine and its equivalents, safflower yellow components, carthamin, safflower Ct components	safflower + Amur cork tree
	4	pink	pattern	berberine and its equivalents, carthamin, safflower Ct components	safflower + Amur cork tree
	5	reddish brown	ground	rutin, isorhamnetin-rutinoside, Nowik type A & C components, sappanwood component, sulfuretin ?	sappanwood + pagoda bud + smoketree ?
TPM-1	1	purple	pattern	potentially synthetic purple colourants	potentially a synthetic dye
	1	blue	pattern	potentially synthetic green and purple colourants	potentially a synthetic dyes
	1	red	pattern	no characteristic dye components detected	
	2	red	pattern	potentially synthetic red colourants and an potentially synthetic yellow colourant of a small amount	potentially a synthetic dye
TPM-2	1	yellow	ground	rutin, isorhamnetin-rutinoside	pagoda bud
	2	blue	ground	isatin, indigotin, indirubin	indigo
TPM-3	1	blue	ground	indigotin, indirubin	indigo
	2	white	pattern	—	
TPM-4	1	yellow	ground	four potentially synthetic yellow components	potentially a synthetic dye
	2	green	pattern	berberine, indigotin, indirubin	Amur cork tree + indigo
V&A-1	1	yellow	ground	no characteristic dye components detected	
V&A-2	1	yellow	metal thread core	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, quercetin	pagoda bud
	2	dark green	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, indigotin, indirubin	pagoda bud + indigo

Table 4. 3 Identification results of natural dyes in historical samples (continued)

	3	light green	pattern-top	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, indigotin, indirubin	pagoda bud + indigo
	4	lighter green	pattern-bottom	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, indigotin, indirubin	pagoda bud + indigo
	5	apricot yellow	ground-weft	Nowik type A & C components, curcumin, desmethoxycurcumin, bisdesmethoxycurcumin	sappanwood + turmeric
	6	red	ground-weft	berberine and its equivalents, carthamin	safflower + Amur cork tree
	7	apricot yellow (faded)	ground	Nowik type A & C components, curcumin, desmethoxycurcumin, bisdesmethoxycurcumin	sappanwood + turmeric
V&A-3	1	yellow	stitching thread for buttons	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside, quercetin	pagoda bud
	2	yellow	metal thread	core missing	
	3	apricot yellow	lining	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin, turmeric component, carthamin	safflower + turmeric
	4	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	5	—	pattern	core missing	
V&A-4	1	yellow	ground for cuff	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	2	yellow	ground-weft ?	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	3	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud

Table 4. 3 Identification results of natural dyes in historical samples (continued)

V&A-5	1	red	ground	four unknown yellow components	unknown natural dye
	2	green	pattern	indigotin, berberine ?	Amur cork tree ? + indigo
	3	yellow	metal thread core	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin, turmeric component	turmeric
	4	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	5	pink	pattern	carthamin, safflower components	safflower
V&A-6	1	yellow	metal thread core	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	2	yellow	ground for cuff	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	3	pink	lining	carthamin	safflower
	4	grey	pattern	probably berberine	Amur cork tree ?
	5	dark blue	ground	indigotin, laccaic acid A and its equivalents	indigo + lac
	6	black	ground-thick edge	ellagic acid	acorn cup
	7	black	ground-thin edge	gallic acid	gallnut
	8	black	stitching thread?	ellagic acid	acorn cup
	9	pink	stitching thread	carthamin	safflower
V&A-7	1	green	pattern	berberine and its equivalents, indigotin, indirubin	Amur cork tree + indigo
	2	red	ground	Nowik type A & C components, carthamin, curcumin, desmethoxycurcumin, bisdesmethoxycurcumin	sappanwood + safflower + turmeric
	3	black	pattern	ellagic acid and its equivalent	acorn cup

Table 4. 3 Identification results of natural dyes in historical samples (continued)

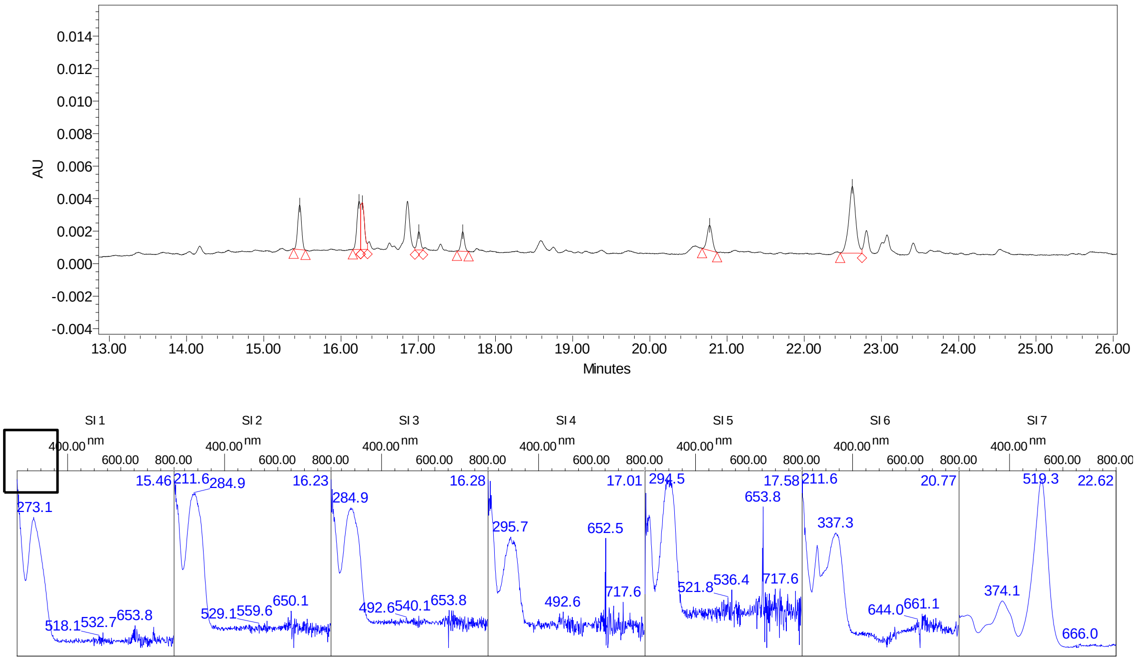
	4	yellow	metal thread core	curcumin, desmethoxycurcumin, bisdesmethoxycurcumin	turmeric
V&A-8	1	pink	ground	potentially synthetic red components	potentially a synthetic dye
V&A-9	1	yellow	ground	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	2	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	3	reddish brown	pattern-for metal thread	Nowik type A & C components, ellagic acid	sappanwood + acorn cup
V&A -10	1	reddish brown	pattern	Nowik type A & C components, sulfuretin, fisetin, rutin	sappanwood + smoketree + pagoda bud
	2	green	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside indigotin, indirubin	pagoda bud + indigo
	3	pink (faded)	lining	carthamin	safflower
	4	yellow	pattern	rutin, isorhamnetin-rutinoside, kaempferol-rutinoside	pagoda bud
	5	red	pattern	berberine and its equivalents, carthamin, safflower components	safflower + Amur cork tree
	6	purple	pattern	Nowik type C component, indigotin	sappanwood + indigo
	7	blue	ground	indigotin, indirubin	indigo
	8	pink	stitching thread	berberine, carthamin, safflower Ct component	safflower + Amur cork tree
	9	red	pattern	berberine and its equivalents, carthamin, safflower component, safflower Ct component	safflower + Amur cork tree
	10	blue	pattern	indigotin, indirubin	indigo
	11	green	ground	berberine and its equivalents, indigotin, indirubin	Amur cork tree + indigo

Table 4. 3 Identification results of natural dyes in historical samples (continued)

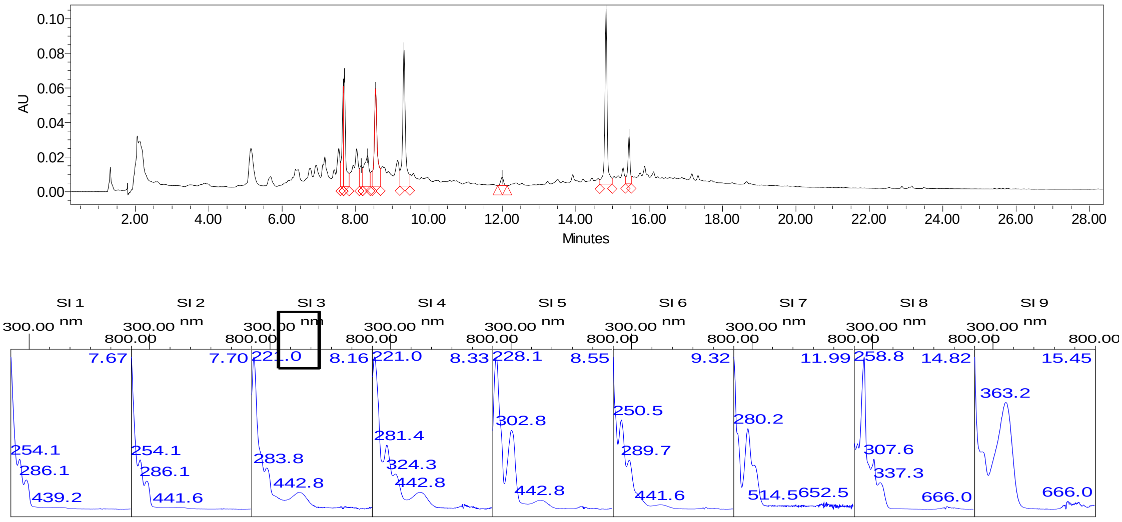
	12	pink	pattern	carthamin	safflower
V&A -11	1	yellow	metal thread core	no characteristic dye components detected	
	2	dark purple	pattern-metal thread edge	potentially synthetic red colourants	potentially a synthetic dye
	3	yellow	lining	rutin , isorhamnetin-rutinoside, kaempferol-rutinoside, quercetin, curcumin, desmethoxycurcumin, bisdesmethoxycurcumin, turmeric component	turmeric + pagoda bud

4.3.1.2 Dyes identified

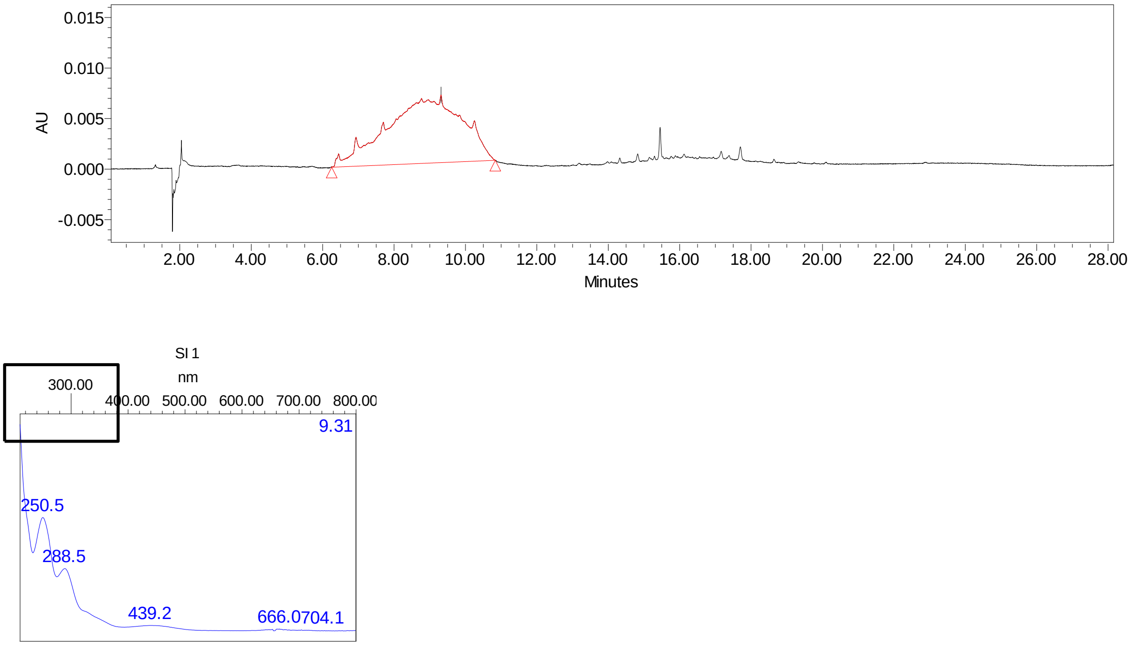
The most frequently identified dyes included safflower, sappanwood, Amur cork tree, pagoda bud, turmeric, indigo as well as a dye containing ellagic acid (examples presented in Fig 1). The dye containing ellagic acid is probably acorn cup because acorn cup is the dye containing ellagic acid recorded most frequently in the historical dye recipes. Gallnut and smoketree were also identified. Examples of analytical data showing the identification of these dyes are presented in Figure 4. 3a to i.



(a) An example of the analytical result of a historical sample dyed by safflower (V&A-5-5, monitored at 295 nm). Safflower yellow components, safflower Ct component, safflower component and carthamin were detected.

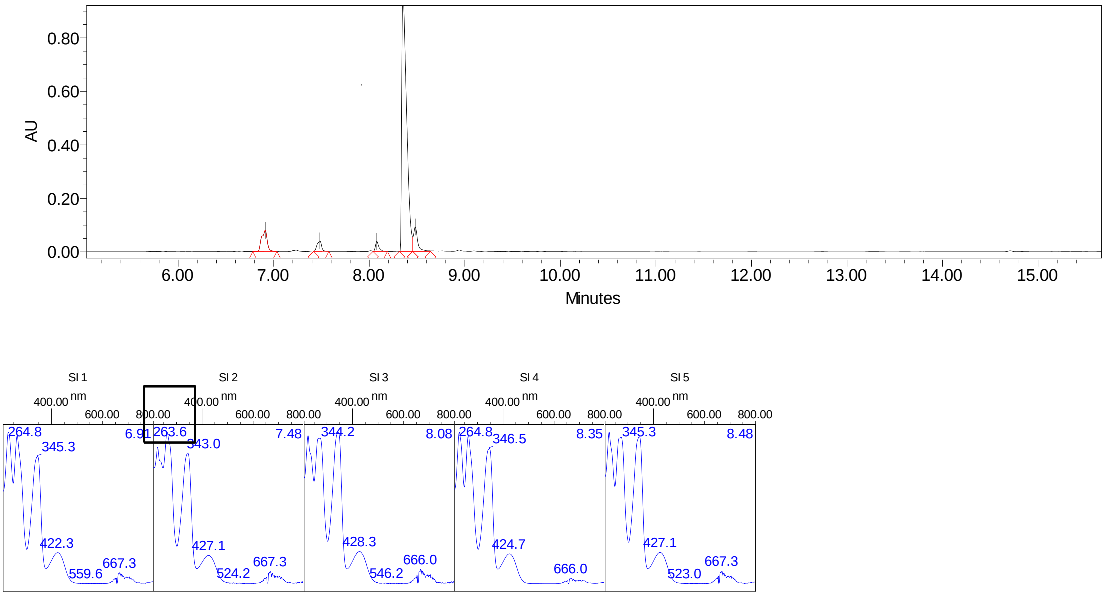


(b-1)

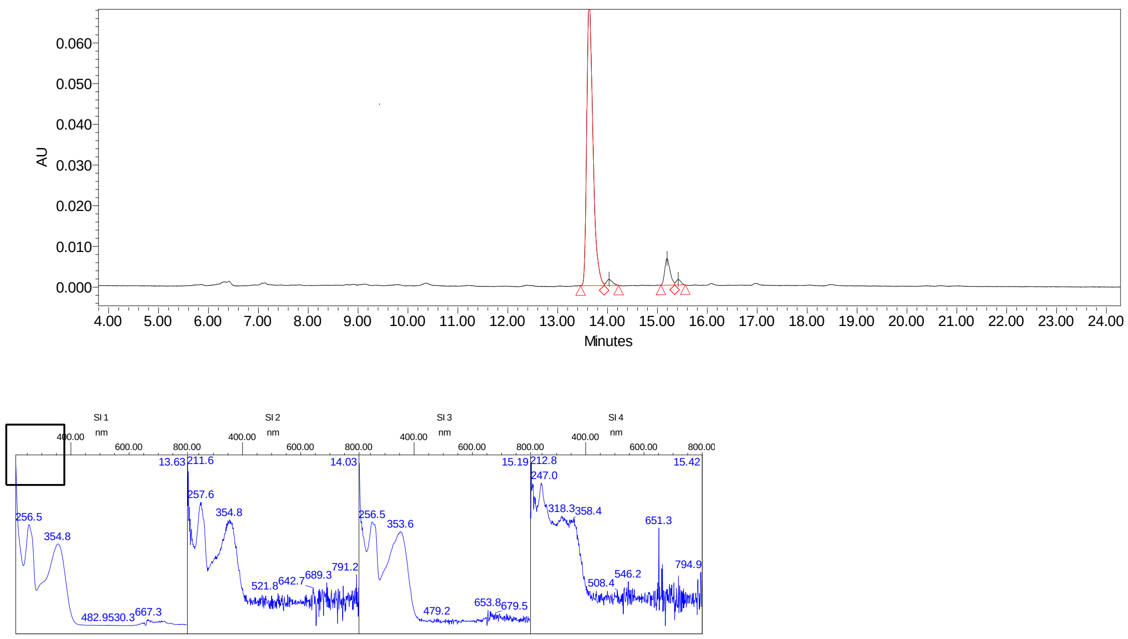


(b-2)

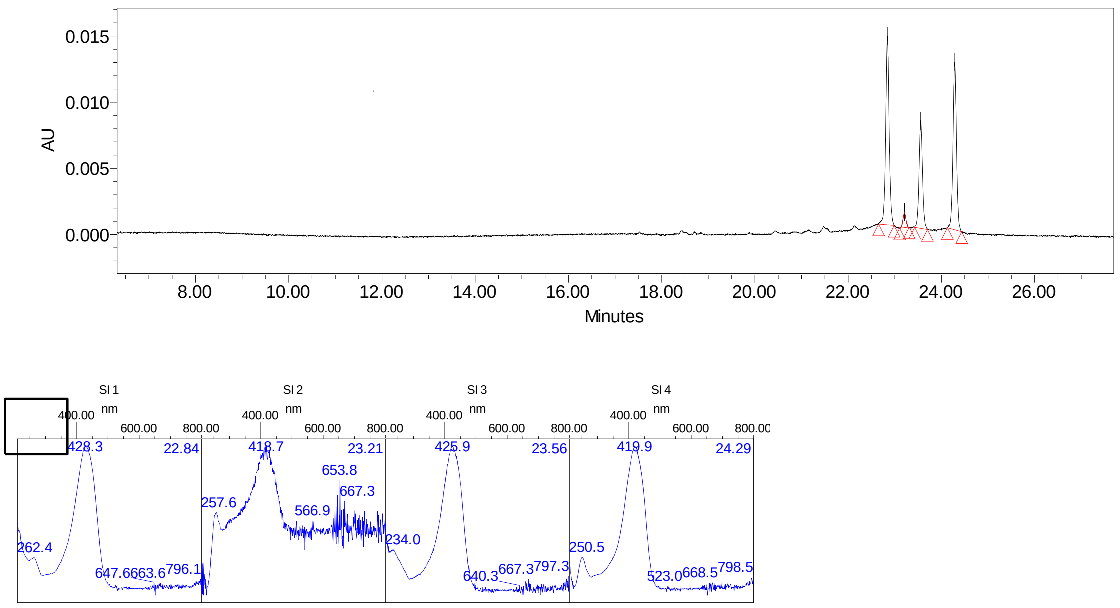
(b) An example of the analytical result of a historical sample dyed by sappanwood (JSL-3, monitored at 295 nm (b-1) and 430 nm (b-2)). Brasilein, Nowik type A components, Nowik type C component and sappanwood components were detected.



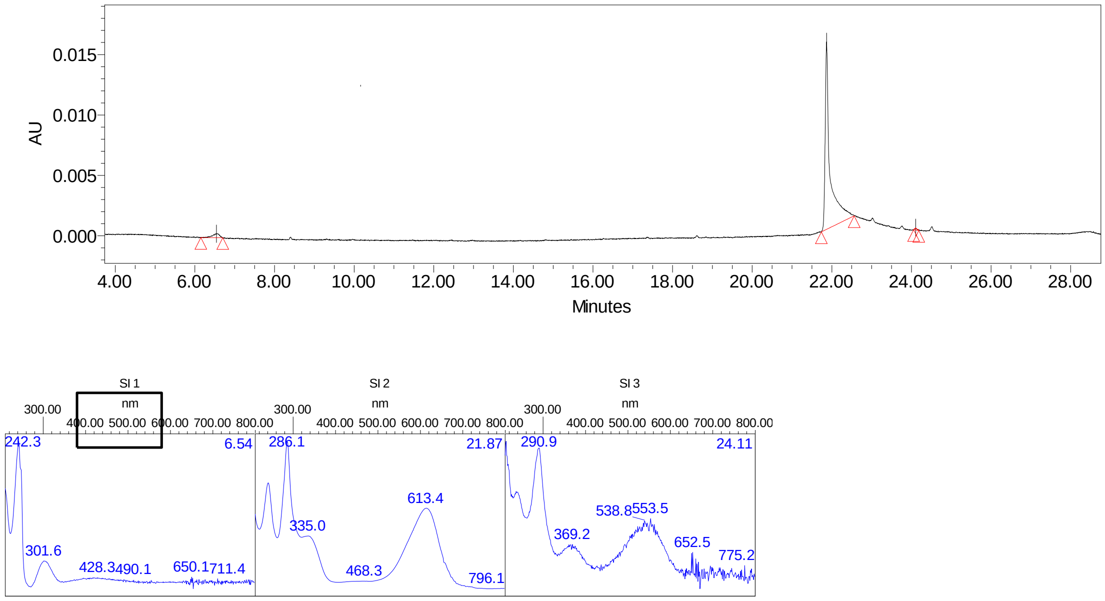
(c) An example of the analytical result of a historical sample dyed by Amur cork tree (BC-1, monitored at 350 nm). Berberine and its equivalents were detected.



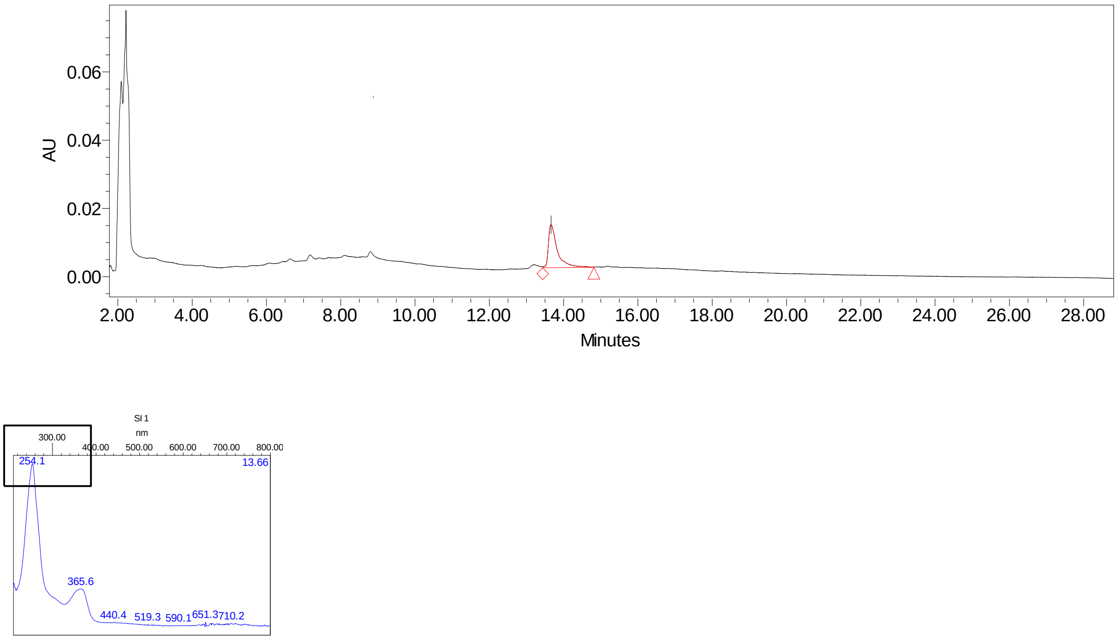
(d) An example of the analytical result of a historical sample dyed by pagoda bud (NMS-9-1, monitored at 350 nm). Rutin, its equivalent, isorhamnetin-3-rutinoside and kaempferol-3-rutinoside were detected.



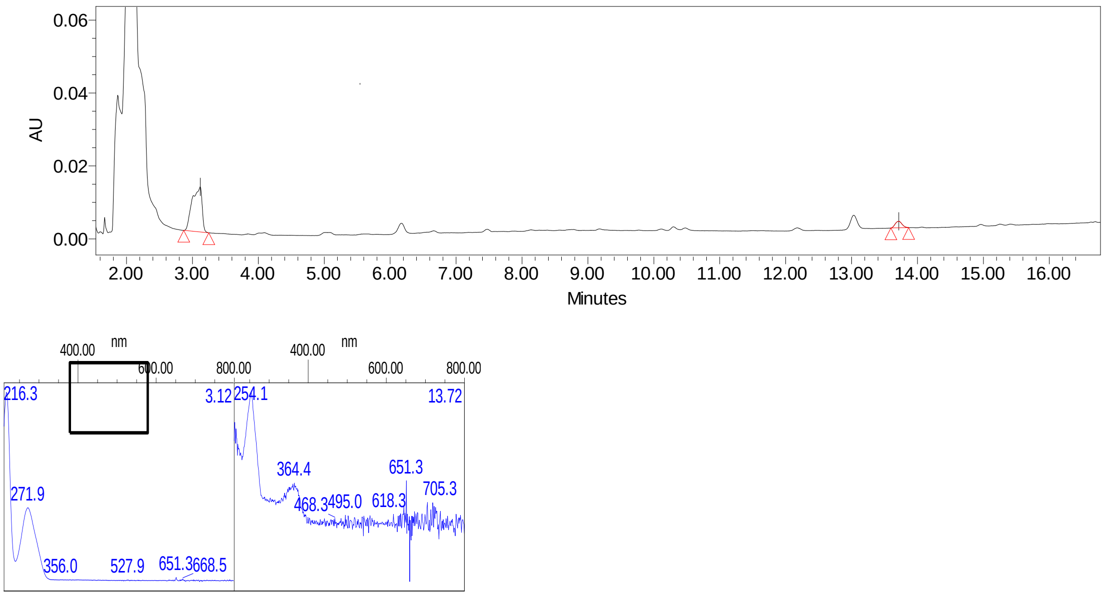
(e) An example of the analytical result of a historical sample dyed by turmeric (NMS-9-2, monitored at 425 nm). Curcumin, desmethoxycurcumin, bisdesmethoxycurcumin and a turmeric component were detected.



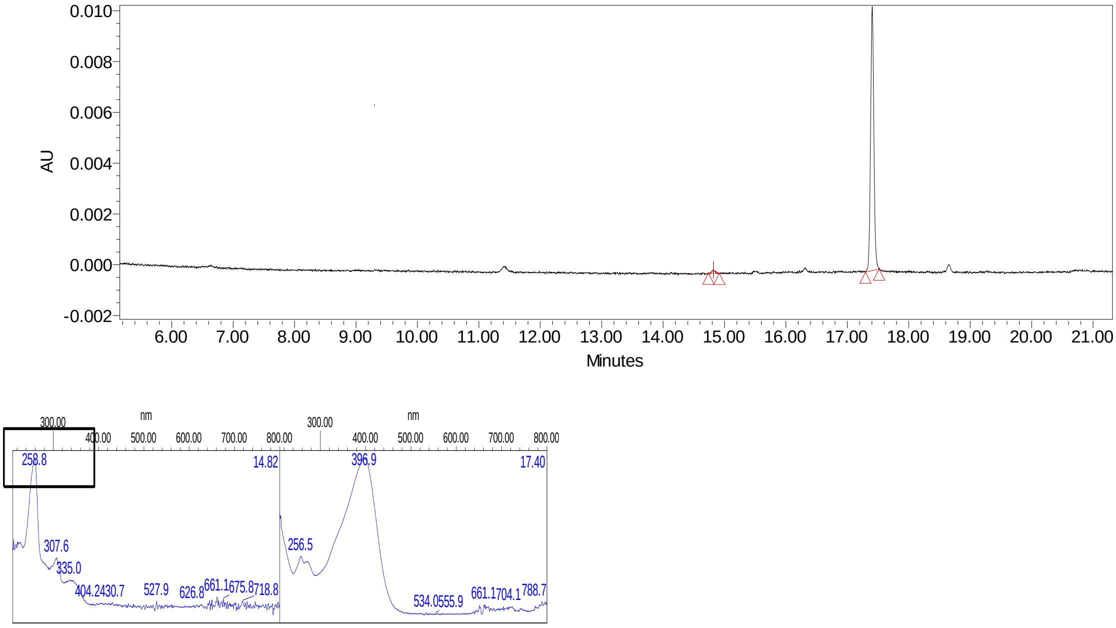
(f) An example of the analytical result of a historical sample dyed by indigo (BC-2, monitored at 425 nm). Isatin, indigotin and indirubin were detected.



(g) An example of the analytical result of a historical sample dyed by acorn cup (NMS-13-2, monitored at 350 nm). Ellagic acid was detected.



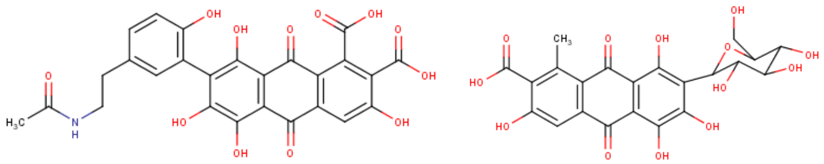
(h) An example of the analytical result of a historical sample dyed by Chinese gallnut, together with acorn cup (V&A-6-7, monitored at 350 nm). A gallic acid monomer and ellagic acid were detected.



(i) An example of the analytical result of a historical sample dyed by smoketree, together with sappanwood (V&A-10-1, monitored at 425 nm). Sulfuretin, Nowik type C component, and other characteristic components of sappanwood (when monitored at 295 nm) were detected.

Figure 4. 3 Examples of the analytical results of historical samples respectively dyed by safflower, sappanwood, Amur cork tree, pagoda bud, turmeric, indigo, acorn cup, Chinese gallnut and smoketree

Apart from these dyes, lac and cochineal were identified, respectively twice and once. Relevant information on the botanical source and use history of the frequently identified dyes are presented in detail in the previous three chapters. The three less common dyes are discussed in detail as following.



laccaic acid A carminic acid

Figure 4. 4 Chemical structures of the major dye components of lac and cochineal

Lac

Laccaic acid A (Figure 4. 4) and its equivalents were detected in two of the historical Chinese textiles, indicating the use of lac for dyeing (Figure 4. 6).[307] It was found that lac was used alone to dye wool for an intense red ground in NMS-6 (dragon cloak, 19th century); and for the purple ground colour of silk in V&A-6 (women's jacket, 1736-1795) in combination with indigo (Figure 4. 5). In ancient China, indigenous lac was the gum of Chinese lac (*Kerria chinensis* (Mahdihassan, 1923)), a parasitic insect distributed on the tree *zi kuang* (紫矿, *Butea monosperma* (Lam.) Kuntze) in southwest China. During the Ming and Qing Dynasties, other *Kerria spp.* were often imported from southeast Asia countries as well.[308] The earliest record of using lac for dyeing was in the Jin Dynasty (265-420 AD).[309] Apart from textiles dyeing, lac was also used as a colourant for

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[307] Wouters and Verhecken, "The Coccid Insect Dyes: HPLC and Computerized Diode-Array Analysis of Dyed Yarns," 189-200.

[308] Yong Lu and Yu Cui, "Zhongguo Gudai Zijiaochong Yuanchandi Kaobian Ji Liyong Tanxi," [Research on the original producing area of Laccifer lacca (Kerr) and application in ancient China], *Agricultural Archaeology* 29, no.1 (2009): 261-265.

[309] Zhao, "Zhongguo Gudai Ranse Huaxueshi," 637,640.

architecture paintings, drawings, rouge and ink.[310] How the detection of lac could help provenance the textiles needs further investigation.

Figure 4. 5 Lac was detected in the red ground of NMS-6 (left) and in the purple ground of V&A-6 together with indigo (right)

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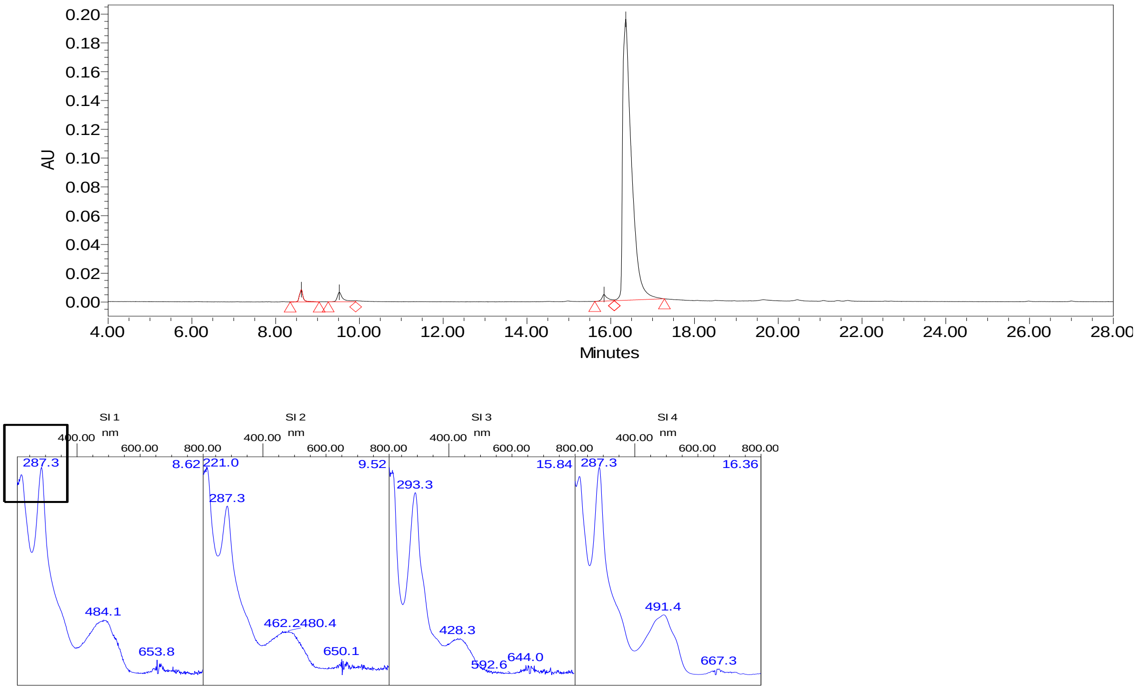

(a) Lac dyed wool reference sample

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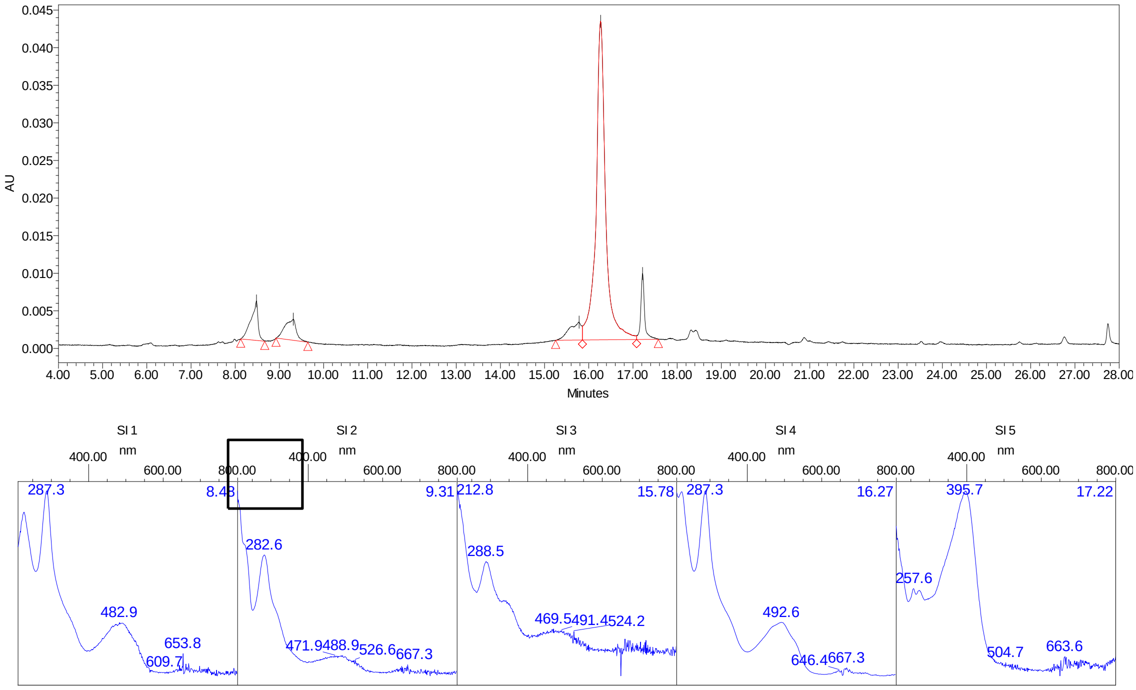
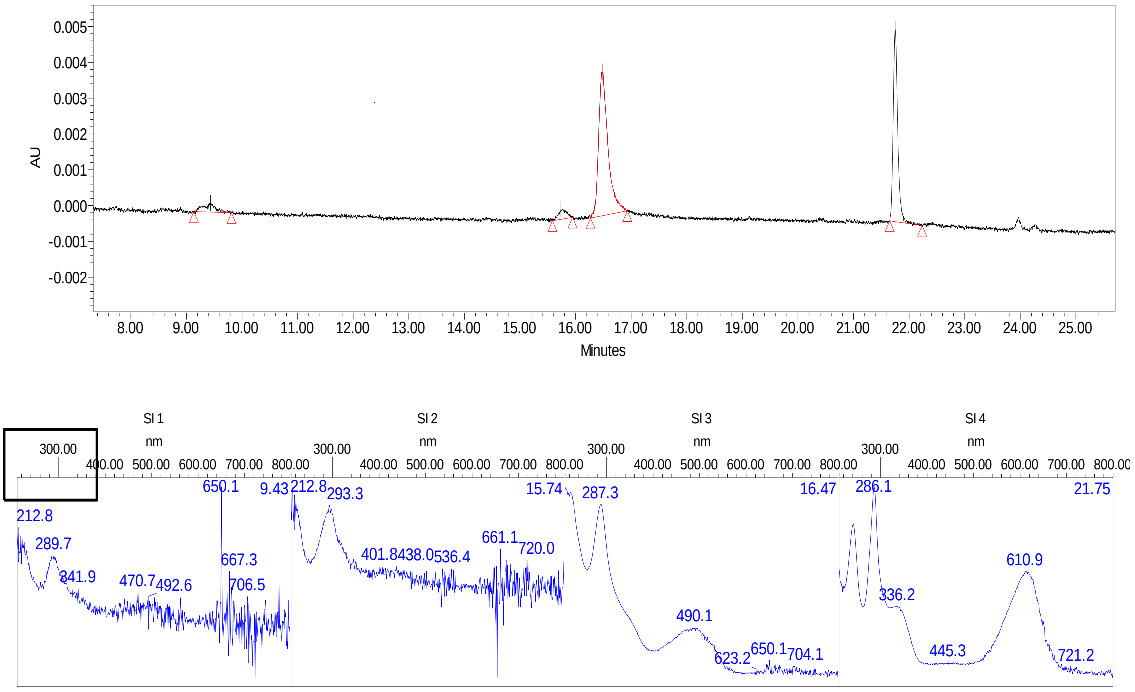
[310] Lu and Cui, "Zhongguo Gudai Zijiaochong Yuanchandi Kaobian Ji Liyong Tanxi," 261-265; Jinyu Wang, "Zhonghua Gudai Dui Zikuang De Kaifa Yingyong," [Development and application of lac in ancient China], *China Historical Materials of Science and Technology* 21, no.3 (2000): 222-227.



(b) NMS-6-1



(c) V&A-6-5. Indigotin was also detected in this sample.

Figure 4. 6 UHPLC-PDA chromatograms (monitored at 350 nm) of the extracts of the lac dyed wool reference sample (a), NMS-6-1 (b) and V&A-6-5 (c) and the UV-Vis spectra of their main constituents

Cochineal

Cochineal, an insect dye of the anthraquinone group, was identified in a sample taken from the brown ground of the dancer's skirt NMS-7 (Figure 4. 7), along with ellagic acid, and a synthetic dye, probably magenta (magenta discussed in section 4.3.2). The main component of cochineal, carminic acid, and several minor characteristic components were detected (Figure 4. 8), but it is not certain whether this dye is American cocineal (*Dactylopius coccus*) or another carmine scale insect of *Porphyrophora* spp.[311] On the one hand, it is known that the sophora carmine scale insect *Porphyrophora sophorae* (Archangelskaja, 1935), called *yan zhu jie* 胭珠蚧 in Chinese, is indigenous in China.[312] On the other hand, American cochineal (called *yan zhi chong* 胭脂蟲 in Chinese) was a very precious dye only traded to China with small amounts, mainly through the port of Canton.[313] Similar to this finding, cochineal was detected in a piece of theatre costume of the Qing Dynasty collected at the Museum of Arts and Design (Madrid), together with several other natural dyes and synthetic dyes.[314] Whether the cochineal dyes identified were indigenous in China and whether these findings could help provenance the textiles need further investigation.

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[311] Wouters and Verhecken, "The Coccid Insect Dyes: HPLC and Computerized Diode-Array Analysis of Dyed Yarns," 189-200; Ana Serrano *et al.*, "Analysis of Natural Red Dyes (Cochineal) in Textiles of Historical Importance Using HPLC and Multivariate Data Analysis," *Analytical and Bioanalytical Chemistry* 401, no.2 (2011): 735-743.

[312] Cardon, 653.

[313] Feian Yu and Leyuan Liu, *Zhongguohua Yanse De Yanjiu* [Research on the colour of Chinese paintings] (Beijing: Shijie tushu chuban gongsi, 2013), 20; Leanna Lee-Whitman, "The Silk Trade: Chinese Silks and the British East India Company," *Winterthur Portfolio* 17, no.1 (1982): 21-41; Elena Phipps, *Cochineal Red: The Art History of a Color* (New York: Metropolitan Museum of Art, 2010), 40-41; Robin Arthur Donkin, "The Insect Dyes of Western and West-Central Asia," *Anthropos* (1977): 847-880.

[314] Estrella Sanz Rodríguez *et al.*, "Characterization of Natural and Synthetic Dyes Employed in the Manufacture of Chinese Garment Pieces by LC-DADand LC-DAD-QTOF".

Figure 4. 7 Photo of NMS-7 showing the brown ground colour for stripes, where cochineal, magenta (probably) and ellagic acid were identified

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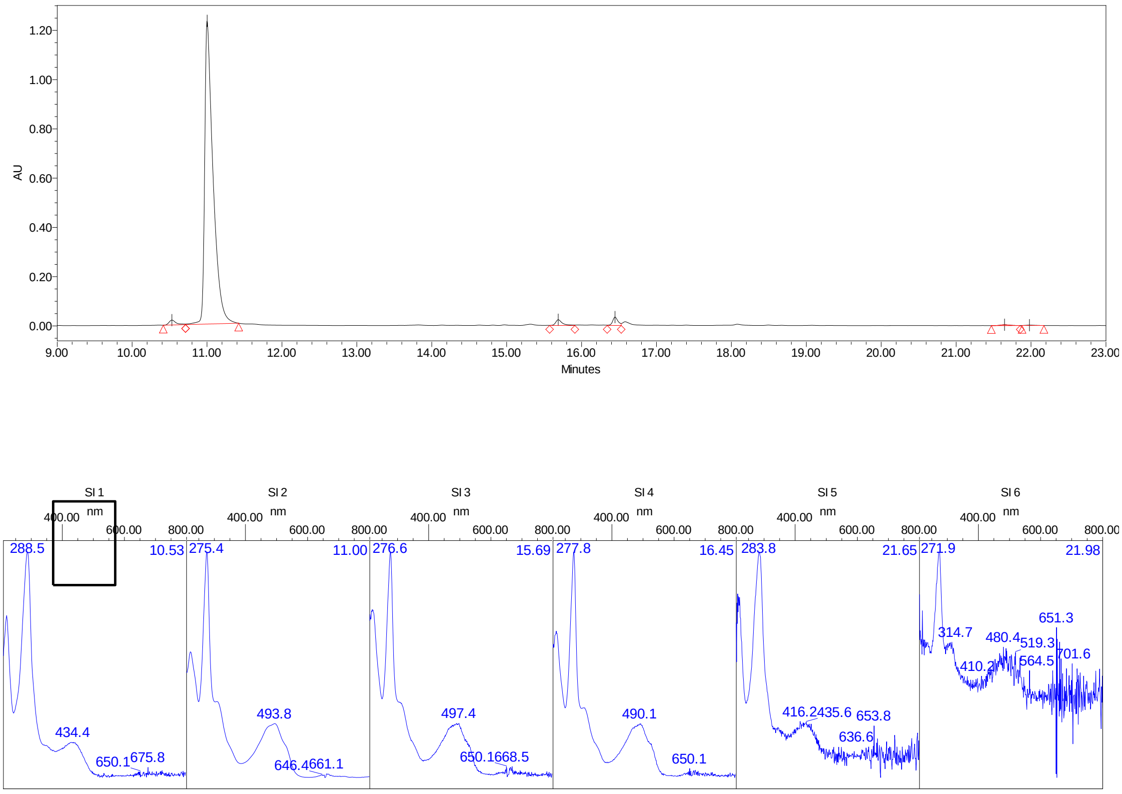
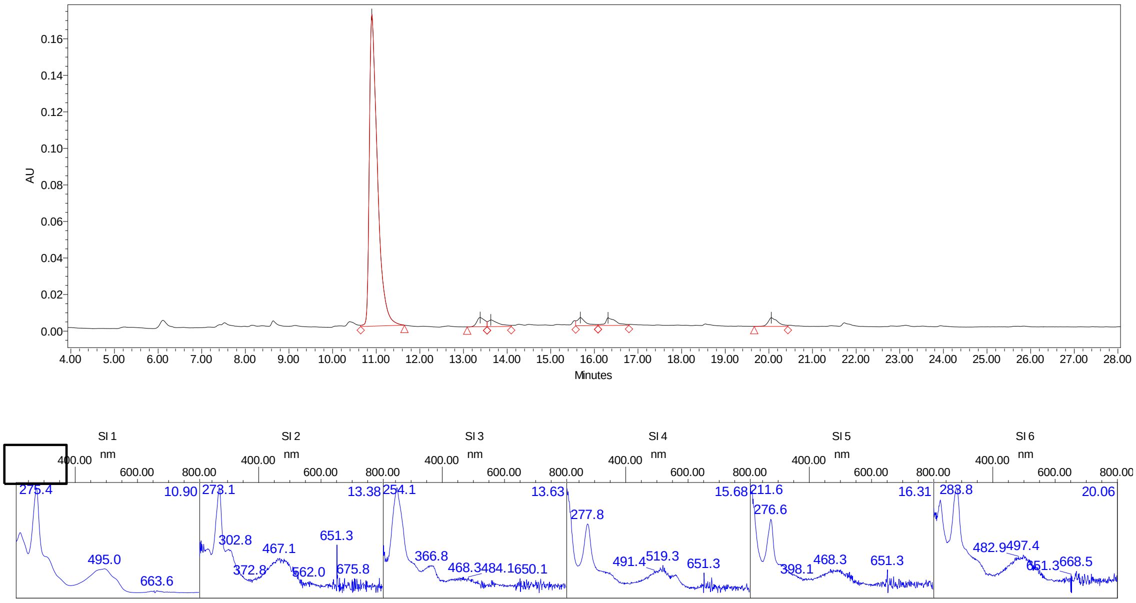
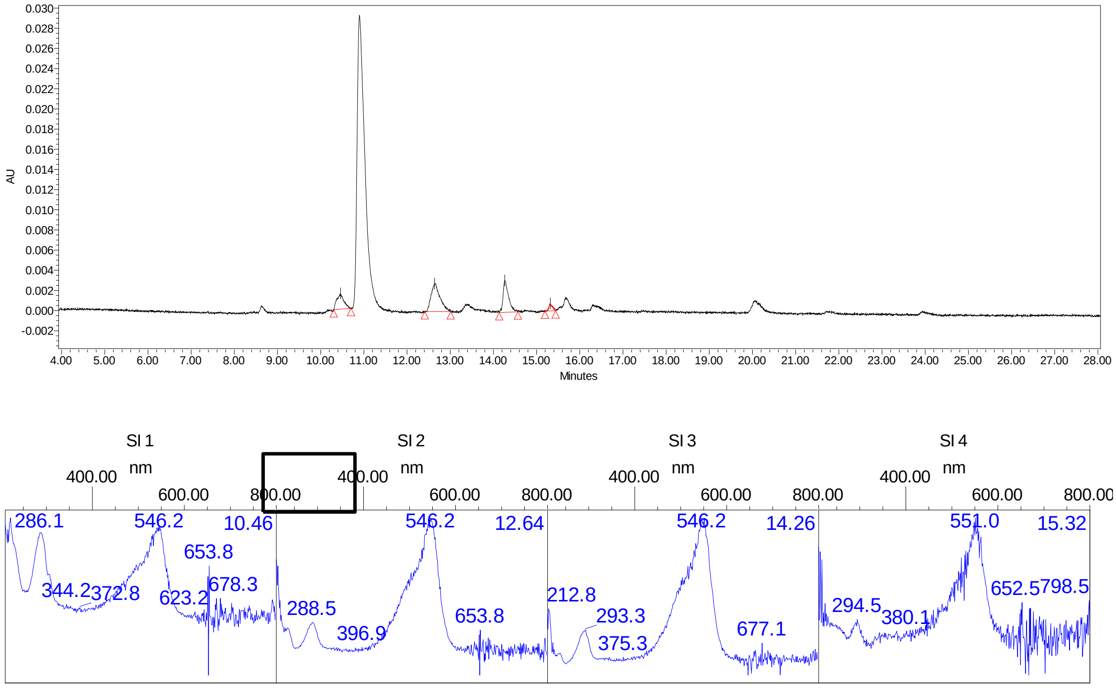


(a) American cochineal dyed wool reference sample. dc II (10.5 min), carminic acid (11.0 min), dc IV (15.7 min) and dc VII (16.4 min), kermesic acid (21.6 min) and flavokermesic acid (22.0 min) were identified.



(b-1) NMS-7-2, monitored at 275 nm. Carminic acid (10.9 min), ellagic acid (13.6 min) and some minor characteristic components of cochineal were detected.



(b-2) NMS-7-2, monitored at 515nm. Four characteristic components of magenta of small amounts were detected.

Figure 4. 8 UHPLC-PDA chromatograms of the extracts of the American cochineal dyed wool reference sample (a) and NMS-7-2 (b), and the UV-Vis spectra of their main constituents

4.3.1.3 Dyeing methods proposed

Among the 119 historical samples identified and exclusively dyed by natural dyes (the 3 duplicate samples for fading study were not counted), 60 samples are dyed by one dye, 56 samples are dyed by two dyes and 3 samples are dyed by three dyes. Established practice to achieve various shades is found. Usually for red, yellow, blue and black shades one dye is used, for other shades a mixture of two dyes are used. The results for the identified dyes are now discussed by colour.

Yellow shades by yellow dyes

Yellow samples are usually dyed by a single yellow dye: pagoda bud is the most frequently used one (for 24 samples), followed by turmeric (9 samples) and Amur cork tree (3 samples). Occasionally two yellow dyes are used together for more subtle yellow shades: two samples are dyed by the combination of pagoda bud and turmeric and one sample is dyed by pagoda bud and smoketree (Figure 4. 9).

Apricot yellow samples are usually obtained by a mixture of red and yellow dyes. Four samples are dyed by the combination of sappanwood and turmeric and two by safflower and turmeric. In JSL-2-4, a set of four samples of apricot yellow shades from light to deep are all dyed by safflower and Amur cork tree. In some apricot yellow samples only a red or yellow dye was detected: in NMS 2-7 and 7-3 only sappanwood was detected; in CBL-1 only turmeric was detected. Probably another dye was used but its amount was too small to detect.

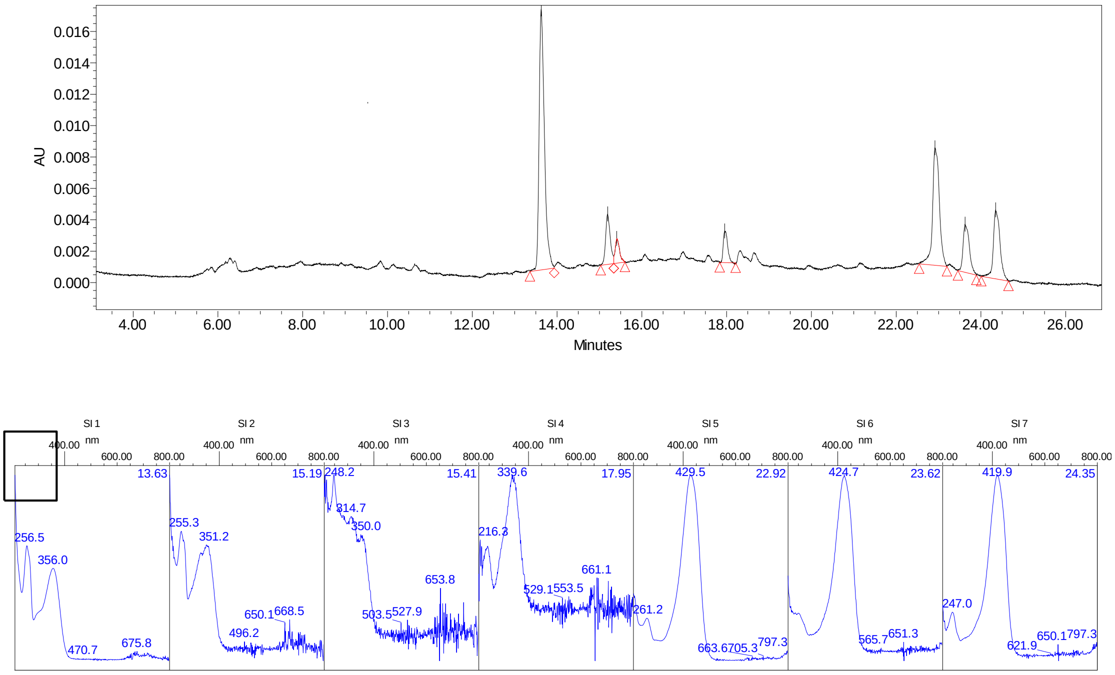


Figure 4. 9 An example of the analytical result of a historical sample (NMS-13-3) dyed by two yellow dyes (pagoda bud and turmeric) for yellow, chromatogram monitored at 350 nm

Red and pink shades

Safflower was detected in most red and pink samples. Amur cork tree is sometimes used with safflower to brighten the shade: all the red samples and two pink samples are dyed by safflower and Amur cork tree together (Figure 4. 10). Small amounts of safflower yellow components were detected in four red samples. Usually yellow components in safflower were discarded before dyeing because of their poor lightfastness, therefore the ratio between the amount of carthamin and those of safflower yellow components may indicate the quality of safflower dyeing.

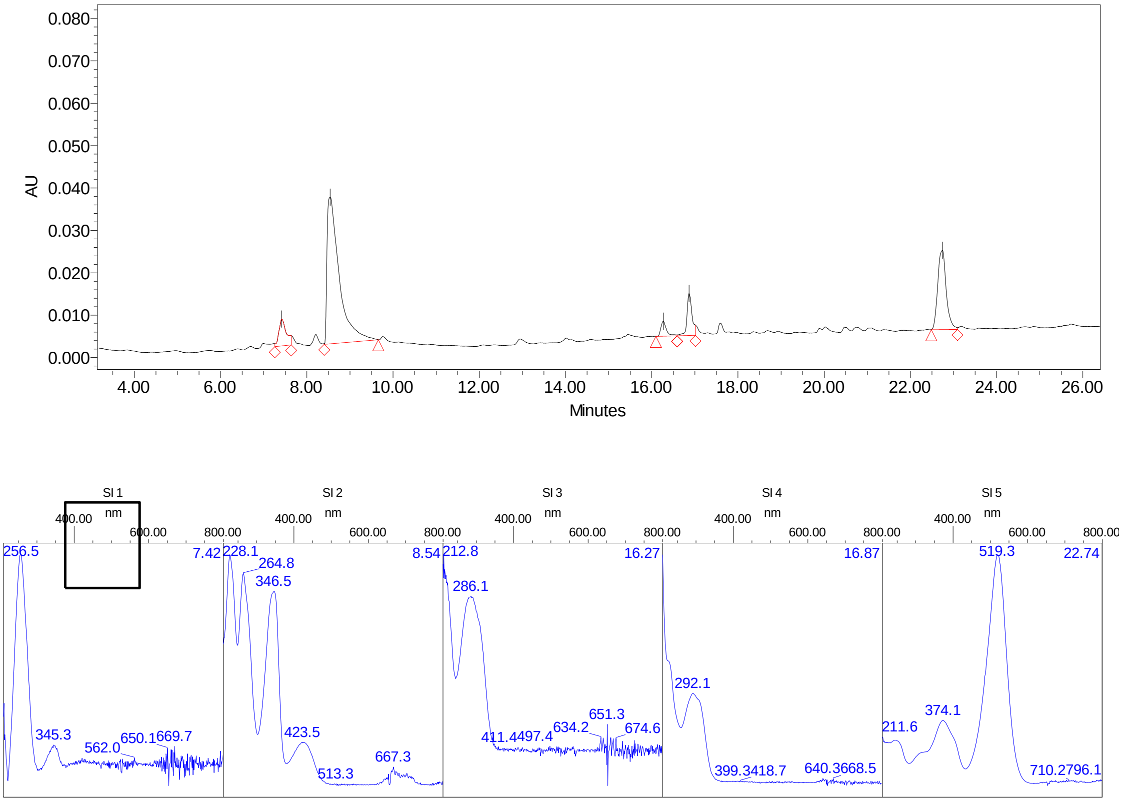


Figure 4. 10 An example of the analytical result of a historical sample (JSL-1-2) dyed by safflower and Amur cork tree, chromatogram monitored at 254 nm

Blue, purple and green shades

In all the blue samples, indigotin is the main colourant, indicating the dye source of indigo. All the purple samples are dyed by sappanwood and indigo together. Green shades are always achieved by the combination of indigo and a yellow dye, usually Amur cork tree (for 6 samples) or pagoda bud (for 7 samples) (examples presented in Figure 4. 3 and Figure 4. 11). There is no obvious difference in shade between the two kinds of combinations.

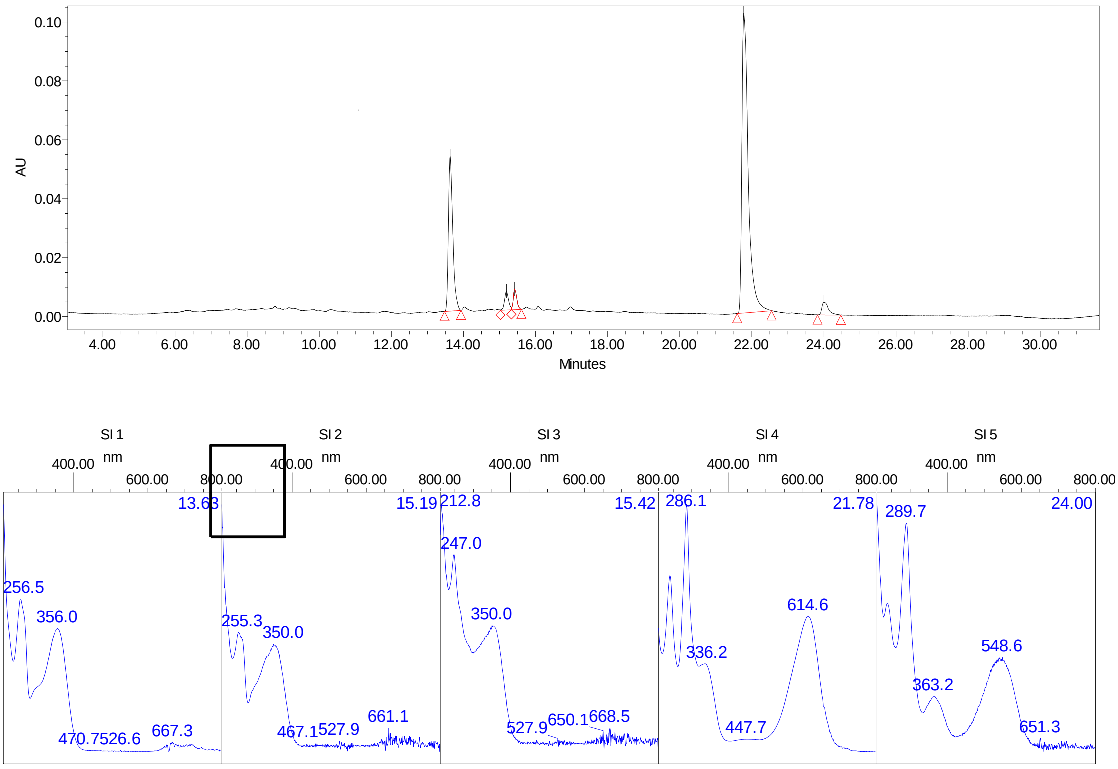


Figure 4. 11 An example of the analytical result of a historical sample (NMS-13-3) dyed by pagoda bud and indigo, chromatogram monitored at 350 nm

Black and brown shades, with or without tannin

Black samples are usually dyed with tannin, with iron sulphate as the expected mordant. 7 black samples contain ellagic acid (probably from acorn cup), and 1 sample has gallic acid (probably from gallnut). The 2 black samples from the ground and stitching thread of NMS-5 dyed by the combination of sappanwood and indigo may indicate good quality of dyeing because the use of iron sulphate makes fabrics brittle.[315]

Brown shades are always achieved by the use of multiple dyes, including the red dye sappanwood, various yellow dyes and a dye/dyes containing tannin, depending on the desired shade:

- the use of sappanwood alone or with tannin, usually for reddish brown (Figure 4. 12);

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[315] Cardon, 410.

- the combination of yellow dyes for yellowish brown;

- the combination of sappanwood and yellow dyes together for reddish or yellowish brown (examples in Figure 4. 13 and Figure 4. 14).

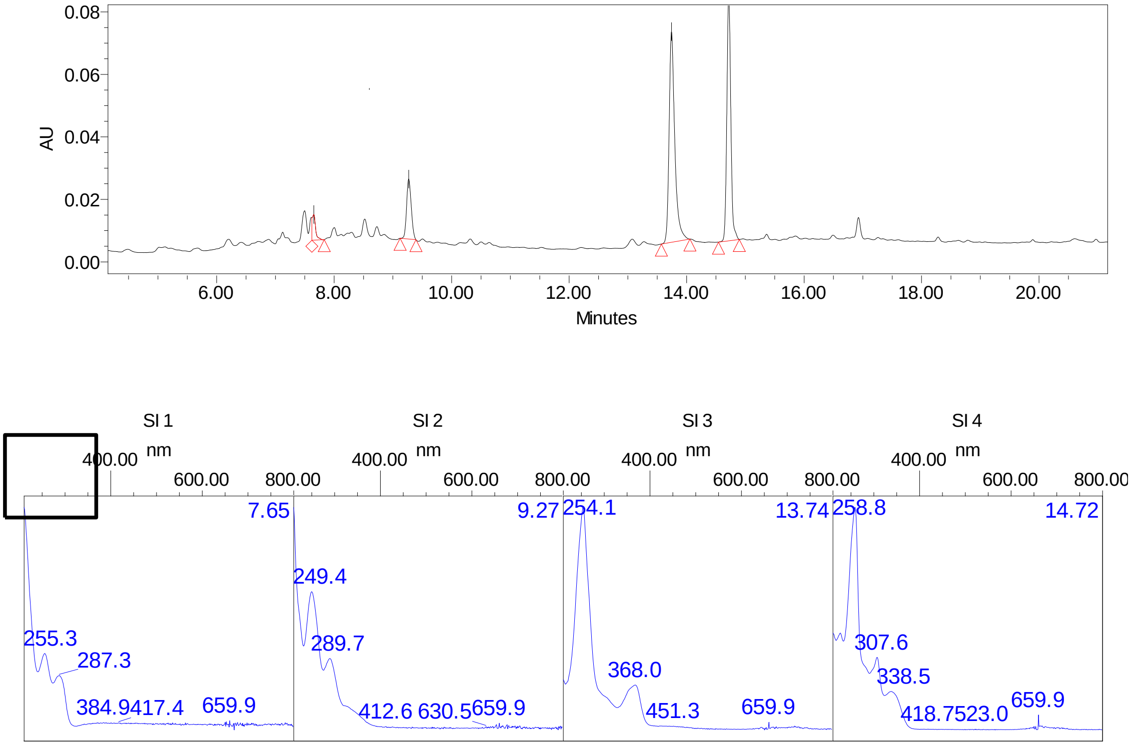

Figure 4. 12 An example of the analytical result of a historical sample (V&A-9-3) dyed by sappanwood and acorn cup, chromatogram monitored at 275 nm

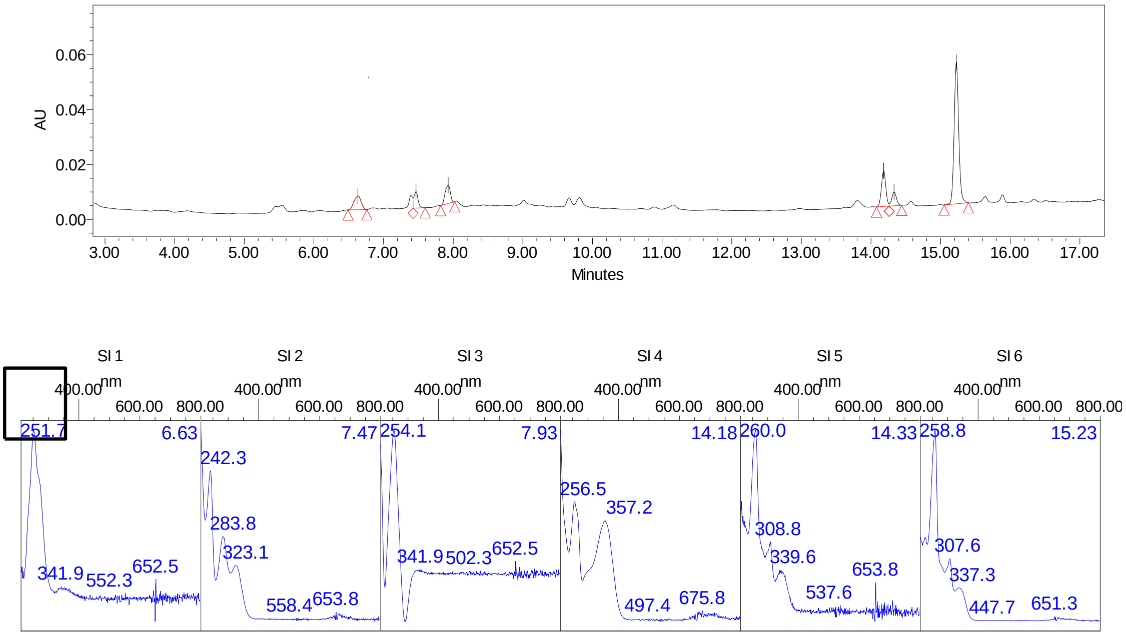

Figure 4. 13 An example of the analytical result of a historical sample (NMS-3-1) dyed by pagoda bud and sappanwood, chromatogram monitored at 254 nm

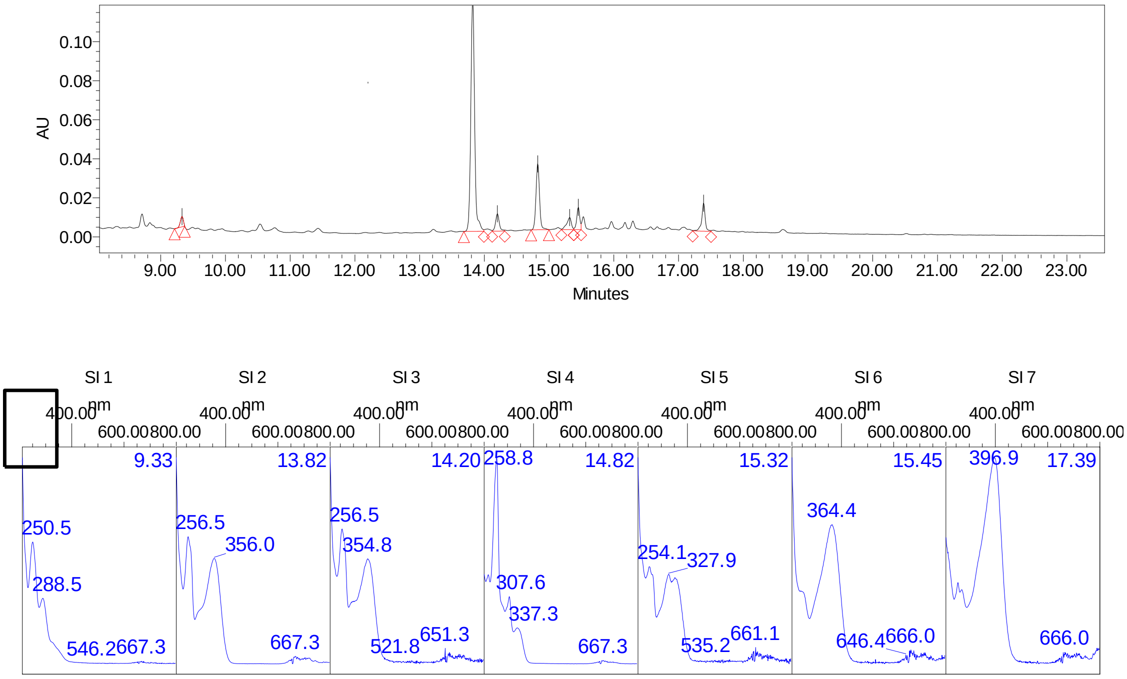

Figure 4. 14 An example of the analytical result of a historical sample (PC-3-5) dyed by three dyes, respectively sappanwood, pagoda bud and smoketree, chromatogram monitored at 350 nm

4.3.1.4 Summary of identified natural dyes and proposed dyeing methods identified from the historical textile samples

The natural dyes most commonly identified from the historical textile samples included safflower, sappanwood, Amur cork tree, pagoda bud, indigo, acorn cup and turmeric. Chinese gallnut, smoketree, lac and cochineal were also found. Based on a thorough review of previous research to date, this is the first time that smoketree and lac have been detected in historical Chinese textiles. The dyes were used alone or with another dye, with specific rules, to obtain certain shades, with occasional cases of using three dyes together.

4.3.2 Synthetic dyes in historical textile samples

4.3.2.1 Introduction to synthetic dyes

Dyes made from chemicals extracted from coal tar and natural materials are classed as synthetic dyes. Technically indigo sulphonic acid, derived by treating natural indigo with sulphuric acid, was the first synthetic dye. It was used commercially in Europe from around 1740.[316] The 19th century was the era of the most significant discoveries and uses of synthetic dyes in Europe and America starting with the yellow dye picric acid which was made from aniline fractioned from coal tar and in commercial use from around 1850. There was also the purple dye murexide, derived from muriatic acid in bird excretions (guano) in commercial use from the 1850s.[317] The synthetic dye that marked the emergence of synthetic dye industry was mauve (also called mauveine, aniline purple and Tyrian purple). It too was derived from aniline extracted from coal tar, and was first synthesised in 1856 by the English chemist W.H. Perkin. By 1857 it was in commercial

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[316] Jaime Wisniak, "Dyes from Antiquity to Synthesis," *Indian journal of history of science* 39, no.1 (2004): 75-100.

[317] Peter JT Morris and Anthony S Travis, "A History of the International Dyestuff Industry," *American Dyestuff Reporter* 81(1992): 59.

production.[318] Since then, synthetic dyes quickly became popular in textile dye industry because of their cheap prices and good colouring effects. A succession of synthetic dyes derived from other fractions of coal tar followed, with many new commercial dyes increasing becoming available to commercial dyers from the 1860s onwards and used alongside natural dyes in Europe and America until the end of the 19th century, when eventually almost all of the natural dyes were superseded by the synthetics.

Synthetic dyes were introduced to China in the late 19th century. The earliest record of a considerable quantity of commercial dyes imported to China found so far is in Shanghai Customs' report that about 2.5 tons of aniline dyes were imported to Shanghai from Europe in 1871.[319] It was also found that in 1885, German company BASF, one of the companies trading with China for the longest period of time, entered Chinese market. After that, more companies entered Chinese market with increasing variety of synthetic dyes.[320] The dates and process by which synthetic dyes were introduced to China still needs further investigation.

Heritage science research for the identification of early synthetic in historical textiles is relatively recent, with a growing need for more research of detailed compositional analysis, and chemical variability through comparative analysis to enable more confidence in the identification of unknowns.[321] The analysis done in this research was a short investigative study, and the data warrants more detailed interpretation of the data to reveal the use of synthetic dyes in China in the 19th century.

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[318] Ibid; Anthony S Travis, *The Rainbow Makers: The Origins of the Synthetic Dyestuffs Industry in Western Europe* (London: Associated University Presses, 1993), 67; Anthony S Travis, Edelstein Center, and Leo Baeck, "Mauve and Its Anniversaries," *Bulletin for the History of Chemistry* 32, no.1 (2007): 35.

[319] Schuyler Cammann, "The Making of Dragon Robes," *T'oung Pao* 40, no.4/5 (1951): 297-321.

[320] Matthijs de Keijzer and Regina Hofmann-de Keijzer, "German Synthetic Dyes Go East and West, Period 1860-1913" (paper presented at *Dyes in History and Archaeology 33*, Glasgow, 2014).

[321] Micaela M Sousa *et al.*, "A Study in Mauve: Unveiling Perkin's Dye in Historic Samples," *Chemistry-A European Journal* 14, no.28 (2008): 8507-8513; Anita Quye and Jing Han, "Typically Variable? A Chemical Study of Commercial Aniline Dyes in a 19th C Sample Book" (paper presented at *Dyes in History and Archaeology 34*, Thessaloniki, 2015); Souto, "Analysis of Early Synthetic Dyes with HPLC-DAD-MS: An Important Database for Analysis of Colorants Used in Cultural Heritage"; van Bommel *et al.*, "High-Performance Liquid Chromatography and Non-Destructive Three-Dimensional Fluorescence Analysis of Early Synthetic Dyes," 260-272.

4.3.2.2 Synthetic dyes identified

Potential synthetic dyes were detected in 20 samples from 11 pieces of historical costume and textiles and altogether 15 samples from 7 pieces were tentatively identified (Table 4. 4). The synthetic dyes identified included three triarylmethane dyes bonded with amine groups including magenta, malachite green and an aniline violet type dye, as well as one nitro dye, picric acid (Figure 4. 15), though further research is needed to clarify the chemical structures of their main dye components. Magenta, one of the most significant early aniline dyes,[322] also turned out to be the dye identified most frequently in these historical samples. It was detected in 8 samples from 7 pieces of textiles. Malachite green and aniline violet type dyes were respectively identified in 3 samples from 2 pieces of costumes and in 4 samples from 2 pieces of costumes. Picric acid was identified in 3 samples, all from one piece of costume. These dyes are either used alone or used with other synthetic or natural dyes.

It is difficult to decide whether an unidentified dye is natural or synthetic, especially when the dye is from textiles of the late Qing Dynasty when synthetic dyes began to be in commercial use in China. It should also be noted that some dye components could be obtained from both natural and synthetic sources, in this research, indigotin. Indigotin was found with magenta in JSL-4-6, dated to Tongzhi period (1862-1874). If the textile is accurately dated, this sample of indigotin must be natural because synthetic indigo was imported to China around 1887,[323] after the time period of this costume. Research is needed to reveal the differences between natural and synthetic indigo so that their detections may help with dating.

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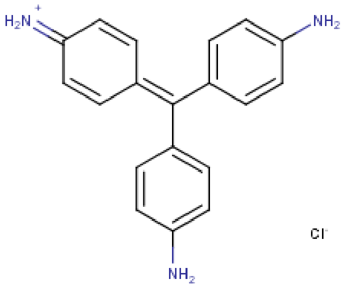
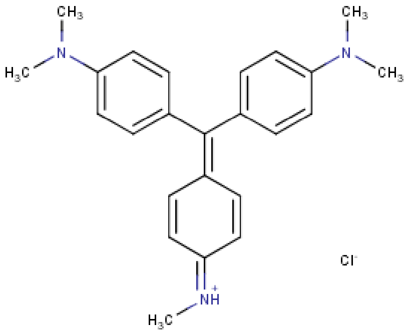
[322] Travis, 67.

[323] Zhenyu Cao, "Hecheng Ranliao Chuanru Woguo Wenti Tanxi," [Study on the Introduction of Synthetic dyes to China], *Market Modernization*, no.33 (2008): 255-256.

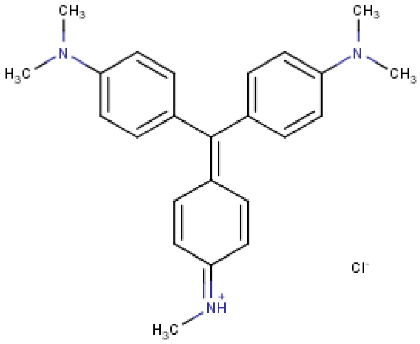
Table 4. 4 Identification results of synthetic dyes in historical samples

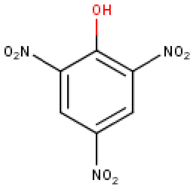
Textile reference code	Sam-ple code	Colour	Use of thread	Proposed dye source(s)
JSL-4	6	dark purple	pattern	magenta (with indigo)
JSL-5	1	dark purple	ground	an aniline violet type dye
	2	light purple	ground	magenta
NMS-1	3	yellow	stitching thread for gold	potentially a synthetic dye
NMS-7	2	brown	ground	magenta of a small amount (with cochineal and acorn cup)
	5	purple	stitching thread	magenta for purple (and turmeric for yellow)
NMS-8	3	green	pattern	picric acid + malachite green
	4	purple	pattern	magenta
	5	yellow	pattern	picric acid (with turmeric)
	6	green	pattern-lace pattern	picric acid + malachite green
	7	pink	ground	potentially a synthetic dye
	8	blue	ground	an aniline violet/blue type dye
NMS-10	1	purple	stitching thread	magenta
NMS-13	4	red	stitching thread	potentially a synthetic dye
TPM-1	1	purple	pattern	an aniline violet type dye
	1	blue	pattern	malachite green + an aniline violet type dye
	2	red	pattern	magenta
TPM-4	1	yellow	ground	potentially a synthetic dye
V&A-8	1	pink	ground	potentially a synthetic dye
V&A-11	2	dark purple	pattern-metal thread edge	magenta





pararosanilin in magenta malachite green





methyl violet picric acid

Figure 4. 15 Main parent molecules of the proposed synthetic dyes

Magenta

Magenta (CI 42510, Basic Violet 14) was a triarylmethane dye first discovered in 1859 and began to be in commercial use in the same year.[324] The reference dyed sample of magenta (K&R, 1893:97) showed four components respectively eluting at 10.45, 12.62, 14.26 and 15.32 min with similar UV-vis absorption spectra, indicating similar chemical structures (Figure 4. 16). Their maximum absorptions are respectively at 543, 545, 549 and 551 nm (with the spectral resolution of 1.2 nm). Seven historical samples with similar chromatographic and spectra characteristics were found, though the relative amounts of the four components are slightly different from the reference sample and the seven historical samples (*e.g.* JSL-5-2, analytical results shown in Figure 4. 17). Since no other reference

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[324] Travis, 67.

dyes accessible so far have similar chromatographic and spectra characteristics, all these seven historical samples were tentatively identified as being dyed with magenta. The reason is as following.

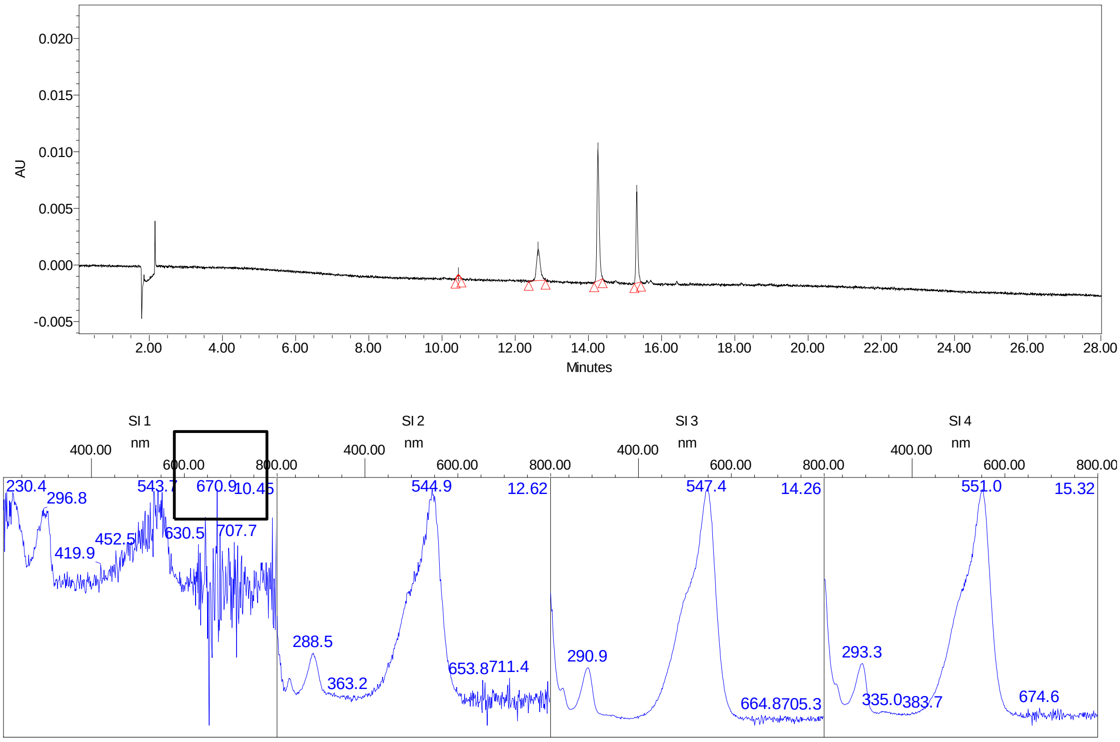

Figure 4. 16 UHPLC-PDA chromatogram (monitored at 515 nm) of the reference magenta and UV-Vis spectra of its main constituents

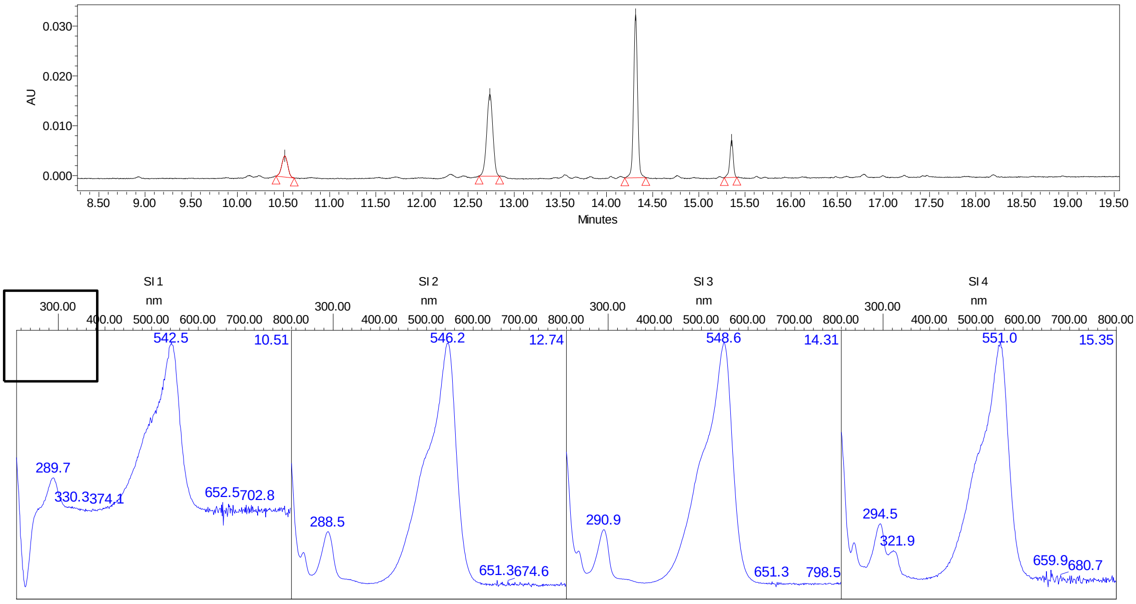

Figure 4. 17 UHPLC-PDA chromatogram (monitored at 515 nm) of JSL-5-2 and UV-Vis spectra of its main constituents

Early synthetic dyes are a complex series of chemical components, arising during their manufacture as by-products and isomers from the synthesis reactions. Different chemical qualities of starting materials as well as unregulated experimental practices in commercial production and use of the early synthetic dyes in the mid- to late 19th century make their chemical composition even more complex.[325] The level of confidence in the identification of a certain synthetic dye is on a case-by-case basis, mainly depending on whether there are other dyes with similar chemical composition. If so, the chemical constituents and their relative amounts of these dye references need to be compared to determine criteria to differentiate them. Further research is needed in this aspect to establish criteria for the accurate identification of synthetic dyes.

Malachite green

Malachite green (CI 42000, Basic Green 4), first synthesised in 1877,[326] is another triarylmethane dye. It is different from the copper mineral malachite, $Cu_2CO_3(OH)_2$, with the dye having been named to indicate its colour rather than chemical composition. The reference of malachite green dyed wool sample from the reference manuscript was mainly composed of two co-eluting blue components (maximum absorption at 607 and 620 nm respectively) and two yellow components (maximum absorption at 354 and 362 nm respectively) (Figure 4. 18). All the four components were detected in three historical samples, NMS-8-3, 8-6 (Figure 4. 19), and TPM-1-1-blue, though there are differences in the area ratio between the blue peaks and the main yellow peak among the reference sample and the three historical samples. The green dyes in the three historical samples were tentatively identified as malachite green.

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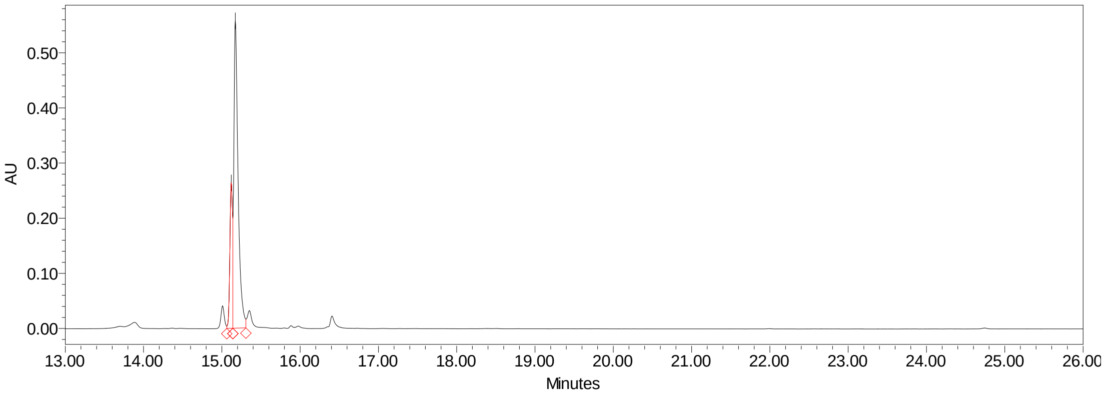
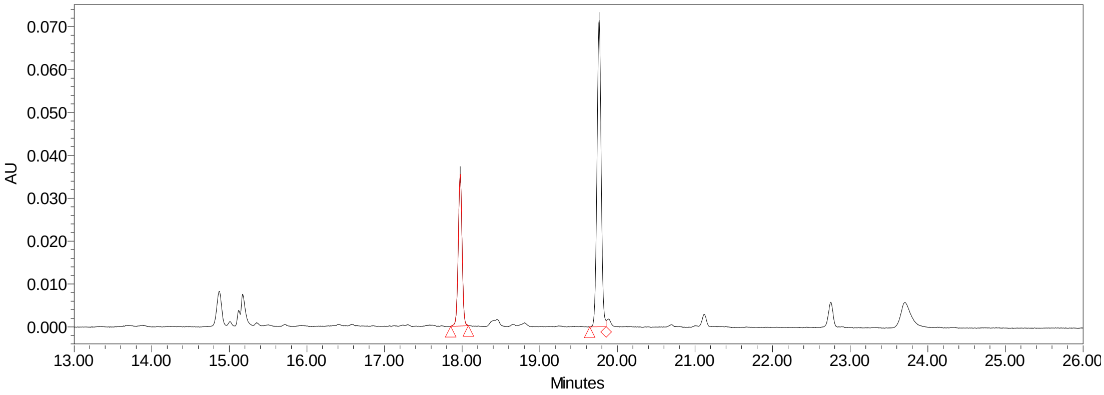
[325] Quye and Han, "Typically Variable? A Chemical Study of Commercial Aniline Dyes in a 19th C Sample Book."

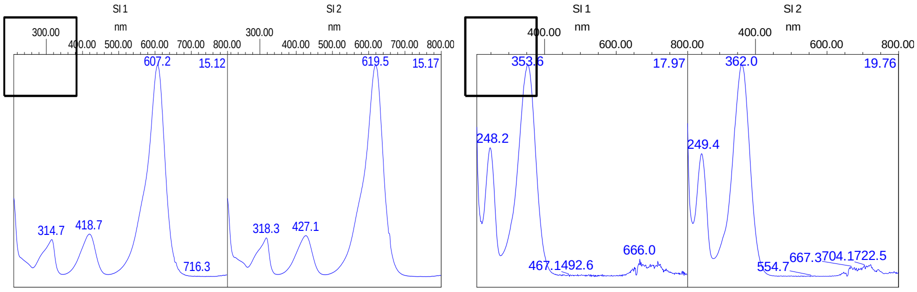
[326] Society of Dyers and Colourists and American Association of Textile Chemists and Colorists, vol. 4, 4380.



(a) 610 nm

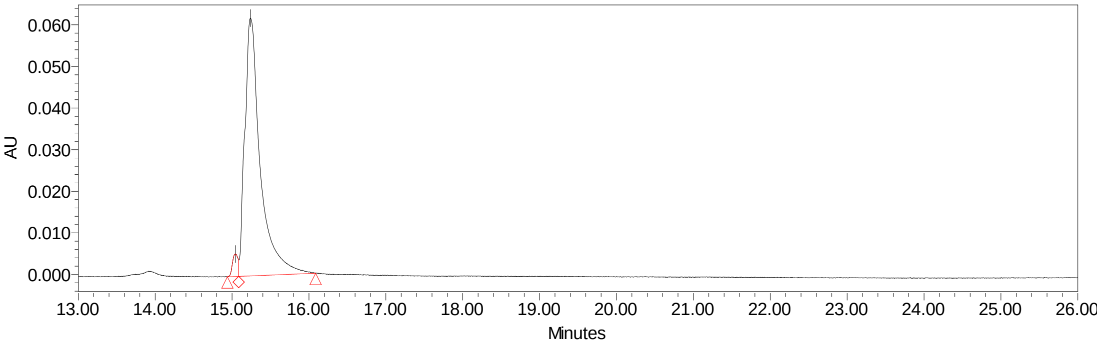


(b) 350 nm

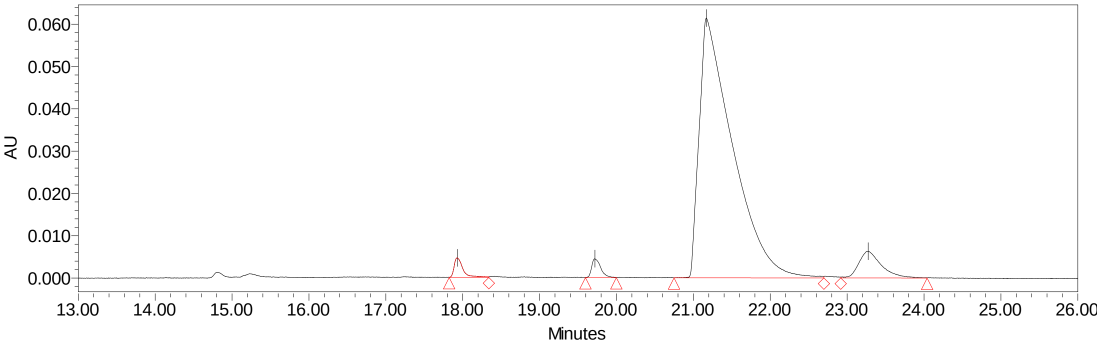


(c) UV-vis spectra of its main components

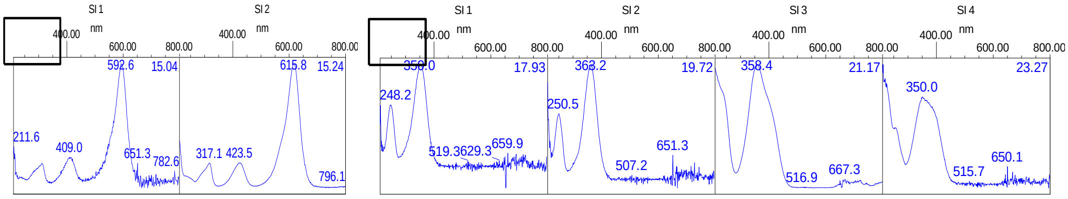
Figure 4. 18 UHPLC-PDA chromatogram (monitored at 350 nm, shown in black, and at 430 nm, shown in blue) of malachite green and UV-Vis spectra of its main constituents, including two blue components eluting at around 15 min and two yellow components eluting at 18.0 and 19.8 min



(a) 610nm



(b) 350nm , showing two yellow peaks of malachite green, followed by two yellow peaks of picric acid



(c) UV-vis spectra of its main components

Figure 4. 19 An example of the analytical result of a historical sample (NMS-8-6) dyed by malachite green and picric acid (see the section of picric acid)

Aniline violet type dye

Similar to magenta and malachite green, aniline violet dyes are also of triarylmethane group. A large amount of types of aniline violet dyes were produced. In the Colour Index (Vol. 5, 1976 edition) dozens of similar dye names were recorded in C.I. Basic Violet dyes which vary from Aniline Violet (CI 42535, Basic Violet 1) to Methyl Violet (of the same CI number and CI name with Aniline Violet), Methyl Violet 6B (CI 42555, Basic Violet 3), *etc*.[327] Among these dyes the earliest one, Methyl Violet (CI 42535) was first synthesised in 1861 and was in commercial use from 1866.[328] In the reference manuscript *The English dyer, with instructions on how to dye* there are dozens of types of dyed samples with names including ‘aniline violet’ and ‘aniline purple’, such as Aniline purple R and Aniline violet BB. Chemical analysis of these samples showed that they all contain a series of similar components but the chemical structures and relative amounts of the components vary slightly from sample to sample.[329] Similar chromatographic and spectral characteristics were detected in JSL-5-1 and TPM-1-1 (Figure 4. 20 and Figure 4. 21). Since these reference dyes are not yet differentiated, the dyes in the two historical samples were tentatively identified as aniline violet type dyes.

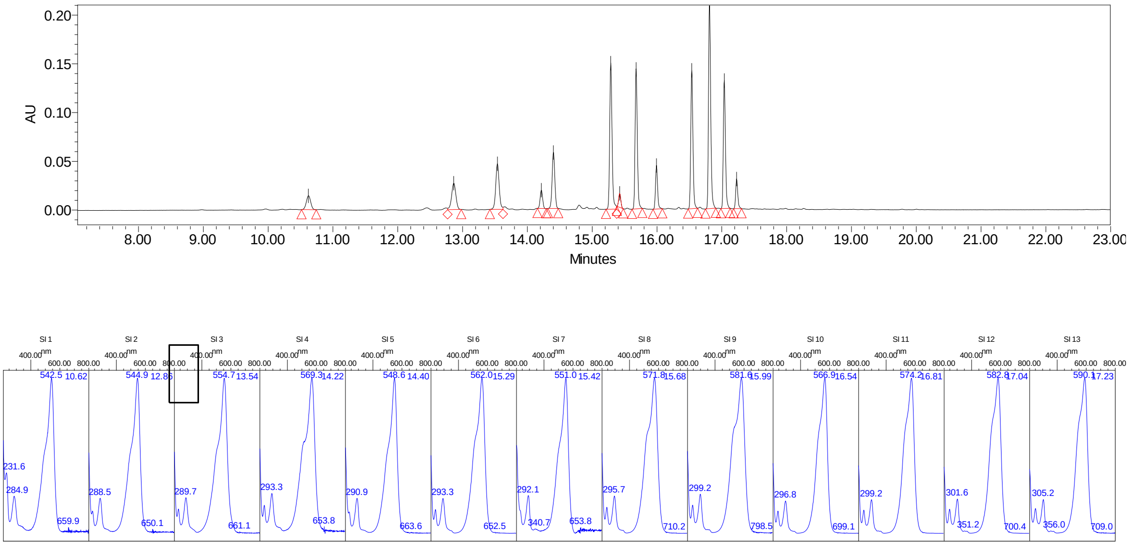


Figure 4. 20 UHPLC-PDA chromatogram (monitored at 515 nm) of JSL-5-1 and UV-Vis spectra of its main constituents

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[327] Society of Dyers and Colourists and American Association of Textile Chemists and Colorists, vol. 4, 5082.

[328] Walter M. Gardner, *The British Coal-Tar Industry Its Origin, Development, and Decline* (London: Williams and Norgate, 1915), 172-3.

[329] Quye and Han, "Typically Variable? A Chemical Study of Commercial Aniline Dyes in a 19th C Sample Book."

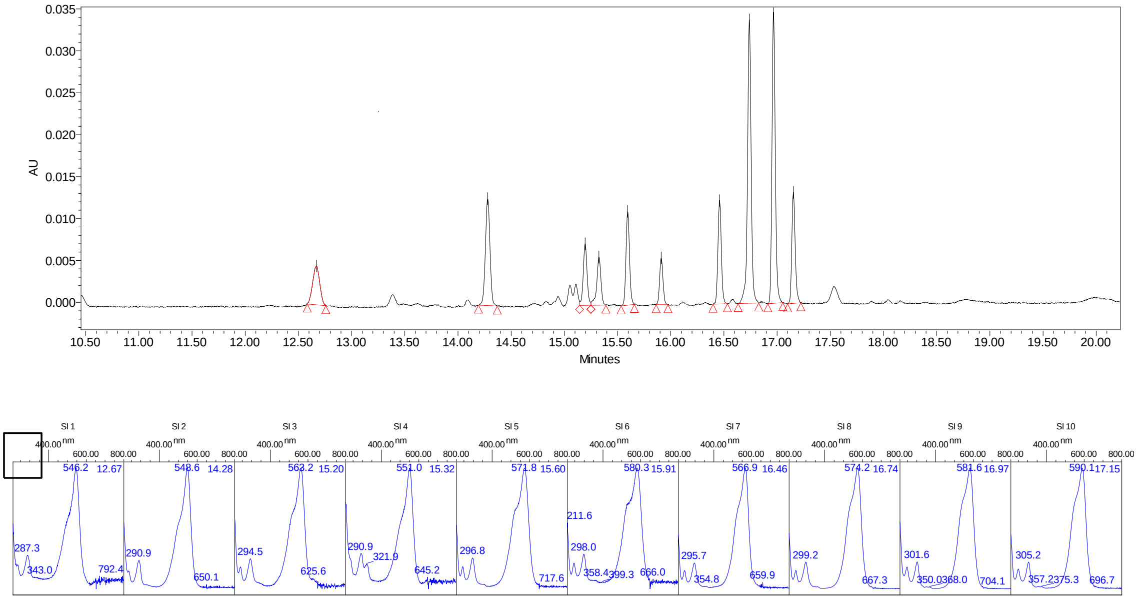

Figure 4. 21 UHPLC-PDA chromatogram (monitored at 515 nm) of TPM-1-1 and UV-Vis spectra of its main constituents

Picric acid

Picric acid is a nitro dye (CI 10305, Acid Dye). It was first synthesised in 1771 by nitration of natural indigotin and then in the 1840s by nitration of phenol from coal tar, the latter leading to its commercial use from around 1850.[330] The chromatogram for the picric acid dyed silk reference in the reference manuscript (called canary in the manuscript) showed two peaks at 21.5 and 23.4 min, with maximum spectral absorption respectively at 358 and 351 nm (Figure 4. 22). The two peaks of picric acid are tailing probably because the dye components with nitro groups are in both forms of molecule and ion in the current system. Three historical samples (NMS-8-3, NMS-8-5 and NMS-8-6) have similar chromatographic and spectra characteristics (Figure 4. 19). Again, the relative amounts of the two components vary among the reference sample and the three historical samples. Nevertheless, picric acid was tentatively identified in the three samples of NMS-8.

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[330] Morris and Travis, "A History of the International Dyestuff Industry," 59; Andrea Bowes, Esther Méthé, and Mary W Ballard, "Important Early Synthetic Dyes: Chemistry, Constitution, Date, Properties," http://www.si.edu/mci/downloads/reports/IESD-CCDP1991.pdf; van Bommel *et al.*, "High-Performance Liquid Chromatography and Non-Destructive Three-Dimensional Fluorescence Analysis of Early Synthetic Dyes," 260-272.

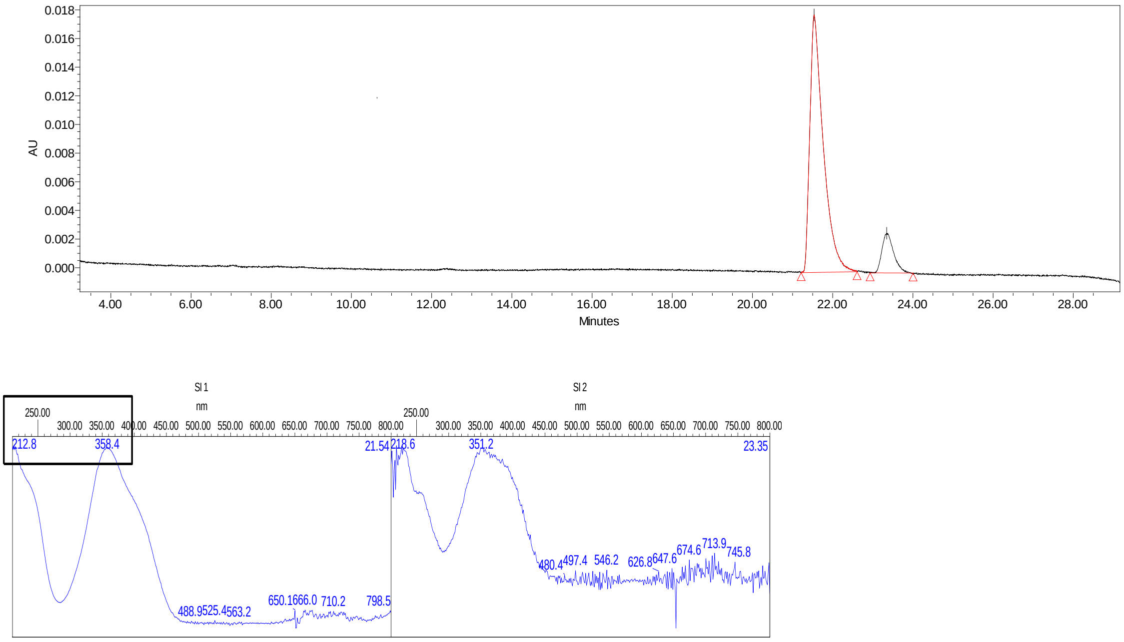

Figure 4. 22 UHPLC-PDA chromatogram (monitored at 350 nm) of reference silk sample dyed by picric acid and UV-Vis spectra of its main constituents

4.3.2.3 Dyeing methods involving synthetic dyes

Among the cases where synthetic dyes were identified, the synthetic dyes are used alone or in combination with other natural or synthetic dyes to obtain certain shades. The combination of picric acid and malachite green was found in a dyed wool reference sample named as aniline green in the Smith book and in historical samples NMS-8-3 and 6. Other examples for the combination of two dyes include magenta and indigo for a purple shade for JSL-4-6 and picric acid and turmeric for yellow for NMS-8-5. The only historical sample identified to be dyed with three dyes including synthetic dyes is from the dancer's skirt NMS-7-2, where a brown ground colour is obtained by a mixture of magenta, cochineal and ellagic acid. The method of using three dyes to achieve specific brown shades is similar with that used for natural dyes.

4.3.2.4 Dating the textiles with synthetic dyes

The identification of synthetic dyes can tentatively date a textile if dates for the beginning of the commercial use of the synthetic dyes are relatively clear. As described above, magenta began to be in commercial use in 1859, aniline violet dyes from 1866 and picric acid from around 1850. When malachite green began to be put into the market was not certain, but 1877, the year for its first synthesis, could be referenced for dating.[331] It should be noted that when these synthetic dyes were first introduced to China and when they began to be put into the Chinese market were not certain, though the earliest date known so far when a considerable quantity of commercial dyes were imported to China is 1871, followed by more evidence of the import of dyes to China in 1880s.[332] Since more research is needed to reveal the exact dates the synthetic dyes were imported to China, in this research the costume and textiles with synthetic dyes were tentatively dated using mainly the date the synthetic dyes began to be in commercial use in Europe. The year 1856 when mauve was invented, which marked the emergence of synthetic dye industry, was temporarily used as the earliest date for the use of the potentially synthetic dyes detected in this research.

Table 4. 5 presents the updated dating for the costume and textiles with synthetic dyes. For three pieces of costumes the original dating were improved, and for another four pieces, their updated dating is in accordance with original dating. The earliest date for NMS-8 and TPM-1 could be updated to 1877 with the detection of malachite green, and that for NMS-7 could be updated to 1859 with the detection of magenta.

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[331] Society of Dyers and Colourists and American Association of Textile Chemists and Colorists, 4380; Estrella Sanz Rodríguez *et al.*, "Characterization of Natural and Synthetic Dyes Employed in the Manufacture of Chinese Garment Pieces by LC-DAD and LC-DAD-QTOF"; Keijzer and Keijzer, "German Synthetic Dyes Go East and West, Period 1860-1913"; Zhenyu Cao, "Zhongguo Jindai Hecheng Ranliao Shengchan Ji Ranse Jishu Fazhan Yanjiu" (PhD thesis, Donghua University, 2008); Morris and Travis, "A History of the International Dyestuff Industry," 59.

[332] Cammann, "The Making of Dragon Robes," 297-321; Keijzer and Keijzer, "German Synthetic Dyes Go East and West, Period 1860-1913"; Cao, 255-256.

Table 4. 5 Dyes identified in individual pieces of textiles and updated dating of these textiles

Textile reference code	**Access-ion number**	**Title**	**Original dating**	**Synthetic dyes identified**	**Beginning of comm-ercial use or date for first synthesis**	**Proposed updated dating**
JSL-4	—	Dragon robe	Tongzhi period (1862-1874)	magenta	1859	in accordance with original dating
JSL-5	—	Pair of sleeve bands	Guangxu period (1871 - 1908)	magenta and an aniline violet type dye	1859 and 1866	in accordance with original dating
NMS-1	A.1971. 675	Dragon robe	late 18th century	potentially a synthetic dye (for a stitching thread sample)	1856 if the uniden-tified dye is synthetic	— (Uncertain if the stitching thread is original or not.)
NMS-7	A.1929. 70	Dancer's skirt	19th century	magenta	1859	more accurate dating to 1859
NMS-8	A.1979. 201	Woman's robe	19th century	magenta, picric acid, malachite green, an aniline violet/blue type dye and a potentially synthetic dye	1859, around 1850, 1877, 1866 and 1856 if the unidentified dye is synthetic	more accurate dating to 1877
NMS-10	A.1966. 511	Woman's skirt	19th century	magenta (for a stitching thread sample)	1859	more accurate dating to 1859 if the stitching thread is original

Table 4. 5 Dyes identified in individual pieces of textiles and updated dating of these textiles (continued)

NMS-13	A.1961.545	Women's robe	19th - 20th century	potentially a synthetic dye (for a stitching thread sample)	1856 if the unidentified dye is synthetic	— (Uncertain if the stitching thread is original or not.)
V&A-8	T.45-1933	Theatre costume	1880-1930	potentially a synthetic dye	1856 if the unidenti-fied dye is synthetic	in accordance with original dating
V&A-11	T.753-1950	Court robe with dragon	1875 -1908 (made)	magenta	1859	in accordance with original dating
PM-1	—	Dragon robe for a Buddha sculpture	late Qing Dynasty	magenta, malachite green and an aniline violet type dye	1859, 1877 and 1866	more accurate dating to 1877

Much caution is needed when dating by synthetic dyes used for stitching threads because of the possibility that the stitching threads were added later for conservation purpose, especially when synthetic dyes were not used for the rest parts of the textiles. For example, from NMS-10, three samples were analysed and results show the stitching thread is dyed by magenta, the two samples taken from its ground and lining are dyed by natural dyes. It is possible that the stitching thread was added later for conservation. Similarly, in NMS-1 and NMS-13, only samples from their stitching threads were found to be dyed by a synthetic dye and the rest of the dyes analysed from the two pieces of robes were all identified as natural dyes. Investigation of the fibre type of these stitching threads and the way they were stitched may confirm whether they were added later or not.

Moreover, the proportion of samples dyed by synthetic dyes may help the provenance and dating of the textiles (when an enough amount of samples is taken). In JSL-4 (dated to Tongzhi period, 1862-1874) only the purple sample is dyed by magenta and indigo together and the other 5 samples are dyed by natural dyes, probably because the robe was made not long after the first synthetic dye was invented, and it took some time for synthetic dyes to be imported to China.[333] Another possible reason is the bright purple was an unusual colour in traditional Chinese palette and thus synthetic dyes were used.[334] In contrast, almost all the dyes identified in NMS-8 are synthetic, indicating later production date. The only natural dye identified in this robe is turmeric, possibly due to the low price of turmeric. The sharp change in the proportion of synthetic dyes used also shows the process of synthetic dyes replacing natural dyes.

The identification results help support and clarify some knowledge of synthetic colours on Chinese costumes. Schuyler Cammann's work in 1951 says that bright reddish purple and vivid green were popular in later embroideries and presents their analysis results by absorption spectra and chemical reaction tests – the bright purple made of methyl violet 2b, and the vivid green of malachite green and picric acid.[335] Analysis results from this research complement for the dye sources for bright purple: The three vivid purple from JSL-4 and JSL-5 are respectively dyed by an aniline violet type dye, magenta and a mixture of magenta and indigo. The analytical results from samples from NMS-8-3 and 6 confirmed that the vivid green shades were dyed by a mixture of malachite green and picric acid.

4.3.2.5 Summary of synthetic dyes in historical textile samples

To date, synthetics have been identified on a limited number of Chinese costumes of the

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[333] Keijzer and Keijzer, "German Synthetic Dyes Go East and West, Period 1860-1913."

[334] Yun Zhu and Xiuzhi Zhu, "Zise Zai Zhongguo Gudai Fuse Zhong De Liubian Ji Qi Wenhua Neihan," [The change of purple in ancient Chinese costume and its cultural connotation], *Journal of Hotan Teachers College* 9, no.3 (2009): 54-56.

[335] Cammann, "The Making of Dragon Robes," 297-321.

Qing Dynasty.[336] Dyes tentatively identified in the historical samples in this research include magenta, picric acid, malachite green and aniline violet type dyes. The data from this study adds further knowledge to the use of synthetic dyes on 19th century Qing Dynasty textiles to build a better picture of the use of early synthetic dyes in China. The findings shed light on the use of early synthetic dyes in late Qing Dynasty and would be a good foundation for further work.

4.3.3 Metal threads in historical textile samples

4.3.3.1 Sample V&A-5-3

Sample V&A-5-3 (Figure 4. 23) is a metal thread with yellow silk thread core, the metal part separated probably made by sticking metal stripes to paper stripes by red glue.[337] To investigate their chemical compositions, spot 10 from the metal layer and area 12 from the red glue layer were analysed.

Figure 4. 23 Micrograph of a metal thread sample V&A-5-3

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[336] Estrella Sanz Rodríguez *et al.*, "Characterization of Natural and Synthetic Dyes Employed in the Manufacture of Chinese Garment Pieces by LC-DADand LC-DAD-QTOF"; Zhenyu Cao, "Yong UPLC-MS Jishu Fenxi Jianding Zhipin Zhong De Jiajizi Ranliao," [Identification of methyl violet dyes in fabrics by UPLC-MS], *Shanghai Textile Science & Technology*, no.8 (2008): 55-57; Cammann, "The Making of Dragon Robes," 297-321.

[337] Qian, 77-82.

On spot 10 from the metal layer (Figure 4. 24), large proportion of gold and small proportion of aluminum, silver and iron were detected. In general natural gold can contain up to 30% silver, which remains in the melting process, and the investigation of traditional Chinese gold craftsmanship shows that silver and sometimes copper are added to alter the colour and characteristics of the gold alloy.[338] This metal thread is probably a gold-silver alloy. Aluminum and iron, together with oxygen and silicon detected may be from the red glue layer underneath (consistent with the following analytical result of area 12 from the glue layer).

The analytical result of the area 12 (Figure 4. 25) from the red glue layer shows that aluminium, silicon, carbon and oxygen were its main elements, followed by iron, calcium and sulfur. In ancient China when making metal threads a special kind of glue, mainly composed of red powder, white clay, vegetable oil and bone glue, was applied to stick metal stripes to paper stripes.[339] Judged from the detected elemental composition of the area 12 and the chemical composition of common red pigments used in ancient China, the red powder is probably hematite (Fe_2O_3).[340] The aluminium, silicon, oxygen and small amounts of calcium and sulfur detected may be from the clay.[341] The organic components of the glue reflect in carbon and oxygen. Therefore, the analytical result of the glue layer confirms current knowledge about tradition metal thread making and helps further identify its chemical composition.

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[338] Haiping Lian, "Chuantong Jinbo Zhizuo Gongyi Diaocha Yanjiu," [Investigation of traditional gold craftsmanship], *Sciences of Conservation and Archaeology* 12, no.14 (2002): 335-348.

[339] Qian, 77-82.

[340] Ibid.

[341] Alfred R. Conklin, *Introduction to Soil Chemistry: Analysis and Instrumentation*, 2nd ed., (Hoboken, N.J.: Wiley-Interscience, 2005), 45-53.

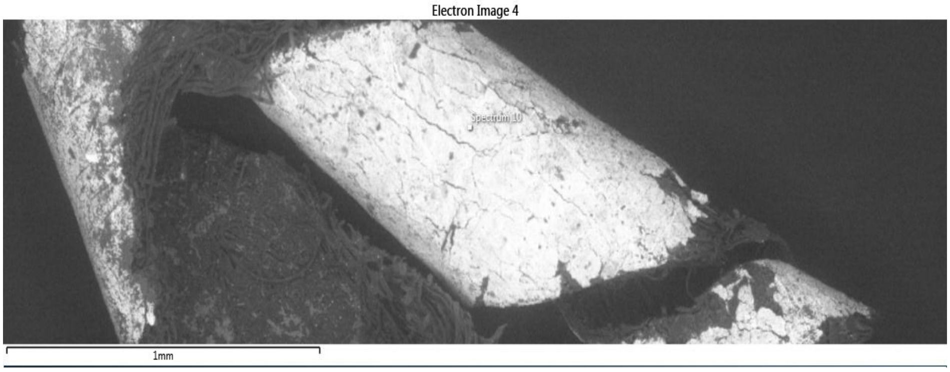


Figure 4. 24 Backscatter electron (BSE) images of sample V&A-5-3 showing spot 10 analysed

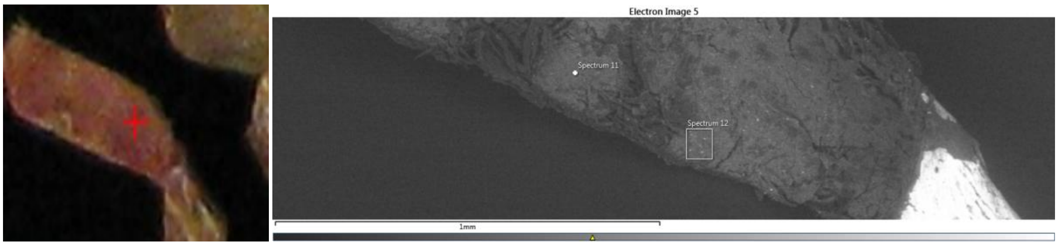
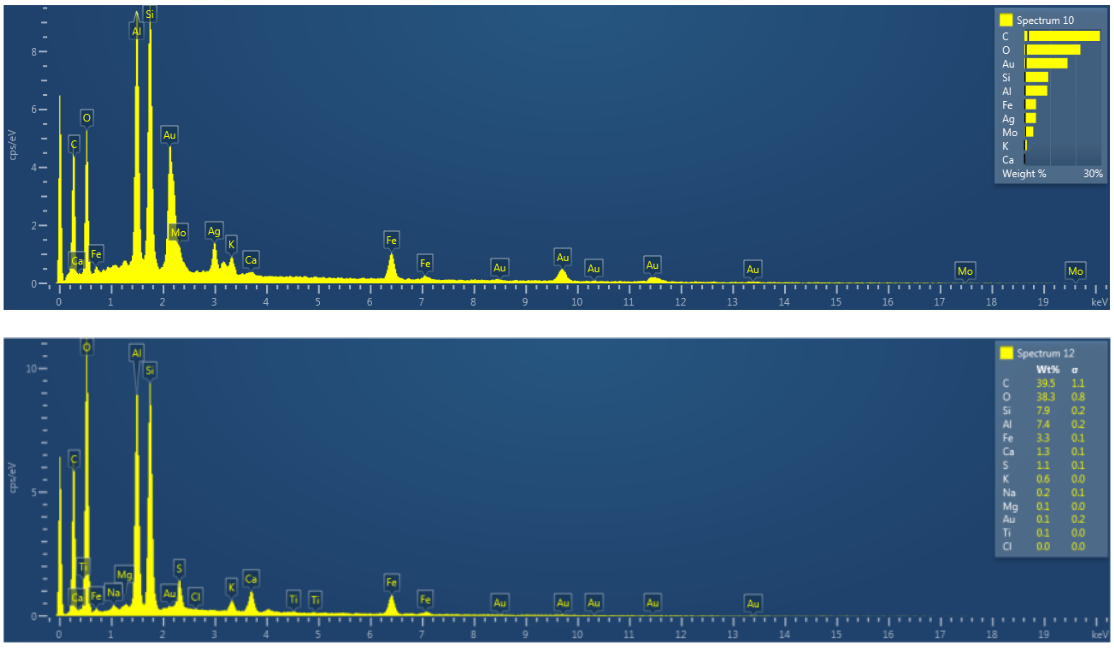


Figure 4. 25 Micrograph of the red layer of the sample V&A-5-3 and its corresponding BSE image showing the location of area 12 analysed



Spectrum 12

	Wt%	σ
C	39.5	1.1
O	38.3	0.8
Si	7.9	0.2
Al	7.4	0.2
Fe	3.3	0.1
Ca	1.3	0.1
S	1.1	0.1
K	0.6	0.0
Na	0.2	0.1
Mg	0.1	0.0
Au	0.1	0.2
Ti	0.1	0.0
Cl	0.0	0.0

Figure 4. 26 SEM-EDX spectra of spot 10 from the metal layer and area 12 from the red layer of the sample V&A-5-3

4.3.3.2 Sample V&A-2-1

Spot 20 from the metal layer of the metal thread sample V&A-2-1 (Figure 4. 27) was analysed and its main metal component is gold, followed by silver, indicating the metal is another gold-silver alloy (Figure 4. 28). Spot 19 from underneath the metal layer is of similar elemental composition with spot 12 from the red glue layer of the sample V&A-5-3, plus some traces of gold and silver, presumably from the upper layer.

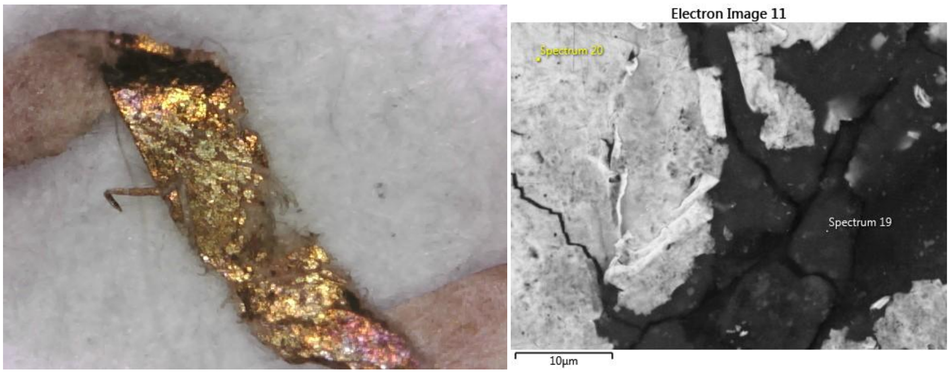


Figure 4. 27 Micrograph and BSE image of sample V&A-2-1

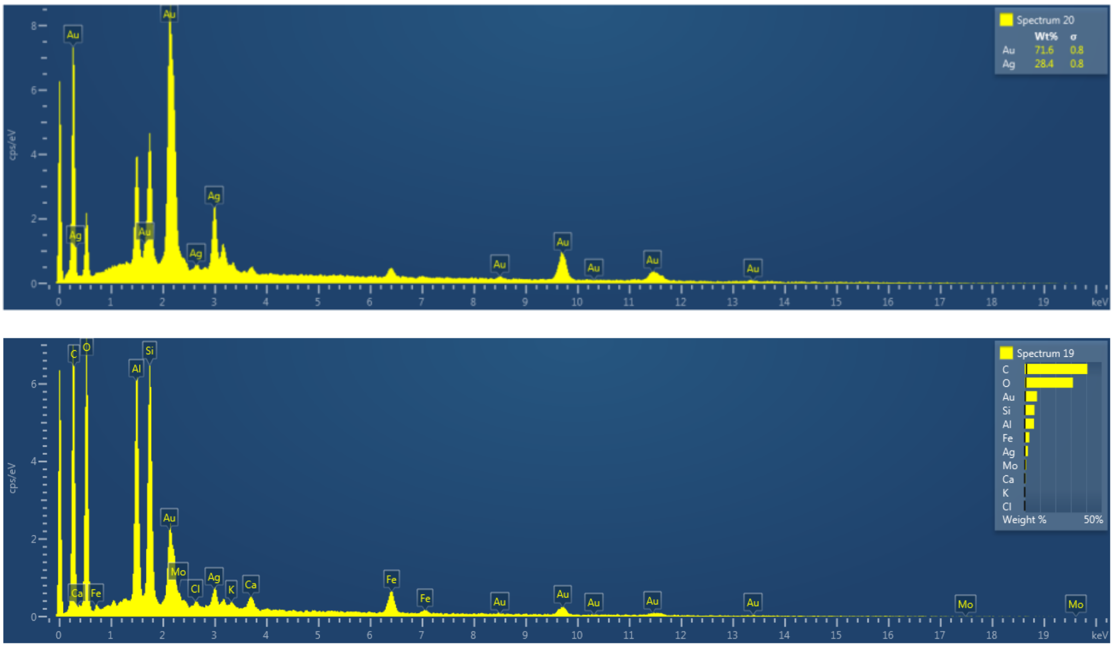


Figure 4. 28 SEM-EDX spectra of spots 20 and 19 of the sample V&A-2-1

In summary, analytical results of the two metal threads showed that the metal threads are all alloys and are mainly composed of gold, with a small amount of silver and sometimes copper present. Hematite was identified as an ingredient for the red glue of two metal thread samples. This is the first report identifying red powder used with glue for metal threads making in China.

4.3.4 Natural dyes in archaeological textile samples

The analysis of archaeological dyes can be very challenging because of the usually poor preservation state of the dyes, especially in wet or alternating wet and dry burial environment. These kinds of burial environments significantly accelerate the degradation of dyes by the participation of water in the degradation process of dyes and by bringing acids and alkalis from the surrounding environment. Water also tends to carry some dye components and degradation products away from their original fibres. Besides, microorganisms that decompose dyes and textiles are more likely to grow in a humid environment. The change of environment during excavation also accelerates the ageing process of dyes. As a result, many fewer dye components survive in archaeological samples than in historical samples. Moreover, various contaminations from burial environment can be present, adding to the difficulty of dye identification.[342] Nevertheless, in the last decade there has been growing research on archaeological dyes in China and worldwide and increasing knowledge has been obtained in terms of the preservation state, analytical protocols and identification of archaeological dyes.[343] The main analytical

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[342] W. Nowik *et al.*, "The Analysis of Dyestuffs from First - to Second - Century Textile Artifacts Found in the Martres-De-Veyre (France) Excavations," *Archaeometry* 47, no.4 (2005): 835-848.

[343] Liu *et al.*, "Identification of Ancient Textiles from Yingpan, Xinjiang, by Multiple Analytical Techniques," 1763-1770; Bai, "Chaoshi Muzang Huanjing Zhong Chutu Sizhipin De Zhiwu Ranliao Jianding Jishu Yanjiu"; Keijzer *et al.*, "Yellow Silk for Buddha – Dye Analysis on Tang Dynasty Textiles from the Famen Temple near Xi'an, Shaanxi Province, China" (paper presented at *Dyes in History and Archaeology 33*, Glasgow, 2014); W. Nowik *et al.*; I. Surowiec, Anita Quye, and M. Trojanowicz, "Liquid Chromatography Determination of Natural Dyes in Extracts from Historical Scottish Textiles Excavated from Peat Bogs," *Journal of Chromatography A* 1112, no.1 (2006): 209-217; Christel M Baldia, "Development of a Protocol to Detect and Classify Colorants in Archaeological Textiles and Its Application to Selected Prehistoric Textiles from Seip Mound in Ohio" (PhD thesis, The Ohio State University, 2005).

method used is HPLC coupled with MS or PDA, or sometimes MS alone. Based on studies in dye recovery methods, these micro-destructive methods helps the detection of dye components on archaeological samples to a large extent by extracting and accumulating dye components in sample preparation through drying/evaporating and reconstituting dye extracts and filtering away insoluble constituents. This is especially important for archaeological samples because they are usually more contaminated and of lower concentration, as discussed above. Additionally, the separation function of HPLC allows better detection of different components. Though it is hard to say with confidence what the original colour would be because archaeological textiles can lose important markers, and we cannot be sure that all the dye components that were originally present are detected, the identified dye components would still help interpret possible original colours of the textiles. Meanwhile, together with the above methods to identify dyes, other analytical methods were applied to the study of archaeological textile samples including optical microscopy and SEM to know about the morphology and elemental composition of the samples, and Fourier transform infrared spectroscopy (FTIR) to identify fibre types of the textiles.

Analytical results show that characteristic components of natural dyes were detected in most of the samples from the two archaeological sites of the Qing Dynasty, while smaller portions of dye components were detected in the samples from the two archaeological sites of the Ming Dynasty. No synthetic dyes were found, which is consistent with the dates for the four archaeological sites (all earlier than the 19th century). The success rate of dyes identified was not calculated for archaeological dyes because it is uncertain whether characteristic components for all the dyes originally present were detected, and some samples may not have been dyed at all. Detailed information on the four archaeological sites and the textiles where samples were taken and the analytical results of the archaeological samples are presented as follows.

4.3.4.1 Shijingshan Tomb

This tomb, in soil, where textiles for sampling come from is located in Shijingshan District, Beijing. The tomb was excavated in 2006. It was found that the owner of the tomb was a 1st grade military official of the mid-Qing Dynasty. A coin of the Kangxi period (1662-1722) was found, therefore the date of the tomb is no earlier than Kangxi period. The coffin was sealed well and the clothes of the mummy were dry. There was body fluids contamination on the clothes. Due to humid climate, after excavation moulds grew rapidly on the textiles. Water, organic solvents and additives were used to clean the textiles, as described in the published conservation reports.[344] Most of the textiles only have light shades, except for relatively intense blue shade on some of the costumes and accessories. A boot and a hat that were sampled also had intense colour. Samples from clothes, accessories and a quilt bag were taken (Table 4. 6). Most of the samples are silk, except for a wool hat and a pair of cotton trousers.

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[344] Chao Chen, "Beijing Shi Shijingshan Qu Chutu Qingdai Ganshi Chaodai Hebao Xiufu Yanjiu Baogao [Conservation Report for a Court Ribbon and Purses of a Mummy of the Qing Dynasty Unearthed in Shijingshan District, Beijing]," http://www.bjww.gov.cn/2012/12-27/1356580605718.html; Chao Chen, "Beijingshi Shijingshanqu Chutu Qingdai Ganshi Fushi Qingli Baohu [Cleaning and Conservation of the Costumes of a Qing Mummy Excavated in Shijingshan District, Beijing]," in *Wenhua Yichan Yanjiu*, ed. Chinese Academy of Social Sciences Institute of Archaeology (Beijing: Science Press, 2013), 86-106.

Table 4. 6 List of textiles sampled from Shijingshan tomb

Textile reference code	**Title of textile**	**Description**	**Photo**
SJS-1	Waistband	Light yellow waist band	
SJS-2 & SJS-7	Hat	Yellow wool hat	
SJS-3	Accessory	A purse and a thumb ring bag	
SJS-4	Quilt head	Dark yellow damask quilt head	
SJS-5	Boot	Black satin boot with white lining	
SJS-6	Underpants	Light yellow underpants	
SJS-8	*Mang* robe	Court robe with a *kirin* badge	
SJS-9	Cotton trousers	Cotton trousers	

Images in this table © Cultural Heritage Institute of Shijingshan District, Beijing

Table 4. 7 shows detailed information on the samples from Shijingshan tomb and their analytical results. Among the 18 samples from this site, dye sources for 12 of them were identified. Altogether four dyes were identified: indigo, sappanwood, Amur cork tree and

ellagic acid (indicating probable dye source of acorn cup). All of them are common dyes used for single-dyeing and multi-dyeing in the Qing Dynasty.

Table 4. 7 Analytical results of the archaeological samples from Shijingshan tomb

Textile reference code	Sample code	Colour	Use of thread	Major dye components identified	Possible dye source(s)
SJS-1	1	light yellow	background	no characteristic dye components detected	
SJS-2 & 7	1	yellow	hat body	berberine, unknown orange and yellow colourants	Amur cork tree + ?
	2	brown	web	berberine and its equivalents, Nowik type C component, ellagic acid, indigotin, indirubin	Amur cork tree is the main dye. Sappanwood, ellagic acid and indigo may be also present.
	3	dark yellow	stitches	berberine and its equivalents, Amur cork tree components	Amur cork tree
	4	dark yellow	hat body	berberine and its equivalents	Amur cork tree
SJS-3	1	light yellow	pattern	trace amount of Nowik type C component, unknown colourless components	possibly sappanwood
	2	light yellow	ribbon of the thumb ring bag	isatin, indigotin and indirubin	indigo (probably from the blue part on the bag)
	3	light yellow	lining	no characteristic dye components detected	

Table 4.7 Analytical results of the archaeological samples from Shijingshan tomb (continued)

	4	light yellow	lining	indigotin, indirubin, isatin, Nowik type C component	indigo and sappanwood
	5	light yellow	ribbon end	no characteristic dye components detected	
SJS-4	1	dark yellow	background	no characteristic dye components detected	
SJS-5	1	white	lining	indigotin, isatin, trace amount of ellagic acid	indigo and ellagic acid, probably both from the front side
	2	black	bottom	indigotin, ellagic acid	indigo and ellagic acid
SJS-6	1	light yellow	background	no characteristic dye components detected	
SJS-8	1	light red	standing wave	Nowik type C component and ellagic acid	sappanwood, ellagic acid
	2	yellow	standing wave	ellagic acid, Nowik type C component, trace amounts of indigotin and indirubin	sappanwood, ellagic acid, trace indigo contamination
	3	yellow	same as 8-2, twisted	no characteristic dye components detected	
SJS-9	1	light yellow, with blue	quilting lines	indigotin	indigo, probably contamination

For the hat SJS-2 (Figure 4. 29), Amur cork tree was found for the hat body and the stitching thread, in accordance with their yellow colours. For the brown web inside the hat used to fix the wool threads, Amur cork tree was found as the main dye, and small amounts of ellagic acid, sappanwood and indigo were also present. This combination is in accordance with dye recipes in *Zhiraju buce* and *Bu jing*, where four dyes were used together to achieve dark shades. It is also possible that one or two dyes are contamination from other objects next to the web.

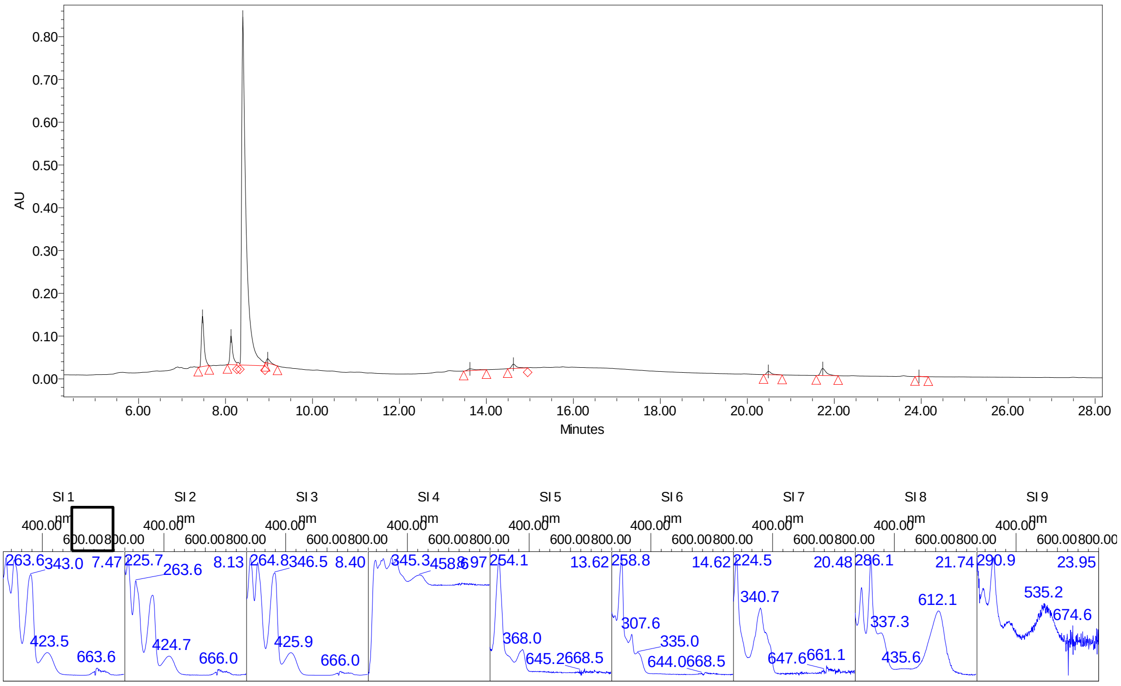

Figure 4. 29 UHPLC-PDA chromatogram (monitored at 350 nm) of the extract of SJS-2-2 and the UV-Vis spectra of its main constituents. Berberine (8.4 min), its equivalents (7.5, 8.1 and 9.0 min), ellagic acid (13.6 min), Nowik type C component (14.6 min), an Amur cork tree component (20.5 min) , indigotin (21.7 min) and indirubin (24.0 min) were detected.

In SJS-3, accessory of a purse and a thumb ring bag, sappanwood and indigo were identified (Figure 4. 30 and Figure 4. 31). Sappanwood was detected from the pattern and lining, indicating their brown shades originally. The original shade may also be apricot yellow if yellow dyes were used. Isatin, indigotin and indirubin were detected on two samples taken respectively from the ribbon of the thumb ring bag and the lining, indicating the presence of indigo. The detected indigo particles may be contaminations from surrounding blue parts like the blue front side of the purse, because the blue shade of the ribbon and the lining are very light and uneven, while the blue on the front side of the purse is very intense. If the lining was originally dyed blue, its blue shade should be preserved better than that of the front side because the lining was probably much less exposed to the external environment which is more likely to cause damage to the dyes.

Figure 4. 30 Photo of the lining of SJS-3

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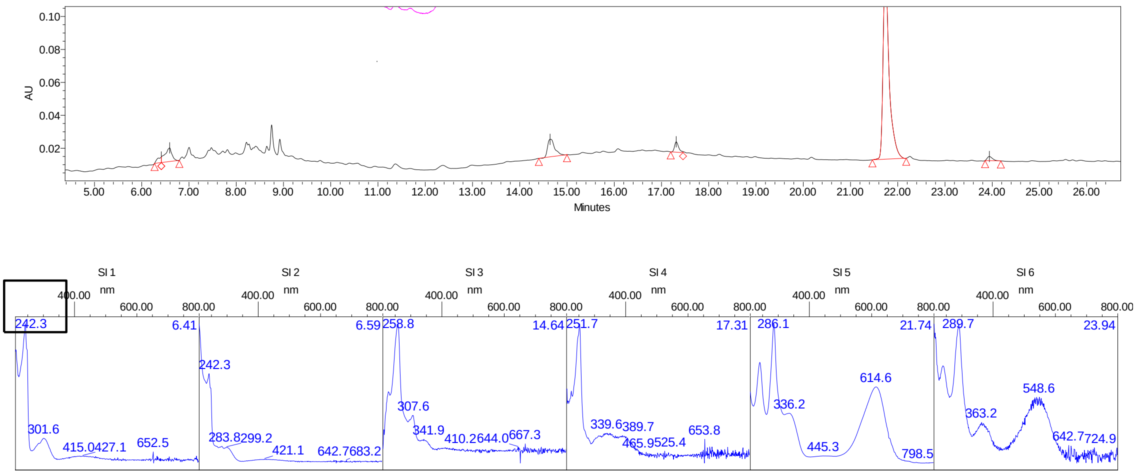

Figure 4. 31 UHPLC-PDA chromatogram (monitored at 254 nm) of the extract of SJS-3-4 and the UV-Vis spectra of its main constituents. Isatin (6.4 min), Nowik type C component (14.6 min), an indigo component (17.3 min), indigotin (21.7 min) and indirubin (23.9 min) were detected.

In SJS-5, a boot, trace amounts of indigotin and ellagic acid were detected (Figure 4.32). No records were found to use indigo and ellagic acid together for a black shade, but according to *Zhiranju buce*, indigo, a yellow dye and tannin were combined to achieve a dark shade. Probably a yellow dye was also used for the deep colour but it had degraded.

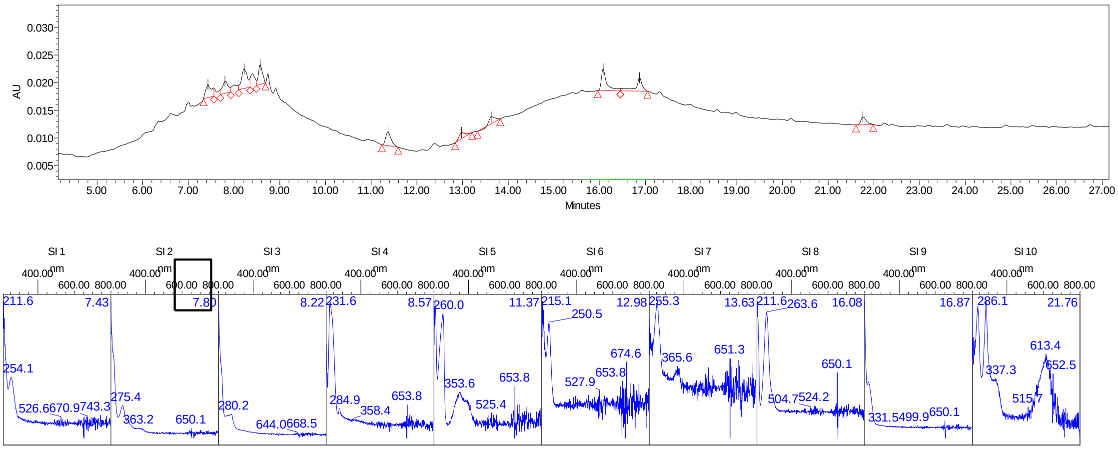

Figure 4. 32 UHPLC-PDA chromatogram (monitored at 254 nm) of the extract of SJS-5-2 and the UV-Vis spectra of its main constituents. Ellagic acid (13.6 min) and indigotin (21.8 min) were detected.

In SJS-8, a *mang* robe, sappanwood, ellagic acid and two unknown yellow components were detected for the two shades of adjacent stripes for standing wave (Figure 4.33 and Figure 4.34). In historical dye recipes, no combination of a tannin dye, a red dye, and a yellow dye was recorded. If sappanwood and ellagic acid are the only two dyes used for the stripes, probably they were originally brown and lighter brown.

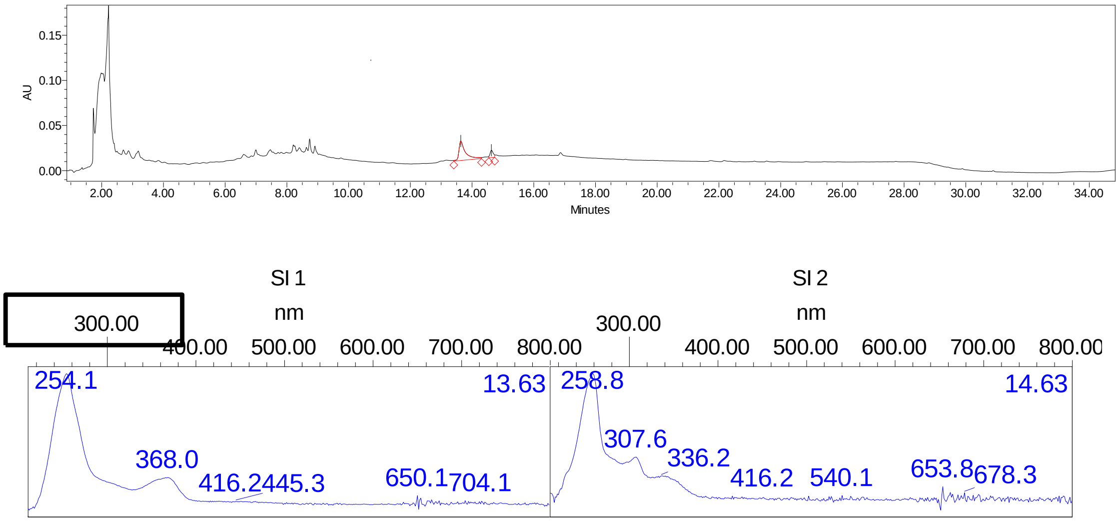

Figure 4. 33 UHPLC-PDA chromatogram (monitored at 254 nm) of the extract of SJS-8-1 and the UV-Vis spectra of its main constituents. Ellagic acid (13.6 min) and Nowik type C component (14.6 min) were detected.

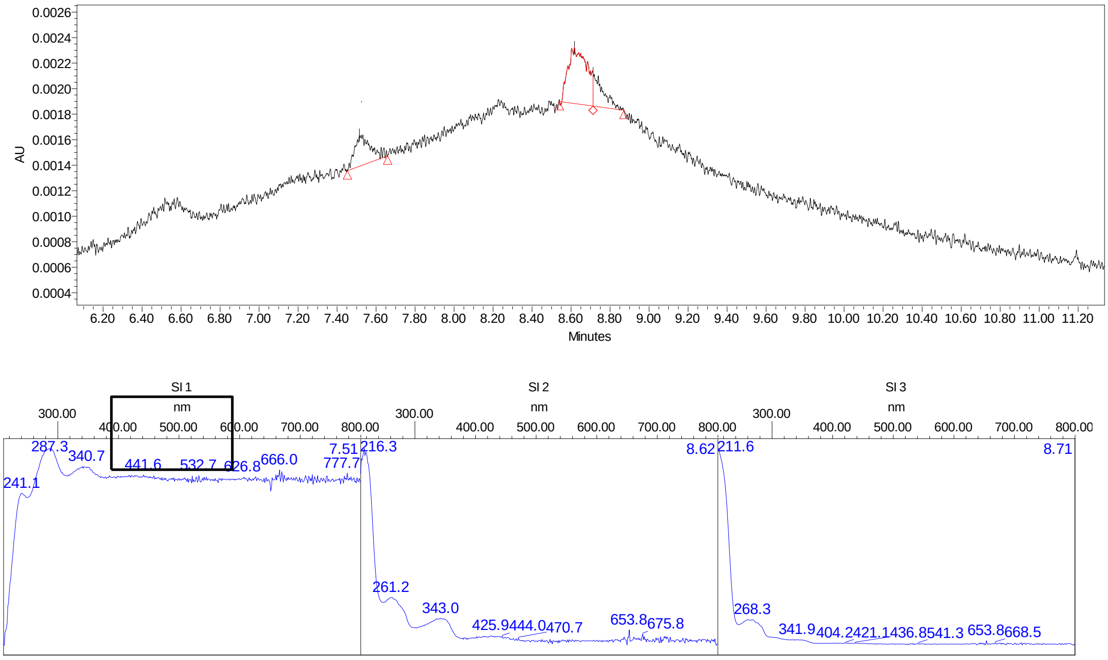

Figure 4. 34 UHPLC-PDA chromatogram (monitored at 430 nm) of the extract of SJS-8-1 and the UV-Vis spectra of its main constituents. Two unknown yellow components (7.5 and 8.6 min) were detected.

No characteristic peaks were found for the waistband, the underpants and the quilting lines. Judged by their light colour compared to the other objects, it is possible that they may not have been dyed or they may have been lightly dyed and traces of dyes have been lost.

4.3.4.2 Heyang Tombs

The tombs, in soil, where the textiles for sampling come from were located in Heyang, Yinan County, Shandong Province. The tombs were excavated in 2013. The owner of the tombs was a 6th grade civil official of the early Qing Dynasty. The textiles were mostly faded, except for some blue shades (Figure 4.35, left). Samples were taken from two pieces of textile fragments in Tomb M3, one piece in Room 2 at the bottom left of the body, with spices, the other piece in a coffin in Western Room, worn by the body (Figure 4.35, middle and right). Both textile fragments were dried naturally after excavation.

Figure 4. 35 Pictures of part of a *mang* robe excavated from the tomb (left) and the two textile fragments where the two samples were taken (middle and right)
© Yinan County Museum

Dye components were detected in both samples (shown in Table 4. 8). In the first sample, unknown orange components, indirubin and trace amount of indigotin were detected, the latter two indicating the presence of indigo (Figure 4. 36). The orange components possibly relates to a dye. In the second sample isatin, indigotin and indirubin were detected, indicating the dye source of indigo. Though the samples looked black, colourants are still present. Further analysis of more samples would help reveal the original colour of this set of textiles.

Table 4. 8 Analytical results of archaeological samples from Heyang tombs

Sample code	**Major dye components identified**	**Possible dye source(s)**
HY-1	unknown orange dye components, indirubin, trace amount of indigotin	indigo + ?
HY-2	isatin, indigotin and indirubin	indigo

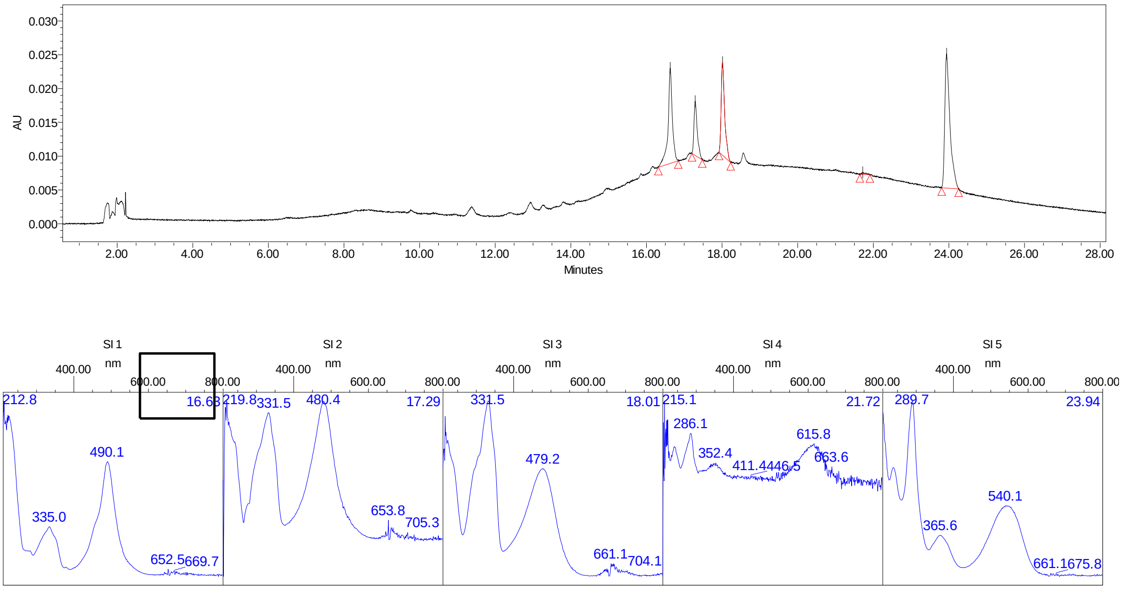

Figure 4. 36 UHPLC-PDA chromatogram (monitored at 254 nm) of the extract of HY-1 and the UV-Vis spectra of its main constituents. Three orange components (16.6, 17.3 and 18.0 min), indigotin (21.7 min) and indirubin (23.9 min) were detected.

4.3.4.3 The tomb of Zhu Tan

The chamber tomb where a piece of textile for sampling comes from is located at Jiulong Mountain in Zoucheng, Shandong Province. The tomb was excavated in 1970-1971 and its owner is Zhu Tan (朱檀) (1370-1390), the tenth son of the first emperor of the Ming Dynasty, Zhu Yuanzhang. The tomb was water-logged when found.[345] After excavation, the textiles found were cleaned and then stored in dark storages. Samples were taken from a piece of silk quilt bag fragment embroidered with flowers and peacocks in a yellow satin background and with gauze lining. The silk fragment was mostly faded except for deep flower core patterns (Figure 4. 37).

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[345] Shandong Museum, "Fajue Ming Zhu Tan Mu Jishi," [Documentary of the excavation of Zhu Tan tomb of the Ming Dynasty], *Cultural Relics* 18, no.5 (1972): 25-35.

Figure 4. 37 Overall (left) and partial (right) photos of the silk quilt bag fragment from Zhu Tan tomb

© Shandong Museum

Table 4. 9 shows the analytical results of the archaeological samples from the tomb of Zhu Tan. In 3 of the 5 samples two coloured characteristic components were detected. Nowik type C component, which indicates the probable use of sappanwood, and an unknown yellow component eluting at 27.05 min with UV-vis absorption at 222, 256, 349 and 442 nm are present in the samples from the front side, lining and stitching threads. If the yellow component indicates the use of a possible yellow dye of unknown source, the quilt bag may have been apricot yellow. If mordants were used for this sample the shade may change. It is to be noted that many natural organic compounds absorb light in the yellow region of the visible spectrum. They could be from plant debris, soil tannins, mould, fungus, *etc*, in the burial environment, as well as yellow degradation products from a dye. The amounts of the two samples from patterns were too small and no identifiable characteristic dye components were detected.

Table 4. 9 Analytical results of archaeological samples from the tomb of Zhu Tan

Sample code	**Visible colour**	**Use of thread**	**Major dye components identified**	**Possible dye source(s)**
ZT-1	dark yellow	lining	Nowik type C and an unknown yellow component	sappanwood + ?
ZT-2	dark yellow	front	Nowik type C and an unknown yellow component	sappanwood + ?
ZT-3	light yellow	stitching thread	Nowik type C and an unknown yellow component	sappanwood + ?
ZT-4	brown	flower pattern	no characteristic components for dyes detected	
ZT-5	light red ?	butterfly pattern	no characteristic components for dyes detected	

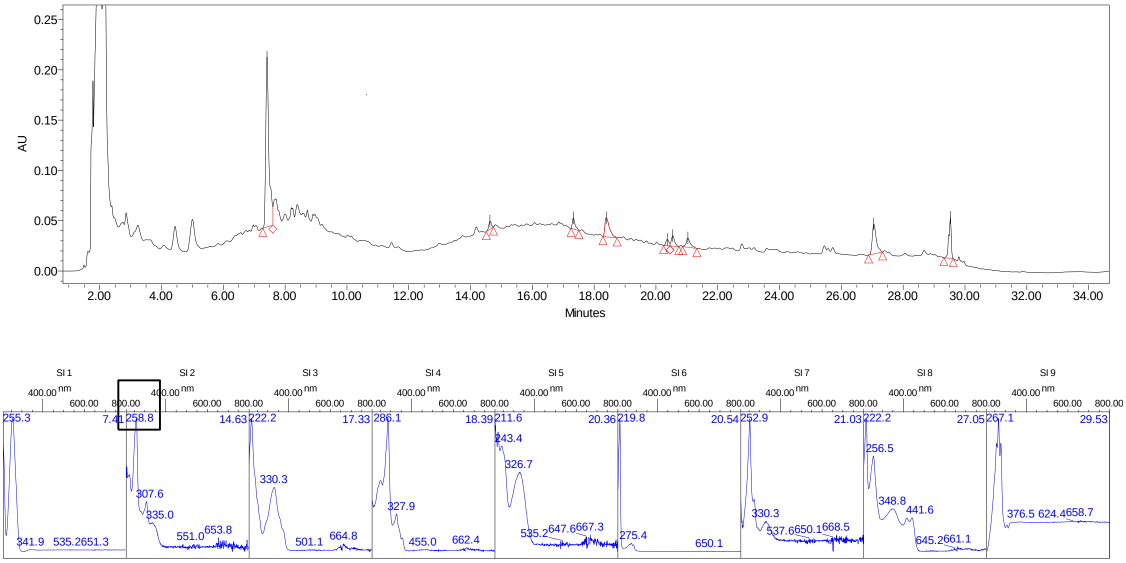

Figure 4. 38 UHPLC-PDA chromatogram (monitored at 254 nm) of the extract of ZT-2 and the UV-Vis spectra of its main constituents. Nowik type C component (14.6 min) and an unknown component (27.1 min) were detected.

4.3.4.4 The clan tomb of Zhu Bingju

The clan tomb of Zhu Bingju (朱秉橘) - the *Fuguo* General (bulwark-general of the State) of enfeoffed King of the Ming Dynasty is located in the southern suburb of Xi’an, Shaanxi Province. It is comprised of four burial chambers. The clan tomb was excavated in 2004-2005. Stelas (inscribed stone tablets) found in tomb M.26 date the deceased to between 1509-1585. Report of archaeological excavation has been published.[346] Nine silk samples ZBJ-1 from tomb M.24 and 20 silk samples from ZBJ-2 from tomb M.26 were collected (Figure 4. 39). M.24 was relatively dry but M.26 was found in a waterlogged condition because of its broken roof by looters and would have been in an alternating dry and wet condition. All the samples from M.26 were detached fragments found floating around the body. Some were also attached to lumps of coffin wood. After excavation the textiles were left to air dry naturally as they had been in long-term fluctuating humid environmental conditions. Some underwent resurgence treatment using water vapour to make them flat. In 2014 the textiles were re-housed in their original excavation boxes in a chest freezer. The samples all look brown. SEM analysis was undertaken on samples ZBJ-1-7 and 10 before dye analysis to investigate contamination and metal fragments on the samples. The analytical results by SEM are presented first followed by dye analysis results.

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[346] Jianyi Xiao *et al.*, "Xi'an Mingdai Qin Fan Fuguo Jiangjun Zhu Bingju Jiazu Mu," [The Clan Tomb of Zhu Bingju —the Fuguo General of Enfeoffed King Qin of the Ming Dynasty], *Cultural Relics* 52, no.2 (2007): 24-38.

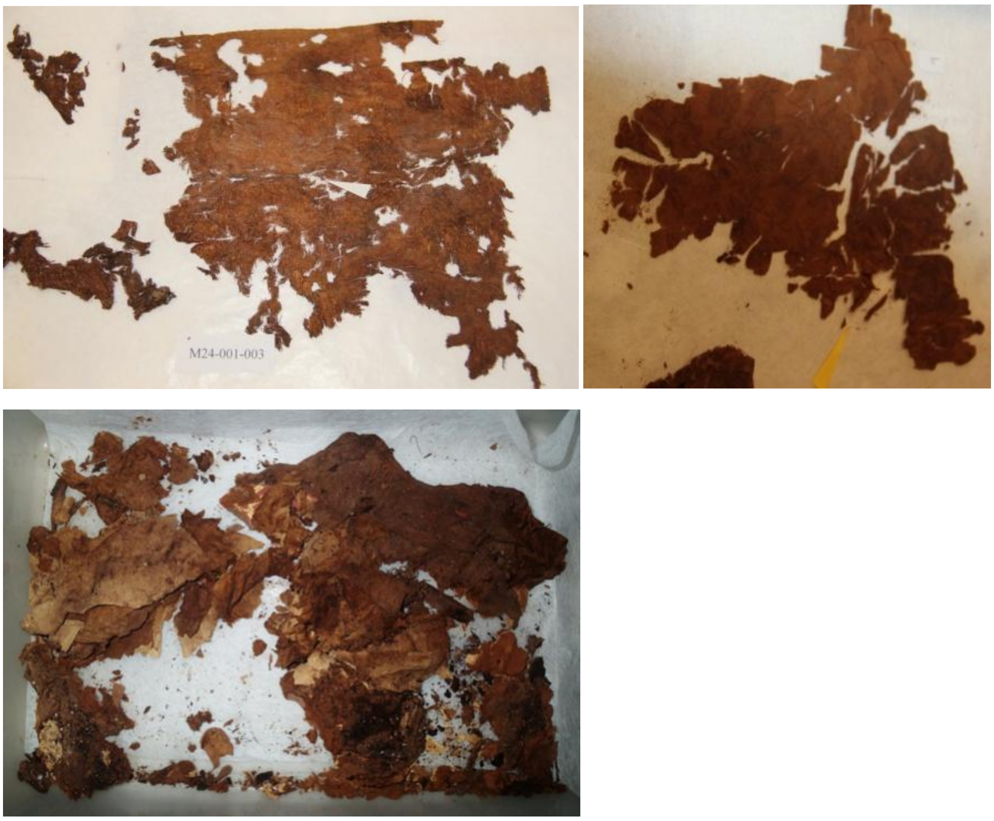

Figure 4. 39 Images of the textile fragments M24-001-003, M24-B14-110b, M26-Box 8 of the clan tomb of Zhu Bingju

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SEM analysis of contamination and metal fragments on two samples

Sample ZBJ-1-7

Sample ZBJ-1-7 is severely contaminated (Figure 4. 40). Spot 8 from a darker side of the sample, spot 7 from a yellow lump and spots 6 and 9 from metal fragments were chosen for examination. First, on spot 8 from the darker side, the elements oxygen, carbon, silicon, aluminium, iron and magnesium were detected. Therefore contamination is probably aluminium silicate. The metal ions may be originally used for the textile as mordants, or contaminations from the burial environment.[347] Iron and alum salts were commonly used as mordants for textile dyeing in the Ming and Qing Dynasties (section 1.3.3.1). It is not possible to say whether the ion and alum ions on this sample are mordants or part of contamination. Second, analytical results of spot 7 from the yellow lump (Figure 4. 41) show that its main elements detected include calcium, carbon, oxygen and phosphorus, indicating the lump is probably from bones, whose main inorganic chemical component is hydroxyapatite, usually expressed in the form of $Ca_{10}(PO_4)_6(OH)_2$.[348]

Third, from spot 6 on a metal fragment, carbon, oxygen and tin were detected. The presence of tin may be from tin coins found in the tomb that were used as funerary objects. In contrast, spot 9 on another metal fragment is predominantly composed of gold and small amounts of silver and copper are also present (Figure 4. 42), indicating that this is probably a metal alloy fragment from a metal thread. It is to be noted that apart from metal threads for textiles, other metal parts and objects were found in the coffins, including jewellery, bronze and tin coins, and gold leaf on wooden fragments of the coffin. These are all possible sources of metal fragments.

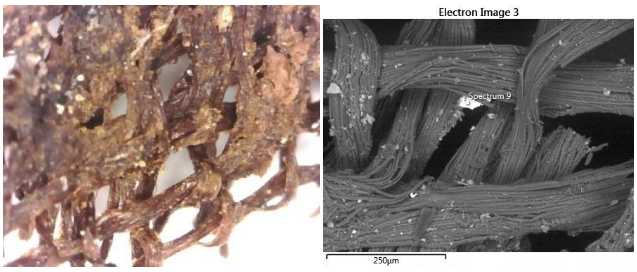

Figure 4. 40 Micrograph and BSE images of sample ZBJ-1-7

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[347] Ineke Joosten *et al.*, "Micro Analysis on Hallstatt Textiles: Colour and Condition," *Microchimica Acta* 155, no.1-2 (2006): 169-174; Ineke Joosten and Maarten R van Bommel, "Critical Evaluation of Micro-Chemical Analysis of Archaeological Materials. Experiences from the Netherlands Institute for Cultural Heritage," *Microchimica Acta* 162, no.3-4 (2008): 433-446.

[348] Simon Mays, *The Archaeology of Human Bones* (London: Routledge, 2002), 1.

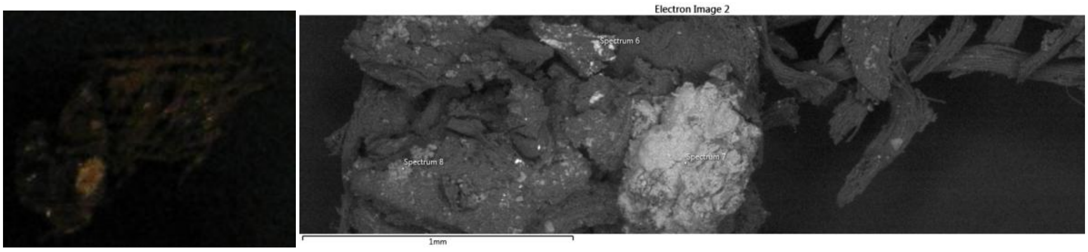

Figure 4. 41 Photo and BSE images of the yellow lump on sample ZBJ-1-7

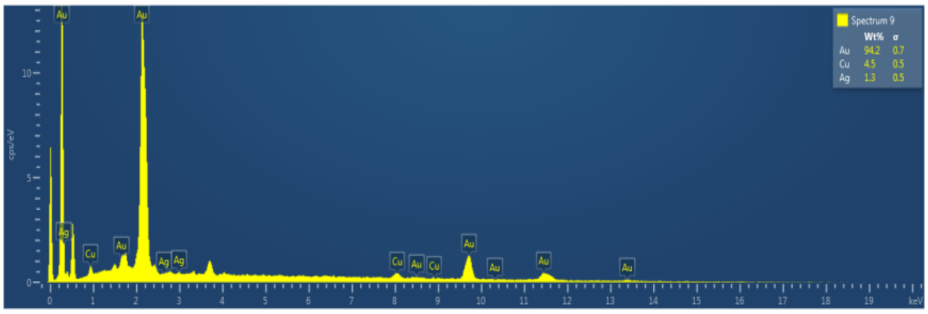

Figure 4. 42 SEM-EDX spectrum of spot 9 from sample ZBJ-1-7

Sample ZBJ-1-10

Sample ZBJ-1-10 was analysed to identify metal fragments and black contamination on the sample (Figure 4. 43). The main elements of spot 2 chosen from the metal fragment are silver and sulfur, probably indicating silver sulfide, the degradation product of silver by reacting with hydrogen sulfide and sulfur dioxide in the surrounding environment. The silver sulfide may be a metal thread fragment or contamination from other objects.

To identify the black contamination on the sample, the elemental compositions of contaminated and non-contaminated spots were compared. Results show that they both contain carbon and oxygen as main elements, which are probably from the fibres, and small amounts of calcium. On area 4, which is more contaminated, there is more silicon and aluminium, indicating the black contamination is probably aluminium silicate, which is a main component of soil.[349]

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[349] Conklin, 45-53.

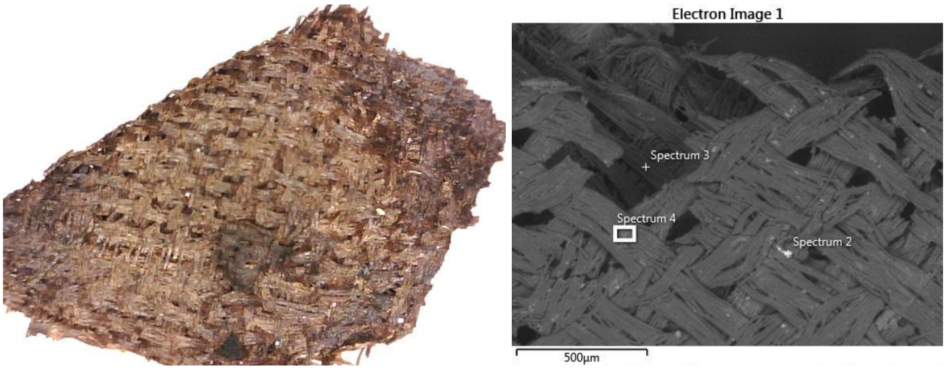

Figure 4. 43 Micrograph and BSE image of sample ZBJ-1-10

In summary, the contaminations of the two samples are mostly from soil in the burial environment. Some metal fragments may also come from surrounding objects. In sample preparation, inorganic contamination and metal fragments on the samples are hardly soluble in the organic extraction solvents for dye analysis therefore it is better to centrifuge the samples before filtering them to prevent blocking the filters.

Dye analysis results by UHPLC-PDA

Table 4. 10 presents the analytical results of the samples from the clan tomb of Zhu Bingju. Trace amounts of coloured components were detected including two yellow components in ZBJ-1-2, a gallic acid equivalent in ZBJ-1-8, and indigotin and a yellow component in ZBJ-2-19 (Figure 4. 44, Figure 4. 45 and Figure 4. 46). As discussed above, the two yellow components detected may indicate the presence of a yellow dye, but they may also come from a variety of sources in the burial environment. The detection of indigotin indicates the probable dye source of indigo, which dyes blue. If there were other dyes, the original shade of the sample would probably be green or purple, judged by existing evidence from historical dye recipes (section 1.3.3.1) and from historical textile samples (section 4.3.1.3). The gallic acid equivalent may be from gallnut, which dyes black or grey, as well as dark shades when used together with other dyes. It is to be noted that in tomb M.24 where

sample ZBJ-1-8 is from, a lot of the wood from the destruction of the coffin lids had also entered the coffins and over time has broken down to wood powder, and thus the gallic acid equivalent could also be tannin leaching out from the wood.

Table 4. 10 The analytical results of the archaeological samples from the clan tomb of Zhu Bingju

Sample code	**Tomb number**	**Textile group number**	**Major dye components identified (and possible dye source(s))**
ZBJ-1-1	M24	001-001	no characteristic dye components detected
ZBJ-1-2	M24	001-003	two trace yellow components (a dye?)
ZBJ-1-3	M24	001-002	no characteristic dye components detected
ZBJ-1-4	M24	001-006	no characteristic dye components detected
ZBJ-1-5	M24	001-010	no characteristic dye components detected
ZBJ-1-6	M24	005-002	no characteristic dye components detected
ZBJ-1-7	M24	005-005	no characteristic dye components detected
ZBJ-1-8	M24-B14	110b	gallic acid equivalent (gallnut?)
ZBJ-1-9	M24-B14	121a	no characteristic dye components detected
ZBJ-1-10	M26	001-002	no characteristic dye components detected
ZBJ-2-1	M26	Box 6	no characteristic dye components detected
ZBJ-2-2	M26	Box 6	no characteristic dye components detected
ZBJ-2-3	M26	Box 6	no characteristic dye components detected
ZBJ-2-4	M26	Box 6	no characteristic dye components detected
ZBJ-2-5	M26	Box 6	no characteristic dye components detected
ZBJ-2-6	M26	Box 6	no characteristic dye components detected
ZBJ-2-7	M26	Box 6	no characteristic dye components detected
ZBJ-2-8	M26	Box 6	no characteristic dye components detected
ZBJ-2-9	M26	Box 6	no characteristic dye components detected
ZBJ-2-10	M26	Box 6	no characteristic dye components detected
ZBJ-2-11	M26	Box 6	no characteristic dye components detected
ZBJ-2-12	M26	Box 6	no characteristic dye components detected
ZBJ-2-13	M26	Box 6	no characteristic dye components detected
ZBJ-2-14	M26	Box 8	no characteristic dye components detected
ZBJ-2-15	M26	Box 8	no characteristic dye components detected
ZBJ-2-16	M26	Box 8	no characteristic dye components detected
ZBJ-2-17	M26	Box 8	no characteristic dye components detected
ZBJ-2-18	M26	Box 8	no characteristic dye components detected
ZBJ-2-19	M26	Box 8	indigotin, a yellow component and colourless components (indigo, with another dye?)

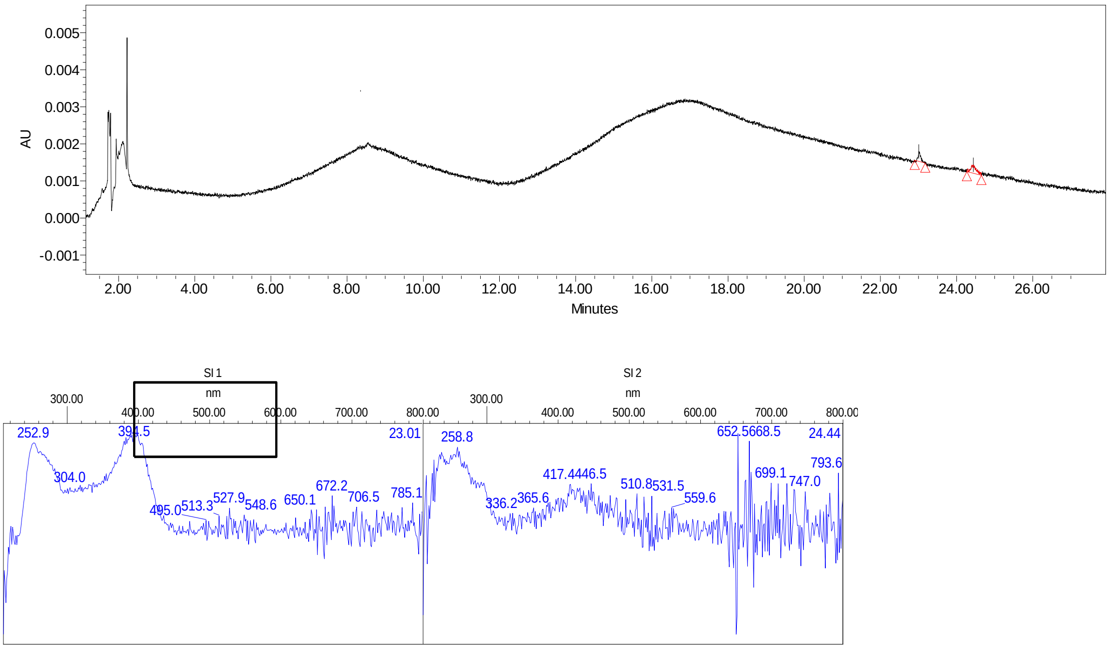

Figure 4. 44 UHPLC-PDA chromatogram (monitored at 350 nm) of the extract of ZBJ-1-2 and the UV-Vis spectra of its main constituents. Two yellow components were detected.

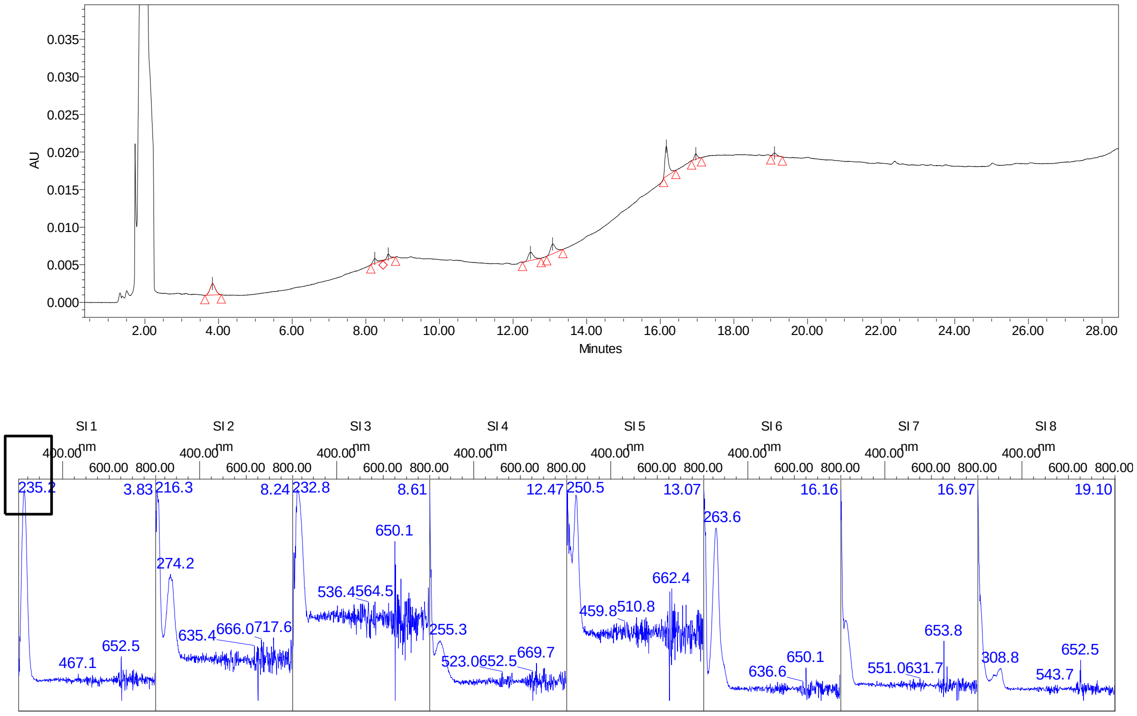

Figure 4. 45 UHPLC-PDA chromatogram (monitored at 254 nm) of the extract of ZBJ-1-8 and the UV-Vis spectra of its main constituents. A gallic acid equivalent (8.24 min) was detected.

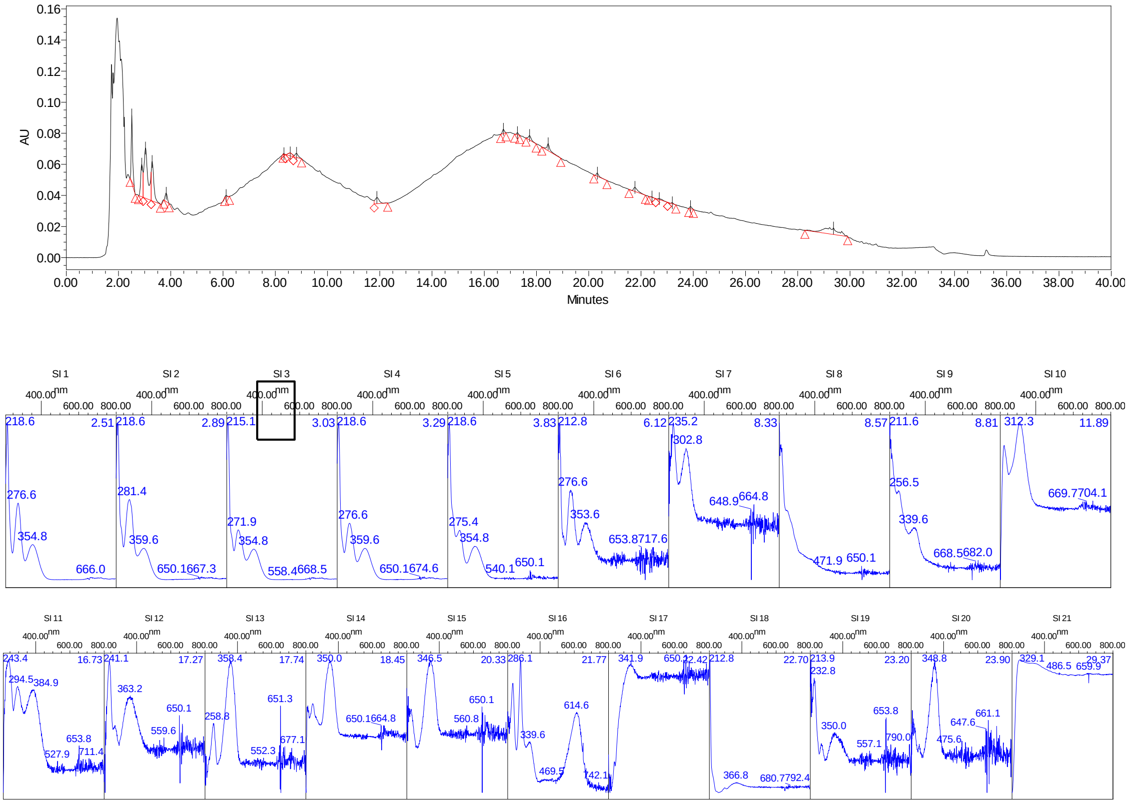

Figure 4. 46 UHPLC-PDA chromatogram (monitored at 350 nm) of the extract of ZBJ-2-19 and the UV-Vis spectra of its main constituents. Indigotin (21.77 min) and two yellow components (16.73 and 17.27 min) were detected.

Trace amounts of colourless components were detected in some of the samples from this site. It was difficult to identify them and whether they are from the dyes is unclear. The compounds could be dye degradation products, but they could also come from the silk, wood, lacquer or body fluid. The low identification rate of the samples from this site probably results from the severe burial environment in the tomb; looters' breaking into the tombs caused severe flooding which accelerated the degradation and dissolution of the dyes on the textiles in the tombs. Additionally, the small amount of some samples (some are fine fibres less than 1 cm) available may also be a reason that few dye components were detected. Besides, it is possible that some of the samples were not dyed.

4.3.4.5 Summary of natural dyes in archaeological textile samples

There has been limited research on archaeological dyes in ancient China. It is the first time that dozens of archaeological textiles from the Ming and Qing Dynasties have been analysed for dyes. Dye components were detected from most of the samples of Shijingshan tomb and Heyang tombs of the Qing Dynasty, while fewer dye components were detected from the samples of the tomb of Zhu Tan and the clan tomb of Zhu Bingju, indicating better a better preservation state in dyes from the former two sites. Dyes identified included indigo, sappanwood, Amur cork tree and possibly acorn cup and gallnut, all of which present alone or together with other dyes. The limited dyes identified and dyeing methods found are consistent with those identified in historical samples. The identification results of the dyes would help interpret possible original colours of the textiles.

4.4 Discussion

4.4.1 Evaluation of the dyes identified relating to the use of thread and the type of textile

Table 4. 11 shows the dyes identified in threads for different uses for individual pieces of historical textiles. So far no significant difference has been found in the use of dyes for threads for various uses from either historical or archaeological textiles. Instead, the use of dyes mainly depends on the colour desired. For example, all the red and pink shades are dyed by safflower, while sappanwood is usually used to dye brown shades, probably because of the pure red shade safflower achieves (1.3.3.2). Nevertheless, some preferences are found for the use of dyes for threads of certain uses: among the yellow dyes, pagoda bud was used most frequently for yellow patterns, but for the five yellow metal thread cores, turmeric was used more frequently than pagoda bud (3 by turmeric and 2 by pagoda bud). The analysis of more samples is needed for quantitative comparison. The common

use of pagoda bud is probably attributed to its good colouing effect, availability and lightfastness (sections 1.3.2 and 5.5.1). Turmeric, a dye of poor lightfastness (section 5.5.1), was used most often for metal thread cores may be because of the fact that the cores were not expected to be exposed to much light and the cheap price and bright colour of turmeric.

Table 4. 11 Dyes identified in individual pieces of historical costume and textiles

Textile reference code	**Pattern**	**Ground**	**Lining**	**Metal thread core yarn**	**Stitching thread**
BC-1	Amur cork tree, indigo, tannin (to cover silver threads)	sappanwood + turmeric	picric acid and unidentified synthetic dyes for conservation patches	—	sappanwood + turmeric
CBL-1	—	—	—	turmeric + ?	—
JSL-1	safflower, pagoda bud, Amur cork tree	pagoda bud	—	—	—
JSL-2	sappanwood + indigo, pagoda bud,safflower, Amur cork tree	—	—	—	—
JSL-3	—	sappanwood	—	—	—
JSL-4	pagoda bud, Amur cork tree, safflower, indigo + magenta	—	—	—	—
JSL-5	—	magenta, an aniline violet type dye	—	—	—
JSL-6	safflower, pagoda bud, smoketree	—	—	—	—

Table 4. 11 Dyes identified in individual pieces of historical costume and textiles (continued)

NMS-1	pagoda bud, safflower, Amur cork tree, sappanwood	sappanwood	—	turmeric	potentially a synthetic dye
NMS-2	pagoda bud,safflower, Amur cork tree, sappanwood, indigo	sappanwood	—	sappanwood + ?	—
NMS-3	pagoda bud + turmeric	sappanwood + pagoda bud	—	—	—
NMS-4	—	—	—	—	—
NMS-5	—	turmeric, sappanwood + indigo for lace ground	safflower + Amur cork tree	—	sappanwood + indigo
NMS-6	—	lac	—	—	—
NMS-7	pagoda bud + indigo	cochineal + magenta + acorn cup	Amur cork tree	sappanwood + ?	turmeric and magenta
NMS-8	turmeric, magenta, picric acid, malachite green	a potentially synthetic dye and an aniline violet/blue type dye	—	—	—
NMS-9	—	pagoda bud	—	—	turmeric
NMS-10	—	safflower + Amur cork tree	pagoda bud + indigo	—	magenta
NMS-11	sappanwood + indigo, acorn cup + ?	turmeric	—	—	turmeric
NMS-12	turmeric + unknown red, safflower, Amur cork tree	acorn cup for lace ground	—	—	—

Table 4. 11 Dyes identified in individual pieces of historical costume and textiles (continued)

NMS-13	—	safflower + Amur cork tree, acorn cup (ground colour for lace)	—	—	turmeric + pagoda bud, potentially a synthetic dye
PC-1	safflower, Amur cork tree	pagoda bud	—	—	—
PC-2	safflower + Amur cork tree	—	—	—	—
PC-3	sappanwood, pagoda bud, safflower, Amur cork tree, smoketree	sappanwood + pagoda bud + smoketree	—	—	—
TPM-1	magenta, malachite green and an aniline violet type dye	—	—	—	—
TPM-2	—	indigo, pagoda bud	—	—	—
TPM-3	—	indigo	—	—	—
TPM-4	Amur cork tree + indigo	potentially a synthetic dye	—	—	—
V&A-1	—	—	—	—	—
V&A-2	pagoda bud + indigo	sappanwood + turmeric, safflower + Amur cork tree	—	pagoda bud	—
V&A-3	pagoda bud	—	turmeric + safflower	—	pagoda bud
V&A-4	pagoda bud	pagoda bud, pagoda bud for cuff	—	—	—
V&A-5	safflower, pagoda bud, indigo + Amur cork tree ?	an unknown natural dye	—	turmeric	—

Table 4. 11 Dyes identified in individual pieces of historical costume and textiles (continued)

V&A-6	Amur cork tree ?	pagoda bud, indigo + lac, acorn cup, gallnut	safflower	pagoda bud	acorn cup, safflower
V&A-7	indigo, Amur cork tree, acorn cup	sappanwood + safflower + turmeric	—	turmeric	—
V&A-8	—	potentially a synthetic dye	—	—	—
V&A-9	sappanwood + ellagic, pagoda bud	pagoda bud	—	—	—
V&A-10	sappanwood, safflower, pagoda bud, Amur cork tree, smoketree, indigo	indigo, Amur cork tree	safflower	—	safflower + Amur cork tree
V&A-11	magenta	—	pagoda bud + turmeric	—	—

In comparing dyes identified in the high-status costume and textiles and in the limited three pieces (NMS-8, TPM-1 and V&A-8) of non high-status costumes, no difference in the use of dyes was found. From NMS-8, the dancer's skirt, dyes identified included pagoda bud, Amur cork tree, turmeric, indigo, sappanwood, ellagic acid, cochineal and magenta. Safflower was the only common natural dye that was not detected, but this is understandable because there are no red or pink or shades. From TPM-1, the dragon robe for a Buddha sculpture, malachite green and an aniline violet type dye were identified. Magenta, malachite green and aniline violet type dyes were all identified in high-status costumes as well. The dye source for the sample from the theatre costume V&A-8 was potentially another synthetic dye, which needs further investigation.

4.4.2 Comparison with historical dye recipes and the overall view of dyes and dyeing methods used in the Ming and Qing Dynasties

Literature records and analytical results are consistent to a large extent in terms of the choice of dyes and the use of dyes for single-dyeing and for multi-dyeing.

4.4.2.1 The choice of dyes

Table 4. 12 shows the comparison result of common dyes recorded in the historical dye recipes and those identified in the historical textile samples. It can be seen that all the main natural dyes identified, except for turmeric, are dyes commonly recorded in the Chinese literature for the period of interest. Turmeric was recorded in five dye recipes in *Bu jing* but not in the other three manuscripts. Though turmeric is not lightfast, its low price and simple dyeing method (direct dyeing) might be the reason turmeric was still used quite often in practice. On the other hand, smoketree and gallnut, frequently recorded in historical manuscripts, were found in limited cases (three times for smoketree and once for gallnut). The poor lightfastness of smoketree may be the reason that this dye was not often used though more investigation is needed to explain this inconsistency (chapter 5.5.1). Gallnut and acorn cup both contain tannin and show no difference in use in historical dye recipes. However, in practice, unpleasant smells generated when boiling gallnut might be a reason why acorn cup was much preferred by dyers. The above inconsistencies may also result from different dyeing practice in various dyeing workshops or places. In terms of synthetic dyes, no synthetic dyes are recorded in the historical dye recipes studied. This is because the two historical manuscripts of the Qing Dynasty were respectively published in 1754 and 1795-1850 before the emergence of the commercialised synthetic dye industry from 1856.

Table 4. 12 Common dyes in the historical dye recipes and in the analytical results

	Dyes commonly recorded in the historical dye recipes	Dyes not commonly recorded in the historical dye recipes
Dyes commonly identified in the analytical results	safflower, sappanwood, pagoda bud, Amur cork tree, indigo, acorn cup	turmeric
Dyes not commonly identified in the analytical results	smoketree, gallnut	gardenia, munjeet, gromwell, *etc*

▨ where literature records and analytical results are not consistent

4.4.2.2 Dyeing with a single dye

In terms of the dyes used for single dyeing, the choice of dyes and shades in historical literature and analytical results are largely consistent (Table 4. 13). One exception is that in literature safflower alone was used to dye red and pink, but in practice it was used alone only to dye pink, and always with a yellow dye for red. This is probably because of the cost saving strategy (section 1.3.2.2) and the brightening effect of a yellow ground for the shade. Another exception is that in reality pagoda bud was used much more frequently than the other yellow dyes, which may result from the bright yellow shade it achieves and its good lightfastness (section 5.5.1).[350]

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[350] T. Padfield and S. Landi, "The Light-Fastness of the Natural Dyes," *Studies in Conservation* (1966): 181-196.

Table 4. 13 Frequencies for dyes used for single-dyeing in historical dye recipes and in analytical results

Dye	**Literature records**		**Analytical results**	
	Number of dye recipes	**Shades obtained and frequencies**	**Number of samples detected**	**Shades obtained**
sappanwood	3	brown 1, purple 2	3	brown
safflower	10	red 4, pink 6	8	pink
pagoda bud	5	yellow 3, dark yellow 1, green 1	24	yellow 23, dark yellow 1
Amur cork tree	5	yellow	3	yellow
smoketree	5	yellow 3, light brown 2	0	
turmeric	1	yellow 1	9	yellow
acorn cup	2	black 2	6	black
gallnut	6	black 6	1	black
indigo	4	blue 2, bluish white 2	5	blue

▨ the use of dyes are not consistent between historical literature records and analytical results
░ same as shown in Table 4.12

4.4.2.3 Multi-dyeing with more than one dye

For multi-dyeing, again, the combination of dye groups is defined by colour. The combination of dyes and shades obtained are largely consistent between historical records and practice (Table 4. 14): orange shades are obtained by a mixture of red and yellow dyes; yellow shades by yellow dyes, with a dye containing tannin for dark yellow; brown and dark red by the mixture of a red dye and a dye containing tannin; and purple/green shades by indigo and a red/yellow dye. The most obvious difference is that in practice red samples are mostly obtained by the combination of safflower and Amur cork tree, but in literature mainly by safflower and turmeric or smoketree. Only one record of dyeing red with safflower and Amur cork tree together was found, in *Wuli xiaoshi* (Small knowledge of the principle of things, late Ming Dynasty). This may be because of the bright shade of Amur cork tree, its antifungal property, good fastness (section 5.5.1) and availability.

Table 4. 14 Dyes for multi-dyeing with two dyes in historical dye recipes and in analytical results

Combination of dyes	**Literature records**		**Analytical results**	
	Number of dye recipes	**Shades obtained**	**Number of samples detected**	**Shades obtained**
Red and orange shades				
safflower + Amur cork tree	0		22	red 16, pink 2, apricot yellow 4
safflower + turmeric	3	red	2	apricot yellow
safflower + smoketree	3	red	0	
sappanwood + pagoda bud	1	light red	2	brown
sappanwood + turmeric	1	apricot yellow	4	apricot yellow
Yellow and yellowish brown				
pagoda bud + turmeric	0	0	2	yellow
pagoda bud + Amur cork tree	1	yellowish brown	2	yellowish brown
pagoda bud + smoketree	3	yellow	1	yellow
pagoda bud + gallnut	1	yellowish brown	0	
smoketree + acorn cup	1	yellowish brown	0	
Dark red and reddish brown				
sappanwood + acorn cup	1	brown	1	brown
sappanwood + gallnut	10	dark red	0	
safflower + acorn cup	2	2	0	

Table 4. 14 Dyes for multi-dyeing with two dyes in historical dye recipes and in analytical results (continued)

Purple and green shades with indigo				
sappanwood + indigo	8	purple	6	purple 4, black 2
safflower + indigo	1	purple	0	
Amur cork tree + indigo	5	green 3, greenish yellow 1, greenish blue 1	6	green
pagoda bud + indigo	6	all for green	7	green

▨	the use of dyes are not consistent between literature records and analytical results
░	same as shown in Table 4.12

4.4.2.4 Dyeing techniques to enrich shades

Physical evidence confirmed literature records of dyeing techniques to enrich shades. Apart from the replacement of dyes and dyeing methods, this is achieved by the variation of the amounts of dyes and the combination of more dyes.

First, it was found in the analytical results that more shades are obtained with the same combination of dyes but of different amounts. Among the three sets of samples with similar shades, two sets were dyed by the same dye/combination of dyes. The combination of safflower and Amur cork tree for four different shades of apricot yellow standing wave of JSL-2 (18th century); pagoda bud and Amur cork tree for yellowish brown standing wave for JSL-4 (late 19th century) (Figure 4. 47 and Figure 4. 48). The same combination of dyes makes the shades consistent and harmony, which is especially important when more than two similar shades comprising a pattern. This is in accordance with the change of dyeing found in historical literature. The number of dye recipe groups with the same combination of dyes for slightly different shades increases from 0 in *Duoneng bishi* and 4 in *Tiangong kaiwu* to up to 13 groups for 46 shades in *Bu jing*. Additionally, for the three green pattern colours for NMS-2 (late 18th century), Amur cork tree and indigo are used for light green and darker green, but pagoda bud and indigo are used for the darkest green (Figure 4. 49), which may indicate that the use of dyes for similar shades may have been flexible.

Figure 4. 47 Safflower and Amur cork tree were used for the apricot yellow shades of JSL-2

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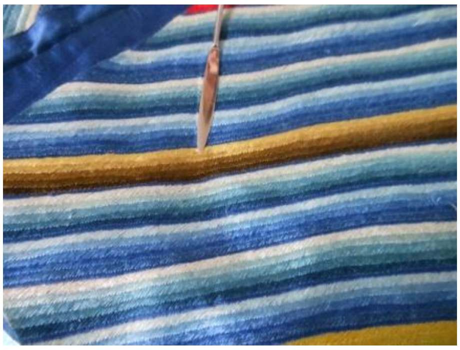

Figure 4. 48 Pagoda bud and Amur cork tree were used for the yellowish brown shades for JSL-4

© Jacqueline Simcox Ltd

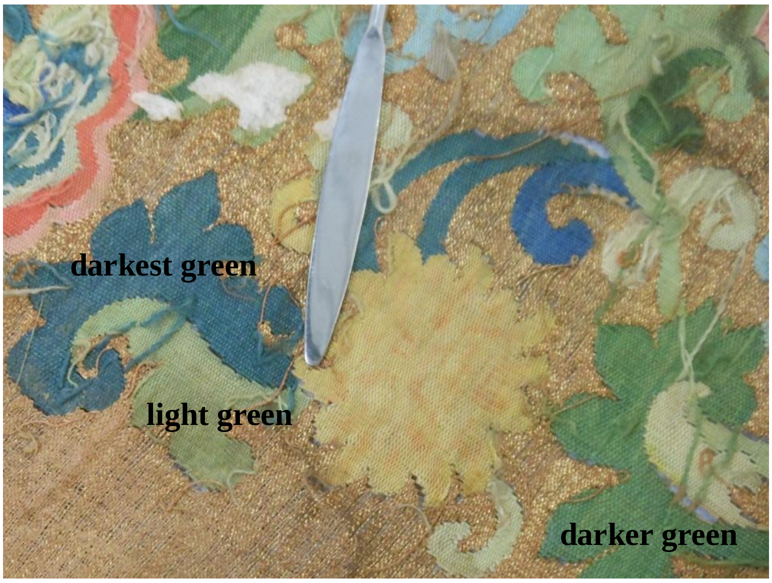

Figure 4. 49 Different combinations of dyes were used for the three green colours for NMS-2

(Permission to reproduce this image has been granted by National Mumseums Scotland.)

Second, the increase of the number of dyes used is found in the analytical results. Analytical results show that the mixture of sappanwood, pagoda bud and smoketree is used for reddish brown for PC-3 and V&A-10 (both 18th century), and the mixture of cochineal, ellagic acid and magenta for NMS-7, altogether counting for 3% of all the samples analysed. In literature a much larger proportion of dye recipes involve three or more dyes (14%) (Figure 4. 50). This difference may result from actual need for colours and the difficulty of controlling shades involving three dyes.

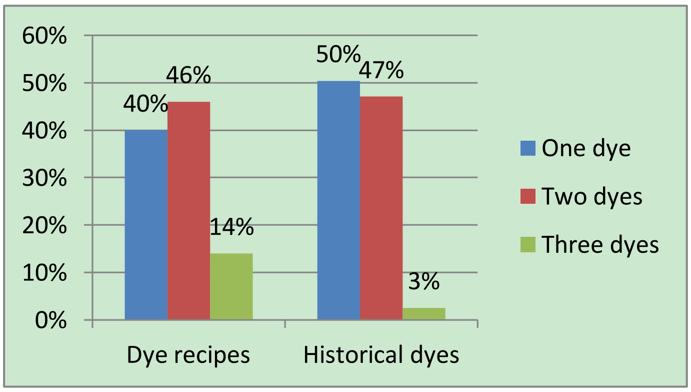

Figure 4. 50 Number of natural dyes used for individual shades in historical dye recipes and historical samples

4.4.2.5 Summary

Overall, literature records and analytical results are mostly consistent in terms of dyes and dyeing methods used. Physical evidence also supports literature records in the enrichment of shades by dyeing over time. The differences between the two are probably due to some practical reasons, such as colouring effects, fastness, operational difficulties and availabilities of dyes. This may also result from differences in the choice and use of dyes among various regions or dyeing workshops.

The overall view of dyes and dyeing methods used in the Ming and Qing Dynasties were revealed by the combined results of literature research and chemical analysis. Dyes commonly used during this period include safflower, sappanwood, Amur cork tree, pagoda bud, indigo, acorn cup, turmeric, Chinese gallnut and smoketree, though turmeric was frequently found in the chemical analysis results but not in historical dye recipes and vice versa for Chinese gallnut and smoketree. Synthetic dyes were used for Chinese costume and textiles from the late 19th century as well. These dyes were used alone or with another dye, with specific rules, to obtain certain shades, with occasional cases of using three dyes together. The development of dyeing techniques included the adoption of better dyes and dyeing methods and the enrichment of colours by variations in the combination and quantity of raw materials.

4.4.3 Indigenous dyes in China and communication in dyeing between China and Europe

4.4.3.1 Comparison of dyes used in China and in other places

Dyes specific and indigenous to China were used extensively, if not exclusively, for the status of clothing analysed. Natural dyes used in China during the Ming and Qing

Dynasties are distinct from dyes used in Europe at the same time period, *e.g.* dyes such as safflower, Amur cork tree and pagoda bud were used in China while dyes such as weld, cochineal and kermes were used in Europe. Meanwhile, China and Europe share several dyes of the same genus but of different species, such as madder (*Rubia tinctoria*) used in Europe and munjeet (*R. cordifolia*) in China, and brazilwood (*Caesalpinia echinata*) in Europe and sappanwood (*C. sappan*) in China. Their slightly different chemical profiles distinguish these dyes in chemical analysis.[351] Furthermore, dyes used in China and dyes used in other Asian counties share more similarities in terms of dyes used, but there are still some differences, such as the use of *Rubia spp.* and gromwell in Japan during the time period of interest.[352] Though detailed comparison of dyes used in China with dyes used in other places during this time period is needed, it can be tentatively concluded that dyes specific and indigenous to China could help provenance Chinese textiles from textiles from other origins.

4.4.3.2 Communication between China and Europe

The dyes identified in this research provide evidence for communication in dyeing between China and Europe during the Ming and Qing Dynasty, especially in terms of dyes introduced by European to China.

From mid-16th century, with the discovery of the Americas, indigenous dyes of the Americas including American cochineal, which has both good colouring effect and good lightfastness[353], and brazilwood were exported to Europe by Spanish and quickly became

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[351] Mouri and Laursen, "Identification of Anthraquinone Markers for Distinguishing Rubia Species in Madder-Dyed Textiles by HPLC," 105-113; Nowik, "The Possibility of Differentiation and Identification of Red and Blue 'Soluble' Dyewoods: Determination of Species Used in Dyeing and Chemistry of Their Dyestuffs," 129-144.

[352] Yoshiko Sasaki *et al.*, "Dye Analysis of Braids Used for Japanese Armour Dating from the 14th to the 16th Century" in *Dyes in History and Archaeology 21*, 2002, ed. Jo Kirby, 119-126 (London: Archetype publications, 2008).

[353] Padfield and Landi, "The Light-Fastness of the Natural Dyes," 181-196.

popular.[354] Soon after mid-16th century American cochineal was traded to Asia and was used for luxury textiles.[355] It was recorded that American cochineal was traded to China from the 16th century.[356] Apart from the one case in this research, cochineal has been identified in only a few cases of historical Chinese textiles, *e.g.* a wedding banner dated 1850-1900,[357] though more investigation is need to confirm their biological sources. Nevertheless, cochineal was probably never used to a large scale in ancient China: it was neither mentioned in the four historical manuscripts with dye recipes nor in the official ware house lists, probably due to the strict trade policy of the Ming and Qing Dynasties.[358] Instead, safflower and sappanwood remained major dye sources for red shades.

From the late 19th century, not long after the invention of synthetic dyes, synthetic dyes were sold by European dye companies to China through merchant business. Synthetic dyes gradually replaced natural dyes and dominated the dyeing market because of their low price, better and more shades, simple dyeing methods and good lightfastness.[359] From 1918 factories for synthetic dyes began to be established in China and synthetic dyes were produced domestically.[360]

Overall, the communication in natural dyes dyeing between China and Europe was very limited, probably because dyeing materials and techniques were relatively equal in the two places. In contrast, synthetic dyes invented in Europe greatly changed dyeing in China because of their huge advantages.

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[354] Phipps, 40-41; Cardon, 287.

[355] Robin Arthur Donkin, "Spanish Red: An Ethnogeographical Study of Cochineal and the Opuntia Cactus," *Transactions of the American Philosophical Society* (1977): 38-40.

[356] Yu and Liu, 20; Lee-Whitman, "The Silk Trade: Chinese Silks and the British East India Company," 21-41.

[357] Phipps, 40-41.

[358] Zhihong Shi, "Ming Ji Qing Qianqi Baoshou Zhuyi De Haiwai Maoyi Zhengce," [The conservative overseas trade policy of the Ming and early Qing Dynasties], *Researches In Chinese Economic History* 19, no.2 (2004): 33-41; Xinxia Lai and Xisuo Li, "Diyici Yapian Zhanzheng Qian Qingzhengfu De Duiwai Maoyi Zhengce," [Qing government's foreign trade policy before the First Opium War], *Journal of Literature, History and Philosophy*, no.2 (1980): 35-42.

[359] Cao, 41.

[360] Ibid.

4.4.4 Relationship between dyeing handicraft and other aspects of the society

During the Ming and Qing Dynasties, dyeing handicraft developed with the evolvement of a colour system and decrees for textiles, the changing organisational structure of textile industry, and a national network for techniques, raw materials and products.

4.4.4.1 Dyeing and the evolvement of colour system and decrees for textiles

The historical literature indicates that during the Ming and Qing Dynasties the textile shades achieved increased dramatically, from dozens of shades in the mid-Ming Dynasty to hundreds of shades at the end of the Qing Dynasty.[361] In terms of colours in official decrees, during the Ming and Qing Dynasties, detailed regulations were made on various yellow shades and corresponding dye recipes were recorded in official documents.[362] According to official decrees, in the Ming Dynasty officials and common people could not wear willow yellow, turmeric yellow or bright yellow.[363] In the Qing Dynasty, yellows were colours for the royal family: bright yellow was worn by emperors, apricot yellow for crown princes (later abandoned) and golden yellow by princes. Women's costume in the court was also correspondingly ranked from bright yellow, apricot yellow, golden yellow and *xiang se* (brownish yellow).[364] From a practical point of view, the colours regulated in decrees should be different enough to show various statuses. Dye recipes for the four yellow shades recorded in the official manuscript *Zhiranju buce* making use of different combination of dyes meet this requirement (Table 4. 15). The other yellow shades obtained

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[361] Fan and Jin, 235.

[362] It is worth noting that except for the yellow shades, which were of the highest status in the Qing Dynasty, it is difficult to draw direct links between the regulations on costume colour and the dye recipes mosly because colour names recorded in the two kinds of documents do not correspond well to each other. In official regulations the colour names are generally more abstract, e.g. blue, while in dye recipes the colour names are more specific, e.g. sky blue and grape blue.

[363] Zhang, "Yu Fu," 68-103.

[364] Yong Yan, "Qingdai Fushi Dengji," [The Grade of Costumes in the Qing Dynasty], *Forbidden City*, no.10 (2008): 70-81. It is to be noted that the colour naming is very complex in the historical dye recipes. Colour names in the dye recipes can be roughly grouped into three types: A. Colour, or adjective + colour, *e.g.* bright yellow. B. Object (indicating colour) + colour, *e.g.* apricot yellow, wood red. C. Object (indicating colour), *e.g.* iron colour, ivory colour, sandalwood. There was no standard system of shades and it is not clear what exact shades the colour names referred to. Colour names in dye recipes did not guarantee one-to-one relationship with combination of dyes. For example, bright yellow in *Zhiranju buce* was obtained by pagoda bud, but in *Bu jing* (The cloth classic) by turmeric, which obtain a shade different from that obtained by pagoda bud.

by smoketree and Amur cork tree respectively have enough distinction in colour from these four shades.

Table 4. 15 Yellow shades and raw materials used recorded in *Zhiranju buce*

Yellow shade	Dyes and mordants used
bright yellow	pagoda bud and alum
golden yellow and apricot yellow	pagoda bud, smoketree and alum of different amounts
qiu xiang se (brownish yellow)	pagoda bud, alum and iron sulphate
mai huang (wheat yellow)	smoketree
kui huang (sunflower yellow)	Amur cork tree

With evidence of historical dye recipes and official decrees, the identification of pagoda bud alone from the yellow ground samples of four pieces of dragon robes and a dragon badge (PC-1, JSL-1, V&A-4, V&A-9 and NMS-9) confirms their original bright yellow shade, even when the original shades were more or less faded. This thus confirms that all these five pieces belonged to emperors and court dowagers of the highest rank like empresses (e.g V&A-9, a robe for female), especially when it is difficult to identify the owner only by patterns.[365] In addition, the yellow ground of two skirts, both of the late Qing Dynasty, were dyed by turmeric. Though during this time period official regulations were broken frequently,[366] turmeric may be used deliberately to distinguish from the regulated bright yellow colour. Since turmeric is light sensitive, this may also indicate the declination of dyeing qualities in the late 19th century. Therefore, on the one hand, the advance of dyeing techniques in obtaining more shades and the ability to control the consistency of these shades makes the detailed decrees possible. On the other hand, the strict requirements in decrees fostered the advancement of dyeing techniques.

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[365] Fernald, 21.

[366] Gau.

4.4.4.2 Organisational structure of the textile industry in China

Textile workshops included official and private workshops. In the early Ming Dynasty, the former was in charge of high-status textiles and the latter mainly for textile commodity.[367] Central and local official workshops have their own responsibilities: the Central Inner Bureau produced textiles for the imperial family, the Central Outer Bureau for officials, and local bureaus for rewards from the court. In the early Ming Dynasty, the main source of labour for official workshops was the levy service of textile craftsman in the form of permanent craftsman or shift craftsman.[368] From the mid-Ming Dynasty, with the development of commodity economy, the pattern of textile production changed: not only was the production scale of textile industry expanded and textile producing techniques improved, but also the production organisational structure changed and division and specialisation strengthened.[369]

Private institutes developed rapidly because of the issue of *yi tiao bian fa* (Single-Whip Method) in 1581 (this decree changed the mandatory service of craftsman to recruitment) and the prosperous economy.[370] Meanwhile, official workshops gradually declined. Only a small part of textiles for the court were produced in official institutes, instead, most of the textiles were customised in private institutes or bought from the open market.[371]

The flourish of economy also fostered the specialisation of dyeing. In the late Ming Dynasty, small numbers of specialised dyeing workshops appeared. In the Qing Dynasty, greater amounts of dyeing workshops appeared and some were of large size. Take dyeing workshops in Suzhou in the Kangxi period (1662-1722) as an example—there were

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[367] Fan and Jin, 241.

[368] Yuquan Wang, Chongri Liu, and Xianqing Zhang, *Zhongguo Jingji Tongshi, Mingdai Jingji Juan* [General history of Chinese economy, Ming economy volume] (Beijing: Jingjiribao chubanshe, 2000), 435-457.

[369] Jinmin Fan, "Mingdai Diyu Shangbang Xingqi De Shehui Beijing," [Social background of the formation of regional commercial groups in the Ming Dynasty], *Journal of Tsinghua University (Philosophy and Social Sciences)* 21, no.5 (2006): 79-92; Li, 37-143.

[370] Qiong Zhang, "Huangquan Yu Jiyi: Qingdai Nei Zhiranju Kaocha," in *Gongting Yu Difang: Shiqi Zhi Shiba Shiji De Jishu Jiaoliu*, ed. Forbidden City and Max Planck Institute for the History of Science (Beijing: Zijincheng chubanshe, 2010), 77-122; Fang *et al.*, 536-539.

[371] Fang *et al.*, 536-539.

hundreds of dyeing workshops with tens of thousands of dyeing craftsmen.[372] With further development, dyeing workshops began to be specialised in certain colours, *e.g.* in Nanjing, various dyeing workshops respectively specialised in dyeing red, black and light shades. Even some cities were specialised in certain colours. Among the cities in Jiangnan area, Nanjing was famous for dyeing black, bronze and sky blue, Zhenjiang for pure red, Suzhou for jade colour, Hangzhou for qing (blue and purple) and light shades and Changzhou for fruit green.[373]

Dyeing techniques and other textile techniques developed together and improved each other. Patterns involving more shades were achieved by the abilities both to obtain a series of shades and to make multiple layers for the pattern by advanced textile woven or embroidery techniques.[374]

4.4.4.3 Circulation of techniques, raw materials and products

In the Ming Dynasty, central and local textile workshops almost spread across the country. The circulation of techniques was realised by the form of shift craftsman.[375] In the Qing Dynasty, because of the changed political situation, *Jiangnan san zhi zao* (the three Jiangnan silk bureaus) became the main official workshops and they were of unprecedentedly large scales.[376] Jiangnan area also became the most important centre for textile commodity production. The recruitment of textile experts from different places, especially Jiangnan area, to official workshops in the capital fostered the communication of techniques across regions. This also provided a good opportunity for craftsman

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[372] Dixin Xu and Chengming Wu, *Zhongguo Zibenzhuyi De Mengya* [Sprouts of Capitalism in China] (Beijing: Renmin chubanshe, 1985), 405.

[373] Fan and Jin, 388.

[374] Dagmar Schäfer, "Silken Strands: Making Technology Work in China," in *Cultures of Knowledge Technology in Chinese History*, ed. Dagmar Schäfer (Leiden: Brill, 2011), 45-73.

[375] Jinmin Fan, "Ming Qing Liangdai Guanying Zhizaoye Shengchan Guimo De Bijiao Yanjiu - Jian Yu Shen Zuwei Xiansheng Shangque," [Comparative study of the production scale of official textile industry of the Ming and Qing dynasties - Discussion with Mr. Shen Zuwei], *Historical Review* 5, no.4 (1990): 59-62, 102.

[376] Zhang, "Huangquan Yu Jiyi: Qingdai Nei Zhiranju Kaocha," 77-122.

specialised in different materials to work together and learn from each other.[377]

The circulation of raw materials and end products was also achieved through a national trade network. Raw materials for textile handicrafts were imported from various places in China to textile centres and textile products were exported all over China and to foreign countries. As the most important raw material for dyeing, dyes were planted in various places in China. Some became tributes to the central government and some were commodity.[378] The form of circulation included both market trading (some controlled by the government) and common commodity trading.[379] In textile trade, business guilds played an important part, the same as for ceramics as has been studied.[380] They either bought end products or customise what they needed.[381] Textile products were transported and sold all over China mainly by boat, sometimes by cart.[382]

4.5 Conclusions

In this chapter, historical and archaeological dyed samples of the Ming and Qing Dynasties, mostly of high-status, were collected and analysed by UHPLC-PDA and SEM analysis. This was the first time to analyse historical and archaeological dyes of relative large amounts and to explore the social background of dyeing in the Ming and Qing Dynasties.

For the 154 historical samples analysed in this study, the success rate of dye identification

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[377] Ibid.

[378] Yuanzhang Zhu, *Zhusi Zhizhang* [Responsibilities of All the Ministries] (1393); Guangwan Tan, "Zhongguo Gudai Zhiwu Ranliao Yanjiu" (Master's dissertation, North West Agriculture and Forestry University, 2009).

[379] Tan, "Zhongguo Gudai Zhiwu Ranliao Yanjiu."

[380] Fan and Jin, 235; Michael Dillon, "Transport and Marketing in the Development of the Jingdezhen Porcelain Industry During the Ming and Qing Dynasties," *Journal of the Economic and Social History of the Orient/Journal de l'histoire economique et sociale de l'Orient* (1992): 278-290.

[381] Jinmin Fan, "Qingdai Jiangnan Sichou De Guonei Maoyi," [Domestic trade of silk from Jiangnan in the Qing Dynasty], *Studies in Qing History* 2, no.2 (1992): 15-21.

[382] Jinmin Fan and Weizhong Xia, "Mingdai Jiangnan Sichou De Guonei Maoyi," [Domestic trade of silk from Jiangnan in the Ming Dynasty], *Journal of Historical Science* 26, no.1 (1992): 29-35; Fan, "Qingdai Jiangnan Sichou De Guonei Maoyi", 15-21; Fan and Jin, 241; Chaofeng Jiang, "Zhongguo Gudai 'Wuliu' Yipie," [A Glance at 'Logistics' in Ancient China], *China Storage & Transport*, no.3 (2006): 44-46.

was 89%, which was a significantly good success rate. Lac and smoketree were identified probably for the first time in historical Chinese textiles. Synthetic dyes were tentatively identified, including magenta, malachite green, picric acid and an aniline violet type dye, showing evidence of synthetic dyes being introduced to China in the late Qing Dynasty. Analytical results by SEM showed that the metal threads are mainly gold alloys and hematite is the ingredient for the red glue of two metal thread samples, being the first report identifying red powder used with glue for metal threads making in China. For archaeological samples, SEM analysis showed that contaminations are mostly from soil in the burial environment and some metal fragments may also come from surrounding objects. Evidence of common Chinese dyes was detected in some of the archaeological samples and this was the first dye analysis of relatively large amounts of textiles of this time period. So far no significant difference has been found in the use of dyes for threads for various uses, despite some potential preferences, or for textiles of different statuses. The analysis of more samples is needed for quantitative comparison.

Literature records and analytical results are mostly consistent in terms of the use of dyes and dyeing methods, and the development of dyeing over time. The combined results of literature research and chemical analysis showed that dyes commonly used during the Ming and Qing Dynasties included safflower, sappanwood, Amur cork tree, pagoda bud, indigo, acorn cup, turmeric, Chinese gallnut and smoketree, though turmeric was frequently found in the chemical analysis results but not in historical dye recipes and vice versa for Chinese gallnut and smoketree. Synthetic dyes were used for Chinese costume and textiles from the late 19th century as well. These dyes were used alone or with another dye, with specific rules, to obtain certain shades, with occasional cases of using three dyes together. The development of dyeing techniques included the adoption of better dyes and dyeing methods and the enrichment of colours by variations in the combination and quantity of raw materials.

By comparing dyes used in China and in other places, it was tentatively concluded that dyes specific and indigenous to China could help provenance Chinese textiles from textiles from other origins. Dyeing in China and in Europe during the Ming and Qing Dynasties was limited in terms of natural dyeing but the invention and trade of synthetic dyes in Europe greatly changed dyeing in China from the late 19th century.

Further research on the social background of dyeing handicrafts during the Ming and Qing Dynasties showed that dyeing handicraft developed with the evolvement of colour system and decrees for textiles. The flourishment of commodities during the mid Ming Dynasty fostered the development of private textile workshops and the specialisation of dyeing workshops. The realisation of dyeing activities also depended on a nationwide network for the circulation of technique, raw materials and products.

This chapter established an overview of dyeing in the Ming and Qing Dynasties from both physical evidences and literature research results. The next chapter investigates the accelerated light ageing of reference Chinese dyes and studies the lightfastness of the dyes, their chemical change during ageing and their ageing products. The conservation, preservation and exhibition of dyed textiles are discussed.

5 Accelerated Ageing Study of Dyes

5.1 Introduction

The fading of natural dyes is a major concern for preserving heritage textiles. During the ageing process, the chemical composition of dyes changes resulting in corresponding changes in colour.[383] Research has been undertaken on the light ageing of natural dyes in the field of conservation science since the 18th century, and in the 20th century the mechanism of ageing and factors affecting ageing were studied.[384] In recent decades the use of analytical techniques such as LC-MS and sometimes GC-MS has allowed more accurate identification of the degradation products of dyes and therefore deeper understanding of possible degradation pathways.[385] Additionally, research carried out in the fields of food chemistry, cosmetics and modern commercial textile production with natural dyes to choose appropriate type of dyes and determine their validities could also be helpful for understanding the degradation of dyes, though it is to be noted that historical dyeing mostly uses the hydrolysed extracts of plants whereas these other industries use and process the plants differently, and major ageing factors for dyed products from these

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[383] Robert L Feller, *Accelerated Aging: Photochemical and Thermal Aspects* (Getty Conservation Institute Los Angeles, CA, 1994), 13.

[384] C.H. Giles and R.B. McKay, "The Lightfastness of Dyes: A Review," *Textile Research Journal* 33, no.7 (1963): 527-577; HCA Van Beek and PM Heertjes, "Fading by Light of Organic Dyes on Textiles and Other Materials," *Studies in Conservation* 11, no.3 (1966): 123-132; Patricia Cox Crews, "The Fading Rates of Some Natural Dyes," *Studies in Conservation* (1987): 65-72.

[385] Ferreira, "New Approaches Towards the Identification of Yellow Dyes in Ancient Textiles"; Hamish McNab *et al.*, "Negative Ion ESI–Ms Analysis of Natural Yellow Dye Flavonoids—an Isotopic Labelling Study," *International Journal of Mass Spectrometry* 284, no.1 (2009): 57-65; Peggie, "The Development and Application of Analytical Methods for the Identification of Dyes on Historical Textiles"; Richard Laursen and Chika Mouri, "Decomposition and Analysis of Carthamin in Safflower-Dyed Textiles," *e-Preservation Science* 10 (2013), http://www.morana-rtd.com/e-preservationscience/2013/Laursen-16-12-2012.pdf; C. Clementi *et al.*, "A Spectrometric and Chromatographic Approach to the Study of Ageing of Madder (*Rubia Tinctorum* L.) Dyestuff on Wool," *Analytica Chimica Acta* 596, no.1 (2007): 46-54; C. Ahn and S.K. Obendorf, "Dyes on Archaeological Textiles: Analyzing Alizarin and Its Degradation Products," *Textile Research Journal* 74, no.11 (2004): 949-954; M.P. Colombini *et al.*, "Colour Fading in Textiles: A Model Study on the Decomposition of Natural Dyes," *Microchemical Journal* 85, no.1 (2007): 174-182; Gibbs and Seddon, "Berberine and Huangbo: Ancient Colorants and Dyes," 30.

different industries vary.[386]

Increasing knowledge about the ageing of natural dyes was obtained by research in the above fields. Nevertheless, knowledge on the fading of Chinese natural dyes was very limited in terms of both the kinds of dyes studied and the mechanism of degradation. The light stability, degradation pathways and degradation products of the dyes remained to be explored to help with the identification, preservation and exhibition of the dyes.

This chapter investigates the ageing of dyes commonly used in ancient China, mainly to identify changes in the chemical profiles of the aged samples to explain differences between the dyed references and the historical samples analysed. Accelerated light ageing is undertaken on reference dyes and aged samples are chemically analysed by UHPLC-PDA, mainly in terms of the decrease and disappearance of dye components and the appearance and increase of degradation products. The identification of the chemical structures of the degradation products is not the primary aim in this research, which would entail a more in-depth chemical study type of project. Instead, factors affecting the ageing of dyes and the kinetics of ageing are discussed because these are more relevant to conservation considerations for preservation of dye colours when historical textiles are exposed to light for display and access. The preservation state of the dyes is investigated and suggestions for the conservation, preservation and exhibition of dyes are provided.

5.2 Principles of accelerated ageing

Accelerated ageing stimulates natural ageing processes and accelerates chemical reactions in materials by initiated and propelled by environmental conditions such as light, heat

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[386] Manuel Carmona *et al.*, "Generation of Saffron Volatiles by Thermal Carotenoid Degradation," *Journal of agricultural and food chemistry* 54, no.18 (2006): 6825-6834; Ana M Sánchez *et al.*, "Kinetics of Individual Crocetin Ester Degradation in Aqueous Extracts of Saffron (Crocus Sativus L.) Upon Thermal Treatment in the Dark," *Journal of agricultural and food chemistry* 56, no.5 (2008): 1627-1637; Erika Pfeiffer *et al.*, "Studies on the Stability of Turmeric Constituents," *Journal of food engineering* 56, no.2 (2003): 257-259.

and/or relative humidity (%RH). For historical dyes on textiles, their material composition is mainly governed by the wavelengths and intensity of the light, and exposure time. The accelerated ageing experiments for this research project focussed on lighting conditions relevant to controlled environmental conditions for textiles in museum exhibition areas and access areas such as study rooms, stores and conservation studios. The currently-accepted conditions are 50 lux to 100 lux, and approximately 20 ^{o}C and 55% RH.[387]

Accelerated light ageing mostly follows reciprocity principle: the total photochemical damage on an object depends on its overall amount of light exposure, which is equal to the intensity of irradiance multiplied by exposure time.[388] The recommended light-exposure for light-sensitive objects, such as dyed textiles, in museums is 50 lux for 3,000 hours (h) a year.[389] Therefore one year's natural light ageing within the standard is comparable to accelerated light ageing using a light source with the average intensity of illuminance at 142,000 lux for 1.06 hours.

5.3 Materials and methods

5.3.1 Reference samples for accelerated ageing

Samples used for accelerated ageing study included reference silk samples dyed with the twelve common dyes (section 3.3.1.1) and an undyed silk sample as reference to monitor the change of silk during ageing process. Nine yarns for each kind of dyed silk (20 cm, approximately 2.5 g) were unwoven from dyed silk fabrics and tied together on a frame of 15 cm × 12 cm made of acid-free card (Figure 5. 1). In this way for each dyed silk sample there were three duplicates of 4 cm (approximately 0.5 mg) the average weight of

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[387] British Standards Institution, *Code of Practice for Cultural Collections Management: Pas 197:2009* (London: British Standards Institution, 2009), 31; May Cassar, *Environmental Management: Guidelines for Museums and Galleries* (London: Routledge, 2013), 88.

[388] Feller, 13.

[389] Garry Thomson, *The Museum Environment* (London; Boston: Butterworths, in association with the International Institute for Conservation of Historic and Artistic Works, 1986).

historical dyed silk samples), allowing for quantitative analysis when needed. Seven sets of samples tied on seven frames were prepared for ageing for different time periods.

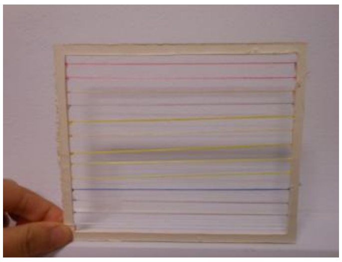

Figure 5. 1 Silk samples tied on a frame ready for ageing

5.3.2 Accelerated ageing: equipments and ageing parameters

In this research, a Q-SUN Xe-1 Xenon Test Chamber with a Full Spectrum Q-Lab Xenon Arc lamp X-1800 (1800w) was used to age the dyed reference samples (Figure 5. 2, left). A X-7462-K Window-Glass Filter blocking most of the UV light was installed to stimulate indoor environment (Figure 5.2, right). The average intensity of illuminance was 0.68 W/m^2 at 420 nm. The temperature inside the test chamber was controlled at 26 ℃ by an internal chiller.

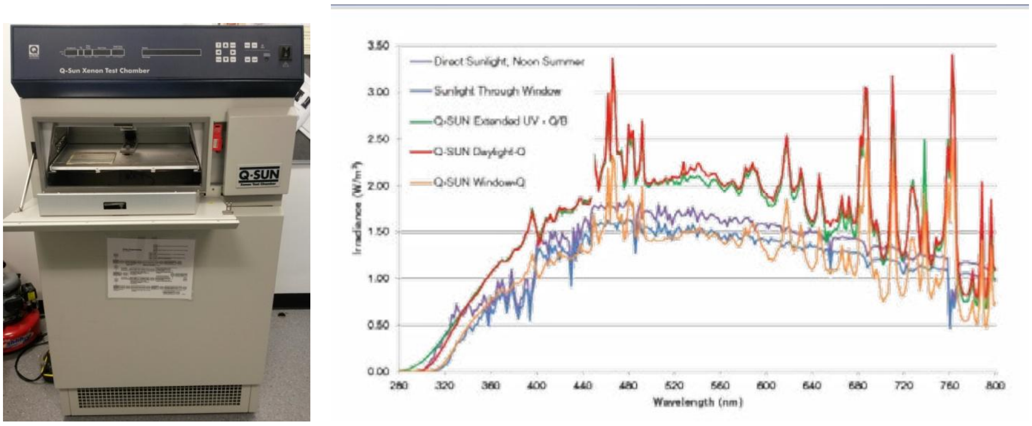

Figure 5. 2 Q-SUN Test Chamber used for the accelerated ageing of dyed reference silk (left) and the spectrum generated by the Xenon Art Lamp with a Window-Glass Filter (orange line) (right)[390]

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[390] Q-Lab Corporation, "Q-Sun Xenon Test Chambers," http://www.q-lab.com/documents/public/41b5935b-d41d-4368-a53e-98a3d528baf1.pdf#page=8.

This research focussed on dyes of the Ming and Qing Dynasties which were produced approximately 100 to 650 years ago and had probably been exposed to light for tens to hundreds of years during their use, preservation and exhibition. Therefore the samples mimicking natural light ageing according to the museum standard for approximately 300 years (292 years in practice) were used as the main set of samples to study the ageing behaviours of the dyes. A set of samples mimicking natural light ageing for up to 500 years was prepared to explore their severe ageing states, especially to study the degradation products of the most stable dyes. Several sets of samples mimicking natural light ageing within 300 years were prepared as well to study the change progress of the chemical composition of the dyes during ageing whenever necessary. To be specific, the sample sets were accelerated aged for seven different time periods, respectively 1) 8 h, 2) 32 h, 3) 48 h, 4) 100 h, 5) 216 h, 6) 308 h and 7) 528 h, comparable to natural light ageing for 1) 8 y, 2) 30 y, 3) 45 y, 4) 95 y, 5) 204 y, 6) 292 y and 7) 500 y. During ageing, the frames were reversed regularly to ensure both front and back sides were aged to the same extent. After accelerated ageing, the sample sets were wrapped in acid-free tissue paper and stored in darkness in a drawer, protected from further light exposure.

5.3.3 Chemical analysis

The solvent extracts of the light-aged samples were analysed by UHPLC-PDA to find out their changes in chemical composition during ageing, especially to detect their intermediates and final products. For each sample 4 cm was cut off (about 0.5 g) and the extraction method of DMSO-OA was applied. The system conditions for UHPLC-PDA were the same as for analysing reference samples (section 3.3.2.2). For data analysis, UHPLC-PDA chromatograms were extracted at the typical wavelength to detect the colourants of the dye and at the screening wavelength of 254 nm to detect both coloured and colourless components. The change of the components were analysed in both qualitative and semi-quantitative ways, especially the decrease and disappearance of characteristic components, the appearance and increase of degradation products, and the change in ratio between certain components during ageing. Since few published degradation products are with UV-vis spectral data, there were some difficulties identifying the molecular structures of the degradation components found in analytical results by UHPLC-PDA analysis, but the major degradation products were added to the UHPLC library to help identify unknown components in historical and archaeological samples.

5.4 Results for accelerated aged samples

5.4.1 The degradation of silk

Figure 5. 3 presents the UHPLC-PDA chromatograms of undyed silk aged for 0, 308 and 528 h. In the unaged silk sample no constituents of silk were detected in the chromatogram, indicating that the constituents of unaged silk connect closely with each other and these connections are not damaged in the dye extraction process. After ageing for 528 h a major component eluting at 7.5 min with maximum absorption at 255.3 nm appears. Apart from this, four minor colourless components eluting at 5.0, 6.0, 9.2 and 9.5 min were found. It is known that silk is mainly composed of fibroin and sericin proteins.[391] Fibroin consists of amino acids, among which glycine and alanine are of the highest relative proportion (29% and 25% respectively).[392] Sericin has been mostly removed during a degumming process before dyeing.[393] During the ageing process, changes including oxidation and degradation occur in the composition of the amino acids of fibroin, usually from amorphous regions to crystallites.**[394]** 4-Hydroxybenzoic acid, most probably the oxidation product of tyrosine,

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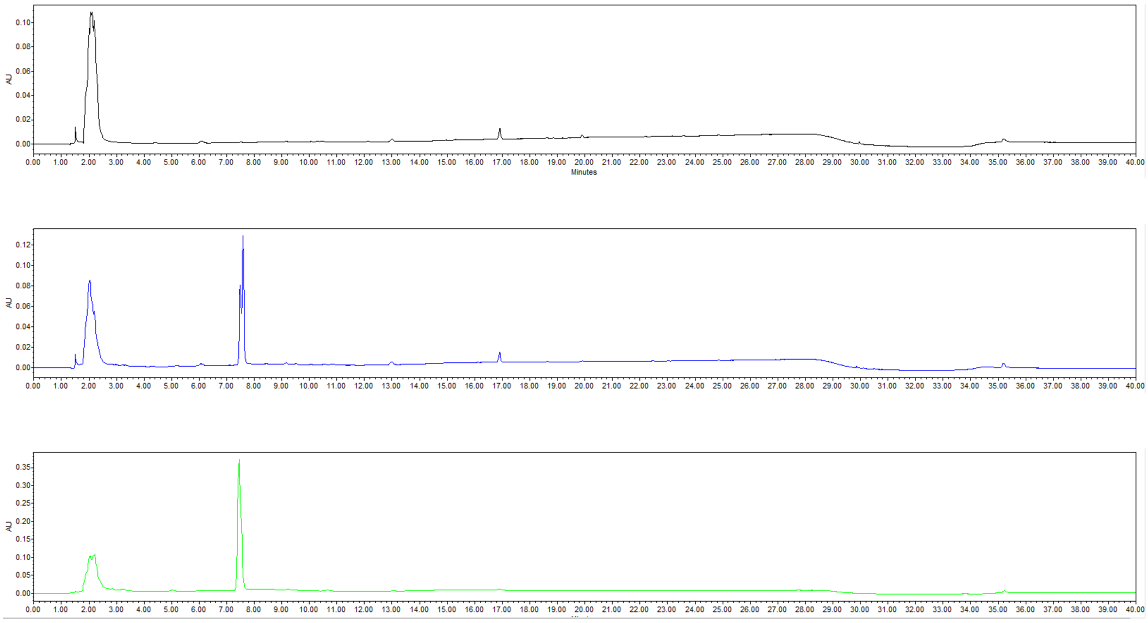
[391] Francisco Vilaplana *et al.*, "Analytical Markers for Silk Degradation: Comparing Historic Silk and Silk Artificially Aged in Different Environments," *Analytical and bioanalytical chemistry* 407, no.5 (2015): 1433-1449.

[392] Stela Baltova and Violeta Vassileva, "Photochemical Behaviour of Natural Silk—Ii. Mechanism of Fibroin Photodestruction," *Polymer Degradation and Stability* 60, no.1 (1998): 61-65.

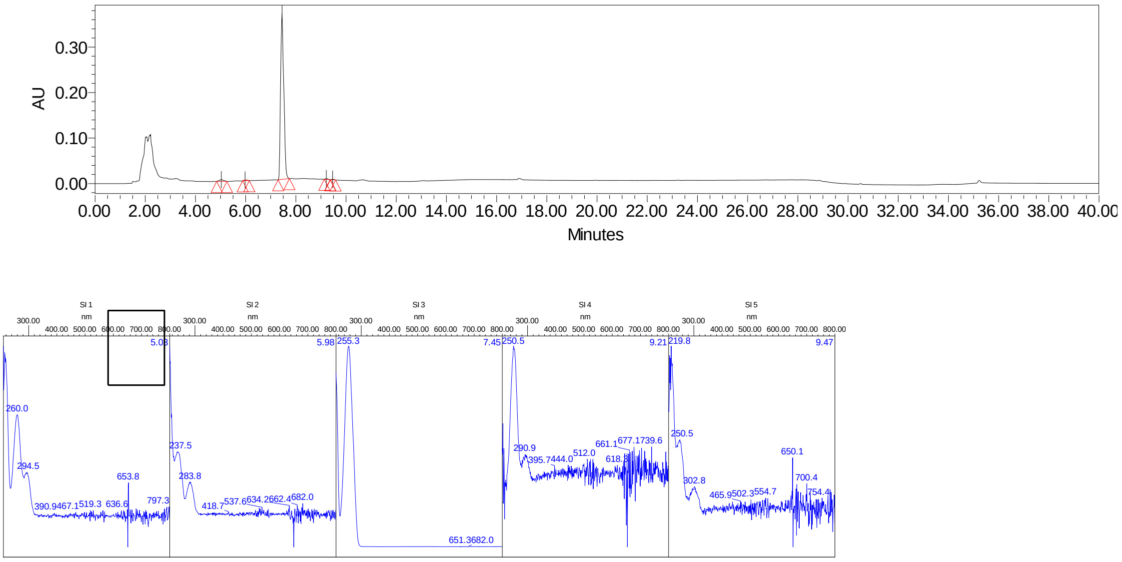
[393] Decai Gong and Haiyan Yang, "The Discovery of Free Radicals in Ancient Silk Textiles," *Polymer Degradation and Stability* 98, no.9 (2013): 1780-1783.

[394] Vilaplana *et al.*, "Analytical Markers for Silk Degradation: Comparing Historic Silk and Silk Artificially Aged in Different Environments," 1433-1449; Ilaria Degano *et al.*, "Historical and Archaeological Textiles: An Insight on Degradation Products of Wool and Silk Yarns," *Journal of Chromatography A*

was detected as a degradation product of silk and can be used as a marker for its extent of degradation.[395]



(a) The UPLC-PDA chromatograms (monitored at 254 nm) of the undyed silk samples aged for 0, 308 and 528 h



(b) The UPLC-PDA chromatogram (monitored at 254 nm) of the undyed silk sample aged for 528 h and the UV-Vis spectra of its main degradation products

Figure 5. 3 Changes in chemical composition of undyed silk during accelerated ageing

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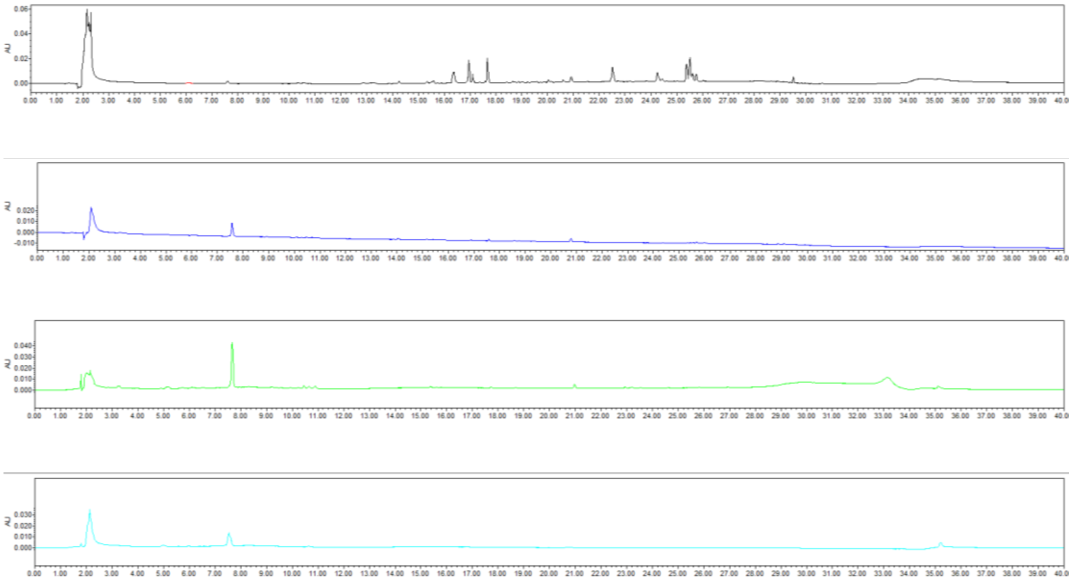
1218, no.34 (2011): 5837-5847; Paul Garside and Paul Wyeth, "Crystallinity and Degradation of Silk: Correlations between Analytical Signatures and Physical Condition on Ageing," *Applied Physics A* 89, no.4 (2007): 871-876.

[395] Degano *et al.*, "Historical and Archaeological Textiles: An Insight on Degradation Products of Wool and Silk Yarns," 5837-5847; Colombini *et al.*, "Colour Fading in Textiles: A Model Study on the Decomposition of Natural Dyes," 174-182.

5.4.2 Red and purple dyes

5.4.2.1 Safflower

The decomposition products and pathways for carthamin during thermal and light ageing were studied and their degradation products were identified separately.[396] In this experiment the ageing of safflower dyed silk was carried out to compare its lightfastness with the lightfastness of the other dyes and to add its degradation information to the library. Figure 5. 4 presents the UHPLC-PDA chromatogram of safflower dyed silk aged for 100, 308 and 528 h. The main dye component of safflower, carthamin, is unstable: it disappeared after ageing for 100 h, indicating this component has changed chemically. Some colourless components are still present after ageing for 308 h, including those for safflower Ct components, which could help identifying degraded safflower.[397] Degradation products appear after ageing for 308 h eluting at 7.9-10.9 min, which are probably from the decreasing peaks of carthamin and the other characteristic peaks of safflower. In the sample aged for 528 h, the Ct component at 17.8 min, a characteristic for safflower, and another component at 20.78 min are still present.



(a) The UPLC-PDA chromatograms (monitored at 295nm) of the safflower dyed samples aged for 0, 100, 308 and 528 h

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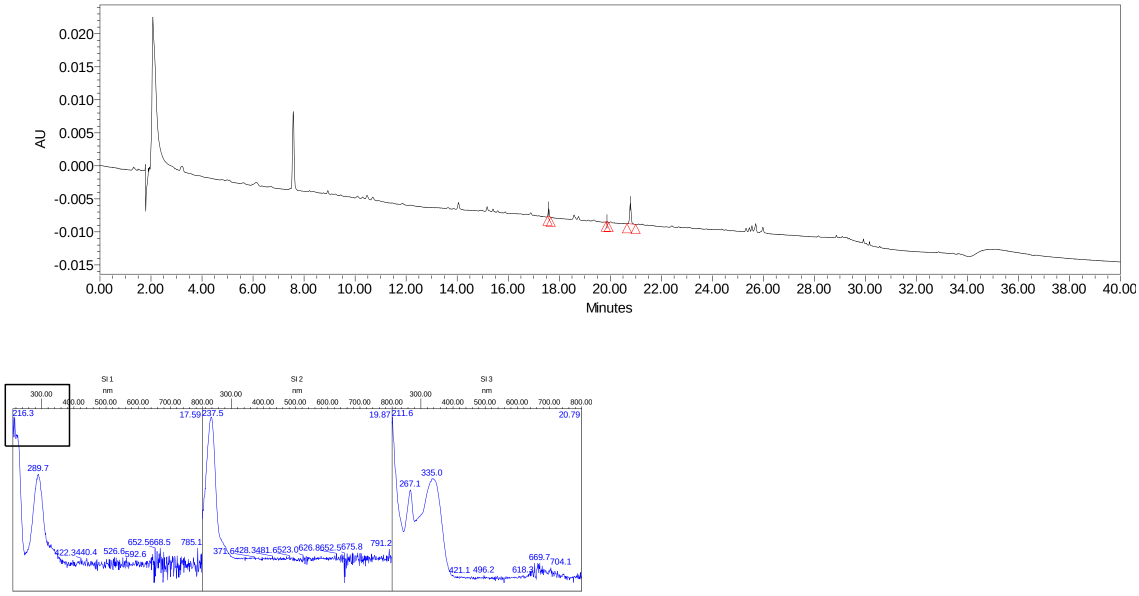
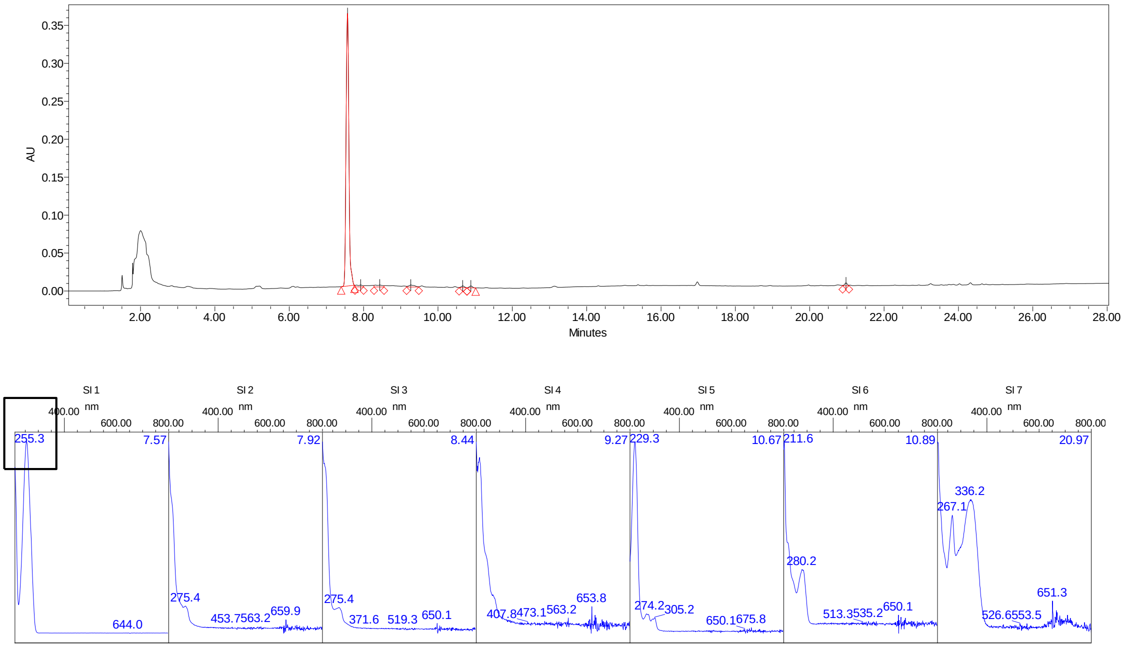
[396] Laursen and Mouri, "Decomposition and Analysis of Carthamin in Safflower-Dyed Textiles".

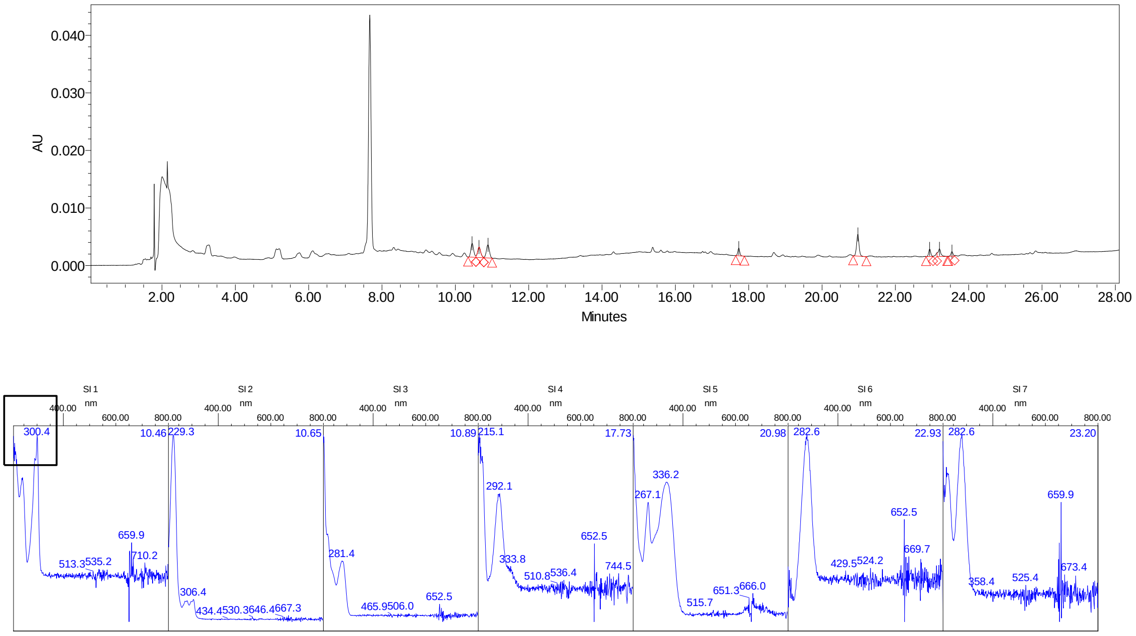
[397] Wouters, Grzywacz, and Claro, "Markers for Identification of Faded Safflower (Carthamus Tinctorius L.) Colorants by HPLC-PDA-MS Ancient Fibres, Pigments, Paints and Cosmetics Derived from Antique Recipes," 186-203.



(b) The UPLC-PDA chromatogram (monitored at 295 nm) of the safflower dyed sample aged for 100 h and the UV-Vis spectra of its main constituents. The three components are respectively a safflower Ct component, a degradation product of the safflower dyed sample aged for 100 h and a characteristic component of safflower.



(c) The UPLC-PDA chromatogram (monitored at 254 nm) of the safflower dyed sample aged for 308 h and the UV-Vis spectra of its main constituents. The main constituents are respectively a degradation product of silk, five degradation products of safflower and a characteristic component of safflower.

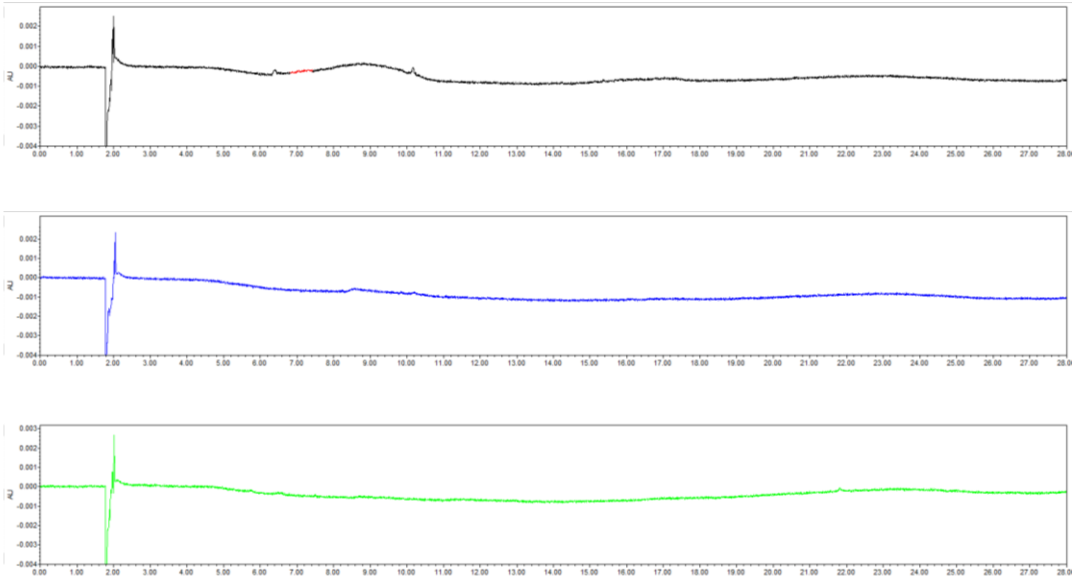


(d)The UPLC-PDA chromatogram (monitored at 295 nm) of the safflower dyed sample aged for 308 h and the UV-Vis spectra of its main constituents. The main constituents are respectively a degradation product of silk, two degradation products of safflower, a Ct component of safflower and three characteristic components of safflower.

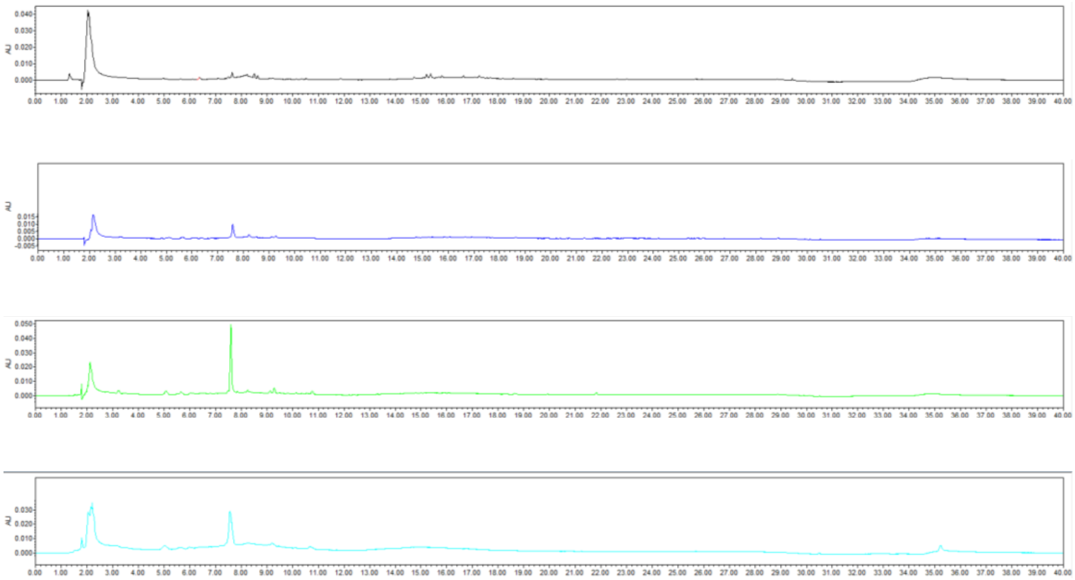
Figure 5. 4 Changes in chemical composition of safflower dyed silk during accelerated ageing

5.4.2.2 Sappanwood

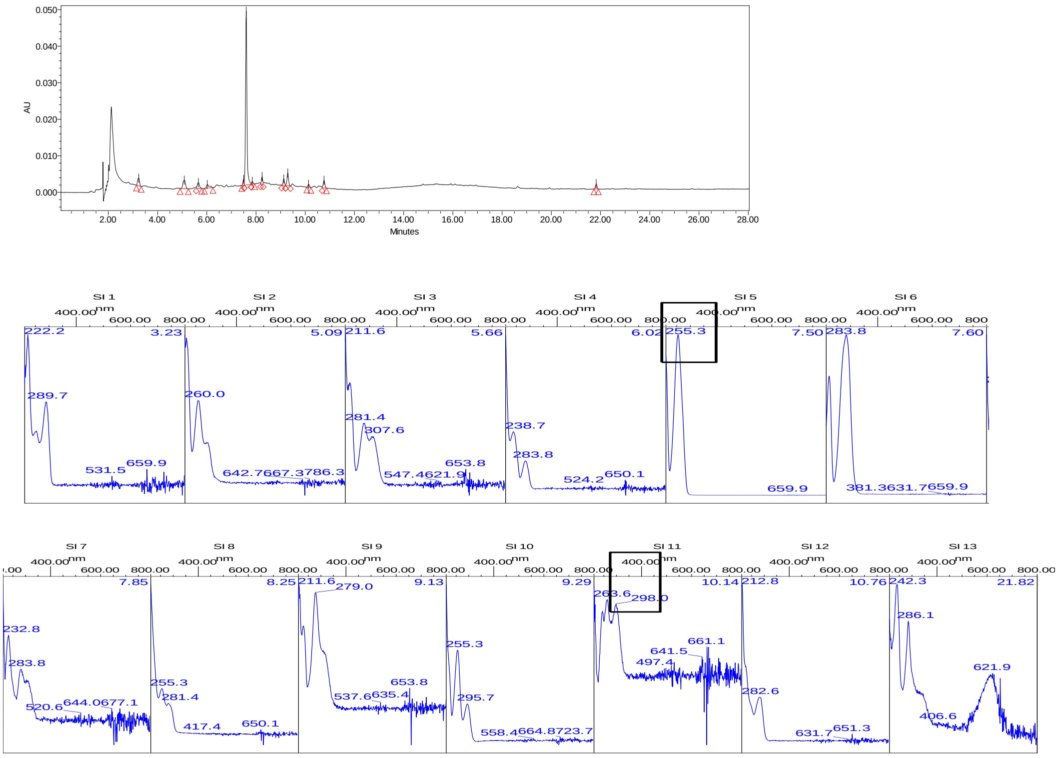
Similar to safflower, sappanwood contains both coloured and colourless characteristic components. The peak for the red component brasilein is still visible after ageing for 100 h but disappears afterwards (Figure 5. 5). The colourless characteristic components type A components (at 8.5 and 8.7 min) and type C component at 14.7 min are present after ageing for 308 h, but disappear after ageing for 528 h. Several intermediate components were detected after ageing for 308 h, and two colourless components in the sample aged for 528 h, which probably indicate the degradation pathways of the lost characteristic components of sappanwood. How these coloured and colourless components degrade over time needs further investigation.



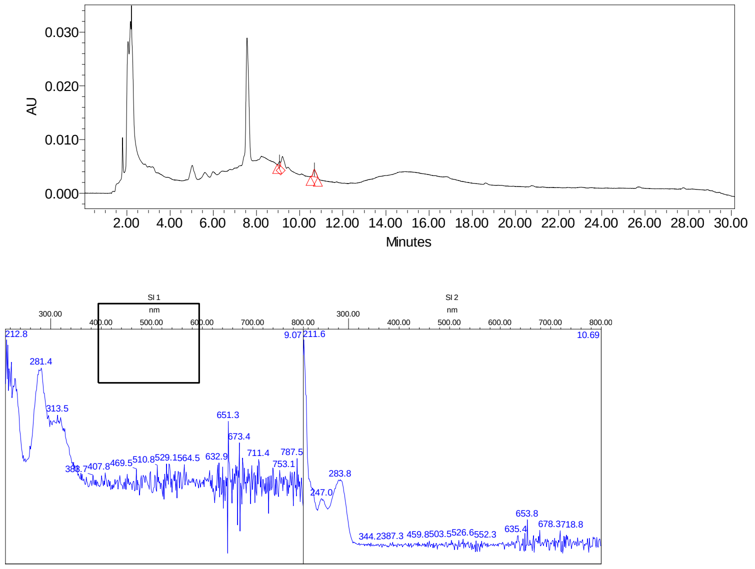
(a) The UPLC-PDA chromatograms (monitored at 450 nm) of the sappanwood dyed samples aged for 0, 100 and 308 h



(b) The UPLC-PDA chromatograms (monitored at 295nm) of the sappanwood dyed samples aged for 0, 100 and 308 h



(c) The UPLC-PDA chromatogram (monitored at 295 nm) of the sappanwood dyed sample aged for 308 h and the UV-Vis spectra of its main constituents. The degradation products of sappanwood elutes respectively at 3.2, 5.6, 7.8, 10.1, 10.8 and 21.8 min. The three components eluting at 8.2, 9.1 and 9.3 min are characteristic components of sappanwood.

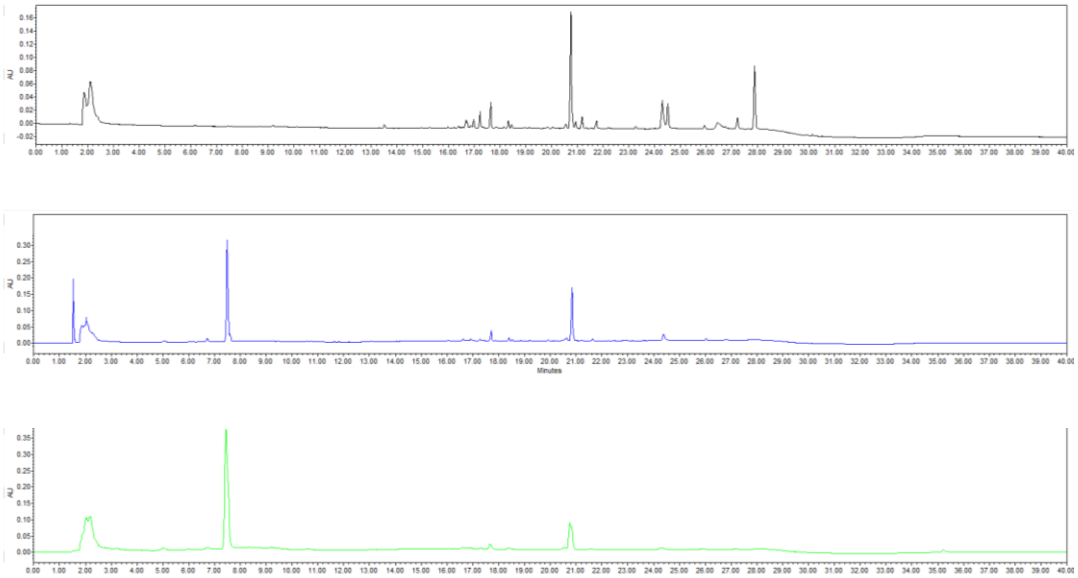


(d) The UPLC-PDA chromatogram (monitored at 295 nm) of the sappanwood dyed sample aged for 528 h and the UV-Vis spectra of its main constituents

Figure 5. 5 Changes in chemical composition of sappanwood dyed silk during accelerated ageing

5.4.2.3 Munjeet

The main coloured components of munjeet are relatively stable (Figure 5. 6). After ageing for 528 h the two main components 6-hydroxyrubiadin-O-Rha-Glc and 6-hydroxyrubiadin-OAc-Rha-Gla (section 3.4.1.4), respectively eluting at 17.6 and 20.7 min, are still present in relatively large amounts. It is known that quinone dyes are of good light-stability because the mutual transformation between quinone and phenolic structures slows the degradation process.[398] Research has been undertaken on the thermal and peroxide/UV degradation of alizarin and more investigation is needed on the ageing of the components of munjeet.[399]



(a) The UPLC-PDA chromatograms (monitored at 430 nm) of the munjeet dyed samples aged for 0, 308 and 528 h

Figure 5. 6 Changes in chemical composition of munjeet dyed silk during accelerated ageing

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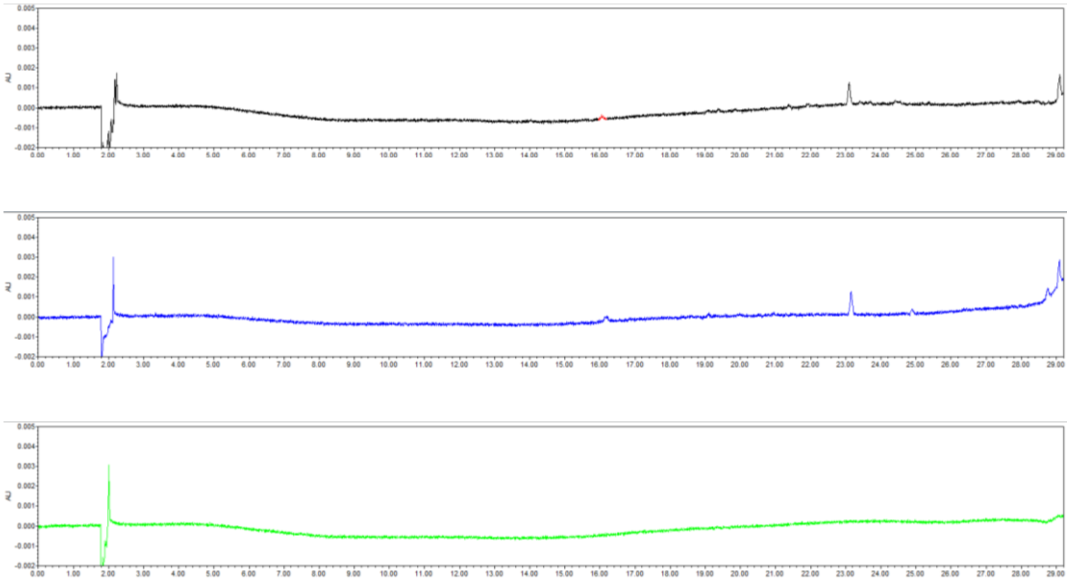
[398] Yongjin Zhang, Bolan Zhang, and Xinyuan Song, "Xianwei Shang Ranliao De Laohua Ziwai Guangpu Fenxi," [UV Spectral Analysis of Dye Degradation on Fibers], *Dyestuffs and coloration* 31, no.5 (2003): 269-271.

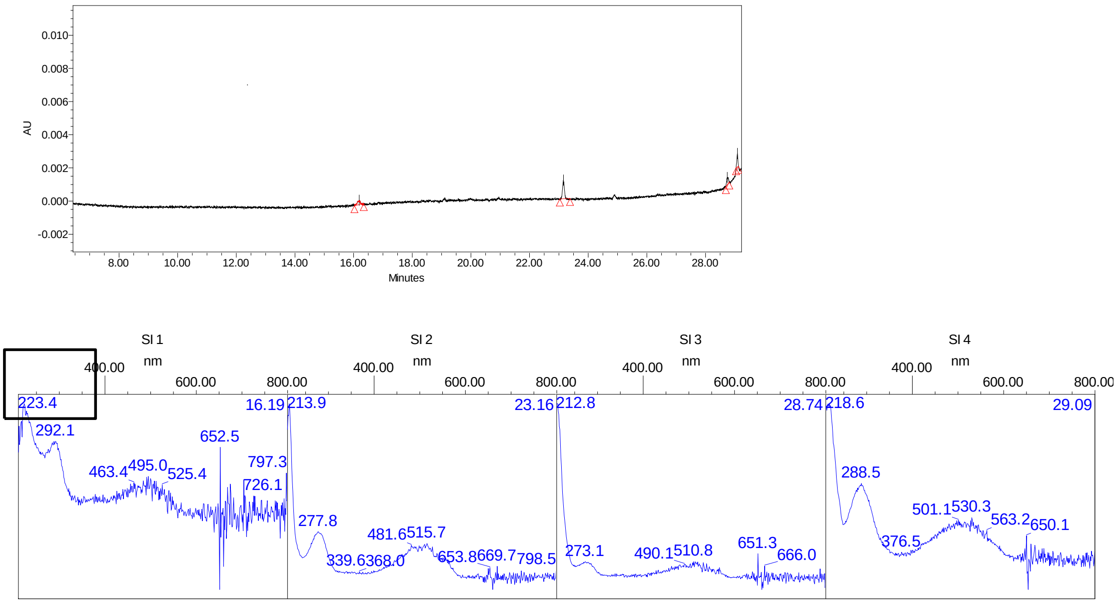
[399] Ahn and Obendorf, "Dyes on Archaeological Textiles: Analyzing Alizarin and Its Degradation Products," 949-954.

5.4.2.4 Gromwell

Gromwell is not lightfast and all the peaks for its characteristic coloured components disappear when aged for 308 h (Figure 5. 7). A shikonin equivalent eluting at 28.7 min appears when aged for 8 h and disappears in the sample aged for 308 h. The degradation products of gromwell needs further research to be characterised.



(a) The UPLC-PDA chromatograms (monitored at 515 nm) of the gromwell dyed samples aged for 0, 8 and 308 h



(b) The UPLC-PDA chromatogram (monitored at 515 nm) of the gromwell dyed sample aged for 8 h and the UV-Vis spectra of its main constituents

Figure 5. 7 Changes in chemical composition of gromwell dyed silk during accelerated ageing

5.4.3 Yellow dyes

5.4.3.1 Pagoda bud

The dye components of pagoda bud are relatively stable (Figure 5. 8). After ageing for 528 h, small amounts of rutin and isorhamnethin-rutinoside remain. Rutin and isorhamnethin-rutinoside are more stable than their aglycones, quercetin and isorhamnethin, judging by the increasing ratio of the peak areas of rutin to quercetin during ageing. This is in accordance to the research result that 3-O-substituted 3-hydroxyflavones are more lightfast than their corresponding aglycones.[400] However, this could not be used directly to identify the preservation state of historical dyes because their original ratio, which varies by such factors as collection time (collecting buds or flowers) and pre-processing activities, is unknown.

Degradation components are generated during the ageing of pagoda bud dyed samples. When the sample is aged for 308 h, several components eluting at 8.5-9.2 min appear. The sample aged for 528 h contains colourless components eluting from 8.0-9.1 min and these components are slightly different from those in the sample aged for 308 h, indicating further degradation. It was found that photooxidation is the main process during the light ageing of flavonols and this may result from radical moieties activated by light or catalysed by mordants.[401] Substituents of the B-ring help identify the original flavonol, for example, the B-ring of quercetin is degraded to 3, 4-dihydroxybenzoic acid and methyl 3,4-dihydroxybenzoate; while the B ring of kaempferol is degraded to 4-hydroxybenzoic acid and its corresponding methyl ester.[402]

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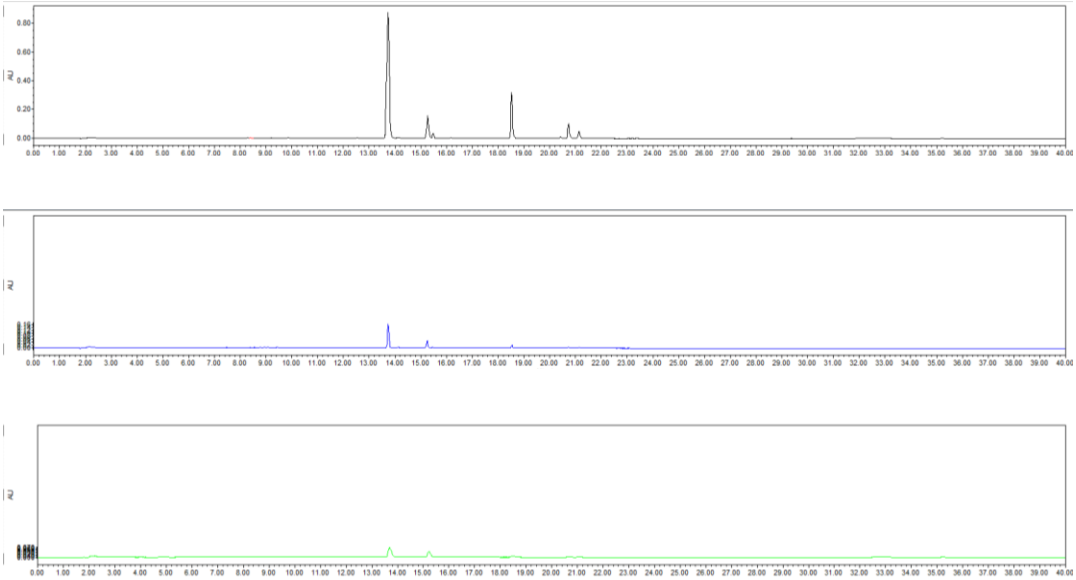
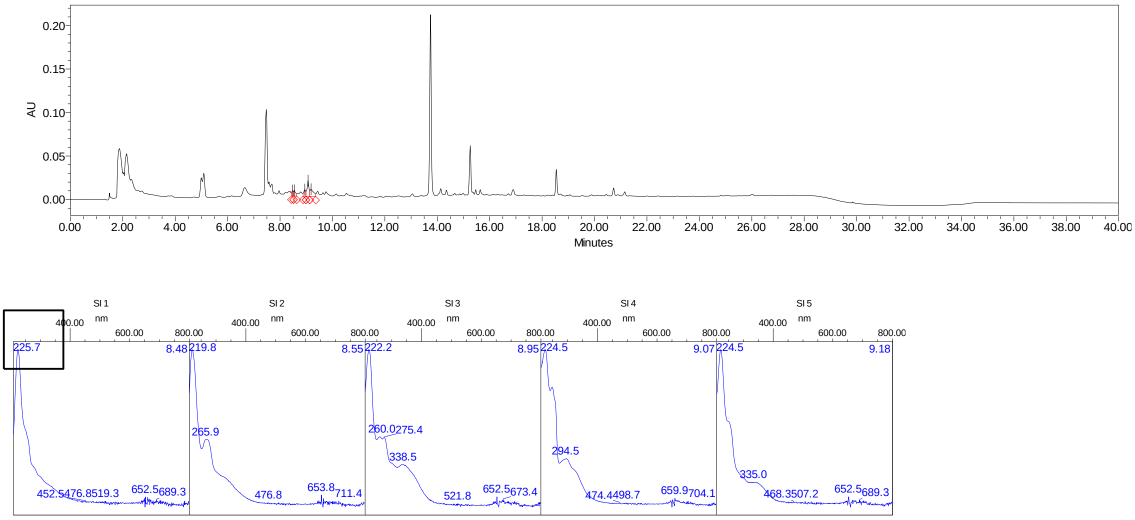
[400] Zhang *et al.*, "The Role of Glycosides in the Light-Stabilization of 3-Hydroxyflavone (Flavonol) Dyes as Revealed by HPLC," 327-334.

[401] Ferreira, "New Approaches Towards the Identification of Yellow Dyes in Ancient Textiles"; Colombini *et al.*, "Colour Fading in Textiles: A Model Study on the Decomposition of Natural Dyes," 174-182.

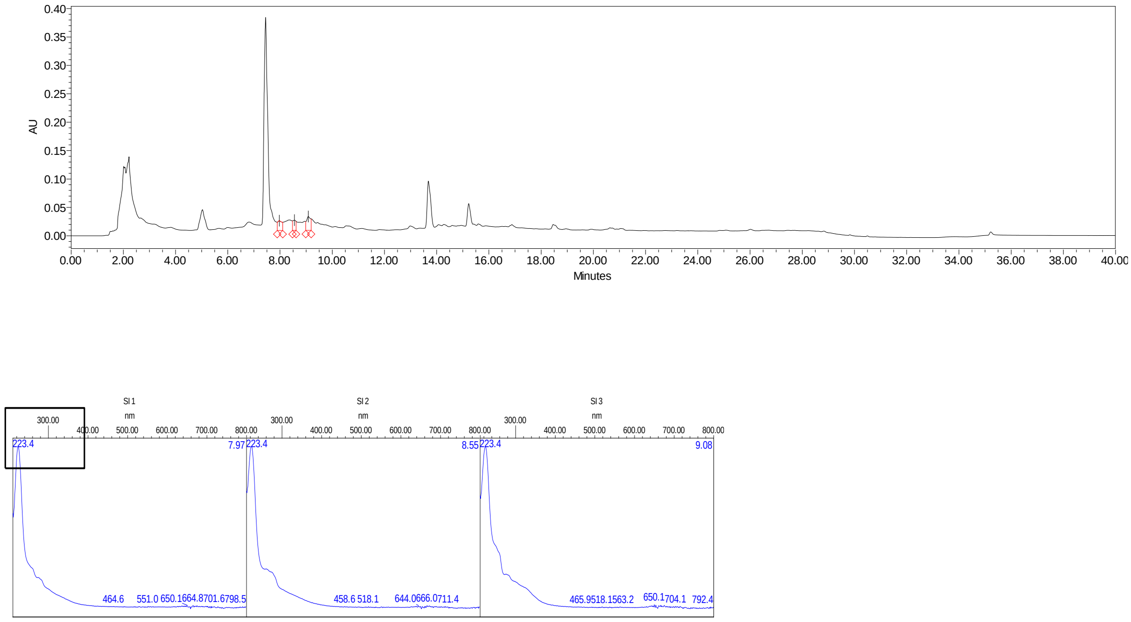
[402] Ferreira, "New Approaches Towards the Identification of Yellow Dyes in Ancient Textiles."



(a) The UPLC-PDA chromatograms (monitored at 350 nm) of the pagoda bud dyed samples aged for 0, 308 and 528 h



(b) The UPLC-PDA chromatogram (monitored at 350 nm) of the pagoda bud dyed sample aged for 308 h and the UV-Vis spectra of its main constituents



(c) The UPLC-PDA chromatogram (monitored at 254 nm) of the pagoda bud dyed sample aged for 528 h and the UV-Vis spectra of its main constituents

Figure 5. 8 Changes in chemical composition of pagoda bud dyed silk during accelerated ageing

5.4.3.2 Smoketree

Smoketree is not as lightfast as pagoda bud: the amount of sulfuretin, its main colourant, decomposes quickly after being aged for 308 h (Figure 5. 9). A degradation product eluting at 9.3 min was detected in the sample aged for 308 h and its amount increases in the sample aged for 528 h. Another new component at 10.8 min appears in the sample aged for 528 h. The small amount of fisetin disappears after being aged for 308 h. It was found that the photo-degradation of this flavonol is in an identical pathway to that of quercetin.[403]

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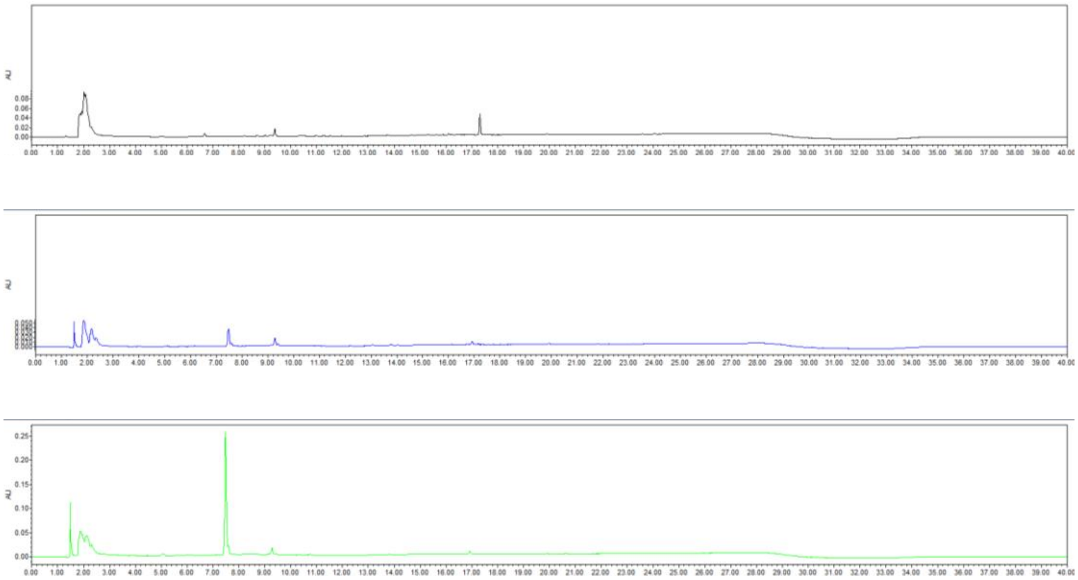
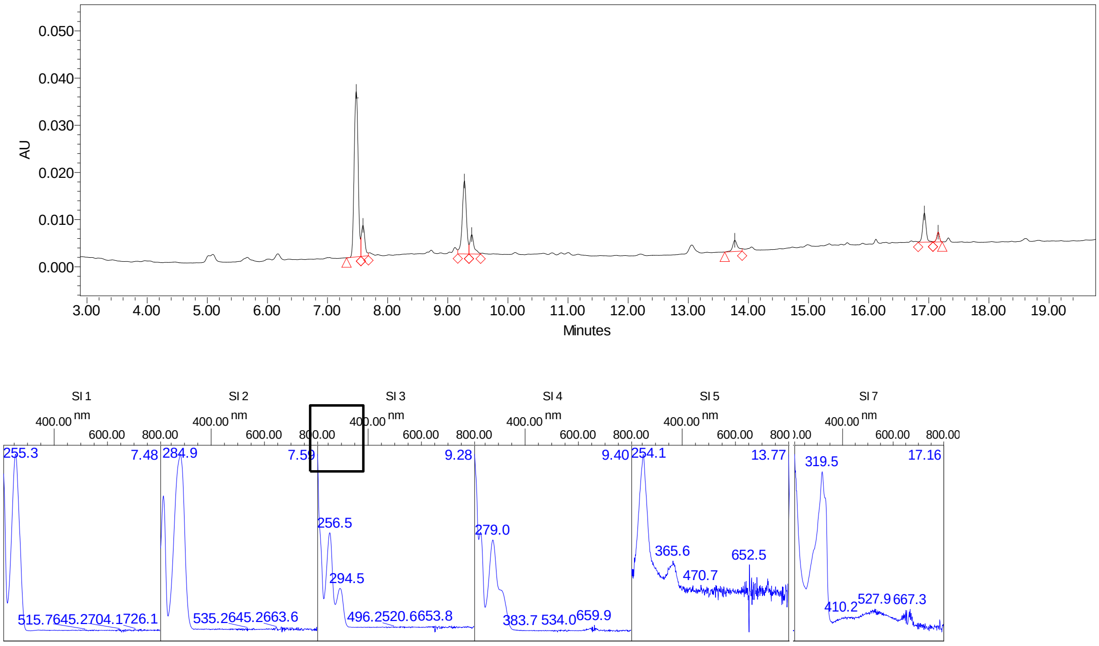
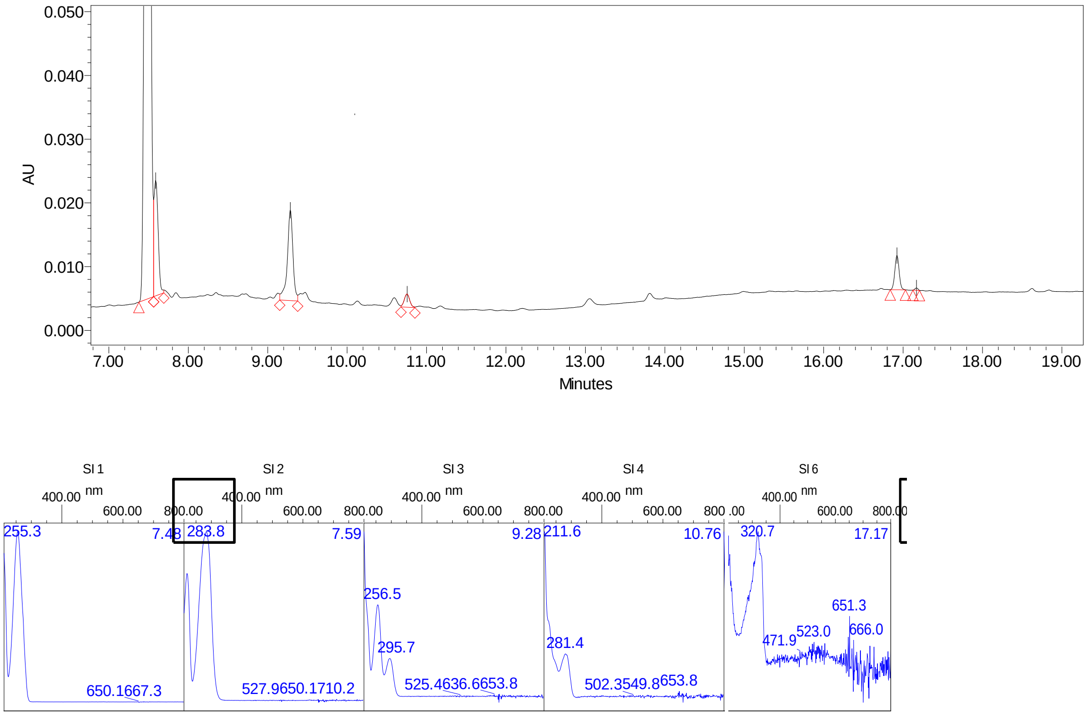
[403] Peggie, "The Development and Application of Analytical Methods for the Identification of Dyes on Historical Textiles."



(a) The UPLC-PDA chromatograms (monitored at 254nm) of the smoketree dyed samples aged for 0, 100 and 308 h



(b) The UPLC-PDA chromatogram (monitored at 254 nm) of the smoketree dyed sample aged for 100 h and the UV-Vis spectra of its main constituents. The main constituents are respectively two degradation product of silk, a degradation product of smoketree, a characteristic component of smoketree, ellagic acid and another degradation product of smoketree.



(c) The UPLC-PDA chromatogram (monitored at 254 nm) of the smoketree dyed sample aged for 308 h and the UV-Vis spectra of its main constituents. The main constituents are respectively two degradation product of silk and three degradation products of smoketree (aged for 100, 308 and 100 h).

Figure 5. 9 Changes in chemical composition of smoketree dyed silk during accelerated ageing

5.4.3.3 Gardenia

Gardenia is relatively lightfast. In the sample aged for 528 h, there are still small amounts of crocins (Figure 5. 10). A minor colourless peak with maximum absorption at 240 nm appears in the sample aged for 528 h. Besides, intermediate degradation products eluting at 10.1 and 18.7 min were found in the sample aged for 308 h. Thermal degradation study has been carried out on crocetin and crocins and their degradation products were identified and degradation mechanisms proposed,[404] which may be of reference value for studying the light degradation of these components.

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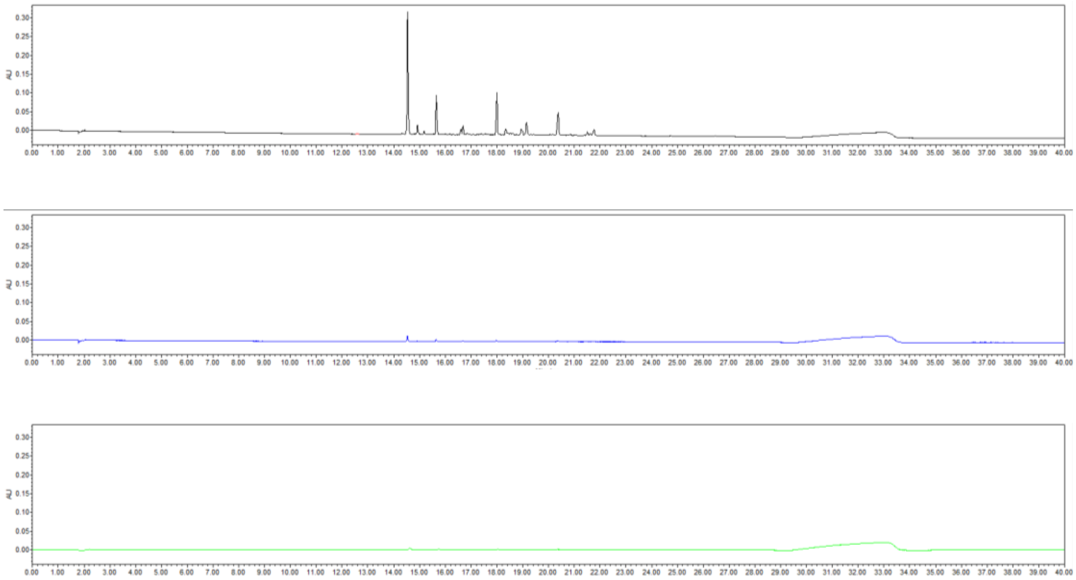
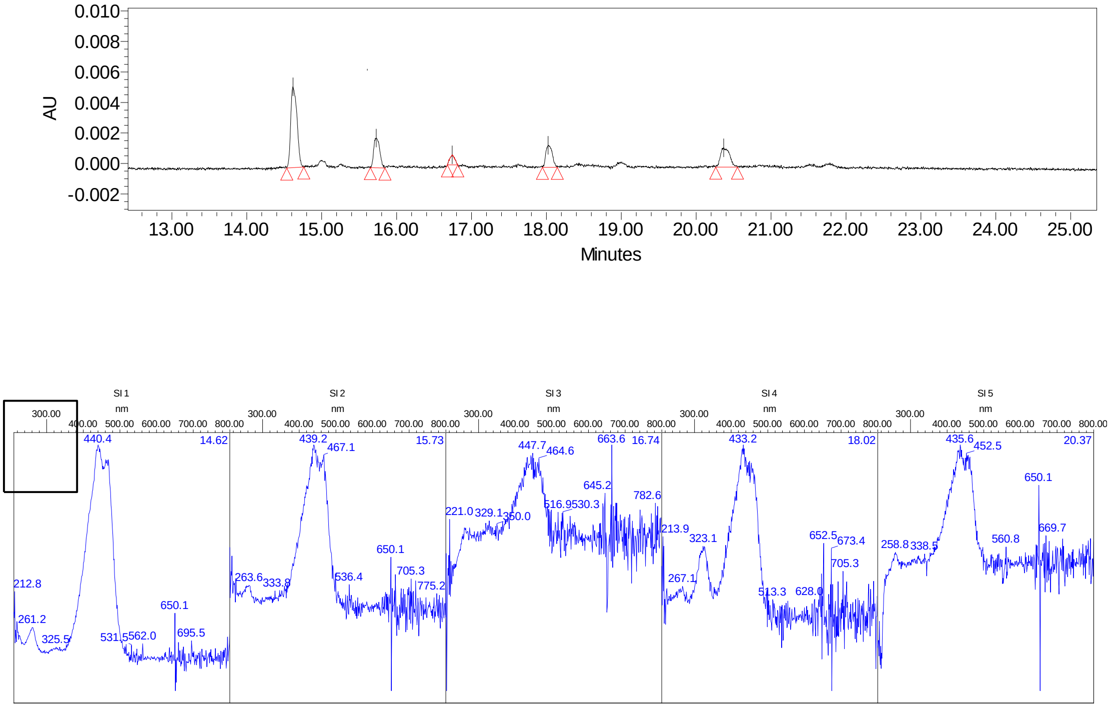
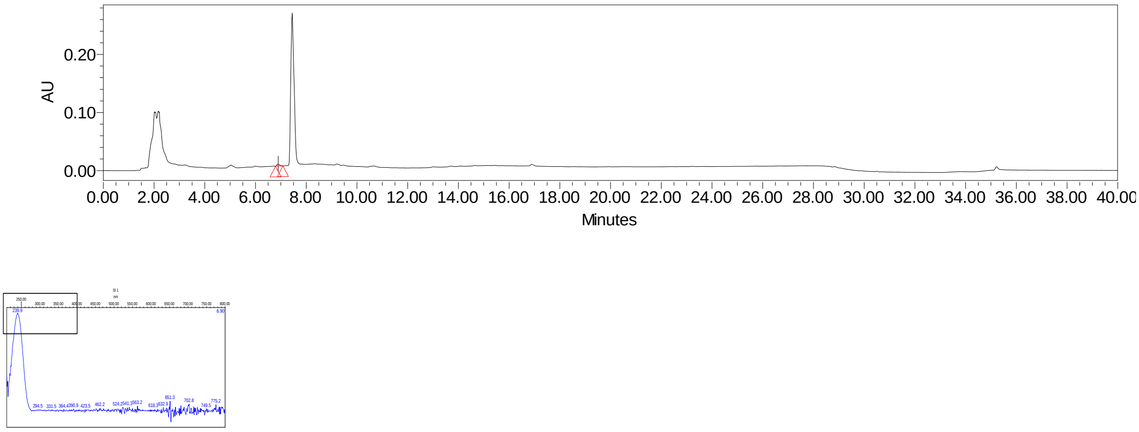
[404] Carmona *et al.*, "Generation of Saffron Volatiles by Thermal Carotenoid Degradation," 6825-6834.



(a) The UPLC-PDA chromatograms (monitored at 450 nm) of the gardenia dyed samples aged for 0, 308 and 528 h



(b) The UPLC-PDA chromatogram (monitored at 450 nm) of the gardenia dyed sample aged for 528 h and the UV-Vis spectra of its main constituents



(c) The UPLC-PDA chromatogram (monitored at 254 nm) of the gardenia dyed sample aged for 528 h and the UV-Vis spectra of its main constituent

Figure 5. 10 Changes in chemical composition of gardenia dyed silk during accelerated ageing

5.4.3.4 Turmeric

Turmeric has long been known as very sensitive to light.[405] The peaks for the main components of turmeric decrease significantly in the UHPLC-PDA chromatogram of the sample aged for 100 h and disappear afterwards (Figure 5. 11). However, a component eluting at 22.9 min remains in the sample aged for 308 h. Several colourless components appear during ageing but all of them are of small amounts.

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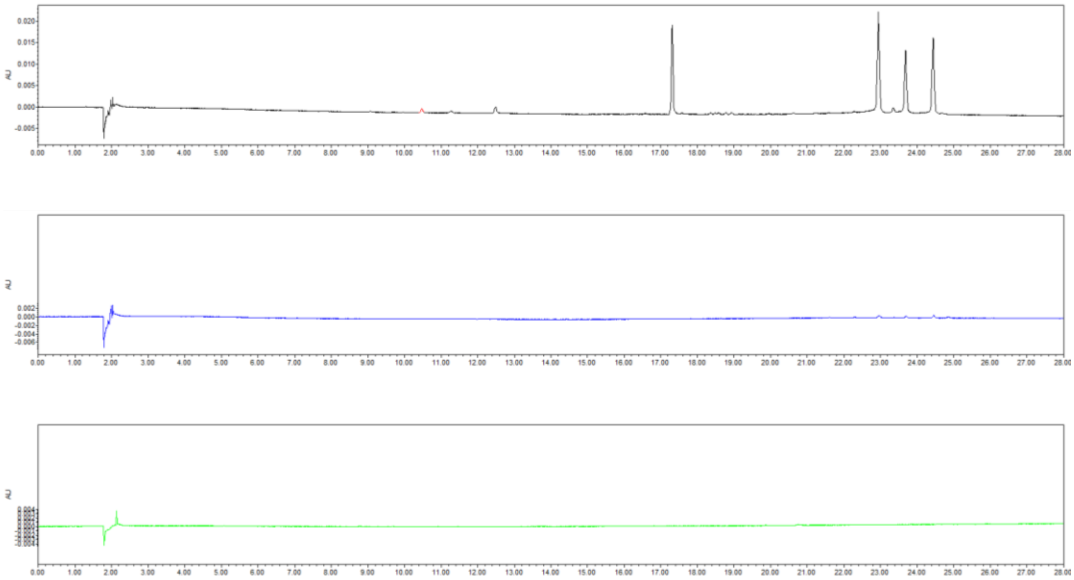
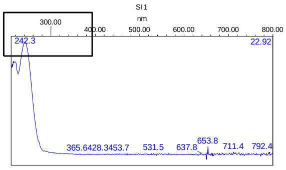
[405] Van Beek and Heertjes, "Fading by Light of Organic Dyes on Textiles and Other Materials," 123-132; GS Egerton and AG Morgan, "The Photochemistry of Dyes II—Some Aspects of the Fading Process," *Journal of the Society of Dyers and Colourists* 86, no.6 (1970): 242-249.



(a) The UPLC-PDA chromatograms (monitored at 430nm) of the turmeric dyed samples aged for 0, 308 and 528 h



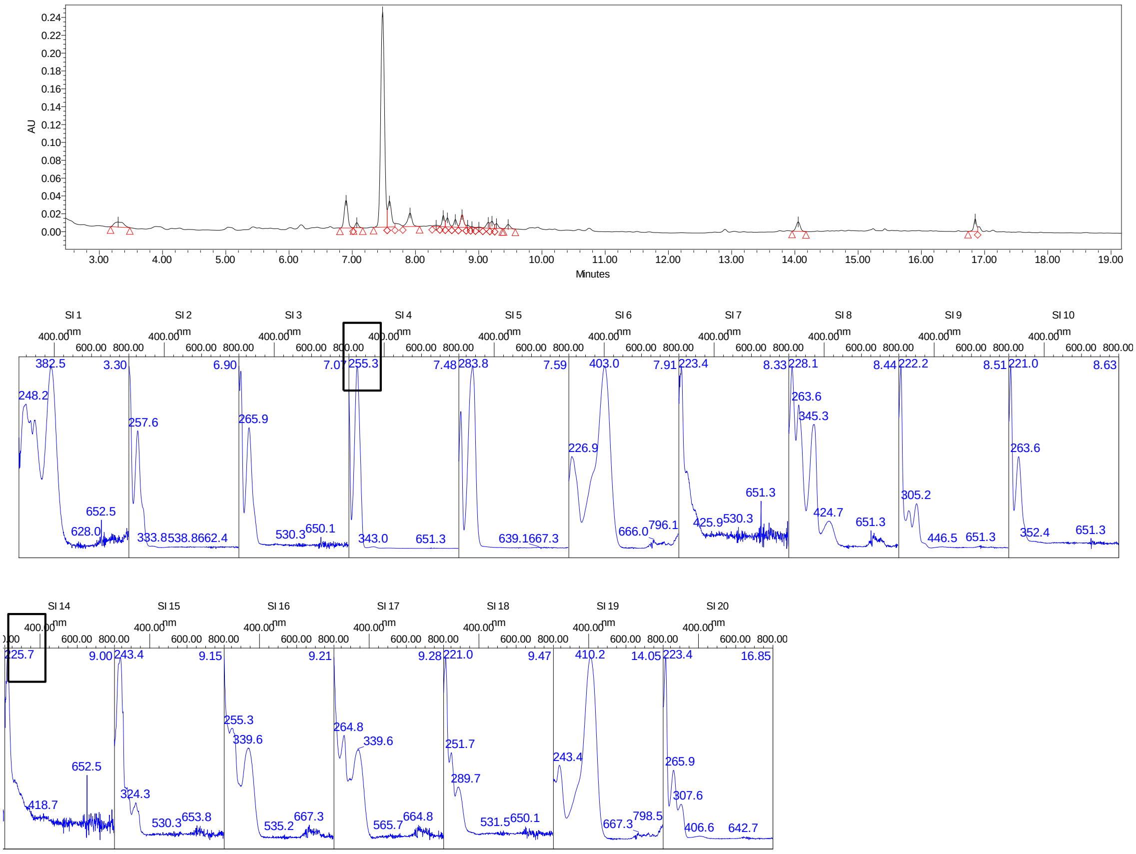
(b)The UV-Vis spectra of the degradation product of turmeric aged for 308 h

Figure 5. 11 Changes in chemical composition of turmeric dyed silk during accelerated ageing

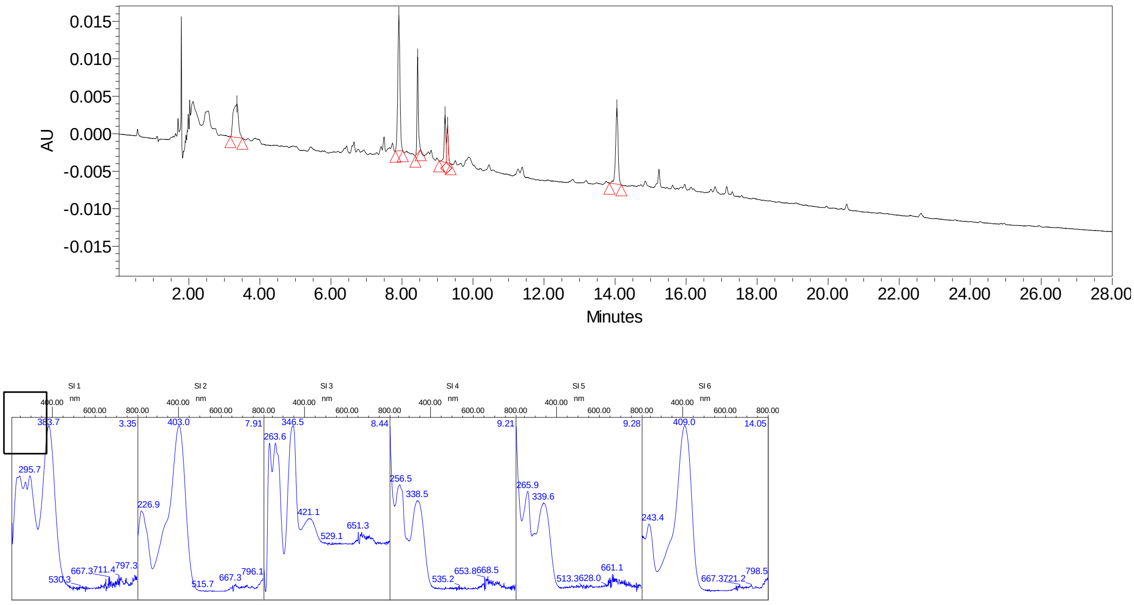
5.4.3.5 Amur cork tree

The colourants of Amur cork tree are not light stable. During ageing, the peak for the main component, berberine, decreases significantly after ageing for 308 h and disappears after ageing for 528 h (Figure 5. 12). When aged for 308 h, a series of yellow and colourless components appear, mainly in the time range of 6.9-9.5 min. When aged for 528 h, almost all these components disappear, except for the two peaks eluting at 3.4 and 8.7 min. Instead, colourless components eluting at 3.3, 6.9, 8.4, 8.7, 9.1 min appear.

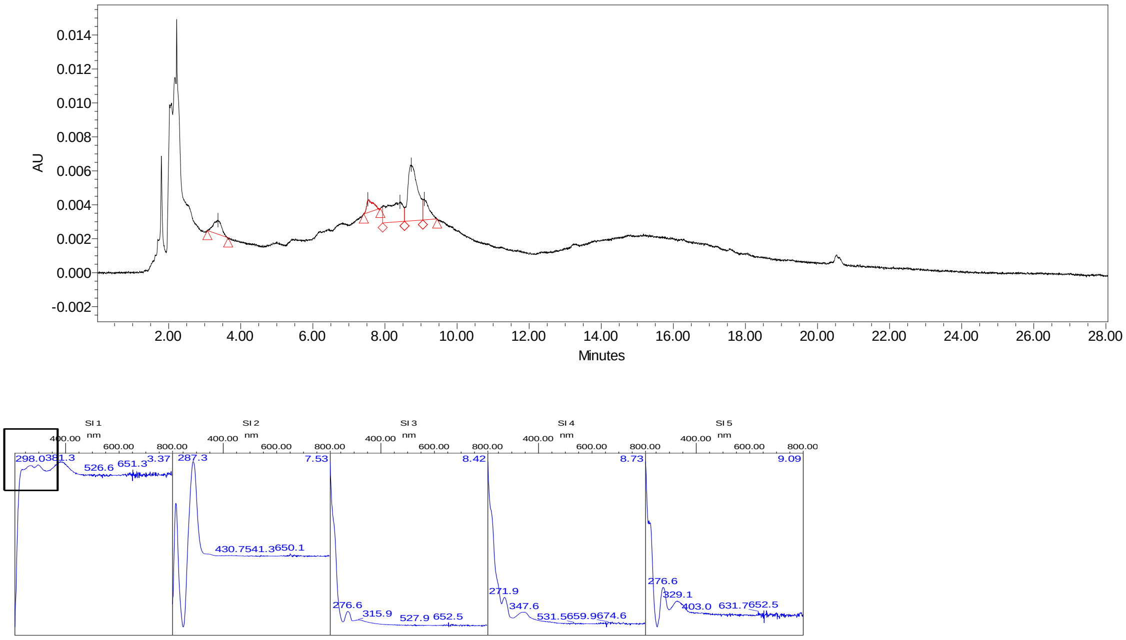
(a) The UPLC-PDA chromatograms (monitored at 350 nm) of the Amur cork tree dyed samples aged for 0, 308 and 528 h



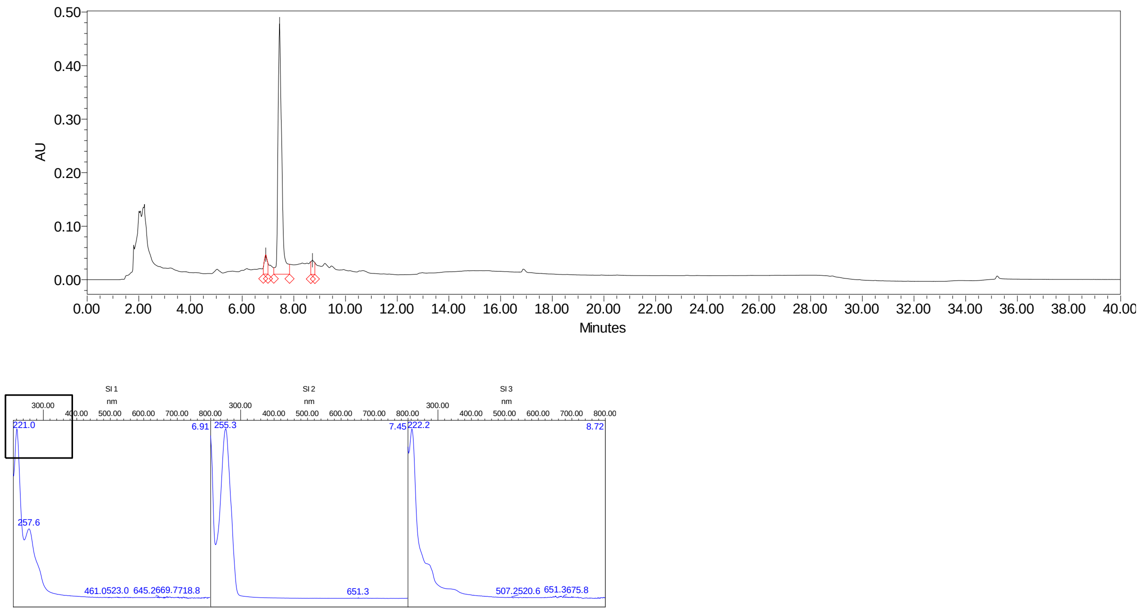
(b) The UPLC-PDA chromatogram (monitored at 254 nm) of the Amur cork tree dyed sample aged for 308 h and the UV-Vis spectra of its main constituents. All these components are the degradation products of the Amur cork tree dyed sample aged for 308 h, except for a small amount of berberine eluting at 8.44 min and the two silk degradation products eluting at 7.5 and 7.6 min



(c) The UPLC-PDA chromatogram (monitored at 350 nm) of the Amur cork tree dyed sample aged for 308 h and the UV-Vis spectra of its main constituents. All these components are the degradation products of the Amur cork tree dyed sample aged for 308 h except for a small amount of berberine eluting at 8.44 min



(d) The UPLC-PDA chromatogram (monitored at 350 nm) of the Amur cork tree dyed sample aged for 528 h and the UV-Vis spectra of its main constituents. The first component appears in the Amur cork tree dyed sample aged for 308 h, the second component is a silk degradation product and the other three components are the degradation products of the Amur cork tree dyed sample aged for 528 h.



(e) The UPLC-PDA chromatogram (monitored at 254 nm) of the Amur cork tree dyed sample aged for 528 h and the UV-Vis spectra of its main constituents. The first component is the degradation product of the Amur cork tree dyed sample aged for 528 h, the second component is a silk degradation product and the third component appears in the Amur cork tree dyed sample aged for 308 h.

Figure 5. 12 Changes in chemical composition of Amur cork tree dyed silk during accelerated ageing

5.4.4 Indigo

Indigo is very stable during ageing. There still remain large amounts of indigotin after ageing for 308 h, though the other components of indigo including indirubin, isatin, and a component eluting at 16.4 min disappear (Figure 5. 13). An ageing product appears at 23.3 min in samples aged for 308 h and 528 h. Indigo is relatively stable because large indigo aggregates even micro-crystals form on the surface of the fibre and the colourants inside the aggregates and micro-crystals are prevented from light fading to a large extent.[406]

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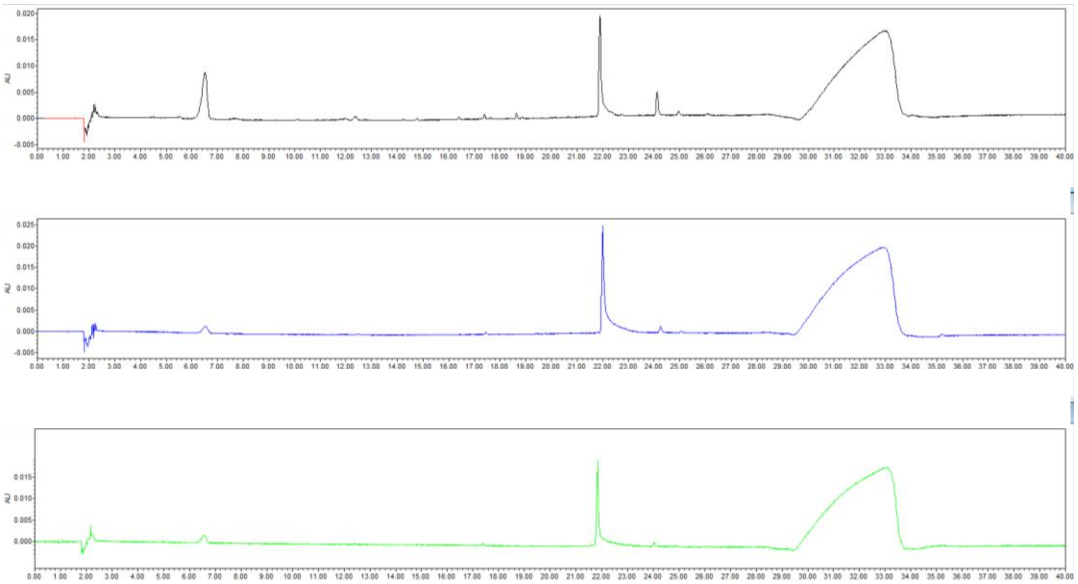
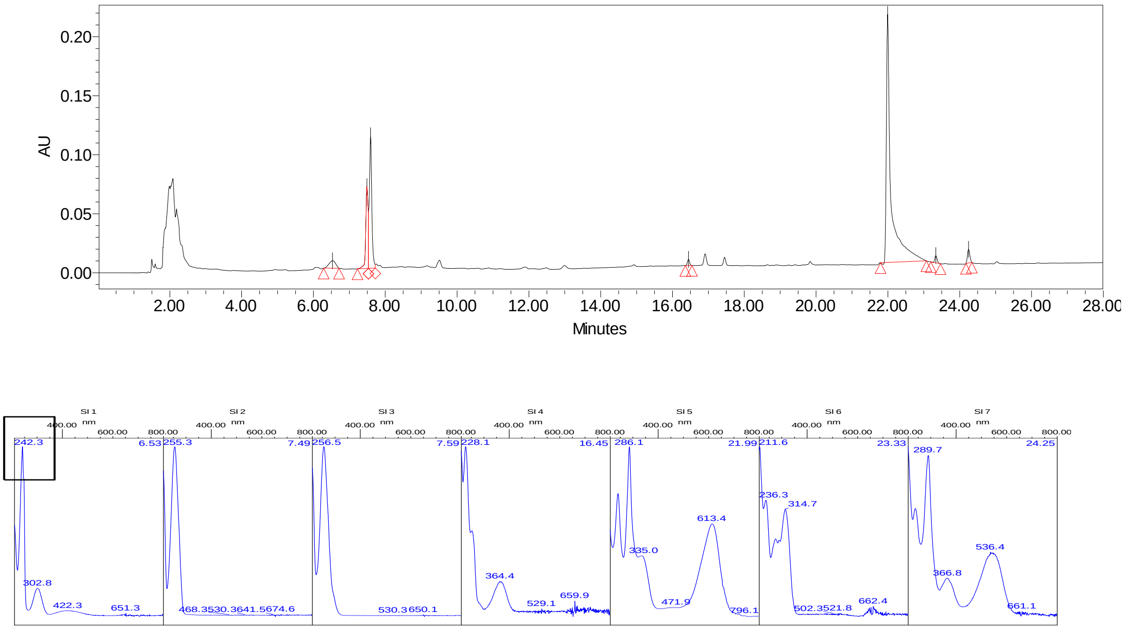
[406] Dianbo Zhang, "Sichou Wenwu Shang Zhiwu Ranliao De Moni Guang Laohua Yanjiu" (Master's dissertation, Zhejiang Sci-Tech University, 2011), 58.



(a) The UPLC-PDA chromatograms (monitored at 425 nm) of the indigo dyed samples aged for 0, 308 and 528 h

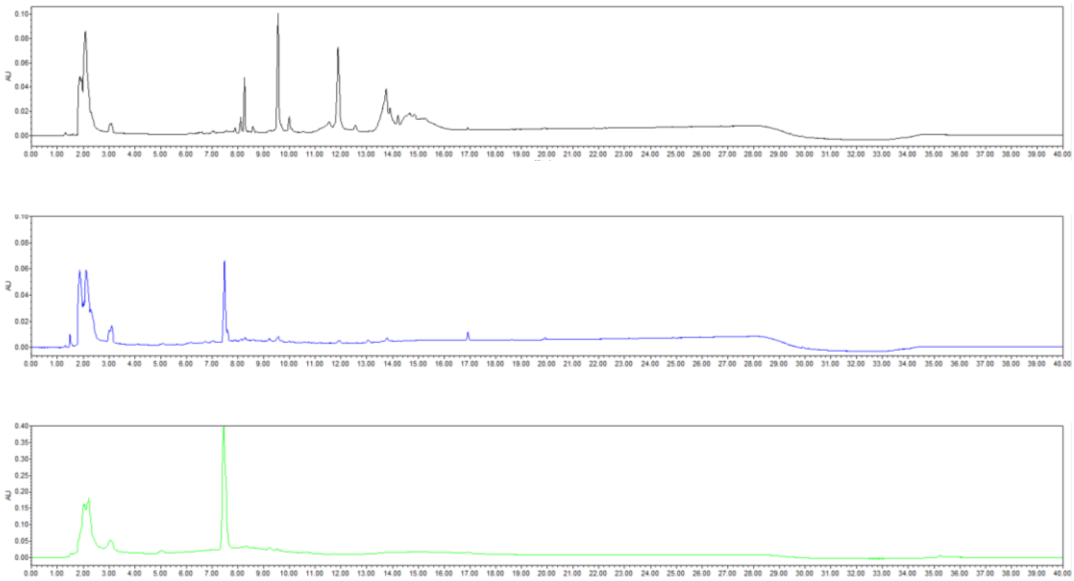


(b) The UPLC-PDA chromatogram (monitored at 254 nm) of the indigo dyed sample aged for 308 h and the UV-Vis spectra of its main constituents. The main constituents are respectively isatin, two silk degradation products, a characteristic component of indigo, indigotin, an indigo degradation product and indirubin.

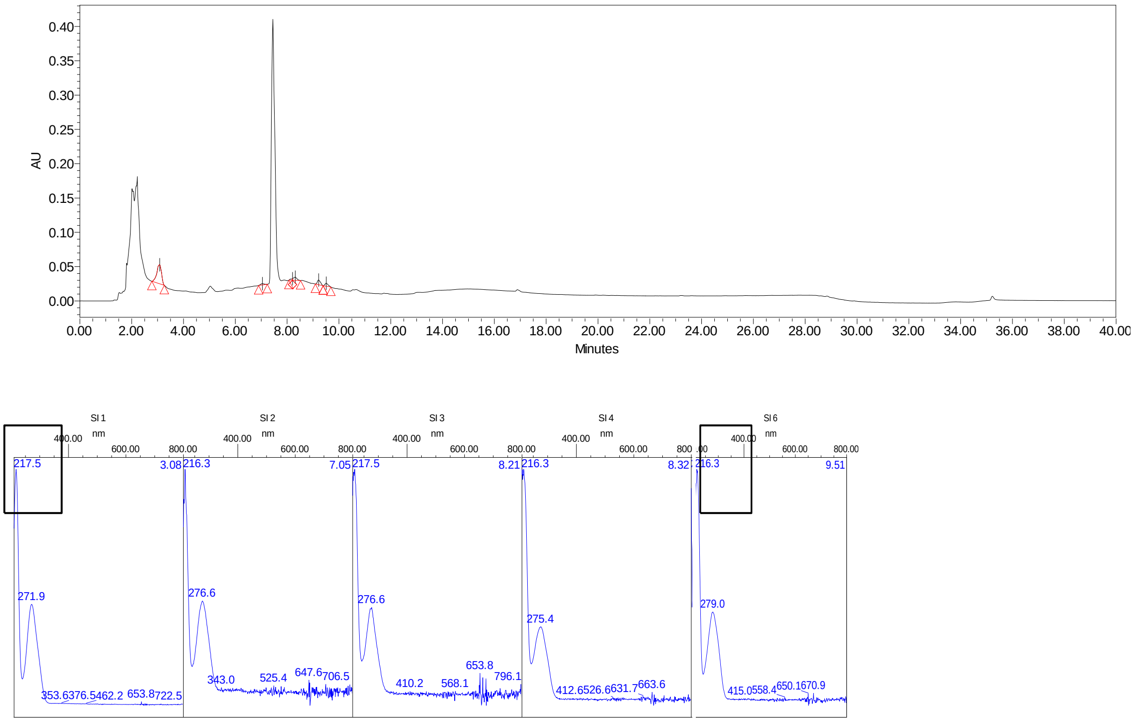
Figure 5. 13 Changes in chemical composition of indigo dyed silk during accelerated ageing

5.4.5 Black dyes containing tannin

The two dyes containing tannin in this research, gallnut and acorn cup, fade during ageing but they are still relatively stable: slight shades are still visible after ageing for 528 h (Figure 5. 14 and Figure 5. 15). In the aged samples of gallnut the peak for gallic acid monomer eluting at 2.1 min increases but the other peaks decrease dramatically, which indicates the decomposition of the polymers to the monomer. For acorn cup, during ageing, peaks for ellagic acid and its equivalent respectively at 13.8 min and 7.6 min decrease and both disappear after ageing for 528 h.

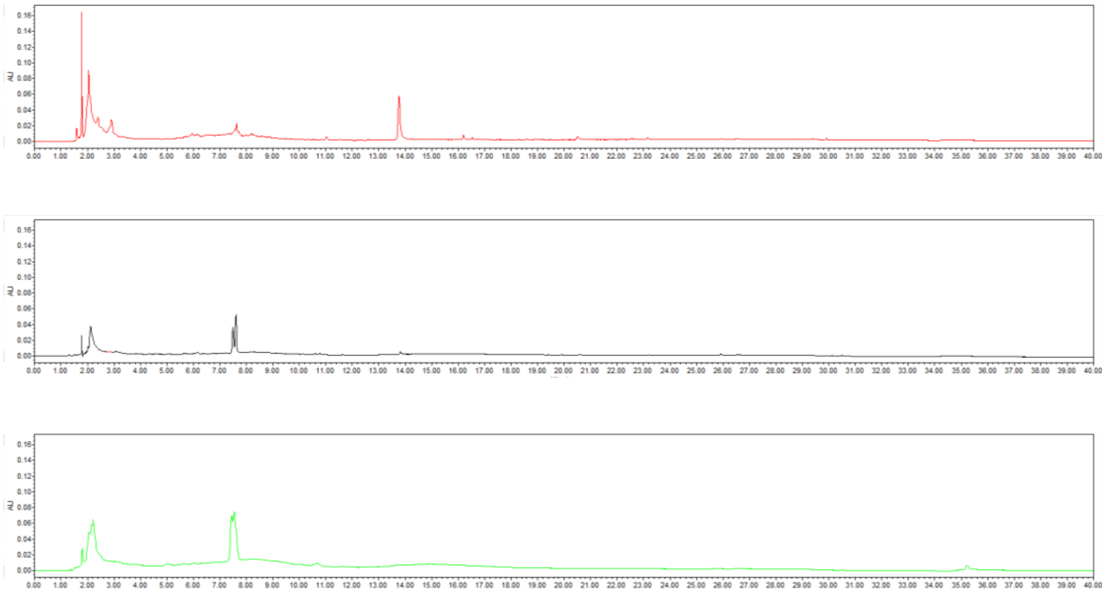


(a) The UPLC-PDA chromatograms (monitored at 254 nm) of the gallnut dyed samples aged for 0, 308 and 528 h

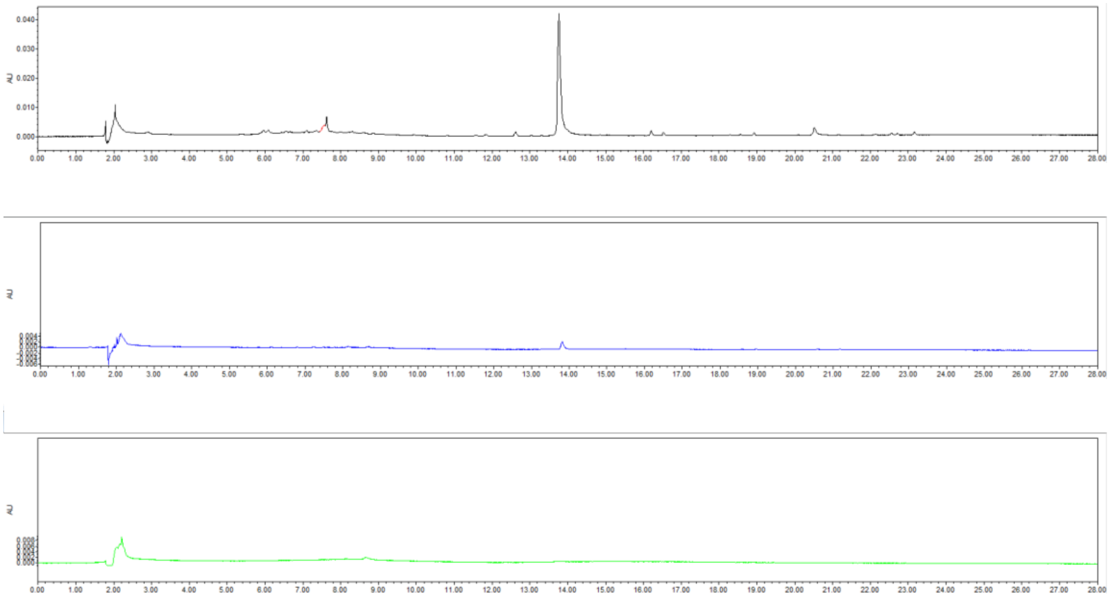


(b) The UPLC-PDA chromatogram (monitored at 254 nm) of the gallnut dyed sample aged for 528 h and the UV-Vis spectra of its main constituents

Figure 5. 14 Changes in chemical composition of gallnut dyed silk during accelerated ageing



(a) The UPLC-PDA chromatograms (monitored at 280 nm) of the acorn cup dyed samples aged for 0, 308 and 528 h



(b) The UPLC-PDA chromatograms (monitored at 370 nm) of the acorn cup dyed samples aged for 0, 308 and 528 h

Figure 5. 15 Changes in chemical composition of acorn cup dyed silk during accelerated ageing

5.5 Discussion

5.5.1 The light stability of the dyes

Accelerated ageing helps rank the light stability of the dyes. Judging from the shades, among the twelve dyes studied, munjeet, Amur cork tree, pagoda bud and indigo are the most stable dyes: for these samples a relatively intense shade remains after ageing for 528 h. The shades of acorn cup, gallnut and gardenia are not as intense but are still visible after ageing for the same period of time, indicating their light stabilities are not as good as the above dyes. Among the twelve dyes the least light-stable dyes are safflower and turmeric.

5.5.2 The shades of the aged samples

Three issues on the shades of the aged samples are to be discussed. First, during ageing, dyes fade because their molecular structures change. As discussed in section 1.3.5, dyes absorb certain portions of the visible light spectrum and thus show colour. When their chemical structures are altered and the dye molecules do not absorb visible light any more, dyes fade. Besides, even though the colours of dyes do not change, they may have already degraded. For example, in the Amur cork tree dyed sample, the yellow components are not berberine and its equivalents, the original components in the dye, but degradation products of these components. This needs attention when handling historical and archaeological textiles. Second, the shades of the dyes fading over time do not change to totally different shades, like changing from red to yellow. This helps us to understand some colour change phenomena for historical and archaeological dyes. For example, the yellow shade of the degraded red lining in NMS-5 (Figure 5. 16) is not because of a dye changing from red to yellow during ageing but because of the use of a yellow dye, in this case, Amur cork tree, for the ground colour underneath. Third, for some dyes, though their shades have completely faded during ageing, some relatively stable characteristic colourless components also helps the identification of the dyes, for example, the Ct components of safflower are still present after ageing for 528 h, though the main colourant of safflower, carthamin, disappear quickly.

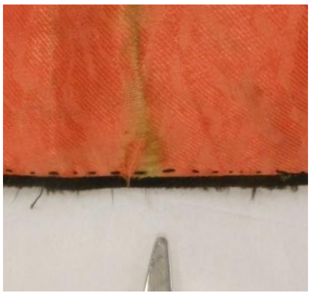


Figure 5. 16 The faded part of the red lining of NMS-5 looks yellow

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5.5.3 Factors affecting ageing

Factors affect ageing include both internal and external factors. Internal factors include the chemical construction and physical state of dyes, mordants used and the type of fibre.[407] The construction of dyes is the most important factor. The electron withdrawing groups of dyes accelerate ageing in reduction processes but slow ageing in oxidation process; vice versa for the electron donating groups of dyes.[408] Substituents may also reduce the reactivity of dyes significantly by such chemical change as the formation of hydrogen.[409] The influence of aggregation state on the light ageing of dyes is mainly reflected in dyed fabric of high concentration. Particularly, the formation of large aggregates within fibers increases the resistance of dyes to ageing.[410] Mordants generally enhance the light- and wash-fastness of dyes and the degrees of impact on fading vary among different mordants.[411] Substrate fibres may lead to different ageing pathways for dyes.[412] Besides, silk slows down the ageing of dyes because some of its active groups (such as hydroxyls, carboxyl groups and amino groups) react first, thus slowing the chemical reactions of dyes on silk.[413]

The external factor for ageing is the environment of dyed fabrics. According to external factors, the ageing of dyes can generally be divided to light ageing, thermal ageing, hydrothermal ageing and biological degradation.[414] Different causes may lead to different ageing pathways and thus degradation products may vary. Light is the major cause for the ageing of historical dyes. During light ageing, dyes undergo a series of photochemical

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[407] Jing Han, "Zhongguo Gudai Tianran Ranliao Fenxi Fangfa Bijiao Yanjiu" (Master's dissertation, Peking University, 2012), 28-29.

[408] Zollinger, 442.

[409] Van Beek and Heertjes, "Fading by Light of Organic Dyes on Textiles and Other Materials," 123-132.

[410] Crews, "The Fading Rates of Some Natural Dyes," 65-72; Y. Ye, L.G. Salmon, and G.R. Cass, "The Ozone Fading of Traditional Chinese Plant Dyes," *Journal of the American Institute for Conservation* 39, no.2 (2000): 245-257.

[411] Patricia Cox Crews, "The Influence of Mordant on the Lightfastness of Yellow Natural Dyes," *Journal of the American Institute for Conservation* 21, no.2 (1982): 43-58; Ana Manhita *et al.*, "Enlightening the Influence of Mordant, Dyeing Technique and Photodegradation on the Colour Hue of Textiles Dyed with Madder–a Chromatographic and Spectrometric Approach," *Microchemical Journal* 98, no.1 (2011): 82-90.

[412] Feller, 178.

[413] Zhang, Zhang, and Song, "Xianwei Shang Ranliao De Laohua Ziwai Guangpu Fenxi," 269-271.

[414] Han, "Zhongguo Gudai Tianran Ranliao Fenxi Fangfa Bijiao Yanjiu," 28-29.

changes, such as photolysis and light isomerization.[415] Light sources affect the rates of fading to a large extent.[416] For archaeological dyes, the major cause of ageing depends on their specific environment. It is to be noted that the difference between accelerated ageing and natural ageing because of different external factors may result in different degradation pathways and degradation products.

In addition, the kinetics of fading for different dyes varies. It was found that most natural dyes fade rapidly at the beginning and then fade slower, and only the most light-stable ones fade at a constant rate.[417] During recent decades, further analysis has been undertaken on the ageing kinetics of dyes by more advanced techniques like LC-MS. As a result, degradation products have been identified and kinetics models for the ageing of dyes have been established.[418]

5.5.4 Conservation, preservation and exhibition of historical and archaeological dyes

5.5.4.1 The preservation state of the historical and archaeological dyes

Knowing how much a dye has already photodegraded based on its chemical components would indicate where it is at its degradation pathway. This can be achieved by detecting degradation products in dyed samples. Degradation products from samples aged for 308 h were found in ten samples, including the degradation product of indigo eluting at 23.3 min found in six samples (TPM-2-2, TPM-3-1, TPM-4-2 and V&A-2-2, 3, 4), the degradation

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[415] Zollinger, 438.

[416] Ferreira, "New Approaches Towards the Identification of Yellow Dyes in Ancient Textiles."

[417] Charles H Giles, Devendra P Johari, and Champaklal D Shah, "Some Observations on the Kinetics of Dye Fading," *Textile Research Journal* 38, no.10 (1968): 1048-1056; Crews, "The Fading Rates of Some Natural Dyes," 65-72.

[418] Ferreira, "New Approaches Towards the Identification of Yellow Dyes in Ancient Textiles"; Sánchez *et al.*, "Kinetics of Individual Crocetin Ester Degradation in Aqueous Extracts of Saffron (Crocus Sativus L.) Upon Thermal Treatment in the Dark," 1627-1637; Manhita *et al.*, "Enlightening the Influence of Mordant, Dyeing Technique and Photodegradation on the Colour Hue of Textiles Dyed with Madder–a Chromatographic and Spectrometric Approach," 82-90.

product of Amur cork tree at 3.3 min found in samples BC-1-1 and BC-1-3 and the degradation product of sappanwood eluting at 21.8 min found in sample NMS-7-3 (see Figures 5.17 - 19 for examples). Though no significant differences in shade were found between the samples with and without degradation products detected, the detection of the degradation products indicates that these dyes have degraded. It is to be noted that dyes may undergo different degradation pathways in different environments and their degradation products vary. Therefore the rest of the samples may also have more or less degraded, in a different way from that caused by the accelerated ageing conditions used in this research. No degradation products were identified in archaeological samples, probably because of a similar reason - the distinct environment in tombs results in different degradation products.

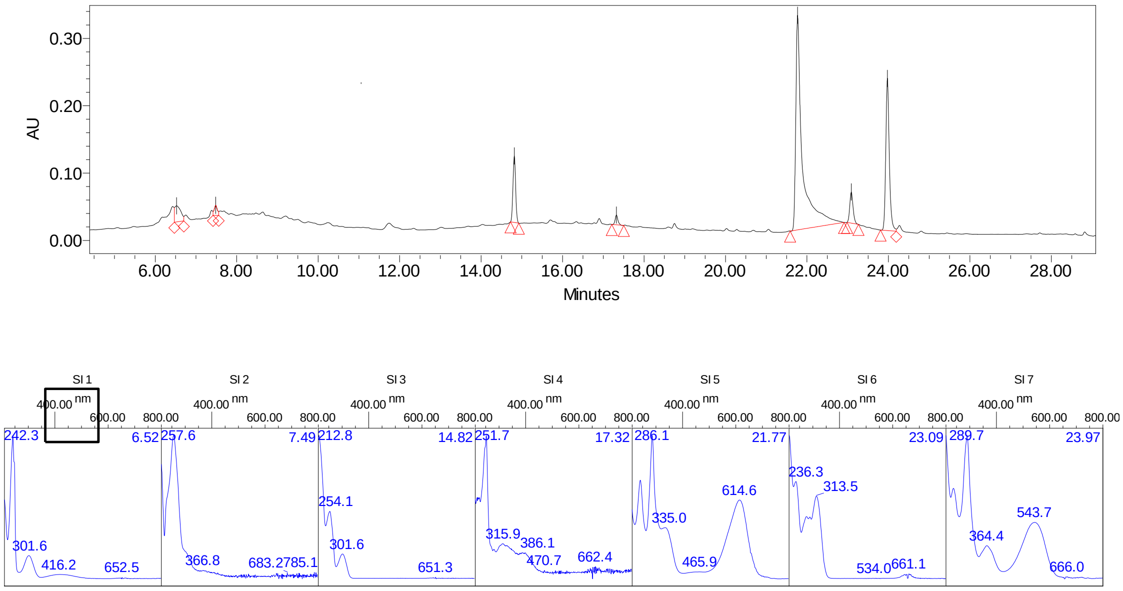

Figure 5. 17 The UHPLC-PDA analytical result of TPM-2-2. Indigo degradation product at 23.1 min was detected.

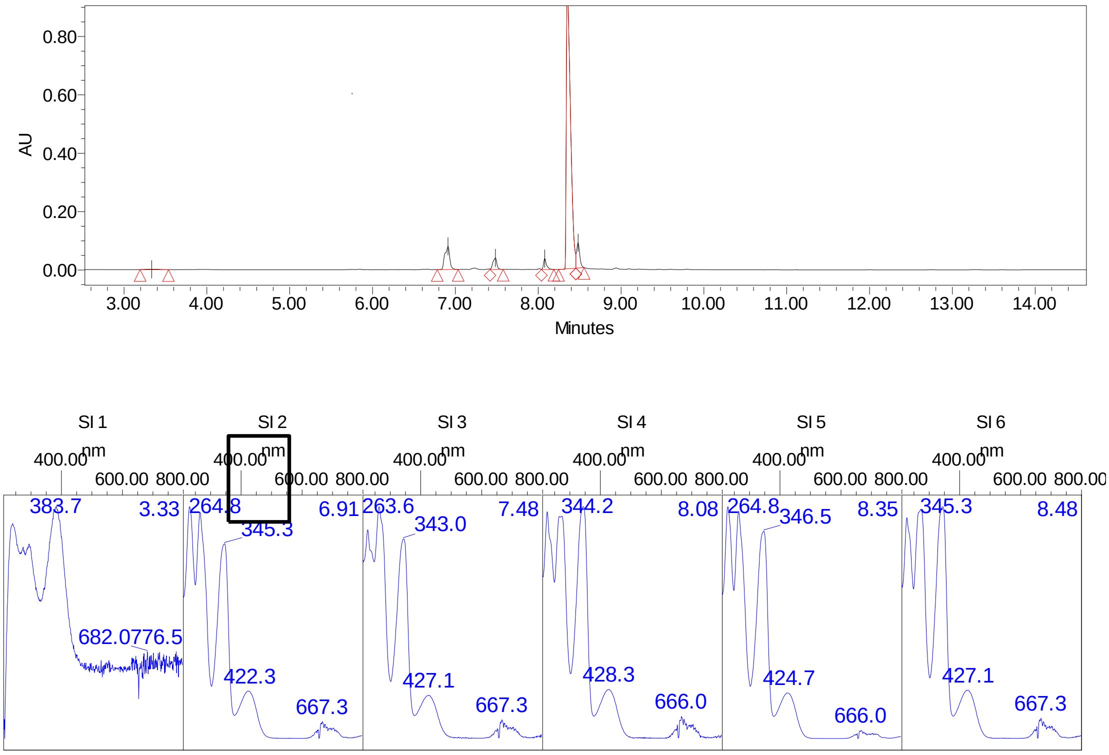

Figure 5. 18 The UHPLC-PDA analytical result of BC-1-1. Amur cork tree degradation product at 3.3 min was detected.

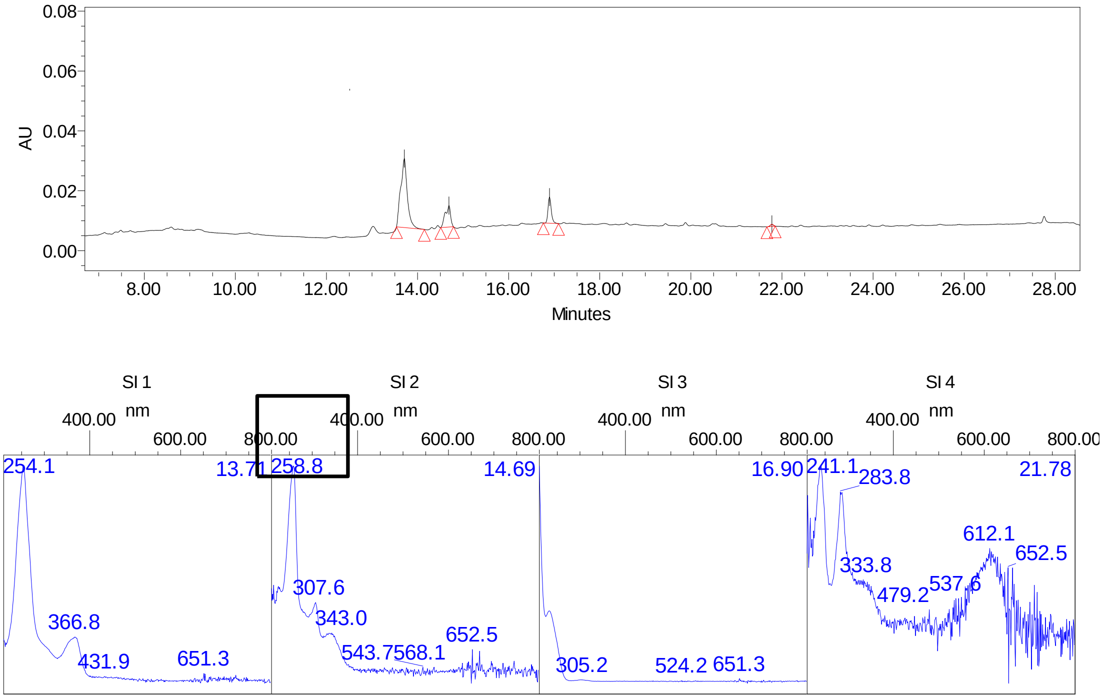

Figure 5. 19 The UHPLC-PDA analytical result of NMS-7-3. Sappanwood degradation product at 21.8 min was detected.

When comparing the three pairs of dyed samples with different preservation state, though no degradation products were found in the three much faded samples, significant decreases in the amount of dye components were found. This could indicate that the dyes in the much faded samples have degraded more severely, based on the assumption that the differences in sample size and in the original amount of dye components between each sample pair are relatively small. For the samples no. 4 and 5 of NMS-5 both dyed by safflower and Amur cork tree, the amounts of berberine and carthamin in sample NMS-5-5 are smaller (Figure 5. 20). As mentioned in section 5.5.2, the sample NMS-5-5 looks partly orange because safflower on the sample has almost completely faded and the yellow shade comes from remaining colourants of Amur cork tree. In the samples V&A-2-5 and 7 dyed by sappanwood and turmeric, the amounts of Nowik type A & C components and curcuminoids in the faded sample no. 7 are smaller. For samples BC-5 and 6, no significant difference is found in the amounts of the colourants detected, which could be because of different sample sizes of the two samples. The decrease of the amount of dye components during the ageing process of historical samples is consistent with the above results obtained by accelerated ageing study.

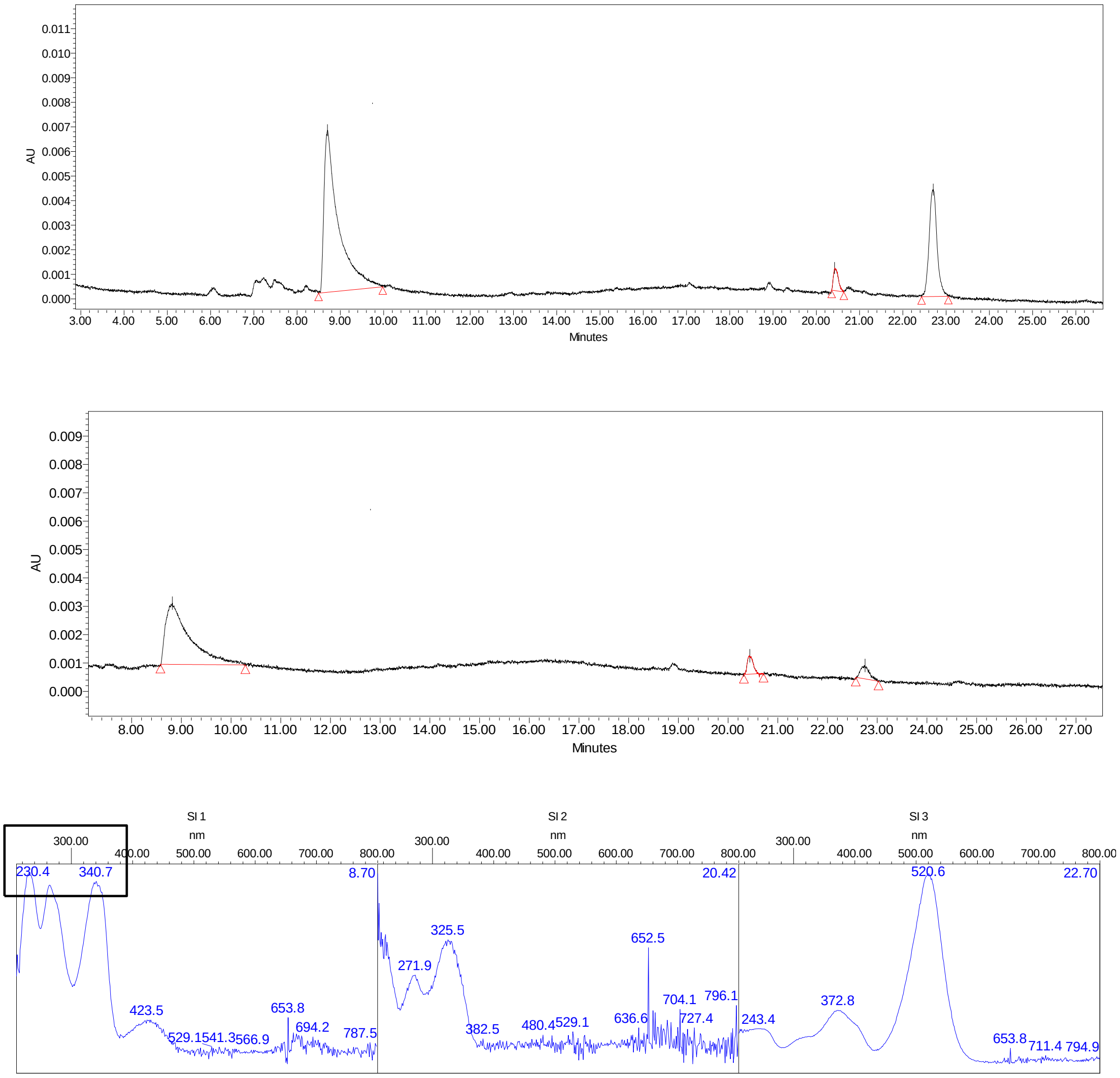

Figure 5. 20 UHPLC-PDA chromatograms (monitored at 350 nm) of the extracts of NMS-5-4 (upper) and 5-5 (severely faded, lower) and the UV-Vis spectra of their main constituents. Berberine, a safflower component and carthamin are present.

5.5.4.2 Implications for conservation, preservation and exhibition

Dye identification could help conservators choose suitable conservation treatments for dyed textiles. First, the wash fastness of dyes is another important factor to consider for conservation when choosing cleaning agents, consolidation, adhesive and during deacidification processes.[419] Generally speaking, direct dyes are easy to dissolve in water, acid dyes like picric acid are soluble in alkali conditions and basic dyes like Amur cork tree are soluble in acidic conditions. Vat dyes, like indigo, can be reduced by reducing agents.[420] Spot tests on the threads of different colours of the part of the textile to be treated by solvents are recommended before solvent treatments to prevent dyes from being dissolved or ‘bleeding’ on the textile. Second, attention needs to be paid on the colour change of dyes with acidity, *e.g.*, turmeric shows yellow in an acid environment and turns orange in an alkaline environment. Third, the identification of previous materials for conservation use by dye analysis helps determine how to treat these different materials. Moreover, since different dyes degrade in different rates, when using multi-dyes for conservation, the use of dyes of similar degrading rates is recommended.[421]

When conserving and exhibiting dyed textiles, it is important to control the environment, especially light source, air composition, humidity and temperature.[422] Light is a main damaging factor for the ageing of textile dyes in museum environment. Sometimes though no obvious colour change is observed, dyes have already degraded. Special attention needs to be paid to textiles with light-sensitive dyes such as safflower and turmeric and light exposure should be limited, *e.g.* at 50 lux for two years. It is to be noted that safflower and turmeric were frequently used for Chinese textiles of the Ming and Qing Dynasties (section 4.3.1), especially safflower, which is present in most of the red and pink samples dyed by natural dyes analysed. Additionally, the light sensitivity of dyes and the total amount of light exposure allowed for each dye can be determined by the method of micro-fading, a fading test on a micro dyed spot.[423] Different light sources are also

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[419] David J Lee, Louise Bacon, and Vincent Daniels, "Some Conservation Problems Encountered with Turmeric on Ethnographic Objects," *Studies in conservation* 30, no.4 (1985): 184-188.

[420] Ágnes Tímár-Balázsy and Dinah Eastop, *Chemical Principles of Textile Conservation* (Oxford: Butterworth-Heinemann, 1998), 96-97.

[421] Jing Han and Xiaomei Zhang, "Gudai Fangzhipin Baohu Zhong De Ranliao Wenti," in *Research on Art Conservation 6th Volume*, ed. Wenzhong Jia (Beijing: Nationalities Publishing House, 2012), 230-234.

[422] NH Tennent, "The Deterioration and Conservation of Dyed Historic Textiles," *Review of Progress in Coloration and Related Topics* 16, no.1 (1986): 39-45.

[423] Bruce Ford and Nicola Smith, "Protecting the Most Important, Most Exhibited and Most Fugitive Museum Objects from Light-Fading," *Research and Technical Studies Specialty Group Postprints* (2010): 30.

recommended according to the kind of dyes and the requirements of exhibition.[424]

5.6 Conclusions

This chapter studied the ageing of reference dyes and creates profiles of their UHPLC-PDA results. During ageing the dyes undergo chemical changes including oxidisation and decomposition, resulting in the decrease and disappear of dye components and the appearance of degradation products. Among the twelve dyes studied, munjeet, Amur cork tree, pagoda bud and indigo are the most lightfast while safflower and turmeric are the least lightfast, consistent with current knowledge to a large extent. The light exposure of textiles dyed with safflower and turmeric needs to be particularly limited. Degradation products were found in some of the historical samples and significant decreases in the amount of dye components were found in faded samples. Dye identification helped choose suitable conservation treatments for dyed textiles as well as suitable strategies for the preservation and exhibition of dyed textiles.

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[424] Hui Feng and Feng Zhao, "Yingxiang Sizhipin Wenwu Zhanchen De Guangzhao Fenxi," [Study on lighting design of silk textile cultural relics], *Silk* 49, no.6 (2012): 41-45; Matthias Farke, Marcello Binetti, and Oliver Hahn, "Light Damage to Selected Organic Materials in Display Cases: A Study of Different Light Sources," *Studies in conservation* (2014): 1-11.

Conclusions

In ancient China, colour was not only an element of fashion, but also an important symbol to distinguish ranks. During the Ming and Qing Dynasties, textile handicrafts developed quickly with the prosperity of commodity economy and the exchange of techniques between China and Europe through world trade. This thesis studied dyeing handicraft in the Ming and Qing Dynasties to reveal dyeing techniques used during this time period and the role of dyeing handicraft in the society. Following the footsteps of existing research on dyes and dyeing techniques in ancient China from 1980s, this research systematically explored dyes and dyeing methods in the Ming and Qing Dynasties for the first time based on the historical and chemical investigation of historical dye recipes and dyes on historical and archaeological textiles.

The novelties of this research include the following aspects.

- The first comprehensive comparative analysis of dye recipes recorded in important historical Chinese manuscripts and dyes on historical and archaeological Chinese textiles (Chapter 1 and Chapter 4).

- Novel approach combining art history and chemistry to interpret and date the textiles to reveal the social background of dyeing handicraft in the Ming and Qing Dynasties (Chapter 4).

- Unprecedented botanical provenance of dye plants recorded in historical documents by investigating the dyeing properties of the dyes and by integrating research from botany and Chinese herbal medicine with research into the dye plants of China (Chapter 2).

- Novel application of UHPLC-PDA and UHPLC-PDA-MS and different extraction methods to the characterisation of reference common Chinese dyes, and the characterisation of less common dyes of relative large scale and dyes from the Li Ethnic Minority for the first time (Chapter 3). Systematic investigation of the lightfastness of reference Chinese dyes (Chapter 5).

The main conclusions of this research are as follows.

Dyes and dyeing techniques revealed by documentary and physical evidence

Through the examination of four important historical manuscripts of dye recipes of the Ming and Qing Dynasties and the chemical analysis by UHPLC-PDA of historical and archaeological dyed yarns from textiles of the period of interest, the overall results of dyes and dyeing methods used in the Ming and Qing Dynasties was revealed. It was found that dyes commonly used during this period included safflower, sappanwood, Amur cork tree, pagoda bud, indigo, acorn cup, turmeric, Chinese gallnut and smoketree, though turmeric was frequently found on historical dyes but not in historical dye recipes and vice versa for Chinese gallnut and smoketree. Synthetic dyes were used for Chinese costume and textiles from the late 19th century. These dyes were used alone or with another dye, with specific rules, to obtain certain shades, with occasional cases of using three dyes together. The development of dyeing included the adoption of better dyes and dyeing methods and the enrichment of colours by variations in the combination and quantity of raw materials.

Further understanding of historical and archaeological textiles and dyeing handicraft of the Ming and Qing Dynasties

Based on the identification of dye sources and dyeing methods by chemical analysis, art history research helped further interpret and date the historical and archaeological textiles. First, by comparing with official dye recipes and official decrees on colour, the owners of dragon robes and dragon badges were confirmed. Second, the findings of common dyes and rare dyes (*e.g.* lac and cochineal) might help provenance the production of the textiles.

Third, the identification of synthetic dyes helped date some of the costume and textiles.

During the Ming and Qing Dynasties, dyeing handicraft developed with the evolvement of colour system and decrees for textiles. The flourish of commodity from the mid Ming Dynasty fostered the development of private textile workshops and the specialisation of dyeing workshops. The realisation of dyeing activities also depended on a nationwide network for the circulation of technique, raw materials and products.

Natural textile dyes for certain social ranks were specific and indigenous to China. Thus identification of dyes in unprovenanced textiles can help distinguish and categorise Chinese textiles from other textiles from different origins. The exchange of dyeing techniques between China and Europe during this time period was limited in terms of natural dyeing while the synthesis and trade of synthetic dyes in Europe influenced dyeing in China to a larger extent.

Botanical provenance of common dye plants used in ancient China

The botanical provenance of common dye plants used in ancient China was clarified mainly by comparing the dyeing properties of the dyes and by introducing relevant outcomes in the field of herbal medicine. Uncertainties about the names, provenance and preferences for the significant dyes in Chinese textile history were resolved for the first time. The most confusing cases of safflower, saffron, sappanwood, smoketree, pagoda bud, turmeric and gardenia were studied in detail and their correct botanical provenances were suggested. It was found that most dye plants refer to one or two major species or variants with ambiguity arising mainly from non-uniform naming conventions, the change of plant names over time and conversion between different taxonomies.

Analytical characterisation of the chemical components of reference dyes

The chemical characterisation of reference dyes by UHPLC-PDA-MS or UHPLC-PDA was undertaken. A database for the chemical composition of twelve common dyes and ten less common dyes was first established and the understanding of their chemical constituents was improved. The investigation of dyes and dyeing techniques of the Li group in Hainan Province showed that dyes of the same kind share similar chemical profiles with the reference samples. Some special dyes and dyeing methods are used by the Li group for cotton dyeing and they also depend on local availability. The analytical protocol used in this research enabled most of the significant dye components for identification to be extracted (from both silk and cotton samples), well-eluted and separated. The presence of particular dye components may not necessarily indicate specific dye sources and further evidence of relative amounts of the components, records of dyes in historical manuscripts and the botanical provenance of the historical dyes can help confirm the dye sources.

Ageing study of reference dyes

The accelerated light ageing study of reference dyes improved the knowledge of the lightfastness of the dyes and their changes in chemical profile during ageing. It was found that among the dyes studied, munjeet, Amur cork tree, pagoda and indigo are the most lightfast while safflower and turmeric are the least lightfast. Ageing results in the reduction and disappearance of dye components and the appearance of degradation products. The detection of degradation products helped identify historical and archaeological dyes as well as their preservation state. Suggestions for the conservation, preservation and exhibition of the dyes were provided.

The original contributions of the thesis include the clarification of dyes and dyeing in the Ming and Qing Dynasties based on literature and physical evidence, the improved understanding of the textiles in terms of ownership and the dating, the social and global context of dyeing, and the names, botanical provenance and preference of dye plants, a database of the chemical profiles of reference Chinese dyes, and the better elucidation of the chemical composition of gallnut, acorn cup, gardenia and munjeet dyed samples.

This research contributes significantly to dyeing history, textile history, colour history and plant history of both China and the world. It is also important for the preservation of dyed textiles and modern practice on natural dyeing.

First, the knowledge of dyes and dyeing methods of the Ming and Qing Dynasties revealed by the unprecented comprehensive study of primary sources of historical dye recipes and dyes on historical and archaeological textiles forms an important part of the dyeing history of China. This is also vital to dyeing history worldwide, in terms of the development of dyeing techniques of a particular place, the exchange of dyeing between China and other places, and the provenance of dyed textiles. The characterisation of the chemical profiles of Chinese dyes and the database established are very helpful for the identification of dyes on historical and archaeological textiles, and contributed to knowledge about similar dyes used worldwide. The investigation of dyes and dyeing techniques of the Li group in Hainan Province improves the understanding of the use of dyes and dyeing techniques in China and marked the start of the chemical research of ethnographic dyeing in China. Besides, the research results of the name, botanical provenance and preference of dye plants complement existing knowledge in the field of Chinese herbal medicine research and plant history.

Second, the research outcomes are very important for Chinese textile history. The production of the textiles in terms of dyeing was clarified, which forms an important part of both technical history of the textiles and Chinese textile handicraft as a section of the social production. The links among high-status people, costume colour and dyed textiles in ancient China by the official decrees of colour grading and official dye recipes were first elucidated, and the development of the official decrees with dyeing techniques was revealed, contributing to the knowledge of the relationship between textile handicraft and other aspects of the society. The research results also improve the understanding of

Chinese historical and archaeological textiles.

Moreover, this research contributes to colour studies in general. Colour is an important visual element, and the understanding of it, its symbolism and practice in different materials evolve closely with science, technology and society.[425] Research undertaken included the use of colour for costume of specific time periods, in terms of their symbolism and social functions,[426] and the fashion, techniques, production and trading of specific colours and relevant influential factors.[427] The outcomes of this research contribute to these colour studies, especially in terms of costume colour in ancient China, and complement existing colour studies on historical Chinese ceramics and architecture.[428]

Besides, research on the lightfastness of the dyes and knowledge of the wide use of safflower and turmeric, both light-sensitive dyes, for Chinese textiles of this time period is very valuable for their preservation. Light exposure on textiles dyed with safflower and turmeric should be limited carefully during display and access.

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[425] Stuart Clark, *Vanities of the Eye: Vision in Early Modern European Culture* (Oxford: Oxford University Press, 2007); John Gage, *Colour and Meaning: Art, Science and Symbolism* (London: Thames and Hudson, 1999); John Gage, *Color and Culture: Practice and Meaning from Antiquity to Abstraction* (Boston: Little, Brown and Company, 1993); Diana Young, "The Colours of Things," in *Handbook of Material Culture*, ed. Christopher Y Tilley (London: SAGE, 2005), 173-185; Andrew Jones and Gavin MacGregor (eds), *Colouring the Past: The Significance of Colour in Archaeological Research* (Oxford: Berg, 2002); Michael T. Taussig, *What Color Is the Sacred?* (London: University of Chicago Press, 2009).

[426] M. Channing Linthicum, *Costume in the Drama of Shakespeare and His Contemporaries* (New York: Russell & Russell, 1963); Jane A Lawson, "Rainbow for a Reign: The Colours of a Queen's Wardrobe," *Costume* 41, no.1 (2007): 26-44; John H Munro, "The Anti-Red Shift–to the Dark Side: Colour Changes in Flemish Luxury Woollens, 1300-1550," in *Medieval Clothing and Textiles*, eds. Robin Netherton and Gale R Owen-Crocker (Woodbridge: The Boydell Press, 2007), 55-95; Ann Rosalind Jones and Peter Stallybrass, *Renaissance Clothing and the Materials of Memory* (Cambridge: Cambridge University Press, 2000).

[427] Susan Kay-Williams, *The Story of Colour in Textiles: Imperial Purple to Denim Blue* (London: Bloomsbury, 2013); Amy Butler Greenfield, *A Perfect Red: Empire, Espionage and the Quest for the Colour of Desire* (London: Doubleday, 2005); Catherine E. McKinley, *Indigo: In Search of the Colour That Seduced the World* (London: Bloomsbury, 2012); Jenny Balfour-Paul, *Indigo in the Arab World* (London: Routledge, 1997); J. R. Harvey, *Men in Black* (Chicago: University of Chicago Press, 1995); Bruce R. Smith, *The Key of Green: Passion and Perception in Renaissance Culture* (University of Chicago Press, 2009); Mary H. M. Hulton, *'True as Coventry Blue'* (Coventry: Coventry Branch of the Historical Association, 1995).

[428] Xiaomin Zhang, "Analysis of the Ming and Qing Polychrome Color Evolution" (Master's dissertation, Jingdezhen Ceramic Institute, 2012); Ding, "Aesthetic Cultural Research on Porcelain’s Color of Yuyaochang in Ming Dynasty"; Lv, "A Research on the Cultural Idea and Cultural Expression of Traditional Chinese Architecture Color."

In addition, the research outcomes of natural dyes from this research could also be informative for modern practice of natural dyes dyeing as well as such modern industries involving natural dyes for colourants as food, cosmetics and interior decorating, faced with the increasing potential of natural dyes globally, as, compared with synthetic dys, natural dyes are more environmental-friendly and safer for both related practitioners and consumers.[429]

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[429] DJ Hill, "Is There a Future for Natural Dyes?," *Review of Progress in Coloration and Related Topics* 27, no.1 (1997): 18-25; T. Bechtold *et al.*, "Natural Dyes in Modern Textile Dye Houses—How to Combine Experiences of Two Centuries to Meet the Demands of the Future?," *Journal of Cleaner Production* 11, no.5 (2003): 499-509.

Future Research

This research comprehensively explored Chinese dyeing history of the Ming and Qing Dynasties for the first time and significantly improved relevant knowledge. Here are some suggestions for future research.

1. Research on the use of less common dyes such as lac and cochineal in ancient China will help provenance the textiles involving these dyes to bring insight as to whether they were indigenous, where the use of these dyes originated, and their spread of use.

2. The chemical analysis of dyes from costume and textiles of particular groups, *e.g.* of lower-status, will complement current knowledge about dyeing in China. Analysis of more textiles of the Ming Dynasty collected in Qufu and at Shandong Museum, and textiles of different periods of the Qing Dynasty collected at the Palace Museum and the Royal Ontario Museum would contribute to the knowledge of dyeing of more specific time periods.

3. Research on the relationship between the development of dyeing and other textile techniques is needed to get a more comprehensive picture of the evolvement of textile handicrafts in the Ming and Qing Dynasties.

4. Research on how dyeing in China and in Europe influenced each other during the 17th-18th century would further reveal the cultural and technical exchange between the two places. During this time period, with the more frequent communication and trade between China and Europe, chinoiserie, emerged as a popular decorative style, and chinoiserie textiles became fashionable.[430] Chinese colour palette enriched the Rococo

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[430] Madeleine Jarry, *Chinoiserie: Chinese Influence on European Decorative Art, 17th and 18th Centuries* (London: P. Wilson, 1981); David Beevers and Royal Pavilion & Museums, *Chinese Whispers: Chinoiserie in Britain, 1650-1930* (Brighton: Royal Pavilion & Museums, 2008).

palette and dyes were transported between China and Europe.[431]

5. Further research on early synthetic dyes used in China would help reveal how synthetic dyes were introduced to China and would contribute to the dating of textiles of the late 19th to early 20th century. Dye recipes recording early synthetic dyes such as *Ran jing* (The Classic of Dyeing, Republic of China) by Wu Shenyin and relevant trade records would help.

6. Further work studying the ageing of natural dyes, treatments for dyes during the excavation and conservation of dyed textiles, and the exhibition of dyed textiles will help better preserve dyes on historical and archaeological textiles.

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[431] Adolf Reichwein, *China and Europe; Intellectual and Artistic Contacts in the Eighteenth Century* (New York: Barnes & Noble, 1968), 43.

Appendix. Publications and Presentations

Publications

J. Han, Botanical provenance research of historical Chinese dye plants. *Economic Botany*, 2015, 69 (3) 230-239.

J. Han, A. Quye, Dyes and dyeing in the Ming and Qing Dynasties (1368-1911) in China: preliminary evidence based on primary chinese documentary sources, accepted by *Textile History* with minor revisions. Under revision.

J. Han, J. Wanrooij, M. van Bommel, A. Quye, Characterisation of chemical components for identifying historical Chinese textile dyes by ultra performance liquid chromatography - photodiode array - electrospray ionisation mass spectrometer, to be resubmitted to *Journal of Chromatography A.*

Conference presentations

J. Han, A. Quye. A study of dyeing in the Ming and Qing Dynasties (1368-1911) from multiple perspectives. Dyes in History and Archaeology 34, Thessaloniki, 22 Oct 2015.

A. Quye, J. Han. Typically variable? A chemical study of commercial aniline dyes in a 19th C sample book. Dyes in History and Archaeology 34, Thessaloniki, 22 Oct 2015.

J. Han, A. Quye. Dyeing practice and the society: a study of historical Chinese dyes of the Ming and Qing Dynasties (1368-1911) by chemical analysis and history of art. Dyes in History and Archaeology 33, Glasgow, 30 Oct 2014.

J. Han, A. Quye. Dyes and dyeing in the Ming and Qing Dynasties (1368-1911) in China: Preliminary evidence based on primary Chinese sources. Dyes in History and Archaeology 32, La Rochelle, 4 Oct 2013.

J. Han, A. Quye. The historical and chemical investigation of dyes in high status sixteenth century to eighteenth century Chinese costume and textiles of the Ming and Qing Dynasties by UPLC. The sixth MaSC (Users' Group for Mass Spectrometry and Chromatography) meeting. University of Pisa, Pisa, 5 Jun 2013. Poster presentation.

J. Han, Y. Chung, 'Colour' and 'technique' of Ming court costume. Life History in the Ming Court symposium, The Palace Museum, Beijing, China, 23 Aug 2012.

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Bechtold, T., A. Turcanu, E. Ganglberger, and S. Geissler. "Natural Dyes in Modern Textile Dye houses—How to Combine Experiences of Two Centuries to Meet the Demands of the Future?" *Journal of Cleaner Production* 11, no.5 (2003): 499-509.

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