Investigation of colour materials applied in Shāhnāma manuscripts of 15th Century by non-invasive analytical methods

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Eidesstattliche Erklärung

Hiermit erkläre ich an Eides statt, dass ich diese Arbeit selbstständig und ohne fremde Hilfe verfasst, keine anderen als die angegebenen Quellen und Hilfsmittel benutzt und die wörtlich und inhaltlich übernommenen Stellen als solche kenntlich gemacht habe.

Ich habe mich erstmals und nur an der Universität Hamburg zur Zulassung zu einer Doktorprüfung beworben. Kein Teil dieser Dissertation ist bislang veröffentlicht.

Hamburg, im September 2021

Mojtaba Mahmoudi Khorandi

To My Wife *Samaneh*

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Preface and Acknowledgments

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Mojtaba M. Khorandi

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Transliteration

For transliteration, the guidelines of the International Journal of Middle East Studies (IJMES) was followed. Names of dynasties and cities for which an established English version is available were not transliterated.

IJMES TRANSLITERATION SYSTEM FOR ARABIC, PERSIAN, AND TURKISH

Consonants

A = Arabic, P = Persian, OT = Ottoman Turkish, MT = Modern Turkish

	A	P	OT	MT		A	P	OT	MT		A	P	OT	MT
ء	ʾ	ʾ	ʾ	—	ز	z	z	z	z	ك	k	k *or* g	k *or* ñ	k *or* n
ب	b	b	b	b *or* p	ژ	—	zh	j	j				*or* y	*or* y
پ	—	p	p	p	س	s	s	s	s				*or* ğ	*or* ğ
ت	t	t	t	t	ش	sh	sh	ş	ş	گ	—	g	g	g
ث	th	s̱	s̱	s	ص	ṣ	ṣ	ṣ	s	ل	l	l	l	l
ج	j	j	c	c	ض	ḍ	ż	ż	z	م	m	m	m	m
چ	—	ch	ç	ç	ط	ṭ	ṭ	ṭ	t	ن	n	n	n	n
ح	ḥ	ḥ	ḥ	h	ظ	ẓ	ẓ	ẓ	z	ه	h	h	h[1]	h[1]
خ	kh	kh	h	h	ع	ʿ	ʿ	ʿ	—	و	w	v *or* u	v	v
د	d	d	d	d	غ	gh	gh	g *or* ğ	g *or* ğ	ي	y	y	y	y
ذ	dh	ẕ	ẕ	z	ف	f	f	f	f	ة	a[2]			
ر	r	r	r	r	ق	q	q	ḳ	k	ال	[3]			

[1] When h is not final. [2] In construct state: at. [3] For the article, al- and -l-.

Vowels

		ARABIC AND PERSIAN	OTTOMAN AND MODERN TURKISH
Long	ا *or* ى	ā	ā (words of Arabic and Persian origin only)
	و	ū	ū (words of Arabic and Persian origin only)
	ي	ī	ī (words of Arabic and Persian origin only)
Doubled	يّ	iyy (final form ī)	iy (final form ī)
	وّ	uww (final form ū)	uvv
Diphthongs	وْ	au *or* aw	ev
	يْ	ai *or* ay	ey
Short	َ	a	a *or* e
	ُ	u	u *or* ü / o *or* ö
	ِ	i	ı *or* i

For Ottoman Turkish, authors may either transliterate or use the modern Turkish orthography.

Abbreviations

FORS	Fibre Optic Reflectance Spectroscopy
XRF	X-Ray Fluorescence
FOMF	Fibre Optics Molecular Fluorimetry
MS	Mass Spectrometry
TLC	Thin Layer Chromatography
SERS	Surface Enhanced Raman Scattering
FTIR	Fourier Transform Infrared
HPLC	High-Performance Liquid Chromatography
NIR	Near Infrared
UV	Ultraviolet
F	Folio
Fig.	Figure
Tab.	Table
MS	Manuscript

CHAPTER 1: The Research in General

1-1 Subject Definition

Illuminated manuscripts are among the most precious Persian artworks. Illumination and decoration of manuscripts in Persian art have a long history. The background of this art in Iran dates back to the Pre-Islamic era that the Persians used for archetypes of books, especially religious books (Pakbaz 2006, p. 43). The first examples of Persian illustrated manuscripts can be seen in the remaining few pages of Aržang of Mani (Arjang) book from the Sassanid era (224 to 651 CE). In the following centuries, with the arrival of Islam in Persia (in the mid seventh century), the tradition of illustrating manuscripts continued in the form of decorating Quran.

One of the most important periods of development of Persian manuscripts is the 15th century, which manuscripts analysed in this study belong to the same period of time. The importance of this period is that After Timūr Gurkānī[1] had attacked Persia and founded the Timurid dynasty in Persia in 1370 CE, Timur transferred a large number of artists, scientists, and craftsmen to Samarkand, his capital. The gathering of these elite people in Samarkand caused an extraordinary cultural evolution in Persia. After the Timur's death (1405 CE), his son Shahrukh chose Herat, as the capital (Ca. 1405 CE), and transferred the artists of Samarkand court there. Shahrukh began to support the production of manuscripts by establishing libraries and workshops for the construction of manuscripts in Herat. As a result, we are witnessing the creation of a new style of Persian painting in Herat.

In the following and the presence of Iskandar Sulṭān and Ibrahim Sulṭān in Shiraz (Ca. 1412 CE), we are witnessing the creation of royal workshops in this city. Patronage of Timurid rulers of the libraries and workshops in Shiraz resulting in the emergence of a new style in Persian manuscripts that has produced manuscripts independently of Herat style. But this is not the end of the road to the developments of manuscripts in this century. Following the weakening of the Timurid government and the rise of Turkmans in the mid-fifteenth century we are witnessing the emergence of a new style of painting in Shiraz and other cities of Iran, known as Turkman style. Finally, in the late 15th century, we are witnessing manuscripts produced separately from the workshops of Turkman kings and known as “the commercial Turkman styles manuscripts”.

[1] Timūr was a Turco-Mongol conqueror and the founder of the Timurid Empire in Persia and Central Asia (1135-1405 CE)

As mentioned, in this century, we have witnessed many ups and downs in the process of manuscript production that have occurred in manuscript manufacturing workshops in different cities, especially in Herat and Shiraz. In this century, manuscripts with two different styles have been produced in parallel in different cities for instance in Herat and Shiraz. Also, in some cases, we see the production of manuscripts with different styles in the same city, which have been produced in parallel in different workshops. It is obvious, the study of colour materials used in each of these cities and workshops has very useful information that will help us understand the evolution of illustrated Persian manuscripts.

Manuscripts produced in the 15th century have been studied and classified into different categories by art historians and codicologists. These scholars have been divided the 15th century Persian manuscripts into different categories based on the structure of the manuscripts, their paintings, and their decorations. However, the manuscripts included in different categories have never been studied in terms of the colour materials used. Obviously, the vacancy of such a study on manuscripts of the 15th century in Iran was very felt, and this point has been mentioned many times by the codicologists. Obviously, identifying and comparing the colour materials used in different cities as well as various workshops includes very useful information for both art historians and codicologists. This information can help these researchers to divide 15th century manuscripts in different styles and also help them better comprehension of the prevailing conditions in manuscript production workshops. Moreover, the scientific information regarding the colour materials used in the different cities and workshops of manuscript production in 15th century may provide scientific strategies for the recognition of them from each other.

In addition, awareness of the colour materials used in different cities and workshops for the production of manuscripts will be very fruitful in the protection and restoration of these manuscripts.

Based on mentioned points the aims of this study were identifying the colour palette of 15th century illustrated Persian manuscripts, compare the colour materials used in manuscripts of different cities, especially the cities of Herat and Shiraz, and compare the colour materials used in different manuscript production workshops in the 15th century.

It should be noted that all the manuscripts analysed in this study belonged to the 15th century. Some of these manuscripts had paintings from the late 14th and 16th centuries, which were also studied. The study of these paintings greatly helped to better understand the colour materials used for 15th century manuscript paintings. On the other hand, except for paintings related to the cities of Herat and Shiraz, paintings belonging to Qazvin and Lahijan, as well as several Indian paintings were also studied. The study of these paintings was very useful in understanding the working conditions of manuscript production workshops and the major differences between royal workshops and other workshops.

Since analysing manuscripts due to their fragile nature is very challenging, another aim of this study was to investigate the capabilities of the combined analytical method of FORS, FOMF and p-XRF to identify the colours used in manuscripts. During this study, the capabilities of this combined analytical method for identification of colour materials used in manuscripts were examined.

The combined analytical method consists of two non-invasive techniques FORS and FOMF is among the best non-destructive ways to identify dyes used in manuscripts. Obviously, the lack of FORS and FOMF spectral databases of the dyes in the Persian manuscripts is one of the reasons why there are few studies in this case. Therefore, to compensate for this lack I have started to create the FORS & FOMF spectral database of some dyes possibly employed in Persian manuscripts (Chapter 4). In order to build up a spectral database devoted to dyes possibly employed in Persian manuscripts that have not been studied before, a set of mock-up samples was prepared based on natural dyestuffs indicated in the comprehensive book, "The art of bibliopegy in Islamic civilization," by Nadjib Māyel Heravi and also "Gulistan-i Hunar ("Rose Garden of Art)," by Qāżi Aḥmad Qomi which collects treatise dealing with penmanship, ink making, paper, gilding and bookbinding.

It should be noted that in this study the selection of manuscripts and analysis techniques were very careful to select the best options. Thus, in this study all nine analysed manuscripts are *Shāhnāma* manuscripts. Because, due to the importance of *Shāhnāma* in Persian culture *Shāhnāma* manuscripts have been produced continuously in different cities and dynasty over time. Therefore, *Shāhnāma* manuscripts have all the required features to achieve the aims of this study.

According to the objectives of this study, in selecting these manuscripts, the place of production of these manuscripts, the date of their production, and the workshop of production of manuscripts was considered. For example, manuscript RAS 239, which is one of the most famous and precious Persian manuscripts of all epochs, contains all the characteristics of the manuscripts of the Herat Timurid school and at the same time is a very prominent example of manuscripts produced in a royal workshop. The two manuscripts Or 420 and Ms 22-1948 produced in Shiraz represent Timurid manuscripts of Shiraz, which were produced in a close period of time but in two different workshops in Shiraz.

The three manuscripts AKM 4, 5, 269 produced in Shiraz represent the full characteristics of Turkman and Turkman commercial style. Manuscript AKM 6 is also one of the most unique Persian manuscripts produced in Turkman commercial style in Lahijan. This unique manuscript is known as the Big Head manuscript. The two manuscripts Persian 9 and Persian 933, are among Indian manuscripts produced in the mid-15th century. These two manuscripts have original paintings belong to the 15th century and also paintings from the late 14th and 16th centuries that were added to these manuscripts after their production in mid-15th century (Table 1-1).

Painters	City	Style	Date	Manuscript	Number of analysed paintings
AKM 4	Shiraz	Turkman	1482	AKM 4	5
AKM 5	Shiraz	Turkman	1494	AKM 5	4
AKM 269	Shiraz	Turkman	1492	AKM 269	13
Or 420	Shiraz	Timurid	1437	Or 420	9
Ms 22-1948	Shiraz	Timurid	1435	Ms 22-1948	5
Persian 933 painter A	Shiraz	Inju	Late 16th century	Persian 933	3
RAS 239 painter A	Herat	Timurid	1444	RAS 239	2
RAS 239 painter B	Herat	Timurid	1444	RAS 239	5
RAS 239 painter C	Herat	Timurid	1444	RAS 239	3
RAS 239 painter D	Herat	Timurid	1444	RAS 239	2
RAS 239 painter E	Herat	Timurid	1444	RAS 239	1
RAS 239 painter F	Herat	Timurid	1444	RAS 239	1
RAS 239 painter G	Herat	Timurid	1444	RAS 239	1
Persian 9 painter A	West India	Jalayerid	Late 14th century	Persian 9	5
Persian 9 painter B	West India	Timurid	Mid-15th century	Persian 9	14
Persian 933 painter B	West India	Timurid	Mid-15th century	Persian 933	4
RAS 239 painter Mughal	West India	Mughal court	End 16th century	RAS 239	2
AKM 6	Lahijan	Turkman	1494	AKM 6	4
Persian 933 painter C	Qazvin	Safavid	16th century	Persian 933	6

Table. 1-1: Manuscripts and paintings analysed in this study

Another point to mention is how to display the information obtained from colour material analysis in this study. Obviously, one of the main reasons for identifying the colour materials used in manuscripts is checking the health status of manuscripts and using this scientific information to adopt the appropriate protection and restoration process for each manuscript. But as you can see, the objectives of this study have been defined in such a way that the information obtained from the scientific analysis can be more considered by researchers in the field of art history and codicology. Because this study can be considered as the first study which specifically designed to investigate and compare the colour materials used in Persian manuscripts of different cities and workshops in a specified timeframe.

Obviously, comparing the colour materials used in manuscripts produced in different cities, different times, different workshops, as well as colure materials used by various painters who have worked together on a manuscript will have useful information for those active researchers in these fields. Therefore, in this dissertation, I tried to express my own personal conclusions from scientific analysis and show these results in such a way that they can be useful for active researchers in the field of humanities, art history and codicology. Therefore, many colour and visual references have been used to make the contents more understandable. Different tables and charts are provided for all analysis and reviews of each manuscript. Even in the interpretation of the analysis performed on each manuscript, it is stated that the colour materials in question have been used for painting what figures are used in the hope that this information may be useful for researchers in other fields.

1-2 Literature review

Compared to the western manuscripts there are few scientific-analytical studies on colour materials used in Persian manuscripts. Research on Persian painting began in European museums in about 80 years ago. Generally, the main purpose of the first studies was the identification of fake and original artworks of the museums. The first example of these research is “Materials in Persian Miniatures” which is published in the journal “*Technical Studies in The Field of The Fine Arts* (vol.3)” by Laurie, A. P. in 1935 CE. Another example of these studies is “The pigments and medium” written by Laurie, A. P. in Vol.3 of book “*A survey of Persian Art*”[2] which is one of the oldest and most comprehensive resource of the history and art in Iran.

The information of these types of research was obtained from the historical evidence or from the personal experience of the masters in their fields and basic scientific investigations. Therefore, they are more relevant from a historical rather than from a scientific point of view.

[2] This book was written by a group of 69 American experts under the supervision of Professor Arthur Upham Pope. These books are written in English and were published in six volumes in 1939.

Two of the first and more relevant studies from scientific analysis on identifying the colour materials on Persian manuscripts are; "A Study of the Materials Used by Medieval Persian Painters" written by Nancy Purinton and Mark Watters which is published in "*the Journal of the American Institute for Conservation* Vol. 30, No. 2 (1991 CE)", and "Raman microscopy applied to the analysis of the pigments used in two Persian manuscripts" by Dan A. Ciomartan and Robin J.H Clark, which is published in "*the journal J. Braz. Chem.* Soc, Vol. 7 (1996)". In these two studies, the colour materials applied in Persian manuscripts were studied based on scientific-analytical techniques.

Among the available scientific studies on Persian manuscripts, no one of them focused on the comparison of colour materials used in Persian manuscripts produced in different cities or workshops. Many of these studies are focused on identifying colour materials of one or more manuscripts.

However, some of them compared colour materials used in two manuscripts or two paintings. These two studies are good example to clarify them; "MOLAB® meets Persia: Non-invasive study of a sixteenth-century illuminated manuscript" by Anselmi et al. (2015). In this study three miniatures belonging to a finely illuminated sixteenth century Persian manuscript, were analysed by the use of multiple analytical techniques at The Fitzwilliam Museum. As well as Muralha et al. (2012) in the study "Raman analysis of pigments on 16–17th c. Persian manuscripts" were analysed the palette of four Persian manuscripts of the 16th and 17th centuries by Raman.

Therefore, the present study can consider as the first study focused on identifying and comparison of colour materials applied in Persian manuscripts produced in different cities and workshops.

One of the most similar studies to the present study is a series of scientific analysis performed on the materials and techniques on Islamic manuscripts in The Harvard Art Museums. These studies contain embellish folios of manuscripts and albums created from 13th through 19th centuries. The result of this studies published in 2018 as a unique article by Knipe et al[3].

Although, this study is not focused on *Shāhnāma* manuscripts either Persian manuscripts, however, a wide range of scientific analysis on several Islamic manuscripts are performed. However, this article has not focused on comparing colour materials. It only has focused on identify and introduce colour materials. Therefore, this research was very helpful to interpret analysis and identify colour materials which are presented in this dissertation.

However, a small number of studies have been done on the Persian manuscripts, and most studies have so far been focused on the pigments and seldom has the research done on the dyes used in the Persian manuscripts.

[3] In this study over 50 works on paper from Egypt, Iraq, Iran, and Central Asia dated from the 13th to 19th centuries were examined and analysed at The Straus Center for Conservation and Technical Studies.

Among the rare studies that have been done on identify dyes used in Persian manuscript, we can mention the studies by Dr. Mandana Barkeshli in “The International Islamic University of Malysia” supported by thorough historical research on bibliographic sources. these series of studies on the materials used in Persian manuscripts have been done by Dr. Mandana Barkeshli between 1996 to 2015 CE. These studies were very helpful to preparing dyes reference samples which presented in the fourth chapter of this dissertation.

The selection of manuscripts under study and their information generally was obtained from a series of catalogues of Persian manuscripts written by B. W. Robinson[4] and research conducted in “The Cambridge *Shāhnāma* Project”[5].

In addition, interpreting FORS and FOMF measurements are based on a set of studies by Aceto et al. on the usage of “UV-visible-NIR reflectance spectrophotometry” on manuscripts in “The Universita degli Studi del Piemonte Orientale”. Also, the book “*I pigmenti nell'arte: dalla preistoria alla rivoluzione industrial*” by Bevilacqua et al. (2010), and “FORS and FOMF Spectral database of Persian dyes” registered by writer this study as master thesis in “The Universita degli studio di Torino” (2014) were very helpful to interpreting FORS and FOMF analysis.

Also, Interpreting XRF analysis is based on information which is obtained from the book “*I pigmenti nell'arte: dalla preistoria alla rivoluzione industrial*” by Bevilacqua et al. (2010), and study “Free XRF Spectroscopy database of pigments checker” by Larsen et al. (2016).

1-3 Overview of this dissertation

The results of this study are presented in six chapters in this dissertation.

1-3-1 The Research in General (Chapter 1)

In the first chapter, we have had an overview of the project's objectives and the work done, as well as the overall structure of this dissertation. Also, the Persian transliteration guidelines has been introduced.

[4] Basil William Robinson, (1912 –2005 CE) was a British art scholar and author, specializing in Asian art and history. He has established a reputation as a leading authority on the art of Persia. His work on Persian manuscript illumination represents one of the most important contributions made in this century to the study of the development of this pivotal branch of Islamic art.

[5] Its start is associated with the opening of the *Shāhnāma* exhibition at The Fitzwilliam Museum in 2010. The establishing of a database of *Shāhnāma* was one of the main aims of this project.

1-3-2 Introduction (Chapter 2)

In the second chapter, we have a brief overview of Persian painting and the studied manuscripts of this study have been introduced. Persian painting is divided by researchers in a wide variety of ways. Some of these classifications are based on the style of the paintings, others are divided based on the historical period of the production of manuscripts, others based on the location of the production of manuscripts, and others based on the events of the index that occurred in the Persian painting (such as the emergence of a particular painter or a very different style of a painting, etc.).

In this chapter, Persian painting is divided and presented based on historical periods, as well as important events occurring in Persian painting in each period. A summary of different periods of Persian painting was briefly described in this chapter and only the developments of 15^{th} century painting, which is the subject of this study, are described in more detail. It should be noted that the methods of naming Persian painting schools have been carried out by researchers based on the centrality of the empire that governs the country. Therefore, the names of Persian painting schools are often the same names of cities. Therefore, in this chapter and dissertation, two words city and school are considered as synonymous and used.

Since all the studied manuscripts of this study are *Shāhnāma* manuscripts, in another part of this chapter, we have had a description of *Shāhnāma* as the text from which the most manuscripts have been produced throughout the history of Iran. Also, some of the most famous *Shāhnāma* manuscripts have been introduced. Finally, nine *Shāhnāma* manuscripts studied in this study have been introduced and the characteristics of each one is described.

1-3-3 Analytical techniques: principles and experimental (Chapter 3)

In the third chapter of this dissertation, an explanation of the material analysis techniques used in this study is presented. In this section, the advantages, and disadvantages of each of these techniques are mentioned. Also, while presenting a brief history of each of these techniques, the general principles of the function of these techniques are briefly explained. In the other part of this chapter, the analytical devices used for each of these analyses are also introduced. It should be noted that in this chapter in addition to the three main analytical techniques used in this study FORS, FOMF, and XRF two SERS-Raman and HPLC-MS techniques are also described. In this study, due to the availability of ten micro samples, it was possible to perform several semi-destructive analyses using these two methods on several specific colours.

1-3-4 Preparation of dyes reference samples (Chapter 4)

In chapter four, how to make dye reference samples is expressed. As mentioned before, in studies on colour materials used in Persian manuscripts, less work has been done on the identification of dyes. Because identifying dyes with non-destructive methods is very difficult.

One of the limited non-destructive methods available for identifying dyes in manuscripts is the combination of FORS and FOMF methods. However, the lack of reference samples for dyes used in Persian manuscripts has caused these methods to be used less in the diagnosis of dyes. In this chapter, several dyes used in Persian manuscripts were reconstructed to compensate for this deficiency by relying on traditional recipes of colour. So, in this chapter, how to make each of these dyes examples is described. Traditional orders for their construction extracted from historical texts are mentioned, as well as FORS and FOMF spectrums taken from each of these colour samples have been presented as reference samples.

1-3-5 Discussion and interpretation of data (Chapter 5)

In the fifth chapter, which is the main part of this study, the results of the analysis performed in this study on manuscripts have been investigated. In the first part of this chapter, possible colour materials used for each colour tonality are mentioned. Their characteristics and composition are described. Then, the method of identifying each of these colour materials is described by three main analysis methods used in this study. Then an example of the XRF spectrum and FORS and FOMF spectrums of each of these colour materials is provided. In fact, to prevent the repetition of several and multiple spectrums of each colour material, an example of the spectrums of each colour material in this section is presented as reference, and the spectrums taken from each manuscript are presented in the appendix.

In the second part of this chapter, the results of each manuscript analysis have been studied separately. In order to better sum up, these studies were conducted based on colour tonality. For example, for each manuscript, it is separately stated what colour materials have been used for blue tonality. Since this study is a comparative study, at the end of the study and interpretation of the analysis performed on each manuscript, a statistical analysis section has been presented for it. In this section, a percentage chart (Pie chart) is presented for each colour tonality.

In order to observe statistical principles and avoid confusion of the dissertation reader and better understanding of the percentages presented in the Pie charts, the number of analyses performed for each colour tonality is mentioned in the text and a brief explanation is provided for each pie chart. Also, in a column charts, the number of times a colour material is identified is shown. It should be noted that in Persian paintings, a variety of coloured tonalities have been used on which naming is very difficult.

As a result, colour references are provided in all parts of this chapter for the colours studied so that the reader can have an understanding of the colour tonality in question. Another point to note is that colour materials used by different painters of the manuscript RAS 239 has been examined separately because of its importance and also because it has been painted by nine different painters. In the conclusion (Chapter 6), it mentioned how a separate review of the colour materials used by each of these painters and comparing them together will help us to better understand the conditions of the workshop in which these manuscripts were produced.

In the third part of this chapter, the results of colour material analysis used in each city are compared with other cities. At the beginning of this section, the colour materials used in the manuscripts produced in Shiraz have been compared based on the production workshop and their production period. In this section, comparisons have been made based on colour tonality. For example, the coloured materials used for blue colour tonality have been compared in different manuscripts.

Five manuscripts Or 420, Ms 22-1948, and AKM 4, 5, 269 as well as Inju style paintings in manuscript Persian 933 have been studied and compared as samples produced in Shiraz (see table 1-1). Then, the colour materials used in Herat were compared with the colour materials used in Shiraz. For this purpose, RAS 239 manuscript as the produced manuscript in The Royal Workshop of Herat has been compared with the manuscripts produced in Shiraz. Firstly, the colour materials used by different painters of this manuscript are compared and then these colour materials are compared with the colour materials used in Shiraz.

After Shiraz and Herat manuscripts, the colour materials used in Indian paintings with the colour materials used in the paintings of Shiraz and Herat have been investigated and compared. In order to investigate Indian paintings, the paintings of four painters were examined. Painter A and B related to the manuscript Persian 9, Timurid painter manuscript Persian 933 and painter Mughal manuscript RAS 239 (see table 1-1). As you can see, Indian paintings exist sporadically in several different manuscripts. Meanwhile, Indian paintings of manuscript RAS 239 were produced at the court of the Mughal kings and added to the manuscript are very different in quality from those of three other painters. They also belong to the late 16th century in terms of production time, but the paintings of three other painters belong to the mid-15th century.

Therefore, in this section, while examining and comparing the colour materials used in Indian paintings with those of Herat and Shiraz, the colour materials used by different Indian painters have also been compared. Comparing the colours used in the Indian paintings of manuscript RAS 239 with the paintings of three other painters is another great example to understand the differences between the productions of royal workshops and other workshops.

Then, the colour materials used in Lahijan paintings with other cities have been investigated and compared. For these comparisons, the manuscript AKM 6 as the only manuscript produced in Lahijan has been investigated. This manuscript is the most famous manuscript produced in Lahijan. The colour materials used in the paintings of this manuscript are compared with the coloured materials used in paintings in other cities. On the other hand, since this manuscript is also one of Turkman manuscripts, comparing the colour materials used in this manuscript with other Turkman manuscripts produced in Shiraz during the same time period was very interesting. Therefore, the colour materials used in this manuscript have also been compared with three Turkman manuscripts produced in Shiraz AKM 4, 5, 269.

Then, the colour materials used in Qazvin paintings were compared with other cities. In manuscript Persian 933, there were six paintings related to Qazvin during the Safavid era. Since these paintings had major differences in terms of production timeframe and style of paintings, comparing the colour materials used in these paintings with those of other cities as well as other times was very useful.

In the last part of this chapter, the results of the comparisons made in the form of a Summery are expressed. In this summery, comparisons have been made based on different colour tonalities and a diagram is displayed for each colour tonality. In this diagram, we have tried to present four factors; the colour material used, the location of the painting production, the time of its production, as well as the number of times it is identified in the form of a diagram. It should be noted that for a better understanding of the content, each chart is described separately for the reader.

1-3-6 Conclusion (Chapter 6)

In the sixth chapter, we had a summary and conclusion of the work done in this study. In this chapter, we have tried to answer the questions raised in this study and new questions are also raised. In the first part of this chapter, to achieve one of the main objectives of this study, i.e., introducing colour palettes for 15th century Persian illustrated manuscript, a summary of the analysis on colour materials used in different cities and workshops is presented.

The purpose of this section was to introduce colour materials used for each colour tonality. Therefore, considering all aspects, a system was designed to represent the results obtained in this study. In this system, a pie chart is considered for each colour tonality, according to which the reader will be able to easily identify the colour materials for which they have the most use. Also, according to this pie chart, common colour materials can be identified between different cities and workshops. It should be noted that for better understanding of the obtained results, an interpretation has been provided for each of these pie charts.

The second part of this chapter is based on the other purpose of this chapter, i.e. examining the ability of combined analysis technique FORS, FOMF, and XRF. In this distribution, the capabilities of this combined analysis technique have been partially investigated. Since XRF technique is very well known, in this section, the capabilities of FORS and FOMF methods are further described when used together. In the final part of this section, the capabilities of this combined analysis technique for the detection of some colour materials are explained in detail. In the third part of this chapter, final results of the comparison of colour materials used in different cities and workshops has been investigated. In fact, it has been investigated what results can be found from the commonalities or differences of colour materials used in different cities and workshops.

The questions raised during this study have been mentioned and an answer has been provided for each of these questions. The majority of these questions are related to the art history basin, which was tried to be answered based on information obtained from the comparison of colour materials in this study and exciting historical and codicological information. For example, based on the analysis and comparisons made in this study and the available information about the status of manuscript production workshops, the importance of manuscript production workshops was investigated. It was tried to express the major differences between royal workshops of manuscript production and other workshops.

For example, given the importance of manuscript RAS 239 as a well-known example of the productions of The Royal Workshop of Herat, there is a lot of codicological information about it. putting this information together along with the historical information about the Royal Workshop in Herat in addition, the analyses performed in this study presented a diagram of the hierarchy of work in royal workshops.

Also, based on the analyses performed in this study and the information of art history in the field of Turkman manuscripts, the concept of Turkman and Turkman commercial style has been investigated. AKM 6 manuscript was another manuscript that has been studied and compared more accurately due to its unique characteristics. However, this manuscript and two manuscripts AKM 4, 5 was produced in the same timeframe and style but in two different cities. Therefore, based on the comparison of these manuscripts together, it was tried to investigate the effectiveness of manuscript production workshops due to their geographical differences or differences between them.

CHAPTER 2: Introduction

2-1 Brief history of Iran

Any scientific study of Persian manuscripts would be meaningless without the review of the art of illustration in Persia[6] and its evolution throughout time. The Persian manuscripts that spring to mind would be written in what we call the modern Persian, i.e. the modern written language of Persian made its appearance between the eighth and tenth centuries in the vast Persian territories incorporated into the growing Muslim world at the end of the seventh century (Grabar 2002, p. 2).

The first well-documented evidence of human settlements in Persia are several caves and rock shelters in The Zagros Mountains (Western Iran) dated back to about 100,000 BCE. Later examples of human activity are spread over much of the Iranian Plateau and in Lowland Khūzestān. Archaeological sites of Tepe Sabz *(تپه سبز)* (center Iran) in Khūzestān, Hajji Firuz *(حاجی فیروز)* in Naqadeh (northwestern Iran), Tepe Godin *(گودین تپه)* in Luristan (northeastern Iran), Tepe Sialk*(تپه سیلک)* on the rim of the central salt desert and Tepe Yahya*(تپه یحی)* in Kerman (southeast Iran) have all yielded evidence of a structured agricultural life (Pakbaz 2006, p.14).

The region now called Iran was occupied by the Medes and the Persians in the 1500 BCE. The Persian king Cyrus the Great (559–530 BCE) overthrew the Medes and founded the Achaemenid (Persian) Empire, which laid from the Indus to the Nile at its zenith in 525 BCE.

Alexander (356–323 BCE) defeated the Persians in 331–330 BCE and then Persia was ruled by the Seleucids (312–63 BCE), the Parthians (247 BCE–226 CE), the Sasanians (224–640 CE) and the Arab Muslims (641 CE). By the mid-800s CE science and culture flourished in Persia, although the relevance of Persia as scientific and cultural center stopped with the Mongol invasion in the 12th century. From 1501 CE to 1722 CE, Persia was ruled by the Safavid dynasty and the dominant religion became Shiite Islam.

After that, the Qajar dynasty ruled the area from 1794 CE to 1925 CE. After that the Persia (Iran, according to the name of the modern political state) was ruled by the Pahlavi dynasty and from 1979 CE by the Islamic Republic of Iran.

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[6] The history of Iran, commonly known as Persia in the Western world, is the history of a larger region, which encompasses the area from Anatolia and Egypt in the west, Ancient India and Syr Darya in the East, Caucasus and the Eurasian Steppe in the north and the Persian Gulf and the Gulf of Oman in the south.

2.2 History of Persian Painting

Like the history of the Middle East or Islam, the history of Persian painting is not easy to follow. If a particular style of painting is associated with a dynasty, a province, even a work, city, or perhaps with a particular social environment or even a painter, this cannot be done in a consistent manner to establish a system (Grabar 2002, p.32). As Grabar 2002 quotes: "Some researchers such as S. Cary Welch, Basil Robinson, and Ernst Grube have proposed the classification of Persian painting by contrasting the contemporary stylistic levels of metropolitan or provincial, high or low, Iranian or Turkman that always existed and have sometimes been interlaced". However, these classifications are too often subjective, even if the contrasts of genre and quality are quite real. Furthermore, it is difficult to frame these contrasts by the political and cultural history of Iran, since for all practical purposes it is not easy to identify the influence of Islam on the different styles of expression. What we can define and describe are the different periods of Persian painting, the distinctive features of each period and their chronological order (Grabar 2002, p.32).

2.2.1 Pre-Islamic Persian paintings

The Pre-Islamic Persia is generally known by the history and art of the Sasanian Dynasty, which dominated Iran from Ctesiphon in Iraq, south of present-day Baghdad, to the eastern frontiers, which were the subject of disputes with various oriental powers. It was also an era marked with wars against the Roman and Byzantine empires for control of Levant and the Indian Ocean commerce. Almost nothing is known of Sasanian painting, although it certainly existed but the art developed within the Manichaeism[7] had a great influence on Islamic art (Pakbaz 2006, p. 43). Some scholars endorse the hypothesis that the Persian-Islamic painting is fully based on the Manichean painting. One can say that the source of the Manichean painting is Mani himself. In fact, he was certainly a great painter since many books tell about his *Arzhang*[8] (*Aržang* ارژنگ) that showed his ability in painting (Upham Pope 1999, p. 27; Pakbaz 2006, pp. 43-48).

Almost all the Manichean drawings that still survive are dated from the nine century and can be seen on walls, fabrics and on papers from the Turfan area (Pakbaz 2006, p. 46, Upham Pope 1999, p. 21). Moreover, some researchers sustain the hypothesis that the Persian-Islamic painting was also influenced by the Sogdian painting. Sogdian rather arbitrarily refers to a vast territory of vague borders extending over a large part of the modern republics of Uzbekistan and Tajikistan as well as certain parts of Turkmanistan and

7 Manichaeism was a major Gnostic religion that was founded by the Iranian prophet Mani (216–276 CE) in the Sasanian Persian Empire.

8 The Arzhang was one of the holy books of the Manichaean religion, written and illustrated by its prophet Mani, in Syriac Aramaic. It was unique in that it contained numerous pictures designed to portray the events in the Manichaean description of the creation and history of the world.

Kazakhstan. Its population was Persian as far as language and culture were concerned, but still numerous Turkic speaking people as well as an entire society of merchants and adventurers from all over Asia were also present (Grabar 2002, p. 33).

The archeological excavations have discovered the main monuments and sites: Panjikent, Afrasiyab, Balalykh Tepe, Varahsha, and Ajina Tepe, which require further studies and supplementary works involving important technique for full appreciation of documents, since they are recent discoveries and only made subject to preliminary reviews (Grabar 2002, p. 33).

This region made its wealth during the heydays of the *Silk Road*, i.e. between the third and the eighth centuries. Extending from east to west, this road became one of the greatest axes of communications of all kinds, allowing silk, spices, and any other merchandise to move from one region to another and paving the way for the intellectual and religious exchanges, such as the spread of Buddhism from India to China (Grabar 2002, p.33; Pakbaz 2006, p. 37). For several reasons, this commerce prospered during the seventh and the eighth centuries, enriching the great oases of Central Asia (Grabar 2002, p.33).

Figure 2-1: Playing Backgammon, early eight century from Panjikent, Hermitage Museum

Photo Copyright © Persian Painting book

This world, which hitherto was dominated by the Persian culture, was first conquered by the Muslim Arabs in the eighth century and threatened by the Chinese Tang armies appearing at its frontiers (Fig. 2-1).

Thus, their revolutionary technique was introduced into the Muslim world, from where it spread to Europe in the pursuing centuries. This revolution causing a great reduction in the costs of bookmaking, simplification and transmission of written words and facilitating the spread of knowledge and ideas (Grabar 2002, p. 33). They may be reason for the endurance of the Persian culture in China and its return with the Mongols in 14th century.

However, the earliest known illustrated manuscript to survive from Persia is *the Suwar al-kawakib al-thabitah* (The Book of Images of Fixed Stars) by Abd al-Rahman al Sufi died 986 CE, copied in 1009 CE (T. Adamova and Bayani 2015, p. 19). The constellations are depicted in this illustrated manuscript as tinted drawings rather than paintings.

2.2.2 The Islamic Middle Ages (700-1290)

The Islamic Middle Ages elapsed between the fall of the Sasanian empire from the Mongol invasion of the 13th century. This era in Iranian history cannot be defined simply. The most important event in this era was the Islamization of the country, that the speed of this event varied in different regions (Grabar 2002, p. 34). From the tenth century the Abbasid caliphate of Baghdad ruled Persia, but this did not prevent the Persians to play an essential role not only in the government but in almost every aspect of the culture as well (Pakbaz 2006, p. 49; Grabar 2002, p. 36). Local dynasties appeared all over, Saffarids and Samanids in the east, Buyids in the center and the west (Pakbaz 2006, p. 51; Grabar 2002, p. 36). From 11th century, the Turkish warrior dynasties of Ghaznavi and then Seljuks took over and often adopted and transmitted the Islamic Persian culture to other territories as they did for example in India. There were always significant differences between Persia's eastern and northeastern regions. (Afghanistan, and Central Asia with the large cities of Bokhara, Samarkand, Merv, Balkh, Nishapur, Herat, and Ghazni) and western Persia, which grew more slowly within the Islamic domain (the regions of Isfahan, Yazd, Shiraz, and Kerman) and between the two was the transitional area that included Rayy (not far from present-day Teheran) (Grabar 2002, p. 36). This period's paintings can be discerned in murals and ceramics discovered during the excavations of Nishapur, Kashan and other places (Pakbaz 2006, p. 51). The murals at Nishapur mostly consist of decorative panels (Fig. 2-2).

Figure 2-2: Lioness and Attendant, tenth century, Nishapur, the Metropolitan museum

In the tenth century, in the northeastern provinces of Iran, an original vegetal motif, Arabic calligraphy of various styles, and even a small number of highly stylized human and animal figures transformed certain utilitarian objects, given their ceramic techniques, into works of pictorial art. The cities of Nishapur, Kashan and Afrasiyab/ Samarkand are generally associated with these ceramics, in spite of the fact that most of these exhibits the earlier techniques of Islamic Iran (Fig. 2-3 & 2-4).

Two significant illustrated manuscript from this period survive today. The first is an Arabic text of al-Sufi's well-known astronomical treatise on the constellations, *Kitab Suwar al-Kawakib al Thabita* (The Book of Images of Fixed Stars) copied in Persia in the year 1009 CE now kept at The Bodleian Library of Oxford (T. Adamova and Bayani 2015, p. 19).

Its numerous illustrations are exquisite depictions, in which, the classical representations of the constellations have been transformed into linear images while respecting the conventions in the representation of clothing that one sees in both Sasanian and medieval silver (T. Adamova and Bayani 2015, pp. 19-20; Grabar 2002, p. 38).

The second manuscript, *The Kitab e Varqa wa Golshāh* (Romance of Varqa wa Golshāh) by the Ghaznavid poet Ayyuqi which was probably dedicated to the Ghaznavid prince Mahmud, tells the story of the two lovers' unhappy affair in an imaginary Arab world (T. Adamova and Bayani 2015, pp. 19-20; Grabar 2002, p. 38). A copy of this text is kept in Istanbul which has 71 miniatures. It is not dated but it seems to be from about the year 1200 CE (Grabar 2002, p. 38) (Fig. 2-5).

Figure 2-5: Varqa wa Golshāh Embracing, ca. 1200 CE, Topkapi Saray Istanbul

Photo Copyright © Persian Painting

The text surrounding the image is the key to its understanding. However, in all appearance the painter lacked the visual model for composition or for the style of representation at his disposal, and unlike the numerous Christian manuscripts. However, these observations still do not conclude with certitude the existence of Persian illustrated manuscripts before the end of 13th century. Surprisingly, while reflecting a work of undeniable technical quality, the Varqa wa Golshah retains the simplicity of its forms making it difficult to place it historically (Lentz and Lowry 1989, p. 83).

2.2.3 The Mongol period

The Mongol invasion in the first half of 13th century and the occupation of Baghdad in 1258 CE, ended the Abbasid caliphate and brought about the Mongol rule in Iran, Transcaucasia, eastern Anatolia, and Mesopotamia. The devastation and depopulation in Iran inevitably targeted the architectures and the arts as well. Despite the early signs of recovery in 1270 CE and 1280 CE, it still took 50 years before the serious reemergence of the cultural life in the region (T. Adamova and Bayani 2015, p. 63).

However, the Mongol invasion of Iran in 13th century did leave its mark on the traditions of arts. The attributes of this period can be observed in the unillustrated manuscript of *Firdawsī's Shāhnāma*, the Persian national epic, which was copied in 1276-77 CE, probably in Kashan. This important artistic center prior to the invasions, reinstituted the production of luster and underglaze-painted ceramics in the 1260s and 1270s CE (T. Adamova and Bayani 2015, p. 63).

In the same years, the Mongols or Ilkhanid rulers constructed a summer palace at Takht-e Sulayman, south of Maragheh, which is currently the only excavated palace from the Mongol period in Iran (T. Adamova and Bayani 2015, p. 61). Unfortunately, most of the painted stuccos of the palace are now destroyed with only a number of glazed tiles remaining. These are notable for their blend of text from the *Shāhnāma* with images inspired from Chinese iconography. Dragons and phoenixes, noted symbols of Chinese sovereignty, as well as lotuses, peonies, motifs from Chinese landscapes and features borrowed from Chinese painting, were henceforth the trend (Komaroff and Carboni 2002, p. 24). The milestone in the future development of painting was the Ghazan Khan, the Mongol ruler's conversion to Islam at the start of his reign in 1295-96 CE, which marked his decision to represent the Ilkhans as successors to the great traditions of the Iranian past and reinforce the legitimacy of Mongol rule in Iran (T. Adamova and Bayani 2015, p. 63). The Mongol ruler Ghazan Khan commissioned his vizier and historian, Rashīd al-Dīn to prepare *The Jāmiʿ al-Tawārīkh* (Fig. 2-6), which has for theme the integration of Mongol history into those of other people in the known world. This work was completed under Sulṭān Uljaytu. The earliest known illustrated manuscripts of the Ilkhanid period dating to the late 13th century were copied and illustrated in Baghdad, the former capital of the Abbasid caliphate and a major cultural center of the Islamic world.

Figure 2-6: Mongol soldiers at the time of Uljaytu, Jāmiʿ al-Tawārīkh, 1310-11 CE, Tabriz

Although it is difficult to attribute any manuscript to early 14th century Baghdad, but the miniatures of the famous manuscript of *Khwājū Kirmānī's* three narrative poems (*Mathnawī*) written in 1396 CE and universally recognized as masterpieces of Persian painting, show that the art of the illustrated book must have been developing in the course of 14th century, reaching its zenith in the second half of the century under the patronage of the Jalayirid dynasty (T. Adamova and Bayani 2015, p. 63) (Fig. 2-7).

The period saw its major development in painting occurring in the Ilkhanid cultural capital of Tabriz. The illustrations of the earliest manuscripts executed in the metropolitan workshops in Tabriz and Maragheh, such as *The Manāfīʿ-i Ḥayawān* of Ibn Bakhtishu' dated 1297 CE or 1300 CE and *al-Biruni's al-Athar al-baqiyah* dated 1307-08 CE combine older, local traditions, particularly in the depiction of human figures, together with landscape features inspired by Chinese art (T. Adamova and Bayani 2015, pp. 63-65).

Figure 2-7: Khwaju Kirmani's mathnawi, 1396 CE, Baghdad, the Brithish Library

Photo Copyright © The British Library Board

2.2.4 The Injuid and Muzaffarid

Shiraz to the south of Iran played a major role in shaping a school of painting in continuation of the high culture traditions from earlier centuries. The highly documented and famed Inju style, is closely related to the painting of the pre-Mongol period. It developed under the Inju dynasty founded around 1303 CE when Sulṭān Uljaytu appointed Sharaf al-Dīn Mahmoud Shah to administer the royal estate in the southern province of Fars from its capital Shiraz (Kargar and Sarikhani 2012, p.114; T. Adamova and Bayani 2015, p. 64). The scholarly literature mostly attributes all manuscripts illustrated in this style to the 1330 CE and 1340 CE (Ilse Sturkenboom 2016, p.222; T. Adamova and Bayani 2015, p. 64; Pakbaz 2006, p. 68). Manuscript "Kalīla wa Dimnā" script dated 1307-08 CE, is one of manuscripts which convincingly attributed to Inju Shiraz (Fig. 2-8). The illustrations and illumination of this manuscript, the earliest known dated work of Injuids Shiraz. These illustrations and illumination are characteristic of the Inju style in its fully developed form, as it's style can easily be associated to many contemporary or later works attributed to Shiraz (T. Adamova and Bayani 2015, pp. 64-67). The Shāhnāma manuscript, dated 1341 CE, is the most well-known Inju manuscript. This manuscript ordered by the minister of Fars, Haji Qawam Bin Hasan. (Fig. 2-9) (T. Adamova and Bayani 2015, pp. 64-67; Pakbaz 2006, p. 68).

Figure 2-8: Kalilah wa Dimnah, 1307 CE, Shiraz, The British Museum

Figure 2-9: Shāhnāma, 1341 CE, Shiraz, the British Museum

2.2.5 The Timurids and Turkman Styles (15th century)

2.2.5.1 Introduction

In the last two decades of 14th century, the Timūr (known in the West as Tamerlane) extended his empire to the Iranian world and its neighboring territories. Choosing Samarkand as his capital, he constructed many splendidly decorated monuments symbolizing the magnificence of his empire and kingship. After his death in 1405 CE, his son Shāhrukh took over the major part of his Iranian domain. He set up his capital in Herat, the most distinguished city of the province of Khurasan, which became the artistic hub of the Islamic world, especially in the arts of the book and painting. After the defeat of the Muzaffarids by Timūr's army in 1393 CE, Fars and other provinces of western Iran came under the Timurid rule, until the invasion of the Qara Qoyunlu (Black Sheep) Turkman in 1453 CE.

Shiraz, the capital of Fars, continued to play a significant role in the advancement and novelty in the arts of the book under the ownership of Timr's grandsons Iskandar Sulṭān (1410-1414 CE) and Ibrahim Sulṭān (1414-1435 CE). Despite several Timurid and Qara Qoyunlu invasions, the west of Iran and Iraq, including Tabriz and Baghdad, were ruled by Sulṭān Ahmad Jalayir until 1410 CE, when he was killed in a battle with Sulṭān Qara Yusuf Qara Qoyunlu. Thereafter, during the 1450s and 1460s CE, both Baghdad, the capital of the Qara Qoyunlu rulers, and Shiraz flourished as important artistic centers.

The Qara Qoyunlu dynasty was overthrown in 1469 CE by the Aq Qoyunlu (White Sheep) Turkman, who ruled from the capital Tabriz until it was captured by the Safavids.

Iran was divided in the second half of the 15th century between the Aq Qoyunlu kings and the Timurid Sulṭān Husayn Bāyqarā. Sulṭān Husayn Bāyqarā dominated Khurasan until 1507 CE before the Uzbeks conquered Herat (T. Adamova and Bayani 2015, pp. 158-160).

2.2.5.2 New style of illustrated Persian manuscripts

The paintings illustrating Khwājū Kirmānī's Khamsa, completed in 1396 CE in Baghdad for Sulṭān Aḥmad Jalāʾir, are the shining examples of this new style (T. Adamova and Bayani 2015, p. 159) (Fig. 2-10).

The full-page illustrations of this manuscript are filled with poems, the human figures are engaged, but they look tiny among the massive architectural structures or large landscapes whose colours dominate the images (Grabar 2002, p. 52).

This new trend was also reflected in Niẓāmī 's Khusraw Wa Shīrīn paintings and in the illustrations of a Divan of Ahmad Jalayir to Sulṭān Ahmad's final years in power in Tabriz (T. Adamova and Bayani 2015, pp. 158).

Figure 2-10: The Khwājū Kirmānī's Khamsah, 1396 CE, Baghdad, the British Museum

2.2.5.3 The Timurid School of painting

Under rule of Iskandar Sulṭān, grandson of Timur, Shiraz became the pioneer of transforming the early Timurid manuscript painting into perfect works of art (Pakbaz 2006, p. 71; T. Adamova and Bayani 2015, pp. 159). The new page-layouts of horizontal and diagonal texts allowed the introduction many decorative motifs such as triangular thumb-pieces and illuminated rectangular panels filled with sprays of flowers and leaves. In this style the illustrations, text and various ornamental motifs were now in complete harmony.

Being the alien rulers like the Mongols the Timurids attempted to establish themselves as the legitimate authority in Iran. Therefore, Sulṭān Shāhrukh tried to revive the precedence of historical works, and so the earliest dated illustrated manuscripts from Herat are of a historical nature (Pakbaz 2006, p. 72; T. Adamova and Bayani 2015, pp. 160). One important Timurid manuscript, now kept in The Topkap Palace Museum Library, Istanbul is a manuscript which is often referred to as the Kulliyāt-i Tārīkhī; a collection of historical works by several authors and supplemented by Sulṭān Shāhrukh 's court historian Ḥāfiẓ-i Abrū (T. Adamova and Bayani 2015, pp. 159). It recounts the history of the Timurids up to 1416 CE.

The paintings in this manuscript, which was probably copied and illustrated around 1416 CE, strongly recall those of the style of the earlier illustrated manuscripts produced in Shiraz for Iskandar Sulṭān (T. Adamova and Bayani 2015, pp. 159; Grabar 2002, p. 56). During the second decade of 15th century, the court library of Herat, like its predecessor in Shiraz, considered the decorative elements in book production as important as illustrations. Unlike the later books in Herat, this illustrated historical manuscript is more closely linked with manuscripts of the early Timurid period in Shiraz underlining a new trend in the production of manuscripts. The term "historical style of Shāhrukh" refers to the archaizing style of manuscripts produced in the workshops of Sulṭān Shāhrukh during the third decade of 15th century. It was based on the main features of *The Majmaʿ al-Tawārīkh* (Fig. 2-11), a historical work by Ḥāfiẓ-i Abrū (1653 CE), which was completed in 1426 CE, and on a number of related manuscripts, influenced by early 14th century works from Tabriz (T. Adamova and Bayani 2015, pp. 159-161).

Figure 2-11: *Majmaʿ al-Tawārīkh*, 1426 CE, Herat, the British Museum

The paintings illustrating these manuscripts consist mostly of the classic Persian literature. They are distinguished by their grand style, refined execution and purity and brilliance of colour, and are often regarded as unrivaled miniature painting masterpieces (T. Adamova and Bayani 2015, pp. 160-161).

Painting flourished in Herat in the latter half of the fifteenth century under the Timurid Sulṭān Ḥusayn Bāyqarā, who ruled all Khurasan from Herat.

The new features associated with the miniatures of the Herat school and notably in the works of Kamāl al-Dīn Bihzād, were the pronounced characterizations of individual figures and the introduction of a multitude of naturalistic details into painting, and scenes that bear no relation to the text (T. Adamova and Bayani 2015, pp. 160-164; Pakbaz 2006, pp. 80-82).

2.2.5.4 The Turkman school of painting

The paintings of Turkman School that appeared at the courts of the Qara Qoyunlu and Aq Qoyunlu rulers of the mid and later 15th century displayed similar features. The Turkman occupied the western territories of Iran from the Timurids and Jalayirids, and established power centers in Tabriz, Baghdad, and Shiraz, where the Turkman School's greatest illustrated manuscripts were created (T. Adamova and Bayani 2015, pp. 160-164; Pakbaz 2006, p. 77; Norihito Yahashi 2012, p. 169). The illustrated manuscripts produced in these workshops ignored the relationship between the text and illustrations to a far greater degree than their contemporary Herat counterpart.

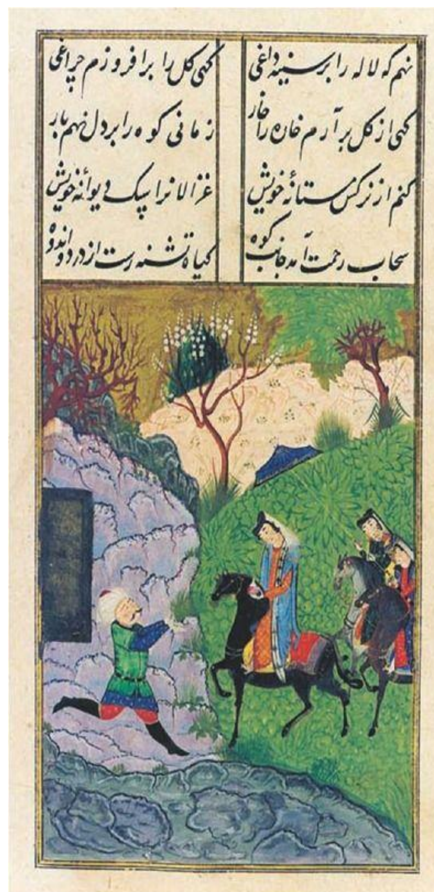

Figure 2-12: Khamsa of Niẓāmī, 1481 CE, Tabriz, the Metropolitan Musuem of Art

Photo Copyright © The Metropolitan Museum of Art

A particular example is the best-known Turkman manuscript, a Khamsa of Niẓāmī completed in 1481 CE, where several illustrated scenes have no relevance to the text (Fig. 2-12). Despite their astonishing beauty, these paintings are devoid of the "classical" measure and the ideal balance between parts of the composition judged so important in the first half of the fifteenth century.

Eleven illustrations from this manuscript were created by Shaykhi and Darvish Muhammad, two leading late 15th century artists from the courts of the Aq Qoyunlu rulers Sulṭān Khalīl and Sulṭān Yaqūb. These paintings and drawings, some on silk, others on paper, have attracted scholars' attention for more than 50 years both for their unusual subject matter and for their artistry, and have generally been attributed to fourteenth century Central Asia.

2.2.5.5 The commercial Turkman styles

Contrary to Herat School, the Timurid paintings of Shiraz and Yazd in the 1430s and 1440s CE, appear archaic and underline the intention to faithfully illustrate the text as accurately as possible. The streamlined and conventionalized style that frequently occurs in illustrated manuscripts created in Shiraz during the Turkman period, particularly in the last quarter of the 15th century, is known as Turkman Commercial Style. The Turkman Commercial Style is made up of three distinct elements: 1. human beings with a stocky shape with round infantile faces; 2. Landscapes with enormous hillocks and pale ground or rocky mountains, flavored with stylized bulbous flowers, are simplified; 3. a basic arrangement with two or three central figures (Norihito Yahashi 2012, p. 172).

After Qara Qoyunlu captured Shiraz in 1452, the style's genuine connection to Turkman tribes became apparent. Pir Budāq, son of Jāhānshāh Qara Qoyunlu, is the first documented Turkman sponsor of illustrated manuscript production (Norihito Yahashi 2012, p. 172).

Firstly, the special features of these manuscripts, such as the close association between the illustrations and the text, reflected the prevailing tendency in the in 15th century court style of Shiraz. Secondly, it is highly probable that the court ateliers produced more than one type of manuscript to both cater for the prestige of the patron by valuable manuscripts that had a specific program of illustrations, and the more modest works of smaller size manuscripts designed to facilitate reading, and with images directly and clearly illustrating the events described in the text (T. Adamova and Bayani 2015, pp. 163-167).

Figure 2-13: Khamsa of Amīr Khusraw, 1478, Shiraz, the Fitzwilliam museum

The 1478 CE Khamsa of Amīr Khusraw, illustrated in the Commercial Turkman style, bears the seal of Sulṭān Ūzūn Ḥasan (Fig. 2-13). Other late 15th century manuscripts of the type of feature ownership marks of some of the most important personalities of the period.

The *Majmaʿ al-Tawārīkh* (The Compendium of Chronicles), written between 1423 and 1426 CE is the most famous work of the historian Ḥāfiẓ-i Abrū composed for the Timurids, Sulṭān Shāhrukh and Bāysunghur Mīrzā. This work is a general history in four parts: the first three cover the history of the world up to the Arab conquest, the Islamic territories from the time of the Prophet to the end of the Baghdad caliphate in 1258 CE, and Iran under the Seljuq and Mongol rules (T. Adamova and Bayani 2015, pp. 163-167).

Figure 2-14: Divan of Hafiz, 1531–33 Tabriz, the Metropolitan Musuem of Art

2.2.6 The Safavids (1501-1629)

The Safavid dynasty ruled Iran for more than two centuries, leaving behind thousands of examples of painting in all techniques, from book illustrations to murals. One may even include in the large frescoes of the Armenian churches of 17th century at Julfa, the Armenian suburb of Isfahan in the Safavid style of painting. Given the numerous emblems and signatures and considering the number of documents dealing with painters, more than one hundred artists and other artisans of painting have been identified. Many of them emigrated to India where the Mughal court was more welcoming and, especially, more generous than the Iranians, particularly at the end of the sixteenth century.

In fact, even the institution of the workshop, or Kitābkhāna, seems to have lost the monopoly in making paintings. The consequence of these overwhelming changes in Safavid era of painting was the great variations in the quality of the works that were produced (Fig. 2-14), which have made it difficult to present a clear and consistent presentation of this art. For the preceding centuries, it is readily organized around the large cities and capitals like Tabriz, or Isfahan, or provincial centers like Shiraz, Mashhad, Herat, and even cities such as Yazd and Sabzevar on the basis of the supposed existence of local traditions or schools, which were maintained despite political upheavals.

It seems that a framework of an introduction is necessary for a different presentation of Safavid painting. The first period, which continued until the death of Shah Abbas in 1629 CE, includes the great masterpieces of Persian painting, whose Timurid roots are evident. The second consists of the rest of the seventeenth century until the Afghan invasion of 1722 CE (Grabar 2002, pp. 80-83).

2.2.7 Persian Paintings From 1630 to 1730

The style developed previously was sustained in the second Safavid century. The old Riza, his son Shafīʿī and, more importantly, his pupil Mu'in Musavvir were still painting. Working between 1635 CE and 1697 CE, the latter left a collection of beautiful pictures in the styles of Riza-yi `Abbasi and Ṣādiq, as well as representations such as the lion attacking a passerby, which is now kept in the Museum of Fine Arts, Boston. Muhammad Zamān 1649-1704 CE who with Mu'in Musavvir was one of the last great painters of the Persian tradition, copied Christian subjects introduced in Iran by Western missionaries and merchants (Fig. 2-15). However, by the end of the century, most of the best artists in this tradition had left for India to contribute to the formation and development of Mughal painting.

Figure 2-15: Kneeling woman counting by Mu'in Musavvir, 1673 Isfahan, the British Museum

In the Central Asia of the Uzbeks, separated from the Iranian world by its religious allegiance to Sunnite Islam and deprived of contacts with the West, artists continued to repeat, less and less well, post-Behzadian images.

The new era in the Iranian painting and the complete break from the past began with the Qajar dynasty 1732 CE. It is important to first recognize the contrast between vertical or diachronic identifications by regions (Khorasan, Azerbaijan, Fars, provinces with artistic rhythms that are variable in intensity but constant) and horizontal or synchronic definitions by dynasty or kinds of authority or government (imperial, aristocratic, urban) by emphasizing continuities within certain regions, which have come back into style with contemporary nationalism.

In any event three “chronological” instances, uniting chronology and space, define the Persian art of painting; Sogdian in Central Asia in about 700 CE, the formation of the Islamic Ilkhanid state about 1290 CE, and the development of Samarkand and Herat as cultural centers at the beginning of 15th century. These are the milestones of Persian painting, the characteristics and consequences of which demand further study and reflection (Grabar 2002, pp. 81-87).

2.3 The *Shāhnāma* (Book of Kings)

The *Shāhnāma* (Book of Kings), has completed in eastern Iran in 1010 CE by *Firdawsī* (935–1020 CE), is a work of mythology, history, literature, and propaganda: a living epic poem that pervades and expresses many aspects of Persian culture. There are hundreds of manuscript copies of the text existing in libraries throughout the world with the earliest dating back to 1217 CE (Melville 2006, p. 10; Brend 2010, p. 122). Large numbers of these manuscripts are illustrated with the most exquisite masterpieces of Persian art. “Indeed, the Shāhnāma offers a panoramic view of Persian painting for well over 1000 years, and it would be possible to trace the whole development of Persian painting and the arts of the book relying purely on examples taken from the Shāhnāma” (Melville 2006, p. 11).

Among the many works of classical literature that form the extensive body of Persian manuscript illustration, *Firdawsī’s Shāhnāma* occupies the prominent place. Hundreds of illustrated volumes survive today, but undoubtedly these are but a fraction of the actual number of the artistic production that began in the Il-khanid (Mongol) period, if not earlier, and continued well into the modern era in both painted and printed form (Robinson 1983, p. 75).

The Shāhnāma is a large text with circa 50,000 verses (bayts, each consisting of two hemistichs, miṣraʿ), and It consists of sections mythical, legendary, and historical. The first includes the establishment of human civilization, the domestication of animals, the battle with the strength of evil, and the determination of Iranian territory against her neighbors.

“The main section of *Shāhnāma* contains the ‘Sistan cycle’ of legends about the hero Rustam and his family, and the continual wars with the lands of Turan (approximately Turkestan or modern Central Asia), Iran’s traditional foe” (Melville 2012, p. 10).

However, the epic stories and characters, including those depicted in pre-Firdawsīan narratives and oral tradition were common in the Persian visual arts well before the practice of illustrating the *Shāhnāma* as a written text (Robinson 1983, p. 68; Hillenbrand 2007 pp. 95-119).

Firdawsī's work generally, is a thorough description of the history of the Iranian world from its creation to the fall of the Persian Empire. The Arab invasion changed the economic, social, and cultural life, however, the *Shāhnāma* offered Iran's new rulers a model of kingship, avoid changing the Persian language and identity, and spread their cultural influence beyond Iran's political borders.

The *Shāhnāma* was translated into Arabic, Ottoman Turkish, and many of the languages. A thousand years after completion of the *Shāhnāma*, it remains one of the most popular texts of poetry in Southwest Asia. "*Shāhnāma* was as a memorial to Iran's glorious past at a time when its memory was in danger of disappearing. Further, one of the main ways that the text could be inspired, along with the ethical messages it conveys, especially concerning just kingship and the benefits of society, was by the illustrated poem manuscript. Illustrated *Shāhnāma* started at least in the middle of the Mongol period (1300 CE) and the production of illustrated copies continued into the late 19th century when lithographic printing slowly replaced the manuscripts" (Melville 2006, p. 74).

2.4 Manuscripts Selection

To achieve the aims of this study the nine *Shāhnāma* manuscripts were selected to analysing. In choosing the manuscripts, four issues played an important role.

The historical period and city (school) in which the manuscripts were produced, also it was important that manuscripts be illustrated, and originality of their paintings already confirmed. Therefore, all these manuscripts are illustrated and belong to the 15th centuries and were produced in important cities (schools of paintings) of manuscripts production.

As well as the originality of paintings of these manuscripts is confirmed by the specialists. Although among them some manuscripts have certain paintings belong to 14th or 16th centuries (Tab. 2-1).

Manuscript	Place of production	Date of production	Date of paintings production	Number of analysed paintings	Paintings style
Ms 22-1948	Shiraz	1435-1440	1435-1440	5	Timurid of Shiraz
Or 420	Shiraz	1437	1437	9	Timurid of shiraz
RAS 239	Herat	1444	1444	15	Timurid of Herat
			Late 16th century	2	Mughal Indian
Persian 9	West India	Mid-15th century	Mid-15th century	14	Timurid
			Late 14th century	5	Jalayerid
Persian 933	West India	Mid-15th century	Mid-15th century	4	Timurid
			Late 16th century	3	Inju of Shiraz
			Late 16th century	6	Safavid of Qazvin
AKM 4	Shiraz	1482	1482	5	Turkman
AKM 269	Shiraz	1492	1492	13	Turkman
AKM 5	Shiraz	1494	1494	4	Turkman
AKM 6	Lahijan	1494	1494	4	Turkman

Table 2-1: *Shāhnāma* manuscripts selection

2.4.1 The *Shāhnāma* MS 22-1948:

Before mid-15th century that western Iran was ruled by two Turkman dynasties, the Herat Timurid style was very influential in Shiraz. The manifestation of these influences can be seen in the manuscripts of Ebrahim's workshop in the second quarter of 15th century.

This manuscript is an example of Timurid manuscripts of Shiraz belong to Ebrahim's workshop. This Timurid manuscript was produced in Shiraz, c. 1435-1440, and is now housed in The Fitzwilliam Museum in Cambridge. It is written in *nastaʿlīq* script and contains 559 folios and 26 paintings (Robinson 1985, p. 24). Five other illustrated pages of this manuscript are preserved at The British Museum (registration no. 1948, 1009, 0.48 to 52), which is in fact a collection of paintings, restored and reimagined in Europe with some text left in between them (*Wormald and M. GilesA* 1982, pp. 301-2).

In the paintings of this manuscript the hilly background and rocky horizon are present, and sometimes we witness the single tree as well[9]. The paintings are close to those produced in Ibrahim Sultan's workshop, especially to the *Shāhnāma* (Oxford, Bodleian Library, Ouseley Add. 176), so although it is not dated, it must have been produced around 1435 or shortly after Sultan Ibrahim's death (Robinson 1985, pp. 15-16). This copy of the *Shāhnāma* is a good example of Timurid Shiraz productions for comparing the differences of colour materials used in Heart workshops of Herat and other manuscripts produced in Shiraz like Turkman style manuscripts of Shiraz (fig. 2-16).

Date: 1435-1440 CE (838 AH)

Origin: Shiraz

Folios extant in manuscript: 34

Columns x Rows: 4 x 23

Page Size (h x w): 246 x 172 mm

Text Size (h x w): 178 x 114 mm

Script: *Nastaʿlīq*

Illustrations in manuscript: 26

Figure 2-16: *Shāhnāma* Ms 22-1948, 1984 Shiraz, The Fitzwilliam Museum

[9] For a reproduction of the British Museum's paintings, see Stchoukine, Ivan, *Les Peintures des Manuscrits Timurides*, Paris, 1954, pls. 24, 28 and 30; Canby, Sheila, *Persian Painting*, London, 1993, p. 55, fig. 31; Robinson, Basil, *Persian Drawings from the 14th through the 19th Century*, New York, 1965, p. 102, fig. 70.

2.4.2 The *Shāhnāma* MS. Or 420

This copy is dated 841/1437-38 in the colophon and although the place of production is not stated, it is very likely one of the Timurid manuscripts produced in Shiraz; however, there are elements of early Turkman style in some of its illustrations.

This is a part of an original manuscript which is now preserved in several collections (Browne 1922, p.129). The manuscript that is kept at the Cambridge University Library, contains the first part of the poem from the beginning to the end of the reign of Kay Khusrau (Browne 1922, p. 129). It comprises 281 folios each containing 25 columns, in *nastaʿlīq* script. The manuscript contains 11 paintings. The manuscript is unpublished, but it is mentioned in an appendix in The Epic of Persian Kings (Brend and Melville, 2010, pp.248-251).

Norihito Hayashi has studied this manuscript in his article on the Turkman Commercial style[10]. Hayashi reports that "the manuscript is in a seriously damaged condition so that all the written area has been cut off from the original pages and stuck onto the brighter white paper.

These have been cut along the rectangular frame, so that we have certainly lost the parts of painting extending to the margin" (Hayashi 2012, pp. 177-178). His assumption that Shiraz is "the most conceivable place for its production" is based on the characteristics of several manuscripts produced in Shiraz in the 1430s and 1440s, such as rocky horizons, simplified landscapes usually with single trees, and stylised bulbous flowers.

However, Hayashi considered this manuscript as a Timurid manuscript of Shiraz (Pre-Turkman) which represent some features of Turkman style. From the point of view of material science, all the 11 paintings of this manuscript are original (fig. 2-17).

This Timurid *Shāhnāma* manuscript of Shiraz is a good example to compare with the other two *Shāhnāma* Ms 22-1948 and RAS 239 which produced almost in same time in Shiraz and Herat. As well as this manuscript as a Pre-Turkman manuscript is a good example to compare with Turkman Commercial style manuscripts.

[10] Norihito Hayashi, The Turkman Commercial Style of Painting: Origins and Developments Reconsidered, Orient, Vol. XLVII (2012): 177-179: DOI: 10.5356/orient.47.169

Date: 1437 CE (840 AH)

Origin: Shiraz

Folios extant in manuscript: 281

Columns x Rows: 4 x 25

Page Size (h x w): 322 x 200 mm

Text Size (h x w): 232 x 130 mm

Script: *Nastaʿlīq*

Illustrations in manuscript: 11

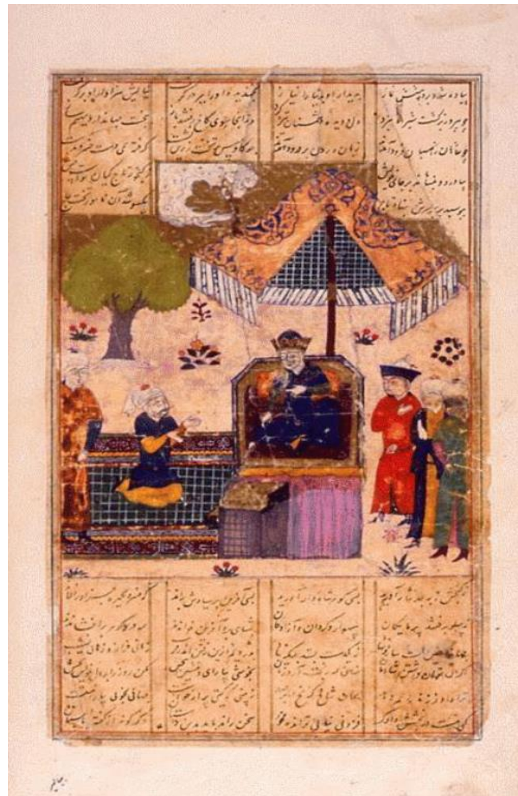

Figure 2-17: *Shāhnāma* Or 420, 1437 Shiraz, Cambridge University Library

2.4.3 The Juki *Shāhnāma* (MS. RAS 239)

This manuscript was commissioned by the Timurid prince Muhammad Juki[11] (1402-1445 CE), son of Shahrukh in 1444 CE. The manuscript belongs to the Royal Asiatic Society in London and is now preserved at The Cambridge University Library. Due to the importance of this manuscript, it has been studied with accuracy by Barbara Brend and published in 2010 in The Royal Asiatic Society in London.

This *Shāhnāma* manuscript is one of the most famous and classically beautiful Persian manuscripts. This manuscript along Baysunghur's *Shāhnāma* is the best example of the manuscript production of the royal workshop of Herat, the Timurid capital of the fifteenth century (Brend 2010, p.1). As Barbara Brend mentioned seven Timurid painters have been worked on this manuscript. These painters are painters of the royal workshop of Herat which some of them also worked on Baysunghur's Shāhnāma. The choice of

[11] The name of Muhammad Juki is mentioned twice in the decorations of two paintings on ff. 278r and 296r.

personages and composition in one of the paintings – Firdawsī and the court poets–shows great resemblance to those of Prince Baysunghur's copy (Rajab Kalta 2011, p.5)[12]. This painting appears in the preface of the Juki *Shāhnāma*, the section which seems to have been copied closely from the Preface to Prince Baysunghur's copy of 1430 CE (Mihan 2018, pp. 205-206)[13]. Folios containing miniatures are detached with the bifolio and stored separately in a box and the manuscript lacks the colophon (Brend 2010, p. 1). This is the only manuscript that Muhammad Juki is known to have commissioned. It is written in *nastaʿlīq* with 536 folios and contains 29 miniatures with two further paintings on f.430v and f.531r, added during the Mughal period (Brend 2010, p. 48) (Fig. 2.18).

From the point of view of material science, this manuscript is an excellent example to know about colour materials used in the royal workshop of Herat. As well as due to its originality, and its well-known painters it is an excellent example to understand the prevailing atmosphere in the bookmaking royal workshops. Further, since it is representative of the colour materials used in the Timurid manuscripts of Herat it is a very good example to compare with the manuscripts which have been produced in other cities and workshops.

Date: 1444 CE (c. 847 AH)

Origin: Herat

Patron: Muhammad Juki

Folios extant in manuscript: 536

Columns x Rows: 4 x 25

Page Size (h x w): 338 x 228 mm

Text Size (h x w): 228 x 135 mm

Script: Nastaʿlīq

Illustrations in manuscript: 31

Figure 2.18: *Shāhnāma* RAS 239, 1444 Herat, The Royal Asiatic Society, London

Photo Copyright © The Fitzwilliam Museum

[12] See Rajab Kalta, M. "Muṭāliʿa-yi taṭbīqī-i dah majlis az Shāhnāma-yi Bāysunghurī bā dah majles az Shāhnāma-yi Muḥammad-i Jūkī" (M.A., Isfahan University of Art, 1390/2011), where he has compared 10 illustrations from Juki's *Shahnama* with similar subject scenes from Baysunghur's *Shahnama* (Ms. 710, Golestan Palace, Tehran).

[13] For more detail, see Mihan, Shiva, *Timurid Manuscript Production: The Scholarship and Aesthetics of Prince Bāysunghur's Royal Atelier (1420–1435)*, (PhD Dissertation, University of Cambridge, 2018): 205-206.

2.4.4 The Shāhnāma MS Persian 9[14]

This is one of the Timurid manuscripts produced in Western India or Southern Iran (probably Shiraz), in the first half of the 15th century, and is kept in the John Rylands Library in Manchester. It comprises 702 folios, written in *nastaʿlīq* and contains 55 paintings.

The manuscript is enclosed in half-calf gilt binding, with lettered spine. It contains both the *Shāhnāma* and the Khamsa, in the central text block and margin, respectively (Robinson, 1980, pp. 72-73). The manuscript contains 42 paintings, 2 preliminary sketches, and 11 blank spaces, which indicates it was intended to have 55 paintings from the outset.

Robinson based on the pictorial features of the paintings of this manuscript judging very likely that two painters had worked on the manuscript: "painter A was probably an Indian, his primitive and naive style recalling Jalayirid work, as is especially evident from his palette (oranges and mauve). Painter B is 'unquestionably Persian' and a competent artist. Either he was a Persian artist visiting India, or an Indian more attuned to Shirazi Timurid style" (Robinson, 1980, pp. 72-74) (Fig. 2-19).

This manuscript is representative some features of Indian manuscripts. Therefore, it is a good example to identify colour materials used in Indian manuscript, also is good example to comparing with manuscripts produced in other cities.

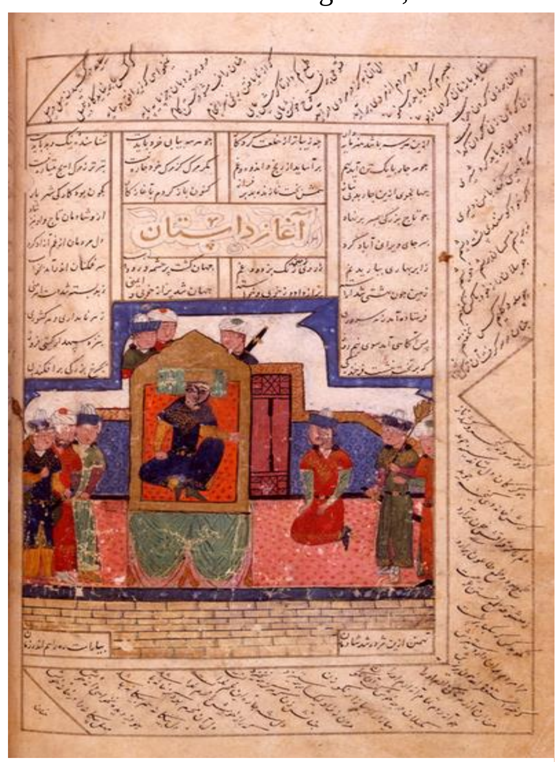

Figure 2-19: Shahnameh Per 9, 15th century Western India or Southern Iran, The John Rylands University Library of Manchester

Date: 15th century (middle)

Origin: Western India or Southern Iran

Folios extant in manuscript: 702

Columns x Rows: 4 x 21

Page Size (h x w): 230 x 158 mm

Text Size (h x w): 157 x 108 mm

Illustrations in manuscript: 55

[14] This manuscript is digitized and available at: https://luna.manchester.ac.uk/luna/servlet/view/search?q=reference_number=%22Persian%20MS%209%22

2.4.5 The Shāhnāma MS Persian 933[15]

This copy is a Timurid manuscript produced in Western India[16] in the 15th century, with 18th-century replacements of the lacunae, dated 1195/1781 CE. The codex is kept at The John Rylands Library, University of Manchester and contains 266 folios, carrying the text of the *Shāhnāma* written in *nastaʿlīq* script. It contains 79 paintings. The majority of paintings of this manuscript are in a rough hurried style of late 16th century. However, this manuscript contains four paintings contemporary with the manuscript (mid-fifteenth century), most probably these paintings which are painted in West India are imitations of the paintings of Ibrāhīm Sulṭān workshop of Shiraz (Robinson 1980, pp. 69-70). The late 16th century paintings are divided into two groups: Safavid Qazvin style and Inju style of Shiraz paintings (Robinson 1980, pp.70-71). Most of its illuminations including the *shamsa*, were evidently added in the late 16th century (Robinson 1980, pp.70-71).

This is the only manuscript analysed in this study which contains miniatures of the Qazvin style and Inju style. Therefore, it is a good example to comparing with manuscripts produced in other cities. As well as to comparing with other manuscripts produced in Shiraz (Fig. 2-20).

Date: 15th century

Origin: Western India

Folios extant in manuscript: 266

Columns x Rows: 6 x 31

Page Size (h x w): 400 x 292 mm

Text Size (h x w): 267 x 197 mm

Script: Nastaʿlīq

Illustrations in manuscript: 79

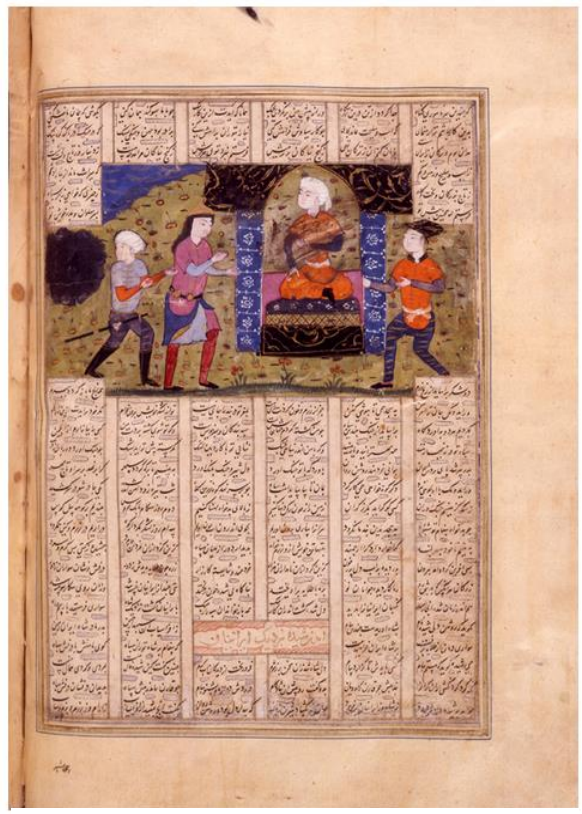

Figure 2-20: Shahnameh Per 933, 15th century Western India or Southern Iran, The John Rylands University Library of Manchester

[15] The manuscript is accessible at https://luna.manchester.ac.uk/luna/servlet/view/search?q=image_number=%22JRL030169tr%22

[16] Eleanor Sims assigns the manuscript to either Southern Iran or Western India, c. 1430-40. (Sims 1992, pp. 50-51)

2.4.6 The *Shāhnāma* AKM 4

This *Shāhnāma* manuscript is a copy in the Turkman style manuscript produced in Shiraz under Aqqoyunlu Turkman patrons in 1482 CE. It is kept in The Aga Khan Museum in Toronto.

This manuscript has all features of Turkman Commercial style manuscript (see section 2.2.5.5). This style of manuscript illustration that can be recognized in the manuscripts of western Iran during the second half of the fifteenth century (S. Graves and Junod 2010, pp. 282-3).

Turkman Commercial Style was first developed under the patronage of Qara Quyunlu rulers and was later introduced into Shiraz and other cities of their territories.

The phrase "Turkman Commercial Style" was used by B.W. Robinson in the 1950s to categorize a specific style of Persian painting in the late 15th century from an elegant style belong to the contemporary Timurid and Turkman courts (Norihito Hayashi 2012, p.169). It "is generally referred to the simplified and conventionalised style which regularly appears in the illustrated manuscripts produced at Shiraz in the Turkman period, particularly in the last quarter of the fifteenth century" (Hayashi, 2012: 172).[17]

This manuscript comprises six detached folios from a dispersed *Shāhnāma* kept at the Aga Khan Museum in Toronto with following register number: AKM45, AKM46, AKM47, AKM48, AKM49.

This manuscript written in *nastaʿlīq*, which include five paintings and a colophon. The scribe signs his name as Murshid b. ʻIzz al-Din Vazan in the colophon (Welch 1972, pp. 113-115).

Other folios of the same copy are held at the Metropolitan Museum of Art, in New York (MS. 40.38.2) (Welch 1972, pp. 113-115) (Fig. 2-21).

This is one of Turkman Commercial style manuscript analysed in this study and is a good example to comparing with manuscripts produced in other cities. As well as to comparing with Timurid manuscripts of Shiraz like manuscript Ms 22-1948 and Or 420.

[17] For a comprehensive study of the Turkman Commercial Style and its origins, see Hayashi, N. "The Turkman Commercial Style of Painting: Origins and Developments Reconsidered", *Orient*, XLVII (2012): 169-190.

Date: 1482 CE (887 AH)

Origin: Shiraz

Calligrapher: Murshid b. ʻIzz al-Din Vazan

Folios extant in manuscript: 6

Columns x Rows: 4 x 21

Page Size (h x w): 324 x 215 mm

Text Size (h x w): 223 x 158 mm

Script: Nastaʿlīq

Illustrations in manuscript: 5

Figure 2-21: *Shāhnāma* AKM 4, 1482 Shiraz, Aga Khan museum Toronto

Photo Copyright ©The Aga Khan Museum

2.4.7 The *Shāhnāma* AKM 269

This *Shāhnāma* is an exquisite manuscript produced under Aqqoyunlu Turkman patrons in Shiraz in 1492 CE. It is preserved in The Aga Khan Museum in Toronto. The fall of Shiraz to the Turkman dynasty in 1452 CE led to the development of a new commercial painting style. So, this manuscript contains both paintings with the influence of Timurid Shirazi painting and paintings of "Turkman Commercial style" (Robinson 1991, p. 26; S. Graves and Junod 2012, p.194).

This manuscript comprises 613 folios, written in *nastaʿlīq* script by the scribe, Na'im al-Din Shirazi ibn Sadr al-Din al-Muẕahhib, who was an accomplished and prolific calligraphy master for Sultan Abu'l-Nasr Qasim Khan (Welch 1982, p. 57; Junod 2007, p.158; S. Graves and Junod 2010, p. 285). This manuscript contains 44 high quality paintings in almost pristine condition (Welch 1972, pp. 28-31). It is a significant example for comparing the colour materials used in Shiraz workshops and under the rule of a Turkman dynasty with those used in the Timurid manuscripts produced elsewhere (Fig. 2-22).

Date: 1492 CE (897 AH)

Origin: Shiraz

Patron: Abu'l-Nasr Qasim Khan

Calligrapher: Na'im al-Din Shirazi

Folios extant in manuscript: 613

Columns x Rows: 4 x 21

Page Size (h x w): 292 x 183 mm

Text Size (h x w): 97 x 172 mm

Script: *Nastaʿlīq*

Illustrations in manuscript: 44

Figure 2-22: *Shāhnāma* AKM 269, 1492 Shiraz, Aga Khan museum Toronto

2.4.8 The *Shāhnāma* AKM 5

This is another example of the Aqqoyunlu Turkman manuscripts produced in Shiraz in 1494 CE. The manuscript is in fact a collection of nine detached folios of a dispersed *Shāhnāma* kept at The Aga Khan Museum in Toronto with following register number: AKM51, AKM52, AKM53, AKM54, AKM55.

This collection also including three folios of text, and a colophon, written in a mediocre *nastaʿlīq*. This manuscript was formerly part of the Demotte collection (Welch 1972, pp. 116-121, Vol. I; Junod 2007, p.143). It is penned by Sulṭān ‘Ali Shirazi, and its six paintings have been assigned to the Turkman Commercial Style (fig. 2-23).

This is another example of Turkman Commercial style manuscript analysed in this study and is a good example to comparing with manuscripts produced in other cities. As well as to comparing with Timurid manuscripts of Shiraz like manuscript Ms 22-1948 and Or 420.

Date: 1494 CE (899 AH)

Origin: Shiraz

Calligrapher: Sulṭān ‘Ali Shirazi

Folios extant in manuscript: 9

Columns x Rows: 4 x 25

Page Size (h x w): 325 x 232 mm

Text Size (h x w): 224 x 149 mm

Script: Nastaʿlīq

Illustrations in manuscript: 6

Figure 2-23: *Shāhnāma* AKM 5, 1494 Shiraz, Aga Khan museum Toronto

2.4.9 The *Shāhnāma* AKM 6

This *Shāhnāma* is a production of the Aqqoyunlu Turkmans in Gilan. It was produced at the court workshop of Sultan ‘Ali Mirza, from the Karkiya dynasty (r. 1478–1505) in 899/1494 CE. It is a collection of five detached, illustrated folios preserved at the Aga Khan Museum, AKM62, AKM63, AKM64, Akm91, and AKM92. Written in neat *nastaʿlīq*, these folios were originally part of the celebrated “Big Head”

Shāhnāma[18] (Welch 1978a, p. 56; Akbarnia et al. 2008, p.287). The term refers to the visual characteristics of the portrayal of human figures with big heads, which is seen in most of its illustrations.

The bulk of the manuscript is housed in two collections in Istanbul: volume one in the Turk ve Islam Eserleri Muzesi (henceforth TIEM), MS 1978, and volume two in the Istanbul University Library, F. 1406 (Welch 1972, pp. 127-128). It is the most prodigiously illustrated of all known *Shāhnāma*s, originally containing about 350 paintings. This copy was penned by Salik b. Sa'id in *nastaʿlīq* script.

The significance of this manuscript lies in its place of production, as it is the only manuscript analysed in this study which was produced in Lahijan. Therefore, it can potentially serve as an important source of information about colour materials used in Gilan Province and can provide a scientific comparison with the manuscripts produced in Shiraz and Herat (fig. 2-24).

Date: 1494 CE (899 AH)

Origin: Gilan (Lahijan)

Patron: Karkiya Mirza ʻAli (or ʻAli Mirza)

Calligrapher: Salik b. Sa'id

Folios extant in manuscript: 5

Columns x Rows: 4 x 23

Page Size (h x w): 346 x 242 mm

Text Size (h x w): 232 x 153 mm

Script: Nastaʿlīq

Illustrations in manuscript: 6

Figure 2-24: *Shāhnāma* AKM 6, 1494 Gilan, Aga Khan museum Toronto

Photo Copyright © The Aga Khan Museum

[18] Melville, Charles, "The "big head" *Shāhnāma* in Istanbul and elsewhere: some codicological and iconographical observations", in *The arts of Iran in Istanbul and Anatolia : seven essays*, ed. Olga Davidson, and Marianna Shreve Simpson (Boston, 2018).

CHAPTER 3: Analytical Techniques: Principles and Experiments

Considering the multi-material structure of the illustrated manuscripts, the multi-technique approach is the optimal strategy to recognize colour materials used in illustrated manuscripts as generally required when dealing with diagnostic in cultural heritage. Therefore, using a combination of methods could create a perfect survey on colour materials used in the illustrated manuscripts. In this study, the non-invasive and micro-invasive analytical techniques have been employed to reach the aims of the project mentioned in the first chapter. It should be noted that in this research analytical techniques have been applied to identify pigments by X-ray Fluorescence (XRF) and Fibre Optic Reflectance Spectroscopy (FORS) techniques and natural dyes and lakes through a combination of FORS, Fibre Optics Molecular Fluorimetry (FOMF), High Performance Liquid Chromatography Mass Spectrometry (HPLC-MS), and Surface-enhanced Raman scattering (SERS) techniques.

3-1 Introduction

"A particular requirement for the investigation of cultural and historical objects is the use of techniques that are non-destructive or only need minimal sampling. The methods should also be fast, universal, versatile, sensitive, and multi-elemental" (Hahn et al. 2007, p. 23). Many spectroscopic methods have been used for cultural heritage objects, including UV/Vis/NIR, FTIR, Raman and XRF spectroscopy. In the field of art and cultural heritage, non-destructive reflection-UV/Vis/NIR spectroscopy has been applied in different ways for pigment identification as well as the study of degradation processes mainly in combination with other techniques (Wilfried and Schreiner 2014, pp. 7-8).

Besides, in situ analytical techniques have often been used in the past years, for the investigation of manuscripts and their decoration; this has especially been the case for Raman spectroscopy, often used together with x-ray fluorescence (XRF) or particle-induced x-ray emission and sometimes in combination with micro-sampling/destructive techniques (Ricciardi et al. 2013, p. 13).

However, one should be aware that a complete investigation of an illuminated manuscript is a difficult task, since illuminated manuscripts are among the most precious and fragile artworks. Many limitations and challenges must be considered. Sampling from miniatures is a hard task and is usually not permitted by possessors and institutions, and thus only in situ analysis can be performed; and applying analytical techniques which touch the surface of manuscripts, like ATR-IR, is usually not possible. Moreover, while carrying out analytical measurements, the lengthened opening of the manuscripts causes stress to illuminated pages and to the manuscript's layout itself, therefore, after some hours, the analytical process must be stopped (Aceto et al. 2014, pp. 1-2). Finally, a fast-analytical process is necessary to minimise interference with the activities of museums and institutions. “Therefore, the techniques of choice must be rapid, non-invasive and available in portable version” (Aceto et al. 2014, pp. 1-2).

In this work a multi-step analytical protocol is proposed for non-invasive in situ characterization of miniature paintings. “Since manuscripts require particular care due to their intrinsic fragility and susceptibility to damage caused by changes in environmental conditions, non-invasive multi-technique approach offers a reliable and sensitive way to study the materials the manuscripts are made of, in situ” (Anselmi et all. 2015, p. 185).

So, the performed protocol allows the identification of coloured materials through its use in a sequence of complementary techniques, to fully exploit the information given by each instrument. The protocol starts with an extensive investigation with Fibre Optics Reflectance Spectroscopy (FORS), collecting spectra from all the most significant painted areas in the manuscript. The second step involves a fresh investigation of painted areas in the manuscript that have been diagnosed like organic material (dyes) by Fibre Optics Molecular Fluorimetry (FOMF), and XRF spectrometry is then performed in the third step to characterize pigments and metal layers, to recognize minor components that may yield information concerning provenance materials and manuscripts. Afterward, HPLC-MS and SERS techniques are performed in the last step for more accurate investigation of dyes and lakes if micro samples are available.

As one of the main analytical techniques applied in the present project, FORS is able to recognize both pigments and dyes. FORS works on the basis of the identification of spectral features of materials (reflectance maxima, transition edges, spectral shape, vibrational features) due to specific electronic transitions of single atoms or ions (inorganic), or molecules (organic). Information relevant to vibrational features (overtones and combinations) can be obtained as well (N. Clark 1999, p. 3).

Yet, another analytical technique used in the project protocol is X-ray fluorescence analysis (XRF). Since XRF contains most of the important requirements of manuscript investigations, its use has increased immensely in the last years (Hahn et al. 2007, p. 23). XRF is a technique able to identify the pigments by recognizing the chemical elements of their components (Ricciardi et al. 2013, p. 14).

Afterwards, ultraviolet, and visible (UV-Vis) spectrofluorimetry, with reference to the variant with optical Fibres or FOMF (Fibre optics molecular fluorimetry) is considered in the project as a complementary analytical technique. FOMF has some features and benefits that make it particularly suitable for the identification of dyes in the illuminated manuscripts. Due to its fast response times and its ease of use, it could at least be considered as a preliminary technique before the application of more complex techniques to identify dyes, in order to determine the number of spots under investigation (Aceto et al. 2014, pp. 1-2).

Therefore, the capability of the combination methods could create a complementary data of the material under investigation, and these methods allows the researchers to identify the various kind of colour materials used in the illuminated manuscripts (Bacci et al. 2004; Aceto et al. 2008; Ricciardi et al. 2009).

Basically, the experimental protocol applied in this project for the analysis of colour materials used in the *Shāhnāma* manuscript included the application of FORS and XRF first to determine the colour materials utilised for illuminated pages, and then the use of FOMF to determine and examine the organic dyes which were recognized by FORS. Finally, to improve precision in the determination of organic dyes and lakes, SERS and HPCR-MS were performed on some micro-samples.

3-2 X-ray Fluorescence (XRF)

This part will present an overview of the role and use of XRF in the collection/acquisition of materials characterization data from the manuscripts.

3-2-1 Introduction

XRF has all the necessary features for the identification of pigments used in manuscripts. Since identifying the pigments present on illuminated manuscripts requires much important data, including information about the working operation of the artists and their chosen palette, XRF helps to discover an unknown time-period of execution by indirect-dating, to recognize any later interventions and to help determine the necessary conservation protocols to protect the work of art in the future (Gebremariam et al. 2013, pp. 462-69; Liss and Stout 2017, p. 55).

Therefore, due to features like ease of use, prompt setup, short acquisition times and portability, XRF as a non-destructive analytical technique, is often one of the first choices for the investigation of colour materials in the field of cultural heritage (Liss and Stout 2017, p. 55). "Indeed, XRF represents one of the most suitable ways to obtain qualitative information on many different materials, such as iron gall inks, carbon inks, or even other drawing and writing materials" (Hahn et al. 2007, p. 23).

The German physicist Wilhelm K. Röntgen (1845–1923) was the first person to discover X-rays which won him the Nobel Prize in 1901 (Röntgen 1898, pp. 1-11). "While X-rays have been used for commercial elemental analysis since the 1950s, X-ray spectroscopy is much older than that, dating back to 1909 when Charles G. Barkla found a connection between X-rays radiating from a sample and the atomic weight of the sample" (Shackley 2011, p. 7).

Thus, X-Ray fluorescence (XRF) technique is commonly used for analysing the elemental composition of paints in various manuscripts. This technique benefits from the availability of a variety of transportable instruments ranging from single spot to high-resolution scanning equipment, as well as from a wealth of knowledge and experience that have been accumulated in the characterization of historical pigments and inks via this technique. Specifically, the development and use of the fingerprint model based on the qualitative and quantitative detection of inorganic components of colour materials allow for their reliable classification. It must be noted that XRF as an elemental spectroscopy cannot recognize organic materials or binding media which are mostly organic materials, and the elemental information given by XRF cannot determine molecular arrangement or precise chemical formulae of the pigments (Hunt and Speakman 2015, p. 1).

There are two methods of X-ray spectroscopy, ED-XRF (energy-dispersive) and WD-XRF (wavelength-dispersive). They differ by the type and function of their detectors and practically by the accuracy of the results they provide (Artioli 2010, p. 34).

3-2-2 Principles and experiments

The x-ray fluorescence technique is based on the detection of characteristic X-rays from the elements present in the sample under evaluation (Guerra et al. 2013, p. 2).

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding it with X rays. When the surface of the materials is exposed to high-energy, short-wavelength radiation (e.g. X-rays), they can become ionized and then will emit characteristic X-rays. When the electrons of an atom shift from their normal or ground state to another state, this atom is called an excitation atom; however, the atom can return to the non-excited state by various processes (Jenkins 1999, p. 55).

Therefore in an atom, if the energy of the radiation which is irradiated to the atom is sufficient to shift an electron from the inner shell, the atom becomes excited and an electron from the outer shell replaces the missing inner electron. In this situation, energy is released because the inner shell electron is more strongly bound compared with the ejected electron (Fig. 3-1) (Shackley 2011, p. 16). The emitted radiation is called fluorescent radiation because its energy is lower than the primary incident X-rays Energy differences between electron shells are known and fixed, so the emitted radiation always has characteristic energy. Detecting this photon and measuring its energy allows us to determine the element through the specific electronic transition from which it originated (Shackley 2011, p. 16).

It must be considered, in performing XRF for identifying pigment, that the support (in this case paper) is always present in the spectrum because the x-ray radiation passes on the tiny layer of pigments, and therefore we have to be aware of major elemental components of the support (Liss and Stout 2017, p. 57).

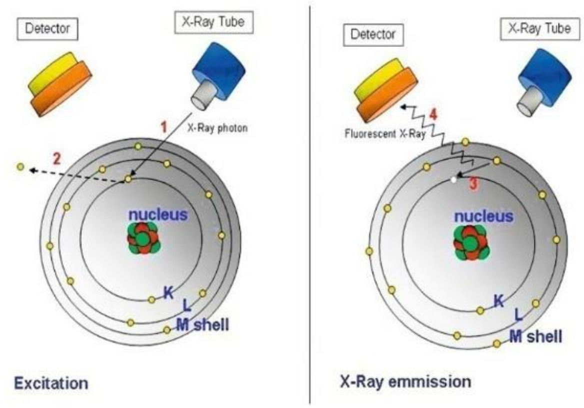

Figure 3-1: Physics of X-ray fluorescence in a schematic representation

3-2-3 Instrumentation

Since *Shāhnāma* manuscripts investigated in this project are kept in various museums and libraries in the world, portable XRF spectroscopy has been chosen by the authors as a well-developed technique to study the colour materials used in the *Shāhnāma* manuscripts.

Considering the improvement of the portability and affordability of the XRF, the portable XRF instrument has become a common analytical technique in archaeological research (Shugar and Mass 2013, pp. 15-17). Portable XRF is a fast and reliable technique to identify the elemental components of pigment materials used on manuscripts and can be considered as part of a multi-technique approach for the identification of the materials colour (Miliani et al. 2010, pp. 729-731). Time available for the analysis and the accessibility of the illustrated folios of *Shāhnāma* manuscripts at the site were significant limiting factors in this study, and therefore a quick survey was designed to cover all of the visible palette colours on each of the selected illustrated manuscripts. This represented circa 1000 individual points studied collectively on nine manuscripts. In this scenario, all pigments were analysed with XRF.

Due to the rules and regulations of different museums and libraries as well as limitations like the availability of the in situ XRF instrument, the availability of a room for performing XRF measurements, the time allotted for measurements and the conservation situation of the manuscripts, three different portable XRF instruments were applied.

In the Cambridge University Library (*Shāhnāma*: RAS 239 and Or. 420) an ELIO® spectrometer (XG-LAB S.R.L, Milano, Italy) was applied, which consists of an air-cooled low-power X-ray tube, poly-capillary X-ray optics (measuring spot size of 1 mm in diameter), a silicon drift detector and a CCD camera for sample positioning. The measurements were conducted by using a 10 W low-power Rh tube, 50 kV, 200 µA, and an acquisition time of 60 s (live time). The XRF scanning equipment employed a mobile XRF probe that was positioned over the manuscript at a distance of 5 mm.

In the Fitzwilliam Museum (*Shāhnāma*: Ms 22-1948) an Artax micro X-ray spectrometer (Bruker) with an Rh anode was used. The X-ray tube was operated either at 50 kV and 600 µA or at 15 kV and 1100 µA with He flush, for better detection of light elements.

The measurements lasted 200 s each and were performed with no filters. The measurement spot size was about 0.65 mm in diameter. Images of each analysed area were captured with the instrument's in-built camera and saved.

In the Aga Khan Museum (*Shāhnāma*: AKM 269, AKM 4, AKM 5, and AKM 6), the XRF measurements were carried out by the X-Ray Fluorescence Spectrometer model "Bruker AXS Handheld Tracer III-SD" which consists of an X-ray tube Rhodium target; 40 kV maximum voltage and a detector; 10 mm^2 XFlash Silicon Drift Detector (SDD); 145 eV resolution at 100,000 counts-per-second, with an analysis window size of approximately 3 mm * 4 mm in diameter.

In case of manuscripts AKM 4-5 & 6, since they were detached manuscript folios, the measurements were carried out with a different strategy. The Handheld XRF instrument was placed on the holder (the desktop stand style) in vertical position (analysis window in upward direction) and illustrated folios were placed in front of the analysis window (Fig. 3-2).

In this strategy, two Lab Jacks were employed to adjust the height and balance the positions. A Passepartout folio with a hole in the centre was also placed between the analysis window and the illuminated folio to protect illuminated folios and to keep a standard distance between the analysis window and the illuminated folio under analysis (Fig. 3-3).

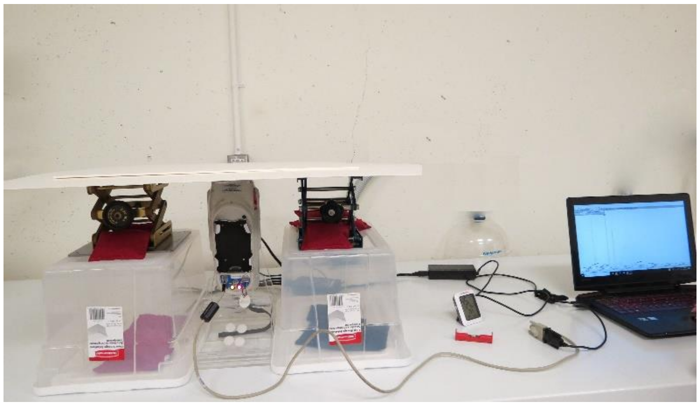

Figure 3-2: Performing XRF measurements on detached manuscript folios

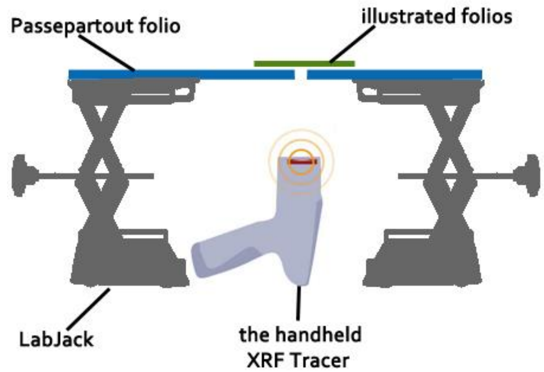

Figure 3-3: Schematic view of strategy of apply XRF on detached manuscript folios

3-3 Fibre Optic Reflectance Spectroscopy (FORS)

This part will present an overview of the role and use of FORS for the identification of pigments and dyes used in the selected *Shāhnāma* manuscripts.

3-3-1 Introduction

To the best of our knowledge, the first application of the Fibre optics to the investigation of paintings was made at the National Gallery of London in the late seventies and early eighties (Picollo et al. 2000, p. 259).

Thanks to the development of conveniently transportable devices, FORS has become a widely used method to identify artwork colour materials in situ [Miliani et al. (2010); Dupuis & Menu (2006); Bacci et al. (2009), Aceto et.al 2012, Anselmi et.al 2015, Acquaviva et al. (2008); Acquaviva et al. (2010), Vetter and Schreiner (2014)].

Fibre-optics reflectance spectroscopy (FORS) is part of a large class of techniques in molecular spectroscopy; it involves the irradiation of the sample with light having a wavelength between 200 and 1.100 nm (more commonly between 200 and 800 nm) and recording the spectrum of the light diffused by the sample.

FORS in the UV, Vis, and NIR regions is a non-invasive technique, effective for analysing artworks. FORS is a non-invasive portable technique able to identify colour materials (pigments and dyes), and appraise colour and colour changes (Bacci et al. 2009, p. 2). Moreover, in this technique, a large number of spectra can be registered in a short time. This feature makes allows for a statistical treatment of the data and is useful for the identification of different colour materials (Picollo et al. 2000, p. 259).

FORS could also be used in combination with other techniques to locate areas for micro-sampling (Bacci et al. 2009, p. 2). The spectra obtained by FORS enable us to identify both organic and inorganic colour materials without the risk of damage to or contamination of the objects under investigation (Vetter and Schreiner 2014, p.7). FORS can be applied largely in order to identify pigments, such as synthetic or natural pigments (Bacci et al. 2009, pp. 4-5). It is also an efficient technique for the identification of dyes, and therefore, several studies have been done for the identification of red, blue, and yellow dyes in artworks by performing FORS (Bisulca et al. 2008, p. 2).

It should be noted that the use of FORS is proposed for the identification of colour materials, by comparing the obtained spectrum to a suitable database (Picollo et al. 2000, p. 259; Dupuis et al. 2002, p. 1329). The diagnosis of the unknown spectrum is usually based on the identification of the characteristic wavelengths of that spectrum in comparison with the spectral database but the ordinates of the spectra are not taken into consideration (Dupuis et al. 2002, p. 1329).

However, regarding the efficiency of the results obtained through FORS, it should be noted that FORS is not able to identify complex mixtures of colour materials very accurately; and in such cases, the position of the absorption bands may be shifted a few nanometers or be reduced in intensity (weakened) (Bacci et al. 2009, pp. 3-4). In addition, when the colour materials (pigments and dyes) are present in low concentrations, the effect of yellowing of the binder or the varnish may significantly move their curve inflection points in FORS spectra. Some materials have similar FORS spectra such as cadmium red and vermilion, therefore, FORS is not able to identify all colour materials accurately (Bacci et al. 2009, pp. 3-4).

3-3-2 Principles and experimental

FORS is based on the analysis of the radiation diffused by the surface in the 200-1100 nm range (Bacci et al. 2009, p. 2). The technique is based on the absorption of the radiation that strikes the sample, which occurs because of electronic transitions to an excited energy level, with the production of electronically excited species. The absorption is a selective phenomenon since it occurs only when the energy of the incident radiation corresponds to the transition energy between two molecular quantum levels of the absorbing chemical species. The frequency of the absorbed radiation is therefore defined by the Bohr condition:

$$h\nu = Ef - Ei$$

Where h is Plank's constant, ν is the frequency of the absorbed radiation, Ef is the energy of the excited level and Ei is the energy of the ground state. The absorption of ultraviolet or visible radiation is usually due to excitation of bonding electrons and then the wavelengths of the absorption bands can be correlated with the types of bond present in the test species. The molecular absorption spectroscopy is useful for identifying functional groups in molecules (Kortüm 1969; Aceto et al. 2014; Poldi and Villa 2006; Braeuer 2015).

The absorption of radiation in the UV-Vis-NIR spectral range occurs due to four classes of transitions that are related to (1) π, σ and n electrons; (2) d and f electrons; (3) electrons in the energy bands of semiconductors; (4) charge transfer transitions (Fig. 3-4). When a beam of electromagnetic radiation strikes a material, part of the radiation is reflected, and the other part that enters the material can be absorbed or diffused. The fraction of the absorbed radiation is a function of wavelength according to the classes of electronic transitions described above (Kortüm 1969; Aceto et al. 2014; Braeuer 2015; Antonioli et al. 2005).

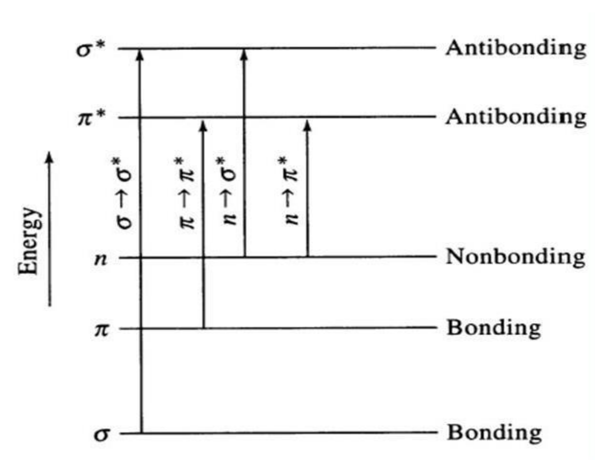

Figure 3-4: Molecular energy levels

The absorption spectrum yields the qualitative information on the nature of the material constituting an object. Information about the absorption properties of an object may derive both from the transmitted radiation through transmittance (defined as: T = Ii/I0 where I0 and Ii are the intensity of the incident beam and the intensity of the light that passed through the sample) or, for opaque materials, from the reflected radiation (Kortüm 1969, pp. 176-77).

The absorption bands in the UV, Vis, and NIR regions are determined by transition between the electronic energy levels, therefore FORS features are defined by different processes, which have either electronic or vibrational origins. For instance, in inorganic pigments, the absorption bands are related to Ligand-Field, Charge Transfer, and Valence-Conduction band transitions. In fact, with these features, it is possible to recognize inorganic pigments (Bacci et al. 2009, pp. 4-5).

However, in reflectance spectra, colourants of similar hue can be recognized by the identification of maximum peaks and inflection points. Moreover, in a mixture of colourants maximum peaks and inflection points are not easily detectable. In such a situation more reliable information is derived from apparent absorbance maxima, which can be obtained through Kubelka–Munk or Log(1/R) transformation (Aceto et al. 2012, pp. 354-356; Kortüm 1969, pp. 176-177).

In painted areas where pure colourants have been used, a correct identification can be made based on FORS spectrum, referencing it against standard spectra. Where the spectrum from a sampled area is significantly different from a standard spectrum it could be related to (e.g. due to a shift in maximum position), an interpretation is needed, taking into account the fact that spectral features in apparent absorbance mode are more reliable than those in reflectance mode. In most cases, the presence of a mixture can be guessed, addressing the application of successive, more powerful techniques (Aceto et al. 2012, pp. 354-356).

Multivariate analysis performed on FORS spectra allows identifying painted areas obtained with the same pigment when dealing with large sets of spectra. Every spectrum is described as a two-column set of data, containing wavelengths and reflectance values, respectively (Aceto et al. 2012, pp. 354-356).

3-3-3 Instrumentation

In this work portable Fibre Optics Reflectance Spectroscopy (FORS) was employed. Therefore, the instrument configuration includes spectrophotometers and spectroanalysers and involves the use of bundle optical Fibres for both the transport of the light beam to the sample, and for the collection of light reflected from it and sent to the detector. The ambient light has a negative influence on the quality of FORS spectra;

therefore, it could be more advantageous if spectra are collected in a dark room (Vetter and Schreiner 2014, p. 10).

In this configuration, the Fibre optics, the dispersive element (grating), and the detector are arranged to collect the backscattered light by the Fibre optics and afterward send them to the dispersive element and then to a suitable detector (Fig. 3-5).

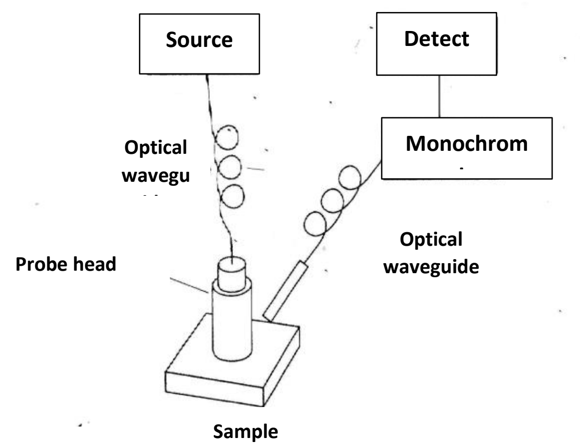

Figure 3-5: Setup for technical FORS instrument equipped with fiber-optic light-gathering reflected by the sample

The difference in the refractive index of light is the reason why light is reflected by the Fibre optics. The Fibre optics bundles contain two extended coaxial cylinders each of which has a different refractive index; the inner one (the "core") has a high refractive index, while the exterior one (the "cladding") has a lower refractive index (Bacci et al. 2009, pp. 298-299; Aceto et al. 2012, p. 353).

Therefore, it is possible to work in diffuse reflectance by collecting the light scattered at a 45°-degree angle to the incident light, to avoid specularly reflected light. This is the radiation that is reflected without interacting with the bulk of the material analysed, so it does not carry any information on chemical composition (Bacci et al. 2009, pp. 298-299; Aceto et al. 2012, p. 353).

As mentioned above, FORS analysis was performed by various portable instruments due to the wide range of manuscripts analysed in this project and their preserving place.

In order to perform FORS in the Cambridge University Library (*Shāhnāma*: RAS 239 and Or 420) and the John Rylands Library in Manchester (*Shāhnāma*: Persian 9 and Persian 933), an Avantes (Apeldoorn, The Netherlands) AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-DH-S-BAL balanced deuterium–halogen light source with a wavelength range of 190–2500 nm were used; the detector and light source were connected to an Ocean Optics (Dunedin, Florida, USA) R-400 model reflection probe with fibre optics.

In this configuration, light is sent and retrieved with a unique fibre bundle positioned at an angle of 45° from the surface normal, in order to exclude specular reflection. The investigated spectral range of the detector was 250–900 nm; depending on the features of the monochromator (slit width of 50 lm, grating of UA type with 300 lines/mm) and of the detector (2048 pixels), the best spectra resolution was 2.4 nm calculated as FWHM. Diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile provided by Avantes and guaranteed to be reflective at 98% or more in the investigated spectral range.

The investigated area on the sample had a 3 mm diameter. In all measurements the distance between probe and sample was kept constant to 1 mm. To visualize the investigated area, a Framos (Agrate Brianza, Italy) WEB1315SI model digital micro camera, connected to a PC via USB, was mounted in the probe. The instrumental parameters were as follows: 30 ms integration time, 50 scans for a total acquisition time of 1.5 s for each spectrum. The whole system was managed by AvaSoft v. 8 dedicated software, running under Windows 7.

In the Fitzwilliam Museum (*Shāhnāma*: Ms 22-1948), the reflectance spectra of the manuscripts were recorded with a FieldSpec4 spectrometer (ASDi/PANalytical) with an integrated light source and a bifurcated Fibre-optic probe kept parallel to the surface normal. The spectral resolution of the instrument was 3 nm at 700 nm, and 10 nm at 1400 and 2100 nm. The instrument included a modular Silicon array and two Peltier-cooled InGaAs detectors. The measurement spot size was about 3 mm in diameter. Sixty-four scans were acquired for each spectrum for a total acquisition time of approximately 8 seconds. Calibration to reflectance was obtained using a Spectralon standard. The spectral interpretation was based on both in-house and published reference databases.

In the Aga Khan Museum (*Shāhnāma*: AKM 269, AKM 4, AKM 5, and AKM 6) FORS measurements were carried out by a light source model HL-2000 (Halogen light source) and a miniature spectrometer model Flame "Ocean Optics (Dunedin, Florida, USA)" with an acquisition range of the spectrum between 350-1200 nm; detector, and light source were connected with Fibre optics Premium-grade Reflection Probes (Dunedin, Florida, USA), the investigated area on the sample was a 3 mm diameter (Fig. 3-6).

Figure 3-6: Setup for technical FORS instrument equipped with fiber-optic

3-4 Fibre Optics Molecular Fluorimetry (FOMF)

This technique was used in some manuscripts in this project as a non-destructive method for recognizing dyes. So, this part will present an overview of the technique.

3-4-1 Introduction

Natural dyes have been used extensively in the past for many purposes, such as to colour papers and fibres, to produce inks, watercolours, and paints, but their use declined rapidly after the discovery of synthetic colours (Acquaviva et al. 2014, p. 1). Due to the relative difficulty of identifying dyes compared to inorganic pigments, very little diagnostic information is available on the presence of organic colourants (dyes and lakes) in the palettes of Persian artists particularly in Persian manuscripts. (Idone et al. 2021, p. 138).

Because of dimension and weight, the FOMF instrument is easily portable and useful for collecting spectra in situ. Moreover, due to its velocity and ease of use, many spectra can be obtained in a short time, which is useful for the identification of different dyes (Picollo et al. 2000, p. 259).

Identification of the natural dyes and lakes is commonly achieved by destructive or micro destructive methods like high-performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FTIR) and SERS which can require time-consuming and complicated sample preparation this fact must also be taken into consideration in the case of manuscripts sampling from miniatures that it is hard to conduct if ever allowed by owners and institutions even in the meaning of micro samples Other issues that make identifying dyes used in manuscripts difficult are the low concentration of the dye and the presence of the binder (Bisulca et al. 2008, pp. 1-2; Aceto et al. 2014, pp. 1488-89). Therefore, the ability to identify dyes with the non-invasive technique is a very important task in the field of cultural heritage objects especially in the case of analysing manuscripts.

As mentioned above, FORS offers many advantages for identifying the dyes and there have already been several published studies on the analysis of the dyes by using FORS (Bisulca et al. 2008, p.2). As a non-invasive and simple method, FOMF is a very useful technique to identify dyes used in manuscripts. In fact, this technique is considered as a complementary technique for helping FORS method to identify dyes. Undoubtedly recognizing dyes by FOMF is not reliable and accurate in comparison with HPLC and SERS but due to some advantages of FOMF like short requests analysis times, being non-invasive, ease of use, portability, etc., it is a good alternative to those powerful but sophisticated techniques for identifying dyes used in manuscripts.

3-4-2 Principles and experiments

Fluorescence occurs when a molecule absorbs light photons from the UV-Vis light spectrum that causes transition to a high-energy electronic state (excitation) and then rapidly (in less than 10^{-9} s) emits light photons as it returns to its ground state (Nahata 2011, p. 2).

Fluorimetry characterizes the relationship between absorbed and emitted photons at specified wavelengths. Some energy is lost through heat or vibration so that the energy of light emitted by fluorescence is lower than the one emitted by the excitation beam, i.e., the emission wavelength is always longer than the excitation wavelength. The difference between the excitation and emission wavelengths is called the Stokes shift (Nahata 2011, p. 2).

The emission properties of a compound are fixed, for a given instrument and conditions, and can be used for identification purposes. The magnitude of fluorescent intensity is dependent on both intrinsic properties of the compound and on the presence of other species in the local molecular environment. Also, the intensity of the absorbed light and concentration of the emitting species play a role.

Of particular relevance is the quantum efficiency (ϕ), which is the percentage of molecules in an excited electronic state that decay to ground state by fluorescent emission. This value is always less than or equal to unity and is characteristic of the molecular structure. A high efficiency is desirable to produce higher relative emission intensity. All non-fluorescent compounds have a quantum efficiency of zero (Aceto et al 2012, p. 355; Poldi and Villa 2006, pp. 157-159).

3-4-3 Instrumentation

In the Cambridge University Library (*Shāhnāma*: RAS 239 and Or 420) and the Manchester's John Rylands Library (*Shāhnāma*: Persian 9 and Persian 933) in order to identify dyes by FOMF, the molecular fluorimetry measurements were obtained by measuring the intensity of the emitted radiation in a broad spectral range for a fixed excitation wavelength produced by an LED source.

In order to record fluorescence spectra, an Ocean Optics (Dunedin, Florida, USA) Jaz model spectrophotometer was employed. The instrument is equipped with a 365 nm Jaz-LED internal light source;

a QF600-8-VIS/NIR Fibre-optic probe is used to drive excitation light on the sample and to recover the emitted light. According to the features of the monochromator (200 lm slit width) and detector (2048 elements), the spectral resolution was 7.6 nm calculated as FWHM. The investigated area on the sample was 1 mm in diameter.

In all measurements, the sample-to-probe distance was kept constant to 1 mm (corresponding to focal length) by a black cylinder inserted on top of the probe. This also excluded contributions from external light. Instrumental parameters were as follows: 2 s integration time, 3 scans for a total acquisition time of 6 s for every spectrum. The system was managed with SpectraSuite software working under Windows 7.

In the Aga Khan Museum (*Shāhnāma*: AKM 269, AKM 4, AKM 5, and AKM 6), FOMF measurements were carried out by a 365 nm light source – for illumination model 365 nm LED and miniature spectrometer model Flame "Ocean Optics (Dunedin, Florida, USA)", a Fibre optics Premium-grade Reflection Probes (Dunedin, Florida, USA), was used to drive excitation light on the sample and to recover emitted light. The investigated area on the sample is 3 mm in diameter.

3-5 High Performance Liquid Chromatography Mass Spectrometry (HPLC-MS)

This part provides an overview of HPLC-MS as a micro destructive analytical technique for the characterization of natural dyes and lakes (Indian lac) used in some of the selected *Shāhnāma* manuscripts. In the present project, a few samples from *Shāhnāma* manuscript RAS 239 (UCL) and *Shāhnāma* manuscripts Persian 9 and Persian 933 (JRL) were analysed by the HPLC-MS technique.

3-5-1 Introduction

Due to the obvious fact that a large number of dyes and lakes have been used to decorate Persian manuscripts, their identification is an important issue for the preservation of the manuscripts as well as historical research. Many methods have been used for the identification of dyes and lakes; however, it must be considered that most analytical techniques able to accurately identify these materials require taking a sample (micro-sample) (Bisulca et al. 2008, p. 1).

At the beginning of dye analyses, techniques such as ultraviolet-visible (UV-vis) spectrophotometry, thin-layer chromatography (TLC), and infrared (IR) spectrophotometry were used One of the best methods in use today is HPLC (Koren 2005, p. 194; Rosenberg 2008, p. 33). This technique has proved its usefulness for the analysis of natural organic dyes and lakes in many instances described in the literature (Lech et al. 2015, p. 855). "Coupling Mass Spectrometry (MS) with chromatographic techniques has always been desirable due to the sensitive and highly specific nature of MS compared to other chromatographic detectors" (J Pitt 2009, p. 19).

Therefore, HPLC-MS is an advantageous micro-invasive technique for identifying dyes and lakes. In this technique, precise information could be obtained by extracting the dye/lake from micro-samples, and in fact, a minute quantity of sample is required (nearly negligible sampling) (Koren 2008, pp. 5-7). While this technique is very sensitive and can definitively identify mixtures of molecules, it requires time-consuming sample preparation (Bisulca et al. 2008, p. 1).

The biggest obstacle to performing HPLC-MS in the identification of dyes and lakes used in manuscripts is its necessity to sample, although the quantities needed for HPLC analysis are truly "nearly negligible". "Hence, the minimal micro-sampling needed is such a negligibly invasive technique that it can certainly be considered nearly non-destructive" (Koren 2008, pp. 5-7).

3-5-2 Principles and experiments

This method is to-date the most efficient one to be used for the analysis of dyes and lakes. All chromatographic methods are similar, as the technique consists of stationary and mobile phases. High-performance liquid chromatography (HPLC), also known as high-pressure liquid chromatography, is an advanced type of LC.

This method is known as high-pressure liquid chromatography due to the high pressures required (up to about 300 atm) in order to push the sample and eluents through the column. The high surface area of the particles in the column provides for high resolution of the separated components, and hence it is known as "high performance" (Koren 2008, p. 5). Among the different LC techniques, a particular feature of HPLC is that the solvent travels under high pressure obtained by means of a pump to overcome the pressure drop in the packed column, which reduces the time of separation.

In the HPLC method, the stationary phase is a highly packed matrix composed typically of a non-polar material. Among the different combinations of stationary phase and mobile phase, the most common is using a non-polar stationary phase (es. C18) and a polar mobile phase typically composed of, etc. (Koren 2008, p. 4).

The linking of mass spectrometry (MS) with HPLC (HPLC-MS) was an obvious extension of liquid chromatography (LC), and therefore generated developed devices equipped with electrospray sources able to analyse complex mixture (Fig. 3-7) (J Pitt 2009, p. 20).

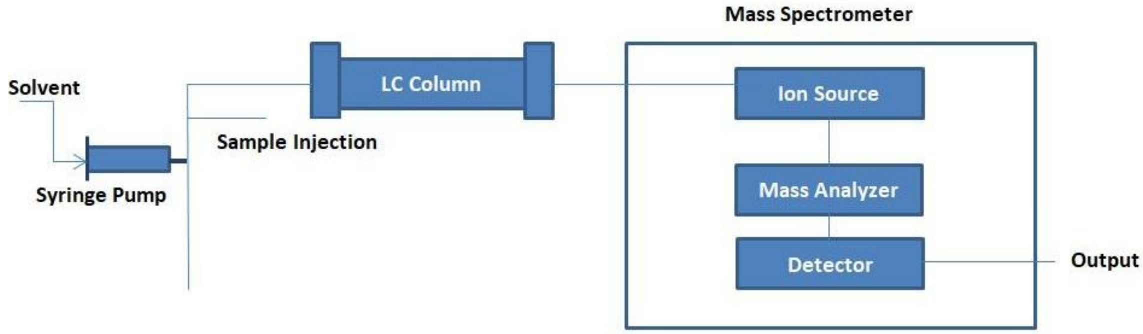

Figure 3-7: Schematic view of an HPLC-MS instrument

HPLC-MS involves separating mixtures due to their physical and chemical features, identifying the components within each peak and detecting them based on their mass spectrum. The complete ionization to maintain the detection sensitivity of the MS, in HPCL-MS starts to decrease beyond 200 μL/min. Therefore, the columns in HPLC-MS are much smaller to accommodate the smaller solvent flow rates and sample volumes.

3-5-3 Instrumentation

HPLC-MS analysis was carried out with an Agilent 1100 HPLC-MSD Ion Trap XCT system, equipped with an electrospray ion source (HPLC-ESI–MS) (Agilent Technologies, Palo Alto, CA, USA). Separations were performed on a Jupiter C18 column 1 × 150 mm with 3-μm particle size (Phenomenex, Torrance, CA, USA). The mobile phase was a gradient between water (A) and acetonitrile (B), both added with 0.1% formic acid; the gradient program was from 5% eluent B to 95% eluent B in 25 min. Flow rate was 50 μL/min with a column temperature of 25 °C. The injection volume was 8 μL. Mass spectra were acquired in the negative ion mode in the 100–800 m/z range.

3-6 Surface-enhanced Raman scattering (SERS)

SERS as a micro destructive analytical technique was applied to identify natural organic dyes used in *Shāhnāma* manuscripts. In the present project, samples from *Shāhnāma* manuscript RAS 239 and from *Shāhnāma* manuscripts Persian 9 and Persian 933 were analysed by the SERS technique.

3-6-1 Introduction

The importance of dyes and their identification in manuscripts has been discussed above. Therefore, surface-enhanced Raman scattering (SERS) as a micro-destructive powerful technique for the detection of natural dyes was performed on some of the micro-samples taken from *Shāhnāma* manuscripts. Since the amount of dye present in historical manuscripts is minimal, identifying this material requires extremely sensitive analytical techniques such as SERS (Leona et al. 2006, p. 981).

"Surface-enhanced Raman scattering (SERS) was first used to identify dyes of artistic and archeological interest by Guineau and Guichard in 1987, when they demonstrated the possibility of obtaining SERS spectra of alizarin extracted from madder-dyed textile samples" (Leona et al. 2006, p. 981).

This is due to the fact that Raman spectroscopy is one of the efficient techniques to identify colour materials used in manuscripts, but it is not useful to identify organic colour materials with the exception of indigo and shellfish (Idone et al. 2021, p. 138). Natural organic materials used as dyes or lake pigments in manuscripts are often fluorescent under normal dispersive Raman measurement conditions (Leona et al. 2006, p. 981). Fluorescence emissions overlapping the Raman signal is a general limitation for Raman spectroscopy especially for identifying minimal concentration materials which is the case with ancient materials. Therefore, a good way to resolve this limitation of Raman could be enhancing the Raman signal through surface-enhanced Raman scattering (SERS) (Bellot-Gurlet et al. 2006, pp. 2-3).

Therefore, Raman analysis exploiting the surface enhancement effect of metal nanoparticles (SERS) is efficient in the identification of organic colourants, but it must be taken into account that SERS requires sampling. However, since it requires only a small sample (< 1 mm), it can be considered to be truly micro-destructive (Idone et al. 2021, p. 139).

The Raman spectrum of many important natural dyes has background obscures; indeed, they are extremely fluorescent even at 785 nm excitation. For instance, the red dyes, madder, cochineal, lac dye, kermes, Brazilwood, alkanna, shikon, litmus, and henna. "These dyes have large π-electron systems or atoms carrying lone electron pairs; both factors can lead them to adsorb metal nanoparticles; they are fluorescent, and hence their conventional Raman spectra are obscured by very high backgrounds; and they are present in any reasonable sample in only microscopic quantities, requiring an ultrasensitive technique" (Leona et al. 2006, p. 981). Therefore, SERS can be considered as an ideal technique for the analysis of natural organic dyes. To mention a negative point of SERS, it must be noted that in SERS, the high enhancement factor is not always reproducible (V. Prikhodko et al. 2015, p. 633).

3-6-2 Principles and experiments

The SERS technique is based on the Raman Effect, which is accepted as a useful phenomenon for the identification of historic colour materials. In this method, a micro-sample which contains organic colour materials is coated with electrically conducting metallic nanoparticles, causing an increase in the electronic response in the Raman spectrometric analysis (Koren 2011, p. 3).

The observation of surface-enhanced Raman scattering (SERS) from molecules adsorbed on silver, gold, and copper electrode opens a new method for studying the phenomenon of dyes adsorbed on metallic colloids in aqueous solutions. Recently, several publications have reported the use of surface-enhanced Raman spectroscopy (SERS) to successfully characterize and identify highly fluorescent dyes and lake pigments. It is well known that the SERS effect significantly enhances the Raman scattering signal (Idone et al. 2013, pp. 5895-6).

SERS is a surface-sensitive technique, can be used in situ and it occurs that molecules are adsorbed on, or in close proximity to, the surface of the certain nanostructured metal (normally silver or gold) substrates (V. Prikhodko et al. 2015, p. 632).

The SERS analysis was performed after sampling and applying Silver colloidal nanoparticles (Lee-Meisel's synthesis) for the characterization and identification of a small quantity of dye from the sample which is put on the glass (Fig. 3-8). The SERS effect allows to avoid the high fluorescence from the dyes, because each dye absorbs radiation in the visible region.

The nanoparticles are produced by the colloid synthesis of silver nanoparticles called Lee - Meisel's reaction which is the reaction of three solutions in pure water. The materials are: Ag_2SO_4 (Baker Analysed Reagent), $AgNO_3$, (MCB), sodium citrate (Mallinckrodt, Analytical Reagent), poly (vinyl alcohol) denoted PVA (Polysciences, hydrolysis 99.0-99.8 mol %), $NaBH_4$, (Alfa Inorganic), HAuCl, (Strem Chemicals), and the dyes (Eastman Kodak Co., laser grade) were used as received (P. C. Lee and D. Meisel 1982, p. 3391).

Preparation of Sols: Ag sols were prepared according to the following procedures: (a) Ag_2SO_4 (80 mg) was dissolved in ca. 200 ml of hot water and then mixed with 5 g of PVA dissolved in ca. 200 ml of hot water. The mixture was then bubbled with Hz at near boiling temperature for 3 h.

The final volume was adjusted to 500 ml. (b) A solution of 5 X l0^{-3} M $AgNO_3$, (100 ml) was added portionwise to 300 mL of vigorously stirred ice-cold 2 * l0^{-3} M $NaBH_4$. A solution of 1% PVA (50 ml) was added during the reduction. The mixture was then boiled for 1 hour to decompose any excess of $NaBH_4$. The final volume was adjusted to 500 ml. (c) $AgNO_3$, (90 mg) was dissolved in 500 ml of H2O and brought to boiling. A solution of 1% sodium citrate (10 ml) was added. The solution was kept on boiling for 1 hour.

Figure 3-8: Preparation the samples with the silver nanoparticles for SERS analysis

2-6-3 Instrumentation

The SERS analysis was performed using a high-resolution dispersive Jobin Yvon (Villeneuve d’Ascq, France) LABRAM HR model spectrophotometer equipped with a confocal Olympus BX 41 microscope 30, a 633 nm excitation laser, a 600 lines/mm dispersive gratings, an 800 mm path monochromator and a Peltier cooled CCD detector. The microscope was equipped with long working distance 10x, 20x, 50x and 80x objectives. The laser output was ca. 5 mW and the exposure time was 10 to 20 seconds, with 1 or 2 accumulations. The parameters changed according to the sample studied. The wavenumbers were calibrated by measuring the Raman signal of a silicon crystal. The software application, LabSpec 5.0, was used for data collection and analysis. The area where vibration modes are found, i.e., 4000-100 cm-1, was the spectral region scanned (Fig. 3-9).

Figure 3-9: Surface-enhanced Raman scattering (SERS), Microscope Raman, Olympus BX 41

CHAPTER 4: Preparation of dyes reference samples

4-1 Introduction

Throughout the course of time a large variety of the organic materials has been used to decorate manuscripts to paint various substrates, to colour human hair and skin and for cosmetics purposes. These organic-coloured matters are known as dyes, but their use declined rapidly after the discovery of synthetic colours (Acquaviva et al. 2010, p.1). Dyes used in the past were obtained from natural sources like plants or animals and may yield different colours through different dying procedures.

The use of mineral and organic materials (plant and animal) to utilize their colour has a long history in Persian territory. Communities living in Iran plateau, since the seventh millennium BC used colour materials, and gradually over time, range of colours was expanded and utilized in various affairs (Pakzad 2017, p. 8).

The tip-top of the use of dyes in Persian territory is evident in the textile and manuscripts. According to the Persian historical documents (book and treatise) which include information about different stages of book-making, it is quite obvious that a large number of dyes were used to decorate the Persian manuscripts: for example, to colour sheets of paper, dyes were applied on the paper to create the favorite tonality of colour; pigments were mixed with dyes to render a shining surface or sometimes the dyes were used as a corrosion inhibitor, fungicide and as a suitable sizing material.

"Historical evidence from the Timurid and Safavid eras, including the Qajar period, has revealed that the paper used for producing books in these years was generally dyed" (Barkeshli 2015, p.195). Knowledge of the dyes used by Persian artists in the manuscripts, however, is not as thorough as is the knowledge of pigments used in Persian manuscript. The lack of non-invasive effective methods to recognize the dyes in the manuscripts, the faded dyes due to their organic nature, and the lack of spectral databases of the dyes have led to the fact that there have been a few studies examining precisely dyes in Persian manuscripts.

Among the rare studies that have been done on identify dyes used in Persian manuscript, we can mention the studies by Dr. Mandana Barkeshli in "the International Islamic University of Malysia" supported by thorough historical research on bibliographic sources.

As explained in chapter two; The combined analytical method consists of two non-invasive techniques FORS and FOMF is among of the best non-destructive ways to identify dyes used in manuscripts. Obviously, the lack of FORS and FOMF spectral databases of the dyes in the Persian manuscripts is one of the reasons why there are few studies in this case. Therefore, to compensate for this lack I have started to create the FORS & FOMF spectral database of some dyes applied in Persian manuscripts since my master dissertation.

Seven mock-up samples were prepared in my master thesis, contain: Saffron (*Crocus sativus*), Anemone (*Anemone coronaria*), Turmeric (*Curcuma longa*), Henna (*Lawsonia inermis*), Rhubarb (*Rheum undulatum*), Madder (*Rubia tinctorum*), and Barberry (*Berberis vulgaris*). In figure 4-2 and 4-3 you can see their registered FORS and FOMF spectra.

Figure 4-1: The plant raw materials used for mock-up samples; A. Barberry (fruits), B. Madder (roots), C. Anemone (flowers), D. Rhubarb (fruits), E. Saffron (stamens), F. Henna (powder of leaves), G. Turmeric (powder of roots)

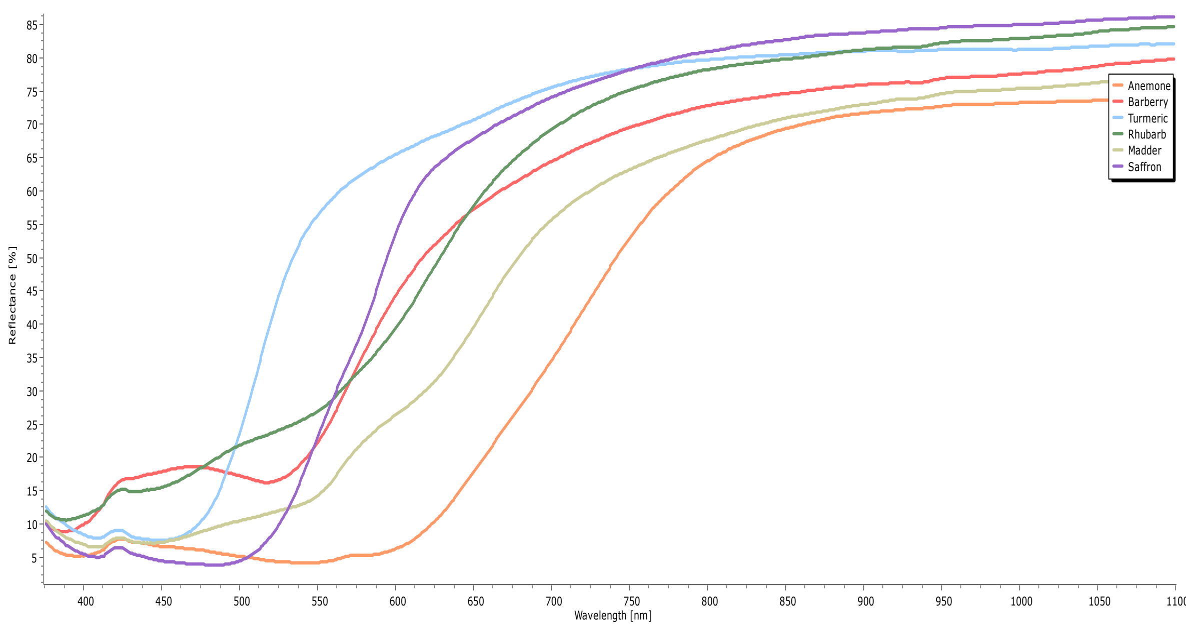

Figure 4-2: FORS spectra obtained of Anemone, Barbary, Turmeric, Rhubarb, Madder, and Saffron reference samples

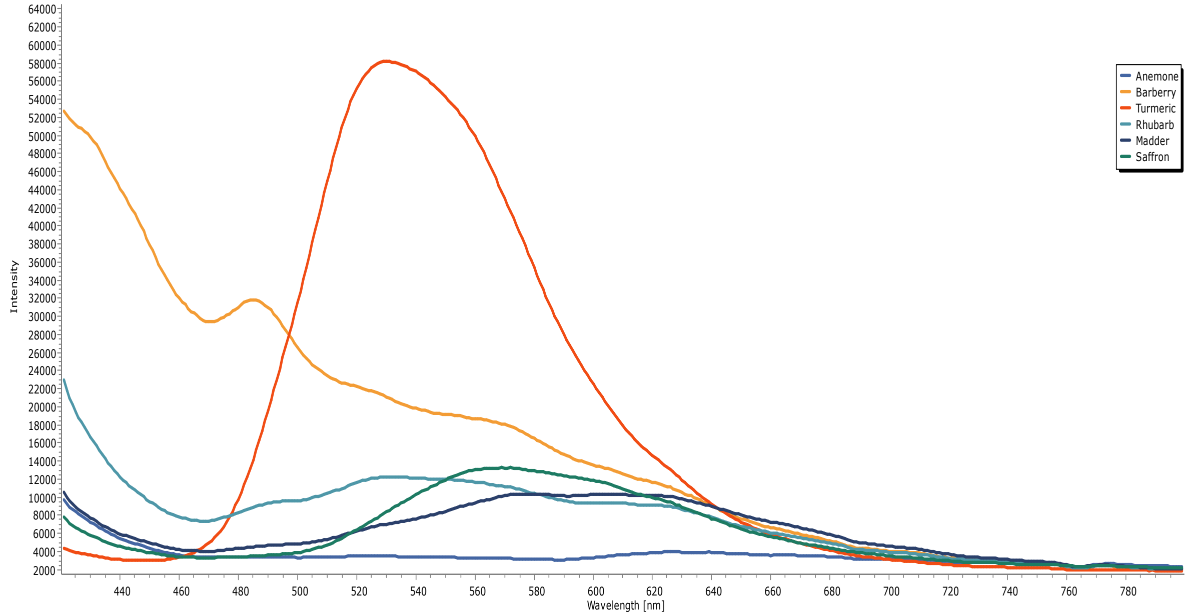

Figure 4-3: FOMF spectra obtained of Anemone, Barbary, Turmeric, Rhubarb, Madder, and Saffron reference samples

In the present study to complete the FORS & FOMF spectral database of Persian dyes five other mock-up samples were prepared contain: Indigo (*Indigofera tinctoria*), Red onion skin, Henna (*Lawsonia inermis*), Mallow (*Althea officinalis*), and Saffron (*Crocus sativus*). All of them have planet origin. As well, due to the different usage of Saffron and Henna in Persian manuscript, these two dyes were reproduced by considering new recipes.

Figure 4-4: The plant raw materials used for mock-up samples; A. Saffron (stamens), B. Mallow (flowers), C. Henna (leaves), D. Red Onion skin (the dry outer skins)

In order to produce the reference samples regarding the traditional methods, natural dyes indicated in the comprehensive book of Nadjib Māyel Heravi “The art of bibliopegy in Islamic civilization”[19] and “*Golestan-e Honar*”[20] (Rose Garden of Art) were used. Moreover, the book "Methods of Making Colour in the Arts and Painting" (Jokar 2006) and “The Arts of the Book & Calligraphy in Iran” (Rahpeyma 2015) were also applied to make the reference samples.

It should be noted since the book “The art of bibliopegy in Islamic civilization” is contain the treatises of the book “*Golestan-e Honar*” and as well as this book is more available in the European libraries for the recipes only this book has been referenced. The following treatises of this book have been used:

Resāleh dar Bayān-e Kāğaḏ Morakkab va Ḥall-e Alvān[21] (pp. 65-80), *Savād al-ḵaṭṭ*[22] (pp. 217-246), *Ādāb al-Mašq*[23] (pp. 248-285), *Golzār-e Ṣafā*[24] (pp.287-312), *Rasala khat va Morakab*[25] (pp. 389-414), *Qanun al-sovar*[26] (pp. 415-430), *Resāleh dar Bayān-e Tariqeye Sāḵtan-e Morakkab va Kāğaḏ-e Alvān*[27] (pp. 619-628), *Resāleh dar Bayān-e Rang Kardan-e Kāğaḏ*[28] (pp. 629-638).

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[19] The book "the Art of Bibliopegy in Islamic Civilization" is edited by Nadjib Māyel Heravi. This book is a collection of 28 treatises on calligraphy, ink making, colour making, paper making and dyeing, gilding and book binding. This valuable book published in the Department of Astan Quds Razavi in Mashhad in 1993.

[20] GOLESTĀN-E HONAR, is a 16th century treatise on the art of calligraphy, with brief biographical notices on a selection of past and contemporary calligraphers and artists, by the Safavid author and historian Qāżi Aḥmad b. Šaraf-al-Din Ḥosayn Monši Qomi Ebrāhimi. It is an important primary source for the history of the art of bookmaking in Persia in the late Timurid to early Safavid period, containing first-hand information on some of the artists and patrons with whom the author and members of his family came into contact.

[21] This treatise is detached part of a valuable book belong to 15th century by a skilled master of the art of bookmaking. A copy of this treatise is in "The Library of Iranian Parliament" (Registered No. 4767) (Māyel Heravi 1993, p. forty-six).

[22] It is a treatise in the field of calligraphy and its derivatives belong to 1504/909 written by Solṭān Aḥmad Majnun Rafiqi Heravi (Māyel Heravi 1993, p. seventy-one).

[23] It is another treatise written by Solṭān Aḥmad Majnun Rafiqi Heravi in five chapter in the field of calligraphy, papermaking, ink making, colour making. A copy of this treatise is in "The Malek National Library" (Registered No. 1269) (Māyel Heravi 1993, p. seventy-two).

[24] It is a treatise in the field of the art of bookmaking written by Ali Seyrafi in the form of poetry (Mathnawi) at ca.1543/950 (Māyel Heravi 1993, p. seventy-three).

[25] This treatise is part of a book Riad al-Abrar by Hossein Aqili Rostamdari belongs to the Safavid dynasty. He was a scientist of the court of the Shah Tahmasp Safavid. A copy of this treatise is in "The Library of Astan Quds Razavi" (Registered No. 2033) (Māyel Heravi 1993, p. eighty-five).

[26] A valuable treatise written by Ṣādeq Bek Afšār in the field of painting techniques, painting tools and etc. that dates back to the Safavid era (before 1600/1010). A copy of this treatise is in "The Malek National Library" (Registered No. 6325) (Māyel Heravi 1993, p. eighty-nine).

[27] This is a treatise that belongs to the Safavid dynasty in the field of painting and calligraphy tools and etc. It briefly mentions the methods for making ink and colouring paper. A copy of this treatise is in "The Malek National Library" (Registered No. 2870) (Māyel Heravi 1993, p. ninety-six).

[28] This is an anonymous treatise about dyeing paper, probably belong to 19th century. Its author has probably written this treatise based on Timurid and Safavid works. A copy of this treatise is in "The Ḵānqah Neʿmatollāhi Library" (Registered No. 304) (Māyel Heravi 1993, p. ninety-seven).

Another valuable resource in the field of the art of bookmaking is contemporary traditional artists. These artists are painters or calligrapher who still working with traditional method and materials.

The working methods of these artists are in fact very valuable information that has been transmitted to us in the system of master and pupils over the centuries. Gholamreza Rahpeyma is one of these artists based on his personal experiences in the three decades study on calligraphy and book layout arts has been published the book “The Arts of the Book & Calligraphy in Iran” in 2015.

This book is a comprehensive study and reviews of scientific and educational remain as well as works of art in the Iranian civilization. This book in some cases was applied to clarifying traditional recipes of reference samples.

4-2 Dyes reference preparation steps

The qualitative determination of the natural sources of dyes employed in manuscripts needs the availability of reference samples that enable the development and the testing of analytical procedures. In particular, in the present study the production of a series of standard samples was carried out, in order to have at disposal dyed paper coloured with the same materials that were possibly employed in the Persian manuscripts.

The possibility of following accurately the ancient procedures for the preparation of the dyes with the plant origin was relatively simple. It generally involved extracting dye from different part of the plant (roots, stems, leaves, flowers, fruits, and seeds) with water then filtering the dye solution and dyeing the paper by immersing it into the coloured liquid (Fig. 4-5).

Obviously, for different dyes, the traditional recipes reported the use of several different materials like stabilizers, softener or a special process for dyeing and drying the paper.

The aim was exclusively making a database of the FORS and FOMF spectra. Therefore, traditional receipts were employed to gain information on raw materials used to obtain the dyes, the extraction process of dye from raw materials, and the paper dyeing process.

Moreover, practical details on how the dyes were used to decorate the paper and the paintings were also recovered and employed to produce the reference samples.

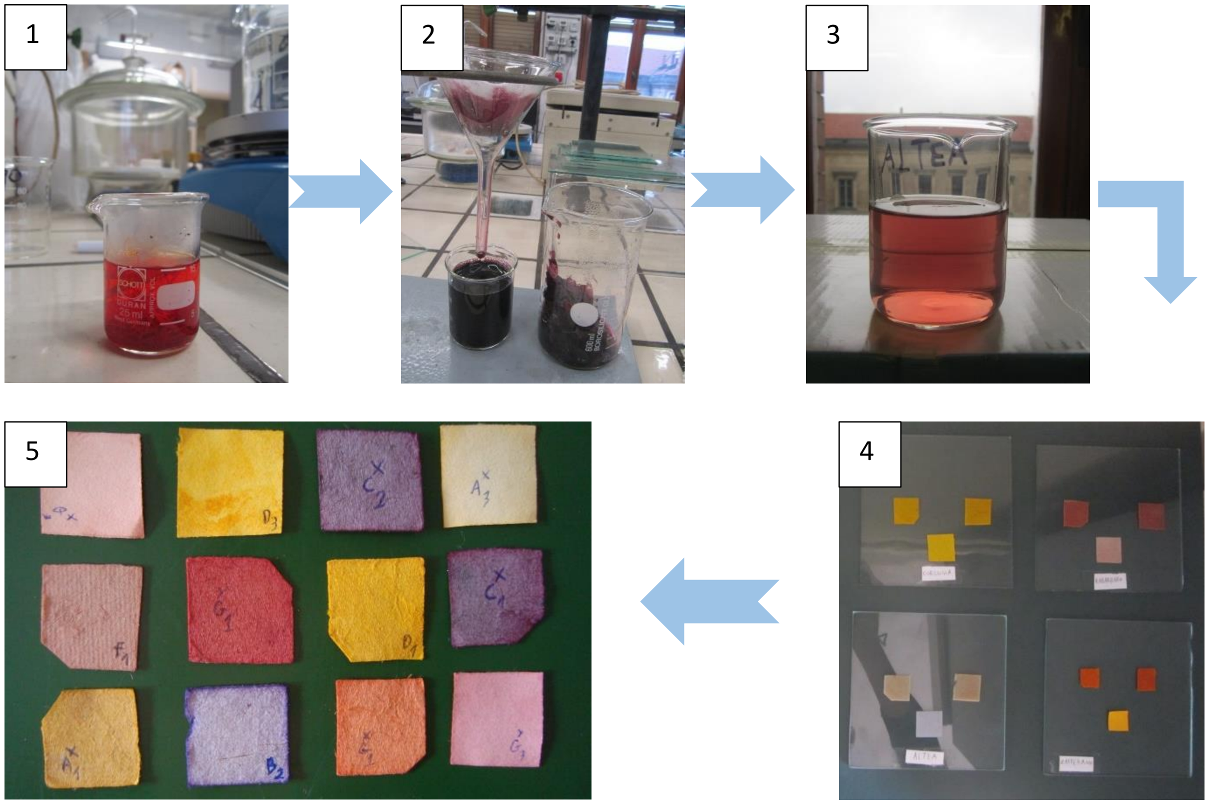

Figure 4-5: general steps of preparation dyed reference samples; 1. dye extraction by water, 2. filtering, 3. immersing paper in dye solution, 4. drying, 5. Prepared dye samples.

Three types of paper were used as a substrate: two were papers made according to traditional procedure employing hemp, with hand-made mechanical treatment in a traditional workshop in Isfahan[29]. One of these traditional papers was then sized with gum tragacanth (sized paper), the other type of paper was used without sizing (non-sized paper). Moreover, also the modern 100% cellulose paper (Whatman) was employed (Fig. 4-6).

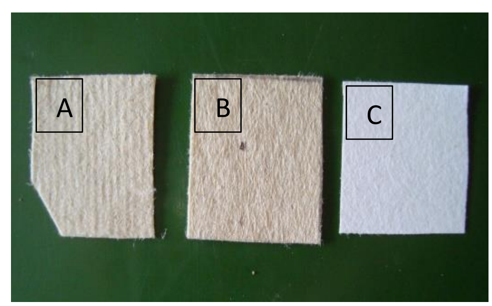

Figure 4-6: three types of paper used for reference samples: A. traditional sized paper, B. traditional unsized paper, C. Whatman paper

In general, dyes were extracted from a series of plants by employing water and the coloured solutions after filtering were used as such to dye paper by immersing it into the coloured liquid. As well as for each dye in addition to the dyed paper sample a paint sample was produced in the meaning of mixing the concentrated dye solution with gum Arabic (binder) and laid the mixture on the paper with a brush (Fig. 4-7).

[29] Karimi workshop Isfahan (Iran)

In order to paint the samples by brush, the coloured solutions obtained from the extraction of the plant were allowed to evaporate in an over at 40 °C until a thick fluid was obtained. This was employed, properly mixed with gum Arabic, to paint the paper. The binder was prepared by treating two grams of the solid gum Arabic with 25 ml of water in a beaker. The beaker was placed on a heated and gently heated for one hour, stirring every 10 minutes, until a smooth gel was obtained.

It is true that the use of dyes with the brush is not mentioned in any historical treatise, but the treatise mentioned the usage of dyes by mixing with pigments and binder. Therefore, the paint references samples were produced to understand the effects of the binder on FORS and FOMF spectra of each dye.

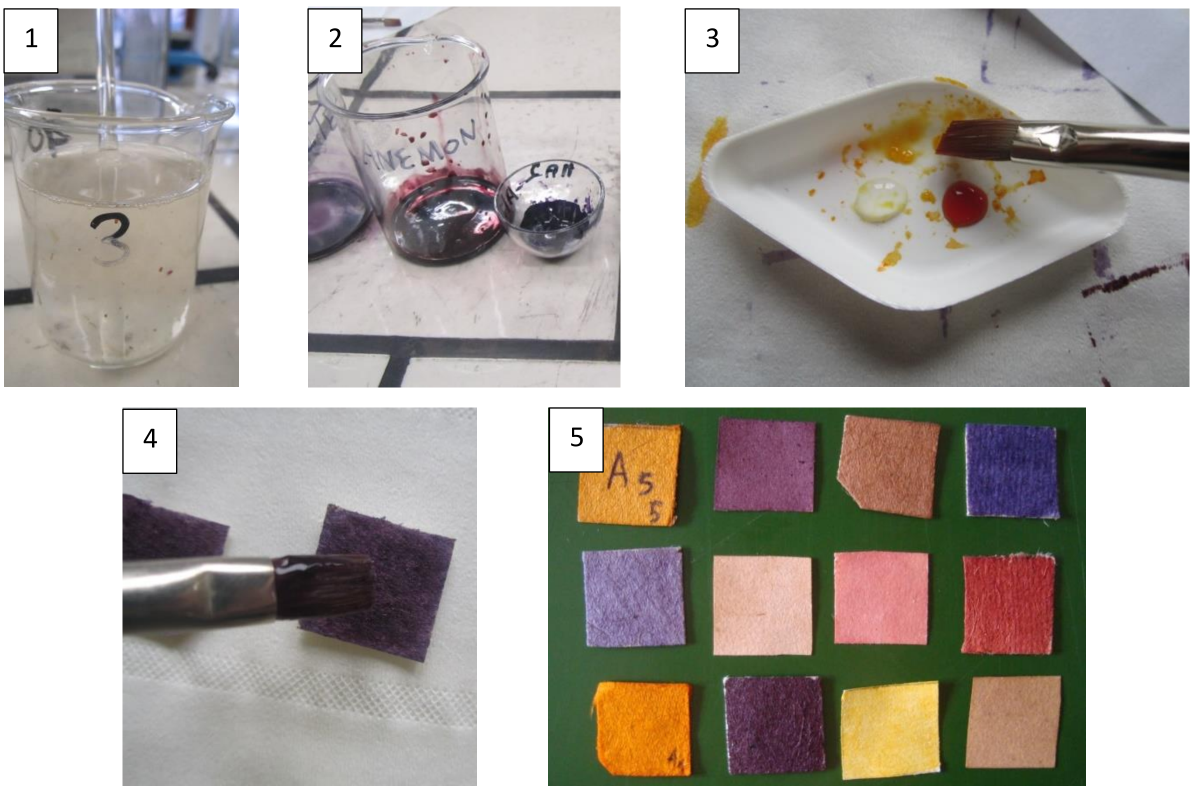

Figure 4-7: General steps of preparation painted reference samples; 1 prepared Arabic Gum (binder), 2. concentrating dye solution, 3. mixing binder with concentrated dye, 4. colouring paper by brush, 5. prepared paint samples

Hence, for each dye, at least six samples were produced (three dyed samples and three painted samples). After examining the samples, it became clear that there is no significant difference in FORS and FOMF spectra of the different dyed and painted samples.

In fact, changes made in the substrate of reference samples and mixing dyes with Arabic Gum did not make a significant effect in apparent absorption in FORS spectra and maximum fluorescence's peak in FOMF spectra of reference samples. Therefore, in order to avoid the presence of spurious signals (noises) in the FORS and FOMF spectra for each dye, only a registered spectrum of traditional sized paper dyed by immersing in the dye solution has been present[30].

Finally, the reference samples were analysed by the means of FORS and FOMF and the resulting a database was employed as a reference for the interpretation of FORS and FOMF spectra recorded on the manuscripts under study.

4-3 Saffron reference sample (*Crocus sativus*)

Saffron is mentioned as a largely employed dye in the illustration of manuscripts. It was largely cultivated in Khorasan (north east of Iran) and used in different epochs for the decoration of manuscripts, alone or in combination with other dyes and pigments (especially gold and Verdigris) for its antiseptic properties and its pleasing scent.

Various treatises described a method for the preparation of Saffron dye (see Māyel Heravi 2018, p. 67, 71, 293, 410, 624, 626, and 634). In accordance with the above-mentioned treatises, one "Mithqāl[31]" (4.68 g) of saffron should be mixed with one "seer"[32] (75 g) water, therefore with an approximate proportion saffron-to-water of 1:16 by weight.

One example of traditional recipes for coloured paper with saffron from treatise *Golzār-e Ṣafā* (see Māyel Heravi 2018, p. 293):

ای رخم زرد زتاب غم تو   در دلم درد زتاب غم تو
هوست کاغذ زرد است اگر   بر رخ زرد من زار نگر
زعفرانی که بود تلخ بسی   ریشه پاک زهر خار و خسی
چون ستانی تو از او یک مثقال   ریزه اش سازی از لطف کمال
آب یک سیر به مثقالی کن   در زجاجش، پس خوشحالی کن
سر آن سخت کن و تا به سه روز   پیش خورشید بمانش در سوز
چون سه روزش بگذاری درشید   شیره اش زرد شود، جرم سفید
پس بیاور قدحی چینی خوب   بکنش پاک و بدارش مرغوب
پس به دستار بپالای روان   بگذارش که بماند ته آن
وانگهی در طبقی پاک بریز   پس نگهدار زگردش به تمیز
پهن کن کاغذ پاکیزه در او   تا رود در جسدش رنگ فرو
مده از پرتو خورشیدش تاب   در رواقیش در افکن به طناب
چون شود خشک، بده آهارش   صیقلی کرده، ببر در کارش

In order to prepare the reference samples, one gram of saffron and 16 ml of

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[30] To see all registered spectrum, please check the appendix 5.
[31] A unit of mass equal to ca. 4.60 grams.
[32] An Iranian traditional unit of weight equal to 75 grams.

warm water were mixed in a beaker and then left until the stigmas of saffron were bleached (3 days) and the dye was extracted and then filtered.

The paper was dyed according to mentioned treatises that indicates the paper should be placed into the coloured solution until it saturates with the dyes. Therefore, portions of about 2x2 cm of traditional paper were dyed by immersing it into the coloured solution for 24 hours.

In FORS the peak of apparent absorption for saffron is an inflection point at 430-450 nm and in FOMF maximum fluorescence's peak is ca. 560 nm (Fig. 4-8).

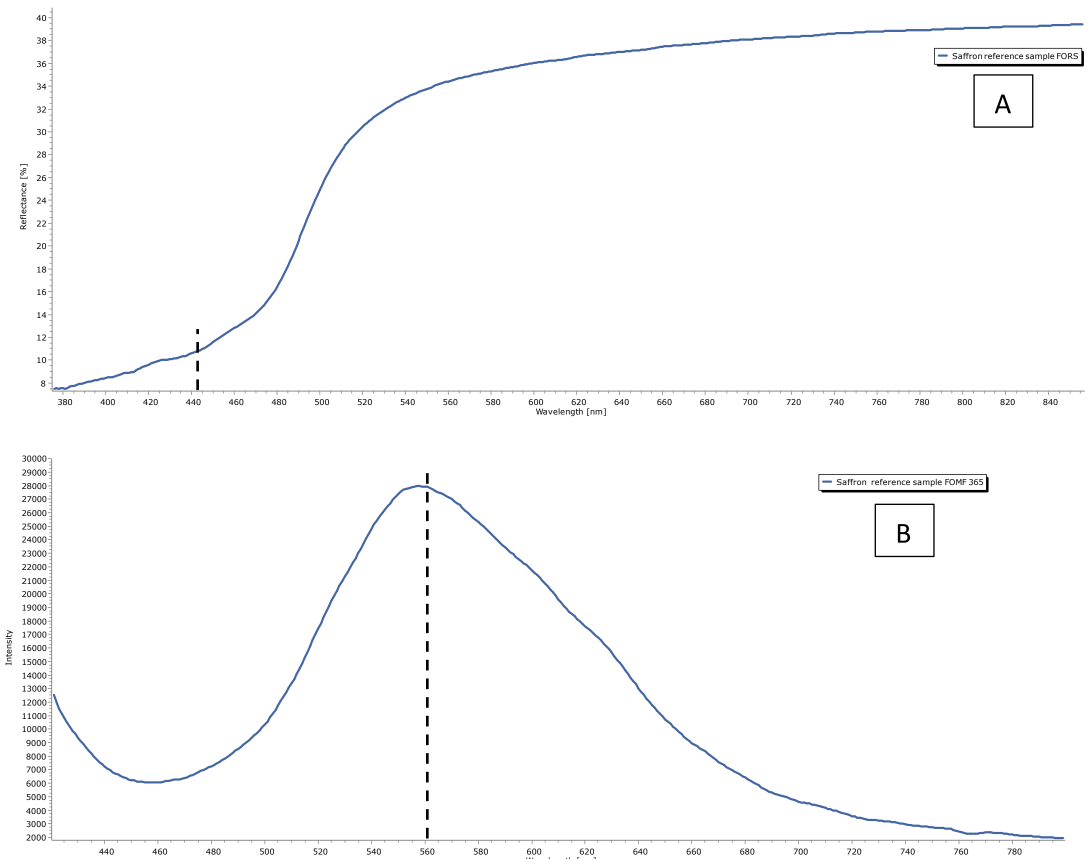


Figure 4-8: FORS(A) and FOMF(B) spectra obtained of Saffron reference samples

4-4 Indigo reference sample (*Indigofera tinctoria*)

Indigo refers to dyes obtained from Indigofera species, among which Indigofera tinctoria is the most popular (Cardon 2007, p.110). It is a perennial herb native of India, which nowadays grows in tropical and subtropical regions from Africa to South-eastern Asia. Indigo is a vat dye, produced by macerating the leaves and stems for several weeks (Hofenk de Graaff 2004, p.200; Cardon 2007, p.110; Rutherford 1966, p.120).

The main colouring agent of indigo is indigotin. Indigo is the most used blue dye all over the world in all periods and it was known in India before the 1st millennium BC. Synthetic indigotin is still employed nowadays to dye blue jeans (Idone et al. 2014, pp.114-115, Rutherford 1966, p.120).

The art of Bibliopegy in Islamic Civilization made references to the ways the paper was dyed with Indigo (see Māyel Heravi 2018, p. 69, 74, 233, 262, and 633).

One example of traditional recipes for coloured paper with indigo from treatise *Ādāb al-Mašq* (see Māyel Heravi 2018, p. 262):

خواهی که ضیاء رنگ ماوی	*آید به لطافت سماوی*
نیلاب لطیف و پاک و صافی	*مقدار دو من که هست کافی*
ده سیر دگر زآب بی غمش	*در وی فکن و ورق در او کش*
کاغذ نه شق و نه نرم باشد	*آبش نه خنک نه گرم باشد*
چون رنگ شود به کام دل باز	*بر آب خنک زن و برانداز*

The ancient treatises mentioned mixing two “Man”[33] (6 Kg) indigo with ten “Seer” (750 g) water. Therefore, approximate proportion indigo-to-water is 8:1 by weight. According to the ancient treatises, 250 g of indigo powder was mixed with ca. 312 ml lukewarm water and cleared through a paper filter. Afterward, traditional paper samples were immersed in a clear blue solution for 24 hours and eventually they were rinsed with cold water.

In FORS the peak of apparent absorption for indigo is located at 660 nm and in FOMF maximum fluorescence’s peak is a weak peak at ca. 735 nm (Fig. 4-9).

[33] It is an Iranian traditional unit of weight that differs in different cities, for example in Isfahan is equal to 6 kg and in Kerman is 3 kg.

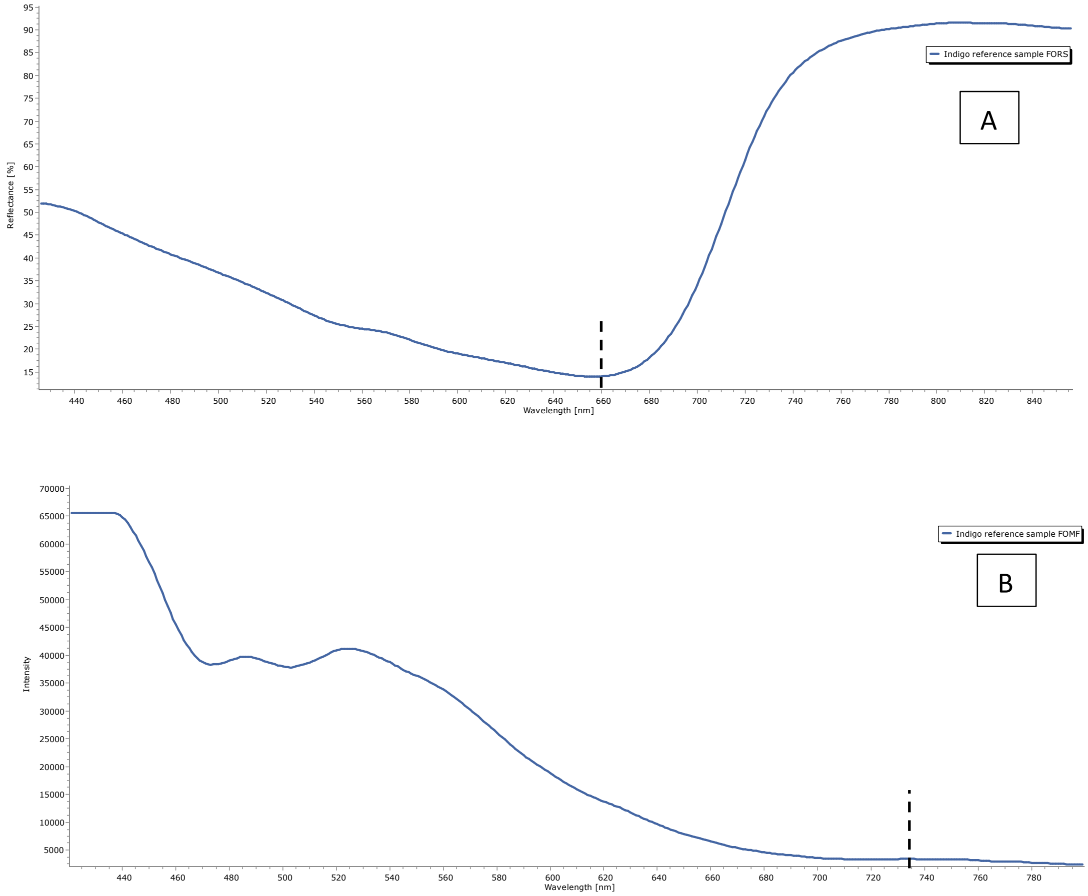


Figure 4-9: FORS(A) and FOMF(B) spectra obtained of Indigo reference samples

4-5 Mallow reference sample *(Althea officinalis)*

According to the Art of Bibliopegy in Islamic Civilization, mallow was mostly used as a softener (Māyel Heravi 2018, p. 71; Rahpeyma 2015, p. 177).

In fact, it makes the paper soft and smooth, and it also enabled the ink to be laid more easily on it. Therefore, mallow was generally mixed with the other dyes and pigment like cinnabar or used to sized paper (Māyel Heravi 2018, p. 117, 230, and 693), although it can also be employed to colour the paper with a light violet hue.

The Art of Bibliopegy in Islamic Civilization describes the various uses of mellow in the preparation of manuscripts (see Māyel Heravi 2018, p. 71 and 302).

One example of traditional recipes for coloured paper with mallow from treatise *Golzār-e Ṣafā* (see Māyel Heravi 2018, p. 302):

تخم خطمی دگری کرده در آب   بگرفته است از آن تخم لعاب

یک شبانروز از آن پس دیگر   کرده اخلاط وی از آب بدر

پس به دستارچه ای پالوده   کاغذ آنگاه به آب آلوده

ولی این خوب و لطیف است بسی   خط بر این گونه نظیف است بسی

Some trials were therefore performed in order to prepare the dyed paper samples, always employing four grams of dried mallow flowers put in 250 ml of water room temperature for one day then filtering (Rahpeyma 2015, p. 177). Nevertheless, reference samples were obtained by immersing the traditional paper for 24 hours into the solution obtained.

In FORS, the peak of apparent absorption for mallow are located at 560 nm & 620 nm and in FOMF Mallow does not have a clear fluorescence peak (Fig. 4-10).

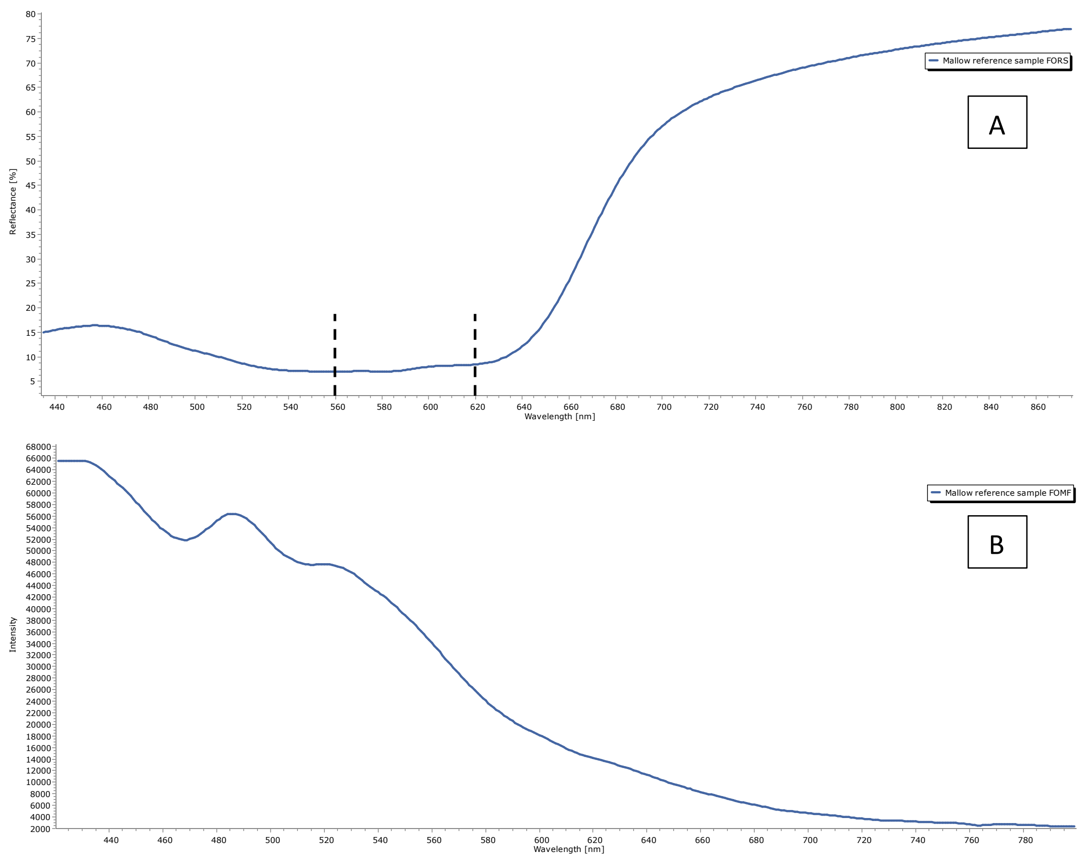


Figure 4-10: FORS(A) and FOMF(B) spectra obtained of Mallow reference samples

4-6 Red onion skin reference sample

The dry outer skins of onions can be used for colouring papers, and it cause an earthy range of colours which is suitable to restore damaged paper of Persian manuscripts.

In order to prepare the reference samples, red onion skin and warm water were mixed in a beaker and then simmered for one hour (Rahpeyma 2015, p.121). The onion skins removed, and the solution filtered, then the papers placed into the coloured solution until it saturates with the dyes.

The paper dyed with red onion skin is used in some traditional methods of manuscript restoration. Therefore, this reference sample could be helpful to recognize restored part of a manuscript.

In FORS the peak of apparent absorption for red onion skin is located at 500 nm and in FOMF maximum fluorescence's peak are at 530 & 560 nm (Fig. 4-11).

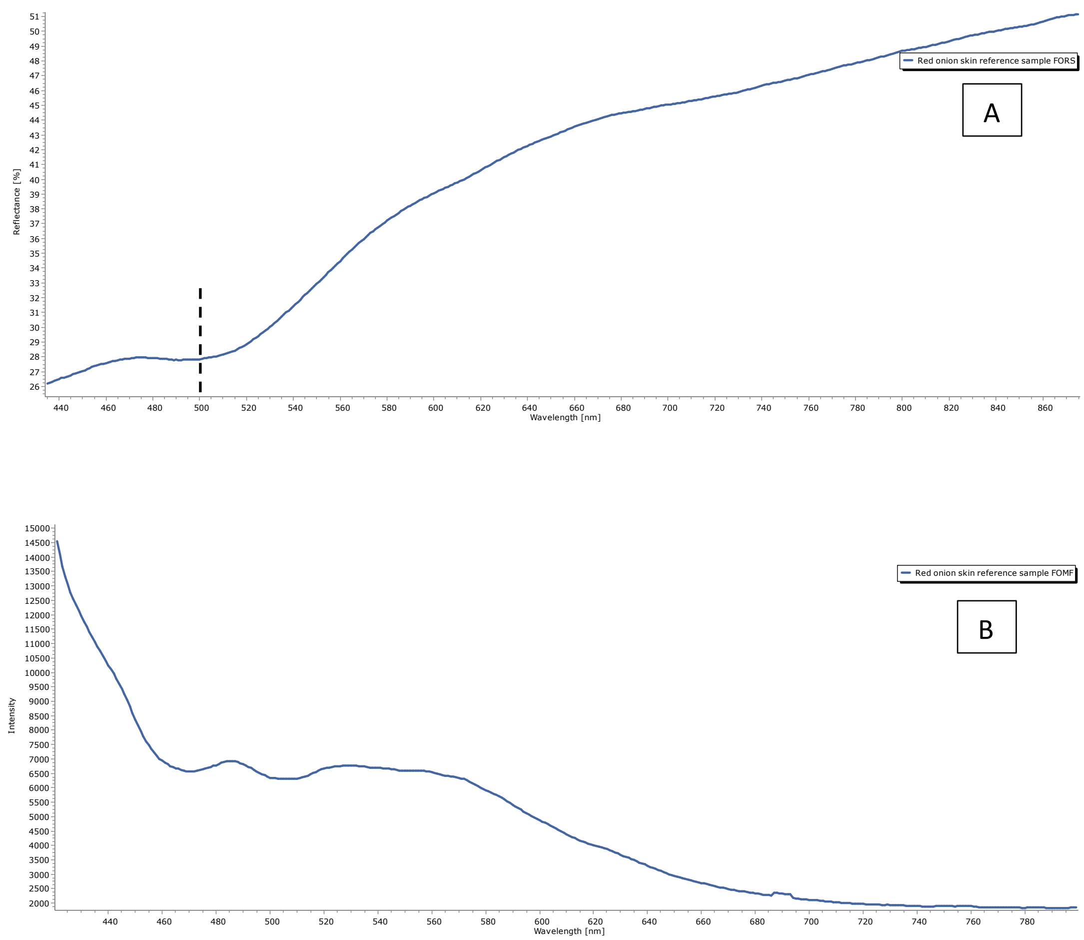


Figure 4-11: FORS(A) and FOMF(B) spectra obtained of Red onion skin reference samples

4-7 Henna reference sample (*Lawsonia inermis*)

One of the methods that have always attracted experts' attention is paper dyeing with natural extracts of henna. This has been used in various ways throughout history. Among the different coloured papers, henna is specifically recommended for making natural colour (k̠odrang) in historical documents either in its pure state or when mixed with saffron (Barkeshli 2015, p. 196).

The art of Bibliopegy in Islamic Civilization provided a lot of information about the way the dye was extracted from leaves of henna and the way the paper was dyed. These books made a reference to henna as k̠odrang (self- colouring) (see Māyel Heravi 2018, p. 69, 297, 408, and 626).

One example of traditional recipes for coloured paper with henna from treatise *Golzār-e Ṣafā* (see Māyel Heravi 2018, p. 297):

کاغذ ای دوست چو خودرنگ کنی	خود به این رنگ هماهنگ کنی
بستان برگ حنا را بسیار	پاک کن وانگهی از گرد و غبار
آب کن گرم در آن رنگ نخست	پس حنا ریز در آن آب درست
وزن آن آب حنا را دریاب	یکی از برگ حنا و ده آب
یک شبانروز به جاییش بنه	صاف کن آب به آن رنگ بنه
کاغذ از رنگ تو گیرد وایه	خشک سازش پس از آن در سایه

Traditional recipes mentioned an approximate proportion henna-to-water of 1:10 by weight. Therefore, one "Seer" (75 g) of leaves of henna was mixed with 750 ml of warm water. In accordance with the recipe, henna and water are put away until the dye is extracted fully extracted (one day). Then the coloured solution was filtered, and the paper samples were dyed and dried in the shade.

In FORS the peak of apparent absorption for Henna is shoulder at 560 nm and in FOMF maximum fluorescence's peak is at 530-550 nm (Fig. 4-12).

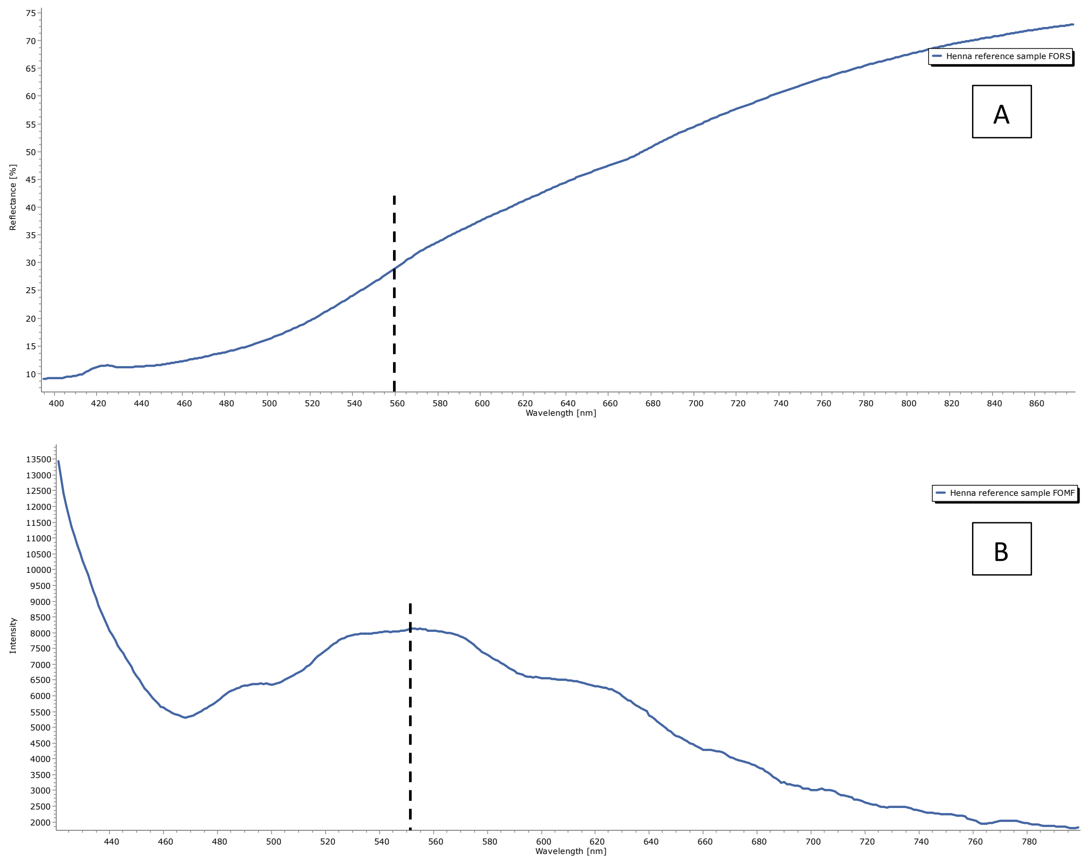


Figure 4-12: FORS(A) and FOMF(B) spectra obtained of Henna reference samples

CHAPTER 5: Discussion and interpretation of data

5-1 Introduction

Persian artists used various materials such as pigments, dyes, paper, binders, and lacquer in their paintings. Generally, the same materials had been used over time, however, some changes were made to their usage and productions because of scientific breakthrough and familiarity with other cultures.

The section 5-2 of this chapter is presented a detailed of chemical, appearance, and spectral features of colour materials (pigments and dyes) as well. This information is identified in *Shāhnāma* manuscripts under study in this project. Besides, the colour materials identified in each *Shāhnāma* manuscript are presented in section 5-3. In section 5-3 to avoid presenting a large number of spectra for each manuscript; XRF, FORS, and FOMF spectrums are assigned to the section 5-2 and appendix.

Since, specifying the name of colours is complicated and many colours could take place in different hue categories, in this chapter for each colour spot is offered a reference colour. As explained in the first chapter, the reader of the dissertation can personally conclude the name of colours. Further, there is a possibility to check the chemical and spectral features of each colour in section 5-2 and appendix. Afterwards, in the last section of this chapter, the obtained data are statistically analysed based on the place and time of the paintings, as well the colour materials applied on motifs and figures. In fact, to achieve the aims of this study a statistical comparison is performed on the colour materials used in the paintings of different *Shāhnāma* manuscripts in various periods and schools (cities).

The historical information about usage of colour materials in Persian manuscript which is presented in section 5-2 has been obtained from historical recipes presented in book "*Golestān-e Honar"*. This book is an important primary source containing first-hand information on the history of the art of bookmaking in Persia in the late Timurid to early Safavid period (see Chapter 4). Also, the book 'The Art of Bibliopegy in Islamic Civilization' has many first-hand information about colour materials used in Persian manuscript, which is very useful in advancing this study (see Chapter 4).

Moreover, the book "A Survey of Persian Art" as one of the first study about Persian art and colour materials used in Persia covering the information about colour materials used in Persian painting presented in this study. The information reported regarding colour materials used in Persian manuscripts in these three books is based on historical sources and experience of traditional masters of Persian art. They are more relevant to a historical point of view rather than scientific data.

Unfortunately, there are few scientific analytical studies on colour materials used in Persian manuscripts. One of the first studies is “A Study of the Materials Used by Medieval Persian Painters” by Nancy Purinton and Mark Watters in 1991. Among these available scientific studies *Shāhnāma* manuscripts were analysed rarely. Therefore, present study can consider as the first study focused on identifying and comparison of colour materials applied in *Shāhnāma* manuscripts.

One of the most similar studies to the present study is a series of scientific analysis performed on the materials and techniques on Islamic manuscripts in the Harvard Art Museums. These studies contain embellish folios of manuscripts and albums created from 13th through 19th centuries. The result of this studies published in 2018 as a unique article by Knipe et al[34]. Although, this study is not focused on *Shāhnāma* manuscripts either Persian manuscripts, however, a wide range of scientific analysis on several Persian manuscripts are performed. Therefore, this research was very helpful to interpret analysis and identify colour materials which are presented in this chapter.

Other studies which are used to analysis the data are; the series of studies on the materials used in Persian manuscripts by Mandana Barkeshli (1996-2015), “The Colourful Past: Origins, Chemistry and Identification of Natural Dyestuff” by Hofenk de Graaff (2004), “MOLAB® meets Persia: Non-invasive study of a sixteenth-century illuminated manuscript” by Anselmi et al. (2015), and “Raman analysis of pigments on 16–17th c. Persian manuscripts” by Muralha et al. (2012).

In addition, interpreting FORS and FOMF measurements are based on a set of studies by Aceto et al. on the usage of “UV-visible-NIR reflectance spectrophotometry” on manuscripts in the Universita degli Studi del Piemonte Orientale. Also, the book “*I pigmenti nell'arte: dalla preistoria alla rivoluzione industrial”* by Bevilacqua et al. (2010), and ‘FORS and FOMF Spectral database of Persian dyes’ registered by writer this study as master thesis in The Universita degli studio di Torino (2014) were very helpful to interpreting FORS and FOMF analysis.

Also, Interpreting XRF analysis is based on information which is obtained from the book “*I pigmenti nell'arte: dalla preistoria alla rivoluzione industrial”* by Bevilacqua et al. (2010), and study “Free XRF Spectroscopy database of pigments checker” by Larsen et al. (2016).

It should note that all the percentages mentioned in the charts of section 5-3 are based on the number of performed analytical measurements on manuscripts. Hence, the percentages are not represented the actual amount of colours which are applied in paintings.

[34] In this study over 50 works on paper from Egypt, Iraq, Iran, and Central Asia dated from the 13th to 19th centuries were examined and analyzed at the Straus Center for Conservation and Technical Studies.

Since the painters of Persian manuscripts have combined white lead with different colours to achieve their desired colour tonality, white lead was skipped in many colour combinations to make the statistical analysis simpler and more understandable. As regards, in all the manuscripts white lead as a white colour and black carbon as a black colour has been applied, the percentages of these two colours were skipped too.

5-2 Colour Materials

In this section, possible colour materials used for each colour tonality are mentioned. Their characteristics and composition are described. Then, the method of identifying each of these colour materials is described.

5-2-1 Green Colours

5-2-1-1 Vergaut (Indigo + Orpiment)

Vergaut is a mixture of blue and yellow. The blue is often indigo, and the yellow pigment is usually orpiment; however, an organic yellow dye can sometimes replace, such as saffron, turmeric, or Indian yellow (Knipe et al. 2018, p.25).

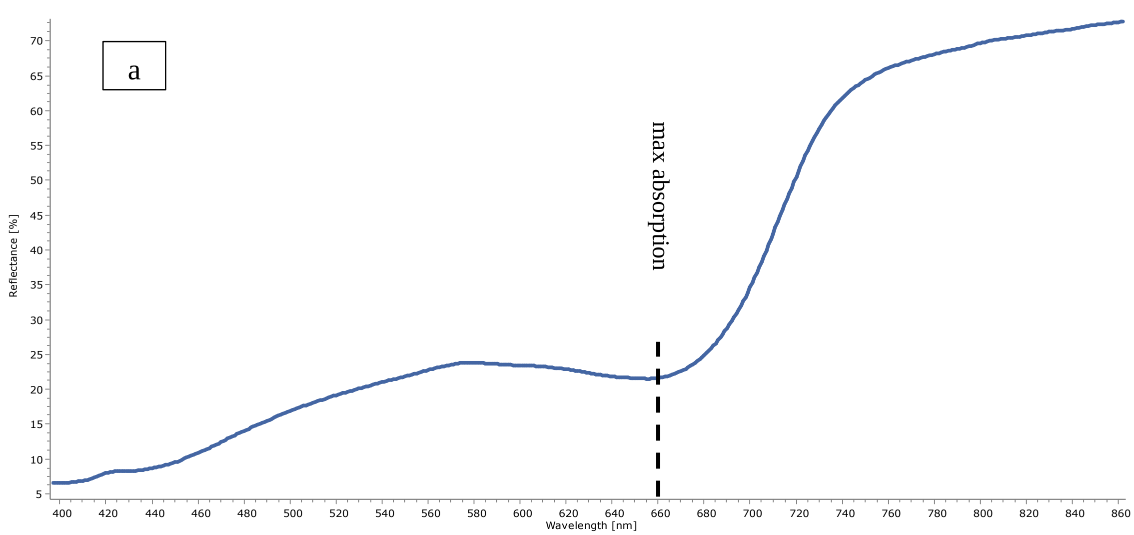
In a folio of the *Shāhnāma* manuscript RAS 239, a mixture of indigo and yellow dye (most probably Indian yellow) was identified, which is the same as the combination identified in Mughal and Bukhara manuscripts, analysed by Knipe et al. (2018). In most of the manuscripts studied in this project, a mixture of indigo and orpiment was used as green, as identified by Anselmi et al. (2015) and Knipe et al. (2018). Some reports have underlined the extensive use of indigo and orpiment mixture in Persian manuscripts and this claim has been demonstrated by analytical studies. Other researchers have also mentioned the preferential application of an orpiment–indigo as green to paint plants and trees whereas the pigment used for clothes was copper-based (Muralha et al. 2012, p. 25; Knipe et al. 2018, p. 25; Anselmi et al. 2015, p. 190). The 13th and 14th centuries offer the greatest diversity of materials for green: most green areas were painted with a mixture of orpiment and indigo, which produces a pale or yellow green. This mixture of green was utilised widely since the 14th century, especially for foliage (Knipe et al. 2018, p. 25).

In the present project, vergaut, as a mixture of indigo and orpiment was identified in all *Shāhnāma* manuscripts, the dominant green on the many manuscripts being mostly a mixture indigo with orpiment, with some cases of white colour (mostly White Lead) blended in to adjust the shade. Therefore, a combination of indigo and orpiment can be considered as the most prised green pigment by Persian painters to use for trees, plants, and foliage.

The blue component of the mixture is indigo, which can be detected by the absorption at 660 nm in FORS spectra, followed by a rise in reflectance with an intense reflectance at $\lambda \geq 800$ nm (Aceto et al. 2014, p. 1495; Bevilacqua et al. 2010, p. 197). The FORS spectrum of vergaut (indigo + orpiment), while showing the reflectance features of a green colourant, still displays the absorption maximum of indigo near 660 nm, and orpiment has an inflection point can be found around 460–490 nm range, and it has intense reflectance at 600 nm (Aceto et al. 2014, p. 1497).

Whereas the yellow component, while the presence of arsenic in the XRF spectra (characterizing As lines are at 10,53 (Kα) and 11,73 (Kβ) keV with the interference of Pb at 10,50 (Lα) keV) contributed to the identification of the yellow component (orpiment) (Fig. 5-1).

In case instead of orpiment, a yellow dye (usually saffron or turmeric) is combined with indigo, the yellow dye can be identified by a combination of FORS and FOMF, although, the identification of yellow dyes with FORS is not very accurate. Their main spectral feature in the UV-Vis for saffron and turmeric is an absorption band, occuring at about 420-435 nm, with a shoulder around 480-485 nm. In FOMF technique, the maximum fluorescence's peak for saffron is located at 560 nm and for turmeric at 530 nm (see 5-4-3) (Aceto et al. 2014, pp. 1494-95).



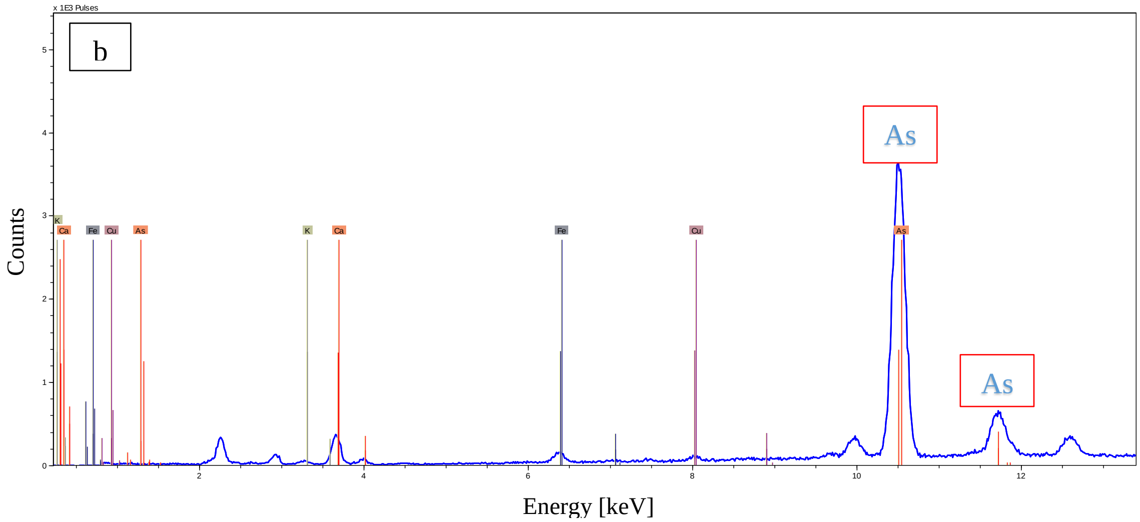


Figure 5-1: An example of a mixture indigo + orpiment identified in this study (manuscript Persian 9) FORS spectra(a), XRF spectra(b)

5-2-1-2 Copper greens

Another type of green colour identified in the *Shāhnāma* manuscripts under study in this project belongs to a family of copper green, although the identification of these pigments is complicated and it is very probable that they were made of different sources, both natural and synthetic.

In Persian manuscripts, copper-based green has normally been deployed to colour garments and architectural components, as mentioned by Knipe et al. (2018). "A variety of mixtures of copper greens were used to colour green robes with subtle variations in colour, including atacamite alone, mixtures of atacamite, malachite and ultramarine, and mixtures of antlerite and ultramarine. This trend shows an increase from the late 14th century…" (Knipe et al. 2018, p. 25).

It must be noted copper-based green pigments, which include copper carbonate (malachite), copper chloride (atacamite), copper sulfate (anterlite, brochantite), and verdigris, can be detected in the XRF spectrum by the existing copper peak, but it is not possible to distinguish them from one another. The same as in FORS technique: copper-based greens have a clear and detectable maximum absorption; but it is not possible to distinguish different types of copper-based greens through this technique either. Due to the limitation of the analytical techniques applied in the present study, I will generally refer to them as copper green.

Since verdigris, as the only green pigment described by historical records, and malachite are the two most widely used copper-based green pigments in Persian manuscripts in my analysis the material and spectral features of them is explained for example it mentioned by Knipe et al. (2018), Barkeshli and Ataie

(2002), and Anselmi et al. (2015). verdigris was used widely in the 15^{th} and 16^{th} centuries, while in the 16^{th} and early 17^{th} century malachite became more common (Knipe et al. 2018, pp. 37-38).

5-2-1-2-1 Verdigris

Verdigris is $Cu(CH_3COO)_2.2Cu(OH)_2$ (copper-(II)-acetate-1-hydrate). It is composed of variously hydrated copper acetates, including the basic copper acetate. Its colour is generated by transitions of type d-d. “According to the historical Persian evidence it was referred to as *Zangar*” (Barkeshli 2015, p. 189). A historical recipe recommends immersing the copper plates in vinegar for a month two meters under the ground (Barkeshli 2015, p. 8). Another recipe includes not only copper and wine vinegar, but also sugar and salt (Mayil Haravi 1993, Qāżi Aḥmad 1973). Different recipes suggest different chemical compositions for verdigris. Due to the presence of acetate ion in the preparation, the pigment in humid conditions can release acetic acid and then cause corrosion of the pictorial support. Therefore, to avoid damage to paper or parchment, in many cases the Verdigris was mixed with saffron, which inhibited the reaction of acetic acid (Knipe et al. 2018, p. 36; Barkeshli 2015, p. 190). It must be noted in many publications, the exact copper type cannot be discerned with certainty, and so the term “Verdigris” is often used generically for green to blue copper corrosion products rather than referring exclusively to the various copper acetates that make up the true Verdigris (Knipe et al. 2018, p. 36).

5-2-1-2-2 Malachite

Malachite is ($CuCo_3.Cu(OH)_2$) is the basic copper (II) carbonate, which is called sabz-e Koohi (meaning mountain green) in Persian. It is a pigment produced by grinding $CuCO_3{\cdot}Cu(OH)_2$, containing homonymous mineral. Its colour is generated by transitions of type d-d. Malachite is naturally found together with azurite. This mineral can be extracted in many places in Iran, from the deposits of carbonate of copper especially in the north of Iran and Afghanistan. The method of using Malachite and azurite was similar (Rutherfor et al. 1966, p. 95; Bevilacqua et al. 2010, p. 117; Pakzad 2016, p. 13).

Malachite has been used by Persian painters mostly as a mixture of malachite and coarse calcite as mentioned by Knipe et. al (2018) or according to Muralha et al. (2012) as a mixture of malachite and indigo. The same mixture was also reported by Anselmi et al. (2015). In all the *Shāhnāma* manuscripts analysed in this project, the copper green was identified, and most likely was used to paint green garments, barding and architectural features, such as floor tiles.

Copper green pigments can be identified on the presence of copper in the XRF spectra, the characterizing Cu lines are at 8,04 (Kα) and 8,90 (Kβ) keV, with traces of Ca, Fe, and impurities of Sb (Lα 3,60 and Lβ 3,97 keV), As (Kα 10,53 and Kβ 11,73 keV), and Zn (Kα 8,63 and Kβ 9,57 keV) (Bevilacqua *et al.* 2010, p.241; Larsen *et al.* 2016, p.661) (Fig. 5-2). The characteristic shape of the FORS spectra of copper green is a deep absorption at 720 to 800 nm followed by maximum reflectance at 485-540 nm (Aceto et al. 2014, p. 1495; Ricciardi et al. 2013, p. 18; Bevilacqua et al. 2010, p. 245) (Fig. 5-2). Since the reflectance maximum can be notably shifted (from 700 to 800 nm) in some instances, for example in mixtures, more accurate identification can be based on the location of the apparent absorption band and the form of the spectrum (Aceto et al. 2014, pp. 1494-96; Bevilacqua et al. 2010, p. 241).

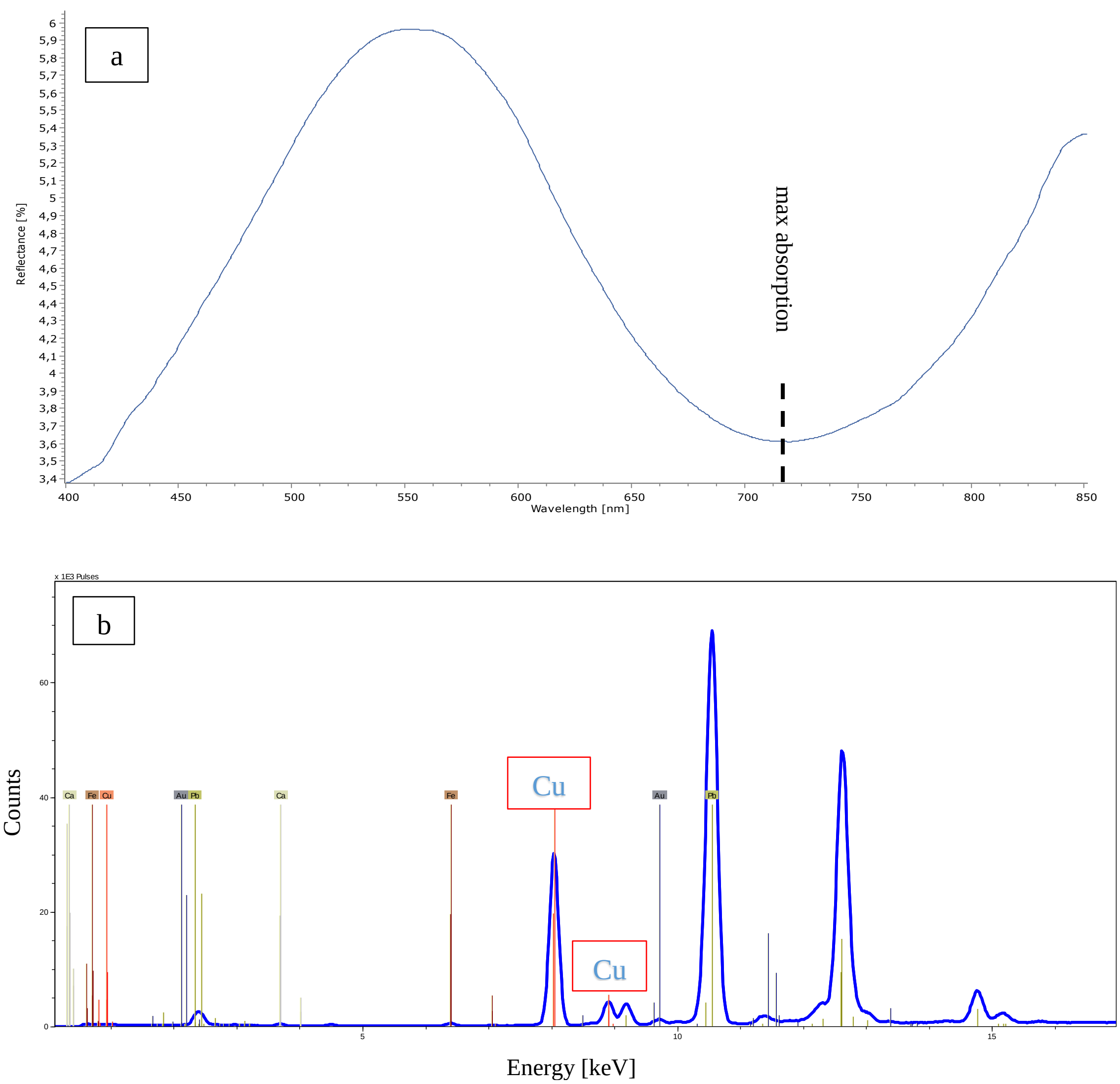


Figure 5-2: An example of a mixture of copper green identified in this project (manuscript AKM 4) FORS spectra(a), XRF spectra(b)

5-2-2 Red, Orange, and Brown Colours

The red palette identified in this and other studies show little variation with place or date, more common colour materials applied by Persian painters to paint the red, orange, and Brown areas are: cinnabar (HgS, either natural from the homonymous mineral or the synthetic vermillion), red lead or minium (Pb_3O_4), red to brown ochres in their several variants and cochineal (organic reds) (Aceto et al. 2016, p. 1491; Muralha et al. 2012, p. 25; Anselmi et al. 2015, p. 190; Knipe et al. 2018, p. 31). Higher concentration of red lead tends to produce a more orange colour, cinnabar (vermilion) and organic reds produce a darker or deeper red, while hematite and red ocher gives a browner tint. In the 15th and 16th centuries, other pigments such as lead white, orpiment or pararealgar were mixed in with the reds to produce a great range of orange or pink shades (Knipe et al. 2018, p. 31).

5-2-2-1 Cinnabar or Vermilion

Cinnabar/vermilion is mercuric sulphide (HgS) and is obtained by grinding the mineral cinnabar (HgS) which it called *Shanjarf* in Persian (Upham Pope et al. 1999, p. 124; Jokar 2006, p. 57). It was used widely in the Eastern Asia since at least the second millennium BC. Its colour is derived from its nature as a semiconductor and then from the transition of electrons between the valence band and conduction band. The ancient recipes (Mayil Haravi 1993; Qāżi Aḥmad 1973) consists of grinding the ore, placing it in a container with water, shaking it and letting it remove any residual dust and dirt. The resulting powder is further ground with the addition of gum Arabic. The natural cinnabar was purchased from Turkmanistan and the synthetic form, vermilion, was produced from several known recipes (Knipe et al. 2018, p. 38; Barkeshli 2013, p. 124).

In addition to the natural form, the artificial pigment named vermilion was produced according to ancient recipes (Mayil Haravi 1993; Qāżi Aḥmad 1973); mercury and sulphur were ground in a mortar and cooked for several hours. Both forms of mercury sulphide are relatively stable chemically, and the addition of white lead does not cause the formation of black sulphides. However, under certain still unclear conditions, the pigment tends to be transformed from α-HgS to α'-HgS, known as meta-cinnabar, to produce black colour. Since it is not possible to distinguish between cinnabar and vermilion without polarized light microscopy (PLM) of samples and this was not undertaken in this project in the present dissertation mercuric sulphide (HgS) pigment referred to as cinnabar.

In in this project, cinnabar was identified in all the *Shāhnāma* manuscripts analysed, and from this aspect, cinnabar is considered as the most prised red pigment, used by Persian painters to paint robes, shield and barding, flowers, architectural components, clothing, and background details. Cinnabar can be identified by the presence of Mercury in the XRF spectra, the characterizing Hg lines are at 9,95 (Lα) and 11,87 (Lβ) keV, with impurities of As (Kα 10,53 and Kβ 11,73 keV), Ba (Lα 4,46 and Lβ 4,99 keV), Zn (Kα 8,63 and Kβ 9,57 keV) (Bevilacqua et al. 2010, p. 223; Larsen et al. 2016, p. 661). The FORS method can easily identify this pigment and there is a well-defined mechanism that defines the absorption of UV-Vis radiation by Cinnabar. As explained by Aceto et al. (2014); "Cinnabar is a semiconductor, it shows a sigmoid-shaped spectrum with an infection point that becomes a maximum peak in the first derivative reflectance spectrum" (Aceto et al. 2014, p. 1492). Cinnabar can therefore, be identified with an inflection point located at 600 nm, and an intense reflectance at $\lambda \geq 630$ nm, and in the first derivative spectrum, cinnabar shows maximum peak cinnabar at 590–605 nm (Fig. 5-3) (Aceto et al. 2014, p. 1492; Bevilacqua et al. 2010, p. 223).

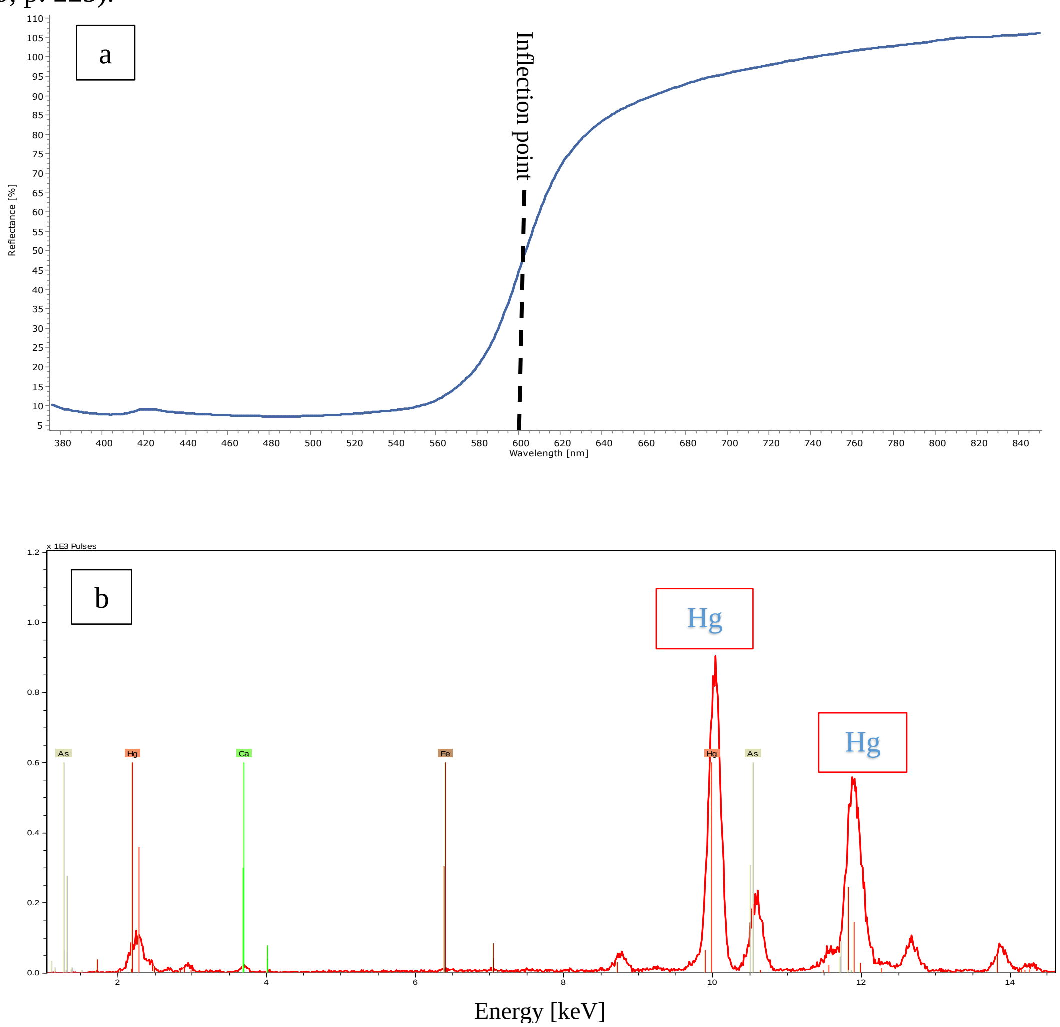


Figure 5-3: An example of cinnabar identified in this project (manuscript RAS 239) FORS spectra(a), XRF spectra(b)

5-2-2-2 Red Lead

Red lead or Minium (Pb_3o_4 or Pbo_2.2Pbo) is lead tetroxide (Pb_3O_4). From as early as the fifth century BC, the Chinese knew the process of its synthesis. It is called *suranj* in Persian (Barkeshli 2013, p. 117).

It has probably derived its name from the *Minius river* in north-west Spain, where there were sources of lead ores. The ancient recipe maintains that it is sufficient to fire lead carbonates, such as white lead and the partial oxidation of lead causes the production of red tetroxide (Mayil Haravi 1993; Qāżi Aḥmad 1973). The pigment was widely used for its low price and ease of preparation, in spite of the fact that red lead can degrade either to PbS in the presence of sulphides, or to lead oxide (PbO_2); both of which are black.

Red lead has been identified in all the *Shāhnāma* manuscripts in this study. It is applied to flowers, clothes, architectural details, and other motifs mostly as a red-orange colour and some time has been mixed with other colour materials to create brown colour.

Red lead (Minium) is clearly recognizable by the relevant amount of lead in the XRF spectrum, the characterizing Pb lines are at 10,50 (Lα) and 12,62 (Lβ) keV with interference of As at 10,53 (Kα) keV (Bevilacqua et al. 2010, p. 221; Larsen et al. 2016, p. 661).

In the FORS technique, since red lead is semiconductors it shows a sigmoid-shaped spectrum with an infection point that becomes a maximum peak in the first derivative reflectance spectrum. Therefore, red lead can be identified with an inflection point located at 565 nm, and an intense reflectance at 620 nm (Fig. 5-4) (Aceto et al. 2014, p. 1492; Bevilacqua et al. 2010, p. 221; Anselmi et al. 2015, p. 189).

However, the main challenge for detecting varieties of red was distinguishing red lead from cinnabar because of the presence of the lead element in most XRF spectra taken from Persian manuscripts. That is due to an extensive use of white lead.

To achieve the desired colour tonality in many cases cinnabar combined with white lead, therefore, the lead observed in the XRF spectrum of this combination might be confused with red lead. Therefore, the presence or absence of mercury in the XRF spectrum, which indicates cinnabar pigments, has a decisive role in identifying the red lead used in the manuscripts.

There are many examples that combine the two pigments of cinnabar and red lead. Therefore, the FORS spectrum of red samples is much of some help in distinguishing these two pigments, because in the FORS technique, red lead has an inflection point at 560 nm and cinnabar has an inflection point at 600 nm.

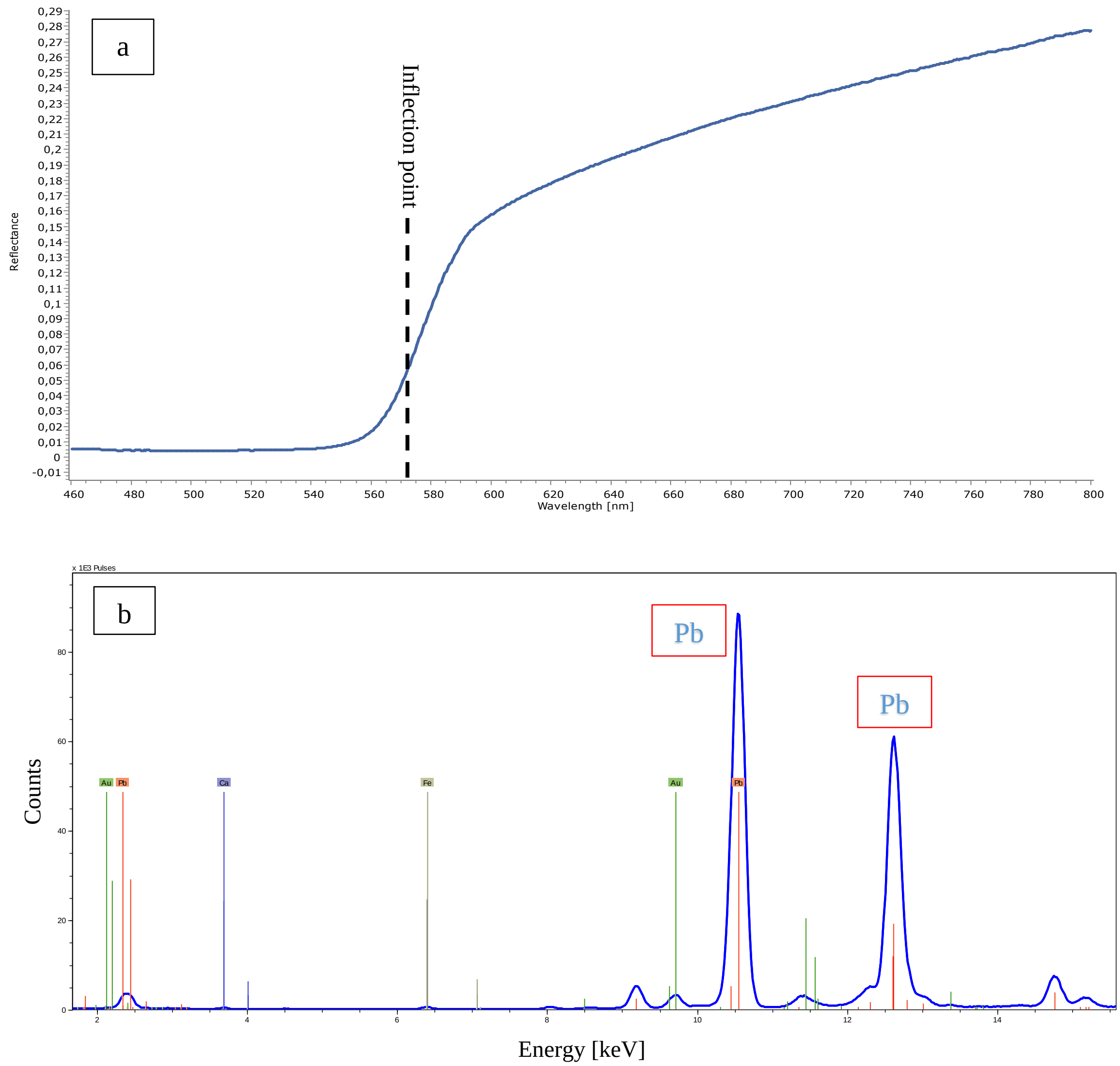


Figure 5-4: An example of red lead identified in this project (manuscript AKM 5) FORS spectra(a), XRF spectra(b)

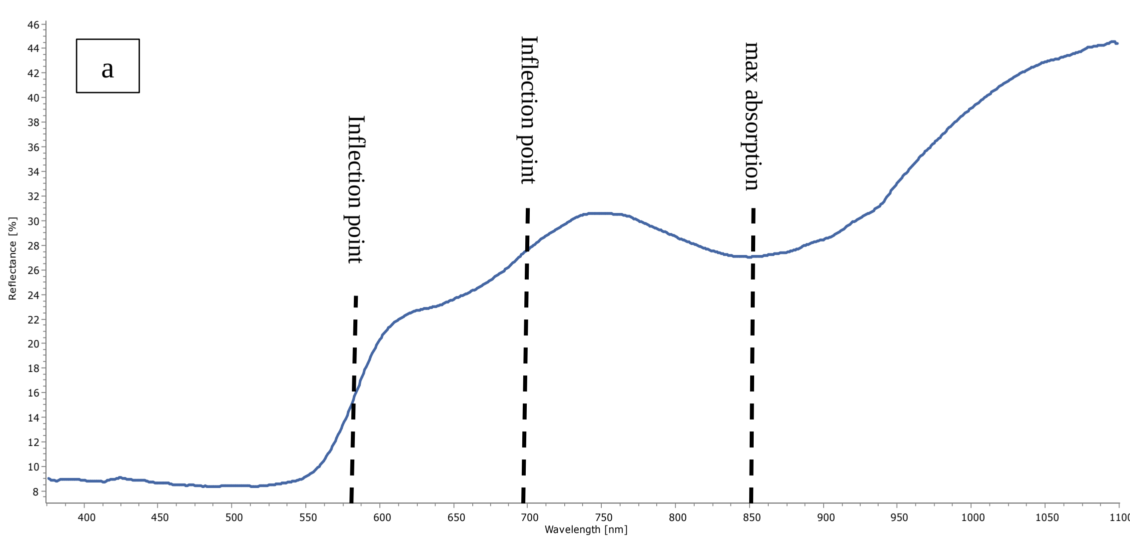
5-2-2-3 Red Ochre or Hematite

Red ochre (Fe_2O_3) is composed mainly of iron oxide or hematite, which is derived from the Greek word *hema* meaning blood (Siddal 2018, p. 5; Bevilacqua et al. 2010, p. 77). In Persian, these iron oxides are called Okhra. Ochres from natural clay deposits were widely available in the Islamic world. The most famous was brown Hormuz clay from the homonymous island in the Persian Gulf, mentioned by a 16th century recipe (Knipe et al. 2018, p. 38; Barkeshli 2013, p. 118). Used from prehistoric times, these permanent pigments can be safely mixed with other colour materials (Bevilacqua *et al.* 2010, pp.77-79; Rutherfor et al. 1966, p. 134). There are a wide range of ochres varying from complete opaque to those valued to use as glaze. Persian artists had a choice of different soils and ochre containing iron oxides in their works. Red ochre/hematite as light and dark brown colour were identified in Persian manuscripts by Knipe et al. (2018), Anselmi et al. (2015), and Muralha et al. (2012). In this study in all the *Shāhnāma* manuscripts ochre is identified as the brown colour used for tree trunks, robes, horses, and architectural components.

Red ochre/hematite is easily recognisable in brown areas by the high amounts of iron in the XRF spectra, the characterising Fe lines are at 6,40 (Kα) and 7,06 (Kβ) keV with interference of Co and Mn and impurities of Ti 4,51 (Kα) and 4,93 (Kβ) keV, Ba 4,47 (Lα) and 5,00 (Lβ) keV, and Ca 3,69 (Kα) and 4,01 (Kβ) keV (Fig. 5-5) (Bevilacqua et al. 2010, p. 209; Larsen et al. 2016, p. 661; Anselmi et al. 2015, pp. 189-190).

In the FORS technique, due to the presence of hematite α-Fe_2O_3 as chromophore, all red iron oxide pigments have similar spectral characteristics. In the first derivative spectrum, the maximum peak is in the range of 575-590 nm and therefore is distinguishable from semiconductors; in addition, their spectra have a characteristic positive slope in the region above 600 nm, producing a less prominent inflection point about 700 nm. Finally, an absorption band due to ligand field transition, centred around 850–900 nm, is usually present (Fig. 5-5) (Aceto et al. 2016, p. 1492; Bevilacqua et al. 2010, p. 210).

It is not possible, however, to discriminate among the different red iron oxide pigments cited only on the basis of their FORS spectra, due to the overlapping of their spectral features which are all determined by the presence of the same chromophore (Aceto et al. 2016, p. 1492; Bevilacqua et al. 2010, p. 210).



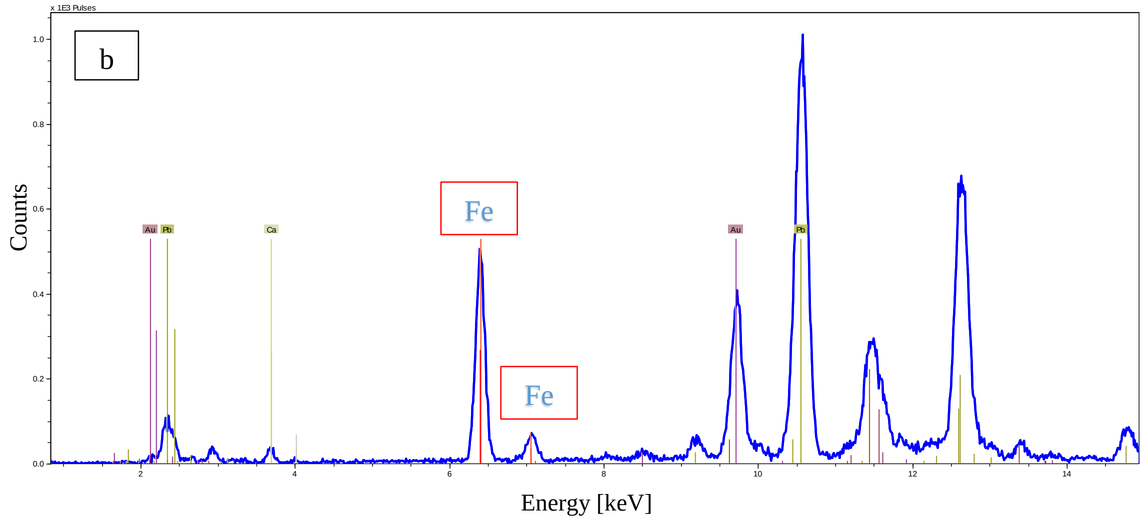


Figure 5-5: An example of red ocher/hematite identified in this project (manuscript Persian 9) FORS spectra(a), XRF spectra(b)

5-2-2-4 Organic reds

Organic red applied in Persian manuscripts contains; insect-based dyes like Indian lac, coccid scale insects (cochineal and kermes) as well as plant-based reds, such as madder, safflower red, and Henna.

Cochineal and Indian lac from coccid scale insects, madder from *Rubia tinctorum*, henna and red safflower, or the red component of the juice from *Carthamus tinctorius* flower, with shades varying from red to purpose and violet, were the most widely used dyes in the illumination of Persian manuscripts. They were either applied alone (in juice or lake form) or as finishing layers (glaze) on other painted areas, but in both cases with little or no hiding power (Knipe et al. 2018, p. 38; Aceto et al. 2016, pp. 1492-93; Rutherford 1966, pp. 123-4 and 154).

Historical records underline the extensive use of organic reds like madder, red safflower, kermes, cochineal, and Indian lac in many Persian manuscripts (Mayil Haravi 1993; Qāżi Aḥmad 1973). This is also maintained by (Knipe et al. 2018, p. 31), who also mentioned that artists added organic reds on other colours to make them more transparent and glassy. The few confirmed identifications of organic reds include carmine as organic red in a late 17th century Persian manuscript (Muralha et al. 2012, p. 27), a red insect-derived anthraquinone dye on a 16th century Persian manuscript (Anselmi et al. 2015, pp. 188-189) and lac as a bright burgundy red and safflower as a peach colour in a 16th century manuscript (Knipe et al. 2018, p. 38).

Another red dye which was mainly used in Persia is Armenian cochineal. It is a mordant dye obtained from *Porphyrophora Hamelii*, an insect of the *Coccoidea* family (1 cm x 7 mm) (Hofenk de Graaff 2004,

p. 207). The coccid insects live on the roots and rhizomes of two grass plants, *Aeluropus littoralis (Gouan) Paul* and *Phragmites communis Trin*., in dry steppes or semi-desert environments of central Asia as well as Turkey, Iran and the Mount Ararat region (Phipps 2010, pp. 6-8). The dye stuff is made by drying the adult females and possibly also the third instars of males. The main dying molecule of Armenian cochineal (0.8% of the dried insect, about 90% of the Colourants) is carminic acid (Figure 5-6) (Hofenk de Graaff 2004, p. 209).

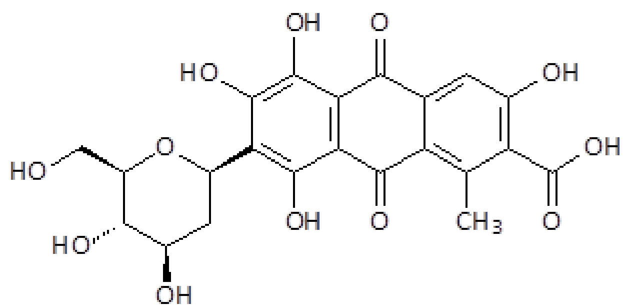


Figure 5-6: Chemical structure of carminic acid

The historical references (Mayil Haravi 1993; Qāżi Aḥmad 1973) mention that organic reds like madder, red safflower, kermes, cochineal, and Indian lac were used in many Persian manuscripts, but these materials are normally detected by complicated destructive or micro-destructive techniques such as SERS Raman, FTIR, and HPLC.

In this study the following strategy was applied to identify red dyes: the absence of detectable elements such as lead, iron, or mercury by XRF analysis in red areas signifies the presence of red dyes, which can then be confirmed by a combination of FORS and FOMF techniques. However, a set of red/violet micro samples of manuscripts RAS 239, Persian 9, and Persian 933 is analysed by Raman (SERS) and HPLC-MS in addition to FORS and FOMF techniques.

In what comes below cochineal and Indian lac are only identified as red dyes in this study. These two red dyes have been used mostly to create pink, violet, and purple in a mixture with other colour materials (see 5-2-6). When used as a red colour, only cochineal was identified in the *Shāhnāma* manuscripts AKM 4, AKM 269, and RAS 239 which they were applied to create dark red to represent red used to colouring blood, small flowers, and background details. Due to the organic nature of cochineal and Indian lac they are not detectable in XRF technique but can be detected by FORS and FOMF techniques.

As mentioned, the combination of FORS and FOMF techniques is a non-destructive way to identify red dyes. Red dyes display a sigmoid-shaped reflectance spectrum with a typical inflection point, similar to red inorganic pigments in the FORS technique, but with a less steep rise in the red area. In addition, in the blue area, a small maximum band is typically present, which explains their hues varying from pure red (Aceto et al. 2016, pp. 1492-93).

In the FORS technique cochineals show two maximum absorbance one at 520–525 nm and 550–565 nm, while two maximum absorbance of Indian lac located at 527–540 nm and 560–585 nm. In fact, differentiation between cochineals and Indian lac by FORS technique is not very accurate but in generally if the first maximum absorption is more than 527 nm, it is an evidence of Indian lac and if the first maximum absorption is around 520-525 nm it indicates cochineal (Fig. 5-7) (Aceto et al. 2016, p. 1493; Anselmi et al. 2015, p. 188).

It must be noted Armenian cochineal is a more common in coccid dyes used in Persian manuscripts but since the FORS technique does not allow us to distinguish among different cochineals (Armenian, Polish and Mexican cochineal) the general terms cochineal is used in the present dissertation. In the FOMF technique cochineal is recognisable by a maximum fluorescence's peak, which is located in 525 and 620 nm and Indian lac by two maximum fluorescence's peaks at 610 nm (Fig. 5-8) (Aceto *et al.* 2014, pp.1491-93; Anselmi *et al.* 2015, p.188). In the Raman (SERS) technique, cochineal sample coated with the Ag colloidal paste substrate (see Chapter 3) show a very strong peak at 1294 cm^{-1} and a less intense one, occasionally observed as a shoulder, at about 1234 cm^{-1}. Other signals can be found at 460 (m) 1083 (w), 1425 (m), 1515 (w), 1630 (w) cm^{-1}. All of them can be attributed to a cochineal and to its major dyeing component, carminic acid, and Indian lac shows a clear peak at 1461 cm-1 and other signals can be found at 451 (m) 1049 (w), 1425 (m), 1222 (w), and 156 (w) cm-1. (Fig. 5-9) (Idone et al. 2013, p. 7).

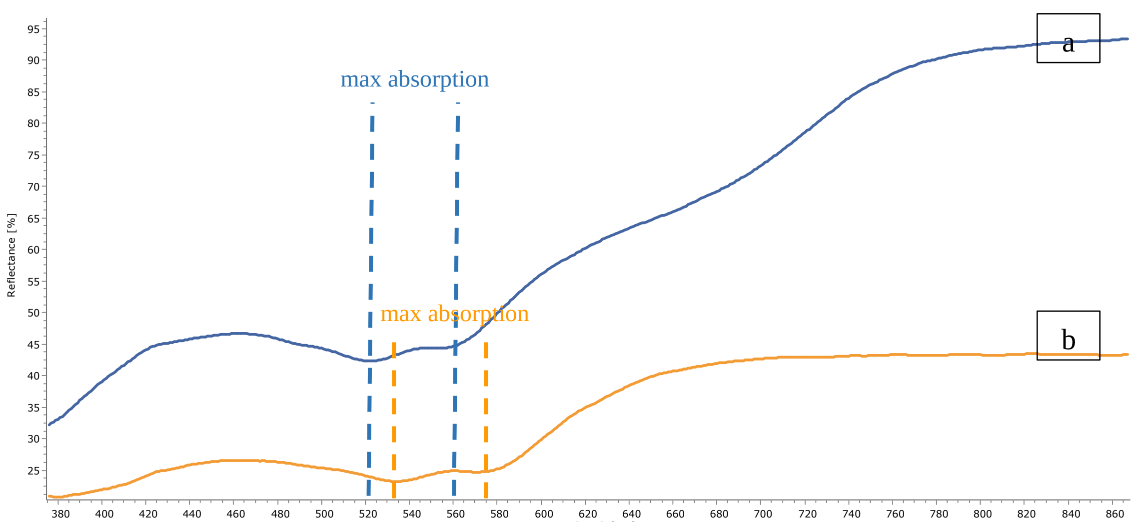


Figure 5-7: FORS spectra of cochineal(a) and Indian lac(b) identified in this project (manuscript Persian 9 and 933)

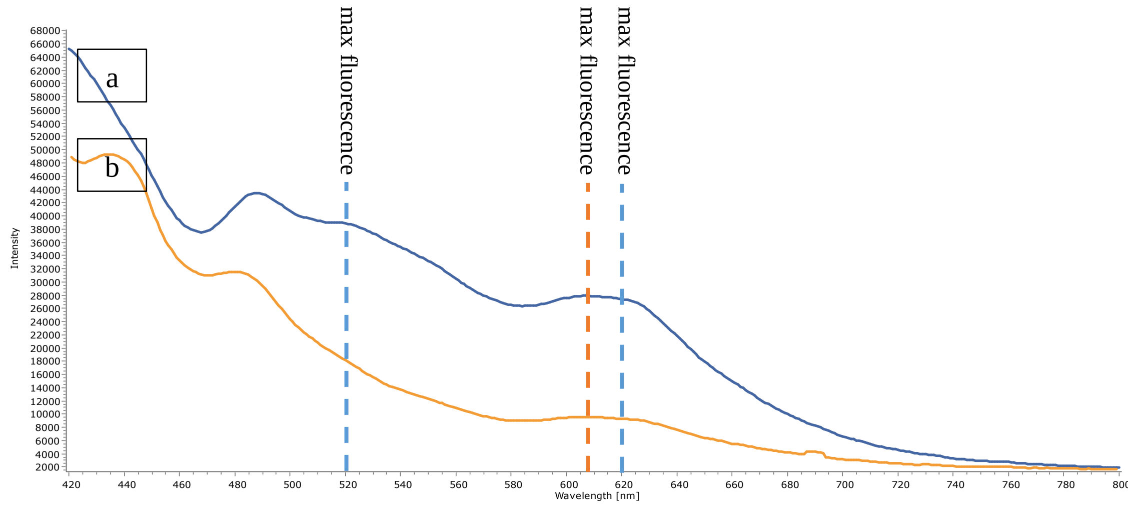


Figure 5-8: FOMF spectra of cochineal(a) and Indian lac(b) identified in this project (manuscript Persian 9 and 933)

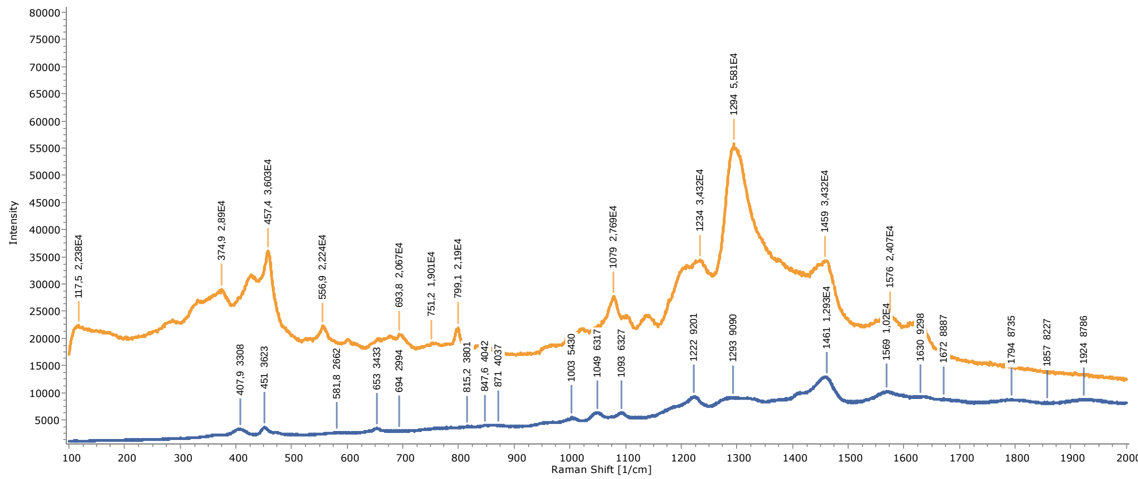


Figure 5-9: SERS-Raman spectra of cochineal(a) and Indian lac(b) identified in this project (manuscript Persian 9 and 933)

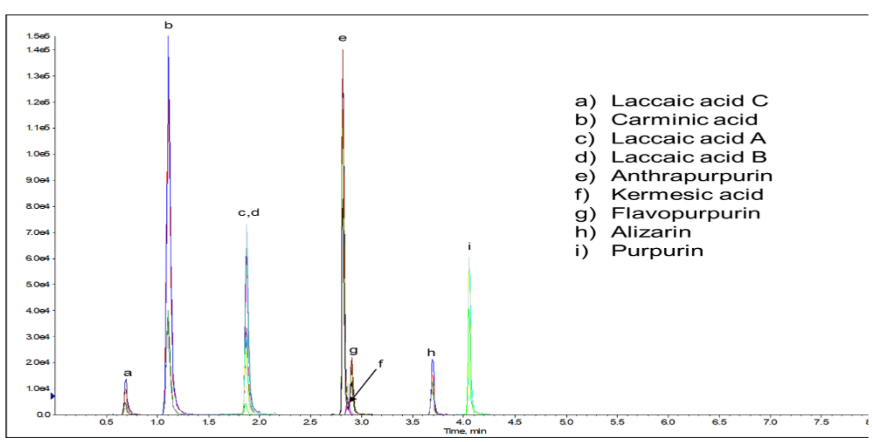


Figure 5-10: HPLC-Mas spectra of cochineal(a) and Indian lac(b) identified in this project (manuscript Persian 9 and 933)

5-2-3 Blue Colours

5-2-3-1 Ultramarine blue

The main blue colour identified in Persian paintings from various periods and regions studies in this research and many other studies is ultramarine, ultramarine in Persian named as *lāzhvard* which derivative of the Persian word *lāzhvard* (blue). This pigment is prepared by grinding lapis lazuli ($Na_8Al_6Si_6O_{24}$), which is a deep blue stone whose name is derived from the Latin word lapis (stone) (Siddal 2018, pp. 17-18). This stone has a complex composition, and it is a mixture of two minerals from the sodalite group:

lazurite, $Na_3Ca\ (Al_3Si_3O_{12})S$ for 25-40%

hauynite, $Na_4Ca_2Al_6Si_6O_{22}S_2\ (SO_4)Cl_{0.5}$.

It also contains calcite and pyrite, which may affect the final colour of the pigment.

Ultramarine was mainly mined from quarries in Badakhshan (the present-day Afghanistan). The abundant use of ultramarine underlines the great system in place for the trade of the stone from the mines across the Islamic lands throughout the entire periods (Knipe et al. 2018, p. 36). The recipes mentioned in medieval treatises have described the ancient recipe in this way: the finely ground mineral, mixed with melted wax, resins, and oils, is wrapped in a cloth and kneaded, the material obtained is immersed in a dilute solution of lye into a container. The blue particles would be collected at the bottom of the container and the impurities and colourless crystals would remain in the ground. The process should have been repeated at least three times ((Mayil Haravi 1993; Qāżi Aḥmad 1973).

Ultramarine as light and dark blue colour has been identified in Persian manuscripts in all studies. In this project in all *Shāhnāma* manuscripts, ultramarine was identified as blue and light blue (combined with white lead) and has been used for many motifs and figures like robes, clothing, sky, background, and etc.

Ultramarine blue is identified by the presence of sodium (Na), aluminium (Al), silicate (Si), and sulphur (S) in the XRF spectrum. However, the XRF system working in the open air and at long distance (20mm) like most porTab XRF instrument used in this project are not capable of detecting the presence of the lighter elements sodium, aluminium, silicon, and sulphur that are expected in ultramarine. It must be noted that only for analysing the *Shāhnāma* MS 22-1948 an Artax micro X-ray spectrometer (Bruker) was applied which is able to detect light elements by using the X-ray tube operated at 15 kV and 1100 μA with He flush (see 3-2-3) (Fig. 5-11). Moreover, ultramarine contains calcite and iron pyrites, from which give rise to the traces of iron and cupper in the XRF spectrum (Bevilacqua et al. 2010, p. 191; Larsen et al. 2016, p. 664). But fortunately, one of the pigments which the FORS technique can easily detect is ultramarine. The absorption of light in ultramarine blue is due to charge transfer, therefore ultramarine blue is recognizable by an apparent absorbance maximum at 600 nm and a maximum reflectance zone blue at 470-490 nm and increases the reflectance $_\lambda$≥700 nm (Fig. 5-11) (Aceto et al. 2014, p. 1495; Bevilacqua et al. 2010, p. 191; Anselmi et al. 2015, p. 188).

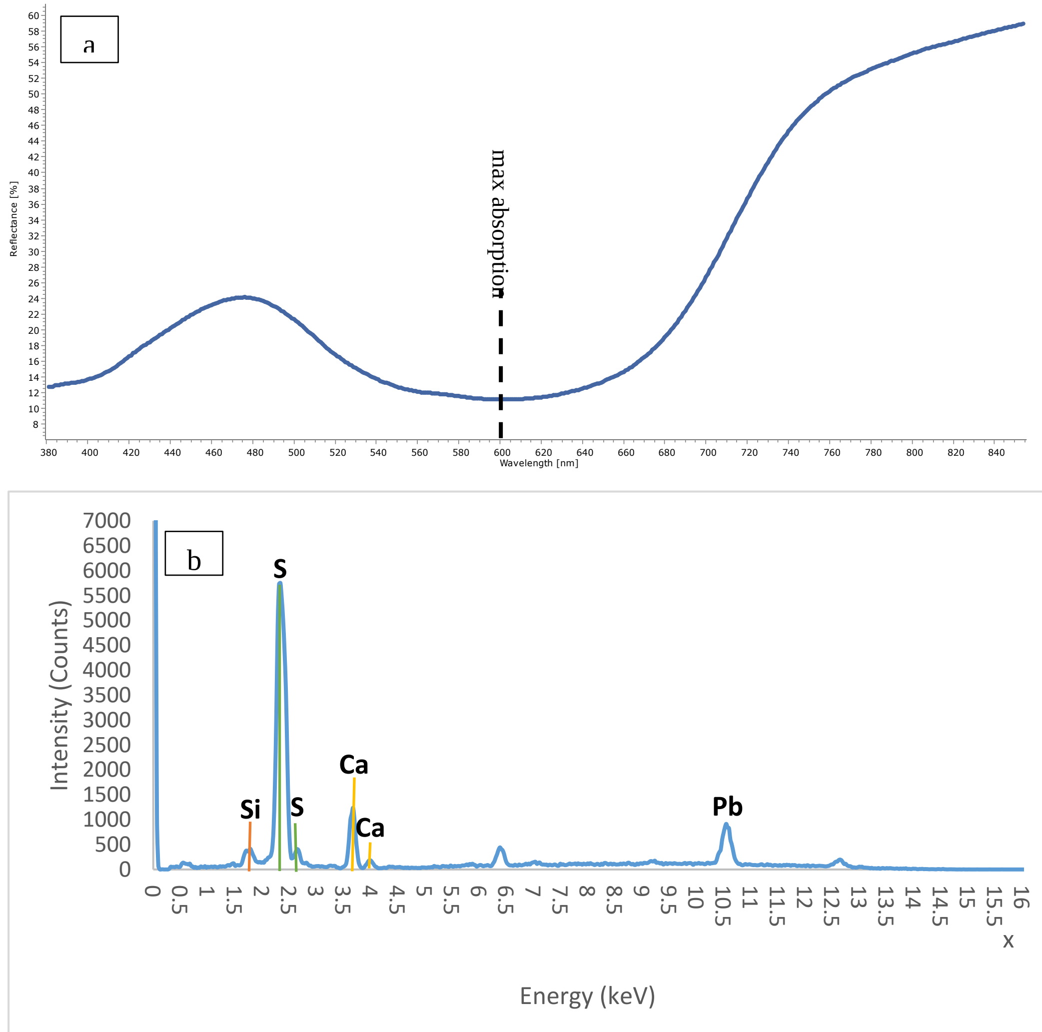


Figure 5-11: An example of ultramarine blue identified in this project (manuscript Ms 22-1948) FORS spectra(a), XRF spectra(b)

5-2-3-2 Indigo

Indigo is the most common blue dye all over the world and was used by Indians as early as the first millennium BC. Synthetic indigotin is still applied today to dye blue jeans (Idone et al. 2014, pp. 114-115, Rutherford 1966, p. 120). Indigo (*Indigotin* $C_{16}H_{10}N_2O_2$) is the dye obtained from *Indigofera* species and particularly from Indigofera tinctoria L. It is a perennial herb native of India, but today it can be found in the tropical and subtropical regions from Africa to South-eastern Asia (Rutherford 1966, p. 120).

Indigo is a vat dye, which requires soaking the leaves and stems for several weeks. Indigotin (Fig. 5-12) is the main colouring agent of indigo (Rutherford 1966, p. 120). The Persian term for Indigo is *nīl* and was probably introduced to Persia in the sixth century (Pkzad 2016, p. 6). Its preparation process is described in old treatises, which also include the production of artificial ultramarine by mixing indigo and lead white (Mayil Haravi 1993; Qāżi Aḥmad 1973). While indigo was also widely used for the plant-based dye stuff, this rarely occurred with a blue pigment. Instead, indigo was blended with yellow orpiment to create a pale or yellow-green or ultramarine to change the colour of blue or to create highlights over other colours, on clothing, and leaves (Knipe et al. 2018, p. 23). As Knipe et al. (2018) have recognized in some cases indigo were used alone in Persian manuscripts, and sometimes indigo were used to paint the sky while ultramarine was used for dark blue areas.

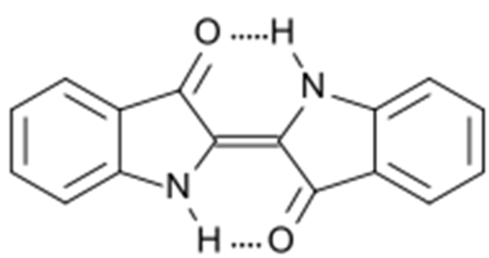


Figure 5-12: chemical structure of indigotin

In this project, indigo was observed mostly in combination with other colour materials to create green, purple, dark blue, and violet, in some cases in the *Shāhnāma* manuscripts AKM 6, Persian 9, Ms 22-1948, RAS 239, and Or 420 indigo was identified independently or mixed with white lead as a hue of blue colour and has been used to paint the sky and background, robes, architectural details or for creating transparent highlights over other colours.

Indigo cannot be identified by XRF but fortunately is clearly recognizable in FORS, delocalized molecular orbitals determine the absorption mechanisms for indigo. Therefore, indigo can be easily identified by an asymmetrical peak close to the violet region and by an overall low reflectance, with a typical steep rise in the far-red region; the absorption maximum is around 660 nm and maximum reflectance at 450-500 nm (similar to Ultramarine Blue), and increases the reflectance $\lambda \geq 700$ nm (Fig. 5-13) (Aceto et al. 2014, p. 1495; Bevilacqua et al. 2010, p. 197).

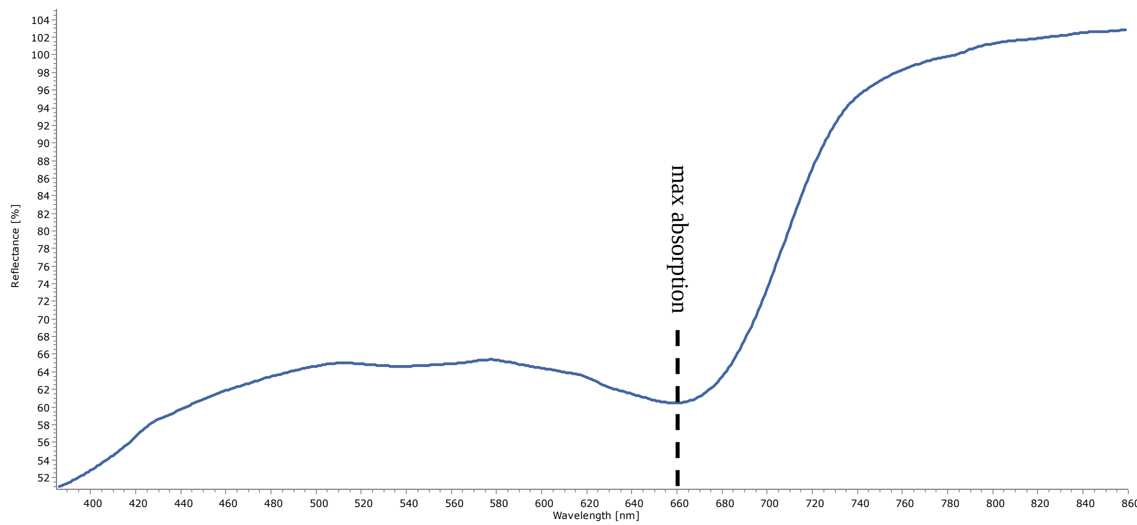


Figure 5-13: FORS spectra of indigo identified in this project (manuscript Or 420)

5-2-3-3 Azurite

This Romans-known mineral pigment is produced by grinding the homonymous mineral consisting of simple copper carbonate ($2CuCo_3.Cu(OH)_2$) (Siddal 2018, p. 14, Rutherford 1966, p. 95). In addition to turning green due to a tendency to transforming into malachite, this pigment, reacts with sulphite to form copper sulphite and becomes blackish in colour. It is called "*abi koohi*" (mountain blue) in Persian, and was used before the 15^{th} century, probably brought from China, which had rich azurite sources. The rich deposits of copper carbonate in north of Iran has also been the sources of raw material to produce azurite locally (Ruthefor et al. 1966, p. 95; Pakzad 2016, p. 12).

The use of azurite did not follow a timeline or geographic pattern, and quite possibly, it depended on the availability of the mineral in association with other sought-after copper pigment such as natural mixed deposits of malachite and azurite. The use of azurite may also be attributed to a preference of a particular shade. The artists applied both darker ultramarine and lighter azurite deliberately for different features (Knipe et al. 2018, p. 36).

Azurite was used in the *Shāhnāma* manuscripts AKM 6, RAS 239 and It was used to paint the robes and backgrounds. In fact, azurite was used to obtain a lighter blue in comparison to ultramarine blue and indigo. Azurite is recognizable in blue areas by the high amounts of copper in the XRF spectra, the characterizing Cu lines are at 8,04 (Kα) and 8,90 (Kβ) keV with impurities of Ba 4,47 (Lα) and 5,00 (Lβ) keV (Fig. 5-14) (Bevilacqua et al. 2010, p. 191; Larsen et al. 2016, p. 664). Azurite in the FORS technique can be identified, in azurite absorption of light is due to ligand field transitions. Therefore, Azurite is recognizable by an apparent absorbance maximum at 640 nm and a maximum reflectance zone blue at 450-490 nm and increases the reflectance $_{\lambda}\geq$900 nm (Aceto et al. 2014, p. 1495; Bevilacqua et al. 2010, p. 189).

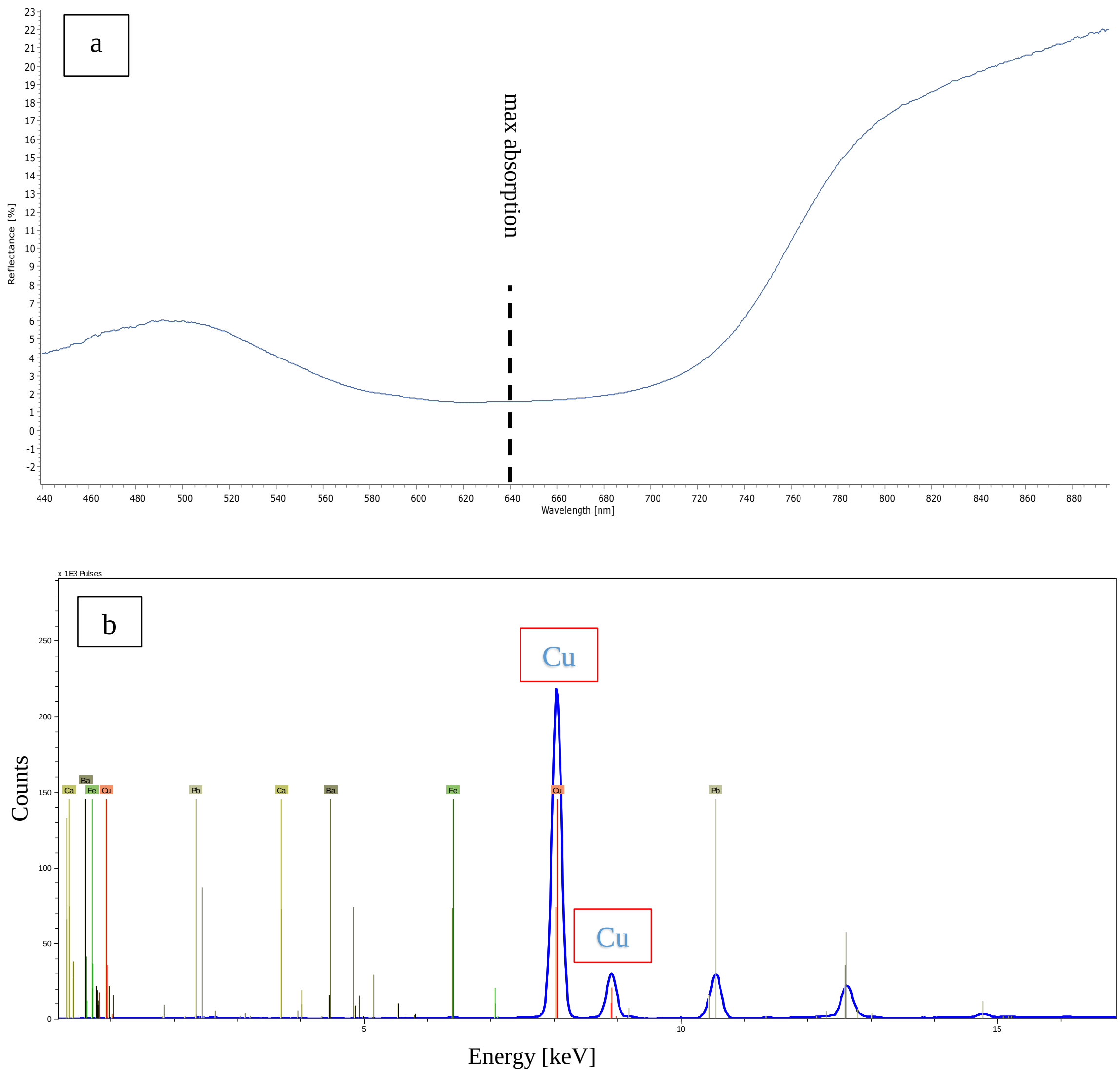


Figure 5-14: An example of azurite identified in this project (manuscript AKM 6) FORS spectra(a), XRF spectra(b)

5-2-4 Yellow Colours

5-2-4-1 Orpiment

Orpiment (arsenic trisulphide, As_2S_3) is undoubtedly the most widely used yellow pigment in Persian manuscripts (Knipe et at. 2018, p. 27). It is produced by milling arsenic sulphide. Due to its rich golden colour, it was known as zarnikh Persian which which is relevant to gold (ZAR), or even *Zard-e Sultani* which means yellow of king. There is evidence of its use as early as the third millennium BC in Egypt, and later in Mesopotamia, India, and China (Rutherfor et al. 1966, p. 135).

There are many references in historical text about the preparation of this pigment, proving its importance in the Persian palette. The historical recipes consist of pulverizing it with water and mixing with gum Arabic until the mixture turns into a soft paste (Mayil Haravi 1993; Qāżi Aḥmad 1973). There was, however, a limitation in its usage because of the negative effects that are created in reaction with white lead, of which Persian painters were aware. Mixing or even just applying in adjacent areas orpiment and pigment containing lead or copper, caused the formation of sulphides of dark colour.

Orpiment is nonetheless the most common pigment used for yellow in Persian manuscripts in almost all regions and periods. This means that natural orpiment could be supplied in abundance, which is not surprising given the presence of several deposits within Persia and nearby countries (including Iraq and Armenia) (Knipe et al. 2018, p. 37). It was applied as a pure yellow, mixed with small amounts of cinnabar/vermilion to adjust the shade and as an addition to indigo to produce green.

In nearly all the *Shāhnāma* manuscript analysed in this project orpiment as a yellow colour was identified either alone or mixed with gold (golden colour without metallic lustre) or yellow dyes, also it was identified as a mixture with other colour material to create green (see 5-1-1) or brown. It was used to paint the robes, cloths, barding, and background and architectural details.

Orpiment is clearly recognizable by the relevant amount of Arsenic in the XRF spectrum, the characterizing As lines are at 10,53 (Kα) and 11,73 (Kβ) keV with the interference of Pb at 10,50 (Lα) keV (Fig. 5-15) (Bevilacqua et al. 2010, p. 225; Larsen et al. 2016, p. 661; Anselmi et al. 2015, p. 189).

Orpiment can be identified by the FORS technique. Light absorption by orpiment is due to ligand field transitions, and the reflectance spectrum is sigmoid-shaped, similar to reds. The inflection point in the spectrum is again the characteristic feature to be used for the identification of yellow pigments. Inflection point can be found around 460–490 nm range for orpiment, and it has intense reflectance at 600 nm (Fig. 5-15) (Aceto et al. 2016, p. 225; Anselmi et al. 2015, p. 189).

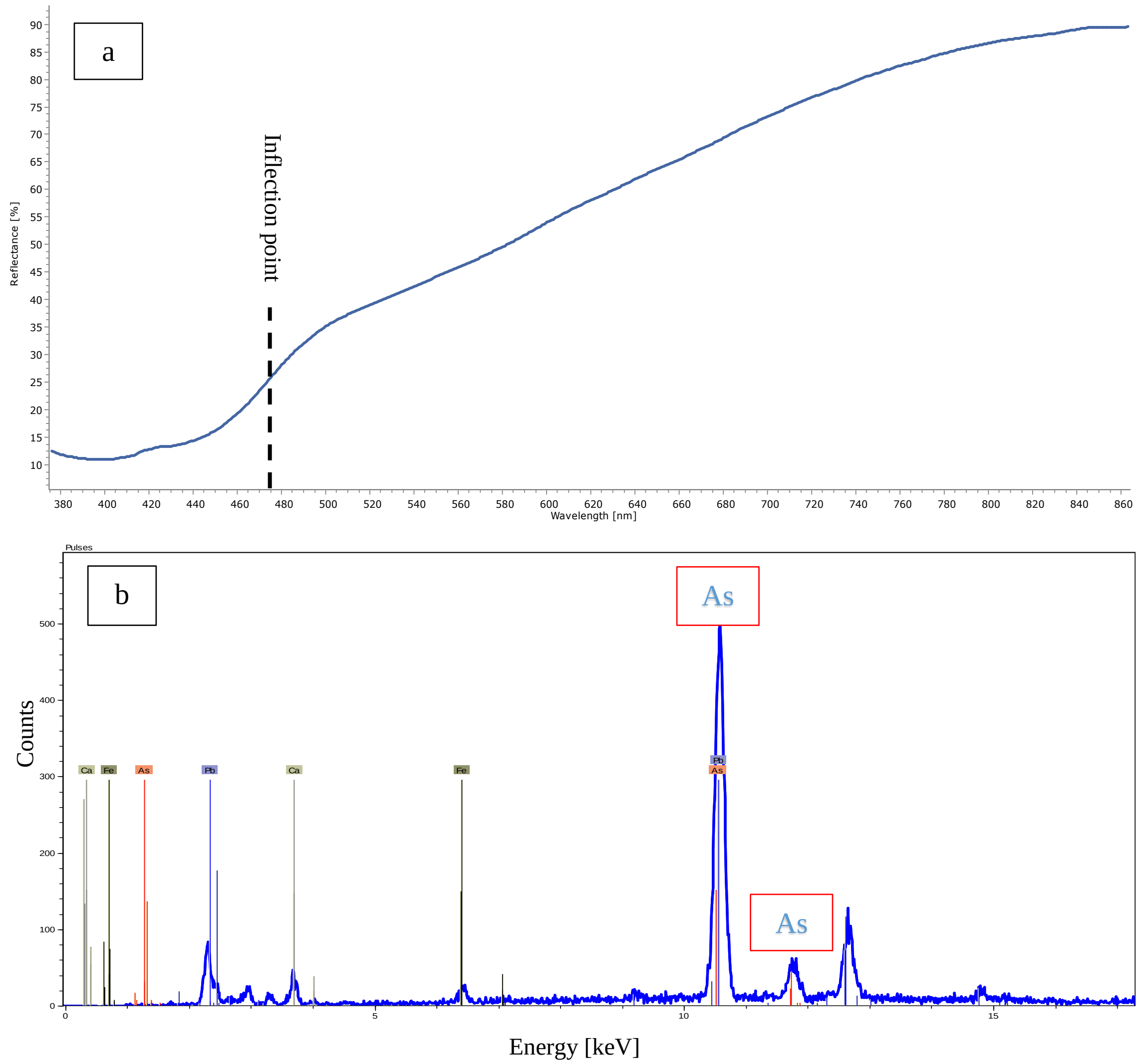


Figure 5-15: An example of orpiment identified in this project (manuscript RAS 239) FORS spectra(a), XRF spectra(b)

5-2-4-2 Indian yellow

Indian yellow, a magnesium euxanthate salt, Indian yellow occurs in Indian artworks from the 16th through 19th century and was likely produced in India from the urine of cows fed exclusively on mango leaves (Knipe et al. 2018, pp. 27-28; Rutherfor et al. 1966, pp. 119-20). The presence of Indian yellow on a small number of definitively Persian manuscripts indicating Indian yellow is used more in Persian manuscripts produced outside of famous Persian painting schools normally outside of present Iran (India, Tajikistan) in late 17th to 18th century special applied in paintings added to Persian manuscripts at the Mughal court in the 17th century (Knipe et al. 2018, pp. 27-28). In Indian works from the 16th to 19th centuries, Indian yellow occurs and has not previously been identified in works firmly ascribed to Iran.

However, Knipe et al. (2018) has identified Indian yellow in two paintings believed to have been produced in Bukhara (present Tajikistan) in the 16th century but later altered in Mughal India and a high-quality manuscript believed to have been produced at the end of the 17th century, probably in Isfahan.

In this project in one painting (folio 200) on the *Shāhnāma* manuscript Persian 933 which belongs to the painting school of Qazvin (17th century) and in the *Shāhnāma* manuscript RAS 239 in one painting belongs to the Mughal court (folio 430) in the 17th century Indian yellow was identified. Indian yellow contains light elements that cannot be detected by XRF, so can be identified by PLM or FTIR analysis identification or the characteristic bright yellow fluorescence in ultraviolet light.

In the FORS technique, Indian yellow has an inflection point at 500 nm (Fig. 5-16), and in the FOMF technique Indian yellow has a strong Max fluorescence and distinct in 555 nm which is the main characteristic of identifying Indian yellow (Fig. 5-16).

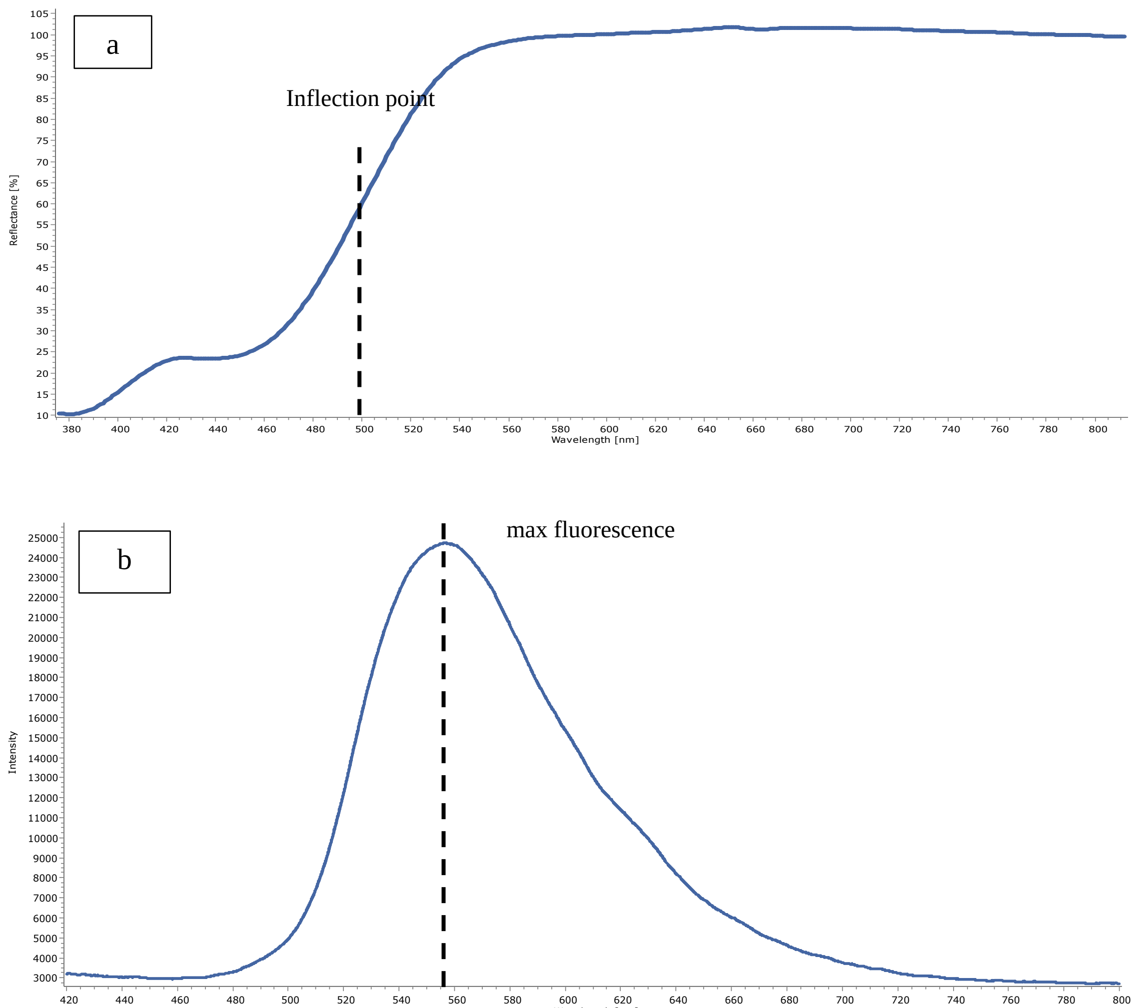


Figure 5-16: An example of Indian yellow identified in this project (manuscript RAS 239) FORS spectra(a), FOMF spectra(b)

5-2-4-3 Yellow dye

It is quite certain that yellow dyes were used widely in Persian paintings given their citation in ancient treatises (Barkeshli and Ataie 2002, p. 157, Barkeshli 2015, pp. 189-91), but since their identification require complicated techniques which are mostly micro-invasive or invasive, the literary information is hard to confirm. Saffron, Turmeric, and rhubarb described in old treatises had more application by Persian painters (Knipe et al. 2018, p. 38; Rahpeyma 2015, p. 121). *Rhubarb* and saffron have been identified as yellow colourants in 16th century Persian paintings and 19th century paint boxes by Barkeshli (2015) and Knipe et al. (2018).

Undoubtedly saffron and turmeric are two more common yellow dyes is used in Persian manuscripts. Many historical recipes for their production and usage are excited (Mayil Haravi 1993; Qāżi Aḥmad 1973), these yellow dyes are mostly used for dyeing papers or mixing with other colour materials (see Chapter 4). However, in this project the yellow dyes in *Shāhnāma* manuscripts AKM 4, AKM 6, AKM 269, Persian 9 and 933, RAS 239, and Or 420 were identified as mixture with orpiment, copper green and gold and applied to dyed paper to paint clothing, flags, and background and architectural details.

Saffron, or in Persian *za'faran*, is the stamen of the plant *Crocus sativus L*., a plant indigenous to Iran, Turkey, and Greece was widely cultivated here under the Sassanid dynasty (III-VII century). The colouring agent is the carotenoid crocetin (Fig. 5-17), obtained by hydrolysis of crocin and located precisely in the stamens of the plant, which were then dried, pulverised, and sometimes pressed in small portions (see Chapter 4) (Rutherford 1966, p. 154). The Persian term *Zard-chube* (yellow wood) refers to turmeric, a natural dye extracted from the roots of *Curcuma domestica L.* and *Curcuma longa L*. These plants grow wild in the tropical zones of South Asia, from India to Malaysia, and are widely planted in many tropical and subtropical regions of Asia and Africa (Cardon 2007, p. 241).

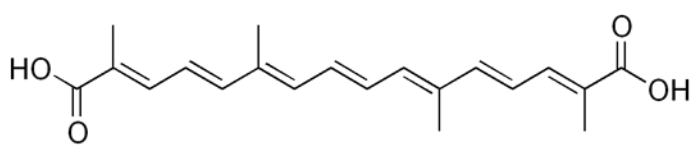
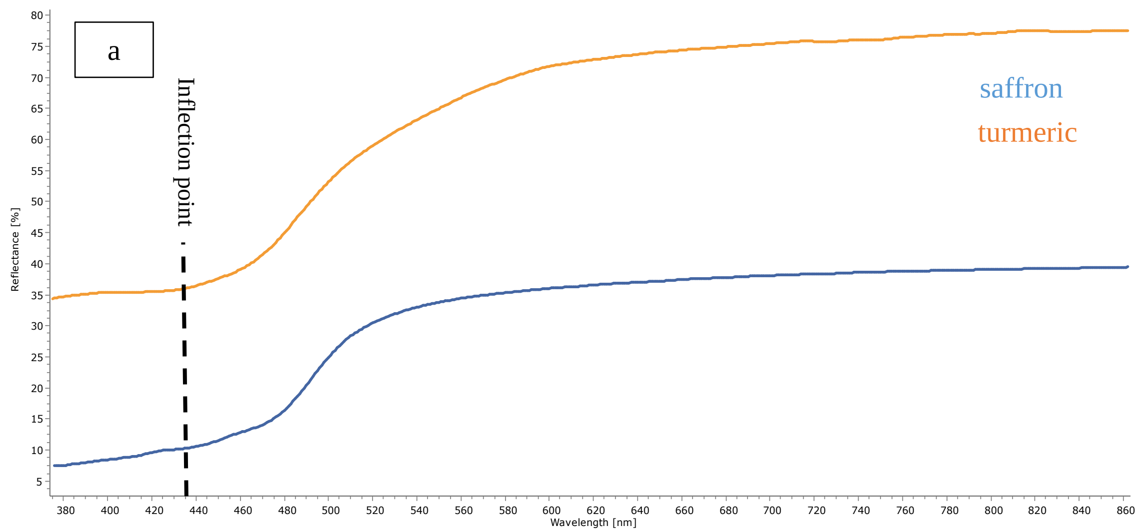


Figure 5-17: Chemical structure of crocetin

As mentioned above identification of yellow dyes with non-invasive techniques is very difficult and cannot be detected by XRF either. Fortunately, with a combination of FORS and FOMF yellow dyes are somewhat recognizable as mentioned by Aceto et al. (2014), Idone et al. (2016), M. Khorandi et al. (2020). The identification of yellow dyes with FORS is difficult. Their key spectral feature is the inflection point in the UV-Vis spectrum but as a result of dilution with a white pigment and of preparation methods, this can differ greatly (Aceto et al. 2014, p. 1494). Yellow dyes in the FORS spectrum have an absorption band in the 400–450 nm. However, the spectral feature for saffron in FORS is an inflection point located at ca. 435 nm with a shoulder around 480 nm that is typical of carotenoids (Fig. 5-18) and in FOMF saffron has a maximum fluorescence's peak is located at 560 nm (Fig. 5-18).

The spectral feature for turmeric in FORS is an inflection point at ca. 420 nm and in FOMF maximum fluorescence's peak is Located at 530 nm (Fig. 5-18) (Aceto et al. 2014; Idone et al. 2016; M. Khorandi et al. (2020). As can see above the FORS and FOMF spectral features of saffron and turmeric are very similar, moreover, maximum absorption at 400-450 nm in the FORS spectrum for yellow dyes occurs in a similar position among the different dyes, so the cited spectral features above should be regarded as indicative only. Therefore, in the present dissertation, all possible identified saffron and turmeric referred to as yellow dye.



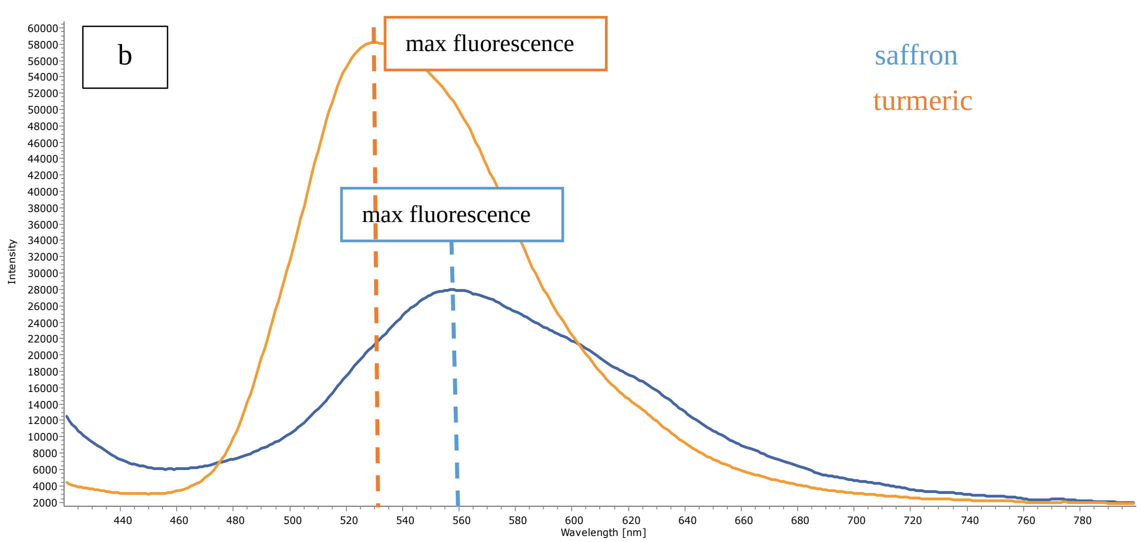


Figure 5-18: An example of yellow dyes identified in this project (manuscript Persian 933) FORS spectra(a), FOMF spectra(b)

5-2-5 Metallic pigments

5-2-5-1 Gold

Gold featured high on the palette of Persian paintings, especially the gold (*Tala* in Persian) obtained from the alluvial queries, which once exited in the Iranian territory. According to historical recipes, gold (tala in Persian) was applied in two forms: with a polished metallic effect (*tala-yi pukhta*) and with a matt finish (*talā-yi khām*) (Rahpeyma 2015, p. 204). Similar to other precious metals gold was used either as a foil applied to the surface with the aid of an adhesive or in the form of powder mixed with a binder. The ancient recipes recommended the use of glue as a binder for gold, and either glue or gum-Arabic (preferred) as a binder for silver (Knipe et al. 2018, p. 31; Pakzad 2016, p. 13). Extensive information is provided in historical references (Mayil Haravi 1993; Qāżi Aḥmad 1973) regarding the method of preparing gold. They further mentioned the use of dyes such as saffron or turmeric on the sheet of gold, also mixing silver powder with gold pigment to reduce costs in less luxuries manuscripts.

In almost all the *Shāhnāma* manuscript analysed in this study, gold was used extensively, both for the background and sky, and for details such as vessels, arms and armour, and some architectural features. In most cases, the gold is of high purity but in some paintings bright high purity gold was deliberately alternated with lighter silver-rich gold to create colour differences or reduce the price. For example, in the *Shāhnāma* manuscript AKM 4, Persian 933, and Or 420 the golden colour used to paint the background and the sky is obtained by combining gold with silver, in the cases which applied this mixture background of the painting has black layers or gold is detached of paper (Persian 933 and Or 420) due to the corrosion of silver.

Mixture of gold + orpiment, gold + yellow dyes, and gold + orpiment and silver also were identified. Gold is clearly recognizable by the relevant amount of gold in the XRF spectrum, the characterizing Au lines are at 9,71 (Lα) and 11,44 (Lβ) keV (Fig. 5-19) (Bevilacqua et al. 2010, p. 225; Knipe et al. 2018, p. 31). Gold can be identified by the FORS technique. It has an inflection point in the range of 510–540 nm and the rise in the yellow region is less steep, so that the whole spectrum appears to be less sigmoid-shaped than that of other yellow pigments, resembling more the spectrum of gold.

It must be kept in mind, though, that the inflection points can vary greatly when these pigments are mixed with a white pigment, so that the values cited must be seen as indicative only (Fig. 5-19) (Aceto et al. 2016, p. 1493).

It must be noted that in many XRF and FORS spectra of other colours, there is evidence of the presence of gold. Therefore, the presence of gold in the FORS spectrum of other colour, especially yellow and red, causes problems in identifying them. Gold is detectable in the FORS technique by the inflection point at 510-540 nm but the presence of gold in the vicinity of other colour or mixed with them, causes problems. For example, it changes the inflection of the orpiment from 480 nm to 490-500 nm, which makes it difficult to distinguish the orpiment from gold.

Moreover, the presence of gold in the FORS spectrum of red lead creates a change in the inflection point of red lead from 565 nm to 590 nm and makes it difficult to distinguish read lead from the other red colour, i.e. cinnabar which has an inflection point at 600 nm.

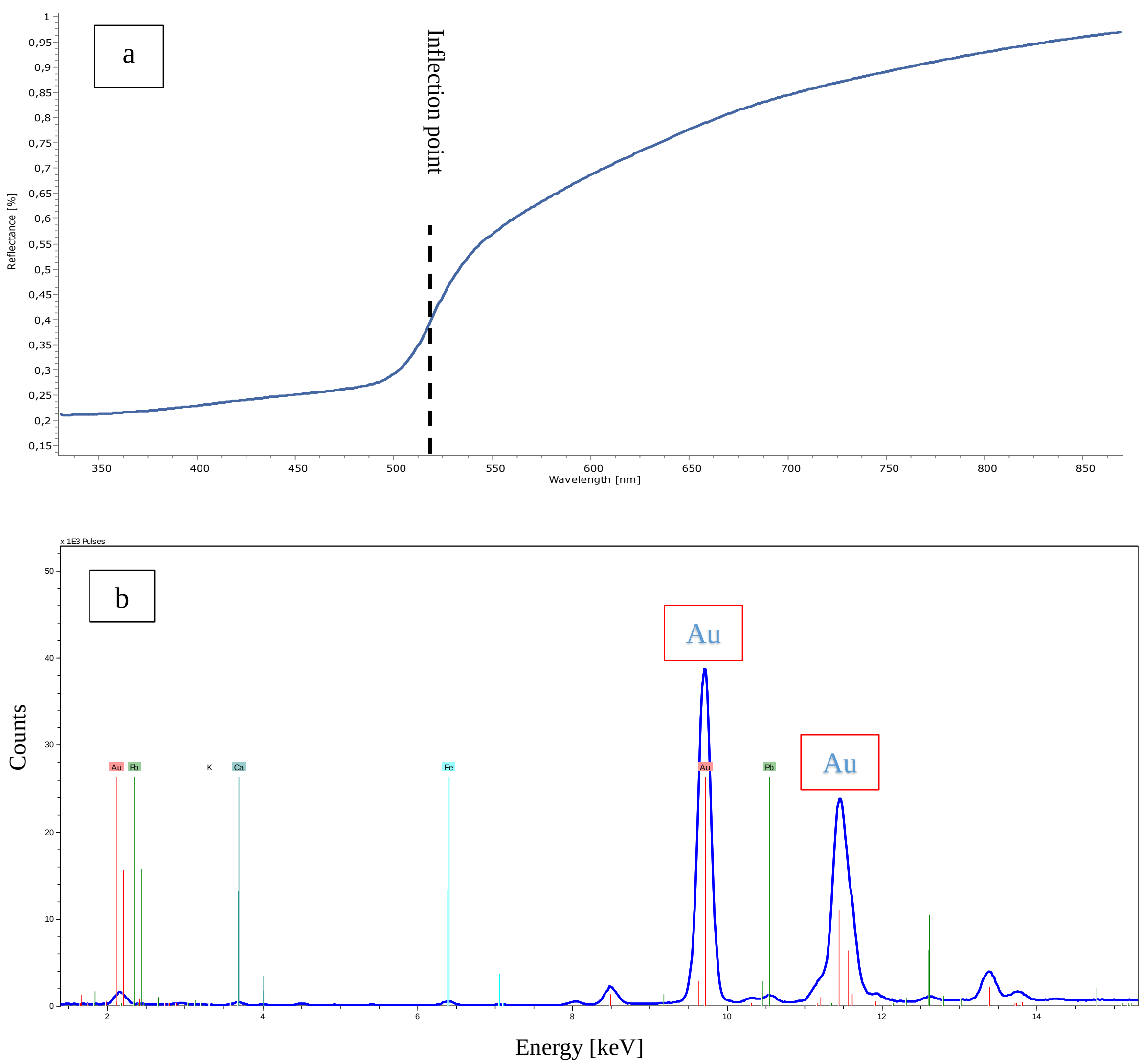


Figure 5-19: An example of metallic gold identified in this project (manuscript Ms 22-1948) FORS spectra(a), FOMF spectra(b)

5-2-5-2 Silver

Another metal pigment identified is silver, which is currently seen as black or dark grey due to its corrosion. Silver Ag (Persian *Noghreh*) is the metal found naturally in its pure, free form (native silver), as an alloy with gold and other metals, and in minerals such as argentite and chlorargyrite (Rutherford 1966, p. 157). Based on treatises references the method of preparation and usage of silver in Persian Manuscripts are those of gold (Mayil Haravi 1993; Qāżi Aḥmad 1973).

According to old recipes, the silver applied in Persian manuscripts was pulverised and mixed with a binder in order to be used as a paint like gold. However, after being exposed to atmospheric gases for some time, silver turns dark resulting in black silver chloride or silver sulphide on its surface. This would make its distinction from dark inks or pigments very difficult (Knipe et al. 2018, p. 31). In many Persian manuscripts silver is seen as dark grey.

Almost in all the *Shāhnāma* manuscripts in this project silver pigment was identified as dark grey except manuscript Or 420. Silver was frequently used for colouring armour, sword, water features, such as rivers and fountains, and architectural features, such as doorways or windows. Silver is clearly recognizable by the relevant amount of Silver in the XRF spectrum, the characterizing Ag lines are at 21,990 (Kα) and 2,97 (Lα) keV (Fig. 5-20) (Bevilacqua et al. 2010, p. 225; Knipe et al. 2018, p. 31). but in the FORS technique silver is not detectable through.

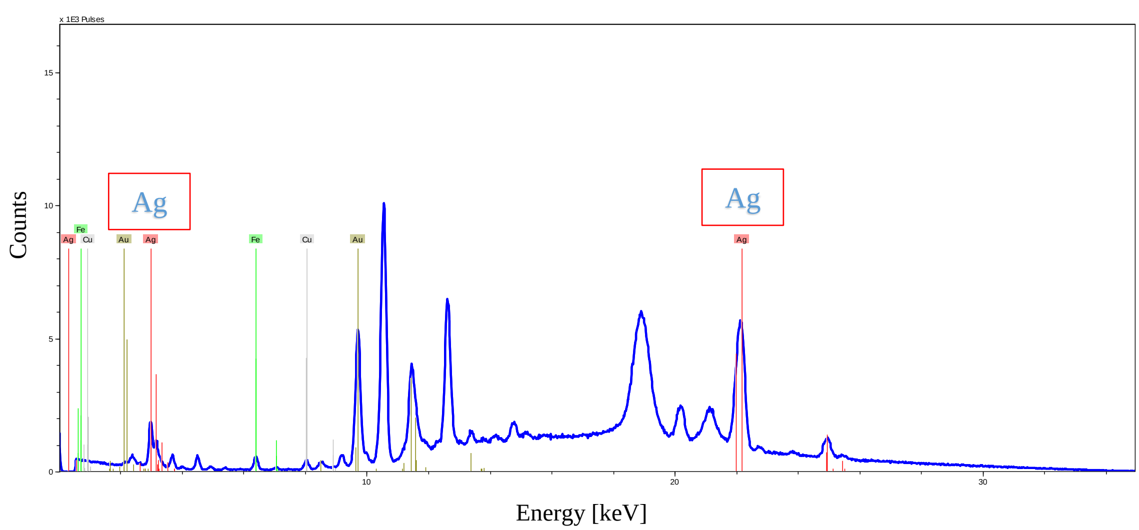


Figure 5-20: An example of XRF spectra of metallic silver identified in this project (manuscript AKM 6)

5-2-6 Pink, Violet, and Purple Colures

Main colour materials were used in Persian manuscripts to create pink and violet are cochineal and Indian lac (see section 5-2-4). Violet and purple hues were usually the results of a mixture of a dye mix with a pigment or other dyes, which according to historical recipes were lac dye (Indian lac) and red dye (cochineal) mixed with ultramarine, cinnabar or indigo mixed with white lead to lightening the tonality of colours (Rahpeyma 2015, p. 187).

As mentioned by Anselmi et. al (2015), very dark purple colour in some Persian manuscripts was obtained by mixing ultramarine blue with an insect-derived anthraquinone dye.

However, there is no specific record of how purple hues were generally obtained by Persian manuscript painters. The only published analytical data refer to the use of a mixture of ultramarine and cinnabar in a purple area is (Muralha et al. 2012, p. 25). Also, Knipe et al. (2018) mentioned a variety of combinations of ultramarine, indigo, cinnabar, red dyes to create violet and purple. Nonetheless with the increases in the non-invasive methods of identification, significant progress will be made towards the identification of organic red colourants on manuscripts (Anselmi et al. 2015, p. 191).

In all *Shāhnāma* manuscripts in this project, different pink, violet, and purple colour materials were identified. For pink hue cochineal, Indian lac, and red lead or cinnabar + white lead and for violet and purple different mixture of colour materials like ultramarine + cinnabar, ultramarine + cochineal or Indian lac, indigo + cochineal or Indian lac, were identified.

A combination of mentioned analytical techniques was used to identify pink, violet, and purple colour s, since spectral features of many of these colour materials has been explained before only spectral features of a more common mixture of these colour materials are shown below.

Unfortunately, the combination of colour materials contributes to a reduction of FORS diagnostic capabilities. A combination of two or more colourants produces a very confusing spectrum in most situations, in which the reflectance characteristics of the individual materials are barely recognizable and maybe completely concealed (Aceto et al. 2014, p. 1496).

5-2-6-1 Indigo + Cochineal or Indian lac

Since both parts of the mixture are dyes they are not recognizable by XRF but in the FORS technique indigo has a maximum absorption at 660 nm, cochineal two maximum absorptions at 510-520 nm, and 560-580 nm and Indian lac has maximum absorptions 527-540 nm and 570/585 nm (Fig. 5-21).

5-2-6-2 Ultramarine + Cinnabar

The blue part of this mixture (ultramarine) is recognizable with a max absorption at 600 nm in FORS technique and the red part of the mixture (cinnabar) is recognizable with the presence of Hg element in XRF spectra.

It must be noted that due to the interaction between ultramarine and cinnabar in the FORS spectra maximum absorption of ultramarine has a hypsochromic shift from 600 nm to 590 nm and cinnabar in this mixture is not recognizable by FORS (Fig. 5-22).

5-2-6-3 Ultramarine + Cochineal or Indian lac

Both parts of the mixture are recognizable by FORS, ultramarine with maximum absorption at 600 nm and cochineal/Indian lac by two maximum absorptions at 820-540 nm and 560-580 nm. It must be noted as mentioned before due to shifting the spectra in this mixture is not possible to distinguish between cochineal and Indian lac (Fig. 5-23).

5-2-6-4 Ultramarine + Indigo

Both parts of the mixture are recognizable by FORS, but ultramarine has a hypsochromic shift from 600 nm to 590 nm and indigo from 660 nm to 640 nm (Fig. 5-24).

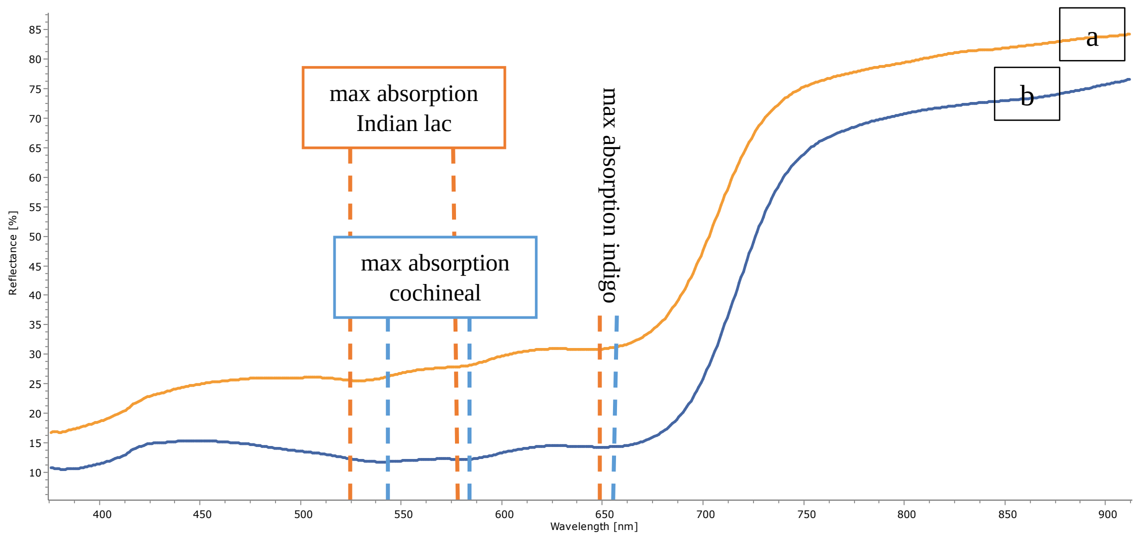


Figure 5-21: An example of FORS spectra of mixture indigo + Indian lac(a) and indigo + cochineal(b) identified in this project (manuscript Persian 9 and 933)

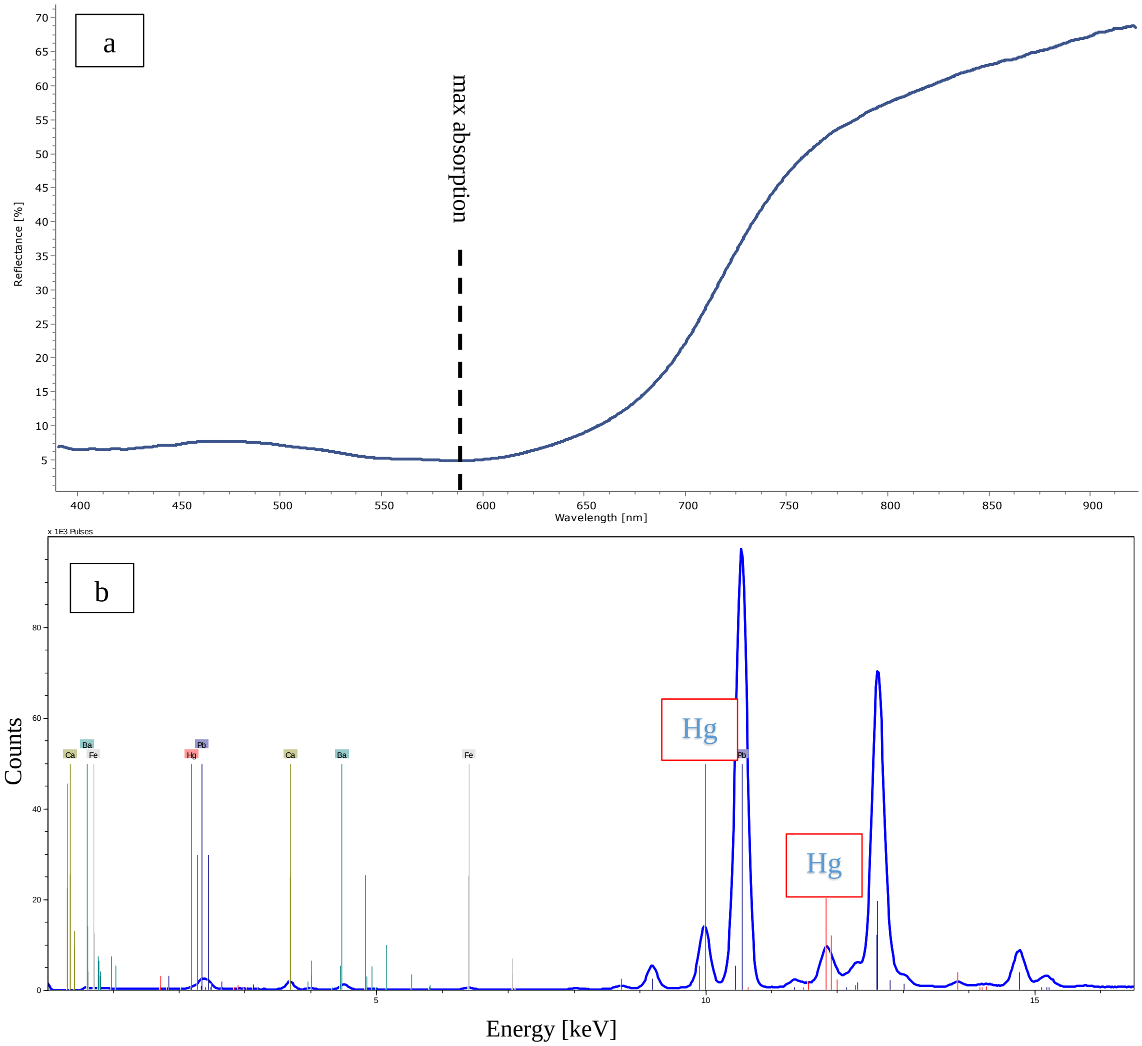


Figure 5-22: An example of mixture ultramarine + cinnabar identified in this project (manuscript AKM 4 and 5) FORS spectra(a), XRF spectra(b)

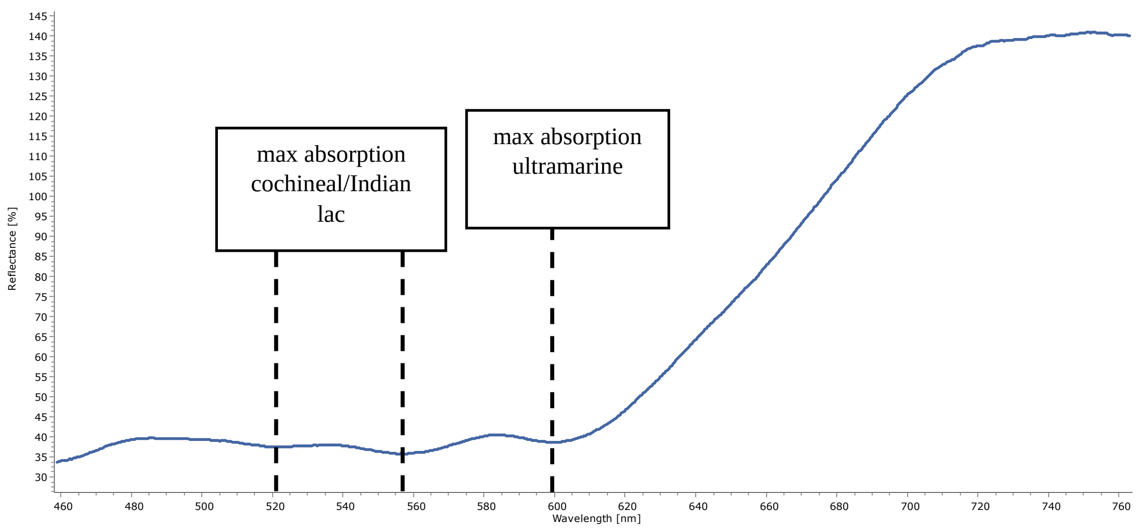


Figure 5-23: FORS spectra of mixture ultramarine + cochineal or Indian lac identified in this project (manuscript AKM 269)

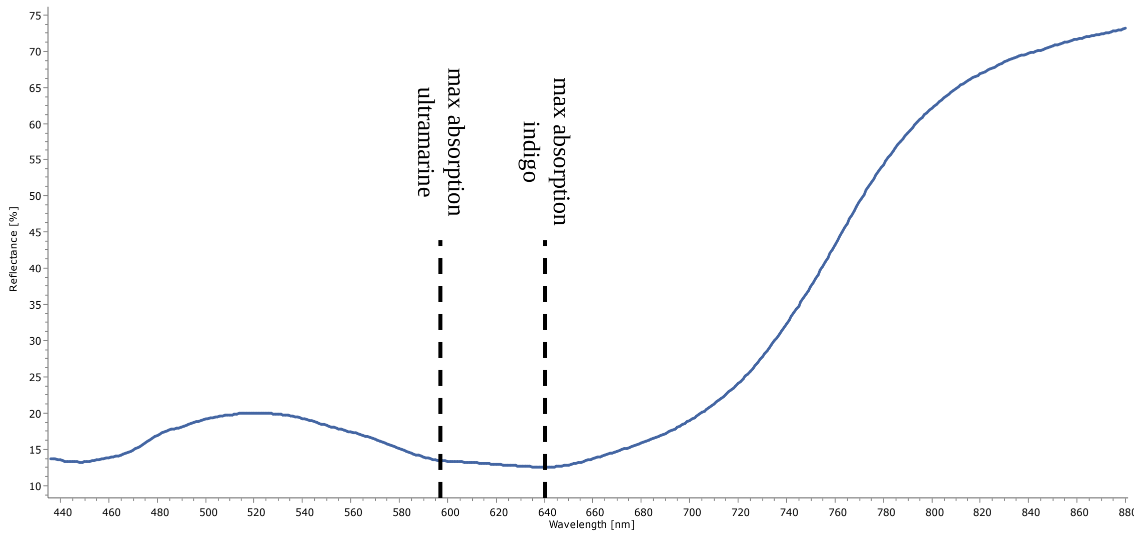


Figure 5-24: FORS spectra of mixture ultramarine + indigo identified in this project (manuscript RAS 239)

5-2-7 White and Black

5-2-7-1 White Lead

White lead ($2PbCo_3.Pb(OH)_2$), or Persian *sefeed-ab* or *sefeed-ab sheikh* is basically lead carbonate with the formula of $2PbCO_3$ $Pb(OH)_2$ (Pakzad 2016, p. 13; Rutherford 1966, pp. 174-5). This artificial pigment is obtained by synthesis from lead or from its ores, but even its natural version, idrocerrusite, is not common for use as pigment. To produce white lead, the materials must be exposed to vinegar fumes and then to carbon dioxide. It degrades in the presence of sulphides with formation of black compounds (Pakzad 2016, p. 13; Rutherford 1966, pp. 174-5). It used as a white pigment either forming a minor constituent in dark areas or mixed with other pigments to obtain lighter hues (Anselmi et al. 2015, p. 188). Like others this study also identified lead white as the primary white phase and the main white mentioned in historic sources, which provided the recipe for its production (Mayil Haravi 1993; Qāżi Aḥmad 1973).

In all the *Shāhnāma* manuscript analysed in this project white lead was used either as a mixture with other colour materials and or in some cases individually to paint architectural details, clothing, and flags. White lead is clearly recognizable by the relevant amount of lead in the XRF spectrum, the characterizing Pb lines are at 10,50 (Lα) and 12,62 (Lβ) keV with interference of As at 10,53 (Kα) keV (Fig. 5-25) (Bevilacqua et al. 2010, p. 179; Larsen et al. 2016, p. 661). As predicted, the main material used in all the analysed points was white lead therefore white lead has been repeatedly detected in all XRF spectrum of the colours analysed in all manuscripts. The lack of colour makes these materials difficult or impossible to identify using UV-Vis FORS. White corresponds to almost complete visible radiation reflection, so the lead white, bone white and gypsum reflectance spectra, three of the most common manuscript illumination pigments, are very close in the near UV and visible range, showing a relatively flat line with high reflectance values (Aceto et al. 2014, p. 1496).

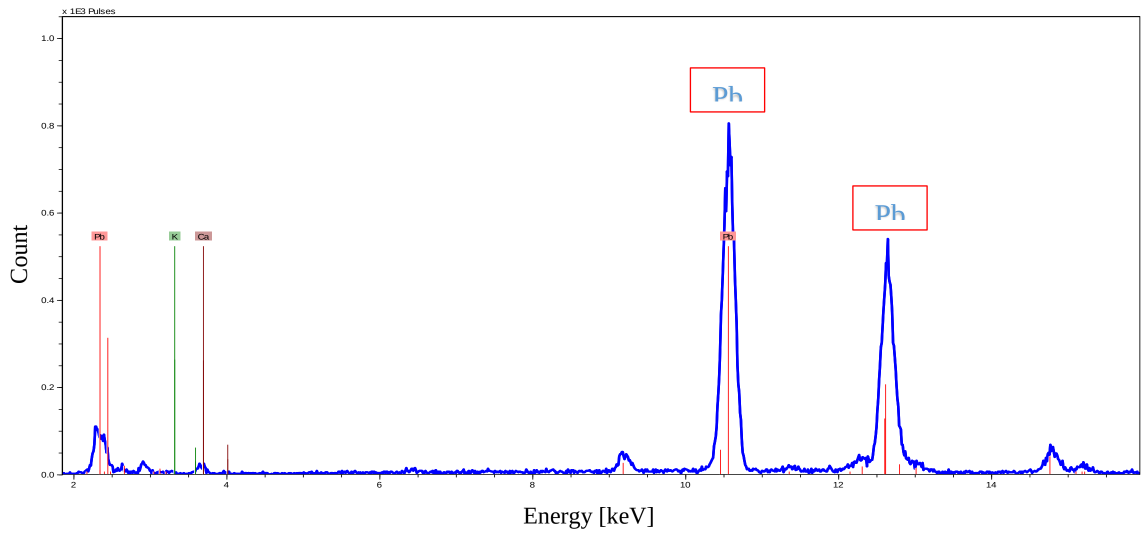


Figure 5-25: XRF spectra of white lead identified in this project (manuscript RAS 239)

5-2-7-2 Black carbon

Black carbon and iron gall ink are most common black colour used in Persian manuscripts. The black carbon is defined by the term soot (or *dūda* in Persian) (Rahpeyma 2015, p. 201; Pakzad 2016, p. 13), and is usually used in the production of inks for text of manuscripts or as colour to paint the miniatures. This organic pigment has been in use since the first century AD and has a very fine appearance: it is composed of 99% amorphous carbon obtained by the combustion of oils, fats and oils and has a discreet covering power (Khosravi 2007, p. 7).

Iron-gall ink in another brown iron-based colourant obtained by adding Fe (II) sulphate to an aqueous extract from gallnuts. Apart from its widespread use in writing from early medieval times, iron-gall ink had also a utility as a colourant in miniature painting, with shades ranging from brown to black (Rutherford 1966, p. 124 and 102-5).

In all the *Shāhnāma* manuscript in this project black carbon (most probably soot) was identified black is often used to show painting details, such as details of buildings, clothes, or horses.

It should be noted that although carbon black (mainly soot) is not detectable by XRF technique, the absence of iron in the XRF spectrum of black spots seemed to be sufficient to prove the use of carbon black since the colour material used as black in Persian manuscripts is limited to carbon black and iron-based black (gall ink). It must also be mentioned that in the FORS technique, these two types of black colour have a smooth and similar peak, and in general, the FORS technique does not have the ability to detect black and white colours.

Note: Therefore, it might be possible to place some of the colours classified in this section in other colour categories, for example, some of the colours classified as pink can be considered as purple, and vice versa. However, based on the project objectives, these colours were placed in three categories: gray, pink, and purple.

5-3 Survey manuscripts from a material science point of view

5-3-1 Shāhnāma manuscript AKM 4[35]

All six samples of blue analysed in this manuscript are made of ultramarine. These colour samples have often been used to paint the sky and clothes (Tab. 5-1). In order to create the desired tonalities, the painter of this manuscript has combined ultramarine with different amounts of white lead and has made colour tones from dark blue to light blue (sky-blue). The blue colour used for the clothes has been prepared with greater amounts of white lead to create a sky-blue colour tone which has been decorated with black, red (cochineal), and gold to mark the details of the clothes.

Since the constituents of ultramarine are light elements such as sulfur (S), silicon (Si), aluminum (Al), etc., the detection of ultramarine is not possible by portable XRF devices (see section 5-3-1) but fortunately one of the pigments which the FORS technique can easily detect is ultramarine (Fig. 5-11). In places where ultramarine is applied to dye clothes, gold is used to specify the detail of the dress, i.e. gold is used on the ultramarine (Fig. 5-26).

[35] In this respect, I would like to thank Branden Cesare Rizzuto who performed the XRF analysis on this manuscript.

Folio number	Description	Colour material	Colour tonality
AKM 45	blue of sky	ultramarine blue	a
AKM 45, 46, 47, 48, 49	robes and clothing	ultramarine + white lead	b

Table 5-1: Distribution of blue colour materials used in manuscript AKM 4

Figure 5-26: Comparison of tonality of different blue colour materials in manuscript AKM 4; ultramarine blue(a), ultramarine blue + white lead (b)

In this manuscript, 15 colour samples including red, orange, and brown tones were analysed. The four pigments used for these colour tones include red lead, cinnabar, red ocher, and cochineal (Tab. 5-2).

Cinnabar and red lead are the two main pigments used for red and orange in Persian manuscripts in all different periods and schools, and as expected, they have been used many times in this manuscript as well. The colour produced by red lead is lighter than cinnabar and is more orangish, and in many cases, it has been used to dye clothes, flags and small orange flowers, while cinnabar, which creates a darker red than red lead has been more used for colouring clothes, barding and red background flowers (Fig. 5-27).

In some cases, the two pigments have also been used as red and orange, one over the other, to specify details. Red ocher pigment has been used to create a brown tint. In this manuscript, the painter has combined red ocher with white lead to create different shades of brown and used them to paint horses, clothes, and tree trunks (Fig. 5-27).

Two vivid cases of used of cochineal as a dark red appear in the manuscript, one on folio 48 for the background and one on folio 46 for blood, though it has been frequently applied as red to highlight the details of clothes, flowers, etc. in the form of fine lines on other colours (Fig. 5-27).

The red lead, cinnabar, and red ocher pigments were detected by a combination of XRF and FORS techniques (see section 5-2-2), and cochineal dye by a combination of FORS and FOMF techniques (see section 5-2-2-4). As mentioned before, the biggest challenge for the detecting varieties of red was distinguishing red lead from cinnabar due to the presence of lead element in most XRF spectra taken from Persian manuscripts since they had used white lead excessively.

Folio number	Description	Colour material	Colour tonality
AKM 45, 47, 48, 49, 46	clothes, flags, flowers	red lead	a
AKM 45, 48, 49, 46	flags, robes, clothing	cinnabar	b
AKM 47, 49, 46	horses, robes	red ocher	c
AKM 48, 46	flowers, blood	cochineal	d

Table 5-2: Distribution of red, orange, brown colour materials used in manuscript AKM 4

Figure 5-27: Comparison of tonality of different red, orange, brown colour materials in manuscript AKM 4; red lead(a), cinnabar(b), red ocher(c), cochineal(d)

According to the analyses (3 spots were analysed), the main material used for yellow colourrs in this manuscript was orpiment (Tab. 5-3). On the dark yellow part of the dress, on folio 45, the painter has used a highlight layer of yellow dye (most probably saffron or turmeric) on the orpiment, and this has caused the yellow colour to become slightly darker (dull yellow). The details of the dress are specified with cochineal on the orpiment. Orpiment has been used to colour clothes and flags (Fig. 5-28). It should be noted that the detection of yellow dyes by the XRF technique is not possible, and their detection is possible only by combining the two techniques of FORS and FOMF (see section 5-2-4-3).

Folio number	Description	Colour material	Colour tonality
AKM 45, 48	clothing, flag	orpiment	a
AKM 45	clothing	orpiment + yellow dye	b

Table 5-3: Distribution of yellow colour materials used in manuscript AKM 4

Figure 5-28: Comparison of tonality of different yellow colour materials in manuscript AKM 4; orpiment(a), orpiment + yellow dye(b)

In this manuscript, the combination of Indian lac with white lead has been used to create pink/violet colour to paint the background and clothes (7 pink, violet, and purple spots were analysed). Unlike many manuscripts analysed in this project, this manuscript uses Indian lac instead of cochineal to create pink and violet (Tab. 5-4). Indian lac is not detecTab by the XRF technique but can be detected by the FORS and FOMF techniques (see section 5-2-2-4).

The two main ingredients of violet and purple in this manuscript are ultramarine and cinnabar, which have been combined with other materials such as white lead and orpiment in accordance with the tonality desired by the painter (Tab. 5-4).

It seems that this colour combination has been achieved in two ways: as a combination of ultramarine and cinnabar, or the use of cinnabar first and then the application of ultramarine on it. In the purple colour sample on folio 48, which has a blue (ultramarine) component of the above-mentioned colour combination, the red colour used can be seen under the blue colour.

This colour combination has been used to paint clothes, flowers, and horse saddles (Fig. 5-29). The pigments used to produce purple can be easily detected by combining the XRF and FORS techniques (see section 5-2-6-2). It should be noted that in the dark purple colour used to colour the clothes on folio 45, a combination of ultramarine with cinnabar, white lead and orpiment has been used.

Folio number	Description	Colour material	Colour tonality
AKM 45, 48, 46	clothing, background, flowers	Indian lac + white lead	a
AKM 45, 47, 48	clothing	ultramarine + cinnabar	b
AKM 45	clothing	ultramarine + cinnabar and orpiment	c

Table 5-4: Distribution of pink, violet, and purple colour materials used in manuscript AKM 4

Figure 5-29: Comparison of tonality of different pink, violet, and purple colour materials in manuscript AKM 4; Indian lac + white lead(a), ultramarine + cinnabar(b), ultramarine + cinnabar and orpiment(c)

Seven samples of the green colour with different tonalities from light green to dark green of this manuscript were analysed. In this manuscript, a copper-based green combination has been used to create a light green colour (close to turquoise colour), which the painter has combined with white lead to achieve the desired tonality (Tab. 5-5). This type of light green has been used for painting horse cover and barding (Fig. 5-30). Copper-based green pigments can be detected by XRF and FORS (see section 5-2-1-2).

In this manuscript, the combination of indigo with orpiment has been used to create dark green, which is the most common colour material used to create green in Persian manuscripts (Tab. 5-5). This colour combination has been used to paint the foliage of trees and the leaves of flowering shrubs (Fig. 5-30). In this colour combination, the yellow part of the combination (orpiment) can be detected through the XRF and FORS techniques and the blue component (indigo) can be identified by the FORS technique (see section 5-2-1-1).

Folio number	Description	Colour material	Colour tonality
AKM 45, 48, 46	the tufts of grass, foliage of trees	indigo + orpiment	a
AKM 45, 48, 46, 47	barding, clothing	copper Green	b

Table 5-5: Distribution of green colour materials used in manuscript AKM 4

Figure 5-30: Comparison of tonality of different green colour materials in manuscript AKM 4; indigo + orpiment(a), copper green(b)

Two types of metallic pigments were detected in the manuscript (5 spots of metallic pigments were analysed) (Tab. 5-6). As expected, like in many other Persian manuscripts, gold has been frequently applied as gold colour with and without metallic luster. In this manuscript gold pigment has been used to paint the background as well as specifying details of clothes and architectural elements, flowers, etc. (Fig. 5-31). The gold used to paint the background and the sky is obtained by combining gold with silver, in the cases which applied this mixture background of the painting has black layers or gold is detached of paper due to the corrosion of silver (see section 5-2-5-1).

Another metal pigment used is silver, which is currently seen as black or dark grey due to its corrosion. This metal pigment has been used to depict river and stream water, swords, and armor (Fig. 5-31). These two metal pigments can be detected in the XRF spectrum by the gold and silver elements, but in the FORS technique silver is not detecTab through (see section 5-2-5).

It should be noted that the light grey colour used to paint the background decoration of folio 47 is a combination of indigo with red lead, which is not a common colour combination to create a grey colour (Fig. 5-31). this coloured spot may have actually been purple (indigo + red lead), which red lead pigment of colour mixture probably has been corroded and became black (see appendix 1). The white colour used in this manuscript (9 white and black spots were analysed), as expected, was a white lead pigment applied repeatedly for colouring the background, clothes, headscarves, and flags (Tab. 5-6). White lead is not detecTab by the FORS technique, but in its XRF spectrum, the element lead is well recognizable (see section 5-2-7-1).

However, it must be noted that since the painters of Persian manuscripts have combined most colours with white lead to change colour tonality, most of the pigments have lead element in their XRF spectrum. Like in other Persian manuscripts, the black colour used in this manuscript is carbon-based pigment (black carbon) (Tab. 5-6), but the black colour used to dye the clothes on folio 49 is a combination of ultramarine and red lead (Fig. 5-31).

It seems that the original colour has been purple (ultramarine + red lead), but its red component, i.e. red lead has been corroded and turned into black, which is why this colour is now seen as black.

Folio number	Description	Colour material	Colour tonality
AKM 45, 48, 46	river water, swords, and armour	degraded silver	a
AKM 47, 48, 49	background, details	gold	b
AKM 47, 49, 46	background, flag, clothing	white lead	c
AKM 46, 47	horses, boat	black carbon	d
AKM 47	clothing	indigo + red lead	e
AKM 49	clothing	ultramarine + red lead	f

Table 5-6: Distribution of metallic, black, white, and grey colour materials used in manuscript AKM 4

Figure 5-31: Comparison of tonality of different metallic, black, white, and grey colour materials in manuscript AKM 4; degraded silver(a), gold(b), white lead(c), carbon(d), indigo + red lead(e), ultramarine + red lead(f)

5-3-1-1 Statistical analysis the Shāhnāma AKM 4

This manuscript as an example of the Turkman style manuscript of 15th century of Shiraz has all features of Turkman painting school (see chapter 3). From the point of view of material science, all of miniatures of this manuscript are original and are good examples to comparison between the colour materials used in ultramarine school whit other schools of Persian manuscripts, therefore, colour materials of all five miniatures of this manuscript were analysed. Indeed 117 single measurements contain; 53 FORS analysis, 53 XRF analysis, and 11 FOMF analysis were performed on this manuscript (see Tab. 5-57).

Due to the structure of Turkman paintings of Shiraz, the colours used in this manuscript are uniformly and the motifs have little details and have been painted simply.

The pigments are simply blended and used. The details of the clothes and motifs are marked with thin lines of metallic gold and thin red lines of cochineal. All five miniatures of this manuscript have a light background with different colour tones.

Due to the historical recipes and other similar articles, three colour materials ultramarine, azurite, and indigo have been used as blue in Persian manuscripts, but in this manuscript, as mentioned below, all 6 samples of blue analysed, i.e. 100 percentage of analysed blue samples contained ultramarine pigment, this percentage for green colour includes 57% copper green pigment and 43% orpiment + indigo. 75% of the grey colours are actually metallic silver pigments that have been corroded and 25% contain indigo + red lead. 60% of the analysed gold samples contain gold pigment with metallic luster and 40% of the samples are composed of a combination of gold and silver and have a less metallic luster, and even in some places due to corrosion of silver, this colour has fallen and turned black.

The materials used for pink, violet, and purple tones in the Persian manuscripts are usually varied and include a wide range of pigments and dyes, but in this manuscript, only two colour combinations have been used to create pink, violet, and purple colours. 57% of the analysed pink, violet, and purple spots are the combination of ultramarine + cinnabar and Indian lac contains 43% of the analysed samples. red lead pigment 37% and cinnabar 31%, red ocher 19%, and cochineal 13% contain the colour samples analysed in red, orange, and brown tones. 67% of yellow samples contain orpiment and 23% of them contain the combination of orpiment + yellow dye.

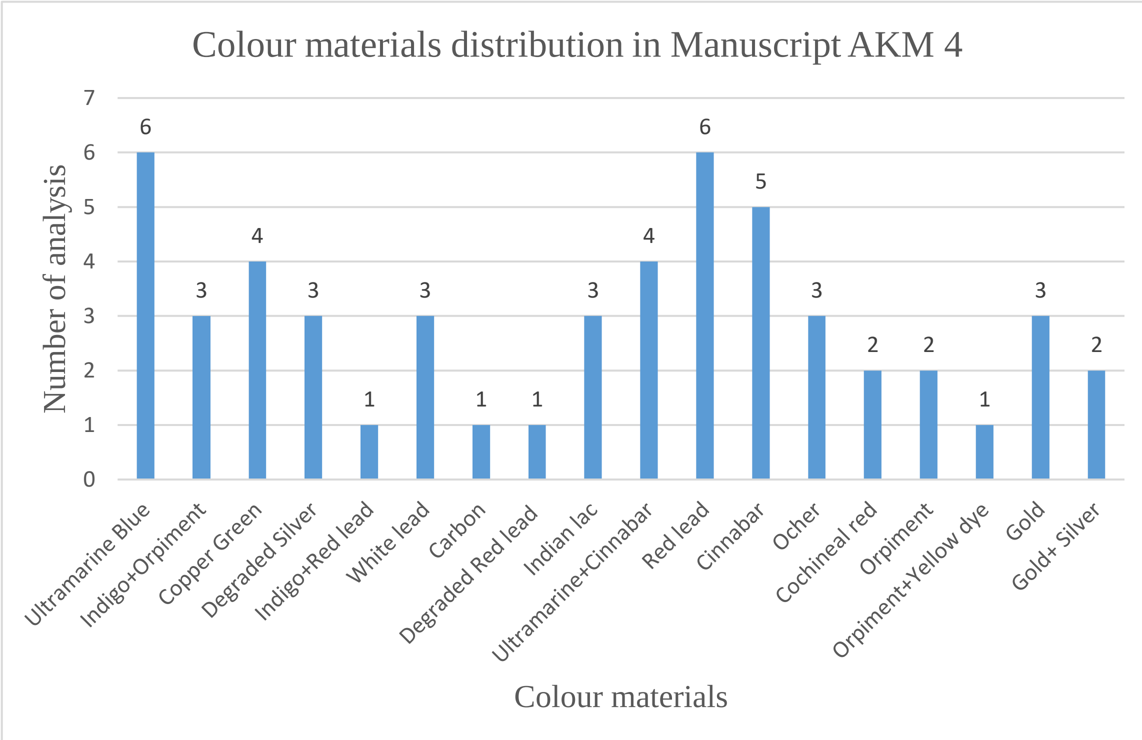
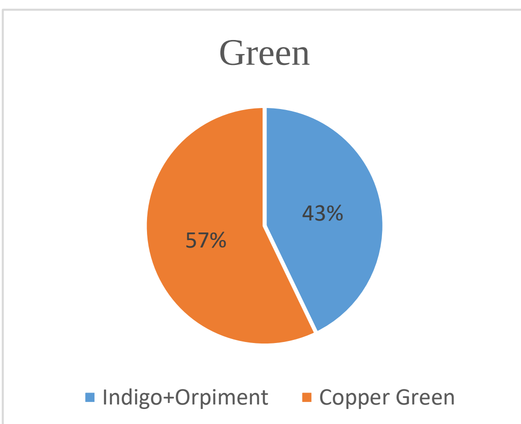
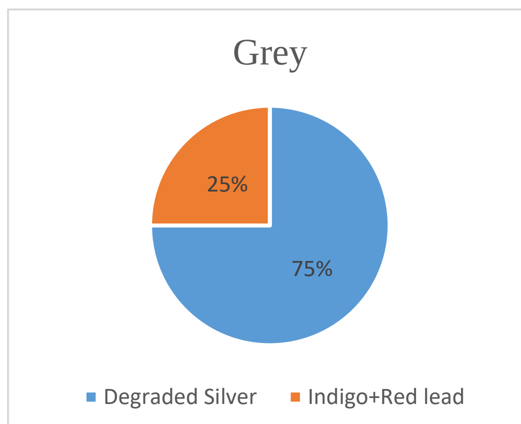
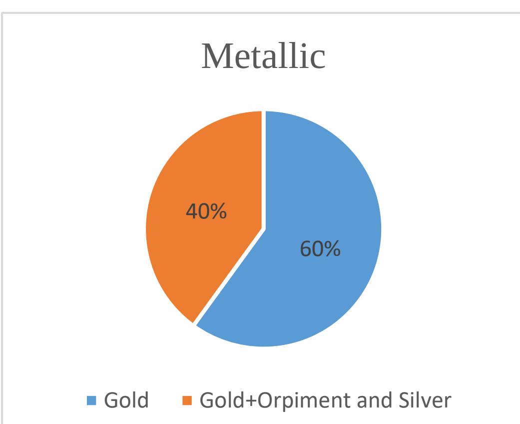
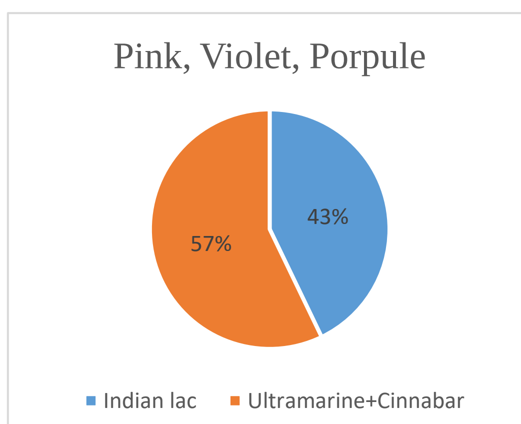


Figure 5-32: Distribution of colour materials used in manuscript AKM 4









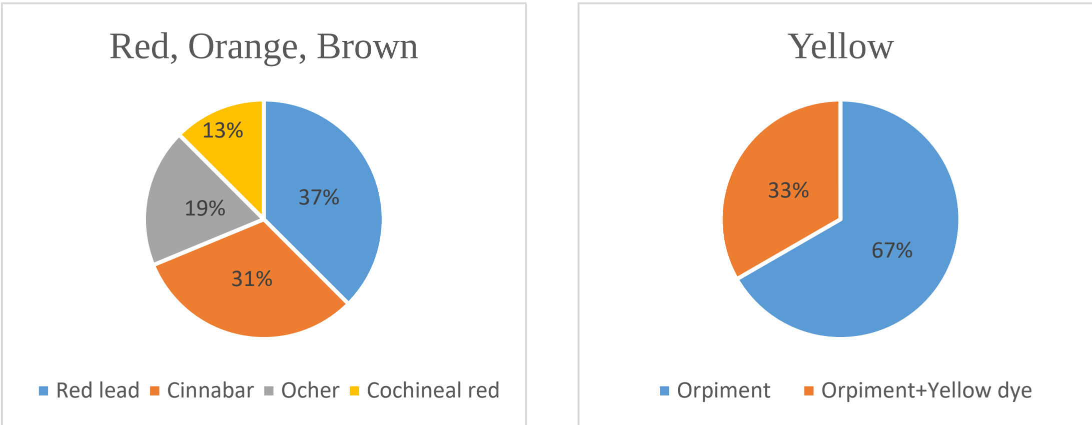


Figure 5-33: Percentage of colour materials used for each colour in manuscript AKM 4

5-3-2 Shāhnāma manuscript AKM 5[36]

Six blue spots with light blue to dark blue tonalities were analysed in this manuscript. The painters of this manuscript have used ultramarine as the main material for painting blue spots and to create different tonalities of blue, they have combined it with different amounts of white lead, and thus different types of blue colours have been created (Tab. 5-7).

The sky is painted with a light blue colour, which is a combination of ultramarine and white lead. This colour combination has also been often used as a light blue for colouring clothes (Fig. 5-34). On folio 53, the turquoise (very light blue) colour of the clothing has been created from a combination of ultramarine and white lead. Ultramarine has also been used separately to paint different clothes. The ultramarine and white lead used to create blue can be easily detected, with a combination of XRF and FORS techniques (see section 5-2-3-1).

Folio number	Description	Colour material	Colour tonality
AKM 51, 52, 54	blue of sky and clothing	ultramarine blue	a
AKM 51, 52, 53	robes and clothing	ultramarine + white lead	b

Table 5-7: Distribution of blue colour materials used in manuscript AKM 5

[36] In this respect, I would like to thank Branden Cesare Rizzuto who performed the XRF analysis on this manuscript.

Figure 5-34: Comparison of tonality of different blue colour materials in manuscript AKM 5; ultramarine blue(a), ultramarine blue + white lead (b)

Like other manuscripts from Shiraz, the three main materials used for the colours red, orange, and brown in this manuscript are cinnabar, red lead, and red ocher (11 spots were analysed) (Tab. 5-8). Generally, the colour produced by cinnabar is dark red, while the colour produced by red lead is orange or orangish red. It should be noted that these two pigments have been used together most of the time and applied on top of each other to specify the details of the design.

The painters of this manuscript have used these two pigments to paint clothes, flags, backgrounds, flowers, and bards (Fig. 5-35). On folio 53, cinnabar has been used to create a dark red colour to paint blood, while most manuscripts have employed cochineal to show blood, which is interesting in its kind. These two pigments can be easily detected with a combination of XRF and FORS techniques (see section 5-2-2). Red ocher has been used to create a brown colour (Tab. 5-8). The painters of this manuscript have used red ocher to paint tree trunks, horses, shoes, and some clothes (Fig. 5-35). Red ocher can be detected by a combination of XRF and FORS techniques (see 5-2-2-3).

Folio number	Description	Colour material	Colour tonality
AKM 52, 53	clothes, robe, ground cloth	red lead	a
AKM 45, 48, 49, 46	flags, robes, clothing, flower, barding, blood	cinnabar	b
AKM 47, 49, 46	horses, tree trunk, clothing	red ocher	c

Table 5-8: Distribution of red, orange, brown colour materials used in manuscript AKM 5

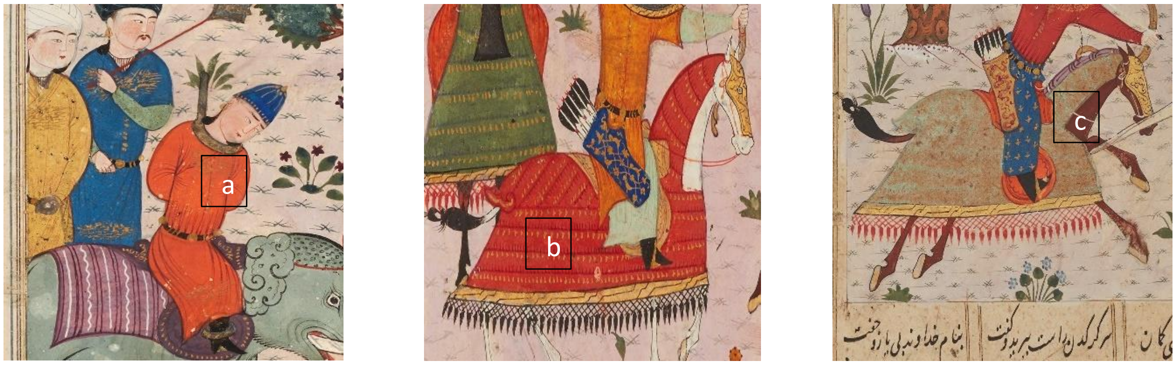


Figure 5-35: Comparison of tonality of different red, orange, brown colour materials in manuscript AKM 5; red lead(a), cinnabar(b), red ocher(c)

The main colour material used for yellow in this manuscript is orpiment (6 yellow spots were analysed) (Tab. 5-19). Interestingly, the painters have used a highlight red layer (red lead) on the orpiment in two orangish yellow spots on folios 51 and 52 (Fig. 5-36). This highlight red layer, which can also be seen with the naked eye, has caused the change in the FORS spectrum of the orpiment inflection point from 480 to 510-530 nm (Fig. 5-37). The painters of this manuscript have used orpiment to paint clothes, flags, and ground cloths. As mentioned before, orpiment can be detected by a combination of XRF and FORS techniques (see section 5-2-4-1).

Folio number	Description	Colour material	Colour tonality
AKM 51, 52, 53	clothing, flag, ground cloth	orpiment	a
AKM 51, 52	robes	orpiment + transparent red layer	b

Table 5-9: Distribution of yellow colour materials used in manuscript AKM 5

Figure 5-36: Comparison of tonality of different yellow colour materials in manuscript AKM 5; orpiment(a), orpiment + transparent red layer (b)

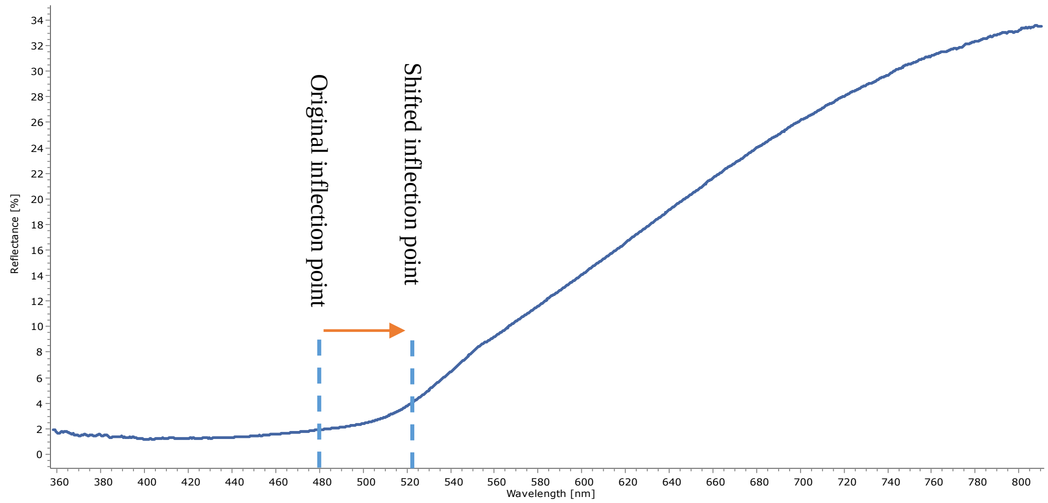


Figure 5-37: FORS spectra of orpiment under highlight layer of red lead

In this manuscript, 8 pink, violet, and purple colour samples were analysed. The combination of Indian lac and white lead has been used to create different tones of light pink. To make the light pink used for painting people's faces, the painters have applied a combination of red lead and white lead, but to create the light pink in the background (pink white), they have first painted the background with white lead and then used a very fine highlight Indian lac over white in order to create a light pink colour (Tab. 5-10).

On folios 51 and 53, the pink colour used to dye clothes is a direct combination of Indian lac with white lead. It should be noted that like the previous manuscript, Indian lac has been used instead of cochineal in this one as well, and as explained before, Indian lac can be detected by a combination of FORS and FOMF techniques (see section 5-2-2-4).

The painters of this manuscript have applied a combination of ultramarine blue and cinnabar to create the colour purple, which is used to colour robes and flags (Fig. 5-38). This colour combination can be detected by combining the XRF technique with FORS (see section 5-2-6-2).

Folio number	Description	Colour material	Colour tonality
AKM 51, 52, 53	robes, background	Indian lac + white lead	a
AKM 52	faces	red lead + white lead	b
AKM 51, 53, 54	robes, flag, ground cloth	ultramarine + cinnabar and orpiment	c

Table 5-10: Distribution of pink, violet, and purple colour materials used in manuscript AKM 5

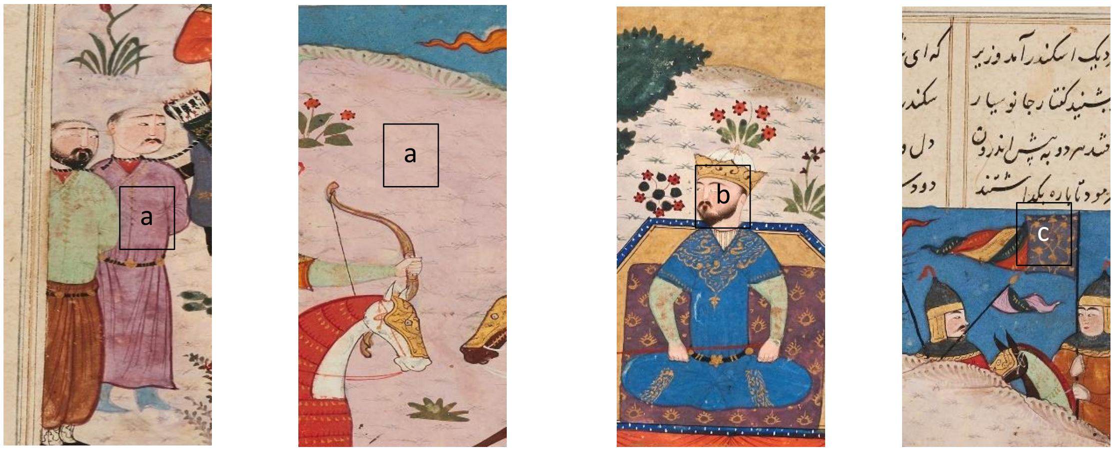


Figure 5-38: Comparison of tonality of different pink, violet, and purple colour materials in manuscript AKM 5; Indian lac + white lead(a), red lead + white lead(b), ultramarine + cinnabar(c)

In this manuscript, 10 colour spots with green tonality were analysed. As expected, the combinations of indigo with orpiment and copper-based green have been used as the two main materials to create green, and only in one case has the painter combined ultramarine with orpiment to make dark green (Tab. 5-11). The painters of this manuscript have created different shades of green from light green to yellowish green to dark green by combining different amounts of indigo with orpiment.

The orpiment used for this combination seems to have had large granulation because on folio 51, the yellow grains of the orpiment painted with this colour combination can be seen clearly in a part of the horse barding. This colour combination has been used to paint tree foliage, background grass, and horse barding (Fig. 5-39). This colour combination can be detected with a combination of XRF and FORS techniques (see section 5-2-1-1). The green colour produced by copper-based greens is a very light turquoise green, and is often used to colour robes, bow holders, and horse barding (Fig. 5-39).

The interesting point about the copper-based greens used in this manuscript is the corrosion of paper on all the spots coloured by copper green. In Persian manuscripts, copper-based green is usually combined with saffron to prevent corrosion of the paper by copper. Considering that corrosion can be seen in all the coloured areas painted with copper green, it can be concluded that all these copper green have been not combined with saffron to prevent corrosion of paper (Fig. 5-40).

Copper-based greens can be detected by a combination of XRF and FORS techniques, but it is not possible to distinguish between different types of copper greens (see 5-2-1-2). The painters of this manuscript have also used a combination of ultramarine and orpiment in a sample on folio 52 to create the dark green colour used to paint the foliage of the trees.

Folio number	Description	Colour material	Colour tonality
AKM 51, 52, 53, 54	the tufts of grass, foliage of trees	indigo + orpiment	a
AKM 51, 53, 54	barding, clothing	copper green	b
AKM 52	foliage of trees	ultramarine + orpiment	c

Table 5-11: Distribution of green colour materials used in manuscript AKM 5

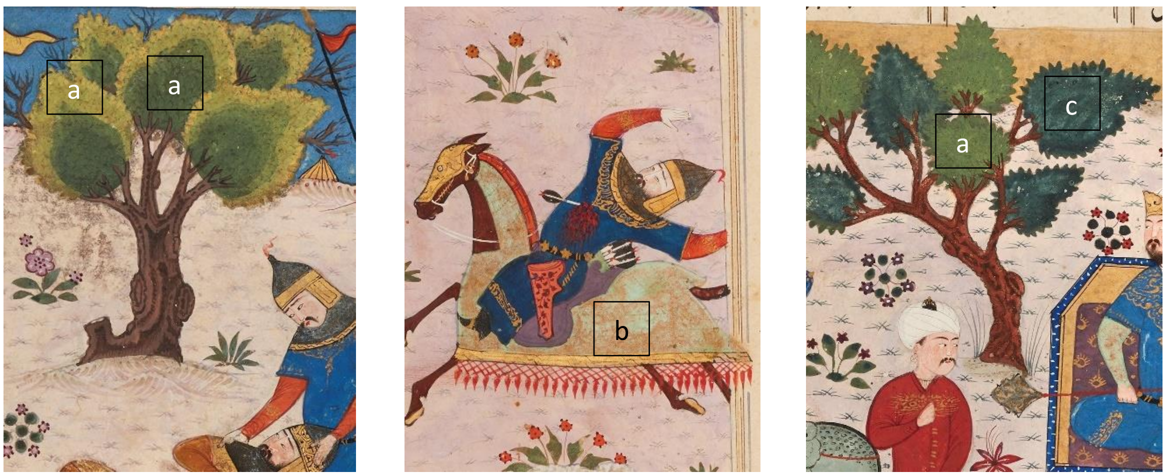


Figure 5-39: Comparison of tonality of different green colour materials in manuscript AKM 5; indigo + orpiment(a), copper green(b), ultramarine + orpiment(c)

Figure 5-40: Corrosion of paper by copper green

Three samples of gold colour used in the background of this manuscript were analysed. According to the results of FORS and XRF analyses of these points, the material used to create them is gold pigments (Tab. 5-12).

In the two samples analysed on folios 51 and 52 in the FORS peak of the colour sample, it can be seen that the maximum absorption falls within the range of 410-420, which indicates the use of yellow dye (probably saffron) in combination with gold; a colour combination applied in many Persian manuscripts. Another metal pigment used in this manuscript is silver pigment, which has been applied to paint armor, shields, swords, and barding (4 grey spots were analysed) (Fig. 5-41).

It should be noted that this pigment does not have a metallic luster due to corrosion and is seen as dark grey. This pigment can be detected by the XRF technique (see section 5-2-5).

It is worth mentioning that the painters of this manuscript have also used two colour combinations of indigo with white lead and ultramarine with white lead to paint the grey spots (Tab. 5-12). These two-colour combinations have been used to create the light grey tones for colouring animals (elephant and unicorn) seen on folios 52 and 54 (Fig. 5-41).

These colour combinations can be detected by an integration of XRF and FORS techniques (Fig. 5-42). The white and black pigments used in this manuscript, like in most Persian manuscripts, have been created with white lead and carbon-based pigments, respectively.

Folio number	Description	Colour material	Colour tonality
AKM 51, 53	swords, barding and armour	degraded silver	a
AKM 51, 52, 54	background, details	gold	b
AKM 52	elephant	indigo + white lead	e
AKM 54	unicorn	ultramarine + white lead	f

Table 5-12: Distribution of metallic, black, white, and grey colour materials used in manuscript AKM 5

Figure 5-41: Comparison of tonality of different metallic, black, white, and grey colour materials in manuscript AKM 5; degraded silver(a), gold(b), indigo + white lead(c), ultramarine + white lead(d)

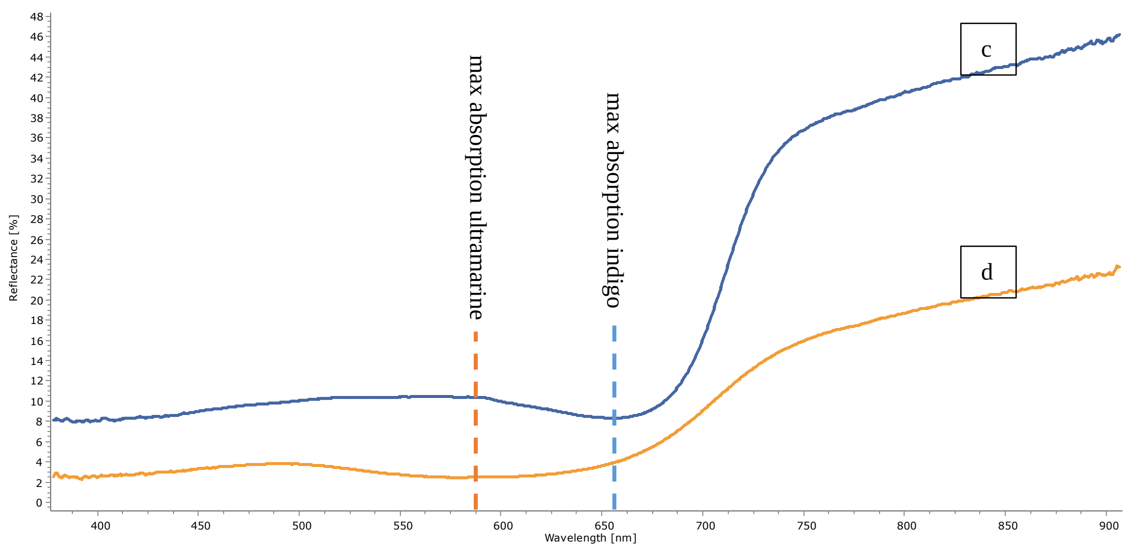


Figure 5-42: FORS spectra of indigo + white lead(c), ultramarine + white lead(d)

5-3-2-1 Statistical analysis the Shāhnāma AKM 5

This manuscript as previous manuscript is (AKM 4) is an example of the Turkman style manuscript of Shiraz dated 1494 CE (see chapter 3). The features of Turkman school in this manuscript are easily identifiable as manuscript AKM 4. The size of miniatures of this manuscript are bigger than other Turkman manuscript analysed (AKM 4 and AKM 269) and It has a higher colour variety compared other mentioned manuscript. From the point of view of material science, colour materials of this manuscript are similar to manuscript AKM 4 just a few differences have been distinguished for example in this manuscript yellow colour has been highlighted by a transparent red layer (red lead), and unlike manuscript AKM 4 in this manuscript cochineal is not used as red. Therefore, colour materials of four existing miniatures of this manuscript were analysed. Indeed 116 single measurements contain; 52 FORS analysis, 52 XRF analysis, and 12 FOMF analysis were performed on this manuscript (see Tab. 5-57).

From the point of view of statistical analysis, ultramarine is the only blue colour used in this manuscript. 60% of analysed green is a mixture of indigo + orpiment, 30% is copper green and 10% is orpiment + ultramarine. Degrade silver contains 50% of grey colour analysed and indigo + white lead, and ultramarine + white lead each 25%. 50% of analysed pink, violet, and purple sample is Indian lac, 37% is a mixture of ultramarine + cinnabar, and 13% is a mixture of red lead + white lead. colour materials identified for red, orange, and brown include 27% red lead, 55% cinnabar, and 18% red ocher. 50% of analysed yellow is orpiment, 25% is orpiment with a highlight red layer of red lead, and 25% is a mixture of yellow dye with gold.

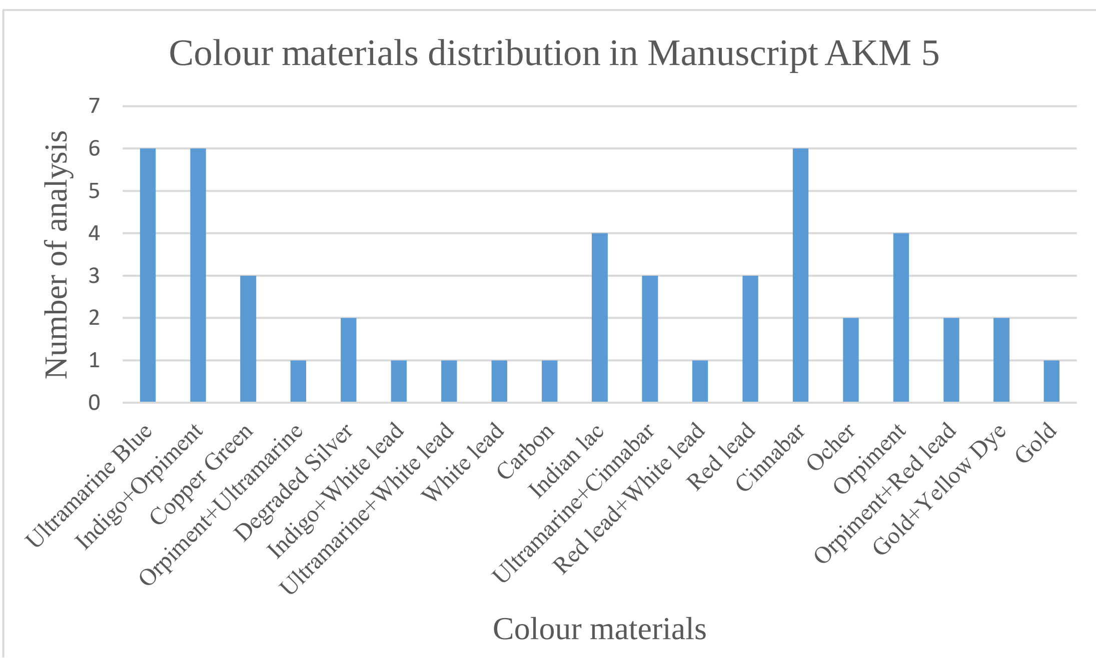


Figure 5-43: Distribution of colour materials used in manuscript AKM 5

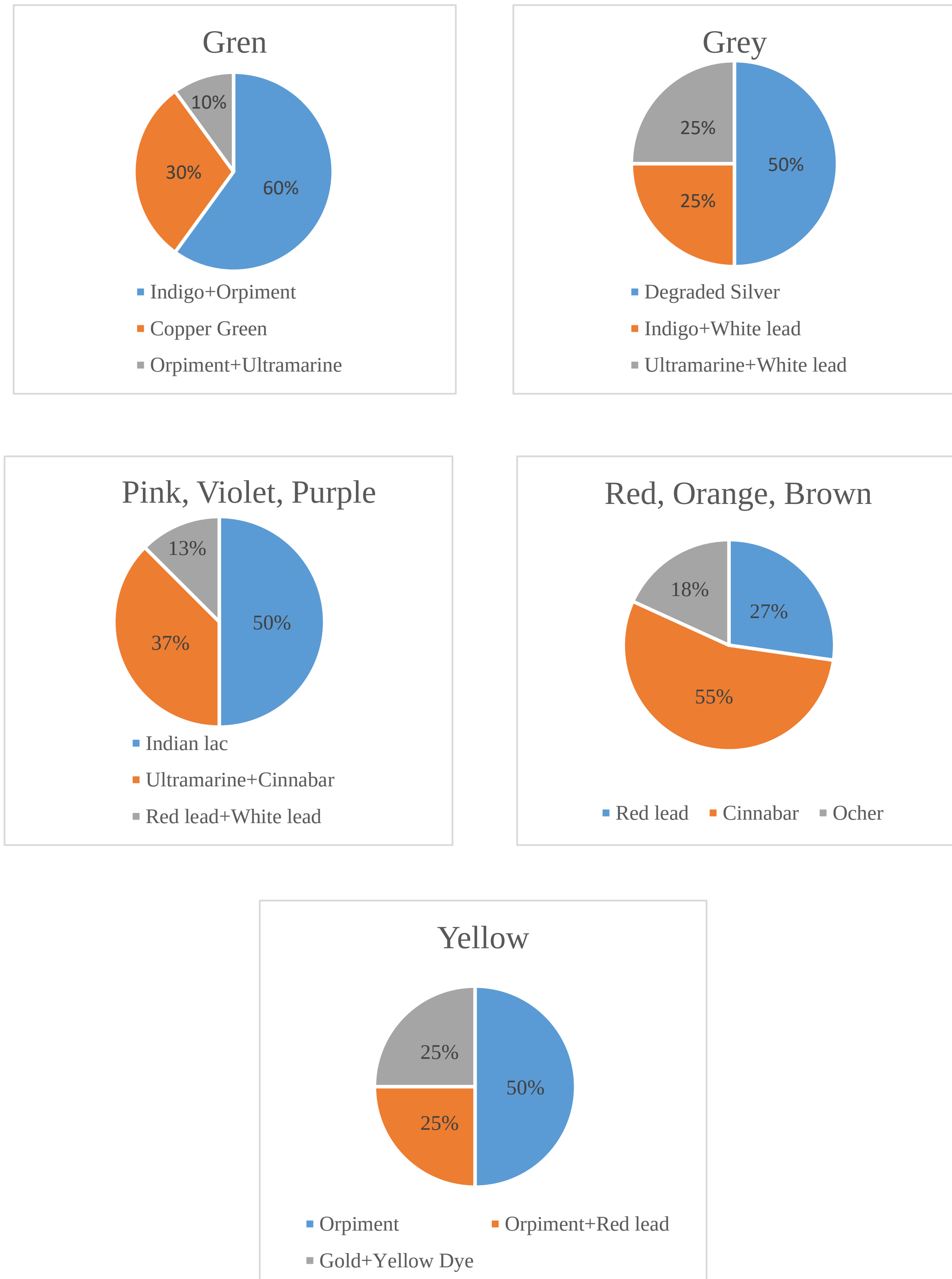


Figure 5-44: Percentage of colour materials used for each colour in manuscript AKM 5

5-3-3 Shāhnāma manuscript AKM 269[37]

The only pigment used to produce blue colour in this manuscript is ultramarine (11 blue spots were analysed) (Tab. 5-13). The painters of this manuscript have used the ultramarine pigment to create different shades of blue, from light blue to dark blue, and to create light blue tonality, they have combined and used ultramarine with different amounts of white lead. The painters of this manuscript have used this colour combination to paint the sky, robes, horse barding, background, architectural components, tent decorations and curtains (Fig. 5-45).

Folio number	Description	Colour material	Colour tonality
Folio 9, 71, 217, 282, 349, 416, 423, 450, 583	building, sky, robes, background, barding and clothing	ultramarine blue	a a
Folio 9, 218, 423	robes, tent	ultramarine blue + white lead	b

Table 5-13: Distribution of blue colour materials used in manuscript AKM 269

Figure 5-45: Comparison of tonality of different blue colour materials in manuscript AKM 269; ultramarine blue(a), ultramarine blue + white lead(b)

[37] In this respect, I would like to thank Branden Cesare Rizzuto who performed the XRF analysis on this manuscript.

More than 15 different colour spots in red, orange, and brown tones were analysed in this manuscript. Red lead has been used extensively as orange and reddish orange in this manuscript (Tab. 5-14). The painters of this manuscript have combined red lead with white lead to produce different tones from orange to red and have used it to paint robes, backgrounds, small flowers, curtains, etc. (Fig. 5-46). cinnabar pigment has also been used to create red and dark red colours.

This pigment has been used by the painters of this manuscript to paint clothes, tents, robes, and small flowers (Fig. 5-46). It must be noted that in the some samples of dark red used to colour small background flowers, small details, as well as blood on folios 58 and 416, cochineal has been used to create a dark red colour (Fig. 5-46). Like in many other Persian manuscripts, red ocher has been used to create different brown tones in this manuscript (Tab. 5-14). Red ocher pigment has been used to colour animals (camels and deer), tree trunks and robes (Fig. 5-46).

The pigments mentioned are easily detecTab by combining the XRF and FORS techniques (see section 5-2-2). The FOMF technique has been used alongside FORS just to make sure about the existence of the cochineal pigment (see section 5-2-2-4).

Folio number	Description	Colour material	Colour tonality
Folio 9, 261, 282, 313, 349, 423, 450	clothes, robe, ground cloth, flower	red lead	a
Folio 9, 218, 261, 423, 583	flags, robes, clothing, flower, barding,	cinnabar	b
Folio 58, 416	flower, blood	cochineal	c
Folio 416, 217, 261	horses, tree trunk, clothing, animals	red ocher	d

Table 5-14: Distribution of red, orange, brown colour materials used in manuscript AKM 269

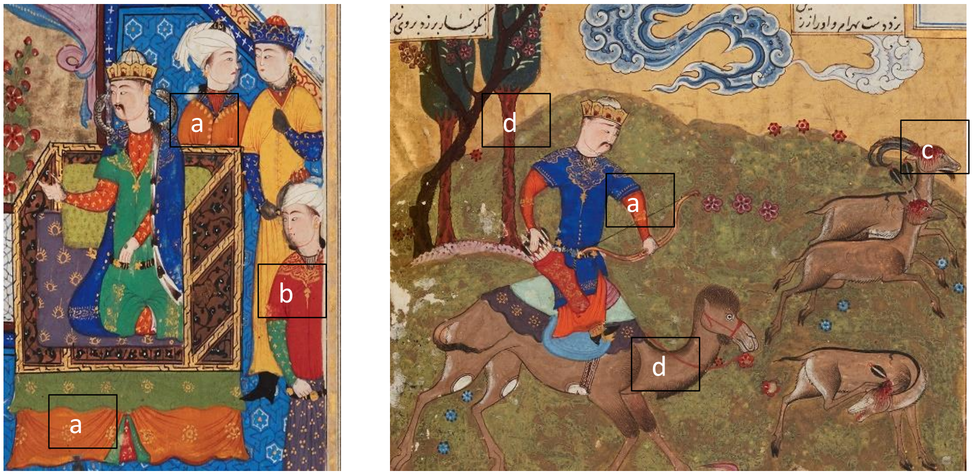


Figure 5-46: Comparison of tonality of different red, orange, brown colour materials in manuscript AKM 269; red lead(a), cinnabar(b), cochineal(c), red ocher(d)

In this manuscript, orpiment has been used as the main material to create the yellow colour (10 yellow spots were analysed). The predominant yellow colour used in this manuscript is a kind of diluted yellow, which seems to have been produced by combining orpiment with white lead (Tab. 5-15). This type of diluted yellow has been used many times for dying clothes, backgrounds, robes, etc. (Fig. 5-47).

It should be noted that on folio 423, a kind of bright yellow colour has been used in painting the tent, which has a major difference in appearance with the other yellow varieties used in this manuscript. In the FORS spectrum of this colour spot, has been seen the absorption maxim in the range of 410 to 420 nm, which indicates that at this point, a significant amount of yellow dyes have been combined and used with orpiment (see section 5-2-4-3). The FOMF spectrum of this colour point confirms the use of yellow dyes.

Folio number	Description	Colour material	Colour tonality
Folio 9, 58, 217, 261, 313, 349, 423, 583	clothing, flag, ground cloth, robes	orpiment	a
Folio 9, 423	tent, Tab	yellow dyes + orpiment	b

Table 5-15: Distribution of yellow colour materials used in manuscript AKM 269

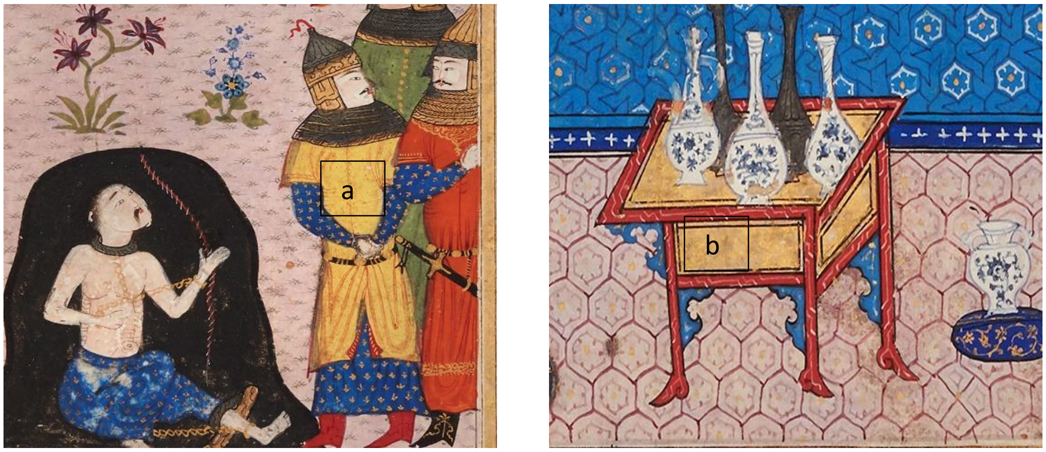


Figure 5-47: Comparison of tonality of different yellow colour materials in manuscript AKM 269; orpiment(a), yellow dyes + orpiment(b)

In this manuscript, a wide variety of pink and purple colours have been used. Thus, a large number of colour samples of this colours tone were analysed (17 pink, violet, and purple spots were analysed). The painters of this manuscript have combined Indian lac with different amounts of white lead to create pink and light pink (whitish pink) (Tab. 5-16). The combination of Indian lac with white lead has been used for painting backgrounds, clothes, robes, architectural components, curtains and so on (Fig. 5-48).

A combination of Indian lac with ultramarine has been used to create a variety of purple colours from light purple to very dark purple (see section 5-2-6-3). This colour combination that creates a variety of tones, from violet to purple, has been used by the painters of this manuscript to colour clothes, backgrounds, ground cloths, tents, and flowers (Fig. 5-48).

It should be noted that the three examples of dark purple (dark greyish) on folios 262, 349 and 583 used to paint robes have been created through the combination of Indian lac with indigo (Tab. 5-16). The Indian lac used in the colour combinations mentioned above was detected by a combination of FORS and FOMF techniques (see section 5-2-6-1). Also, in the FORS spectrum of the colour combination of Indian lac with indigo, in addition to the two absorption maximums mentioned for Indian lac, has been see a maximum absorption at point 660, which indicates the use of indigo in this colour combination (see Fig. 5-21).

Folio number	Description	Colour material	Colour tonality
Folio 9, 58, 217, 261. 282, 313, 341, 349, 416, 450	robes, background, tent, ground cloth, flowers	Indian lac + white lead	a

Folio 262, 349, 583	robes	indigo + Indian lac	b
Folio 9, 58, 261, 416, 423,	robes, background, ground cloth	ultramarine + Indian lac	c

Table 5-16 Distribution of pink, violet, and purple colour materials used in manuscript AKM 269

Figure 5-48: Comparison of tonality of different pink, violet, and purple colour materials in manuscript AKM 269; Indian lac + white lead(a), red indigo + Indian lac(b), ultramarine + Indian lac(c)

Due to the high diversity of green used in this manuscript, 21 spots of the green colour in different tones were analysed. Light green (turquoise) has been used to colour clothes, armor, barding, robes, and backgrounds (Fig. 5-48), and this type of green tonality has been created using copper-based green pigments (Tab 5-17).

The painters of this manuscript have produced different shades of green by combining copper-based green pigment with white lead and used it in this manuscript.

Also, the well-known combination of indigo with orpiment has been used repeatedly to create different tones of green in this manuscript (Tab 5-17). This colour combination is able to produce a dark green (greyish) colour like the colour used in the architectural details on folio 9, to a light yellowish green like the sample used to paint tree foliage on folio 341. The painters of this manuscript have used this colour combination to paint the foliage of trees, backgrounds, clothes, greenery and grass, architectural details etc. (Fig. 5-48).

In addition to the two-colour combinations mentioned, light green (yellowish green) used at two points to colour the robes on folio 9, has been created by combining indigo with yellow dye (probably saffron or turmeric). The above-mentioned colour compounds were detected by a combination of XRF and FORS techniques (see section 5-2-1).

It should be noted that the combination of indigo with orpiment in its FORS spectrum has an inflection point at 480 and a maximum absorption at 660. In fact, the FORS spectrum of this colour combination shows the properties of the indigo and orpiment spectra simultaneously in a FORS spectrum (see Fig. 5-1).

Folio number	Description	Colour material	Colour tonality
Folio 9, 58, 217, 261. 282, 313, 341, 349, 416, 450	the tufts of grass, foliage of trees, robes, tent	indigo + orpiment	a
Folio 9, 58, 217, 261. 282, 313, 341, 349, 416, 450	barding, clothing, robes	copper green	b
Folio 9	robes and clothing	indigo + yellow dye	c

Table 5-17 Distribution of green colour materials used in manuscript AKM 269

Figure 5-48: Comparison of tonality of different green colour materials in manuscript AKM 269; indigo + orpiment(a), copper green(b), indigo + yellow dyes(c)

A set of colour spots (14 spots) containing grey, white, black, and gold (metallic) was analysed in this manuscript. The only metallic pigment used in this manuscript were gold and silver. Gold pigment, which has been repeatedly used to paint backgrounds, clothing details, armor, and architectural features (Fig. 5-49). The gold pigment used in most points has a metallic sheen, but in the gold, sample used for background painting on folio 262 has been seen a dark grey colour (see section 5-2-5).

After the analyses, it was found that in this colour point, the painters have combined and used the pigments of gold and silver, and the dark colour seen in these coloured points is due to the silver pigment used in this colour combination, which has been corroded and created a dark colour. The silver pigment is widely used in this manuscript, and most of the dark grey spots in the manuscript are actually made of silver, which has now become dark due to corrosion (Tab. 5-18). This pigment has been used to paint armor, barding, backgrounds, helmets, swords and river and creek water (Fig. 5-49). The white and black pigments used in this manuscript are, as expected, created with white lead and carbon.

Folio number	Description	Colour material	Colour tonality
Folio 261, 313, 341	swords, barding and armour	silver	a
Folio 9, 423, 261	background, details	gold	b
Folio 9, 423, 450	tent, background, clothing	white lead	e
Folio 71, 217, 423	background, details, horses	carbon-based pigment	f

Table 5-18 Distribution of metallic, black, white, and grey colour materials used in manuscript AKM 269

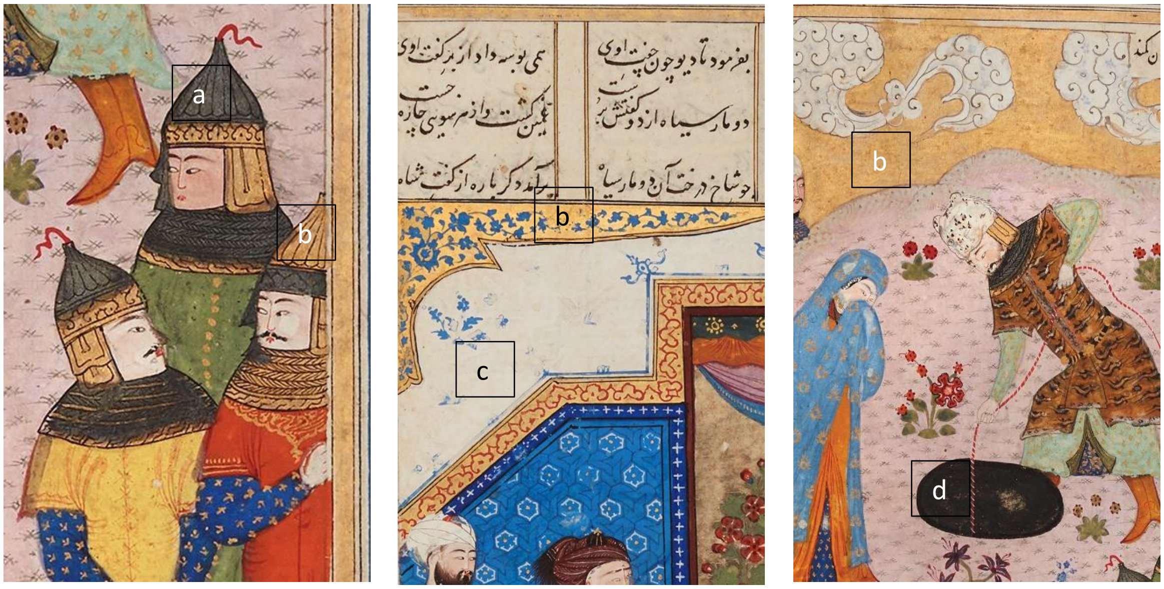


Figure 5-49: Comparison of tonality of different metallic, black, white, and grey colour materials in manuscript AKM 269; degraded silver(a), gold(b), white lead(c), carbon-based pigment (d)

5-3-3-1 Statistical analysis the Shāhnāma AKM 269

This manuscript like manuscripts AKM 4 and AKM 5 is an example of the Turkman style manuscript of Shiraz dated 1494 CE (see chapter 3). From the point of view of material science, colour materials of this manuscript are almost same as manuscript AKM 5, it should be noted that in this manuscripts instead of ultramarine + cinnabar used in AKM 4 and AKM 5 two colour combination of ultramarine + Indian lac and indigo + Indian lac have been used for violet and purple colours. colour materials of 13 miniatures of this manuscript were analysed. Indeed 136 single measurements contain; 100 FORS analysis, 20 XRF analysis, and 16 FOMF analysis were performed on this manuscript (see Tab. 5-57).

all analysed blue spots in this manuscript contained ultramarine pigment. 38% analysed green of this manuscript contain copper green pigment, and 52% orpiment + indigo and 10% indigo + yellow dye. 67% of the grey colours are degraded silver pigments and 33% contain indigo + white lead. 53% of the analysed pink, violet, and purple samples is Indian lac, 35% is the combination of ultramarine + Indian lac and 12% contain indigo + Indian lac. Red lead pigment 40%, cinnabar 27%, red ocher 20%, and cochineal 13% contain the colour samples analysed in red, orange, and brown tones. 80% of yellow samples contain orpiment and 10% of them contain the combination of orpiment + yellow dye and 10% contain orpiment + red lead. 67% of the analysed metallic samples contain gold pigment with metallic luster and 33% of the samples are composed of a combination of gold and silver and have a less metallic luster.

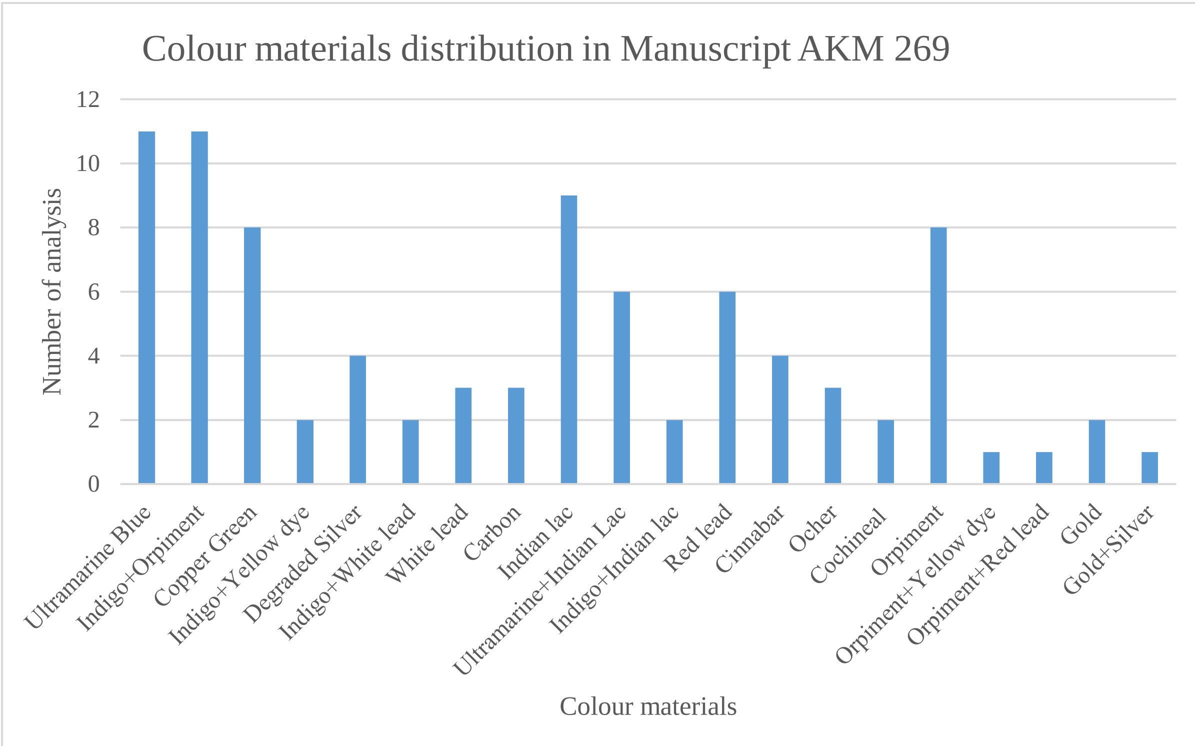
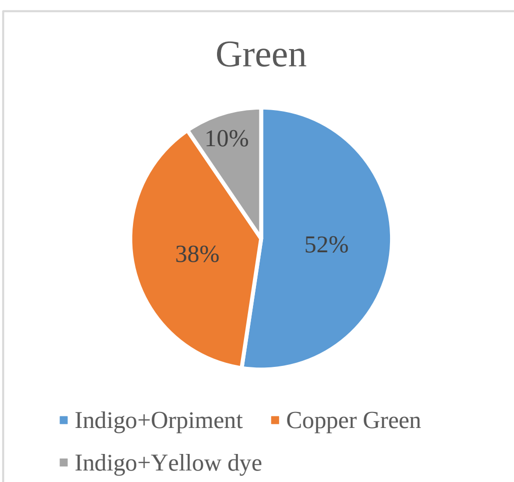
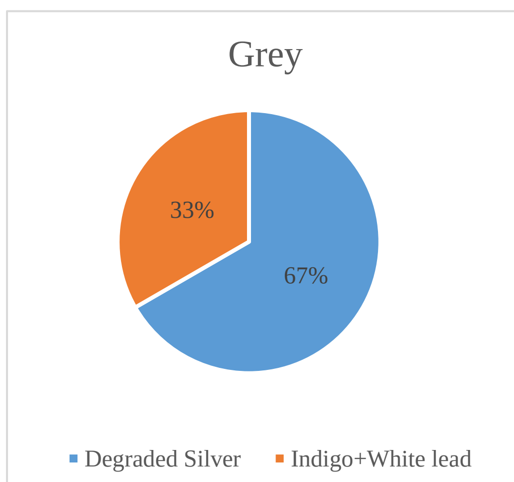


Figure 5-50: Distribution of colour materials used in manuscript AKM 269





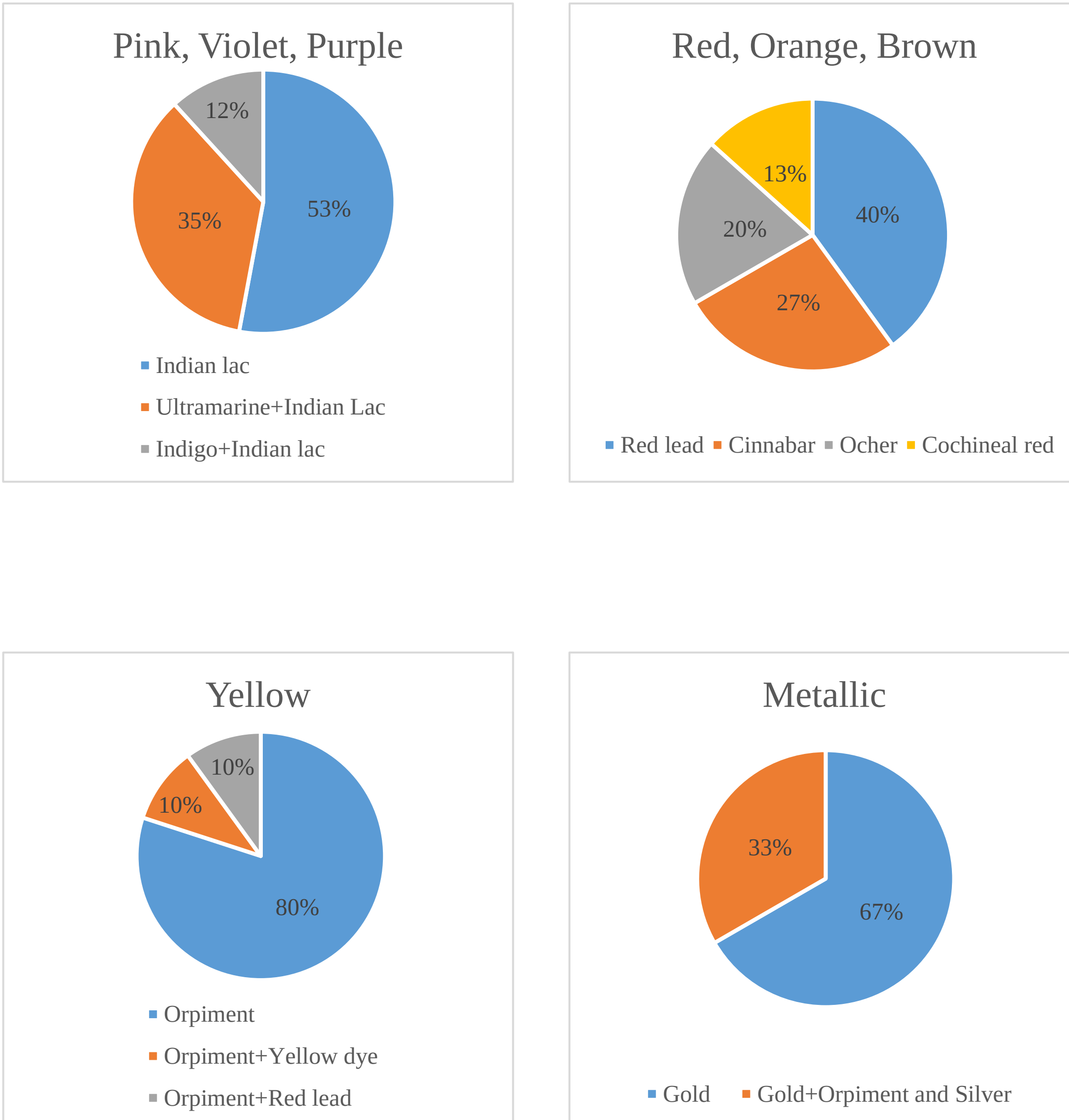


Figure 5-51: Percentage of colour materials used for each colour in manuscript AKM 269

5-3-4 Shāhnāma manuscript AKM 6[38]

Since the tonality of the blue used in this manuscript and the way it had been applied seemed very different from other analysed manuscripts, a large number of blue colour samples were analysed in this manuscript (15 spots). Like in all Persian manuscripts, ultramarine and indigo are the two main materials used in this manuscript (Tab. 5-19). The painters of this manuscript have created different tonalities from blue to light blue by combining different amounts of ultramarine with white lead and have used them to paint clothes, buildings, backgrounds, and small flowers (not seen in other manuscripts) (Fig 5-52).

But as could be predicted by the appearance of some blue spots on folios 62 and 63 of this manuscript, a kind of very dark blue colour has been used, which according to the XRF and FORS spectra taken from these spots, it has been created through a combination of azurite and ultramarine. This colour combination was not seen in any of the other manuscripts. In the FORS spectrum of these dark blue spots, has been seen that the maximum absorption has a shift from 600 to 590 (in the sample taken from folio 62) and from 600 to 610 (in the sample taken from folio 63) (see appendix 2). Also, in the XRF spectrum of the same coloured spots, has been seen a significant amount of the copper element which is characteristic of the azurite pigment. The element barium is also detected as a trace of the azurite pigment in the XRF spectrum (see section 5-2-3-3). This colour combination has been used to paint parts of the tent and robe (Fig 5-52).

In this manuscript, a combination of indigo with light turquoise colour has been created, which has been used for background colouring. In fact, it seems that the painters of this manuscript first painted the background with white lead and then painted a highlight layer of indigo on it, thus making the background of the painting light blue.

Folio number	Description	Colour material	Colour tonality
AKM 62, 63, 64, 92	building, sky, and clothing	ultramarine blue	a b
AKM 62, 63	robes, clothing, and clothing	azurite + ultramarine	c
AKM 62, 63	background	indigo + white lead	d

Table 5-19: Distribution of blue colour materials used in manuscript AKM 6

[38] In this respect, I would like to thank Branden Cesare Rizzuto who performed the XRF analysis on this manuscript.

Figure 5-52: Comparison of tonality of different blue colour materials in manuscript AKM 6; ultramarine blue(a), ultramarine blue + white lead(b), azurite + ultramarine (c), indigo + white lead(d)

In this manuscript, a wide range of colour tonalities from orange to red and brown tones have been used (15 spots were analysed). According to the analyses, it is clear that red lead, cinnabar and red ocher had been used to create these colour tones (Tab. 5-20). Red lead has been used more to create orange tones and the painters of this manuscript have used red lead to paint clothes, flags, flowers, buildings, armor, and barding (Fig. 5-53). However, cinnabar has been mostly used to create different shades of red from dark red to light red, which can be seen in clothing, architecture, background, shields, and a case of writing in red ink (Fig. 5-53). Red ocher pigment has also been used to create different brown tones. The painters have used it to colour clothes, boots, and clothing details (Fig. 5-53). All the above-mentioned pigments were detected by a combination of XRF and FORS techniques (see section 5-2-2).

Folio number	Description	Colour material	Colour tonality
AKM 62, 63, 64, 92	clothes, robe, ground cloth, flag, flower, barding	red lead	a
AKM 62, 63, 64, 92	robes, shield, barding, architecture, ink	cinnabar	b
AKM 64, 92	robes, boot, flagpole	red ocher	c

Table 5-20: Distribution of red, orange, brown colour materials used in manuscript AKM 6

Figure 5-53: Comparison of tonality of different red, orange, brown colour materials in manuscript AKM 6; red lead(a), cinnabar(b), red ocher(c)

In this manuscript, in most cases, a kind of light-yellow tonality (pale yellow) has been used, which is very different from the other manuscripts analysed (6 yellow spots were analysed). To create this unique yellow, the painters have combined orpiment with other materials such as gold, yellow dyes (possibly saffron or turmeric), gold and gypsum (Tab. 5-21).

In the two-colour samples analysed from folios 62 (the background) and 92 (the flag), the painter has created the desired tonality by combining orpiment, yellow pigment, and gold (Fig. 5-54). In the XRF spectrum of these two colour points, the presence of gold and arsenic (orpiment) is clearly recognizable, but in the FORS spectrum of these two colour points, especially in the sample on folio 62, has been see the intersection of the gold inflection point (520 nm) and the orpiment inflection point (480 nm) which makes it impossible to distinguish these two pigments with this technique. However, in the FOMF spectrum taken from these colour points, two max fluorescence were observed at points 530 and 570 nm through which it can be ensured that in the in the compound material used for these colour spots, some amounts of yellow dye has been used (see Fig. 5-18).

In the other colour points analysed, orpiment is still easily recognizable as the main component of the colour compound used in both XRF and FORS techniques (see section 5-2-4-1), but the main difference between the other yellow points analysed and the two previously mentioned points is the absence of the gold peak in the XRF spectrum of these points.

It should be noted that in the XRF spectrum of these points, has been seen a certain peak of Ca and S, which can be a reason for claiming that the painters of this manuscript have combined and used orpiment with gypsum as white colour in order to produce a very bright and pale yellow colour (see appendix 3). In addition, the FOMF spectrum of these points shows that yellow dye has also been used in this colour combination.

The colour combination mentioned has been used to colour the clothes and the details of the tent. This possibility should also be taken into consideration that these yellow points may consist of orpiment and dye, but since this colour is very light and pale (a thin and weak layer), the peaks of gold and gypsum seen in the XRF spectrum of these points might be due to the white and gold colours used under them.

Folio number	Description	Colour material	Colour tonality
AKM 51, 52, 53	clothing, flag, ground cloth	orpiment + gold and yellow dyes	a
AKM 51, 52	robes	orpiment + yellow dyes and gypsum	b

Table 5-21: Distribution of yellow colour materials used in manuscript AKM 6

Figure 5-54: Comparison of tonality of different yellow color materials in manuscript AKM 6; orpiment + gold and yellow dyes(a), orpiment + yellow dye and gypsum (b)

A number of different colour combinations have been used to create different tonalities of pink and purple in this manuscript (7 spots were analysed). The main ingredients of these colours are cochineal, red lead, cinnabar, white lead, and ultramarine, which have been combined with one another and used many times (Tab. 5-22). To create the light pink used for colouring faces, red lead and white lead have been combined. But to create the pink of the clothes and the backgrounds, a combination of cochineal and cinnabar has been used, and the painter has lightened it with white lead to achieve the desired tonality (Fig. 5-55).

To create the pink colour used in the background of folio 92, a combination of cochineal and white lead has been used. The painters of this manuscript have used a combination of ultramarine and cinnabar to create the dark purple tones used to colour the robe on folio 63. For a lighter case of violet used to colour the horse barding on folio 92, the painters have combined ultramarine with cochineal (Tab. 5-22).

To create the light violet used for colouring the robe on folio 64, cochineal has been combined with red lead and white lead. The colour materials used for these combinations were detected by integrating XRF and FORS techniques (see section 5-2-6). It should be noted that in addition to FORS, the FOMF technique was also used to detect cochineal.

Folio number	Description	Colour material	Colour tonality
AKM 62, 63, 64, 92	face	red lead + white lead	a
AKM 62	robe, background, ground cloth	cochineal + cinnabar and white lead	b
AKM 63	robes, flag, ground cloth	ultramarine + cinnabar	c
AKM 64	robe	cochineal + red lead and white lead	d
AKM 92	barding	ultramarine + cochineal	e

Table 5-22 Distribution of pink, violet, and purple colour materials used in manuscript AKM 6

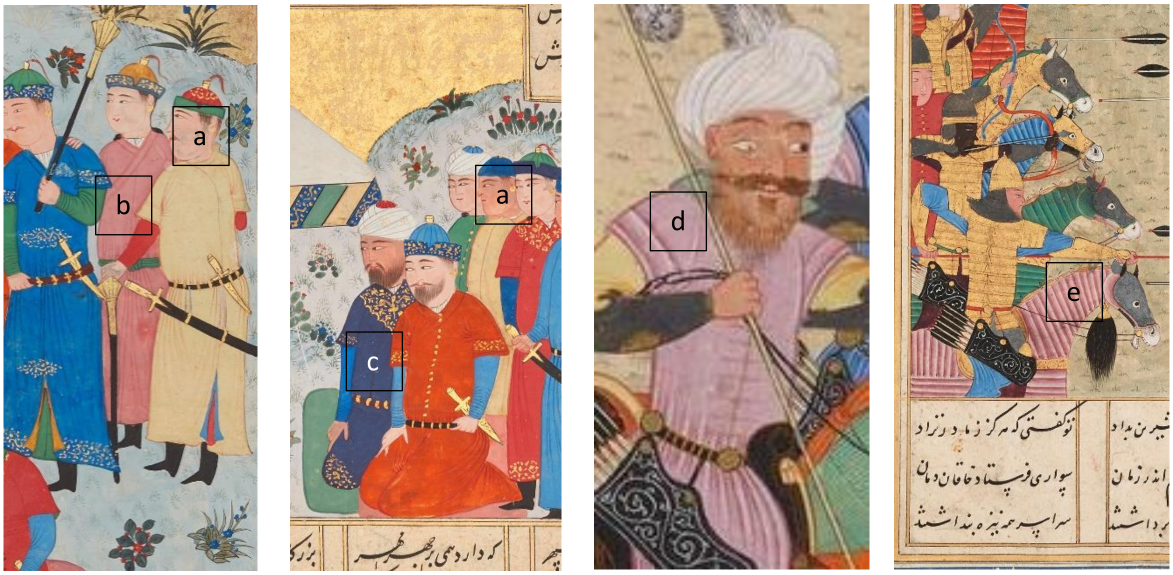


Figure 5-55: Comparison of tonality of different pink, violet, and purple colour materials in manuscript AKM 6; red lead + white lead(a), cochineal + cinnabar and white lead(b), ultramarine + cinnabar(c), cochineal + red lead and white lead(d), ultramarine + cochineal(e)

In this manuscript, a kind of pistachio green colour has been used, which is very different from the other green colours applied in the manuscripts studied in this project (6 green spots were analysed). In this manuscript, this type of green colour has been used repeatedly to paint architectural component, clothes, backgrounds, tent decorations, etc. (Fig. 5-56). In the FORS spectrum of these colour spots, has been seen a maximum absorption in the range of 710 to 720, which is characteristic of copper-based green pigments (see section 5-2-1-2). Also, in the XRF spectrum of these spots, has been seen an intense peak of the copper element. The results of these two techniques clearly show that copper-based green pigment has been used in these colour spots. According to the appearance of this green colour, it can be concluded that this very special shade of green colour has been created by a combination of azurite blue pigment with copper-based green pigment as reported by Knipe et al. (2018).

As mentioned above, in the XRF spectrum of these colour spots, has been seen a very strong copper peak, which also indicates the use of copper green and azurite. Normally in the natural mineral sample of the azurite pigment, it can see a malachite green pigment (Knipe et al. 2018, p.23).

In other words, the two pigments are naturally found together, which means that the painters of this manuscript could have produced the two pigments by pulverizing the ore containing both pigments, or by combining the desired amounts of each of the two pigments.

It should be noted that in this manuscript, there are two cases of a colour substance other than the mentioned combination to create a green colour (Tab 5-23). In one case which appears on folio 62, a combination of indigo and orpiment has been used to create a very dark green (close to grey). On folio 64, a copper-based green alone has been used to colour the horse barding (Fig. 5-56).

The interesting point after comparing the XRF peaks of these two colour samples is that the copper peak related to the sample colour combining azurite with malachite is much more intense than the peak of the sample made of copper-based green alone (see appendix 4).

Folio number	Description	Colour material	Colour tonality
AKM 62, 63, 92	architecture, robes, details of tent, ground cloth	malachite + azurite	a
AKM 64	barding, clothing	copper green	b
AKM 62, 63	foliage of grass	indigo + orpiment	

Table 5-23: Distribution of green colour materials used in manuscript AKM 6

Figure 5-56: Comparison of tonality of different green colour materials in manuscript AKM 6; malachite + azurite(a), copper green(b), indigo + orpiment(c)

All the metallic colour samples analysed in this manuscript (9 spots) were gold pigments used extensively to paint the background, the armor, the buildings, the details of clothing and the architecture (Tab. 5-24).

It should be noted that silver pigments have also been used in many spots in this manuscript for colouring the armor, the barding, the quivers, the helmets, etc. (see section 5-2-5). But the silver pigment has lost its metallic luster over time and is now seen as a dark grey (Tab. 5-24). Only one case of dark grey was identified on folio 62, which has used a combination of indigo and orpiment (Fig. 5-57). As in most Persian manuscripts, the white and black colours used in this manuscript have been created by white lead and carbon.

Folio number	Description	Colour material	Colour tonality
AKM 64, 64, 92	swords, barding, quiver, and armour	degraded silver	a
AKM 62, 63, 64, 92	background, details of architecture and clothing	gold	b
AKM 62	background	indigo + white lead	c

Table 5-24: Distribution of metallic, black, white, and grey colour materials used in manuscript AKM 6

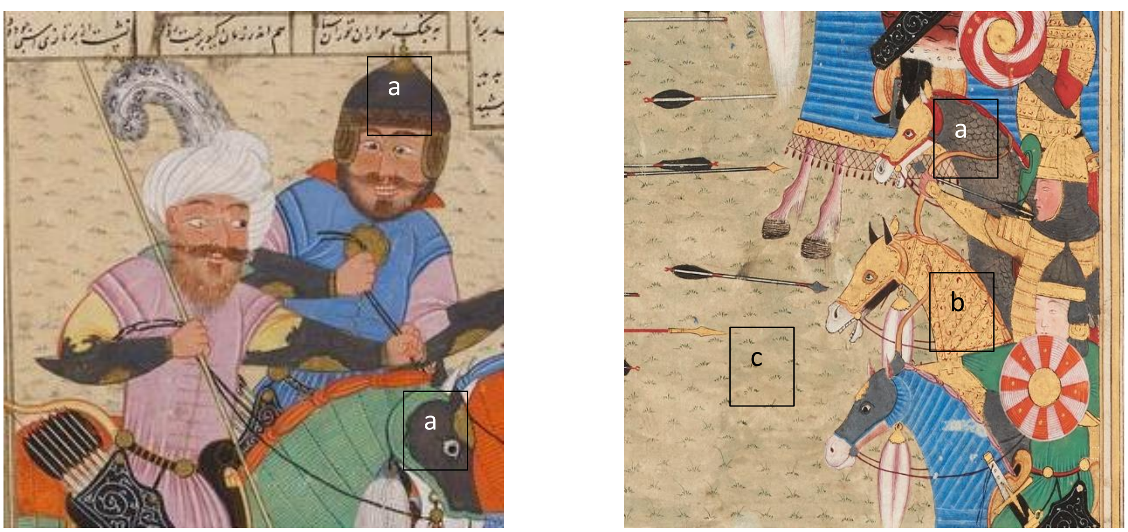


Figure 5-57: Comparison of tonality of different metallic, black, white, and grey colour materials in manuscript AKM 6; degraded silver(a), gold(b), indigo + white lead(c)

5-3-4-1 Statistical analysis the Shāhnāma AKM 6

This manuscript is the only example of manuscript of Lahijan dated 1494 which analysed in this project (see Chapter 3). From the point of view of material science, colour materials used in this manuscript has significant differences comparison the colour materials used in Shiraz (manuscripts AKM 4, 5, and 269) and Herat school (RAS 239) of Persian manuscripts. For example, colour materials used for green, blue, and yellow colours have characteristic features which explained above.

Therefore, colour materials of four miniatures of this manuscript were analysed. Indeed 146 single measurements contain; 65 FORS analysis, 65 XRF analysis, and 16 FOMF analysis were performed on this manuscript (see Tab. 5-57).

53% of blue colour materials analysed in this manuscript is ultramarine, 27% is indigo and 20% is azurite + ultramarine. as well as for green colour 67% analysed green colour is indigo + orpiment, 17% is copper green and 16% is malachite + azurite. This percentage for grey colour includes 80% degrade silver and 20% indigo + white lead. 43% pink, violet, and purple colour analysed is ultramarine + cinnabar, 29% red lead + white lead, 14% cochineal, and 14% ultramarine + cochineal. Also 47% red, orange, and brown colour analysed is red lead, 33% is cinnabar and 20% is red ocher. For analysed yellow colour this percentage includes 17% orpiment, 33% orpiment + yellow dye, and 50% orpiment + yellow dyes and gypsum.

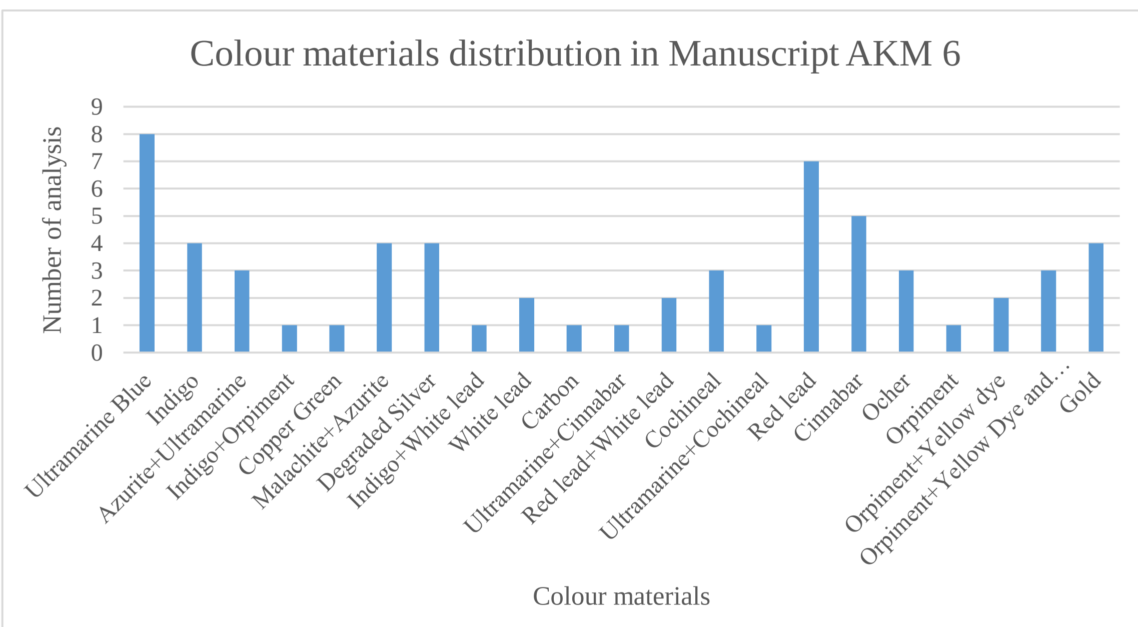


Figure 5-58: Distribution of colour materials used in manuscript AKM 6

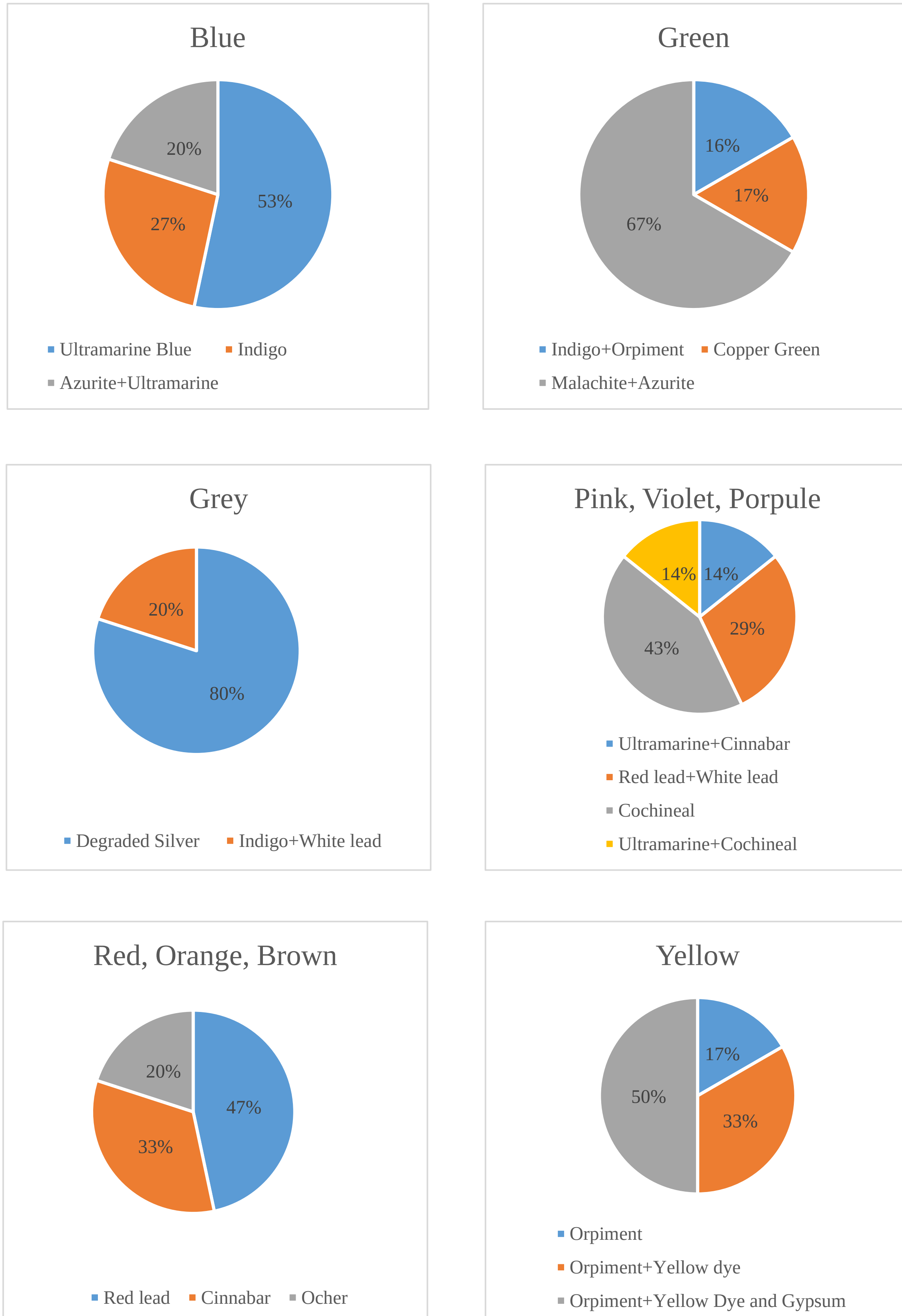


Figure 5-59: Percentage of colour materials used for each colour in manuscript AKM 6

5-3-5 Shāhnāma manuscript Or 420[39]

In this manuscript, nine colour spots with different tonalities of green were analysed. The three green mixture identified in this manuscript consist of the combination of indigo + orpiment, indigo + yellow dye, and copper-based green pigment used by painters in different tonalities (Tab. 5-25).

The indigo + orpiment combination is often used to paint the leaves of trees, shrubs, and meadows (in the background) and barding (Fig. 5-60). The colour combination of indigo + yellow dye (probably saffron) has also been used to colour the shrub leaves on folio 33, which can be seen as a yellowish light green. At first glance, this colour can be accepted as a kind of yellow which like the green colour mentioned above is observable without any damage or shedding. In the FORS technique, the maximum absorption can be seen in region 430 nm and in region 660 nm for this colour combination, which represents a combination of indigo with a yellow dye (saffron) (see section 5-2-4-3).

In addition, the absence of significant elements for yellow pigments in the XRF spectrum, such as arsenic, etc., as well as the clear detection of indigo in the FORS technique can be itself an indication of the use of a yellow dye such as saffron or turmeric along with indigo by the painter of this manuscript to create a certain tone of green.

But the copper green that has been used to paint clothes is a kind of deep bluish green, which in all cases spotted on folios 69, 148 has been damaged to some extent (Tab 5-25). The damages appear in the form of blurring or shedding of the paint at some points and can be due to the use of improper clamps, as well as the specific properties of the copper in this paint, which in some cases has also caused corrosion of the paper (Fig. 5-60). This pigment was detected as copper based green due to the presence of significant amounts of copper (see section 5-2-1-2).

Folio number	Description	Colour material	Colour tonality
17, 69, 85, 148	the tufts of grass, Foliage of trees, Barding	indigo + orpiment	a
33	shrubs	indigo + yellow dyes	b
69, 148, 273	robes, flag	copper green	c

Table 5-25 Distribution of green color materials used in manuscript Or 420

[39] In this respect, I would like to thank Professor Dr Ira Rabin and Dr Olivier Bonnerot who performed the XRF analysis on this manuscript.

Figure 5-60: Comparison of tonality of different green colour materials; indigo + orpiment (a), indigo + yellow dye (b), copper green (c)

In this manuscript 12 colour spots of the red, orange, and brown in different tonalities were analysed. As mentioned before, the colour materials used for different red, orange, and brown tones in different periods and different places are very limited. These colour materials include cinnabar, red lead, and red ocher and sometimes cochineal as dark red (Tab. 5-26). In this manuscript three types of red pigments, namely cinnabar, red lead, and red ocher and a cochineal dye were identified. Cinnabar detected in all places has been used to colour clothes and robes in this manuscript (Fig. 5-61).

Cinnabar pigment was easily identifiable due to the presence of significant amounts of mercury in the XRF spectrum (see section 5-2-2-1), and given that in the XRF spectrum of the red spots observed on folios 69 and 148 of this manuscript, some lead is also recognizable, it can be concluded that the painter has mixed the cinnabar pigment with white lead in order to achieve the desired colour tonality.

In this manuscript, red lead has been used to paint horse barding, flags and flowers painted in the background (Fig. 5-61). Detection of red lead in Persian manuscripts is challenging due to the high use of white lead pigment, and thus much attention was paid in identifying this pigment (see section 5-2-2-2).

The cochineal pigment was detected in only one case on folio 171, used by the painter to colour the sleeves of the shirt (Fig. 5-61). It is a pinkish red colour, which has been damaged or completely disappeared or fallen in some areas. Cochineal was identified by a combination of FORS and FOMF techniques (see section 5-2-2-4). It should be noted that due to the large amount of lead in the XRF spectrum of these colour spots, it can be concluded that the painter has mixed the cochineal pigment with white lead to achieve the desired colour tonality.

As could be predicted beforehand, red ocher and red lead, were the main pigments used to create brown in this manuscript (Tab. 5-26). The detected red ocher has been mostly used to paint the trunks of trees and horses, and generally has a dark brown colour (Fig. 5-61). Red ocher can be recognized by XRF and FORS (see section 5-2-2-3). It should be noted that in the XRF peak of the red ocher identified on folio 69, in addition to iron, some amounts of arsenic and lead were visible.

It can be concluded that the painter of this manuscript has mixed red ocher with orpiment and white lead and used the compound colour to achieve his desired tonality. It should be noted that in the sample of brown colour used on folios 148, 33, and 171 a mixture of red lead was used to create brown colour (Tab. 5-26). In brown colour folio 148 which has a yellowish tint, in addition to lead, significant amounts of gold can be seen in its XRF spectrum, the main reason for which may be the fall or destruction of this colour in that area.

Folio number	Description	Colour material	Colour tonality
17, 69, 148	robes	cinnabar	a
171	clothing details	cochineal	b
236, 273, 17	barding, flag, flower	red lead	c
33, 148, 171	clothing, background, horses	red lead	c
69, 85	tree trunk, horses	red ochre	d

Table 5-26 Distribution of red, orange, and brown colour material used in manuscript Or 420

Figure 5-61: Comparison of tonality of different red, orange, and brown colour materials used in manuscript Or 420; cinnabar (a), cochineal (b), red lead (c), red ocher(d)

12 blue spots were also analysed in this manuscript. These Colour spots had different colour tones from very light blue to dark blue (Tab. 5-27). The two main materials used by the painters of this manuscript are ultramarine and indigo, which have been mixed with different amounts of white lead to create different blue tonalities. Ultramarine has been used to paint various motifs and figures such as the sky, carpets (backgrounds), clothing, buildings, horses, barding, and even in one case (on folio 69) to write manuscript text (Fig. 5-62).

As previously explained, due to the fact that ultramarine is composed of light elements, it is not possible to identify these elements with portable XRF devices in many cases, so ultramarine was detected by the maximum absorption at 600 nm in the FORS technique (see section 5-2-3-1). In the XRF spectrum obtained from light blue spots on folios 17 and 116, due to the presence of a large amount of lead, it can be assumed that the painter has combined ultramarine with white lead to create a light tone of blue.

However, it should be noted that this amount of calcium observed in the XRF spectrum may be due to the use of low-quality ultramarine since calcium is known as one of the by-products (impurities) of ultramarine. Indigo colour was identified in three folios. Generally, it has a darker tone than ultramarine and has been used to paint clothes and backgrounds (mountains, hills) (Fig. 5-62). Since indigo cannot be detected by the XRF technique, the FORS technique was used to detect it (see section 5-2-3-2).

In addition, it should be noted that on folio 273, due to the presence of a significant amount of lead in the XRF spectrum, it was concluded that the painter had mixed indigo with white lead to create a very light tonality of turquoise.

Folio number	Description	Colour material	Colour tonality
17, 33, 69, 116, 148, 171, 236, 273	sky, carpets, clothing, barding, buildings, horses, text	ultramarine blue	a
17, 116, 148	background, horse	ultramarine + white lead	b
148	background	indigo + white lead	c
33, 148	robes, tent	indigo	d

Table 5-27 Distribution of blue colour material used in manuscript Or 420

Figure 5-62: Comparison of tonality of different blue colour materials used in manuscript Or 420; ultramarine blue (a), ultramarine + white lead (b), indigo + white lead (c), indigo (d)

Nine yellow spots with different tonalities were analysed in this manuscript. orpiment is the main material used for the yellow colour in this manuscript, and in most cases, orpiment has been used to create dull yellow (Tab. 5-28). The painters of this manuscript have used orpiment to paint clothes, backgrounds, horses, and barding (Fig. 5-63). As previously explained, the identification of yellow colours by the FORS technique has many challenges and difficulties due to the limitations of this technique (see section 5-2-4-1).

Therefore, in the identification of orpiment in this manuscript, its point of inflection changed from 480 nm to 500-510 nm due to the presence of significant amounts of gold, which made it difficult for FORS to identify orpiment, but fortunately significant amounts of arsenic seen in the XRF spectrum of yellow spots was a great guide for distinguishing gold from orpiment (see Fig. 5-15).

It is noteworthy that in the yellow colour spot of folio 273, due to the significant amount of gold seen in its XRF spectrum as well as the inflection point at 510 and the maximum absorption at 420 in the FORS technique, the dye used to create this spot was identified as a combination of gold pigment and yellow dye (which is most likely saffron) (Tab. 5-28). Also, the light yellow colour used on folio 148 was detected as yellow dye due to the absence of any significant elements in XRF and the maximum adsorption of the yellow pigment (saffron or turmeric) seen at point 420 in the FORS technique.

Folio number	Description	Colour material	Colour tonality
17, 33, 69, 116, 171, 273	clothing, barding, background, horses	orpiment	a
273	background	gold + yellow dye	b
148	tent	yellow dye	c

Table 5-28 Distribution of yellow colour material used in manuscript Or 420

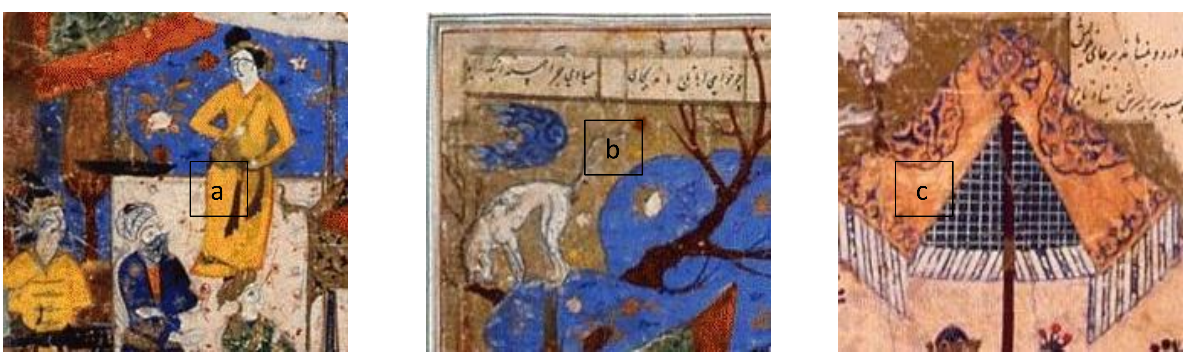


Figure 5-63: Comparison of tonality of different yellow colour materials used in manuscript Or 420; orpiment (a), gold + yellow dye (b), yellow dye (c)

In this manuscript, 6 colour spots of pink, violet, and purple tones were analysed (Tab. 5-29). The pink and violet colour applied in this manuscript has been used to paint the background (textile and surface coverings) and small background flowers, and the material used for all these colour spots is cochineal, which according to the colour tonality desired by the painter has been combined with different amounts of white lead (Fig. 5-64).

The cochineal used in these colour spots can be identified by FORS and FOMF (see section 5-2-2-4). It should be noted that the purple colour spot identified on folio 116 in the FORS technique had a maximum absorption at point 660 nm, which indicates the use of indigo at this colour point, and also an absorption maximum of about 530 nm, which indicates the presence of Indian lac (see section 5-2-6-1).

Folio number	Description	Colour material	Colour tonality
17, 148, 236, 273	clothing, background, flowers	cochineal cochineal + white lead	a
116	background	indigo + Indian lac	b

Tab. 4-29 Distribution of pink, violet, and purple colour material used in manuscript Or 420

Figure 5-64: Comparison of tonality of different pink, violet, and grey colour materials used in manuscript Or 420; cochineal + white lead (a), indigo + Indian lac (b)

Gold and silver are the main metal pigments used in the Persian manuscripts. In this manuscript, two spots of metallic gold colours were analysed (Tab. 5-30). the gold pigment has been used to dyed background. It must be noted that a mixture of gold + yellow dye has been used to paint the background in folio 273 (Fig. 5-65).

three spots of grey colour of this manuscript were analysed, and unlike most of manuscript analysed in this project there is no evidence of the use of silver pigment (Tab. 5-30). In fact, a mixture of indigo + white lead has been used to create grey colour. Also, the dark grey colour spot analysed on folio 236 had significant amounts of lead in its XRF spectrum, which indicates the use of white lead at this spot, but in the FORS technique has been seen a maximum absorption at 600 nm at the same colour spot, which indicates the presence of ultramarine at this spot.

So, it can be concluded that the material used at this spot contained blue colour, but it has been damaged and turned grey. The reason for this damage and discolouration could be degradation of red lead due to the use of low-quality materials by the painters of this manuscript which has been seen also that the ultramarine used has fallen and disappeared over time.

Four white and black colour samples were examined in this manuscript. The painters of this manuscript have used white lead to paint the characters' hats and headscarves, backgrounds, as well as their faces (Fig. 5-65). As predicted, the main material used in all the analysed points was white lead. White lead has been repeatedly detected in the XRF spectrum of the colours analysed in this manuscript.

It has frequently been used by painters to create light tones of different colours, and sometimes it has been used separately to create white. It should be noted that in the pinkish white sample used for the faces of the characters in the paintings of this manuscript, a mix of white lead with a very small amount of cochineal has been used.

In this manuscript, black is often used to show painting details, such as details of buildings, clothes, and horses and as predicted, carbon black was the main material used as the colour black (Tab. 5-30). It should be noted that although carbon black (mainly soot) is not detectable by XRF technique, the absence of iron in the XRF spectrum of black spots seemed to be sufficient to prove the use of carbon black since the colour material used as black in Persian manuscripts is limited to carbon black and iron-based black (gall ink) (see section 5-2-7-2).

It must also be mentioned that in the FORS technique, these two types of black colour have a smooth and similar peak, and in general, the FORS technique does not have the ability to detect black and white colours.

Folio number	Description	Colour material	Colour tonality
171, 148	clothing, background, faces, animals	white lead	a
171, 273	background	indigo + white lead	b
171, 273	background, details	carbon	c
236	robe	ultramarine + white lead	d

Table 5-30 Distribution of white and black colour material used in manuscript Or 420

Figure 5-65: Comparison of tonality of different white and black colour materials used in manuscript Or 420; white lead (a), indigo + white lead(b), ultramarine + white lead(c), black carbon (d)

5-3-5-1 Statistical analysis the Shāhnāma Or 420

This manuscript is an example of the Timurid manuscripts of Shiraz dated 1437 CE (see Chapter 3). From the point of view of material science, since many of colour materials of this manuscript are damaged or detached it can be concluded colour materials used in this manuscript has low quality comparison with materials used in other Shiraz manuscripts and Herat manuscripts.

For example, the ultramarine pigment which has in many cases fallen or changed colour to become grey. Most probably, the colour materials used for this manuscript have not had much of a high quality. Also, many instances of improper restoration can be seen in this manuscript. For example, on folio 273, the right side of the painting has been completely destroyed and has been totally repainted again. The same is true about the top of folio 148. Indeed, nine paintings of this manuscript were analysed, and 122 single measurements contain; 56 FORS analysis, ca.56 XRF analysis, and ten FOMF analysis were performed on this manuscript (see Tab. 5-57).

67% blue colour materials analysed in this manuscript is ultramarine, 33% is indigo. as well as for green colour 56% analysed green colour is indigo + orpiment, 33% is copper green and 11% is indigo + yellow dye. This percentage for grey colour includes 67% indigo + white lead and 33% ultramarine + white lead. 83% pink, violet, and purple colour analysed is cochineal, and 17% indigo + Indian lac. Also 46% red, orange, and brown colour analysed is red lead, 23% is cinnabar and 23% is red ocher and 8% is cochineal. For analysed yellow colour this percentage includes 78% orpiment, 11% yellow dye, and 11% yellow dye + gold.

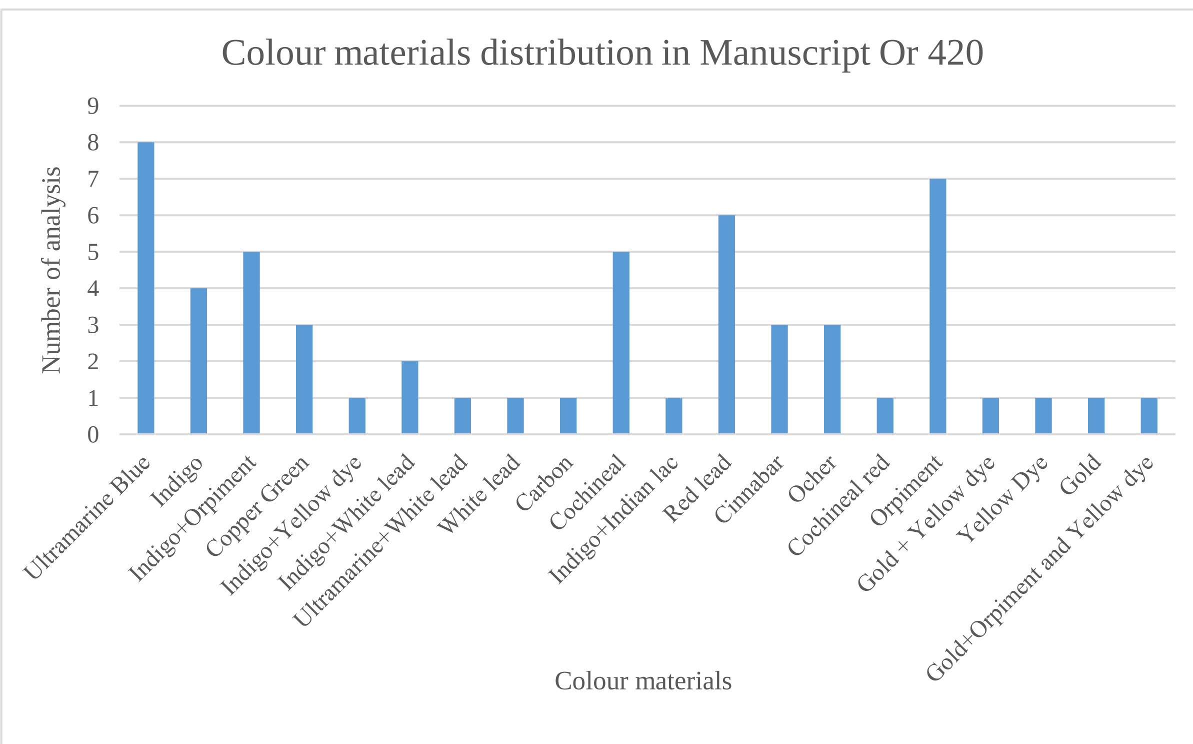


Figure 5-66: Distribution of colour materials used in manuscript Or 420

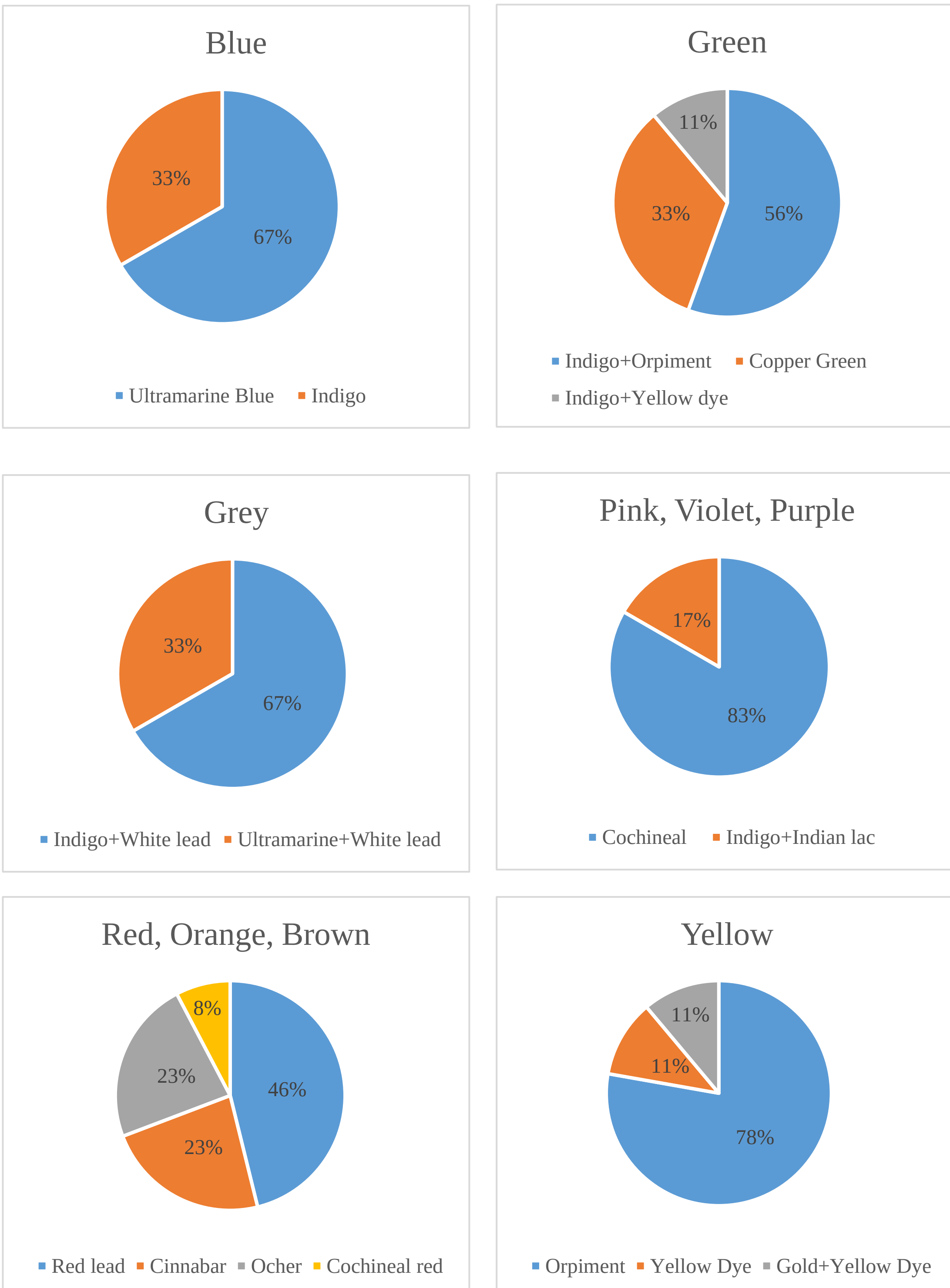


Figure 5-67: Percentage of colour materials used for each colour in manuscript Or 420

5-3-6 Shāhnāma manuscript MS 22-1948[40]

19 coloured spots in red, orange, and brown tonalities were analysed in this manuscript. In this manuscript like many other Persian manuscripts has been used cinnabar as the main pigment to create red colour, red lead as the main pigment has been used to create orange colour, and red ocher has been used as the main pigment to create brown colour (Tab. 5-31) (see section 5-2-2).

Only the light brown colour used to colouring the bird in folio 11 is a combination of red lead with orpiment. the mentioned colour combination has been used many times for colouring clothes, barding, robes, flowers, tents, underlays, carpets, etc. (Fig. 5-68).

Folio number	Description	Colour material	Colour tonality
11, 12, 14, 15, 18, 20, 22, 25	clothes, background, robes	red lead	a
11, 12, 14, 15, 18, 20, 22, 25	robes, barding, clothing, background, tent, flowers, text	cinnabar	b
14, 15, 22, 25	architecture, tree trunk	red ocher	c

Table 5-31: Distribution of red, orange, brown colour materials used in manuscript Ms 22-1948

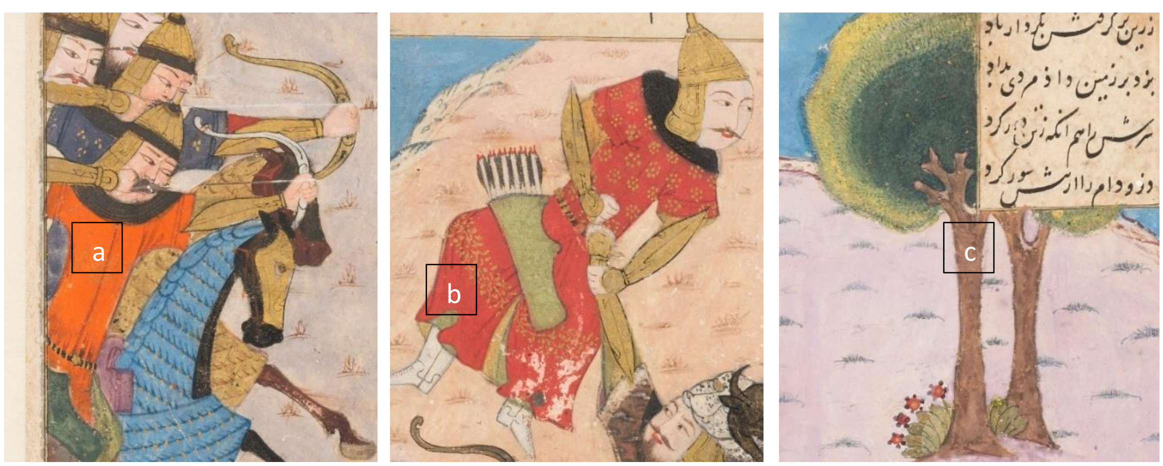


Figure 5-68: Comparison of tonality of different red, orange, brown colour materials in manuscript Ms 22-1948; red lead(a), cinnabar(b), red ocher(c)

[40] I would like to thank Dr Paola Ricciardi who performed the XRF and FORS analysis and helped me in the evaluation of the spectra.

In general, the amount of yellow is so little in this manuscript, therefore four yellow coloured spots of this manuscript were analysed (Tab. 5-32). Only yellow tones are relevant to the yellow spots where the painter has tried to specify the details of his images and has used yellow to a very small extent (Fig. 5-69).

Two yellow colour material has been used in this manuscript; one is the use of orpiment pigment for colour yellow at the outermost part of the tree's foliage in folio 11 and also the use of combination of orpiment with gold to create a special yellow colour which has non-metallic luster and has been used to paint the flag on folios 14 and 20 of this manuscript (Fig. 5-69).

Folio number	Description	Colour material	Colour tonality
11, 20	background, details, tree foliage	orpiment	a
14, 20	flags	orpiment + yellow dye	b

Table 5-32 Distribution of yellow colour materials used in manuscript Ms 22-1948

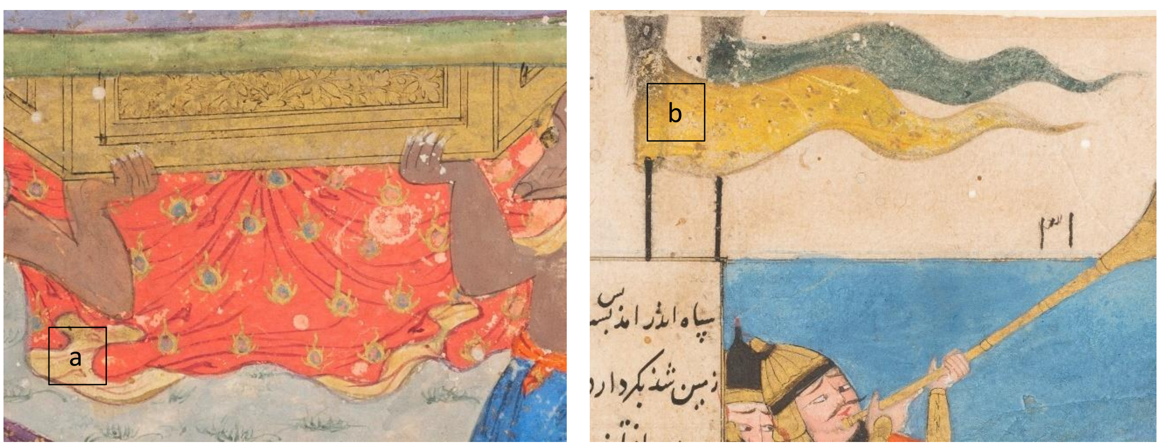


Figure 5-69: Comparison of tonality of different yellow colour materials in manuscript Ms 22-1948; orpiment(a), orpiment + gold(b)

11 blue-coloured spots of this manuscript were analysed. The painters of this manuscript have used ultramarine to create various tonalities of dark blue to light blue (Tab. 5-33).

Ultramarine has been used as the main blue pigment in this manuscript and several times has been combined with white lead to create light blue tonalities (Fig. 5-70). It should be noted that in this manuscript indigo also has been used in two deep blue spots to coloured robe and clothing in folios 14 and 11(see section 5-2-3).

Folio number	Description	Colour material	Colour tonality
11, 12, 14, 15, 18, 20, 22, 25	blue of sky, background, robes	ultramarine blue ultramarine blue + white lead	a
11, 14	robes and clothing	indigo	b

Table 5-33 Distribution of blue colour materials used in manuscript Ms 22-1948

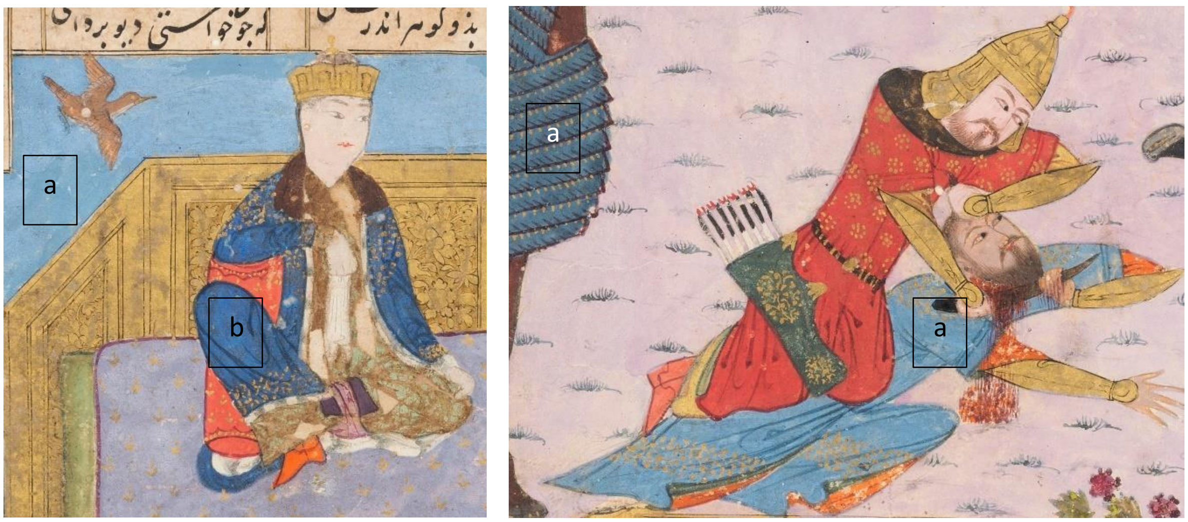


Figure 5-70: Comparison of tonality of different blue colour materials in manuscript Ms 22-1948; ultramarine blue(a), indigo(b)

Ten colour spots of pink, violet, and purple colour were analysed in this manuscript. This manuscript has various tonalities of pink and purple colours that are obtained from different combinations of coloure materials (Tab. 5-34). For example, to create light pink hue and violet a combination of cochineal with white lead has been used, and to create purple and dark purple colour tonalites a combination of cochineal with indigo has been used (see section 5-2-6).

These colour combinations have been used for colouring clothes, barding, robes, backgrounds, underlays, etc. (Fig. 5-71). It should be noted that for creation the light purple colour used for the background of folio 15 as well as the dark purple used for clothing on folio 20 a combination of cochineal with indigo has been used (see section 5-2-6).

Folio number	Description	Colour material	Colour tonality
11, 12, 14, 20, 22	robes, background, barding, clothing	cochineal + white lead	a
11, 12, 18, 20	barding, clothing, rugs, shield	cochineal + ultramarine	b
15, 20	background, clothing	cochineal + indigo	c

Table 5-34: Distribution of pink, violet, purple colour materials used in manuscript Ms 22-1948

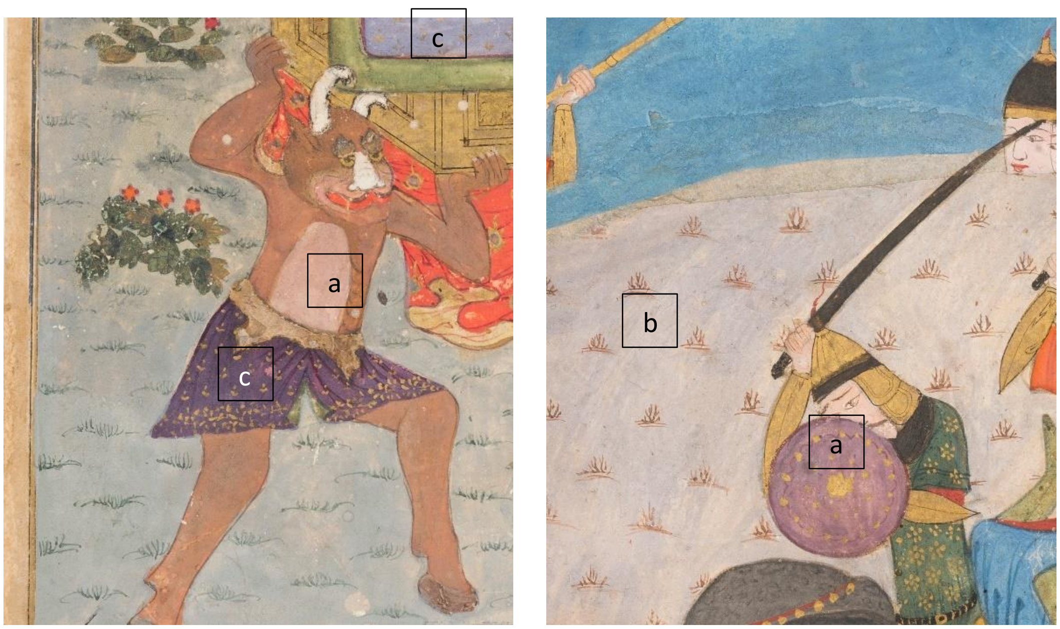


Figure 5-71: Comparison of tonality of different pink, violet, purple colour materials in manuscript Ms 22-1948; cochineal + white lead(a), cochineal + indigo(b), cochineal + ultramarine(c)

Ten green spots with different tonalities were analysed in this manuscript (Tab. 5-35). Painters of this manuscript combined different amounts of orpiment pigment with indigo to create various green tonalities from light green to dark and has been used this mixture for colouring the tufts of grass, the foliage of trees, clothing, underlay and carpets as well as for flower leaves (Fig. 5-72).

It should be noted that only the green pigment based on copper (copper green) has been used for Colouring the light green saddle in folio 12 (see section 5-2-1).

Folio number	Description	Colour material	Colour tonality
11, 14, 15, 18, 20	the tufts of grass, Foliage of trees, clothing	indigo + orpiment	a
14	saddle	copper green	b

Table 5-35: Distribution of green colour materials used in manuscript Ms 22-1948

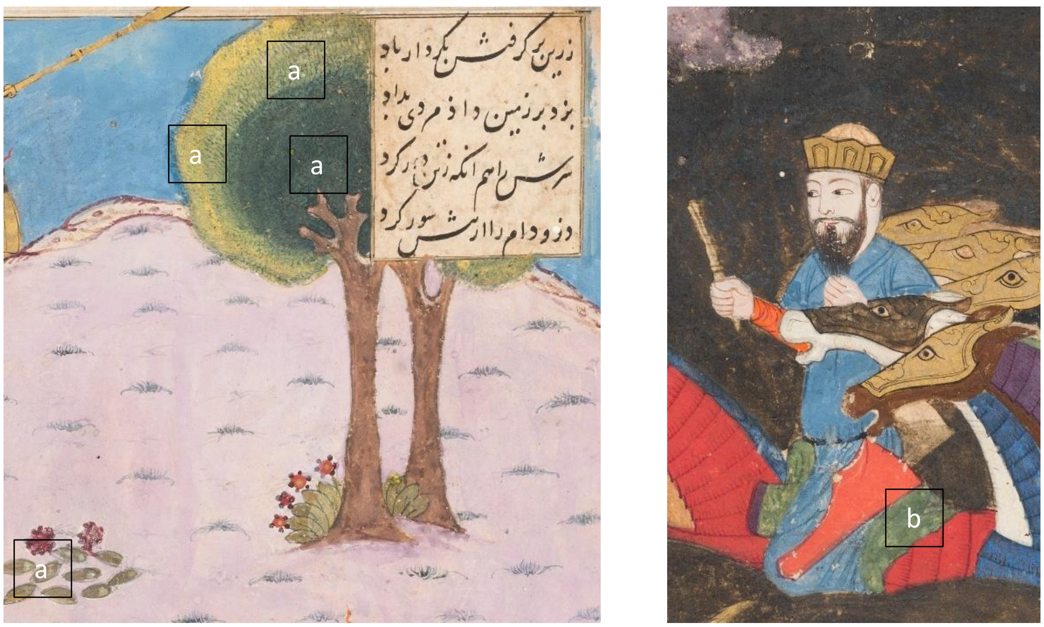


Figure 5-72: Comparison of tonality of different green colour materials in manuscript Ms 22-1948; indigo + orpiment(a), copper green(b)

11 colour samples were analysed in black, white, grey, and also metallic tonality in this manuscript (Tab 5-36). In this manuscript only gold pigments are used to create metallic luster colours (see section 5-2-5-1). It should be noted that the colour tone is dark grey, and light created on folio 12 (for background) and folio 20 (elephants and swords) by silver metal pigment that is degraded over time and became dark grey (Fig. 5-73).

Also, the light grey colour used for the background in folios 11 and 12 is obtained from a mixture of indigo with white lead (Tab. 5-36). Also, in folio 11 to create a dark brownish-grey hue for colouring one of the demons has been used a combination of red ocher pigment with red lead (Fig. 5-73). It looks like the painter for achieving to the desired tonality at this point, it has combined and used red ocher pigment with red lead. The white and black colours used in this manuscript is white lead and black colour material is carbon based black.

Folio number	Description	Colour material	Colour tonality
12, 20	background, elephants, sword	degraded silver	a
11, 12	background	indigo + white lead	b
11	demond	red ocher + red lead	c
11, 12, 14, 15, 20	background, clothing, details	gold	d

Table 5-36: Distribution of black, white, grey, and metallic colour materials used in manuscript Ms 22-1948

Figure 5-73: Comparison of tonality of different black, white, grey, metallic colour materials in manuscript Ms 22-1948; degraded silver(a), indigo + white lead(b), red ocher + red lead(c), gold(d)

5-3-6-1 Statistical analysis of the Shāhnāma MS 22-1948

This manuscript is an example of the Timurid manuscripts of Shiraz dated 1435 CE (see Chapter 3). This manuscript as manuscript Or 420 is an example of the Timurid manuscript of Shiraz but clearly, the quality of colour materials used in this manuscript also the quality of miniatures are higher than manuscript

Or 420. From the point of view of material science, the colour materials of this manuscript are more similar to other manuscripts of Shiraz like AKM 4, not Or 420.

For example, unlike manuscript Or 420 in this manuscript, a little amount of yellow dye and a high amount of silver pigment has been used. Therefore, the colour materials of five existing miniatures of this manuscript were analysed. Indeed 126 single measurements contain; 63 FORS analysis and 63 XRF analysis were performed on this manuscript (see Tab. 5-57).

From the point of view of statistical analysis, ultramarine and indigo are the only blue colour used in this manuscript 82% of analysed blue colour is ultramarine and 18% is indigo. 90% of analysed green is a mixture of indigo + orpiment, 10% is copper green. Degrade silver contains 57% of grey colour analysed and indigo + white lead contains 29%, and red ocher + red lead contains 14% of analysed grey colour. 40% of analysed pink, violet, and purple sample is cochineal, 40% is a mixture of ultramarine + cochineal, and 20% is a mixture of cochineal + indigo. colour materials identified for red, orange, and brown include 32% red lead, 53% cinnabar, and 10% red ocher, and 8% cochineal. 50% of the analysed yellow is orpiment, and 50% is a mixture of orpiment + gold.

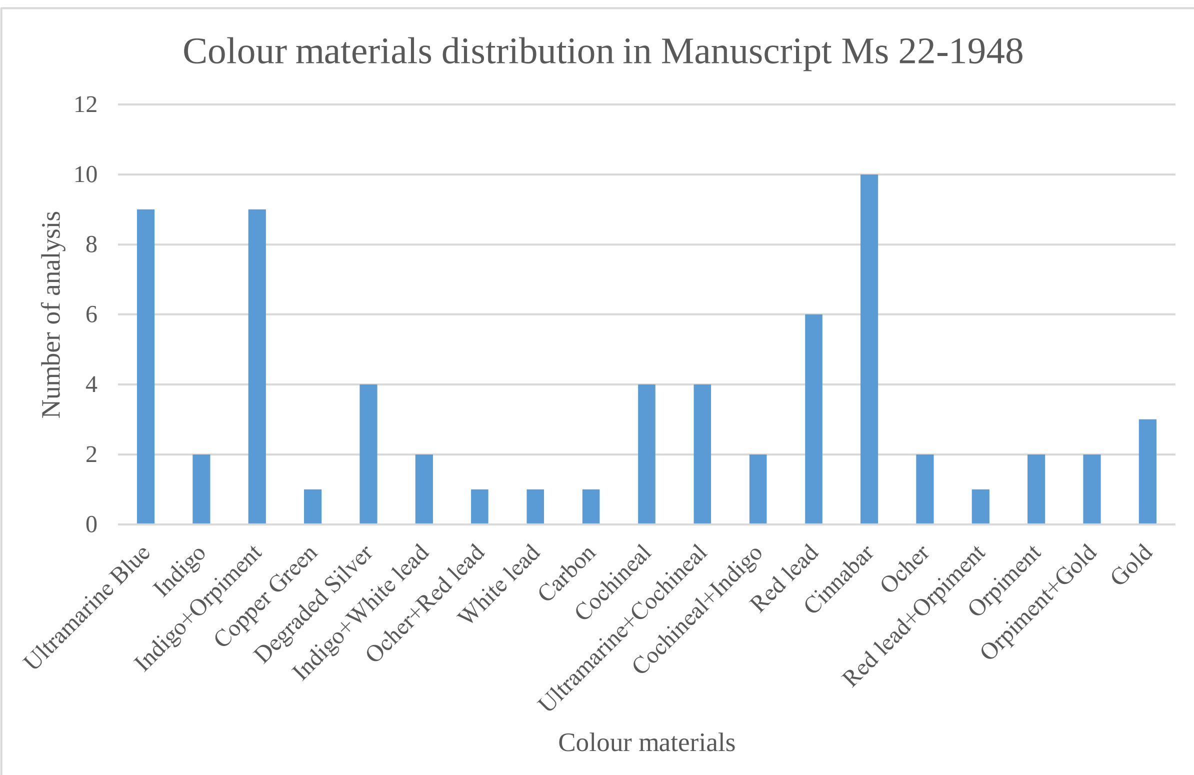


Figure 5-74: Distribution of colour materials used in manuscript MS 22-1948

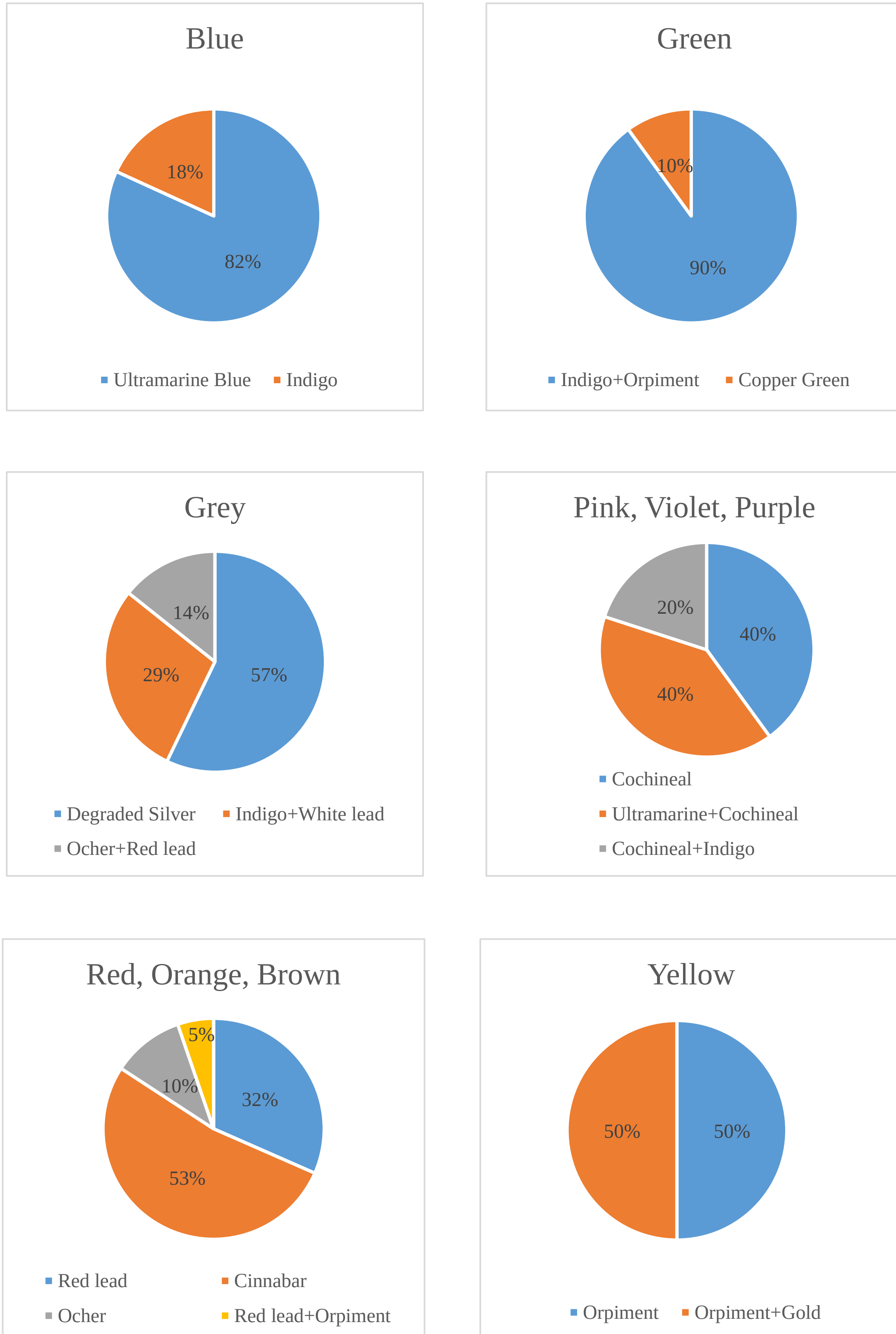


Figure 5-75: Percentage of colour materials used for each colour in manuscript MS 22-1948

5-3-7 Shāhnāma manuscript Persian 9[41]

15 different colour samples in red, orange, and brown colour tonalities were analysed in this manuscript (Tab. 5-37). This manuscript was painted by two different painters in two completely different styles. Painter A who according to his painting style (very simple and primitive designs, uniform and flat colours, and colours limited to brown, orange and purple (mauves)) is an Indian painter recalling Jalayirid painting style (late 14th or early 15th century) (see Chapter 2).

As mentioned before, this painter used a very small number of colours. That three red, orange, and brown colour are among the main colours used by this painter. Painter A to create colour tonality red to brown has used the two pigments cinnabar and red lead alternately (Tab 5-37). Pigment cinnabar to create colour red and dark red have been used, and mostly it is used for background colouring, architectural components, clothes (Fig. 5-76).

It should be noted that in only one case in folio 429 this painter used cinnabar to create the brown colour of the rug. This painter used red lead to create orange and used it to paint clothes, backgrounds, and architectural components (Fig. 5-76). Painter B, who according to his painting style is an Iranian painter belonging to the Timurid painting style of Shiraz school, whose paintings have far higher quality and colour variety than painter A (see Chapter 2). Painter B used cinnabar to create red and dark red and has used it to paint clothes, flowers, backgrounds, robes (Fig. 5-77).

This painter also in order to create the orange colour used red lead and used it to paint robes and background (Fig. 5-77). As well as to create colour tones light and dark brown used red ocher pigment and used it to paint architectural components (Fig. 5-77). All mentioned pigments can be identified by a combination of XRF and FORS techniques (see section 5-2-2).

Folio number	Description	Colour material	Colour tonality
18, 94, 429	clothes, background, robes	red lead	a
18, 28, 94, 348, 575	robes, clothing, background, flowers	cinnabar	b
94, 158	architecture	red ocher	c

Table 5-37: Distribution of red, orange, brown colour materials used in manuscript Persian 9

[41] In this respect, I would like to thank Professor Dr Olivier Bonnerot who performed the XRF analysis on this manuscript.

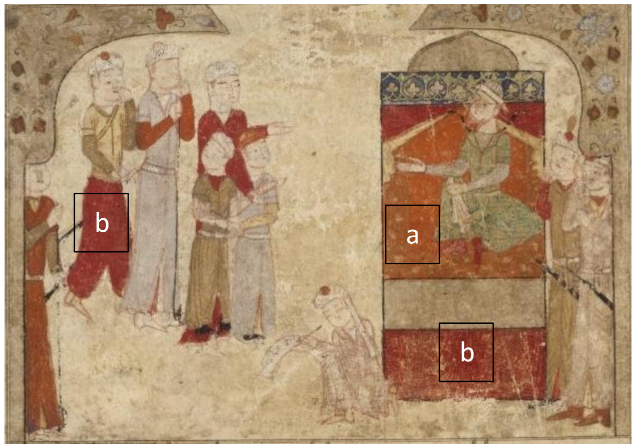


Figure 5-76: Comparison of tonality of different red, orange, brown colour materials in manuscript Persian 9 (Painter A); red lead(a), cinnabar(b), red ocher(c)

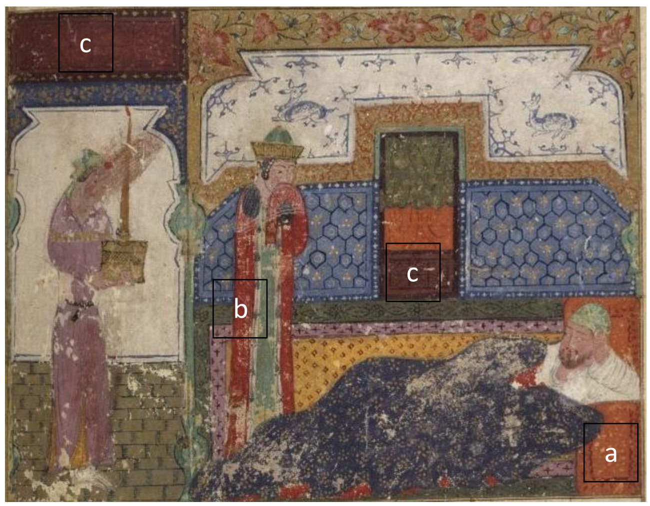


Figure 5-77: Comparison of tonality of different red, orange, brown color materials in manuscript Persian 9 (Painter B); red lead(a), cinnabar(b), red ocher(c)

Nine yellow spots colour from both painters A and B were analysed in this manuscript. The main material used by both painters to create the yellow colour is orpiment (Tab. 5-38). Painter A, to change the yellow tonality and lighten its orpiment yellow mixed and used it with different amounts of yellow dyes. The colour created from this combination is very light and is mostly used for background colouring and clothes (Fig. 5-78). Yellow dye used in this manuscript is most like saffron, turmeric, or Indian yellow.

But unfortunately, with the techniques used in this project, it is not possible to distinguish these dyes from each other (see section 5-2-4). Technique used in this project to identify yellow pigments are FORS and FOMF techniques, however, the FORS and FOMF spectra of saffron and turmeric are very similar (see Fig. 5-18). Therefore, it is only possible to prove the use of yellow dyes, but it is not possible to distinguish them from each other. Painter B also used orpiment as the main pigment to create the yellow colour (Tab.

5-38). The main difference between the two painters in the use of orpiment is that the painter B mixed orpiment with white lead to change the colour tone of the orpiment and to create a bright yellow (Fig. 5-79).

Folio number	Description	Colour material	Colour tonality
18, 28, 158, 217, 313	clothing, background, saddle, architecture	orpiment	a
18, 169	robes	orpiment + yellow dye	b

Table 5-38: Distribution of yellow colour materials used in manuscript Persian 9

Figure 5-78: Comparison of tonality of different yellow colour materials in manuscript Persian 9 (painter A); orpiment(a), orpiment + yellow dye(b)

Figure 5-79: Comparison of tonality of different yellow colour materials in manuscript Persian 9 (painter B); orpiment(a)

14 blue colour samples were analysed in this manuscript. The results of these analyses show that both painters of this manuscript used ultramarine and indigo as blue colour (Tab. 5-39). The painter A used ultramarine to paint the sky and robes (Fig. 5-80). However, this ultramarine colour has been fallen in many places. The phenomenon of ultramarine falls is seen in many Persian manuscripts, but since most of the paintings done by painter A have been severely damaged and due to low quality of paintings of this painter, it can be concluded that the fall of the ultramarine is due to the use of low quality ultramarine or poor painting techniques.

In addition to ultramarine, indigo has also been used to create a blue colour in this manuscript by painter B (Tab. 5-39). This painter to create light blue tonalities combines ultramarine with white lead and to create very light blue (Turquoise) tones used in the background, in many cases has used a combination of indigo with white lead. This painter has used these colour combinations for colouring sky, background, clothes, robes (Fig. 5-81). These colour combinations were identified by combining of XRF and FORS techniques (see section 5-2-3).

Folio number	Description	Colour material	Colour tonality
18, 28, 94, 148, 158, 221, 313, 348	blue of sky, robes, background, clothing	ultramarine blue ultramarine + white lead	a b
80, 196	robes and background	indigo + white lead	c

Table 5-39: Distribution of blue colour materials used in manuscript Persian 9

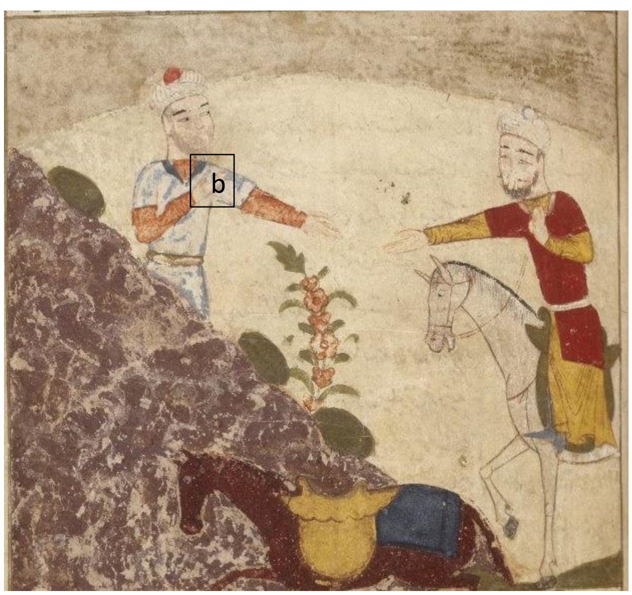


Figure 5-80: Comparison of tonality of different blue colour materials in manuscript Persian 9 (painter A); ultramarine blue(a), ultramarine blue + white lead(a)

Figure 5-81: Comparison of tonality of different blue colour materials in manuscript Persian 9 (painter B); ultramarine(a), ultramarine blue + white lead(b), indigo + white lead(c)

18 coloured spots in pink, violet, and purple tonality were analysed in this manuscript. As mentioned, the coloured pallet used by painter A is very limited, so only three pink and purple colour samples used by this painter were found (Fig. 5-82).

Very dark purple colours (greyish) which is used in folios 169 and 429 to paint the background. To create these colours dark purple is a combination of ultramarine with white lead. A sample of dark pink of robe which painted by the painter A on folio 429 were analysed, this painter has used a combination of cinnabar and white lead for this colour point (Tab. 5-40). But Painter B has used a variety of pink and purple tones to paint the background and clothes (Fig. 5-83).

This painter has used the colour combination of Indian lac with white lead to create different tones of pink and violet, and the combination of Indian lac with indigo to create purple to dark purple, which are mostly used for background colouring and clothes (Tab. 5-40).

It should be noted that this painter used a pale pink colour for painting faces and has used a combination of cinnabar with white lead (Fig. 5-83). Also, pink (peach) used for background and robe in folios 151, 221, 575 are obtained from a combination of cinnabar with orpiment and white lead.

It should be noted, according to the high importance of the colours of the purple to pink spectrum of this manuscript for comparison with other manuscripts analysed in this project, a number of micro samples of pink and purple colours were prepared and examined by SERS and HPLC-MS techniques (see section 5-2-6).

As previously mentioned, this project uses a combination of FORS and FOMF techniques to identify dyes. But it is not possible to distinguish Indian lac from cochineal by using these two combinations, but SERS and HPLC-MS techniques are very precise and of course sophisticated techniques through which it is detected that red dye is used to create colour pink and purple in this manuscript is Indian lac and not cochineal (see Fig. 5-7).

Folio number	Description	Colour material	Colour tonality
28, 94, 148, 196, 217	robes, background, clothing	Indian lac + white lead	a
94, 105, 138, 393, 525	robes, background, clothing	Indian lac + indigo	b
105, 158, 221, 575, 429	background and robes	cinnabar + orpiment and white lead	c
429,169	background	ultramarine + white lead	d

Table 5-40: Distribution of pink, violet, and purple colour materials used in manuscript Persian 9

Figure 5-82: Comparison of tonality of different pink, violet, purple colour materials in manuscript Persian 9 (painter A); cinnabar + white lead(c), ultramarine blue + white lead(d)

Figure 5-83: Comparison of tonality of different pink, violet, purple colour materials in manuscript Persian 9 (painter B); Indian lac + white lead(a), Indian lac + indigo(b), cinnabar + orpiment and white lead(c)

14 green samples were analysed in different tonalites in this manuscript. Painter A has used green to a very limited extent only on folios 44 and 429. This painter uses only copper-based green pigment to create green colour (Fig. 5-84). But Painter B, in addition to the copper-based green pigment, also used a combination of orpiment and indigo to create the green colour (Tab. 5-41). Copper-based green is mostly used for robe and background colouring, combining orpiment with indigo for colouring the foliage of trees and backgrounds (Fig. 5-85).

Interestingly, this painter has created completely different colour fulfilments from the combination of different percentages of indigo. For example, in the folios 28, 148, and 222 this painter to colour the leaves of the trees first mixed a large amount of indigo with a very small amount of orpiment and in this way the desired green colour of the central part of the tree leaves has formed and continues to create the greenish yellow required for the outer part of the tree leaves uses a large amount of orpiment combined with a small amount of indigo to create the desired tonality, it should be noted this colour combination is recognizable by XRF and FORS (see section 5-2-1-1).

Folio number	Description	Colour material	Colour tonality
18, 28, 44, 94, 138, 348, 429	robes, background, clothing	copper green	a
28, 80, 94, 148, 221, 348	tree foliage and background	indigo + orpiment	b

Table 5-41: Distribution of green colour materials used in manuscript Persian 9

Figure 5-84: Comparison of tonality of different green colour materials in manuscript Persian 9 (painter A); copper green(a)

Figure 5-85: Comparison of tonality of different green colour materials in manuscript Persian 9 (painter B); copper green(a), indigo + orpiment(b)

16 coloured spots of grey (six spots), black and white (three spots), and metallic gold (seven spots) were analysed in this manuscript. In this manuscript, like most Persian manuscripts, has been see the uses of two metallic pigments, gold, and silver (Tab. 5-42).

Painter B has used gold in all colour spots with metallic luster, but painter A has used a combination of gold, silver and orpiment, so these coloured spots can be called semi-metallic and like other analysed versions of these coloured spots they do not have metal glow (Fig. 5-86). It should be noted that in some of the less valuable Persian manuscripts, painters used mixture of silver and gold to reduce costs or create a certain colour fulfilment such as painter A in this manuscript (see section 5-2-5-1).

As previously mentioned, this is a manuscript due to the low quality of the materials used in it, especially the colour materials has used by Painter A, it suffers from serious damage in many folios, the coloured material used for it has been detached. In the analysis of coloured spots grey, coloured by Painter A revealed that many of the spots that are currently seen in light grey have in fact another colour, and their current colour is actually a trace of the colour what remains (Fig. 5-86).

For example, in folio 18, two coloured robes are seen as light grey, that according to the analyzes performed, their main colours were blue (ultramarine) and yellow (orpiment), and their current grey colour is actually a remnant of their original colour that has been disappeared. However, the coloured spots of painter B paintings are grey and actually degraded silver, for example the dark grey used for creek water in folio 217 (Tab. 5-42). This painter also created different shades of dark grey (greyish green) by combining indigo with white lead and sometimes with orpiment (Fig. 5-87). It should be noted that like many Persian manuscripts, the white and black colours used in this manuscript are white lead and carbon.

Folio number	Description	Colour material	Colour tonality
18	robes, clothing	detached colour/grey	a
217	water	degraded Silver	b
18, 28, 429	background	gold + orpiment and silver	c
348, 575	background and robes	indigo + orpiment	d

Table 5-42: Distribution of black, white, grey, and metallic colour materials used in manuscript Persian 9

Figure 5-86: Comparison of tonality of different black, white, grey, and metallic colour materials in manuscript Persian 9 (painter A); detached colour/grey(a), degraded silver(b), gold + orpiment(c), indigo + orpiment(d)

Figure 5-87: Comparison of tonality of different black, white, grey colour materials in manuscript Persian 9 (painter B); detached colour/grey(a), degraded silver(b), gold + orpiment(c), indigo + orpiment(d)

5-3-7-1 Statistical analysis of the Shāhnāma Persian 9

this manuscript is an example of the Timurid manuscripts of Western India or Southern Iran (probably Shiraz), in the middle of the 15th century (see Chapter 3). As mentioned, paintings of this manuscript have been painted by two painters; painter A (Indian painter recalling Jalayirid painting style) and B (Iranian painter of Timurid painting style of Shiraz) as explained above.

Therefore, in this manuscript colour materials of two different painting styles were analysed, and many differences of colour materials used by these two painters were recognized. In general, colour materials which have been used by painter B are more diverse than painter A and his paintings are more complex comparison with painter A with very simple paintings.

Indeed 19 miniatures of this manuscript (Painter A; 5 miniatures and Painter B; 14 miniatures) were analysed, in fact, 197 single measurements contain; 88 FORS analysis (painter A; 27, painter B; 61), 88 XRF analysis (painter A; 27, painter B; 61), 11 FOMF analysis (painter A; 4, painter B; 7), and ca.5 SERS-Raman and HPLC-MS were performed on this manuscript (see Tab. 5-57).

The differences in colour materials used by these two painters can be seen in the below charts. Painter A has used only of ultramarine as a blue colour but 77% of the blue colour of painter B which were analysed is ultramarine and 23% is indigo. Painter A has used just of copper green as a green colour but for painter B only 31% of analysed green spots are copper green and the rest 69% is a mixture of indigo + orpiment. 67% analysed pink, violet, and purple colour spots of painter A is a mixture of ultramarine + white lead and 33% is cinnabar + white lead this percentage for painter B are; 29% Indian lac, 29% indigo + indian lac, 12% ultramarine + white lead, 6% cinnabar + white lead, 6% red lead + white lead, and 18% cinnabar + orpiment. 57% of analysed red, orange, and brown colour spot of painter A is cinnabar and 43% is red lead, but painter B in addition to cinnabar 63% and red lead 12% has used also of red ocher 25%. 60% analysed yellow colour of painter A is orpiment and 40% is orpiment + yellow dye, but painter B just has used of orpiment as a yellow colour.

Both painters have used gold as a metallic pigment, but painter A has used just of a mixture of gold + silver but 75% analysed metallic colour of painter B is gold pigment and 25% is a mixture of gold + silver and orpiment. The grey colours of the miniatures of painter A are not really grey colour material, their current colour is actually a trace of the colour what remains put degraded silver contains 75% of analysed grey colour of painter B, and the rest 25% is a mixture of indigo + white lead.

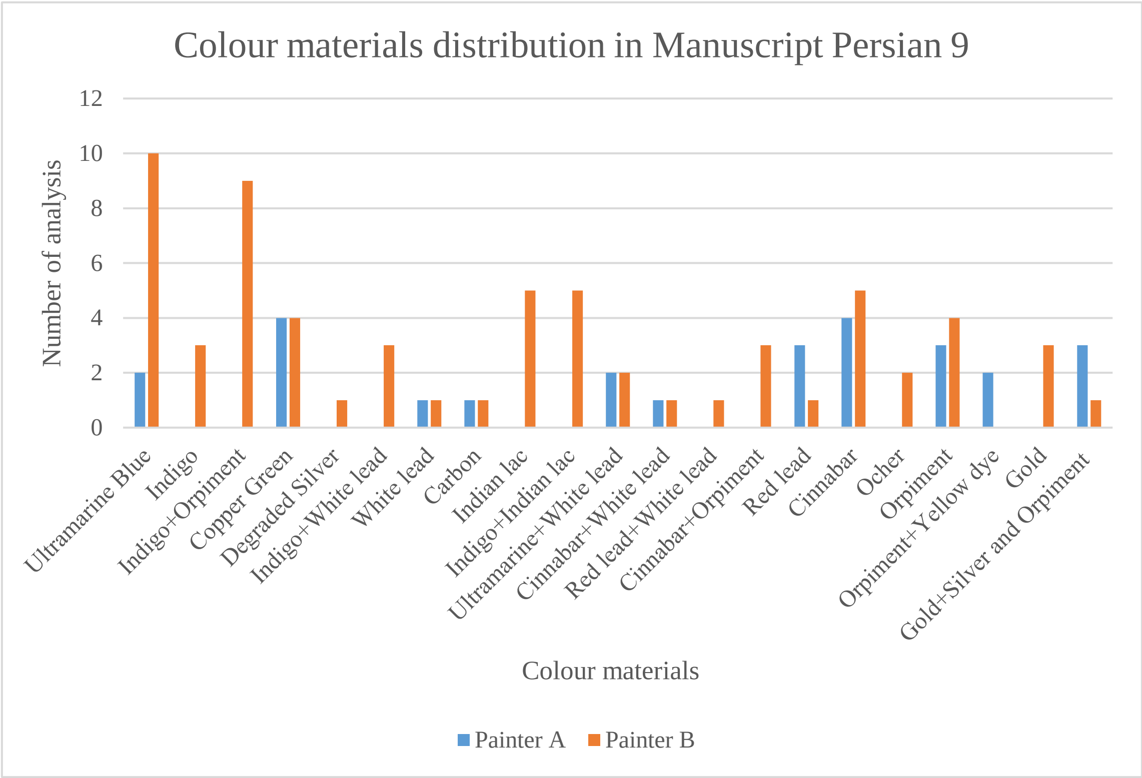
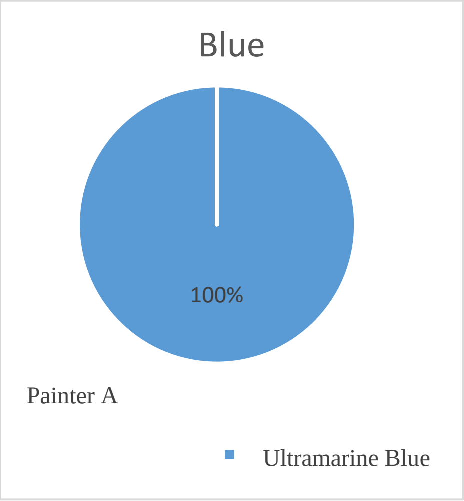
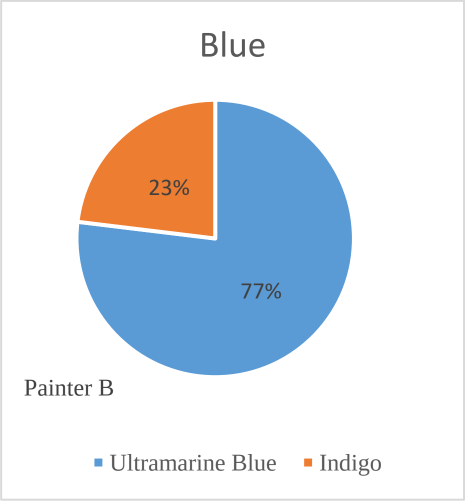
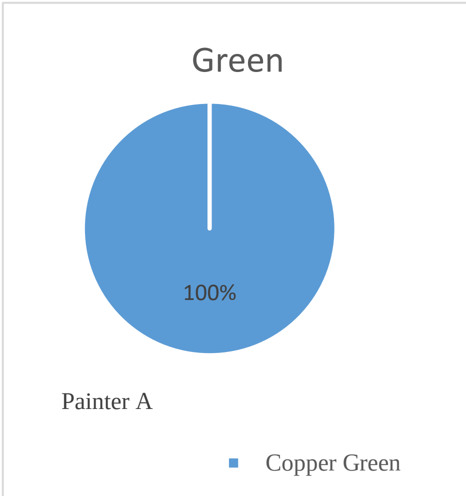
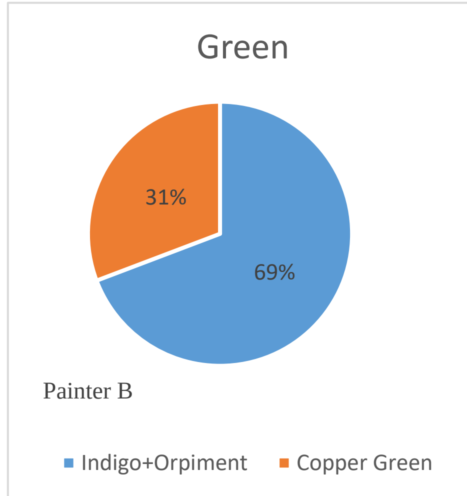


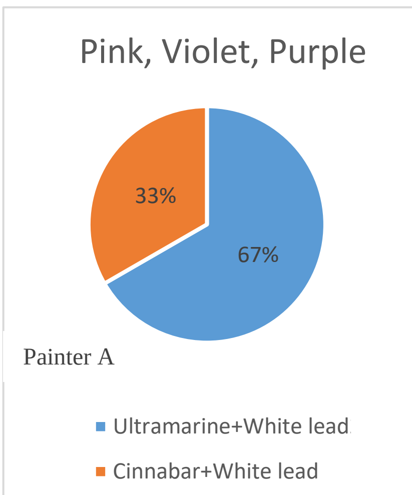
Figure 5-88: Distribution of colour materials used in manuscript Persian 933

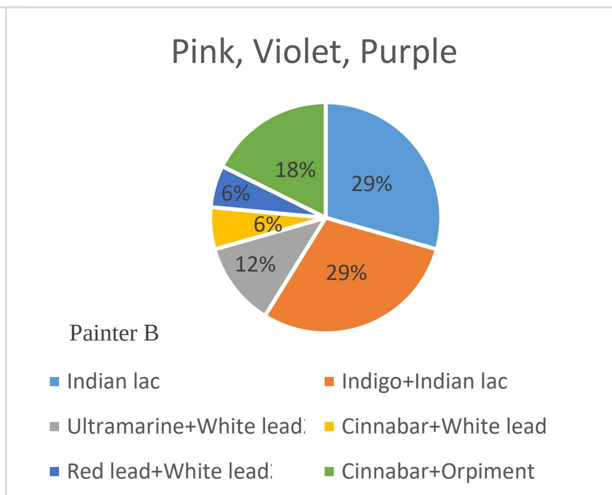


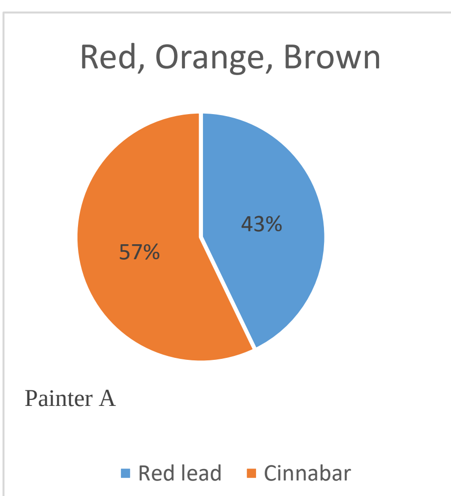


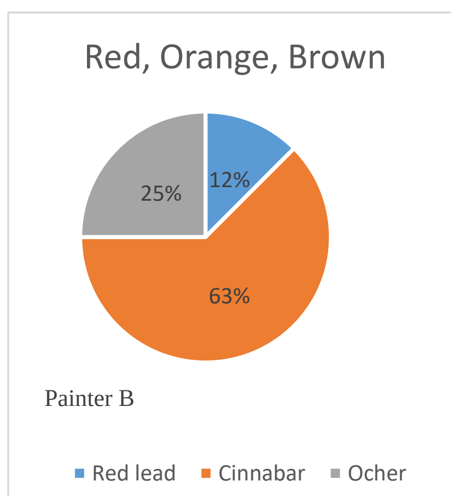

Green
100%
Painter A
Copper Green


Green
31%
69%
Painter B
Indigo+Orpiment
Copper Green


Pink, Violet, Purple
33%
67%
Painter A
Ultramarine+White lead
Cinnabar+White lead


Pink, Violet, Purple
18%
29%
6%
6%
12%
29%
Painter B
Indian lac
Indigo+Indian lac
Ultramarine+White lead
Cinnabar+White lead
Red lead+White lead
Cinnabar+Orpiment


Red, Orange, Brown
43%
57%
Painter A
Red lead
Cinnabar


Red, Orange, Brown
25%
12%
63%
Painter B
Red lead
Cinnabar
Ocher

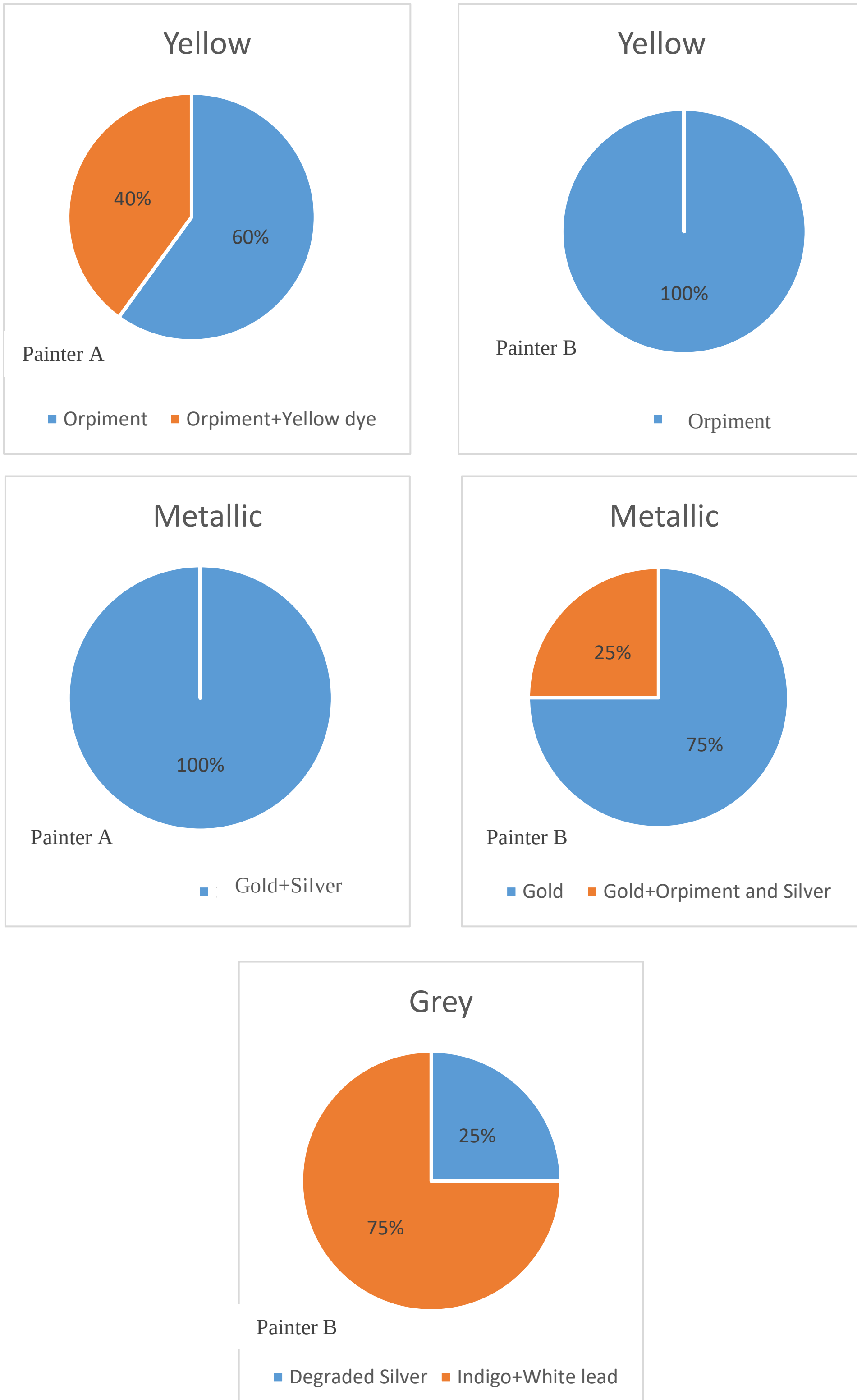


Figure 5-89: Percentage of colour materials used for each colour in manuscript Persian 9

5-3-8 Shāhnāma manuscript Persian 933[42]

As explained in chapter two, the text of this manuscript corresponds to the Timurid period. But the manuscript's paintings include paintings from the 14th century of Inju period, Shiraz school of the 15th century Timurid painter, and Qazvin school of the Safavid period of the 16th century. In this manuscript, 18 coloured spots including orange, red, and brown tonality were analysed. As mentioned above, red lead, cinnabar, and red ocher are common colour materials used for these colour tonalities in most Persian manuscripts (Tab. 5-43).

So, the painters of all three schools mentioned above have used of cinnabar to create dark red and brown colours, and to create orange have used red lead. Also, the Timurid painter has used of red ocher to create brown colour, while Inju painter has used a mixture of cinnabar + orpiment to create brown colour (Fig. 5-90, 92). Painters of this manuscript version linearly, to create their desired colour tonalities, combine the mentioned pigments with different amounts of white lead and used them to paint clothes, robes, architectural components, backgrounds (curtains, carpets, rugs), etc. All the mentioned colour materials are recognizable by XRF and FORS techniques (see section 5-2-2).

Folio number	Description	Colour material	Colour tonality
20, 37, 48, 95, 484, 191	clothes, background, robes	red lead	a
15, 25, 48, 196, 200	robes, clothing, background, flowers	cinnabar	b
87	tree trunk	red ocher	c

Table 5-43: Distribution of red, orange, brown colour materials used in manuscript Persian 933

Figure 5-90: Comparison of tonality of different red, orange, brown colour materials in manuscript Persian 9 (Timurid style 15th Century); red lead(a), cinnabar(b), red ocher(c)

42 In this respect, I would like to thank Professor Dr Olivier Bonnerot who performed the XRF analysis on this manuscript.

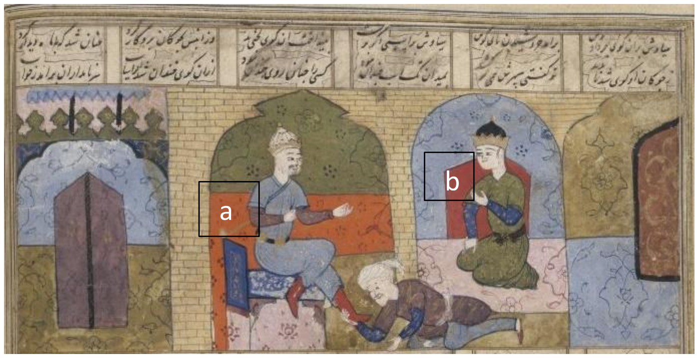


Figure 5-91: Comparison of tonality of different red, orange, brown colour materials in manuscript Persian 9 (Qazvin style 16th Century); red lead(a), cinnabar(b)

Figure 5-92: Comparison of tonality of different red, orange, brown colour materials in manuscript Persian 9 (Inju style 14th century); red lead(a), cinnabar(b), red ocher(c)

Six yellow coloured spots of this manuscript were analysed. According to the analyses performed on this manuscript, the main material used by Timurid painter and Inju painter for creation a yellow colour is orpiment (Tab. 5-44). This pigment has been used for colouring robes and backgrounds (Fig. 5-93, 94). It should be noted, in general, Timurid painter has used yellow colour so little, except to highlight the details of the paintings. Inju painter to paint the yellow underlay in folio 184 used a combination of yellow dye with a significant amount of yellow dye (Fig. 5-47).

The yellow colour of this colour compound can be identified by FORS and FOMF techniques (see section 5-2-4-1). These painters also have created a golden yellow hue from a combination of gold pigment with some orpiment, a golden colour without metallic luster that will be examined in the metallic pigment section. But the Safavid painters to create a yellow colour in addition to orpiment in folio 200 to paint the bright yellow background and saddle has used of the Indian yellow (Tab 5-44). Since the best way to identify Indian yellow is observation on sub-light UV which in this project did not perform a combination of, FORS and FOMF were used to identify Indian yellow (see section 5-2-4-2).

Folio number	Description	Colour material	Colour tonality
30, 37, 95, 184,	clothing, background, architecture	orpiment	a
184	ground cloth	orpiment + yellow dye	b
200	background, saddle	Indian yellow	c

Table 5-44: Distribution of yellow colour materials used in manuscript Persian 933

Figure 5-93: Comparison of tonality of different yellow colour materials in manuscript Persian 933 (Timurid style 15th century); orpiment(a)

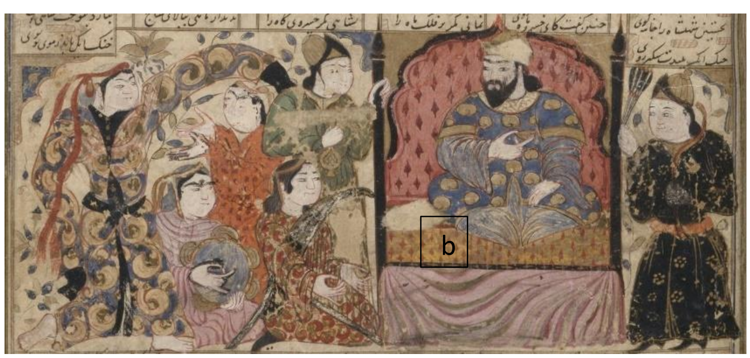


Figure 5-94: Comparison of tonality of different yellow colour materials in manuscript Persian 933 (Inju style 14th century); orpiment(a), orpiment + yellow dye(b)

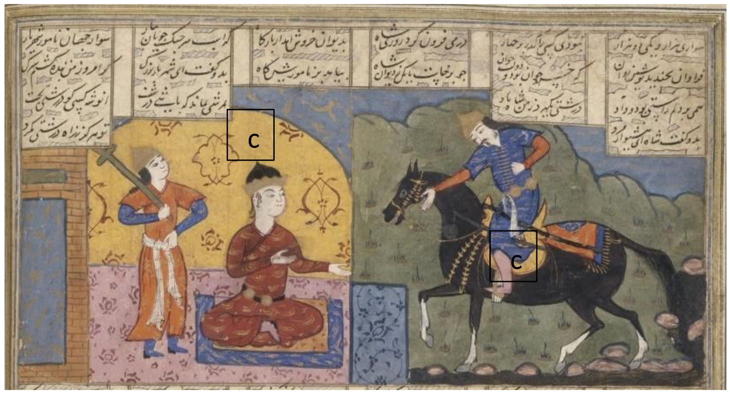


Figure 5-95: Comparison of tonality of different yellow colour materials in manuscript Persian 933 (Qazvin style 16th Century); orpiment(a), orpiment + yellow dye(b), Indian yellow(c)

18 blue samples with different tonality of all periods of this manuscript were analysed. In paintings of all three periods of Timurid, Inju and Safavid ultramarine have been used as the main pigments to create blue colour in different tonalities (Tab. 5-45). All the three painters, according to their desired tonality, combined ultramarine with different amounts of white lead and used it for colouring robes, backgrounds, costumes, sky, architectural details and so on (Fig. 5-96, 97, 98).

Among all analysed spots colour, only Timurtid painters in two places, used mixture of indigo other than ultramarine to create a blue tint (Tab. 5-45). The first case is light blue in the background in folio 25, a combination of indigo and cochineal, However, this combination was identified in other manuscripts as a purple colour, also here would consider as a light purple hue, but it looks more like light blue.

However, Timurid painter of this manuscript has been used this combination to create a light blue colour tone (Fig. 5-96). It should be noted that both are part of this colour sample (dye) and can be identified by a combination of FORS and FOMF techniques (see section 5-2-6-1). second item is related to the very light blue colour is used to colour the robe on folio 37. Timurid painters to create these colours have used a combination of indigo with white lead.

Folio number	Description	Colour material	Colour tonality
15, 20, 25, 37, 43, 48, 87, 95, 194, 191, 196, 200	blue of sky, robes, background, clothing	ultramarine blue ultramarine + white lead	a b

37	robes	indigo + white lead	c
Folio 25	background	indigo + cochineal	d

Table 5-45: Distribution of blue colour materials used in manuscript Persian 933

Figure 5-96: Comparison of tonality of different blue colour materials in manuscript Persian 933 (Timurid style 15th century); ultramarine(a), indigo + white lead(c), indigo + cochineal(d)

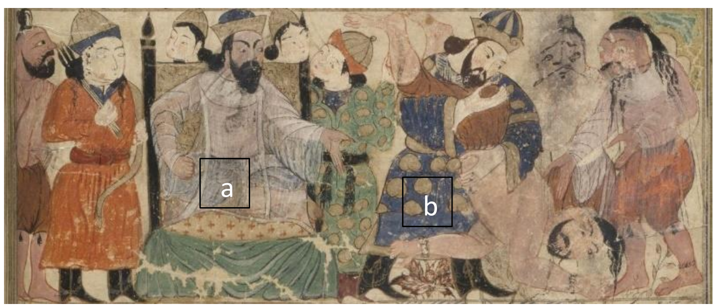


Figure 5-97: Comparison of tonality of different blue colour materials in manuscript Persian 933 (Inju style 14th century); ultramarine(a), ultramarine + white lead(b)

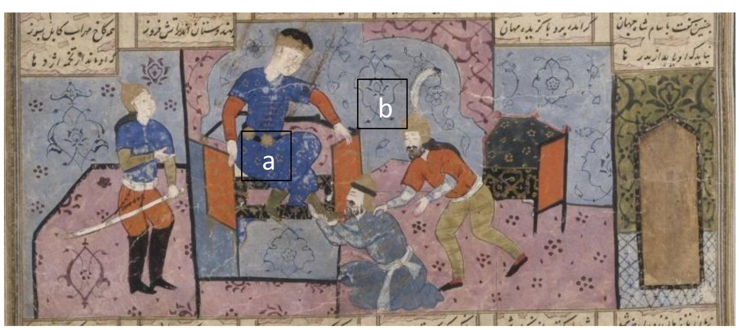


Figure 5-98: Comparison of tonality of different blue colour materials in manuscript Persian 933 (Qazvin style 16 centaury); ultramarine(a), ultramarine + white lead(b)

20 samples of pink, violet, and purple tonality colour were analysed in this manuscript. In paintings of different periods various colour materials has been used to make pink, violet, and purple tonality. Paintings related to the Timurid period have a variety of colours from pink to purple. The main colour material used by Timurid painter for pink and violet colours is cochineal (Tab. 5-46).

The cochineal has been repeatedly used as a violet colour for colouring clothes, backgrounds, and architectural components (Fig. 5-99). As well as Timurid painter produces a variety of pink to dark violet tonalities by combining cochineal with white lead and used it for background and clothes colouring. It should be noted that Timurid painter compared to other painters in this manuscript to create pink tones used more various combinations. For example, the orange-pink (peach) colour of the horse in folio 25 is a combination of cinnabar and white lead. Also, the purple and dark purple colours used to colour the robes on folio 37 created by combining cochineal composition with indigo (Tab. 5-46).

Also, pink-orange (peach) used to paint wall bricks in folio 43, it is obtained by combining cochineal with orpiment and white lead. Safavid painter of this manuscript like Timurid painter to reach to desired tonality of pink and violet combined cochineal with different amounts of white lead (Tab. 5-46) and use it for colouring clothes and background (Fig. 5-101). This painter only has two violet coloured spots in folio 20 (background) and folio 30 (robe) to achieve somehow pink and dark violet cochineal has been mixed with yellow dye (possibly turmeric) and used (Tab. 5-46).

It should be noted that the combination of FORS technique with FOMF was used to identify this combination of pigments (see section 5-2-6). Inju painter of this manuscript, like the other two other painters, combines cochineal with white lead and have created different tones of pink and purple and the only major difference between Inju painter of this manuscript is because, unlike the previous two other painters, he has used cinnabar to create pink tones (Fig. 5-100).

For example, in folio 184 to create an orange-pink colour (peach) used for underlay decorations from a combination of cinnabar with yellow dye is used, also it is used on folios 191 and 196 to create a light pink colour (Fig. 5-100). For The face and skin of the people and the underlay the combination of cinnabar and white lead is used. It should be noted that all the compounds mentioned, analysed, and identified by a combination of XRF, FORS and FOMF techniques (see section 5-2-6).

Folio number	Description	Colour material	Colour tonality
25, 37, 43, 48, 87, 196, 200	robes, background, clothing, architecture details	cochineal	a

25, 37, 43, 48, 87, 196, 200	robes, background, clothing	cochineal + white lead	b
37	robes	indigo + cochineal	c
20, 30	background, clothing	cochineal + yellow dyes	d
25, 191, 196	background, horse, and face	cinnabar + white lead	e
184	background	cinnabar + yellow dyes	f

Table 5-46: Distribution of pink, violet, purple colour materials used in manuscript Persian 933

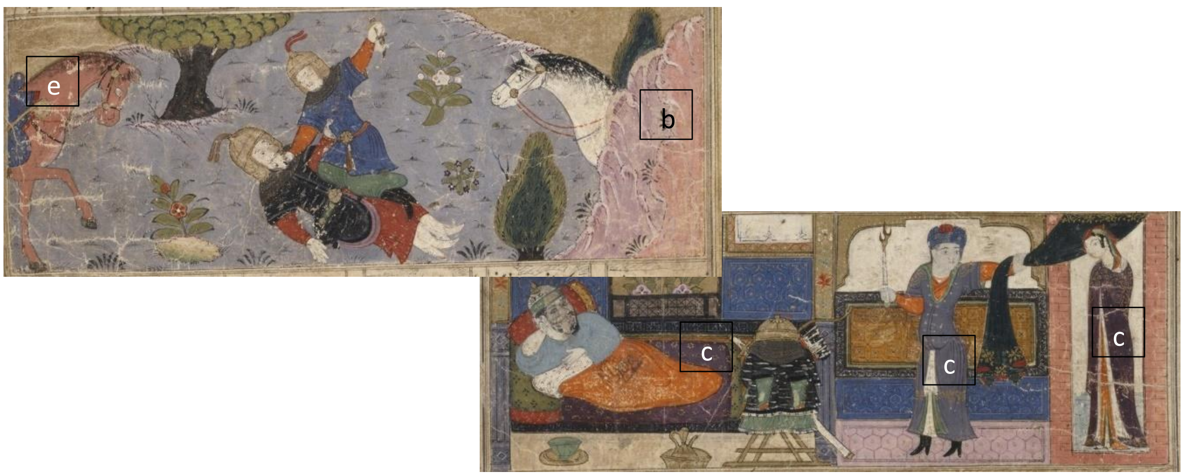


Figure 5-99: Comparison of tonality of different pink, violet, purple colour materials in manuscript Persian 933 (Timurid style 15th century); cochineal + white lead(b), indigo + cochineal(c), cinnabar + white lead(e)

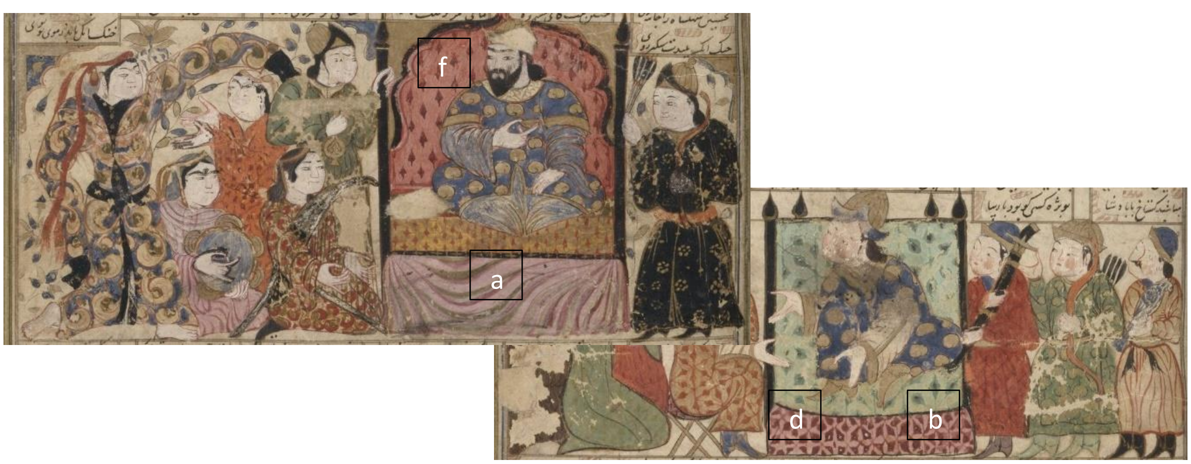


Figure 5-100: Comparison of tonality of different pink, violet, purple colour materials in manuscript Persian 933 (Inju style 14th century); cochineal(a), cochineal + white lead(b), cochineal + yellow dye(d), cinnabar + yellow dye(f)

Figure 5-101: Comparison of tonality of different pink, violet, purple colour materials in manuscript Persian 933 (Qazvin style 16th century); cochineal(a), cochineal + white lead(b), cochineal + yellow dye(d)

Ten coloured green spots of this manuscript were analysed. Among the various colour materials used to create green, copper green and indigo + orpiment combination have the most used in this manuscript (Tab. 5-47). Timurid and Safavid painters used many times the combination of indigo + orpiment to create bright tones to dark green.

These painters tend to combine these two colours with different amounts of dark green to light green toward yellow and used it to paint tree foliage, clothes, and backgrounds (Fig. 5-102, 103). It should be noted only in folio 37 Timurid painter have used copper green for light green. But the Inju painter unlike two other painters in this manuscript only used copper green to create green (Tab. 5-47). These painters combine copper green with white lead to created different tonalities and used it to paint clothes and backgrounds and have created different tones of green colour and have used it to colour clothes and backgrounds (Fig. 5-104).

As previously mentioned, because of copper pigments cause corrosion of paper in many manuscripts, to prevent this corrosion painter added copper green with saffron dye, but in this manuscript version, all the spots dyed with copper green are corroded and has fallen. Therefore, it can be concluded that the Inju painters, unlike the Timurid painters of this manuscript, did not use saffron dye in this manuscript for preventing the paper corrosion. all the compounds mentioned, analysed, and identified by a combination of XRF, FORS and FOMF techniques (see section 5-2-1).

Folio number	Description	Colour material	Colour tonality
37, 184, 191, 196,	robes, background, clothing	copper green	a
15, 25, 30, 87, 200	tree foliage and background	indigo + orpiment	b

Table 5-47: Distribution of green colour materials used in manuscript Persian 933

Figure 5-102: Comparison of tonality of different green colour materials in manuscript Persian 933 (Timurid style 15th century); copper green(a), indigo + orpiment(b)

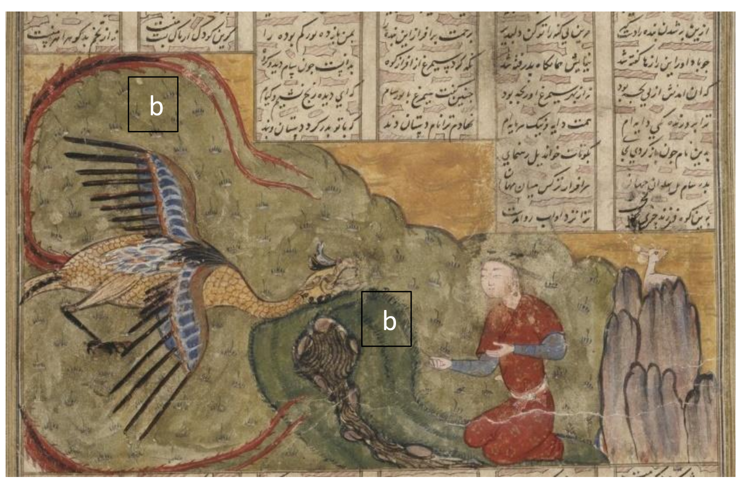


Figure 5-103: Comparison of tonality of different green colour materials in manuscript Persian 933 (Qazvin style 16th century); copper green(a), indigo + orpiment(b)

Figure 5-104: Comparison of tonality of different green colour materials in manuscript Persian 933 (Inju style 14th century); copper green(a), indigo + orpiment(b)

One metallic colour spot of each painters of this manuscript were analysed. Like most Persian manuscripts in all periods, gold pigment has been used in paintings of all three different periods (Tab. 5-48). The only thing to note is that the gold pigment used in the paintings of the Timurid period of this manuscript has higher quality and purity than the paintings of the other two periods.

There is some silver in the gold pigment used in Safavid paintings that indicated that gold powder has been combined with silver powder to reduce the cost of manuscripts (Tab. 5-48). Also, in gold pigments of Inju period orpiment also was identified, which indicates that the gold powder is combined with orpiment and then have been used (Tab. 5-48).

For this reason, the gold colours of these paintings have a semi-metallic (semi-bright) state. It should be noted except metallic pigment only in one case in folio 200 silver pigment was used to paint the creek water which, of course, is now corroded and became dark grey (six grey, white, and black spots were analysed). Also, in folio 87 for colour creation of light grey a combination of indigo with white lead is used to paint the demon. Like most Persian manuscripts in paintings of all three periods of this manuscript, white lead and black carbon have been used to create white and black colours.

Folio number	Description	Colour material	Colour tonality
15, 25, 43, 87, 184	background, architecture	gold gold + silver gold + orpiment	a
15, 25, 43, 184	horses, clothing, background details	black carbon	b
87	bogey	indigo + white lead	c

348, 575	background, faces, architecture, horses, and robes	white lead	d

Table 5-48: Distribution of white, black, grey, metallic colour materials used in manuscript Persian 933

Figure 5-105: Comparison of tonality of different white, black, grey, metallic colour materials in manuscript Persian 933 (Timurid style 15th century); gold(a), black carbon(b), indigo + white lead(c), white

Figure 5-106: Comparison of tonality of different white, black, grey, metallic colour materials in manuscript Persian 933 (Inju style 14th century); gold + orpiment(a), black carbon(b), white

Figure 5-107: Comparison of tonality of different white, black, grey, metallic colour materials in manuscript Persian 933 (Qazvin style 16th century); gold + silver(a), black carbon(b), white lead(d)

5-3-8-1 Statistical analysis of the Shāhnāma Persian 933

This manuscript is an example of the Timurid manuscripts of the Western India dated middle of 15th century (see Chapter 3). As mentioned in in Chapter 3 the text of this manuscript is for mid-15th century, but paintings of this manuscript are belong to three style; Timurid style which are contemporary with the text of manuscript, Inju style (mid-14th century), and Safavid style of Qazvin in the 16th century.

Therefore, the colour materials used for each of three painting style were analysed, in fact 13 miniatures of this manuscript were analysed. four paintings of Timurid style, three paintings of Inju style, and six paintings of Safavid style. Indeed 188 single measurements contain; 80 FORS analysis and 80 XRF analysis, 18 FOMF analysis, and five SERS-Raman and HPLC-MS were performed on this manuscript (see Tab. 5-57).

From the point of view of material science the variety colour materials used in the Timurid paintings are more than Safavid and Inju paintings, therefore Timurid paintings have several common colour materials with both of other painting styles but colour materials used in Safavid and Inju miniatures rarely have common colour materials. From the point of view of statistical analysis, ultramarine and indigo are the only blue colour used in this manuscript 67% of analysed blue colour of Timurid paintings are ultramarine and 33% is indigo in Safavid and Inju paintings only ultramarine has been used. Also 67% of analysed green Colour of Timurid miniatures is a mixture of indigo + orpiment, and 33% is copper green but in the Safavid paintings only a mixture of indigo + orpiment has been used and in the Inju paintings only copper green has been used. Degrade silver contains 50% of analysed grey Colour of Timurid miniatures and indigo + white lead contains the rest 50%, but in the Safavid and inju miniatures only degraded silver have been used.

In each of the different style of paintings of this manuscript different colour material have used to create pink, violet and purple tonalites, 50% of analysed pink, violet, and purple sample of Timurid paintings is cochineal, 25% is a mixture of cochineal + indigo, 13% is a mixture of cinnabar + orpiment and 12% is a mixture of cinnabar + white lead. this percentage for Safavid miniatures contains 71% cochineal and 29% cochineal + yellow dye, and for Inju miniatures the percentage contains 40% cochineal, 40% cinnabar + white lead, and 20% cinnabar + orpiment. 34% of analysed red, orange, and brown sample of Timurid miniatures is red lead, 33% is cinnabar, and 33% is red ocher. this percentage for Safavid miniatures contains 43% red lead and 57% cinnabar, and for Inju miniatures the percentage contains 40% red lead, 40% cinnabar, and 20% cinnabar + orpiment. In the Safavid miniatures a series of mixture have used to create yellow colour, 20% of analysed yellow colour of Safavid paintings is orpiment, 20% is a mixture of orpiment + yellow dye, 40% is Indian yellow, and 20% is a mixture of orpiment + gold, in the Timurid miniatures only orpiment has been used and in the Inju miniatures only a mixture of orpiment + yellow dye has been used.

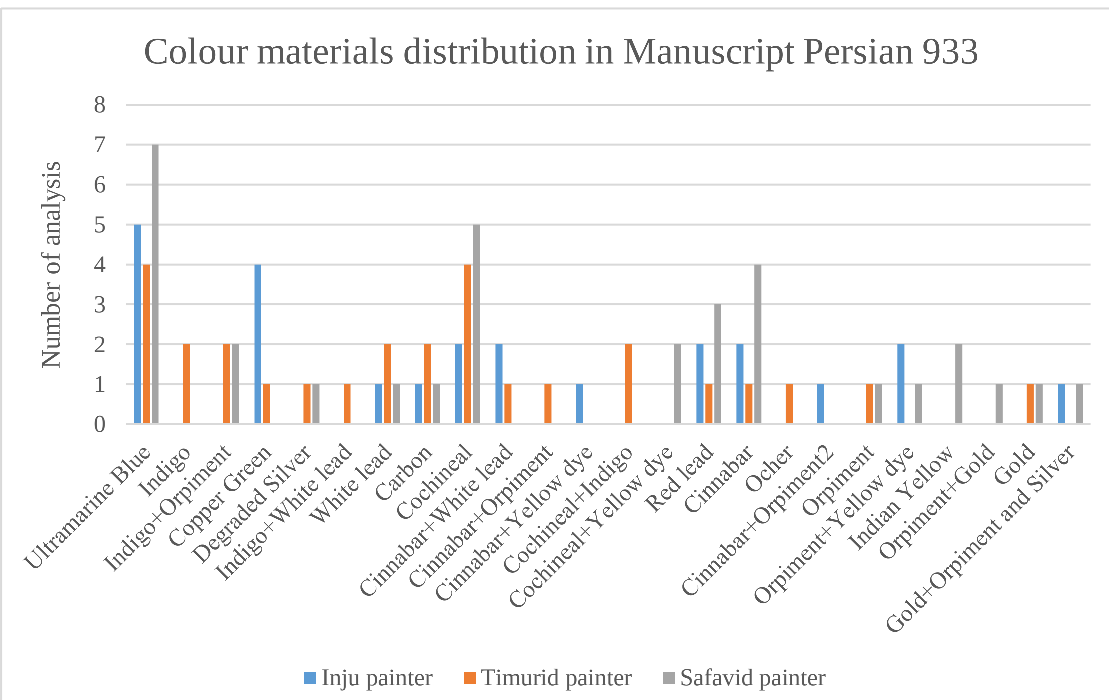
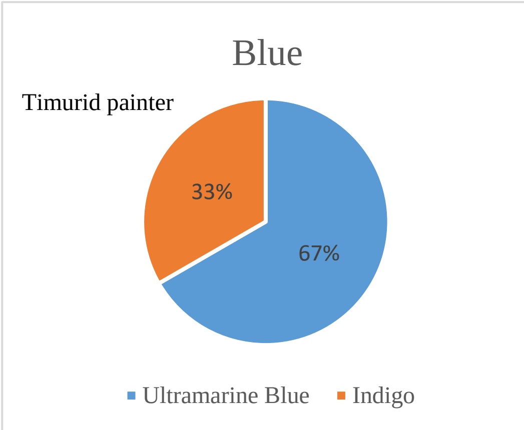
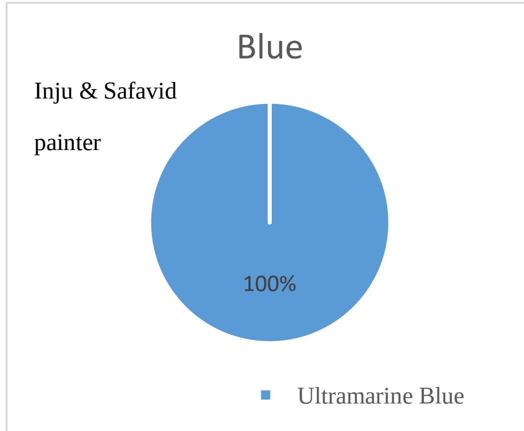
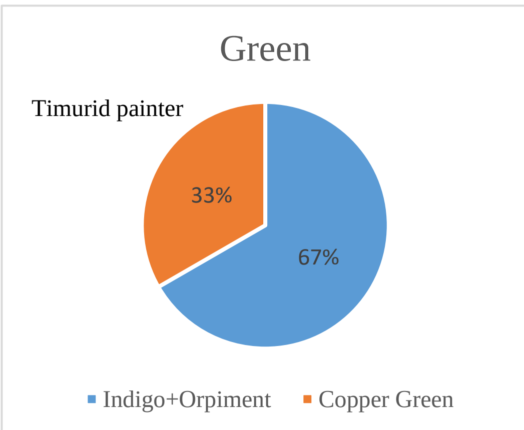
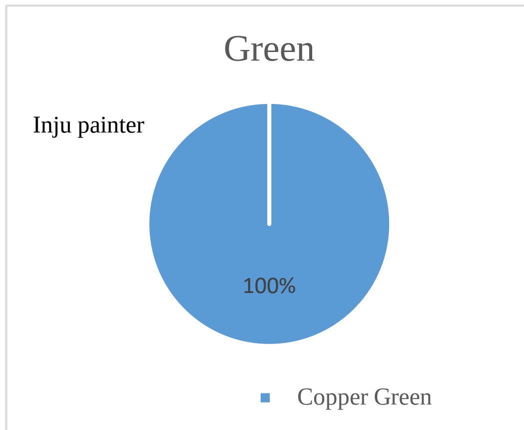


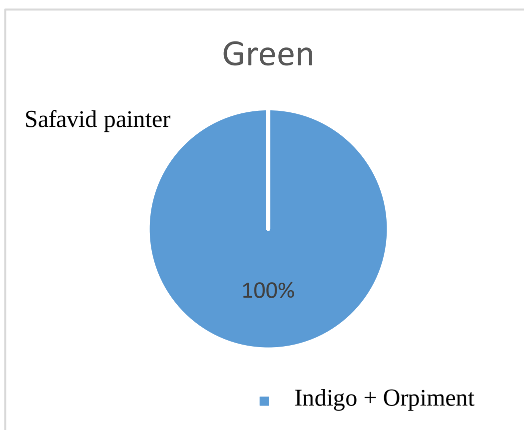
Figure 5-108: Distribution of colour materials used in manuscript Persian 933

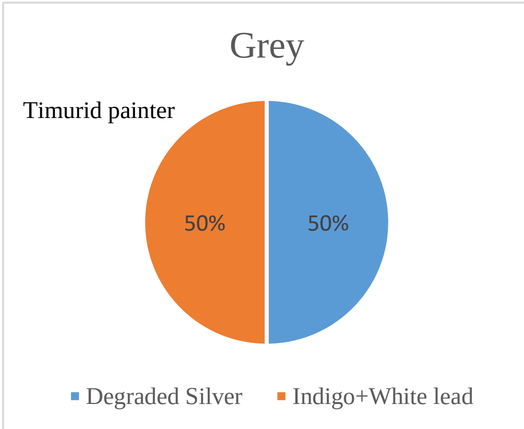

Blue
Timurid painter
33%
67%
Ultramarine Blue
Indigo

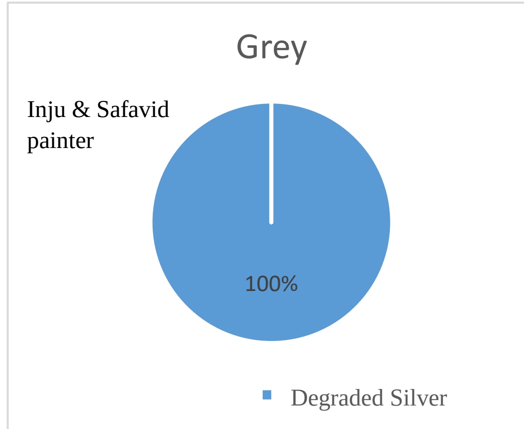

Blue
Inju & Safavid
painter
100%
Ultramarine Blue

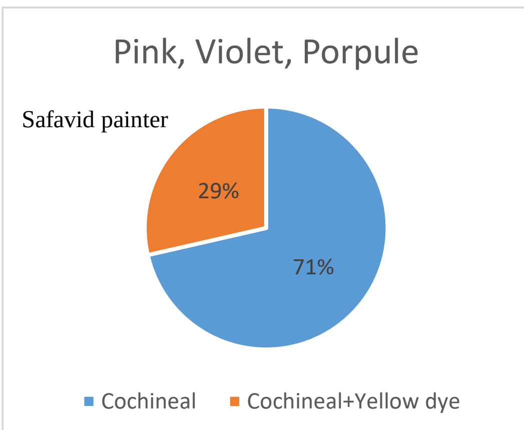

Green
Timurid painter
33%
67%
Indigo+Orpiment
Copper Green

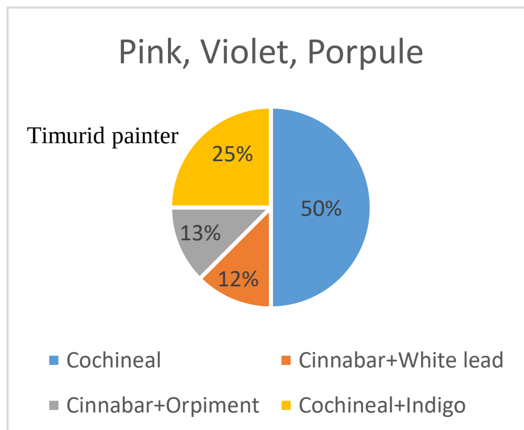

Green
Inju painter
100%
Copper Green

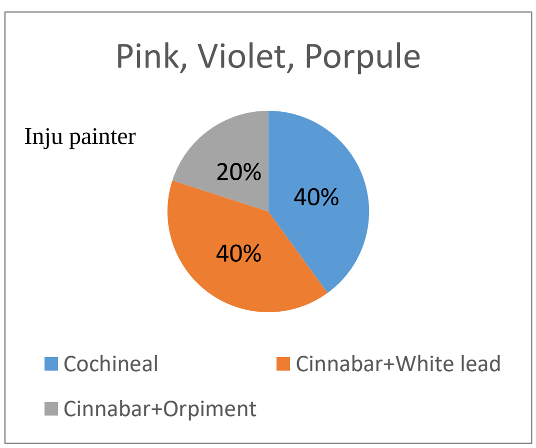

Green
Safavid painter
100%
Indigo + Orpiment

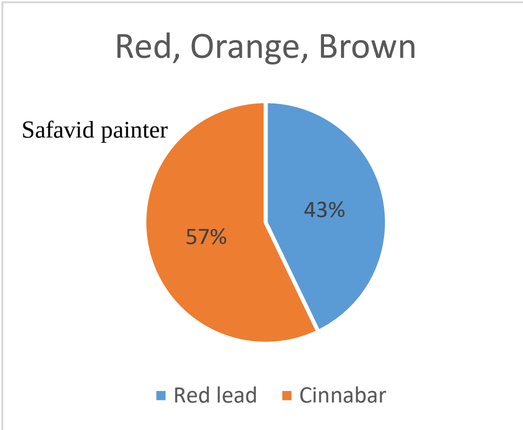

Grey
Timurid painter
50%
50%
Degraded Silver
Indigo+White lead

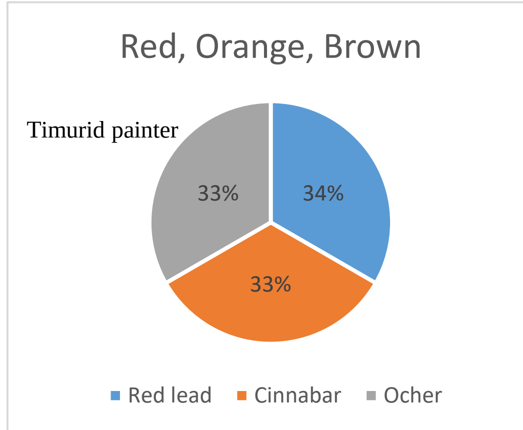

Grey
Inju & Safavid painter
100%
Degraded Silver

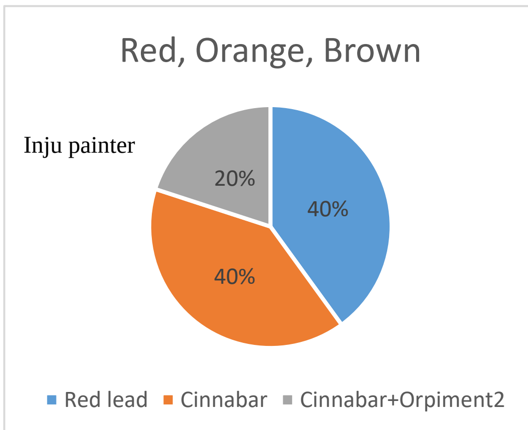

Pink, Violet, Porpule
Safavid painter
29%
71%
Cochineal
Cochineal+Yellow dye

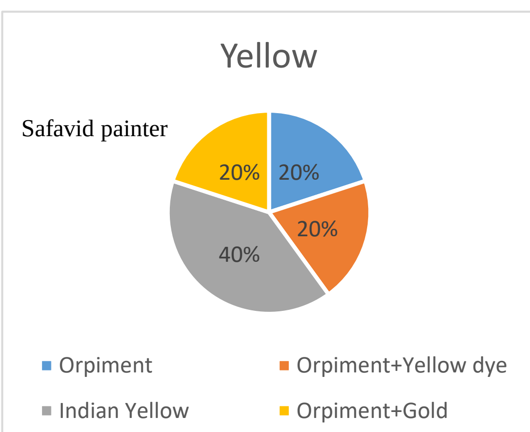

Pink, Violet, Porpule
Timurid painter
25%
50%
13%
12%
Cochineal
Cinnabar+White lead
Cinnabar+Orpiment
Cochineal+Indigo

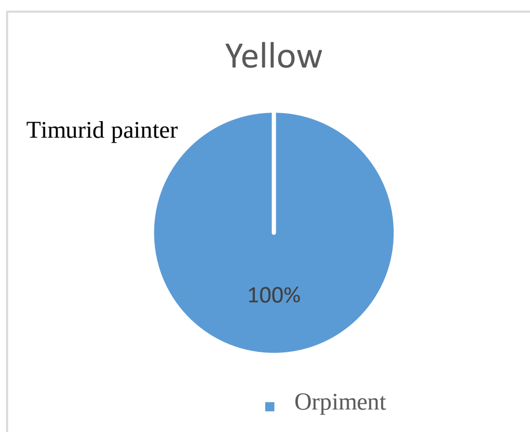

Pink, Violet, Porpule
Inju painter
20%
40%
40%
Cochineal
Cinnabar+White lead
Cinnabar+Orpiment


Red, Orange, Brown
Safavid painter
43%
57%
Red lead
Cinnabar


Red, Orange, Brown
Timurid painter
33%
34%
33%
Red lead
Cinnabar
Ocher


Red, Orange, Brown
Inju painter
20%
40%
40%
Red lead
Cinnabar
Cinnabar+Orpiment2


Yellow
Safavid painter
20%
20%
20%
40%
Orpiment
Orpiment+Yellow dye
Indian Yellow
Orpiment+Gold


Yellow
Timurid painter
100%
Orpiment

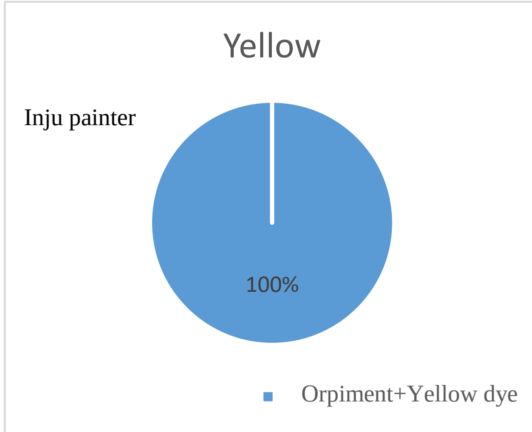


Figure 5-109: Percentage of colour materials used for each colour in manuscript Persian 933

5-3-9 Shāhnāma manuscript RAS 239[43]

As explained in chapter two, this manuscript is a brilliant example of the Timurid manuscripts of Herat dated in 1444 CE. The paintings of this manuscript are painted by eight different painters contains seven Timurid painters and a Mughal painter (ca. 1602). Due to importance of this manuscript unlike other manuscripts in below colour materials applied by each of these painters were surveyed individually.

5-3-9-1 Painter A

In this manuscript, painter A, like many other Persian painters in this manuscript has used two pigments cinnabar and red lead, to create red, brown, and orange tones, these pigments have been used for colouring robes and backgrounds (four spots were analysed). The only thing worth mentioning is not using red ocher pigment, commonly used to create brown colour. But the painter used cinnabar instead of red ocher to create brown. ultramarine is used to create colour blue and for light blue tones (two blue spots were analysed), ultramarine is combined with white lead, and for dark blue tones, indigo is used (Tab. 5-49). The painter used a combination of red lead and white lead to create a light pink colour to paint people's faces and backgrounds (Fig. 5-110). This painter also used a combination of Indian lac with white lead to create a variety of purple tones (four pink, violet, and purple spots were analysed). Green colour, like many other

[43] In this respect, I would like to thank Professor Dr Ira Rabin and Dr Olivier Bonnerot who performed the XRF analysis and some FORS analysis on this manuscript.

Persian manuscripts, is created from indigo + orpiment combination and is used to colour tree foliage (Fig. 5-110).

Other green pigments used to dye clothes and the background is copper green (three green spots were analysed). The combination of indigo with white lead is used to create a grey colour and it is used in the background and clouds (two grey spots were analysed). As it was expected, gold and white lead were used to create the golden and white colours.

Folio number	Description	Colour material	Colour tonality
16 and 135	clothes, robe, background	red lead	a
16 and 135	clothes, robe, background	cinnabar	b
16 and 135	sky	ultramarine Blue	c
16 and 135	background	indigo	
16 and 135	background, faces	red lead + white lead	e
16 and 135	background, clouds	Indian lac + white lead	f
16 and 135	tree foliage	indigo + orpiment	g
16 and 135	background, clothing	copper green	h
16 and 135	background	indigo + white lead	k
16 and 135	background	gold	l

Table 5-49: Distribution of colour materials used in manuscript RAS 239 by Painter A

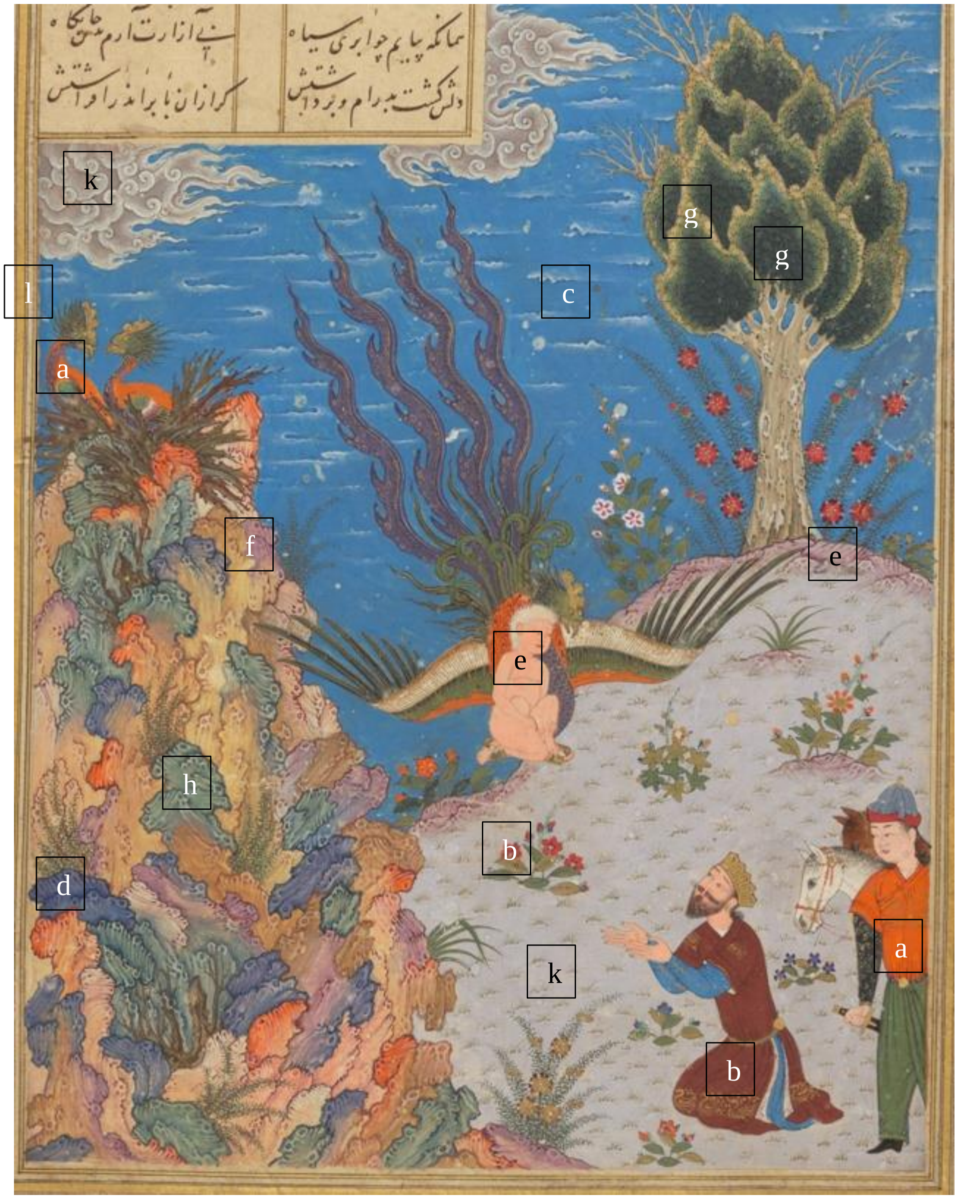


Figure 5-110: Comparison of tonality of different colour materials in manuscript RAS 239 by Painter A; red lead(a), cinnabar(b), ultramarine blue(c), indigo(d), red lead + white lead(e), Indian lac + white lead(f), indigo + orpiment(g), copper green(h), indigo + white lead(k), gold(l)

5-3-9-2 Painter B

Since Painter B is known as the main painter of this manuscript and has more paintings in this manuscript many of the colours used by this painter were analysed in different colour tones. For example, 17 different colour spots were analysed in red, brown, and orange tones.

This painter many times has used cinnabar and red lead pigments to create red and orange colour (Tab. 5-50). And only in one case in folio 270 he used cochineal to colouring stain blood (Fig. 5-111). Interestingly, this painter, like painter A, did not use red ocher to create brown colour, and has used various combinations of cinnabar and red lead to create light to dark brown tones (Tab. 5-50).

To create light blue to dark blue only ultramarine is used, which is combined with different amounts of white lead according to the desired tonality of this painter (11 blue spots were analysed). Due to the different tones of blue used by this painter, it seems that this painter had a wide range of ultramarine available comparison other painters. He had different access to ultramarine and used it to paint the sky, clothes, barding, backgrounds, etc. (Fig. 5-111).

Unlike blue tones, which only ultramarine is used, to create pink to purple tones from a wide variety of combinations is used (ten pink, violet, and purple spots were analysed). For example, to create pink and light pink, commonly used in the background, the combination of red lead + white lead and Indian lac + white lead has been used. To create purple and light purple (violet) colour, combination Indian lac + white lead as well as indigo + red lead is used, and to create a dark purple colour (purple) the composition of ultramarine + red lead and ultramarine + Indian lac were used (Tab. 5-50).

Often light green colours were created by copper green pigments (seven green spots were analysed) for colouring clothes, architectural components, barding, and backgrounds and the dark and light green colour were used for foliage of trees and shrubs is created from the colour orpiment + indigo (Fig. 5-111). It should be noted this painter compared to other painters, has created a very diverse green colour tone by combining green copper pigments with white lead.

The painter used two metallic pigments (four metallic colour spots were analysed), one gold pigment, which is often used usually for background painting, Architectural components, costumes, barding and specify details (Tab. 5-50) as well as silver metallic pigment for colouring armor, swords, river water and background have been used (seven grey spots were analysed), of course this metal pigment is already looking like dark grey due to its corrosion.

It should be noted to create grey colour in addition to silver, a combination of indigo and ultramarine with white lead is also used, these two-colour combinations are mostly used to create a light grey in the background (Fig. 5-111). Also, in order to create white and black colours, white lead and black carbon have been used (three white and black spots were analysed).

Folio number	Description	Colour material	Colour tonality
30, 76, 243	clothes, robe, background, barding, fruits	red lead	a
30, 76, 243	clothes, robe, background, architecture, horses	cinnabar	b
30, 76, 223, 243	sky, barding, robesm, architecture, background	ultramarine blue	c
30 and 270	background	red lead + white lead	d
30 and 243	background, clothing	Indian lac + white lead	e
30	Robes	ultramarine + indigo	f
30	Robes	ultramarine + Indian lac	g
30 and 243	tree foliage, grass	indigo + orpiment	h
30, 223, 243, 270	background, clothing, architecture, barding	copper green	k
243	background, animals	indigo + white lead	l
223, 243	Water, armor, sword	degraded silver	m
30, 76, 223, 243, 270	background	gold	n

Table 5-50: Distribution of colour materials used in manuscript RAS 239 by Painter B

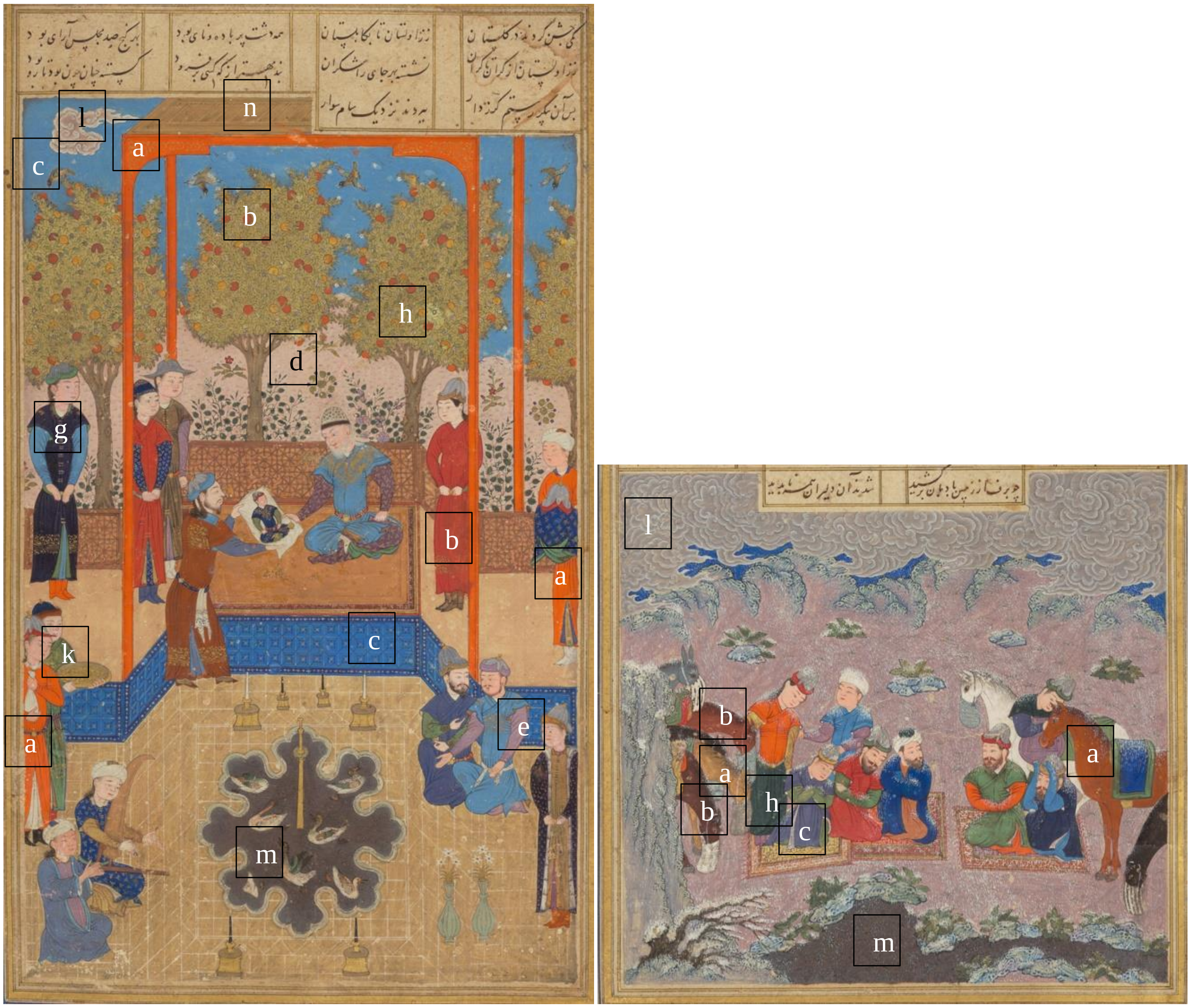


Figure 5-111: Comparison of tonality of different colour materials in manuscript RAS 239 by Painter B; red lead(a), cinnabar(b), ultramarine blue(c), red lead + white lead(d), Indian lac + white lead(e), ultramarine + indigo(f), ultramarine + Indian lac(g), indigo + orpiment(h), copper green(k), indigo + white lead(l), degraded silver(m), gold(n)

5-3-9-3 Painter C

Painter C along with painter B has drawn the most paintings in this manuscript, hence the significant number of colour samples used by this painter was analysed. To create the red, orange, and brown tones (17 red, orange, and brown spots were analysed) this painter like two previous painters, used cinnabar for red and red lead for orange and reddish orange, but unlike these two painters, the painter also used red ocher pigment to create the dark brown colour for tree trunks and robes (Tab. 5-51). This painter also used azurite pigment to create a blue tint next to ultramarine (11 blue spots were analysed) at two points in folios seven and 394 which had never been seen before (Fig. 5-112). Other common colour materials between this painter and two previous painters are coloured materials used for tonality dark green to light green (seven green spots were analysed). Orpiment + indigo is used to create the green colour for the foliage of trees, shrubs and clothes, and copper green is used to create the light green colour in the background, architectural components, and clothes (Fig. 5-112). Like Painter B, this painter has used a variety of colour combinations to create pink to purple colours (ten pink, violet, purple spots were analysed). But Painter C, unlike painter B, used cochineal dye instead of Indian lac (Tab. 5-51). This painter uses the colour combination of cochineal + white lead to create the pink and light pink colours used for the flowers and the background, the colour combination ultramarine + red lead used to create the dark purple colour for the underlayment, and the clothes, the colour combination ultramarine + indigo coloured was used to create the violet colour, For underlays and architectural components, and he has used the colour combination red lead + white lead to create a light pink colour for people's faces and walls (Fig. 5-112).

It should be noted that this painter, unlike painters B and A, has used yellow individually more (4 yellow spots were analysed). The Orpiment pigment was used by this painter to create yellow, although in one case in folio 7 to create a non-metallic luster yellow was used to paint a pitcher from combination of gold and yellow dyes (Tab. 5-51). Also, in folio 394, to create a very soft yellow is used to paint the bricks, according to the observations of the FOMF and FORS spectra (see section 5-2-4-3), the colour combination yellow dye + white lead has been used to paint the bricks. Like previous two painters, this painter has used two metallic pigments of gold and silver (two metallic colour spots were analysed). As previously explained, the silver pigment, often was used to paint water, swords, and armor, it is now corroded and turned to dark grey (Fig. 5-112). But the interesting thing about this painter is that s/he used a combination of silver and indigo to paint the water in folio 7, which is not seen in other paintings of this manuscript. White lead and black carbon have also been used as white and black colours. In general, it can be said that the colour materials used by this painter are significantly different from other painters working in this manuscript.

Folio number	Description	Colour material	Colour tonality
7, 56	clothes, robe, background, barding	red lead	a
7, 56	clothes, robe, background, architecture, horses	cinnabar	b
7	tree trunk, robe	red ocher	c
7, 56, 394	sky, barding, robes, architecture, background	ultramarine blue	d
7, 394		azurite	e

56, 394	Background4	red lead + white lead	f
7	background, clothing, flowers	cochineal + white lead	g
56	robes, ground cloth, architecture	ultramarine + indigo	h
56	robes, ground cloth	ultramarine + red lead	k
7, 56	tree foliage, grass	indigo + orpiment	l
7, 56	background, clothing, architecture, barding	copper green	m
7	water, armour, sword	degraded silver	n
56, 394	architecture, background	orpiment	o
7, 56, 394	background	gold	p

Table 5-51: Distribution of colour materials used in manuscript RAS 239 by Painter C

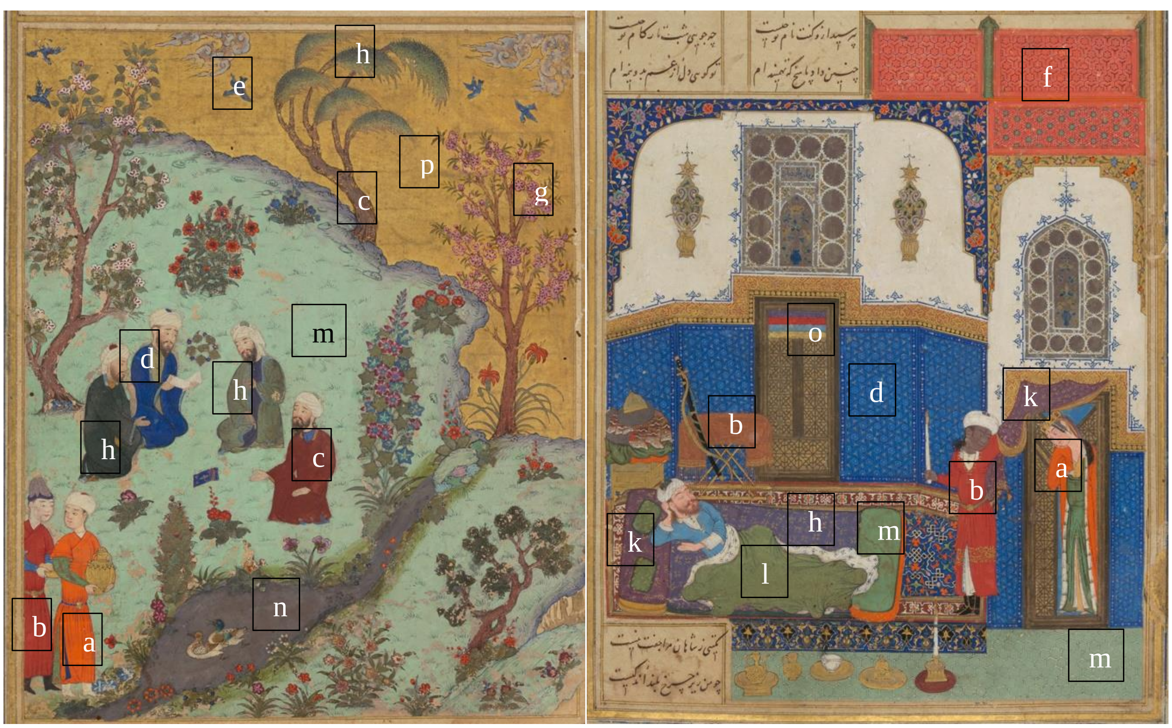


Figure 5-112: Comparison of tonality of different colour materials in manuscript RAS 239 by Painter C; red lead(a), cinnabar(b), red ocher(c), ultramarine blue(d), azurite(e), red lead + white lead(f), cochineal + white lead(g), ultramarine + indigo(h), ultramarine + red lead(k), indigo+ orpiment(l), copper green(m), degraded silver(n), orpiment(o), gold(p)

5-3-9-4 Painter D

Although Painter D has fewer paintings in this manuscript than painters C and B, but the variety of colours used by this painter is very high (Tab. 5-52). This painter used red lead and cinnabar to create red, orange and brown like other painters (5 red, orange, and brown spots were analysed), and s/he used cinnabar to create brown like painters B and A, not pigment red ocher (Tab. 5-52). Ultramarine is the only blue pigment used by this painter (3 blue spots were analysed) and the painter has combined ultramarine blue with white lead to create different tonalities (Fig. 5-113).

Like previous painters, for creating green colour (two green spots were analysed) needed for colouring tree foliage, shrubs, grasses, and clothing the combination of orpiment + indigo have been used, and copper green pigment has been used to paint architectural components, clothing, and backgrounds (Fig. 5-113). This painter has used three colour combinations of red lead + white lead to create pink and purple tones (six pink, violet, purple spots were analysed) to create pink and light pink, from the colour combination red lead + indigo to create dark purple (Tab. 5-52).

s/He has used the colour combination red lead + copper green to create purple (violet). Among these three-colour combinations, the combination of red lead + copper green has been used only by this painter, which has created a kind of greenish purple colour (Tab. 5-52). Gold and silver are two metal pigments (2 gay and three metallic colour spots were analysed) used by this painter and like painter B and A, this painter seldom used yellow individually for some details (Tab. 5-52). Unlike previous painters, this painter rarely used the combination of indigo + white lead to create the light grey colour used in the backgrounds, and the backgrounds are mostly light pink (Fig. 5-113). Two pigments white lead, and black carbon, have also been used to create black and white colours.

Folio number	Description	Colour material	Colour tonality
145, 206	clothes, robe, background, barding	red lead	a
145, 206	clothes, robe, background, architecture, horses	cinnabar	b
145, 206	sky, barding, robes, architecture, background	ultramarine blue	c
145, 206	background	red lead + white lead	d

206	background, clothing, flowers	red lead + copper green	e
206	robes, ground cloth, architecture	red lead + indigo	f
145, 206	tree foliage, grass	indigo + orpiment	g
145	background, clothing, architecture, barding	copper green	h
206	water, armour, sword	degraded silver	k
145, 206	background	gold	l

Table 5-52: Distribution of colour materials used in manuscript RAS 239 by Painter D

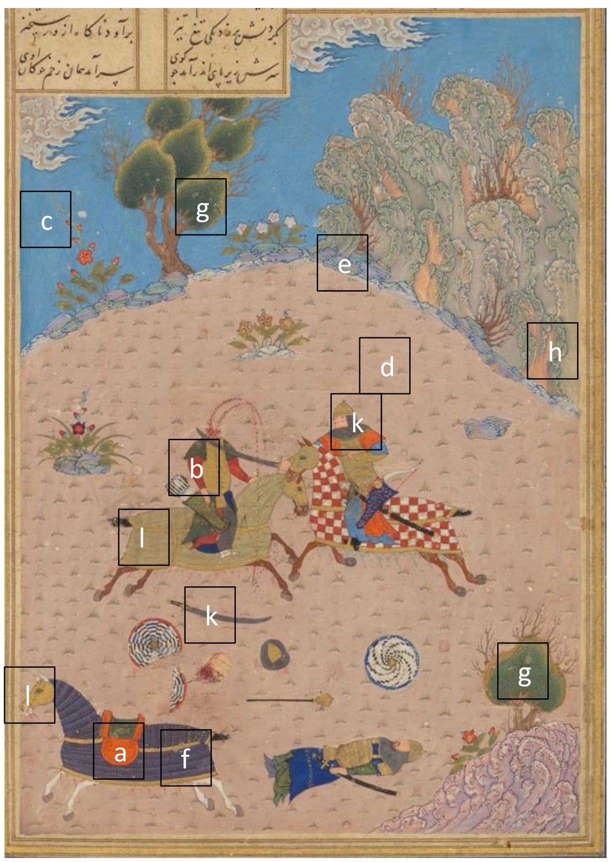


Figure 5-113: Comparison of tonality of different colour materials in manuscript RAS 239 by Painter D; red lead(a), cinnabar(b), ultramarine blue(c), red lead + white lead(d), red lead + copper green(e), red lead + indigo(f), indigo + orpiment(g), copper green(h), degraded silver(k), gold(l)

5-3-9-5 Painter E

Painter E in this manuscript has only one painting in folio 291 (Fig. 5-114). The predominant colour used by this painter is green, so that unlike other paintings in this manuscript, the background is light pink or light grey, the background of this painter is light green (seven green spots were analysed). From two common colour combinations, indigo + orpiment, are used to colour the foliage of trees, shrubs, and grasses, and copper green is used for background and clothing (Tab. 5-53).

The painter used red lead and cinnabar pigments for red, orange, and brown (5 red, orange, and brown spots were analysed) and, like Painter B and A, used a combination of orpiment and cinnabar to create the light and dark brown colour for tree trunks and horses (Fig. 5-114). Ultramarine pigment is the only blue pigment used by this painter (two blue spots were analysed) and unlike other painters, pink and purple tones have been used very little (only one spots were analysed).

The only colour combination used for this colour tone is red lead + white lead, which was used to create a light pink colour (Fig. 5-114). Like other painters, two metallic pigments of gold (two grey and three metallic colour spots were analysed) and silver have been used in this painter's paintings (Tab. 5-52) and carbon black and white lead pigments have been used as white and black colours.

Folio number	Description	Colour material	Colour tonality
291	clothes, robe, background, barding	red lead	a
291	clothes, robe, background, architecture, horses	cinnabar cinnabar + orpiment	b
291	sky, barding, robes, architecture, background	ultramarine blue	c
291	background	red lead + white lead	d
291	tree foliage, grass	indigo + orpiment	e

291	background, clothing, architecture, barding	copper green	f
291	water, armour, sword	degraded silver	g
291	Background, details	gold	h

Table 5-53: Distribution of colour materials used in manuscript RAS 239 by Painter E

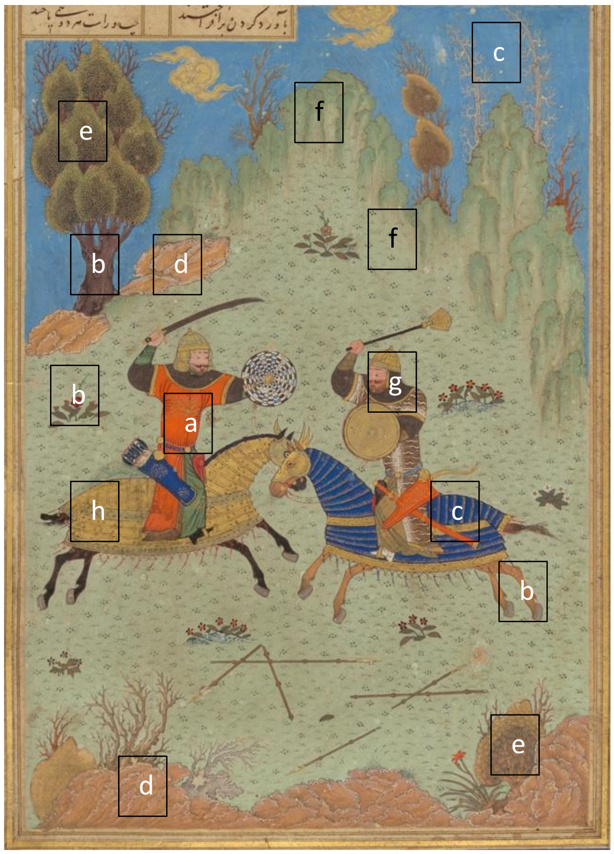


Figure 5-114: Comparison of tonality of different colour materials in manuscript RAS 239 by Painter E; red lead(a), cinnabar(b), ultramarine blue(c), red lead + white lead(d), indigo + orpiment(e), copper green(f), degraded silver(g), gold(h)

5-3-9-6 Painter F

Painter F has only one painting in this manuscript (Fig. 5-115). The colours used by this painter are very similar to the colours used by painter E. This painter has used red lead and cinnabar pigments for red, orange, and brown tones (three red spots were analysed). This painter also used cinnabar pigment to create light and dark brown colours for painting tree trunks and horses' feet, which is combined with orpiment or red lead according to the tonality desired by the painter (Tab. 5-54). It should be noted that the black colour used to paint the horse's foot at the bottom of the folio, according to the FORS and XRF spectrum taken from this colour point, is definitely red lead, in fact, the red lead colour combination has been used at this point with cinnabar that has been corroded and turned to black (Fig. 5-115).

The painter used ultramarine pigment for blue (four blue spots were analysed) and copper green and indigo + orpiment for green (three green spots were analysed). The use of pink to purple tones by this painter is more than the painter E (four green spots were analysed) and the colour combinations of red lead + white lead for pink and purple (violet) and the combination of ultramarine + red lead for dark purple have been used (Tab. 5-54).

The two pigments gold and silver are the only metallic pigments used by this painter (two metallic colour spots were analysed). The silver pigment that is currently seen in dark grey (three grey spots were analysed) has been used many times by this painter (Fig. 5-115). It should be noted that this painter used the combination of indigo + white lead to create a light grey colour for painting the elephant and the background (Fig. 5-115). Like other painters, carbon black and white lead are used for black and white colour.

Folio number	Description	Colour material	Colour tonality
155	clothes, robe, background, barding	red lead	a
155	clothes, robe, background, architecture, horses	cinnabar cinnabar + red lead	b
155	sky, barding, robes, architecture, background	ultramarine blue	c
155	background, clothing	red lead + white lead	d
155	tree foliage, grass	indigo + orpiment	e

155	background, clothing, architecture, barding	copper green	f
155	water, armour, sword	degraded silver	g
155	elephant	indigo + white lead	h
155	horses	degraded red lead	k
155	background, details	gold	l

Tab. 5-54 Distribution of colour materials used in manuscript RAS 239 by Painter F

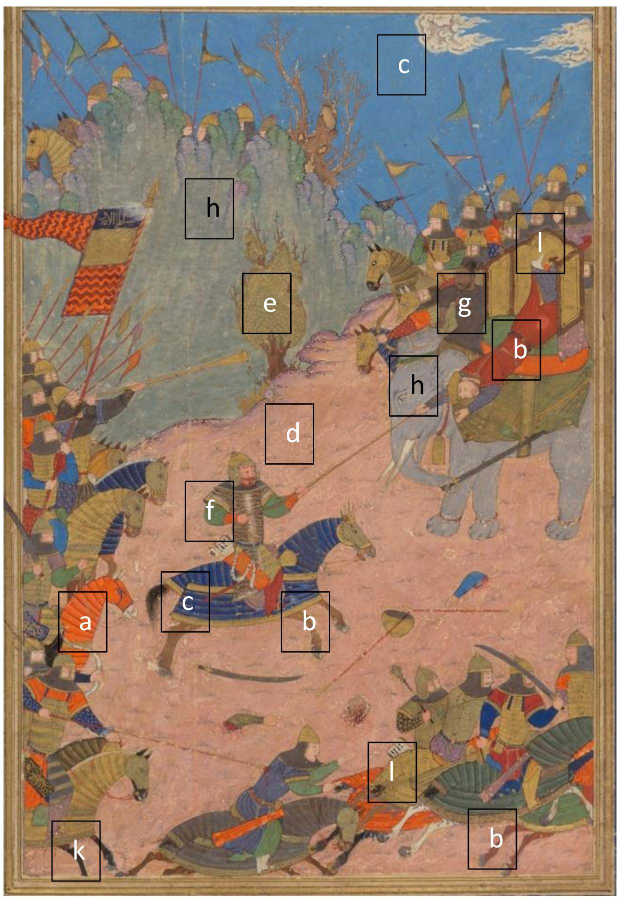


Figure 5-115: Comparison of tonality of different colour materials in manuscript RAS 239 by Painter F; red lead(a), cinnabar(b), ultramarine blue(c), red lead + white lead(d), indigo+ orpiment(e), copper green(f), degraded silver(g), indigo + white lead(h), degraded red lead(k), gold(l)

5-3-9-7 Painter G

Painter G has only one painting in this manuscript (Fig. 5-116). The colour material used by this painter is very similar to Painter A. This painter has used red lead and cinnabar pigments to create red, orange, and brown (five red, orange, and brown spots were analysed). Like Painter A, this painter has used azurite in several cases in addition to ultramarine to create blue (two blue spots were analysed), which is interesting in its kind (Tab. 5-55). The colour materials used by this painter for pink and purple tones are limited to two colour combinations (two spots were analysed) red lead + ultramarine and red lead + white lead, which have been used by this painter to paint backgrounds, clothes, flags and barding (Fig. 5-116). It is interesting to note that this painter used copper green to create a variety of green tones (five green spots were analysed) and did not use another indigo + orpiment green colour combination that is common in Persian manuscripts. This painter also used only two metallic pigments of gold and silver (three metallic colour spots were analysed). It should be noted that this painter used a combination of orpiment with a small amount of gold to create a bright yellow colour for the background (only one yellow spot were analysed).

To figure out the use of gold for this colour combination because of higher amount of orpiment have been used, the created yellow colour has no metallic luster and is seen as a faint yellow (Fig. 5-116). In this manuscript white lead is used as a white pigment and black carbon is used as a black pigment, but in one case, the black colour used to paint the shoes is red lead pigment, which is seen as black due to corrosion (Fig. 5-116). Detection of red lead at this colour point was not expected due to its black colour, but according to the FORS and XRF spectra taken from this point, the use of red lead is approved as seen in the painting of this painter.

Folio number	Description	Colour material	Colour tonality
190	clothes, robe, background, barding	red lead	a
190	clothes, robe, background, architecture, horses	cinnabar	b
190	sky, barding, robes, architecture, background	ultramarine blue	c
190	tree trunk	azurite	d

190	background, clothing	red lead + white lead	e
190	flag, clothing, barding	red lead + ultramarine	f
190	background, clothing, architecture, barding	copper green	g
190	water, armor, sword	degraded silver	h
190	shoes	degraded red lead	k
190	Background	orpiment + gold	l
190	Background, details	gold	m

Table 5-55: Distribution of colour materials used in manuscript RAS 239 by Painter G

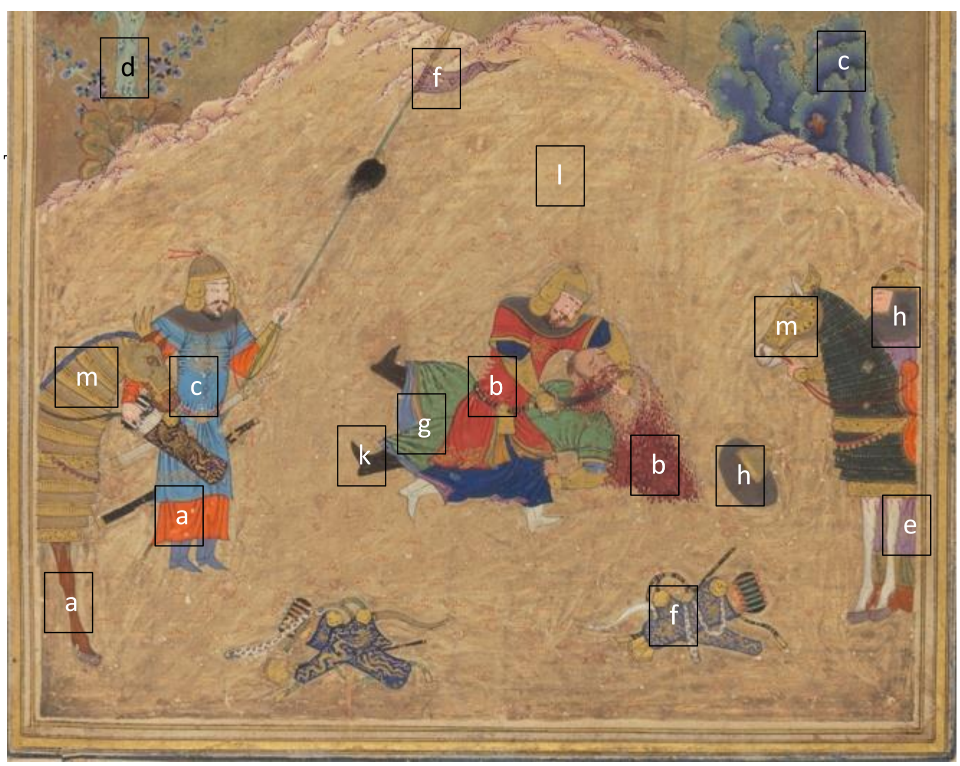


Figure 5-116: Comparison of tonality of different colour materials in manuscript RAS 239 by Painter F; red lead(a), cinnabar(b), ultramarine blue(c), azurite(d), red lead + white lead(e), red lead + ultramarine(f), copper green(g), degraded silver(h), degraded red lead(k), orpiment + gold(l), gold(m)

5-3-9-8 Mughal Painter

According to the available evidence and research of this manuscript three paintings were added to this manuscript after the production of this manuscript in 1444 CE in the Mughal period around the end of the 16^{th} century (see Chapter 2). According to the analysis of these paintings, differences were observed in the type of paint materials used by Mughal painters. In Mughal period paintings, cinnabar was used to create red (three red, orange, and brown spots were analysed), red lead was used for various orange colours, and red ocher pigment was used to produce light to dark brown colours (Tab. 5-56).

Also, the only blue pigment used in these paintings is ultramarine (three blue spots were analysed), which is combined with white lead to create brighter tones of blue (Fig. 5-117)). The pink to purple tones used in these paintings are very diverse (three pink, purple spots were analysed).

To create a variety of pink and purple tones, two colour combinations of red lead + white lead and Indian lac + white lead has been used (Tab. 5-56). Some of these colours are very special and have not been seen in other paintings of this manuscript, and their uses are different from other paintings in this manuscript, for example, using a kind of reddish light pink for clothing and using pale pink for colouring horses (Fig. 5-117). In these paintings, two colour combinations of copper green and indigo + orpiment has been used to create green colour (three green spots were analysed).

Like many other paintings of this manuscript, the grey colours of these paintings (three grey spots were analysed), in addition to degraded silver, also include ultramarine + white colour combination for painting elephants as well as backgrounds have been used.

The noteworthy thing about these paintings is the heavy use of yellow (two yellow spots were analysed) for clothes and background, which is not seen in other paintings in this manuscript (Tab. 5-56). Two colours, Indian yellow and orpiment, have been used to create these yellow colours, which Indian yellow has not been seen in any of the manuscript paintings before.

Also, the gold pigment used in these paintings has a different colour than other paintings (only one spot were analysed), which can be due to the use of lower grade gold or the use of yellow dyes on gold. Unfortunately, these possible yellow pigments used on gold cannot be identified by the analysis techniques used in this research but considering the visual effect of the gold pigment used in these paintings seems probable.

Folio number	Description	Colour material	Colour tonality
430, 531	clothes, robe, background, barding	red lead	a
430, 531	clothes, robe, background, architecture, horses	cinnabar	b
430	tree trunk, horses, clothing	red ocher	c
430, 531	sky, flag, barding, robes, background	ultramarine blue	d
430	background, clothing, horses	red lead + white lead	e
430, 531	flag, clothing, barding	Indian lac + white lead	f
430, 531	background, clothing, architecture, barding	copper green	g
430	Tree foliage, grass, clothing, background	indigo + orpiment	h
430, 531	water, armour, sword	degraded silver	k
430	elephant, background, horses	ultramarine + white lead	l
430, 531	background, clothing, details, robes	orpiment	m
430, 531	background, clothing, details	Indian yellow	n
430, 531	background, details	gold	o

Table 5-56: Distribution of colour materials used in manuscript RAS 239 by Mughal Painters

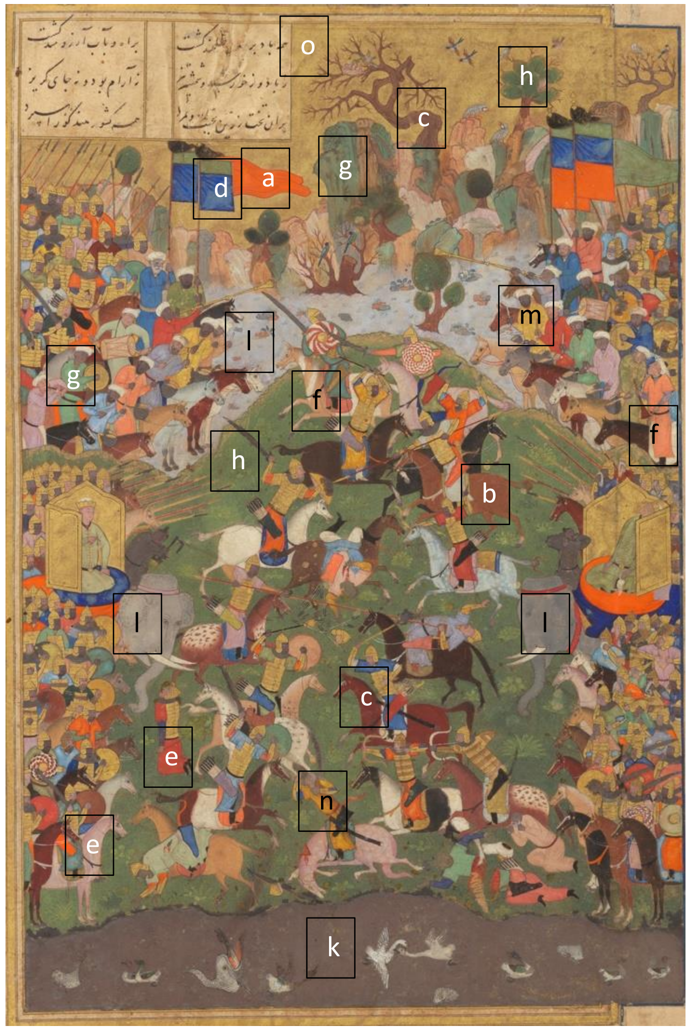


Figure 5-117: Comparison of tonality of different colour materials in manuscript RAS 239 by Mughal Painters; red lead(a), cinnabar(b), red ocher(c), ultramarine blue(d), red lead + white lead(e), Indian lac + white lead(f), copper green(g), indigo + orpiment(h), degraded silver(k), ultramarine + white lead(l), orpiment(m), Indian yellow(n), gold(o)

5-3-9-9 Statistical analysis the Shāhnāma RAS 239

This manuscript is the only example of the Timurid style manuscript of Herat dated 1444 CE (see Chapter 2) analysed in this study. as explained in chapter two eight painters painted the paintings of this manuscript and this manuscript is a brilliant and famous *Shāhnāma* manuscript which ordered and supported by Timurid prince Mouhamad Juki. From the point of view of material science, the quality of paintings of this manuscript from an artistic and scientific point of view is very high. the variety of colour materials used in this manuscript is higher than other manuscripts analysed in this study and has features of a manuscript produced in a royal workshop.

A wide range of ultramarine, a wide mixture of yellow colours, pink to purple colour is applied in this manuscript. Therefore, the colour materials of 17 miniatures of this manuscript were analysed. Indeed ca.482 single measurements contain; ca.214 FORS analysis, ca.214 XRF analysis, 44 FOMF analysis, and ca.10 SERS and HPLC-MS were performed on this manuscript (see Tab. 5-57).

88% of analysed blue spots in this manuscript contained ultramarine, 9% contain azurite and 3% are indigo. 44% analysed green of this manuscript contain copper green pigment, and 56% orpiment + indigo. 61% of the grey colours are degraded silver pigments and 28% contain indigo + white lead and 11% ultramarine + white lead. 17% of the analysed pink, violet, and purple samples are Indian lac, 3% is the combination of ultramarine + Indian lac, 44% contain red lead + white lead, 3% contain cochineal, 8% contain indigo + ultramarine, 5% contain red lead + indigo, 17% ultramarine + red lead, and 3% red lead + copper green. Red lead pigment 34%, cinnabar 48%, red ocher 4%, cochineal 4%, cinnabar + orpiment 4%, and cinnabar + red lead 4% contain the colour samples analysed in red, orange, and brown tones. 28% of yellow samples contain orpiment, 18% contain Indian yellow, 18% contain yellow dye, 9% contain orpiment + gold, and 18% contain yellow dye + gold. All the analysed metallic samples contain pure gold pigment with or without a metallic luster.

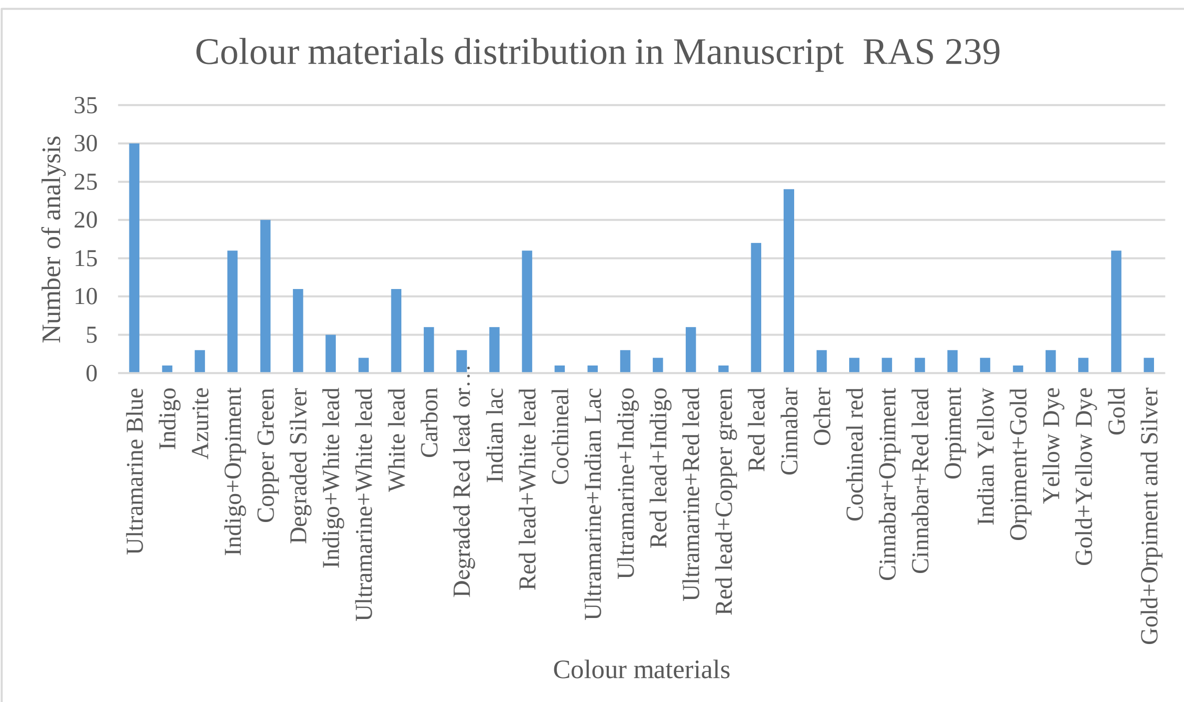
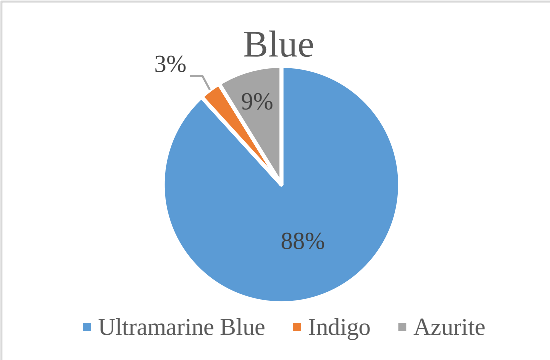
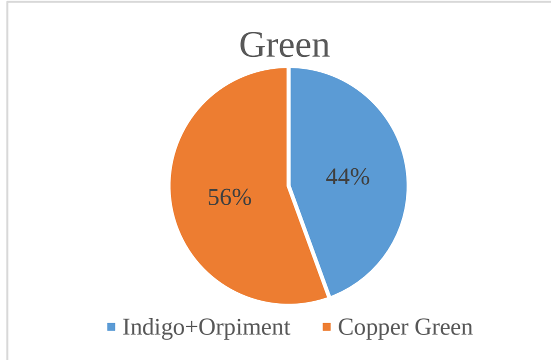
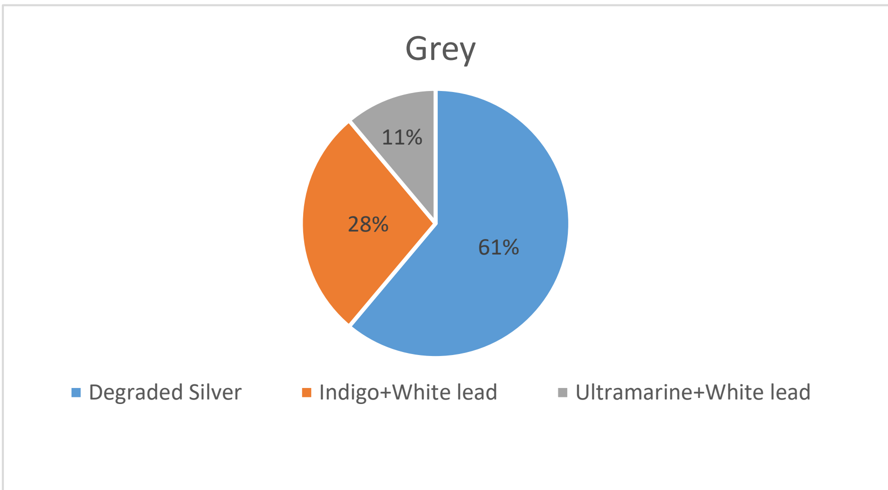
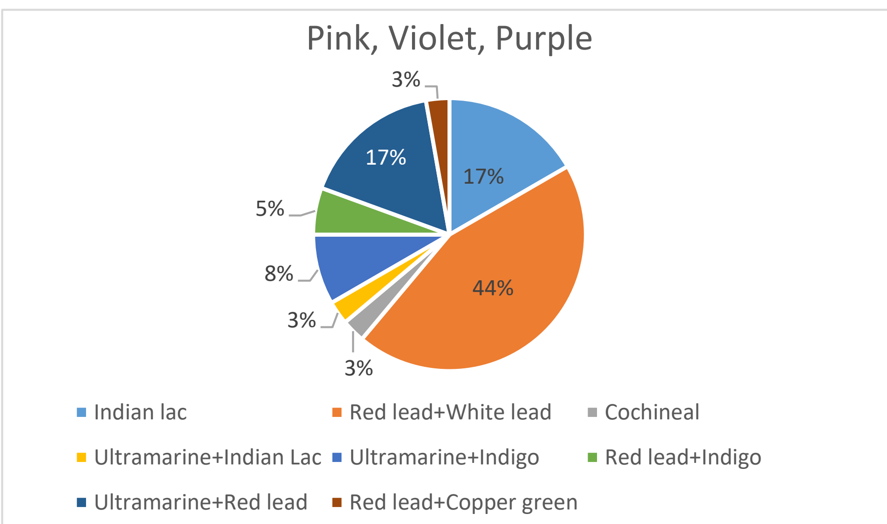


Figure 5-118: Distribution of colour materials used in manuscript RAS 239


Blue
3%
9%
88%
Ultramarine Blue
Indigo
Azurite


Green
44%
56%
Indigo+Orpiment
Copper Green


Grey
11%
28%
61%
Degraded Silver
Indigo+White lead
Ultramarine+White lead


Pink, Violet, Purple
3%
17%
17%
5%
8%
44%
3%
3%
Indian lac
Red lead+White lead
Cochineal
Ultramarine+Indian Lac
Ultramarine+Indigo
Red lead+Indigo
Ultramarine+Red lead
Red lead+Copper green

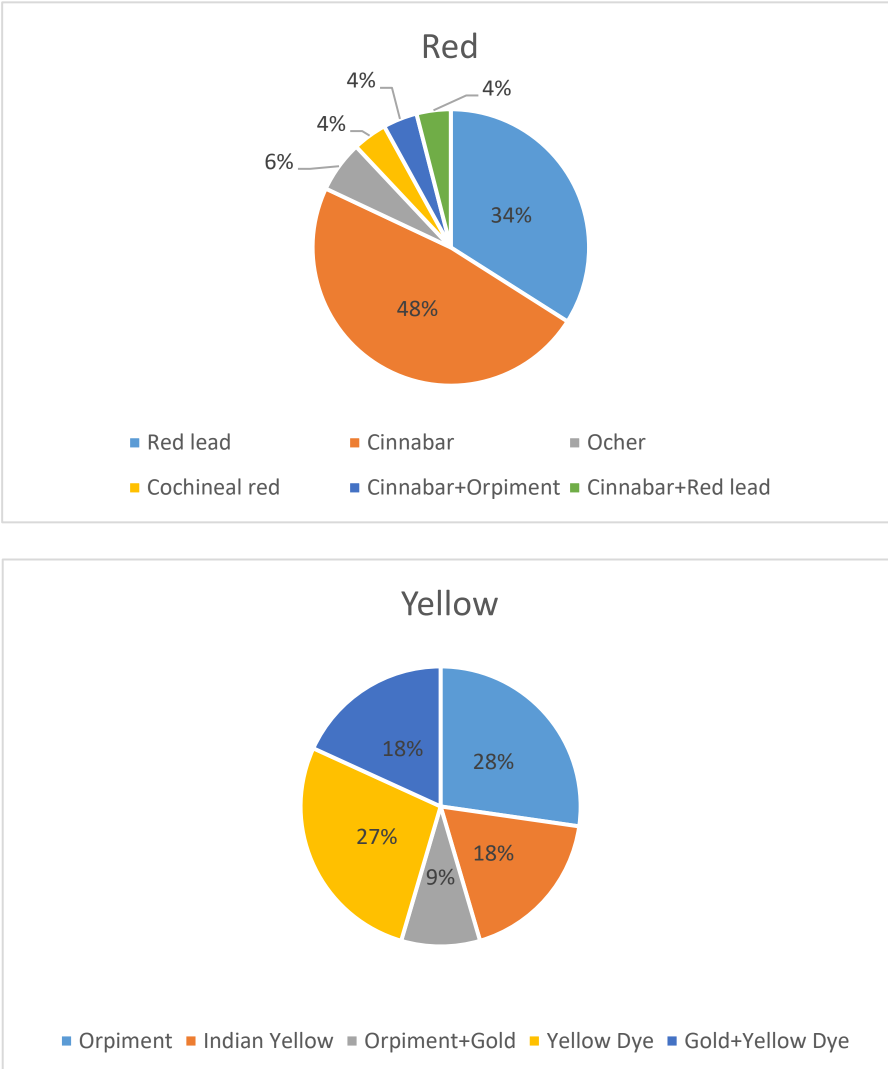


Figure 5-119: Percentage of colour materials used for each colour in manuscript RAS 239

Manuscripts	Analysed Miniatures	No. of XRF measurements	No. of FORS measurements	No. of FOMF measurements	No. of SERS Raman measurements	No. of HPLC-Mass measurements
RAS 239	17	ca. 214	ca. 214	44	10	3
AKM 4	5	53	53	11	-	-
AKM 5	4	52	52	12	-	-
AKM 6	4	65	65	16	-	-
AKM 269	13	20	100	16	-	-
Persian 9	19	88	88	11	3	2
Persian 933	13	80	80	18	3	2
Ms 22-1948	5	63	63	-	-	-
Or 420	9	56	ca. 56	10	-	-
Sum	89	Ca.691	Ca.691	138	16	7

Table 5-57: Overview of number of performed analysis

5-4 Comparison between colour materials used in different cities (schools) of Persian paintings

5-4-1 Shiraz

In this study, 39 paintings produced in Shiraz were analyzed. These paintings have been painted by six different painters (Tab. 5-58). In the terms of style and time of production these paintings can be divided into three categories: Inju style paintings in the late 16th century, Timurid paintings in the early 15th century, and Turkman style paintings in the mid-15th to end 15th centuries (see chapter II). These paintings have major differences in terms of appearance, especially Shiraz Inju style paintings, which have major differences with the other two styles of paintings in terms of colour variety and painting technique. These paintings are related to the *Shāhnāma* manuscript Persian 933 (Painter A), which has a medium size and wavy, vivid, and sometimes very simple and raw hand-drawn images. These paintings also have a limited colour variety, the predominant colour of which is a group of warm colours such as red-brown, and yellow. Their colour is incoherent, and the scenery in them is often dreamy and imaginative, but they have limited conventional elements. Timurid and Turkman paintings have similarities which are more visual. Although, in general, Turkman paintings are often emotional, while Timurid school paintings are purely logical and rational. Shiraz Timurid paintings are related to *Shāhnāma* manuscripts Or 420 (nine paintings) and Ms 22-1948 (five paintings) (Tab. 5-58). The analyzed Turkman paintings are related to *Shāhnāma* manuscripts AKM 4 (five paintings), AKM 5 (four paintings) and AKM 269 (13 paintings) (Tab. 5-58).

5-4-1-1 Blue

Ultramarine and Indigo are the most widely used blue which are used in Shiraz paintings. In the terms of time, three Inju style paintings (*Shāhnāma* manuscript Persian 933) are the newest examples of paintings made in Shiraz that have been analyzed in this study. As mentioned, the Inju style painter has used a limited number of colour tones in these paintings. For example, the only blue tonality colour existed in these paintings is a kind of dark blue created by ultramarine (Fig. 5-120).

Figure 5-120: An example of blue tonalities used in Inju paintings of Shiraz

While in every Timurid style paintings in Shiraz, in addition to ultramarine, also indigo has used to create blue (Fig. 5-121). Unlike the previous three paintings (Inju Style), in these paintings, light and dark blue tones have been used to a great extent to paint the backgrounds, sky, clothes, barding, armour, etc.

The main colour material used by both Timurid painters is ultramarine, which is combined with different amounts of white lead and has created different colour tones. Timurid painters of Shiraz also used indigo as a blue colour, which has not been used by painters of Inju and Turkman style in Shiraz (Fig. 5-123). The colour indigo, which has a kind of dark blue (deep blue), has been used by these two painters only for painting robe and in one case tent (Fig. 5-121).

Turkman style paintings produced in Shiraz belong to three *Shāhnāma* manuscripts AKM 4-5-269. The blue tones used in these paintings are not much different from the Timurid style paintings of Shiraz, but from the point of view of materials science, the dark blue tones (deep blue) in these paintings are created by different types of ultramarine (Fig. 5-122).

Also, Turkman painters, unlike the Timurid painters of Shiraz, did not use indigo as a blue colour (Fig. 5-123). According to the available visual evidence and analyzes, it can be concluded that the common blue colour used in Shiraz in all periods is ultramarine.

In general, the Timurid and Turkman style paintings have many similarities in the terms of visuals and materials used for blue colour, but Shiraz Inju style paintings have major differences with the other two styles, especially from a visual point of view.

It should be noted that Shiraz Turkman painters have used indigo as part of the composition to create purple or as a transparent colour to fade painting figures, but Shiraz Timurid painters have used indigo alone as a dark blue in addition to the mentioned uses. Another notable difference about blue is the low quality of the ultramarine used by the painter Or 420 (Timurid style).

The ultramarine used by this painter has fallen in many cases, unlike the other Timurid painters and Turkman style painters who have used a wider range and higher quality of ultramarine.

Figure 5-121: An example of blue tonalities used in Timurid paintings of Shiraz

Figure 5-122: An example of blue tonalities used in Turkmen paintings of Shiraz

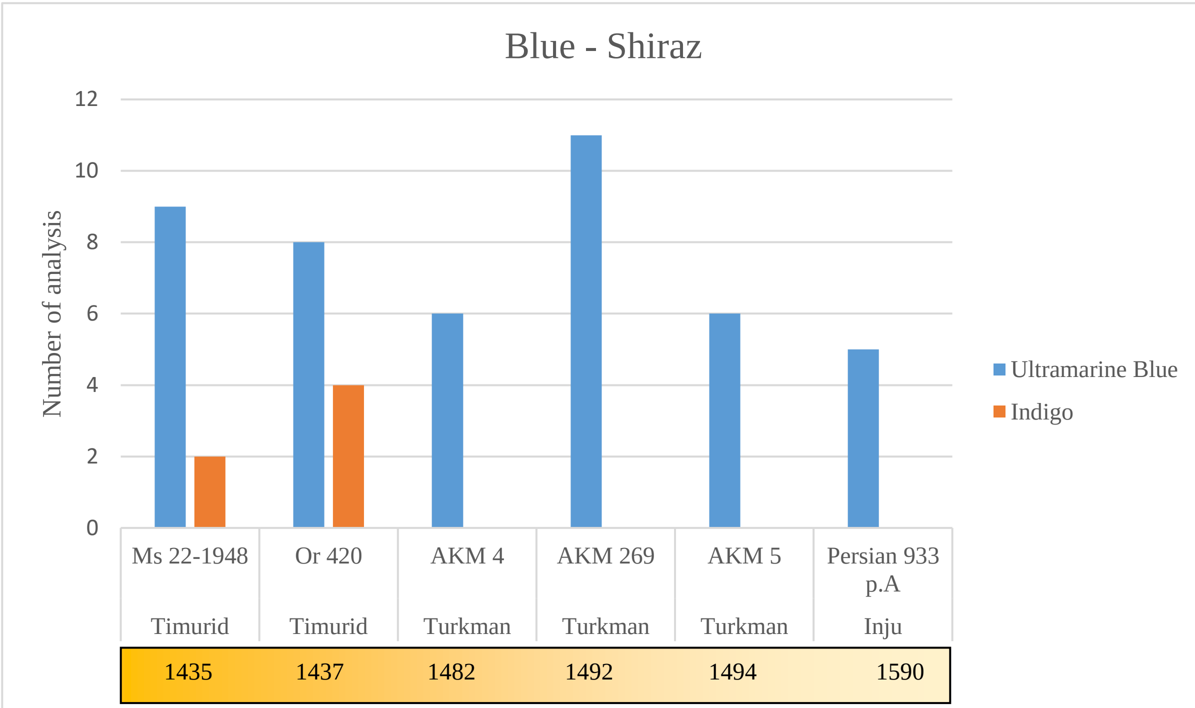


Figure 5-123: Blue colour used in Shiraz

5-4-1-2 Green

In Inju style paintings, only copper green is used as a green colour for painting robe and background (Fig. 5-127). In almost all places where copper green has been used, the paper has been damaged and, in many places, the green colour has been fallen (Fig. 5-124), which may be due to the lack of the use of saffron as an anti-corrosion agent by Inju style painter. It was usual to combine saffron with copper-containing pigments by many Persian painters to prevent paper corrosion.

Painters of both Timurid and Turkman styles of Shiraz have used the combination of indigo + orpiment and copper green as green (Fig. 5-125). In general, it can be said that Turkman style painters are more inclined to use copper green than other painters (Fig. 5-127).

The green colour used in the paintings of *Shāhnāma* manuscript Or 420 has fallen like the example used by the Inju painter, but due to the fall of other colours in this manuscript, it cannot be considered simply as a result of not combining saffron with copper green. Especially that in one case, this painter used a combination of indigo with yellow dye to create light green (yellowish green), the yellow colour of which is most likely saffron.

It should be noted that the colour combination indigo + yellow dye in the Shāhnāma manuscript AKM 269 has also been used by a Turkman painter. In the *Shāhnāma* manuscript AKM 5 (Turkman style) in one case, the colour combination of ultramarine + orpiment was used to create the dark green colour of the tree leaves. This colour combination was completely unique by AKM 5 painter and has not been used by any of the other painters in Shiraz or other cities.

Figure 5-124: An example of green tonalities used in Inju paintings of Shiraz

Figure 5-125: Two examples of green tonalities used in Turkmen and Timurid paintings of Shiraz

Based on the analysis done in this study and considering all three different styles of paintings produced in Shiraz, it can be stated that the colour combination of indigo + orpiment has been used more than copper green in Shiraz. This colour combination has been used most for painting tree leaves, robe, grasses, and background plants. Shiraz Turkman painters have repeatedly used this colour combination to paint tree leaves. By changing the amount of orpiment in this colour combination, these painters have produced a yellowish green colour that was used on the outside part of the leaves of the trees to a dark green colour on the inside part of the leaves (Fig. 5-126).

Figure 5-126: create different green tonalities by changing the amount of orpiment in colour combination orpiment+indigo

In contrast, copper green has been mostly used for colouring robe, background, and barding. According to the analysis done in this study, it can be generally confirmed that in the 15th century CE, the use of indigo + orpiment in Shiraz increases. Considering that the copper green tonality is completely different from the indigo + orpiment green tonality, it should be mentioned that in addition to the time factor, the motifs and figures in each painting also play a decisive role in the green colour material used by the painters. In fact, since in all the cases analyzed, the green colour of the leaves of trees and shrubs is from indigo + orpiment and the green colour used for barding and armour is copper green, the presence or absence of these figures can be known as a reason for the presence or absence of two coloured substances.

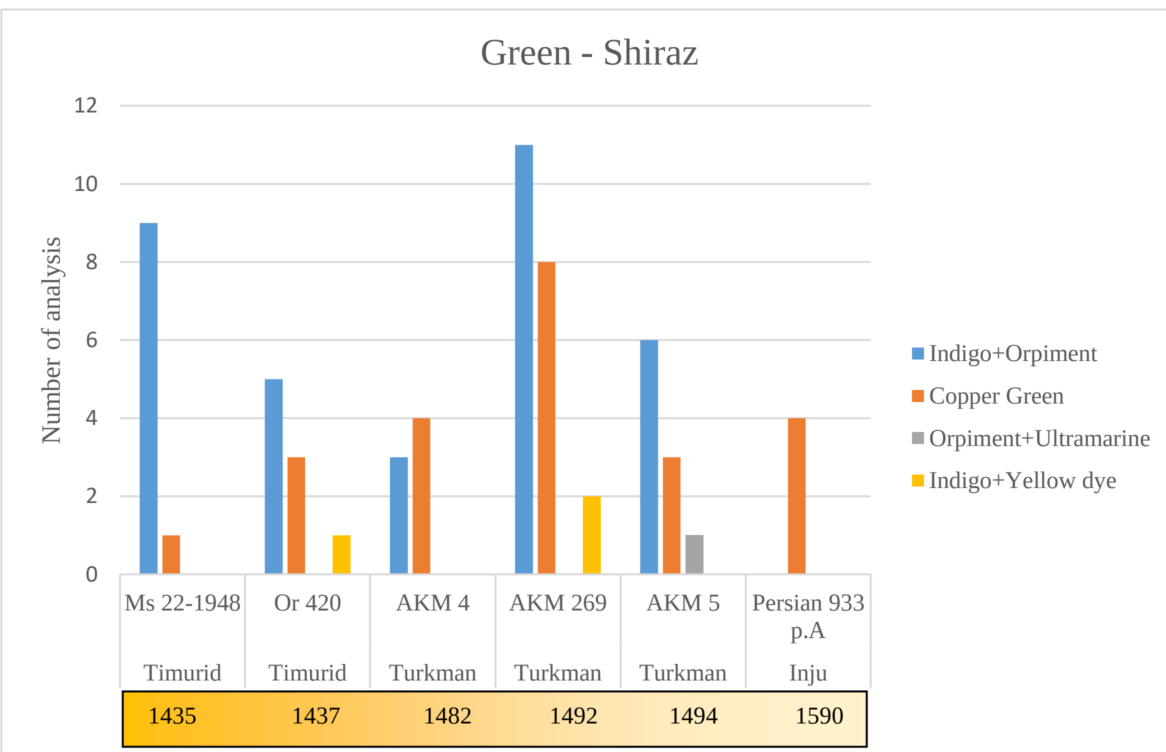


Figure 5-127: Green colour used in Shiraz

5-4-1-3 Red, Orange, and Brown

The two pigments cinnabar and red lead have been used in all three painting styles of Shiraz as red and orange (Fig. 5-129). In fact, the results of this study once again confirmed that these two pigments have been used by painters as red and orange in all cities and historical periods. Therefore, it can be summarized that the only differences regarding the use or non-use of the ocher pigment is as brown and cochineal pigment is as dark red. The Timurid and Turkman painters of Shiraz used ocher to create a brown colour, while the Inju style painter used the combination of cinnabar + orpiment instead of ocher to create a brown colour (Fig. 5-129). Ocher colour has been used by Timurid and Turkman painters of Shiraz to paint the trunks of trees, horses, and robe. Cochineal dye has been used as a dark red colour only by a Turkman painter and a Timurid painter in Shiraz. These two painters have used cochineal as a red colour to a limited extent for staining blood and background details or clothe details. In Shiraz, cochineal has been used mostly as a pink/violet colour or as a part of a combination for purple and its use as a red colour is only relevant to figures with a small area. It should be noted that the Timurid style painter of Shiraz in the *Shāhnāma* manuscript Ms 22-1948 has used the combination of red lead + orpiment as a brown colour that has not been used by any other painters in Shiraz or other cities.

As mentioned, there is no major difference in the use of red tones in different periods and different cities, and in fact the only notable case is the colouring of blood and very small flowers, which in some paintings have been coloured by cochineal, and in some cases by cinnabar.

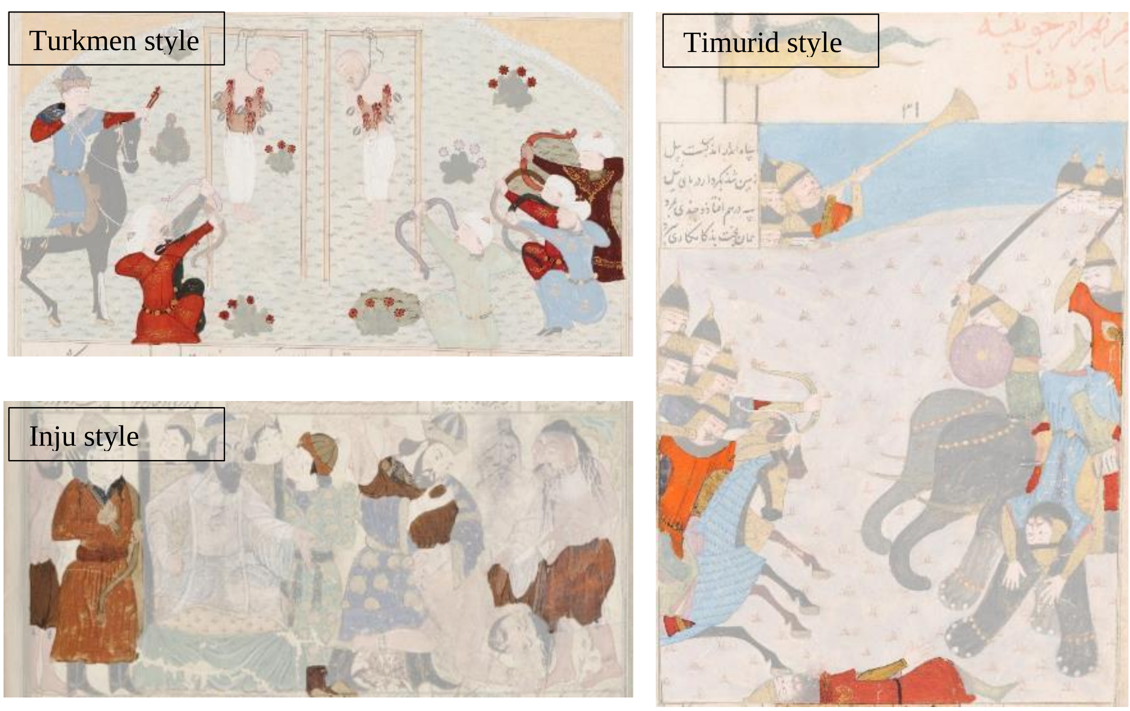


Figure 5-128: Three examples of red, orange, and brown tonalities used in Inju, Turkmen and Timurid paintings of Shiraz

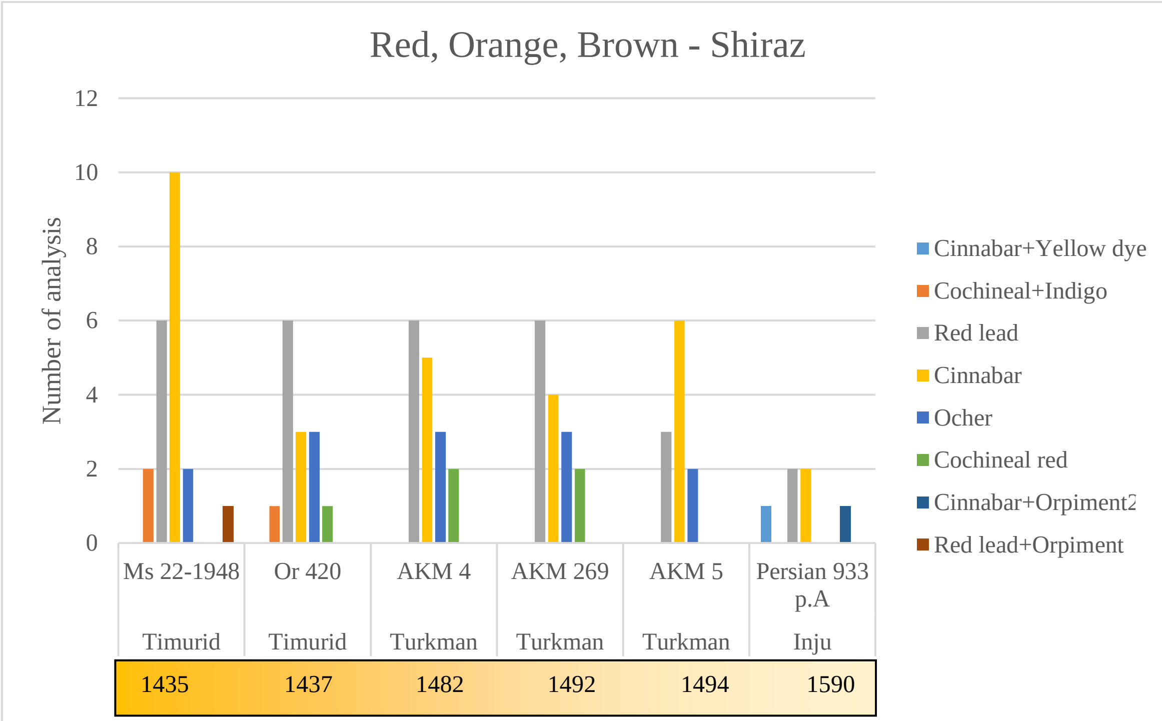


Figure 5-129: Red, orange, brown colours used in Shiraz

5-4-1-4 Pink, Violet, and Purple

In the paintings of all three styles of Inju, Timurid and Turkman of Shiraz, different colour combinations have been used for pink, violet, and purple tones (Fig. 5-133). The comparison of materials used for these colour tones is very important because painters have used different colour combinations to achieve this colour tone at different times and cities.

As mentioned, in Shiraz, different colour combinations have been used at different times to create different pink/violet and purple tones. Cochineal and Indian lac are the only dyes that have been used purely or only in combination with white lead to create pink or violet. Interestingly, many Persian manuscript painters have either used cochineal or Indian lac for these colour tonalities. None of the painters studied in this study have used both colours simultaneously. For example, Turkman painters in Shiraz have used cochineal, and Timurid and Inju Shiraz painters have used Indian lac.

Figure 5-130: An example of pink, violet, and purple tonalities used in Turkmen paintings of Shiraz

These two colours in all three styles of painting in Shiraz have been used by painters for painting background and robe. Shiraz painters have mostly used these two colours as a transparent or semi-transparent layer on other colours to determine the details of the background and clothes. Interestingly, although the appearance and many of the colour materials used by the Timurid and Turkman painters of Shiraz are very similar, but the colour materials used for the pink/violet and purple tones in the Timurid and Inju styles have more in common than the Timurid-Turkman. For example, the colour combination of ultramarine + cinnabar is the most widely used purple colour combination used by Turkman painters (Fig. 5-130), while Timurid and Inju Shiraz painters have used cochineal-based compositions to create purple tones (Fig. 5-131).

Figure 5-131: An example of pink, violet, and purple tonalities used in Timurid paintings of Shiraz

For example, the colour combination of cochineal + ultramarine and cochineal + indigo has been used by the Timurid painter in the *Shāhnāma* manuscript Ms 22-1948 for purple. The Timurid painter also used the colour combination cochineal + indigo to create purple in the Or 420 *Shāhnāma* manuscript. Inju style painter has used the same limited colour materials to create a light pink and peach colour (Fig. 5-132).

This painter has used the combination of cinnabar + white lead for the pink colour used to paint people's faces and cinnabar + yellow dye for the peach colour. It should be noted, unlike the Inju style painter, painters of Turkman *Shāhnāma* manuscript of AKM 5 have used the combination of red lead + white lead to paint the face. These purples and pink/violet colour combinations have been used by Shiraz painters to paint backgrounds, robes, flags, clothes, etc. According to the analysis performed in this study, it can be concluded that in Shiraz in the early 15th century to the middle of the 15th century, cochineal was used more, while from the middle of the 15th century with the advent of the Turkman, the use of Indian lac instead of cochineal has been increased. In other words, in none of the samples of pink and purple colours analyzed in this study before the middle of the 15th century CE in Shiraz, the colour Indian lac has not been identified. Also, based on the analysis done in this study, it can be concluded that the number of colour combinations used for this colour tonality is directly related to the artistic quality and the importance of the manuscript of the paintings. Hence, the painter of the Timurid-style *Shāhnāma* manuscript Or 420 used only cochineal and the combination of cochineal + indigo to create this colour tonality. Also, the Inju style painter used only cochineal and a combination of cinnabar with white lead or yellow dye to create this colour tonality. Due to the great destruction of the paintings of these two manuscripts, it can be easily concluded that, the qualities of the paintings of these two *Shāhnāma* manuscripts are lower than other *Shāhnāma* manuscripts.

Figure 5-132: An example of pink, violet, and purple tonalities used in Inju paintings of Shiraz

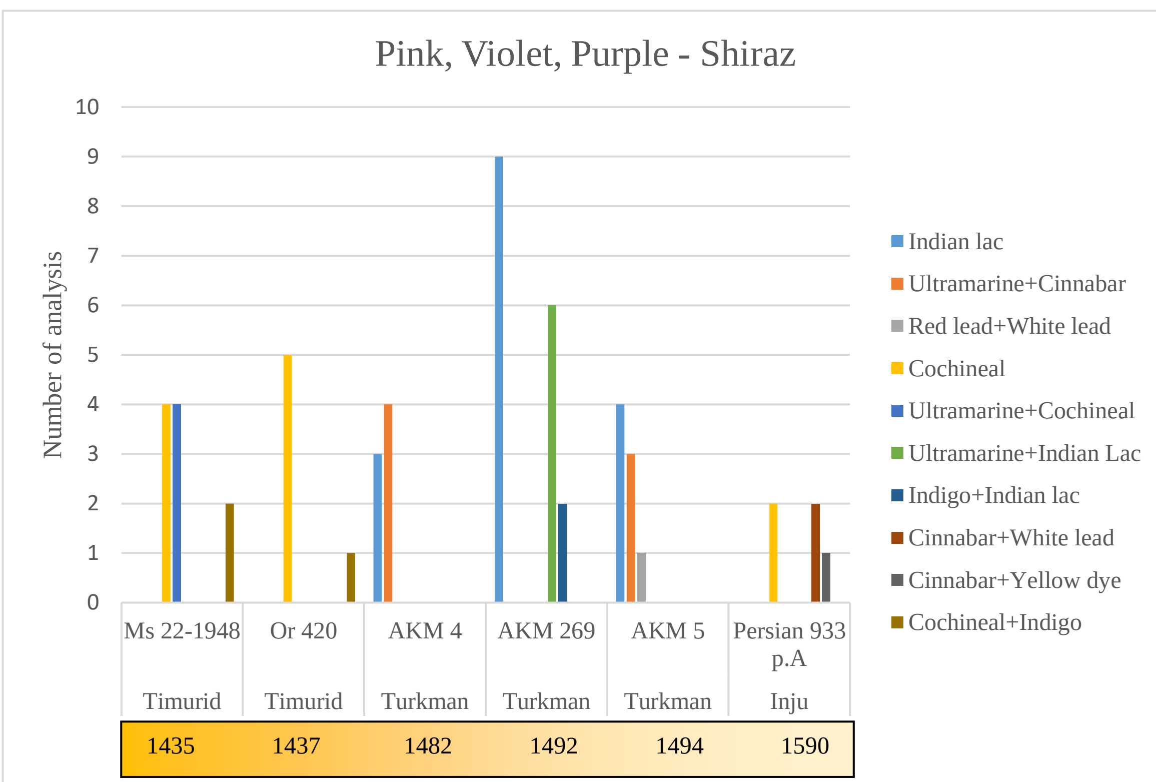


Figure 5-133: Pink, violet, purple colours used in Shiraz

5-4-1-5 Yellow

In Shiraz, like other manuscript production centers, orpiment has been used as the main material for yellow colour. In the paintings of all three different styles of Shiraz, orpiment has been used as the main material of yellow colour (Fig. 5-135). The Timurid and Turkman painters of Shiraz have used orpiment in pure form or in combination with other coloured materials, but the Inju style painter has never used orpiment in pure form.

This painter used orpiment in combination with yellow dye. In the *Shāhnāma* manuscripts MS 22-1948, the Timurid painters created a dull yellow from the combination of orpiment and gold, which was used to paint the flags (Fig. 5-134).

The interesting point is that the Inju style painter uses the same colour combination, but with a colour tone that is closer to golden than yellow. Turkman style painters have used more orpiment than Inju and Timurid style painters of Shiraz (Fig. 5-134). These painters have used orpiment both individually and in combination with yellow dye. It should be noted that in the Turkman style paintings of the *Shāhnāma* manuscript AKM 5, the combination of orpiment + red lead has been used, which has not been used in any other paintings, neither in Shiraz nor in other cities.

This unique colour combination has been used to colour robe that has a dull yellow (orange) colour. It seems that the Turkman painter in this *Shāhnāma* manuscript used orpiment to produce this colour tonality and covered it with a thin layer of red lead. Another colour substance that plays a decisive role in the study of yellow colour is yellow dyes.

As in Section 5-2-4 it was explained in this study it was not possible to distinguish between different types of yellow dyes, but based on historical evidence, saffron and turmeric are the two main candidates for yellow dye used in Persian manuscripts.

According to the analysis, only the Timurid style painter used from yellow dye individually in Or 240 *Shāhnāma* manuscript. While Turkman style painters have mostly used yellow dye in combination with orpiment. It should be noted that the Turkman style painters of *Shāhnāma* manuscript AKM 5 also used a combination of gold + yellow dye.

Figure 5-134: Two examples of yellow tonalities used in Turkmen and Timurid paintings of Shiraz

Based on the analysis done in this study, it seems that some painters were not interested in using yellow in large dimensions. Shiraz Turkman painters have used yellow extensively to paint robes, clothes, backgrounds, and flags. But the Inju style painter has rarely and only in one point has used yellow to paint the background (underlayment).

The interesting thing about Shiraz Timurid painters is that they had a different approach and interest in yellow. Timurid painter version of the *Shāhnāma* manuscript Or 420 has used a great deal of yellow for robe, clothing, background, and barding, while the painter of the *Shāhnāma* manuscript Ms 22-1948 has rarely used yellow and in very small quantities. Based on the analysis of yellow colours in this study, it can be concluded that over time, orpiment has always been known as the main yellow pigment. It should also be noted that from the beginning of the 15th century to the middle of the 15th century (Timurid) Shiraz, in general, the yellow tonality was less considered and was used in very small dimensions. Based on the analysis done in this study, the increase in interest in yellow colour from the middle of the 15th century by the Turkman style painters of Shiraz is obvious.

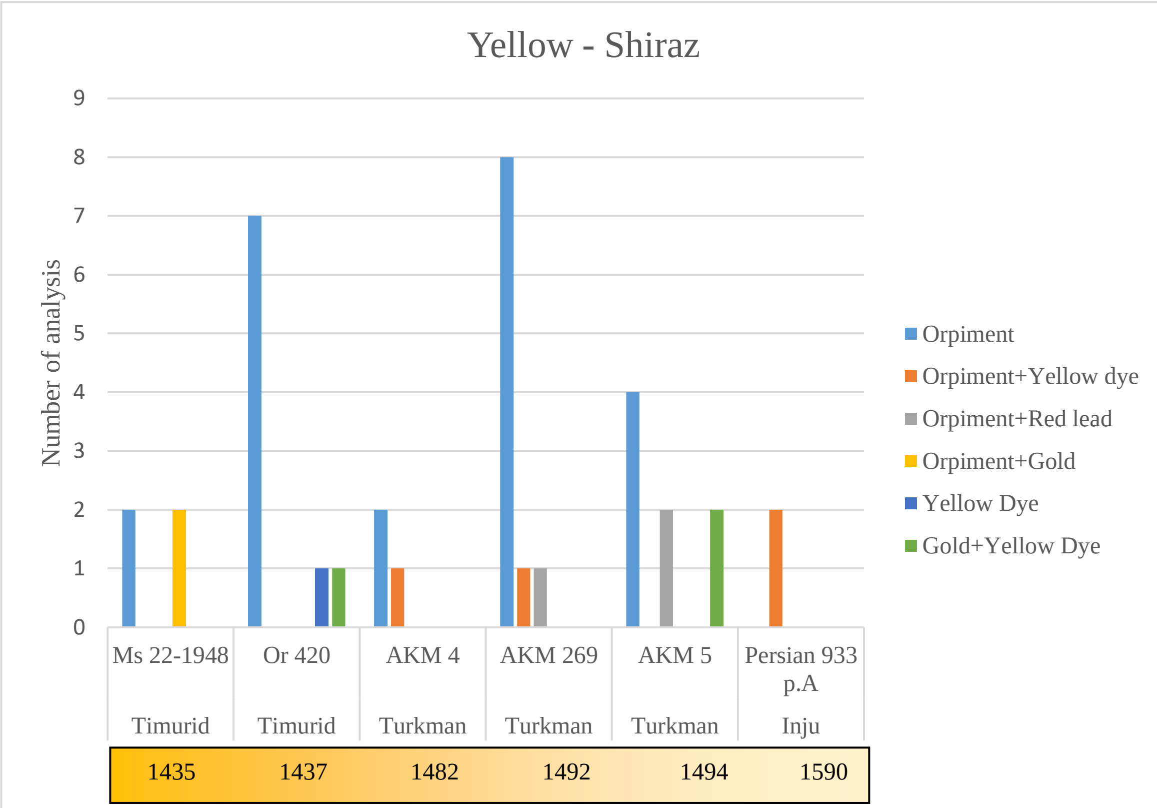


Figure 5-135: yellow colours used in Shiraz

5-4-1-6 Metallic pigments and Grey

Gold and silver are the only metallic pigments that have been used in paintings of different styles in Shiraz in different periods. Gold has been used as a widely used pigment in Persian manuscripts over time in different cities and at different times. Painters of all three different styles of Shiraz have used gold pigment. The only difference in the gold pigment used by these painters is the amount of gold metallic polish or unpolished used.

As in Section 5-2-5 It was explained that Shiraz painters also reduced the metallic luster of gold by grinding (beading) gold or by adding silver or orpiment. For example, the Inju style painter, the Timurid style painter of Or 420 *Shāhnāma* manuscript and the Turkman style painter of the *Shāhnāma* manuscript

AKM 4 have used a combination of gold with silver or orpiment to reduce the brilliance of gold and achieve the desired tonality (4-140).

It should be noted that the addition of silver to gold by Shiraz painters, in addition to achieving the desired colour tonality, could also be due to reduce the costs. Silver is another metal pigment that has been used in various styles of painting in Shiraz. As mentioned before, the silver used in the manuscript is now seen as dark grey due to corrosion (Fig. 5-138). The Inju style painter did not use any grey tones, but most of the dark grey colours used to paint swords, armour, streams, and shields in the paintings of the Timurid and Turkman painters of Shiraz were created by silver pigments (Fig. 5-138).

Figure 5-136: An example of gold pigment used in Turkmen paintings of Shiraz

It should be noted that the Timurid style painter of the *Shāhnāma* manuscript Or 420 did not use silver pigment to create grey colour, this painter used a combination of indigo + white lead and ultramarine + white lead to create a light grey. These two colour combinations have been used as a light grey colour by other Timurid style painters and some Turkman style painters. In some of Shiraz paintings, the colour compositions that have red lead have become dark grey over time due to the corrosion of red lead. For example, in the Turkman style paintings of the *Shāhnāma* manuscript AKM 4 and Timurid paintings of the *Shāhnāma* manuscript Ms 22-1948, to create, the grey colour in two points the colour combination red lead + indigo and red lead + ocher was used respectively. Based on the analysis performed in this study, it can be concluded that the amount and method of using the two metallic pigments of silver and gold have not been changed over time in Shiraz. The same is true of paintings of other cities. Also, very little change is seen in the motifs and figures painted by these metallic pigments over time. Especially in the case of silver pigment, which silver has been used in the

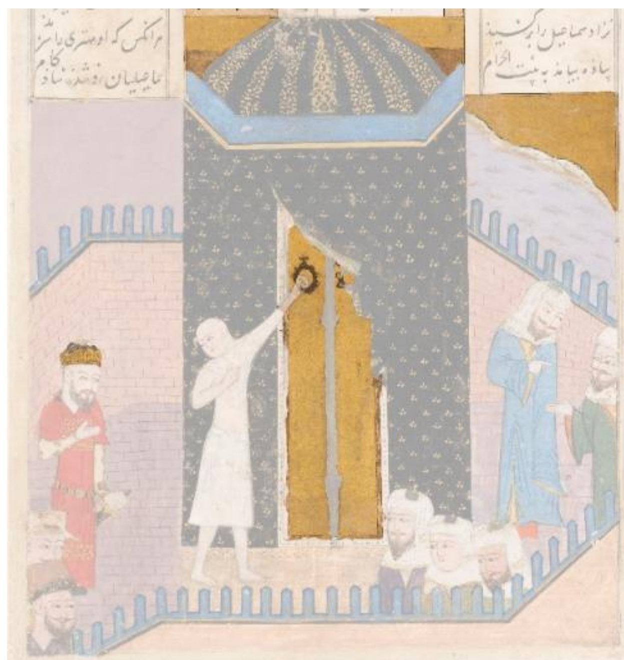


Figure 5-137: An example of gold pigment used in Timurid paintings of Shiraz

paintings of all cities in different periods to paint streams, swords, armour. Another colour combination of grey used by Shiraz painters is the composition of indigo + white lead, which creates a much lighter grey colour than silver. This colour combination has been used in Shiraz paintings, unlike silver, for background of paintings or animals such as elephants or unicorns. It should be noted that in Shiraz, like other cities, white lead and carbon have been used as white and black.

Figure 5-138: Two example of silver pigment used in Turkmen and Timurid paintings of Shiraz

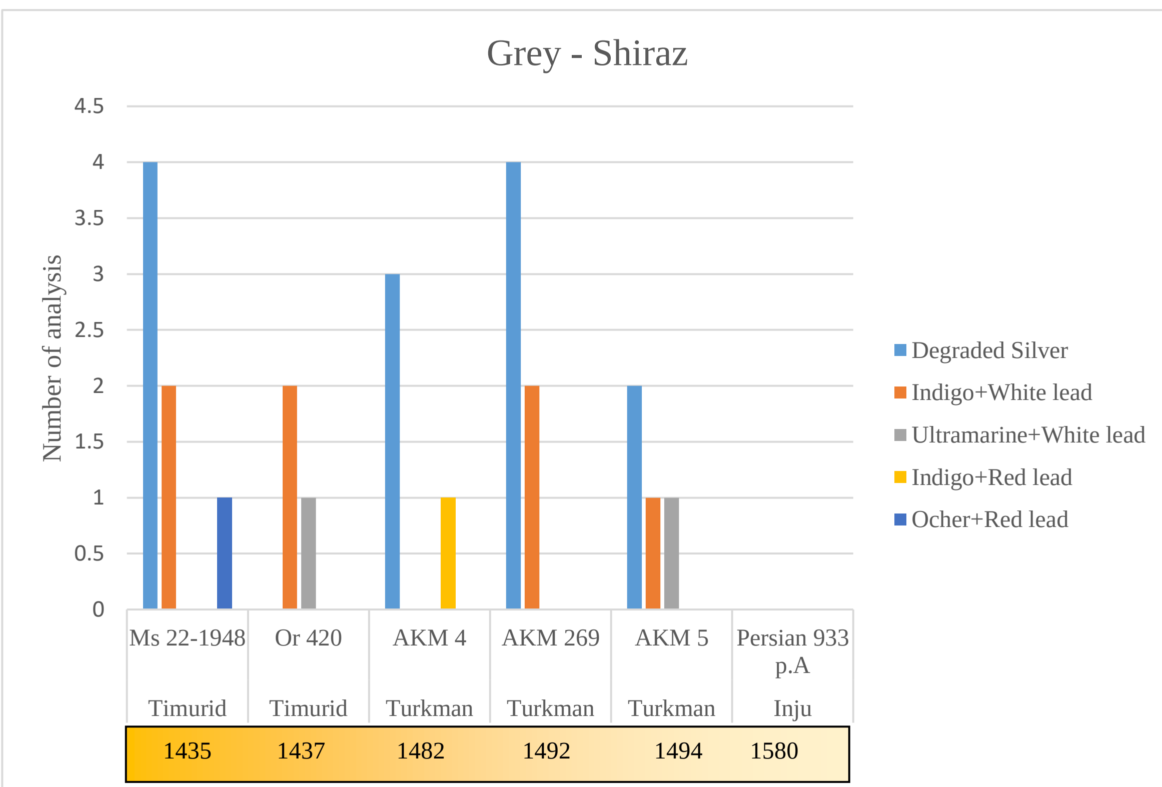


Figure 5-139: Grey colours used in Shiraz

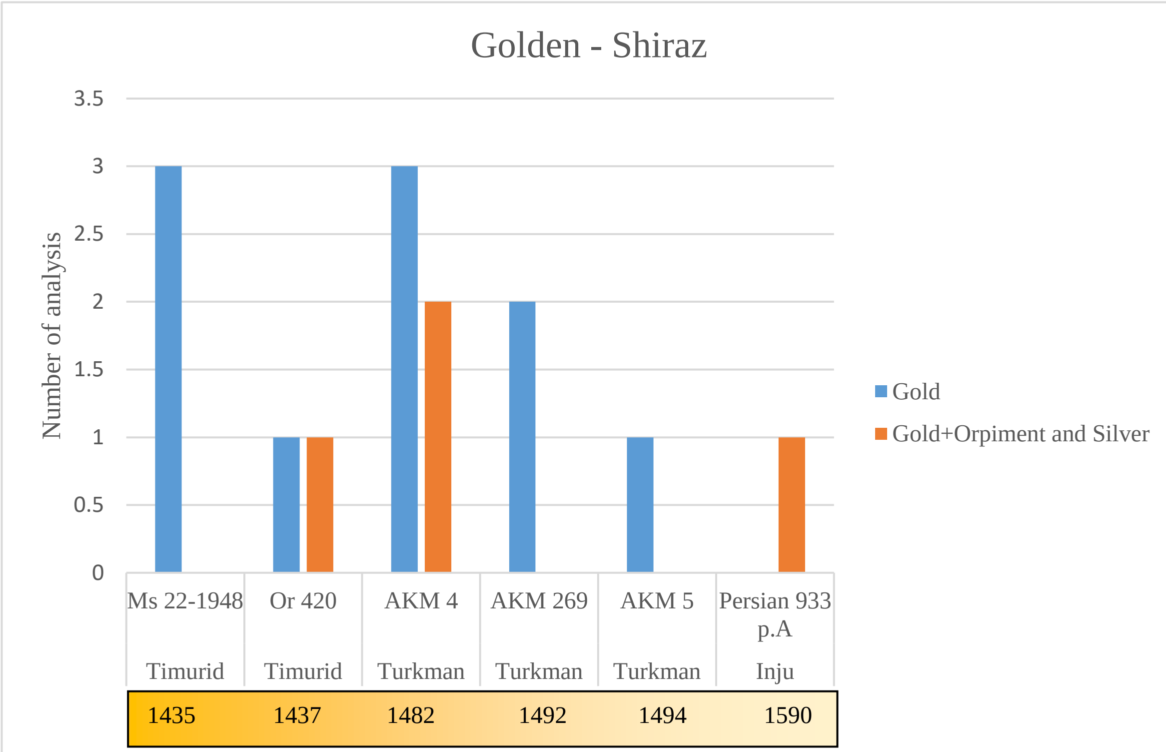


Figure 5-140: Golden colours used in Shiraz

5-4-2 Herat

In this study, 15 paintings by seven different painters in Herat were analyzed. All these paintings are related to the *Shāhnāma* manuscript RAS 239, which was produced in the royal court of the Timurid court in Herat in 1444 CE (Tab. 5-58). All these painters are part of the *Bāysunghur's* Royal Atelier in Herat, known as the Dar al-Sanayeh, which is a book-making center where many of celebrated Persian manuscripts such as the *Shāhnāma* of *Bāysunghur* and *Shāhnāma Joki* (RAS 239) have been produced.

The paintings of these painters express all the characteristics of the paintings of Herat school of painting. The predominant colour of these paintings includes dark blue to light blue (turquoise) and golden. Other unique features of these paintings include symmetrical and asymmetrical compositions, realism in drawing flowers and plants, variety of colours, details in architecture, and skill in drawing body design. Therefore, it can be easily concluded that the paintings of these seven painters clearly show all the characteristics of Herat Timurid style paintings in 15th century.

5-4-2-1 Blue

As expected, the variety of colour materials used in Herat paintings is very high. The colours used for blue in Herat paintings are no exception to this rule. In addition to ultramarine and indigo used in Shiraz, azurite is also used as a blue pigment in Herat. As expected before, ultramarine has been used extensively by all seven painters of *Shāhnāma* manuscript RAS 239 (Fig. 5-143). According to the visual condition of the paintings, it can be clearly understood that the ultramarine used in Herat has a higher quality and variety than the ultramarine used by Shiraz painters, especially the Inju style and Timurid painters of Shiraz.

On the other hand, indigo has been used by only one of these seven painters as a blue colour for background painting, while indigo has been used more by Shiraz painters. Azurite pigment, on the other hand, has been used by four Herat painters. The colour tonality created by azurite is a light bluish green that has been used for small figures such as birds and small flowers or backgrounds. It should be noted that one of the Herat's painters used Azurite with a colour tone close to green (turquoise) to paint the tree trunk, which has not been seen in any other paintings (Fig. 5-141).

Figure 5-141: The only example of used green (turquoise) to paint the tree trunk

The only similar case is related to the Lahijan painter's paintings in the *Shāhnāma* manuscript AKM 6, which is a combination of malachite + azurite (see section 5-4-4-2).

Based on the analysis performed in this study, it can be concluded that ultramarine has been used equally in the paintings of both Herat and Shiraz, but the amount of indigo used in Shiraz has been more than Herat. On the other hand, Herat painters have also used azurite, which has not been used by any painter in Shiraz. Blue can also be considered as the dominant colour in Herat paintings, which has been used to paint the background, sky, architectural components, and clothing in large dimensions (Fig. 5-142).

Figure 5-142: An example of blue colour tonalities used in Herat paintings

In fact, the blue colour used in Shiraz and Herat is similar, with the difference that the blue colour in Herat includes figures and motifs with larger dimensions.

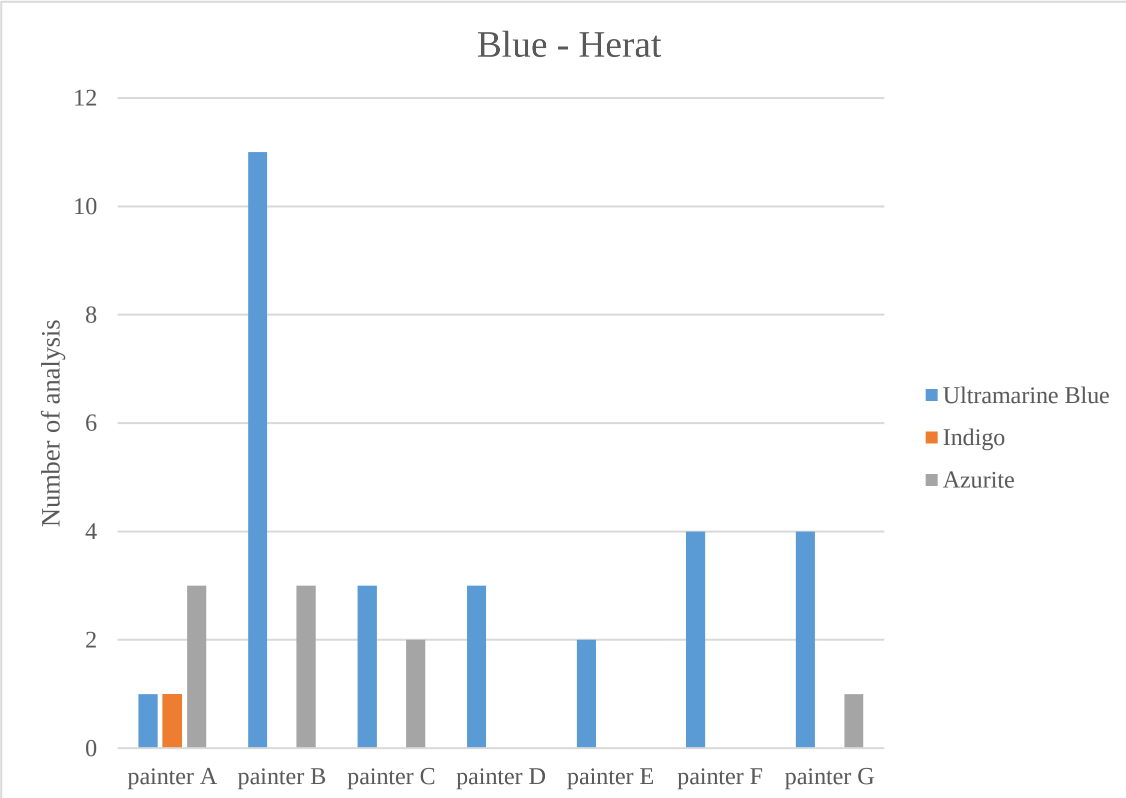


Figure 5-143: Blue colours used in Herat

5-4-2-2 Green

In Herat paintings, to create green tonalities the colour combination of indigo + orpiment and copper green is used to the same extent (Fig. 5-145). The only difference is in the use of these colours to paint different figures. In fact, the composition of indigo + orpiment has been used more to colour the leaves of trees, shrubs, and grasses, but copper green has been used more to colour backgrounds and clothes (Fig. 5-144). It should be noted that there is a unique case in the painting of painter G who used the colour combination of Azurit + malachite to create a blue-green (turquoise) colour[44], which has been used only by the Lahijan style painter in the *Shāhnāma* manuscript AKM 6. As mentioned above, this colour combination

[44] This colour can consider as blue or green hue

has been used in an unusual case to paint the trunk of a tree, that the similar case has not been seen in any other paintings (Fig. 5-141).

Based on the analysis done in this study, it can be concluded that the variety of green tones used in Herat paintings is higher than the green tones used in Shiraz paintings. This difference in green tones can have two main reasons: the large number of trees, shrub and plant figures in Herat paintings compared to Shiraz paintings, and the personal interest of Herat painters in green tones.

For example, the predominant colour of the painting's painter E is green. This painter has obviously used the colour green in such a way that even the background of his painting is a very soft green colour that the similar example has not been seen in other paintings.

Figure 5-144: An example of green colour tonalities used in Herat paintings

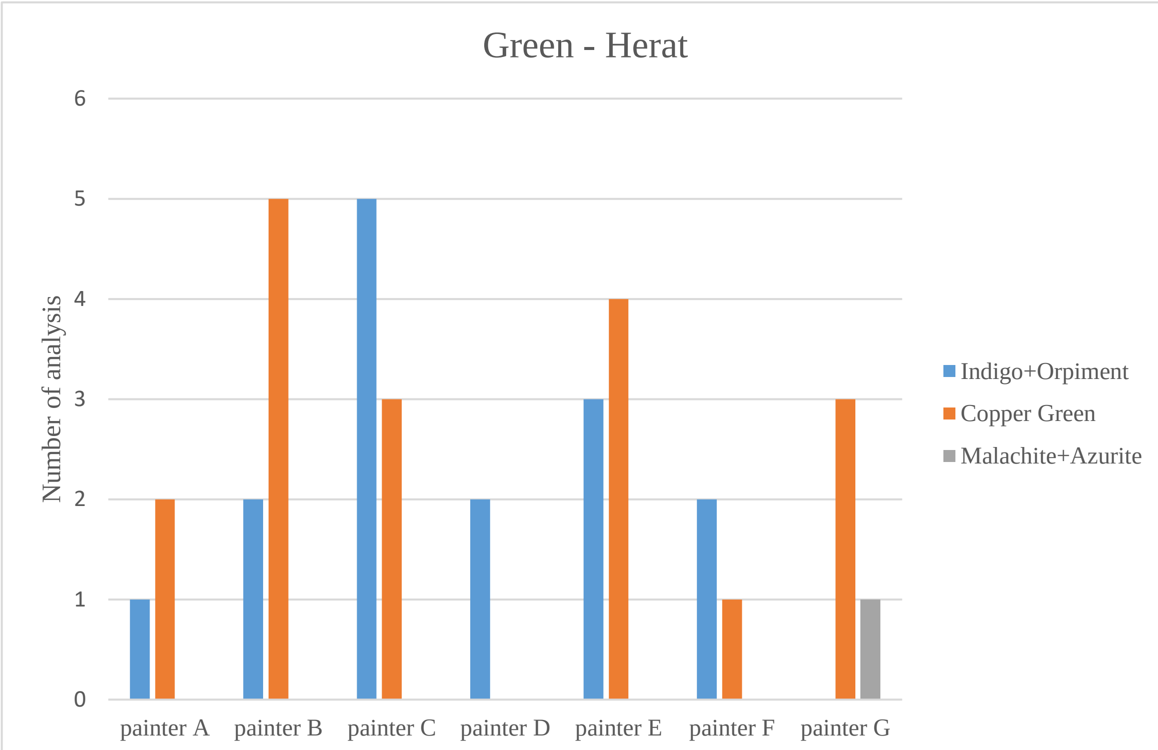


Figure 5-145: Green colours used in Herat

5-4-2-3 Red, Orange, and Brown

In Herat's paintings, cinnabar and red lead are used equally (Fig. 5-147). These two pigments, such as Shiraz, have been used as orange and red. But the interesting thing is the low use of ocher in Herat. Few painters in Herat have used ocher. Most Herat painters have used cinnabar + orpiment or cinnabar + red lead as a brown colour. Also, only two painters have used cochineal as a red colour and used it to paint blood and small flowers like Shiraz painters (Fig. 5-146).

Based on the analysis performed in this study, it can be concluded that the amount and method of using red, orange, and brown materials in the paintings of Herat and Shiraz are similar. One of the differences is that Herat painters have used less ocher than Shiraz painters.

Perhaps the main reason for this is that the painters of Herat painted the trunks of the trees, which is the main part of the use of brown in the paintings, with a different tone of brown, which is very different from the ocher brown. Also, Shiraz painters have used cochineal as a red colour more than Herat painters. But cochineal uses are common in both cities.

Figure 5-146: An example of red, orange, and brown colour tonalities used in Herat

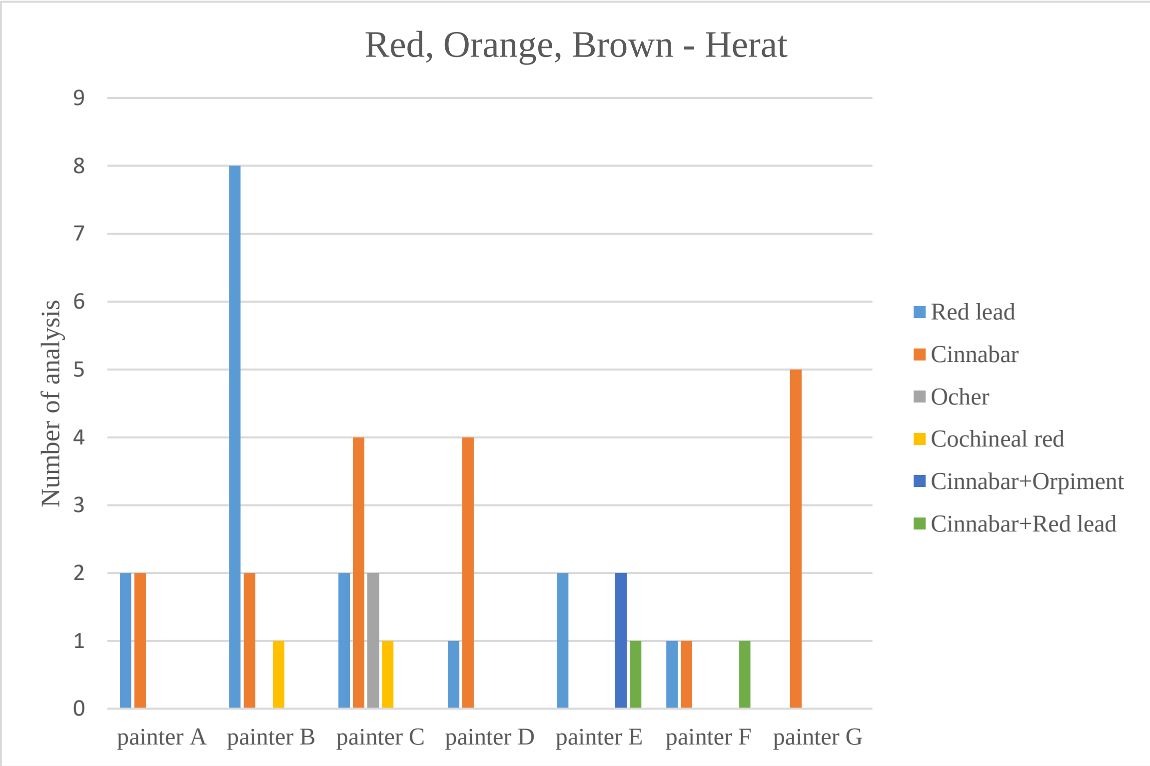


Figure 5-147: Red, orange, and brown colours used in Herat

5-4-2-4 Pink, Violet, and Purple

Diversity in the colour materials used for the pink/violet and purple tones in Heart's paintings is higher than Shiraz`s paintings (Fig. 5-148). The colour combination of red lead + white lead has been mostly used to produce pink and violet colours in Herat paintings. This colour combination is mostly used for colouring the background and face of people and clothes (Fig. 5-147).

This combination has also been used to create a peach colour tonality that has been used to paint walls and architectural components and background. Two Herat painters have used Indian lac to create pink and violet, and one painter has used cochineal, which is a small amount compared to the use of these colour in Shiraz. It should be noted that ultramarine-based colour combinations have been used for purple. Herat painters have combined ultramarine pigment with Indian lac or indigo or red lead to create purple. Also, two colour combinations of red lead + indigo and red lead + copper green has been used.

Based on the analysis done in this study, it can be concluded that the use of Indian lac and cochineal in Herat paintings is less than Shiraz. Herat painters have used red lead + white lead instead of these colour materials. Also, the colour combination of ultramarine + cinnabar, which has been used as purple in Shiraz many times, has not been used at all in Herat. Also, the colour of peach, created in Shiraz from the combination of cinnabar + yellow dye, in Herat, the same colour tonality is created from the combination of red lead + white lead.

Figure 5-147: An example of pink, violet, and purple colour tonalities used in Herat paintings

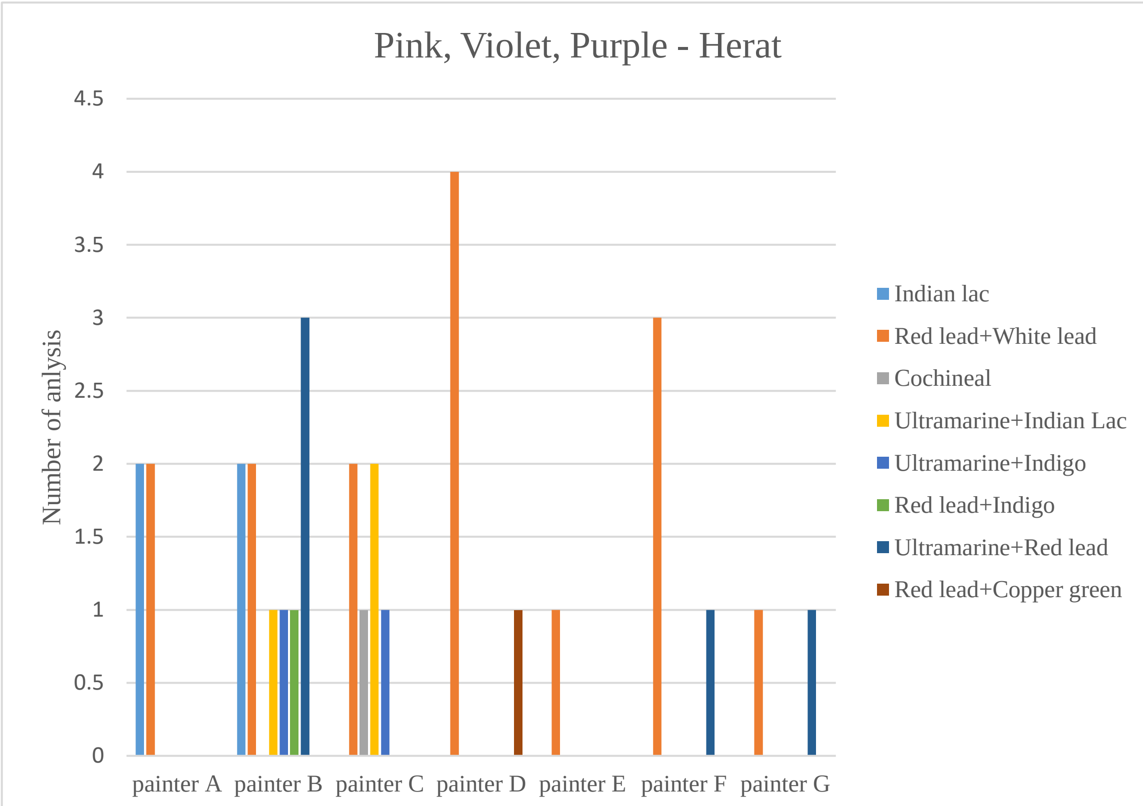


Figure 5-148: Pink, violet, and purple colours used in Herat

5-4-2-5 Yellow

It seems that Herat painters were not very interested in using yellow. In general, the yellow hue is very low in Herat paintings and is seen small in size (Fig. 5-149). Only two painters out of a total of seven painters in Herat have used yellow in a large scale to paint architectural and background elements. Like other cities, Herat painters have used orpiment as main material of yellow (Fig. 5-150).

Yellow dye is another colour material that has been used as a yellow colour in Herat paintings. Herat painters have combined yellow dye with gold or white lead to produce a very soft yellow tone (close to beige) and used it to paint the roof bricks. The combination of orpiment + gold was also used by a painter to paint the background.

Based on the analysis performed in this study, it can be concluded that the use of yellow colour in Herat paintings is much less than Shiraz. Perhaps the main reason is the overuse of gold by Herat painters, as many of the figures painted in yellow in Shiraz are painted in gold in Herat or in colour combinations containing gold.

The use of yellow in Herat and Shiraz is also very different. For example, in Shiraz, yellow has been used many times to paint robes and clothes, while in Herat, not a single case of yellow clothes or robes has been observed (Fig. 5-149). Herat painters have created a combination of gold with other materials such as yellow dye or orpiment or bead (grinding) the surface of gold to create different yellowish tones and have used it as yellow colour.

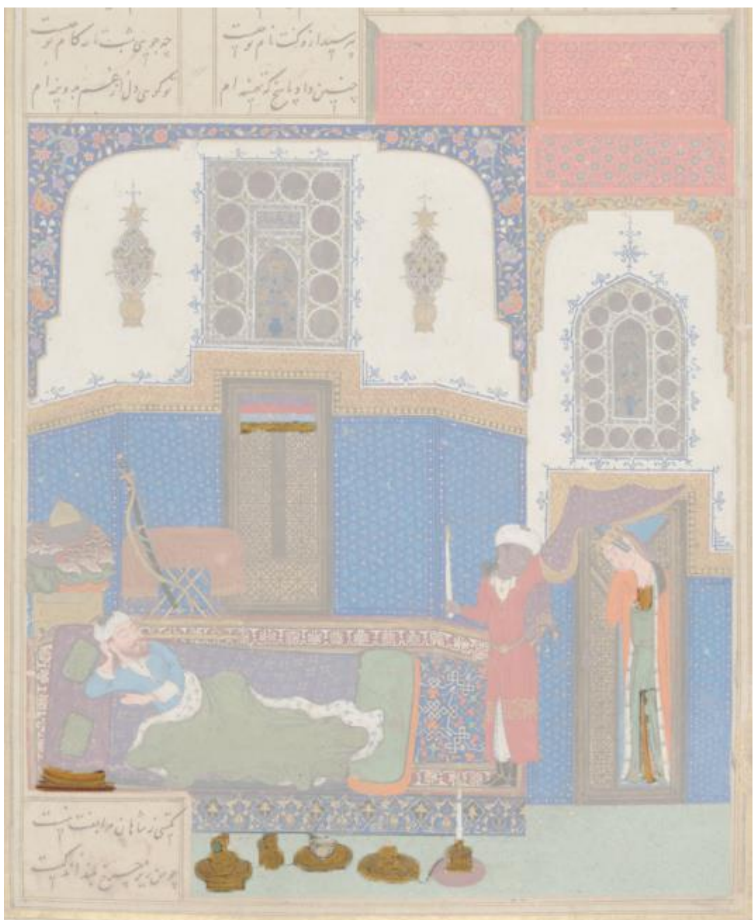


Figure 5-149: An example of yellow colour tonalities used in Herat paintings

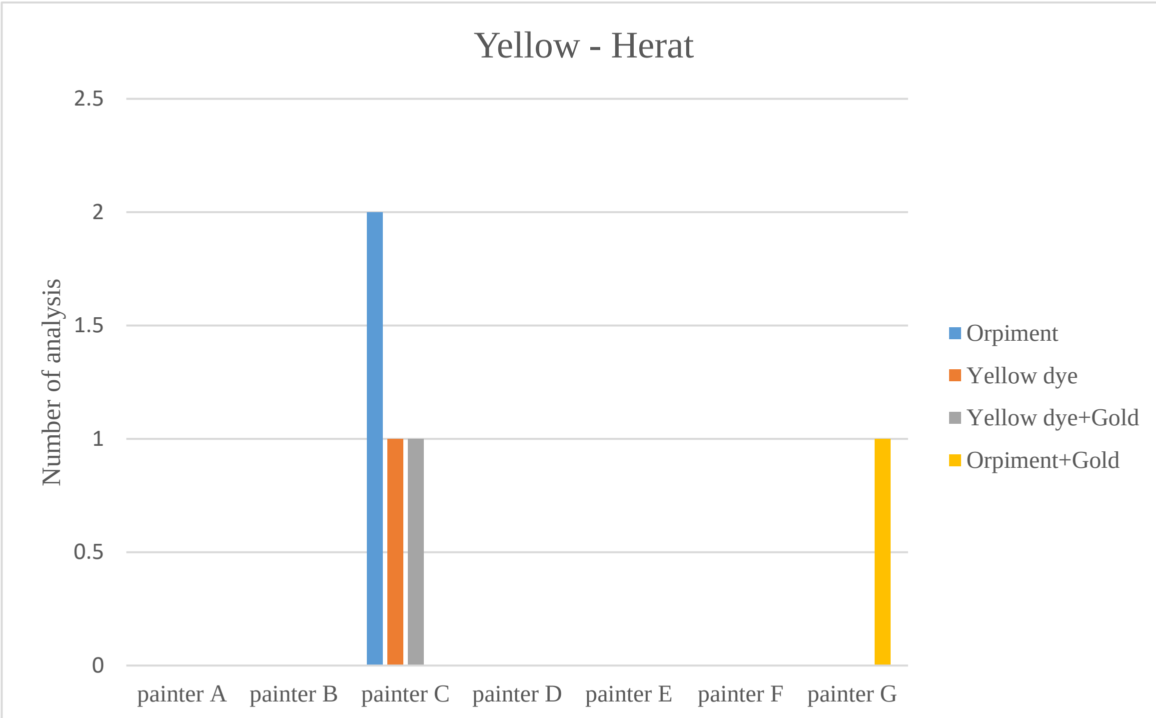


Figure 5-150: Yellow colours used in Herat

5-4-2-6 Metallic pigments and Grey

As mentioned before, gold pigment along with ultramarine has been used most in Herat paintings. Gold has been used exaggerated in Herat paintings. Herat painters have created a golden colour with or without metal polish by beading only gold and have painted various figures and motifs with it (Fig. 5-151). Another metal pigment used is silver, which, as previously described, is now seen as dark grey. Herat painters have used a lot of silver to paint streams, swords, and armour (Fig. 5-152). It should be noted that Herat painters have used the combination of indigo + white lead as a light grey colour. One Herat painter used ultramarine + white lead to create a bluish grey colour that has been widely used for background painting (Fig. 5-153). Herat painters, like painters in other cities, have used white lead and black carbon as white and black colours.

Based on the analysis performed in this study, it can be concluded that the metal pigments used in Herat and Shiraz are common and the only difference between them is the exaggerated use of gold pigments by Herat painters. The colours used for grey are common in Herat and Shiraz paintings. For example, Herat painters, like Shiraz painters, have used the combination of indigo + white lead to paint animals such as elephants and backgrounds. Also, the use of the colour combination ultramarine + white lead, which is used as a bluish grey colour, can be seen in the paintings of both cities.

Figure 5-157: An example of golden colour tonalities used in Herat paintings

Figure 5-152: An example of silver pigment used in Herat paintings

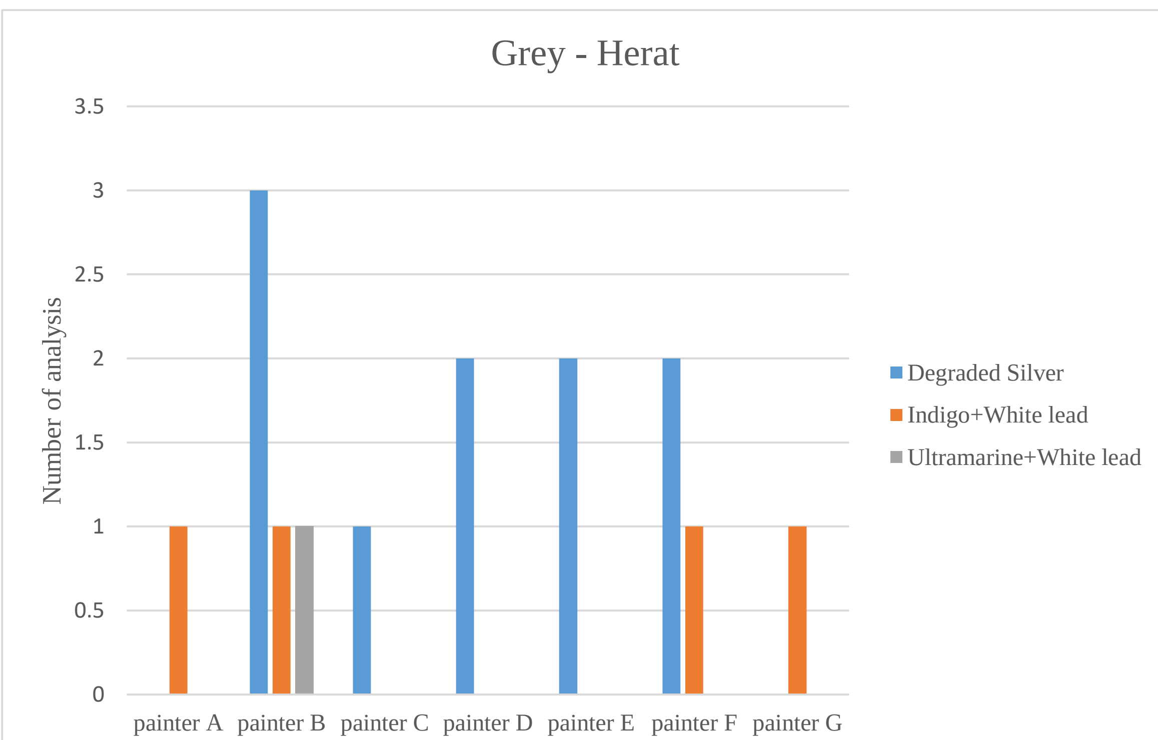


Figure 5-153: Grey colours used in Herat

5-4-3 India

In this study, 25 paintings produced by four different painters in India (mostly western India, eastern Iran) were analyzed (Tab. 5-58). These paintings belong to three *Shāhnāma* manuscripts Persian 9 (two painters and 19 paintings), Persian 933 (one painter and four paintings), and RAS 239 (one painter and two paintings). Unfortunately, the exact place of production of these paintings is not known, but because of the characteristics of their paintings and the manuscripts in which these paintings are drawn, they have been attributed to western India by art historians (see Chapter 2). These paintings were painted in the period from the late 14th century to the late 16th century. The oldest of these paintings is paintings of painter A belong to the *Shāhnāma* manuscript Persian 9 (painter "Persian 9A") at late 14th century. This painter according to Robinson`s claim, is an Indian painter who tried to imitate glossy paintings. Another painter is painter B of the *Shāhnāma* manuscript Persian 9 (painter "Persian 9B") which is a Timurid painter at mid-15th century who, according to Robinson, is either a Persian Shiraz Timurid painter who worked in India or an Indian painter interested in imitating Shiraz Timurid paintings. The "painter 933A" or "Persian 933 ti" of the Shāhnāma manuscript Persian 933 is another painter belongs to the mid-15th century of west India. Then the two analyzed paintings from the *Shāhnāma* manuscript RAS 239 which are produced by "painter Ras 239 Mughal" are belong to the Mughal period of India. These two paintings have a much higher artistic quality than other paintings, and about the year 1600 CE were produced and added to this *Shāhnāma* manuscript at Mughal court.

5-4-3-1 Blue

In all Indian paintings which has been studied in this study ultramarine and indigo used to create a blue tone. Indian painters, like Shiraz painters, have used two colours, ultramarine and indigo, as blue, but unlike Herat painters, Indian painters have not used azurite. "The Persian 9A" painter and "the Ras 239 Mughal" painter have used only ultramarine, and in general these two painters used less blue tonality than the other two painters (Fig. 5-155).

Based on the analysis performed in this study, it can be concluded that the blue colour materials used by Indian painters are more similar to Shiraz painters than Herat painters. Also, like the paintings of Shiraz and Herat, in Indian paintings, blue colour has been used more to paint the sky, background, robes (Fig. 5-154). The passage of time does not seem to have had much of an effect on the blue colours used in Indian paintings. It should be noted that according to the available visual evidence, it can be concluded that the quality of ultramarine used in Indian paintings is much lower than the ultramarine used in Shiraz and especially in Herat, except for Mughal paintings. In many paintings, the ultramarine used has fallen off.

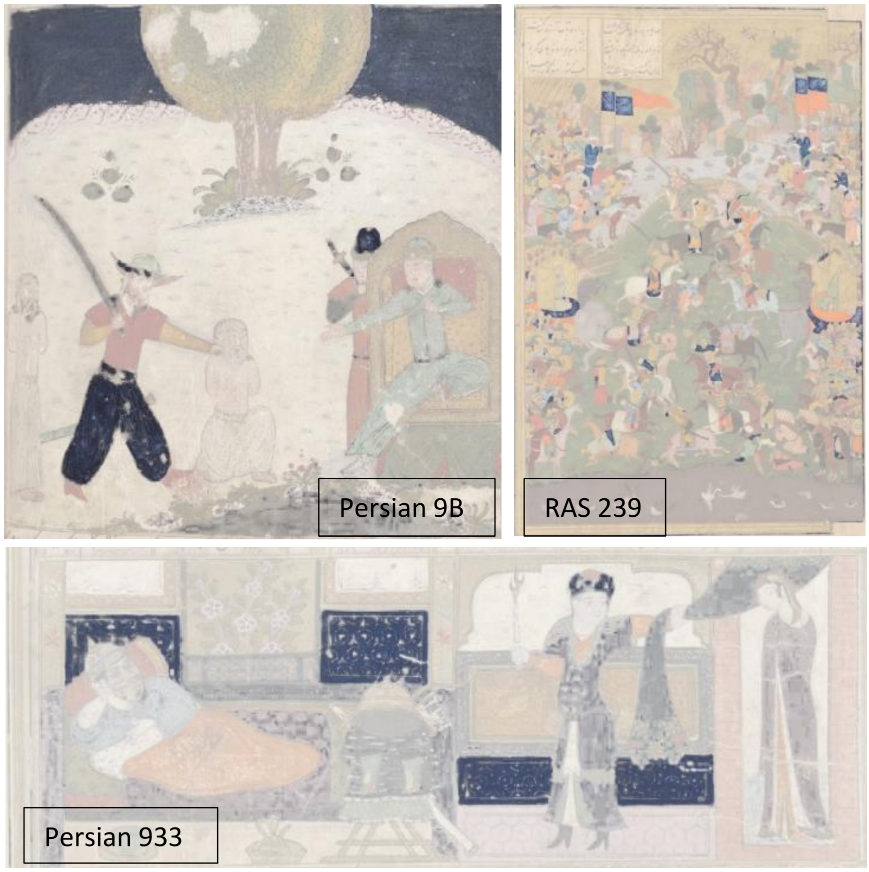


Figure 5-154: Three examples of blue colour tonalities used in west India

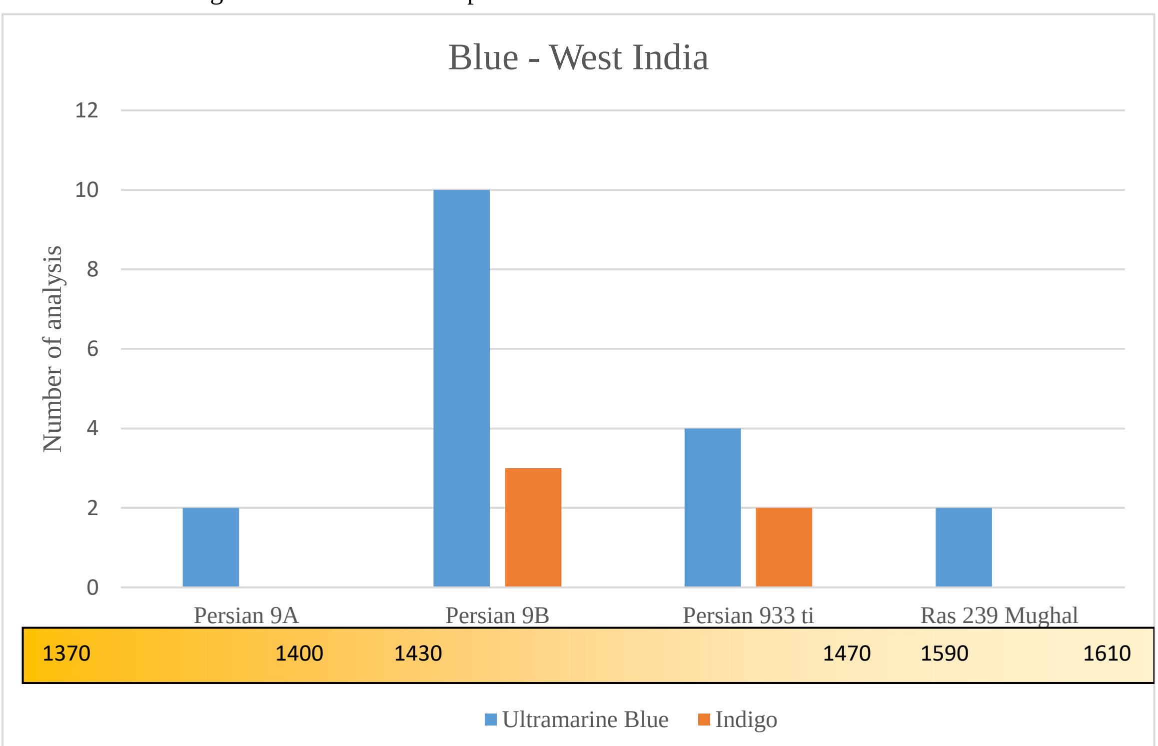


Figure 5-155: Blue colours used in west India

5-4-3-2 Green

Indian painters have used two colours, indigo + orpiment and copper green, to create almost the same amount of green. At the late 14th century "painter 9A" used only copper green as the colour green, but the other three painters used both colours equally (Fig. 5-157).

Based on the analysis done in this study, it can be concluded that the green colours used by Indian painters are not much different from the samples of Shiraz and Herat, and it seems that the main difference is in the quality of the materials used (Fig. 5-156). For example, the "painter 9B" wherever he/she has used copper green the paper has been corroded, so it can be concluded that this painter did not combine copper green with saffron to prevent the paper from corroding by copper. The use of copper green also seems to have been more common in western India until the late 14th century. Of course, not using the colour combination indigo + orpiment has a direct relationship with the absence of trees and shrubs in the glossy style of painting (late 14th century) because the green colour used for the leaves of trees and shrubs is always from this colour combination. The same is true of Mughal paintings (the *Shāhnāma* manuscript RAS 239*)*, which have very few trees

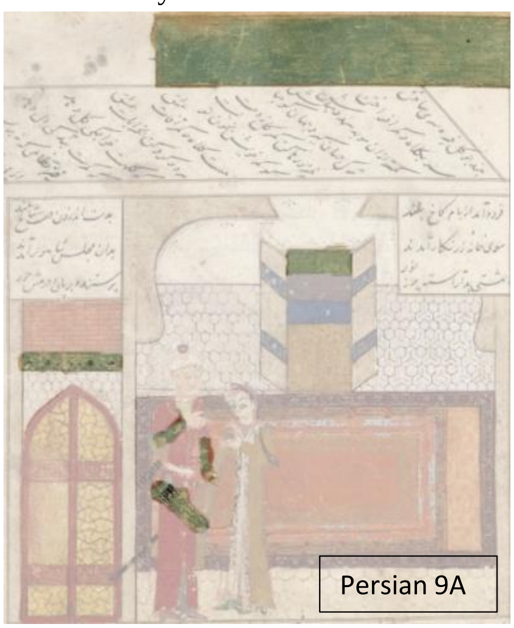


Figure 5-156: Four examples of green colour tonalities used in west India

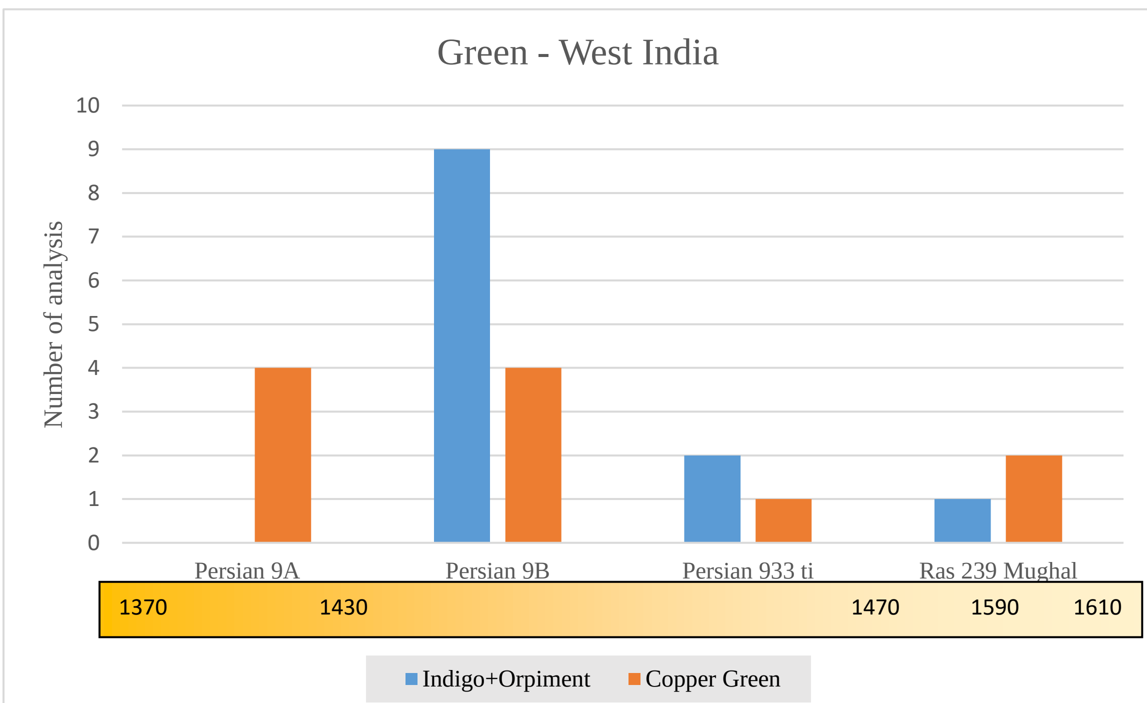


Figure 5-157: Green colours used in west India

5-4-3-3 Red, Orange, and Brown

All four Indian painters used cinnabar and red lead as red and orange (Fig. 5-159). None of these four painters used cochineal as red. For the brown tones, except “the Persian 9A” painter belonged to the late 14th century, other painters used ocher. This ocher is mostly used for painting tree trunks and architectural components. Painter “Persian 9A” has used a colour combination based on cinnabar to create brown tones (Fig. 5-158).

Based on the analysis done in this study, it can be concluded that the red, orange, and brown colour used by Indian painters are not much different from the Herat and Shiraz painters. The only notable difference is the non-use of cochineal by Indian painters, which has been used by Herat and Shiraz painter in small dimension. It should also be noted that the ocher used to paint the tree trunk by the painter “Persian 9B” has created a very dark brown tint that is very different from the brown colour used for the tree trunk by other painters.

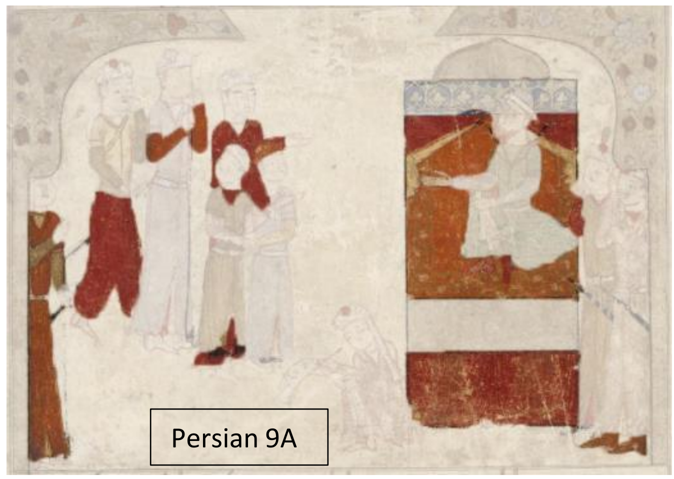


Figure 5-158: four examples of red, orange, and brown colour tonalities used in west India

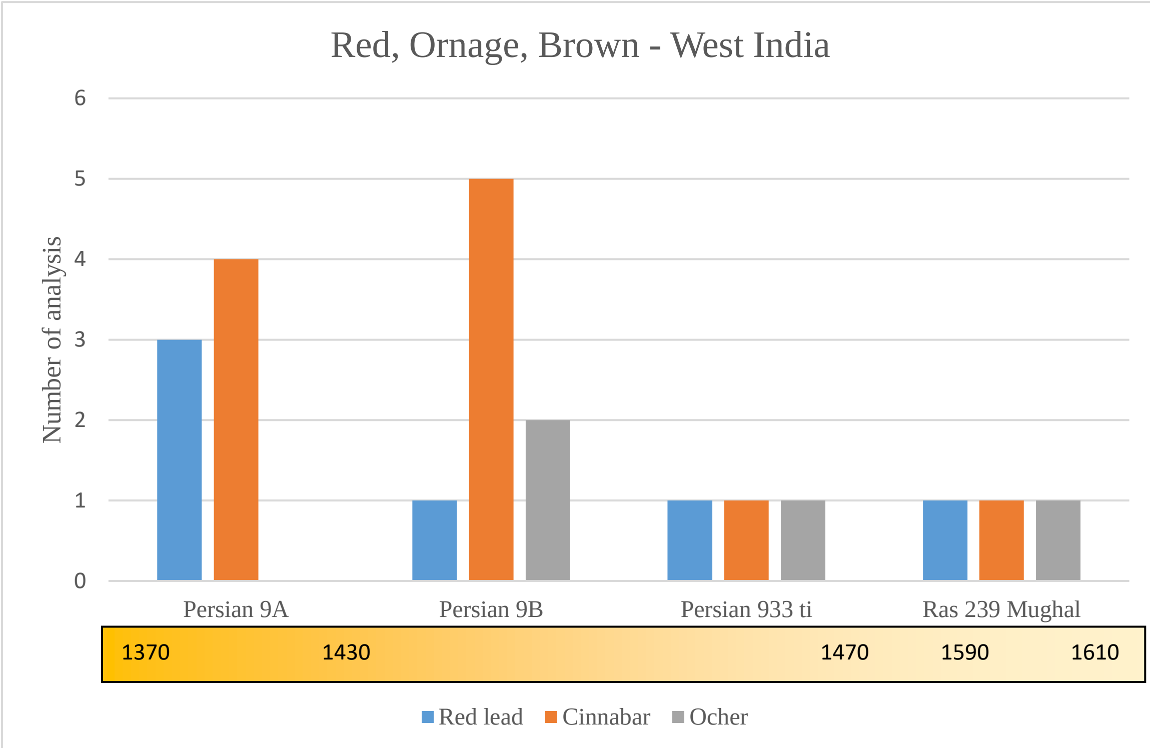


Figure 5-159: Red, orange, and brown colours used in west India

5-4-3-4 Pink, Violet, and Purple

The most common colour used by Indian painters to create pink and violet is Indian lac (Fig. 5-161). The painter "Persian 9B", in addition to using pure Indian lac, has used the combination of Indian lac + indigo to create a purple colour. Instead of Indian lac, the Timurid painter "Persian 933 ti" has used cochineal to produce pink and violet and cochineal + indigo to create purple instead of Indian lac. But at the late 14th century painter "Persian 9A" did not use either these two dyes and instead used a combination of cinnabar + white lead to create pink and violet (Fig. 5-161). In general, this painting has used violet and purple colour tones so little. The interesting point is that this painter and other Indian painters in the *Shāhnāma* manuscript Persian 9 have used a kind of dark ultramarine as purple colour, a similar example of which has not been used by any other painter. The colour combination of cinnabar + white lead has also been used by Indian painters to create pink and violet. These painters used the combination of cinnabar + orpiment to produce a peach colour (Fig. 5-160).

Based on the analysis done in this study, it can be concluded that Indian painters have used different colour combinations to create pink/violet and purple tones. These painters used Indian lac more than cochineal. These painters used the combination of indigo + Indian lac instead of the colour combination ultramarine + cinnabar, which was used as purple in Shiraz. The tendency for Indian painters to use pink and violet tones seems to have increased since the early 15th century. This colour tone is mostly used for background colouring and clothes in all cities. Interestingly, the Mughal and the Persian 933 Timurid painters used a peach colour to paint the horse, a similar example not seen in any other painting.

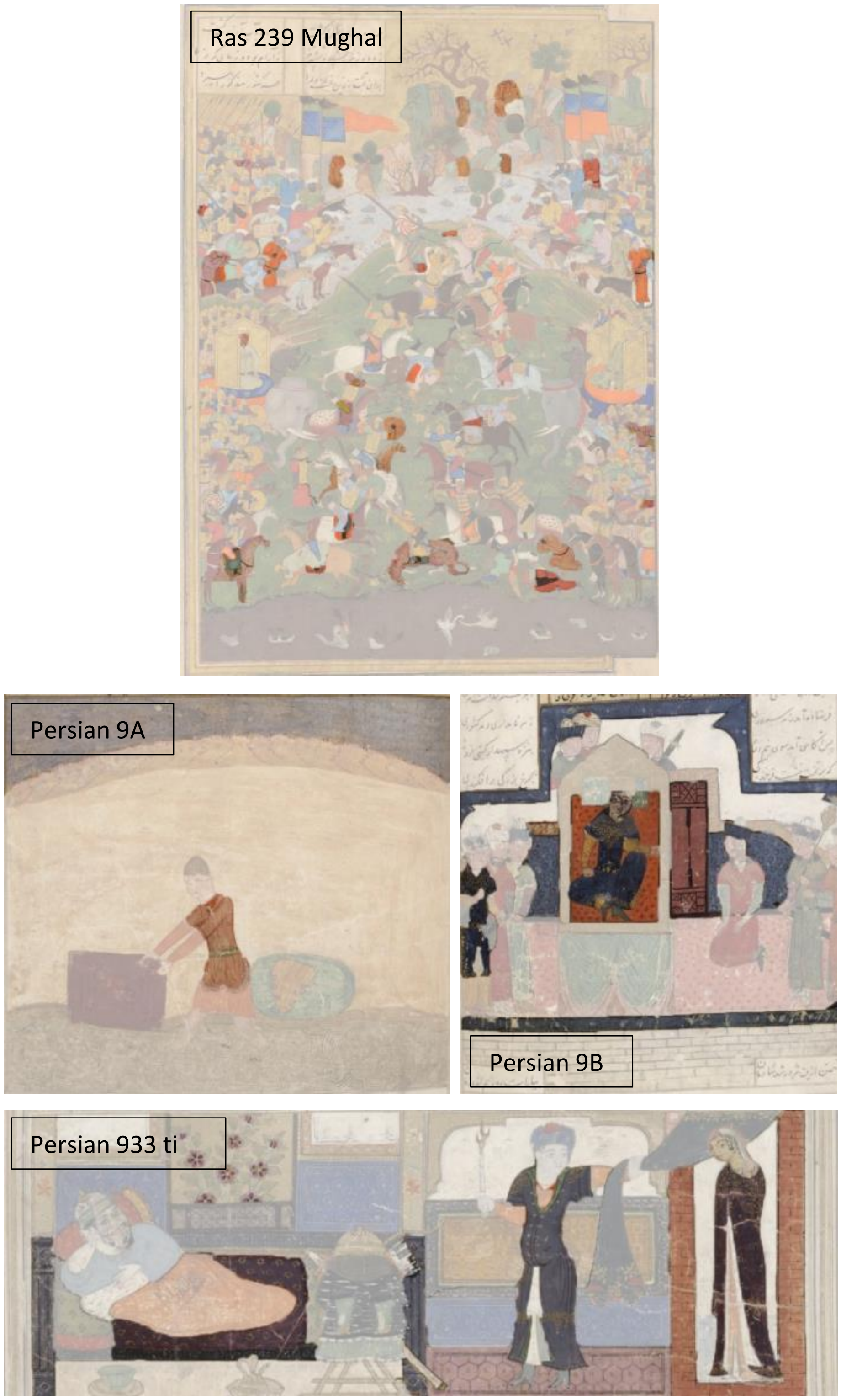


Figure 5-160: Four examples of pink, violet, and purple colour tonalities used in west India

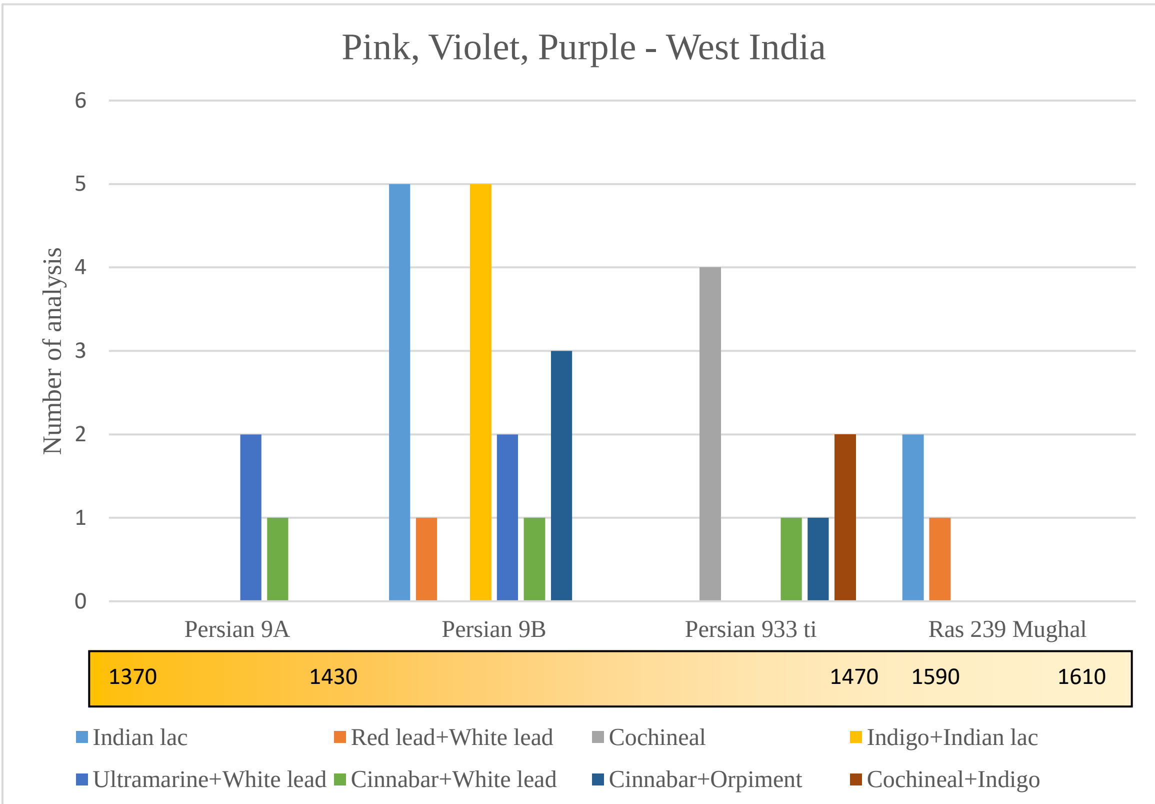


Figure 5-161: Pink, violet, and purple colours used in west India

5-4-3-5 Yellow

Unlike Herat painters, Indian painters have used a variety of yellow tones in their paintings (Fig. 5-162). These painters, like the painters of Shiraz and Herat, have used orpiment as the main material to create the colour yellow (Fig. 5-163). The use of yellow dye by these painters is much more than the painters of Shiraz and Herat. The late 16th century Mughal painter (*Shāhnāma* manuscript RAS 239) used a wide range of yellow tones. These painters have combined and used yellow dye with gold or orpiment to create different tonalities. But the most interesting point of this paintings is usage of Indian yellow, which has not been used by any of the other Indian painters or Shiraz and Herat painters. In this paintings Indian yellow has used on a large scale to paint the background. Indian yellow is recognizable by its obvious visual differences in the Mughal paintings.

Based on the analysis done in this study, it can be concluded that Indian painters, like other painters, have used orpiment as the main material for yellow. But the amount use of yellow dye by these painters is more than the painters of Herat and Shiraz. It should be noted that the use of Indian yellow and yellow dye in Mughal curt seems to have been very common in the late 16th century in India.

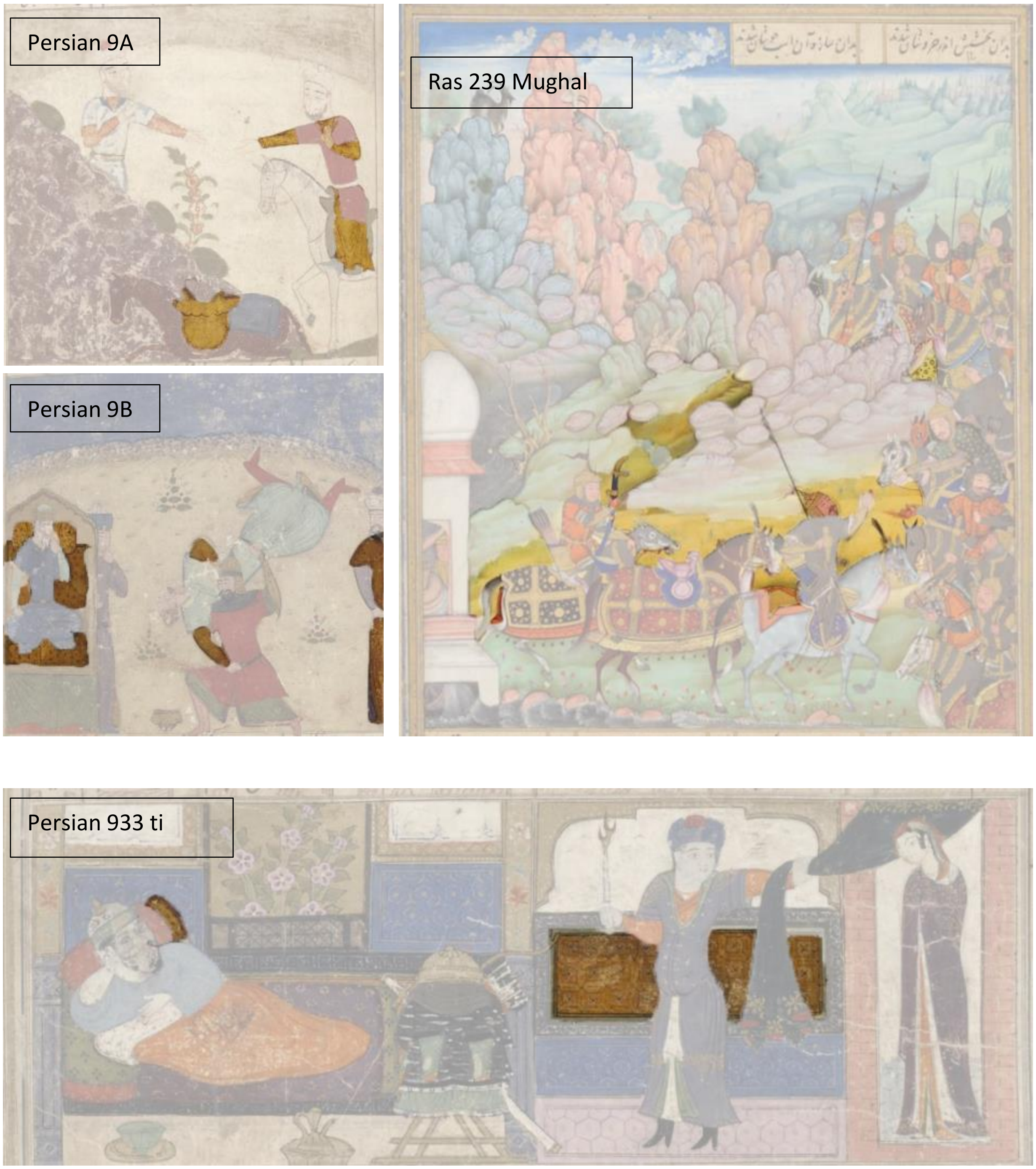


Figure 5-162: Four examples of yellow colour tonalities used in west India

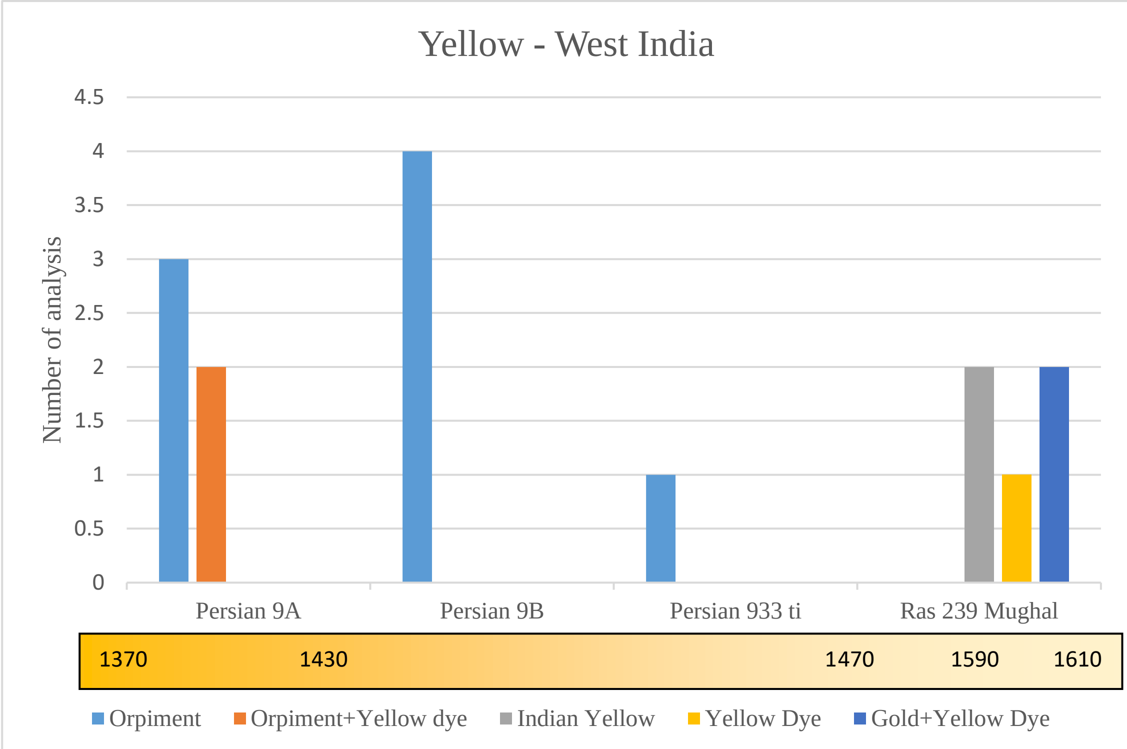


Figure 5-163: Yellow colours used in west India

5-4-3-6 Metallic pigments and Grey

Indian painters, like other painters in many periods, have used a lot of gold pigment (Fig. 4-163). These painters used a lot of gold combined with silver and orpiment (Fig. 4-164). The use of pure gold by these painters and the combination of gold with other colour materials is almost equal. For example, the painter "Persian 9A" and "Ras 239 Mughal" painter used only gold pigment combined with silver or orpiment. Other metal pigment used by Indian painters is silver, which can be seen as dark grey in many paintings (Fig. 4-165). Like other painters, Indian painters used silver to paint streams, swords, and armour. The combination of indigo + white lead has also been used as a light grey colour in Indian paintings (Fig. 4-166). This light grey colour is mostly used for background colouring and animals such as elephants. In addition to the colour combinations mentioned, "the Ras 239 Mughal" painter also used ultramarine + white lead as a grey colour.

Based on the analysis done in this study, it can be concluded that Indian painters have used a combination of gold with other colour materials almost as much as they have used pure gold. As a result, gold is used in many Indian paintings, either without metallic luster or with very little metallic luster. It seems that the gold pigment used by Indian painters has lower quality than the painters of Shiraz and Herat. Silver and the colour combination of indigo + white lead are other materials used by Indian painters such as Shiraz and

Herat to create light and dark grey. White and black, as expected, are created by white lead and black carbon.

Figure 5-164: Three examples of golden colour tonalities used in west India

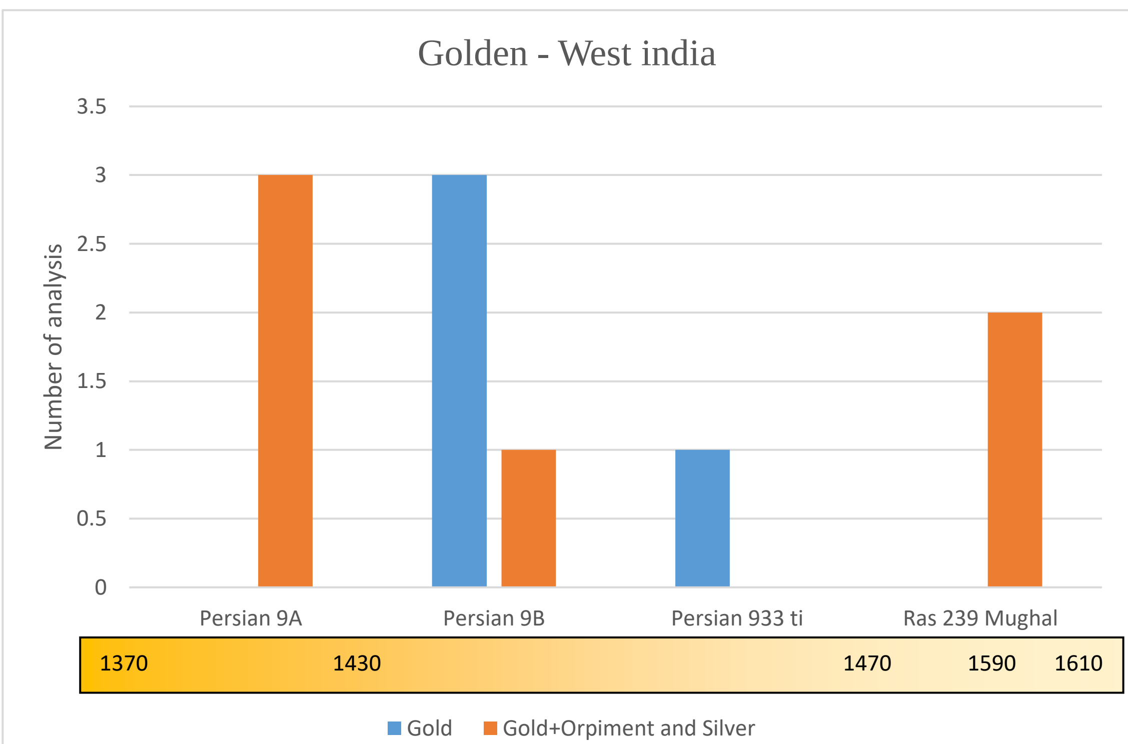


Figure 5-165: metallic golden colours used in west India

Figure 5-166: Three examples of grey colour tonalities used in west India

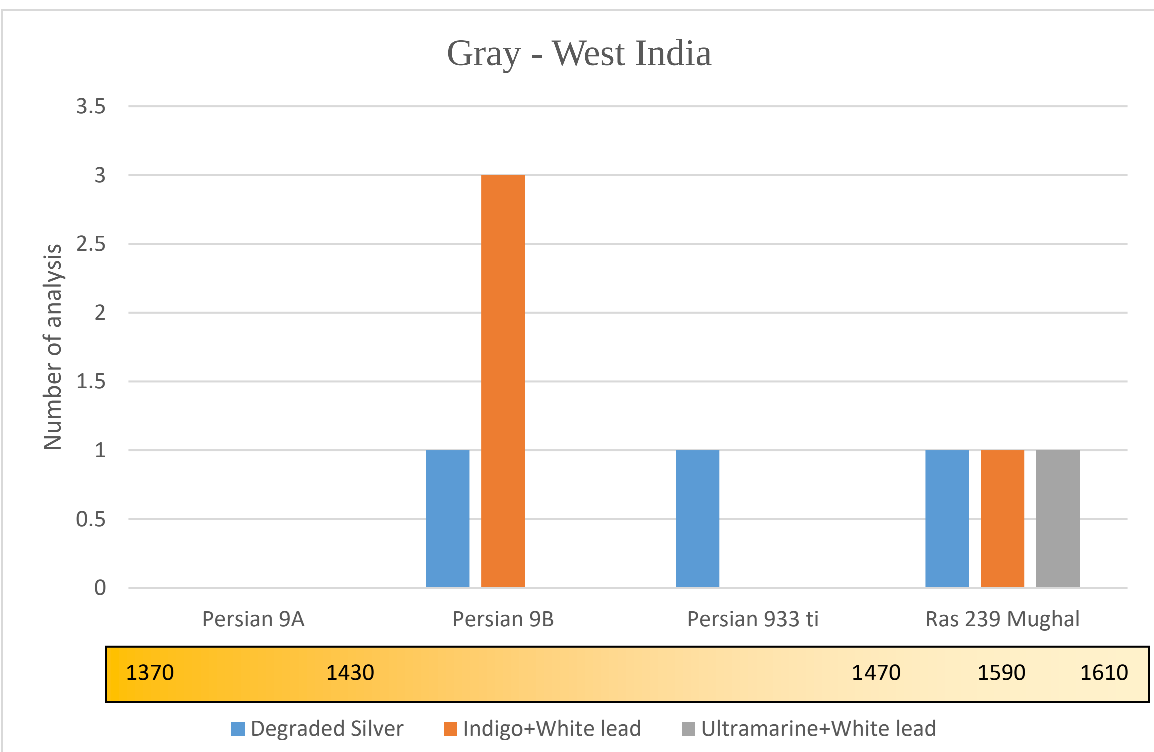


Figure 5-167: metallic grey colours used in west India

5-4-4 Lahijan

The Shāhnāma manuscript AKM 6 is a unique and famous Turkman style manuscript that was produced in 1494 CE in Lahijan. This famous manuscript was prepared for Sultan Ali Mirza, one of the bosses of Gilan. 350 paintings of this *Shāhnāma* are depicted in two formats, in one of which the heads are exaggeratedly large. For this reason, this *Shāhnāma* is known as "*Big head*". Another distinguishing feature of this *Shāhnāma* from other *Shāhnāmas* is its bright and shiny colours, fat and large bodies, the regular growth of grasses, and the disregard for the relationship between space and individuals; but, as it is expected from such orders, the drawings, compared to other commercial orders of the Turkman period, were painted with great care and obsession. To study the colours used by Lahijan painters, four paintings of this famous manuscript were analyzed in this study (Tab. 5-58).

5-4-4-1 Blue

Lahijan paintings have a high variety of blue tones (Fig. 5-168). In Lahijan paintings, like the paintings of Herat, Shiraz and west India, ultramarine and indigo have been used as blue colours (Fig. 5-175). The amount use of indigo in Lahijan paintings is more similar to Indian and Shiraz paintings than Herat paintings. In Lahijan paintings, the combination of indigo + white lead has been used for background painting. The interesting point is the use of a kind of dark blue (deep blue) in Lahijan paintings, which has been used to paint robes. This blue tonality is obtained from the combination of azurite + ultramarine, which is unique and has not been used by any other painter in any city.

Figure 5-168: An example of blue colour tonalities used in Lahijan

Based on the analyzes performed in this study, it can be concluded that in Lahijan paintings, such as Herat paintings, different tonalities of blue have been used a lot. Although azurite pigment is used in Herat manuscript, the colour combination of azurite + ultramarine has been observed only in Lahijan paintings. Another important point is the painting of small background flowers with ultramarine blue, a similar example has not been seen in any other painting.

5-4-4-2 Green

Since the tree figure is not drew in Lahijan paintings, only the uses of indigo + orpiment colour combination includes small background plants of these paintings (Fig. 5-169). Therefore, unlike most of Herat, Shiraz and west Indian paintings, Lahijan paintings have the colour combination of indigo + orpiment to a very small extent.

In these paintings a kind of light green colour (pistachio) attracts a lot of attention. This special colour tone is obtained from the colour combination of Malachite + Azurite (Fig. 5-175). These two copper-based pigments, one blue and the other green, cause the existence of this particular tonality of green (see Section 5-2-1-2). In Lahijan paintings, copper green has been used in only one case for painting green barding.

Based on the analysis performed in this study, it can be concluded that the use of indigo + orpiment and copper green colour combination, which is very common in other paintings, has been used very little in Lahijan paintings. As mentioned, the colour combination of malachite + azurite, which has a special green tint, can be considered as a special pigment in Lahijan paintings. This special tonality of green colour has been widely used in Lahijan paintings and is easily recognizable.

Figure 5-169: An example of green colour tonalities used in Lahijan

5-4-4-3 Red, Orange, and Brown

In Lahijan paintings, like the paintings of other cities, cinnabar and red lead have been used repeatedly as red and orange (Fig. 5-175). Lahijan's painter used ocher to create a brown colour for painting flags, boots and robes. Interestingly, the red colour created by cinnabar in these paintings has a different colour tone than the red colour obtained by cinnabar in the paintings of other cities (Fig. 5-170).

Figure 5-170: An example of red, orange, and brown colour tonalities used in Lahijan

Based on the analyzes performed in this study, it can be concluded that there is no difference in the red colours used in Lahijan paintings with the paintings of other cities. The only noteworthy point is the red tonality obtained from cinnabar, which is significantly different in Lahijan paintings from similar examples in Shiraz, Herat and India. Since in the XRF spectrum of this red sample there was no evidence of another colour combination with cinnabar, it is questionable how painter of Lahijan created this red colour from cinnabar? It should be noted that Lahijan's painter used the combination of red lead + white lead for light orange (peach) colour of the building bricks, like the painters of Herat, while the painters of Shiraz and India used cinnabar with white lead or orpiment or yellow to create this colour tonality.

5-4-4-4 Pink, Violet, and Purple

In Lahijan paintings, cochineal is used as pink and violet and the composition of cochineal + ultramarine is used as purple (Fig. 5-175). These colours have also been used by Shiraz painters. Another colour combination used as purple is the composition of ultramarine + cinnabar, which has been used repeatedly by Shiraz painters. Lahijan painter also used the combination of red lead + white lead as pink and violet.

Figure 5-171: an example of pink, violet, and purple colour tonalities used in Lahijan

Based on the analyzes performed in this study, it can be concluded that different tonalities of pink and purple colours have been used in Lahijan paintings (Fig. 5-171). The materials and colour combinations used in Lahijan paintings are quite similar to Shiraz paintings. Lahijan painter has used only cochineal between cochineal and Indian lac.

5-4-4-5 Yellow

In Lahijan paintings, like the paintings of other cities, orpiment has been used as the main material of yellow colour (Fig. 5-175). The amount use of yellow colour in Lahijan paintings is very similar to Shiraz paintings. But the yellow tone used in Lahijan paintings is completely different from Shiraz (Fig. 5-172). In Lahijan paintings, a very pale yellow is used. In fact, the Lahijan painters, by combining orpiment with yellow dye and gypsum, has prepared this type of pale yellow and used it to paint clothes, robes, underlays and flags.

Figure 5-172: An example of yellow colour tonalities used in Lahijan

Based on the analysis done in this study, it can be concluded that Lahijan painter, unlike other painters, has used less orpiment separately. These painters used a combination of orpiment with other materials such as yellow dye and gypsum to achieve their favorite colour tone. It is worth mentioning that the combination of orpiment + yellow dye has also been used by Shiraz painters, but Lahijan painters to achieve desired tonality has added gypsum to this combination.

5-4-4-6 Metallic pigments and Grey

Pure gold is used in Lahijan paintings. The gold used by Lahijan painters has a luster (not polished), so it is completely different from the samples used in Shiraz (Fig. 5-173). Another metal pigment used in Lahijan paintings is silver, which is seen as dark grey (Fig. 5-174). Like other painters, this painter used silver to paint swords and armour. Also, the combination of indigo + white lead has been used as a light grey.

Based on the analysis done in this study, it can be concluded that Lahijan painters tended to use brilliant gold. This subject has led Lahijan painters to use gold in its purest form without mixing it with other colour materials. Lahijan painters used silver and indigo + white lead like other painters.

It should be noted that although in Lahijan paintings gypsum has been used as a white material to create a yellow with a light tonality, but white lead is used to paint white figures such as clothes and hats. Carbon is also used for black colour.

Figure 5-173: An example of metallic golden colour used in

Figure 5-174: an example of metallic silver used in Lahijan

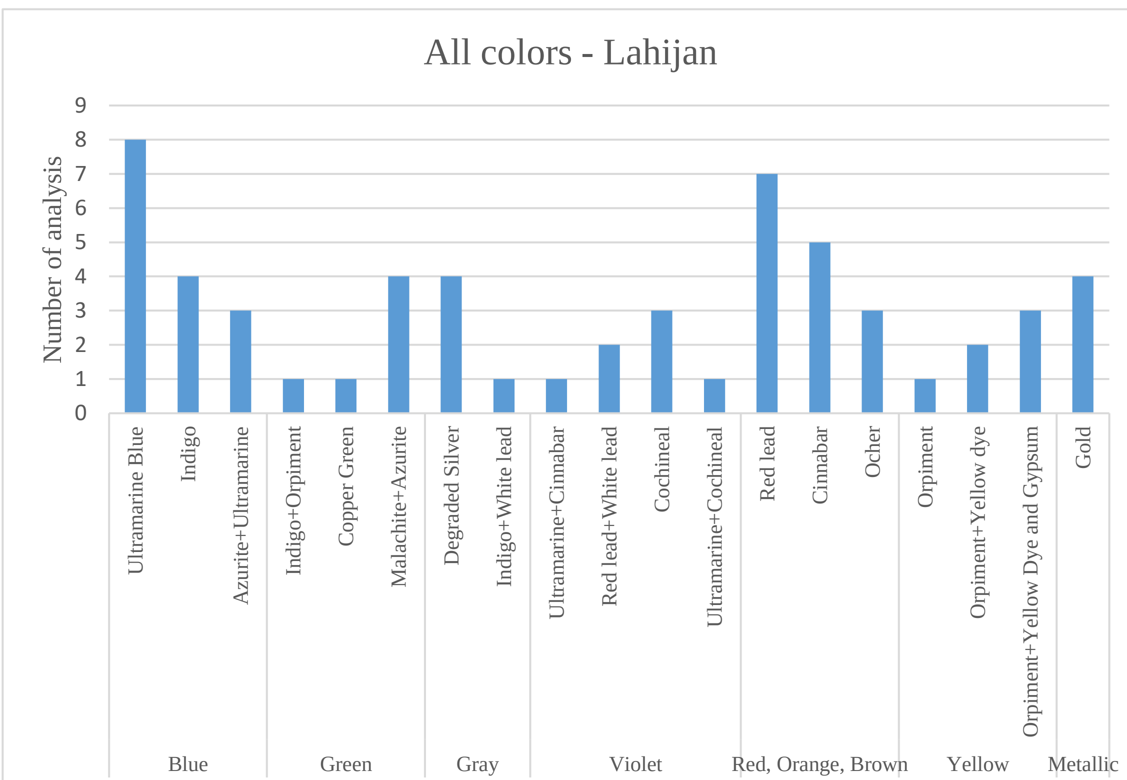


Figure 5-175: All colours used in Lahijan

5-4-5 Qazvin

The paintings of Qazvin analyzed in this study belong to the *Shāhnāma* manuscript Persian 933 (painter C). Six existing paintings of Qazvin style were analyzed in the *Shāhnāma* manuscript Persian 933 belonging to the Safavid period (16th century) (Tab. 5-58). These paintings of Qazvin have a simple structure with figures with low details and colours have been used in large and flat dimensions. In this study, the information obtained about the paint materials used in Qazvin is based on the analysis performed on these six paintings.

5-4-5-1 Blue

In Qazvin paintings, several different tonalities of blue have been used, but all these colour tones have been created by ultramarine (Fig. 5-182). In fact, Qazvin painters have created different tonalities of blue by combining different amounts of ultramarine with white lead or they have access to ultramarines with different colour tones and have used them to achieve the desired tonality (Fig. 5-176).

Based on the analysis done in this study, it can be concluded that in Qazvin paintings only ultramarine is used. Although in these paintings indigo is used to create other colours like purple not as blue colour.

Figure 5-176: An example of blue colour tonalities used in Qazvin

5-4-5-2 Green

The combination of indigo + orpiment is the only colour combination used in Qazvin paintings to create green (Fig. 5-182). Qazvin painters, like Lahijan painters, did not want to use copper green.

Based on the analysis done in this study, it can be concluded that in Qazvin paintings, unlike other paintings, only indigo + orpiment has been used as green colour. It is noteworthy that Qazvin painters used same green tone to paint clothes, backgrounds, tree leaves, bushes and robes (Fig. 5-177). In fact, in all these paintings is used only a green tone and a kind of colour combination.

Figure 5-177: An example of green colour tonalities used in Qazvin

5-4-5-3 Red, Orange, and Brown

In Qazvin paintings, only cinnabar and red lead have been used to create all three colours of red, orange, and brown (Fig. 5-182). Qazvin painters used cinnabar to create red and brown and red lead to create orange tones (Fig. 5-178).

Based on the analyzes made in this study, it can be concluded that ocher has not been used at all in the paintings of Qazvin, unlike the paintings of other cities. Qazvin painters, like Herat painters, used cinnabar to create a brown colour. Although Qazvin painters have used a lot of cochineal to create pink and violet, unlike the painters of Shiraz and Herat, they have never used cochineal as a red colour.

Figure 5-178: An example of red, orange, and brown colour tonalities used in Qazvin

5-4-5-4 Pink, Violet, and Purple

In Qazvin paintings, only cochineal has been used to create pink and violet colours (Fig. 5-182). Cochineal is used purely to create violet and pink colours and to create a pinkish purple colour, the combination of cochineal + yellow dye has been used.

Based on the analysis done in this study, it can be concluded that in Qazvin paintings, like many paintings in Shiraz and Herat, cochineal has been used to create violet colour (Fig. 5-179). Qazvin painter has used a combination of cochineal + yellow dye to create a kind of purulent pink colour. This colour combination is used only by this painter and has not been seen in any other example.

Figure 5-179: An example of pink, violet, and purple colour tonalities used in Qazvin

5-4-5-5 Yellow

In Qazvin paintings, different tones of yellow have been used. Each of these colour tones is created by different colour combinations (Fig. 5-182). Like other painters, Qazvin painter has used orpiment as the main material of yellow colour and has combined yellow with yellow dye or gold to create different tonalities (Fig. 5-180). But the interesting thing is that this painter uses Indian yellow in one of his paintings, which is only seen in Mughal Indian paintings.

Figure 5-180: An example of yellow colour tonalities used in Qazvin

Based on the analysis done in this study, it can be concluded that the variety of yellow tones used in Qazvin paintings is more than other colours used in these paintings. The colour combination of orpiment + yellow dye used by Qazvin painter has also been seen in Shiraz and Lahijan paintings.

Also, the combination of orpiment + gold used by this painter for background painting has also been used by Shiraz and Herat painters. But the most interesting point is the Qazvin painter's use of Indian yellow, which was previously used only by Mughal Indian painters. Due to the geographical long distance between Qazvin and West India, Qazvin and Mughal lived in almost the same historical period (late 16^{th}

century). Perhaps it can be interpreted that the use of Indian yellow in Persian manuscripts from the late 16th century can be seen.

5-4-5-6 Metallic pigments and Grey

In Qazvin paintings, pure gold and gold combined with silver are used (Fig. 5-182). Qazvin painter has used very little shiny gold and only for background details, but he/she has used a combination of gold and silver in larger dimensions and for background painting (Fig. 5-181). Another metal pigment used in this paintings is silver, which is now seen as grey. Qazvin painter did not use any other colour combination to create the colour grey.

Figure 5-181: An example of metallic golden colour used in Qazvin

Based on the analysis done in this study, it can be concluded that in Qazvin paintings, compared to other paintings, very little gold pigment has been used. The gold used by the Qazvin painter is not of high quality and has a significant amount of silver. In one of the paintings of this painter, which gold has been used in large dimensions for background painting, the colour of gold has been darkened. This darkness is due to corrosion of silver and is easily visible. Like other paintings in Qazvin, the painter used white lead and carbon to create white and black.

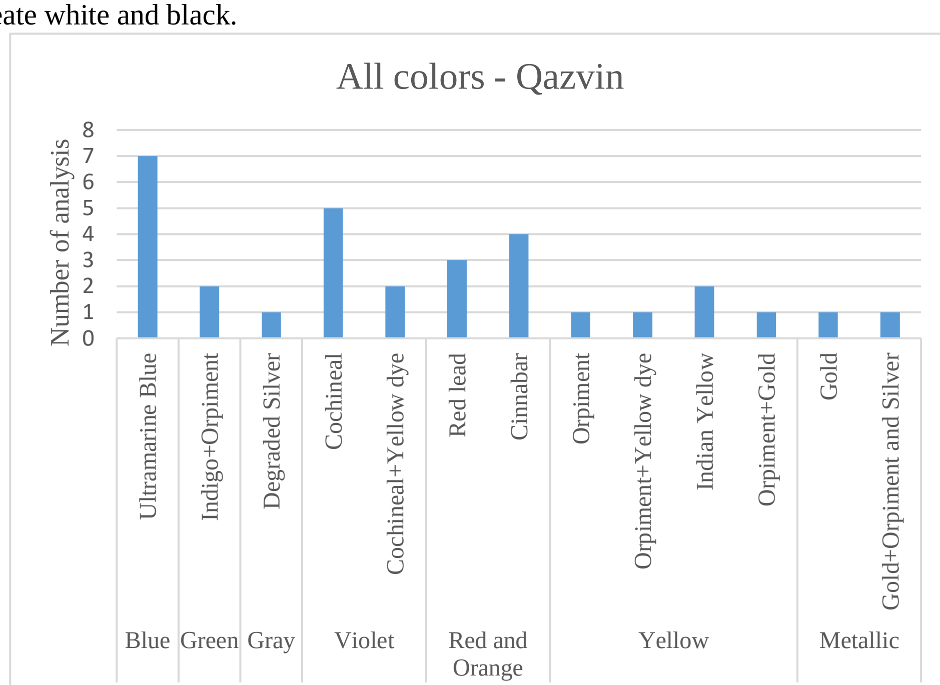


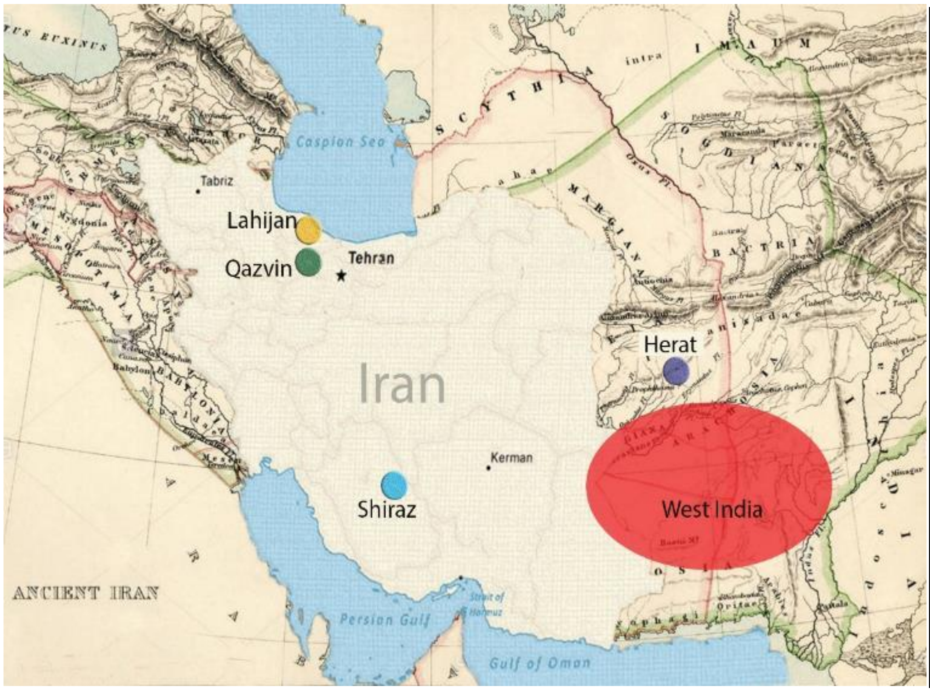
Figure 5-182: All colours used in Qazvin

5-5 Interpretation summary

Below a summary of features of analysed manuscripts, their geographical distribution, and the number of analysed paintings have been presented. Furthermore, to better understand of colour materials dispersion in different places and different time for each colour tonality a graph has been presented.

Painters	City	Style	Date	Manuscript	Analysed Paintings
AKM 4	Shiraz	Turkman	1482	AKM 4	5
AKM 5	Shiraz	Turkman	1494	AKM 5	4
AKM 269	Shiraz	Turkman	1492	AKM 269	13
Or 420	Shiraz	Timurid	1437	Or 420	9
Ms 22-1948	Shiraz	Timurid	1435	Ms 22-1948	5
Persian 933 painter A	Shiraz	Inju	Late 16^{th} century	Persian 933	3
RAS 239 painter A	Herat	Timurid	1444	RAS 239	2
RAS 239 painter B	Herat	Timurid	1444	RAS 239	5
RAS 239 painter C	Herat	Timurid	1444	RAS 239	3
RAS 239 painter D	Herat	Timurid	1444	RAS 239	2
RAS 239 painter E	Herat	Timurid	1444	RAS 239	1
RAS 239 painter F	Herat	Timurid	1444	RAS 239	1
RAS 239 painter G	Herat	Timurid	1444	RAS 239	1
Persian 9 painter A	West India	Jalayerid	Late 14^{th} century	Persian 9	5
Persian 9 painter B	West India	Timurid	Mid-15^{th} century	Persian 9	14
Persian 933 painter B	West India	Timurid	Mid-15^{th} century	Persian 933	4
RAS 239 painter Mughal	West India	Mughal court	End 16^{th} century	Ras 239	2
AKM 6	Lahijan	Turkman	1494	AKM 6	4
Persian 933 painter C	Qazvin	Safavid	16^{th} century	Persian 933	6

Table 5-58: Overview analysed illustrated manuscripts and paintings



Manuscript	City
AKM 4 AKM 5 AKM 269 MS 22-1948 Or 420	Shiraz
RAS 239	Herat
AKM 6	Lahijan
Persian 933 painter C	Qazvin
Persian 9 RAS 239Mughal Persian 933 painter B	West India

Figure 5-183: Geographical distribution of analysed manuscripts

As you can see below (Fig. 5-184), the colour used as blue in different cities (schools) has not changed much over time. In fact, painters of different cities (schools) have used ultramarine to create blue at different times. The only difference is preparation process and usage of ultramarine, which is directly related to the importance of the manuscript and the painter's skill in extracting ultramarine from *Lapis Lazuli*.

Because the preparation process of ultramarine requires mastery. For this reason, the falling of ultramarine is seen in many Persian lower quality manuscripts. Indigo has also been used as a blue colour, but to a much lesser extent as seen in figure 5-184. It seems that after 1500 CE the use of indigo has declined and is less used as a blue colour (Fig. 5-184). Another pigment used for blue is azurite which of has been used only in Herat. As well as the very special blue tonality used in Lahijan manuscript is obtained from the colour combination of ultramarine + azurite (Fig. 5-184).

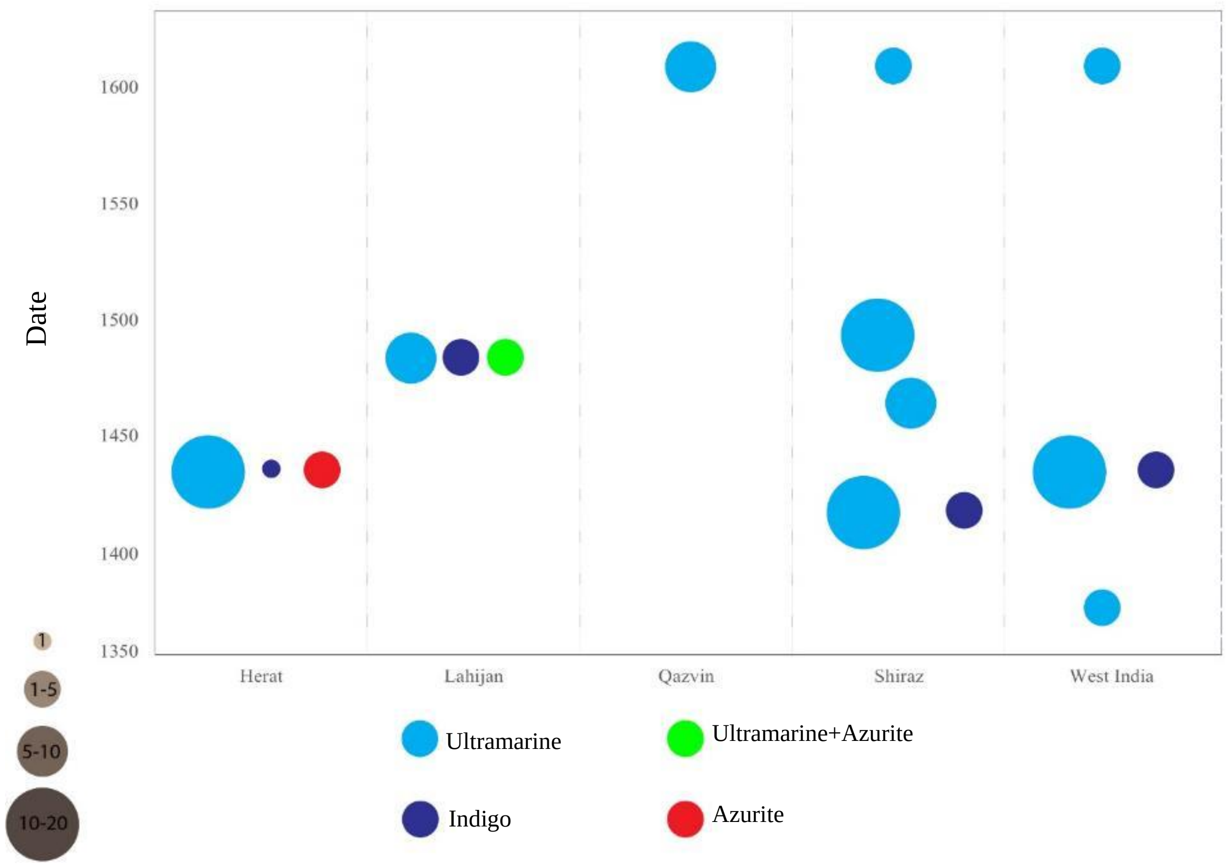


Figure 5-184: Geographical and time distribution of blue colour

As you can see in figure 5-185, the colour combination of indigo + orpiment and copper green are the two main materials that have been used for green over time in different cities (schools). In most of the paintings, these two colour materials have been used equally, but as you can see in the figure 5-185, in Qazvin paintings, only the colour combination of indigo + orpiment has been used.

Also, the Inju painter of Shiraz and one of the Indian painters have used only copper green in their paintings. As well as, according to figure 5-185, it can be concluded that Shiraz and Herat painters at different times tended to use both of these colour combinations, but Indian painters tended to use copper green more. Interestingly, Lahijan painters, unlike painters in other cities (schools), have used a pigment containing two minerals, malachite and azurite, which has created a special colour tone (Fig. 5-185).

This colour combination has also been used by one of Herat's painters and a similar example has been identified by Knipe et al. 2018. Also, as you can see in figure 5-185, in some cases, Shiraz painters have replaced orpiment in the colour combination of orpiment + indigo to achieve a kind of light and pale green.

As in figure 5-185, the combination of orpiment + ultramarine was tried by one of the painters of Shiraz around 1500 CE.

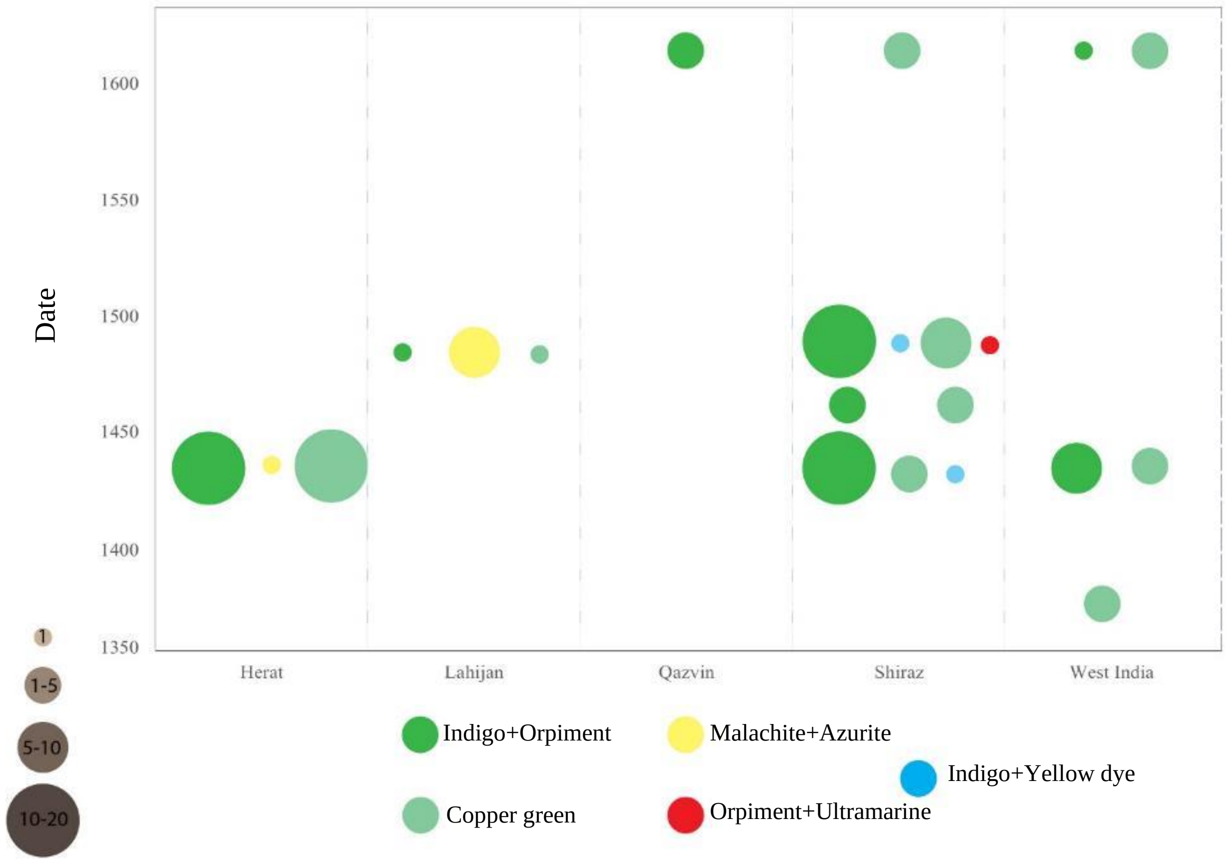


Figure 5-185: Geographical and time distribution of green colour

In figure 5-186 you can see that the three colour red lead, cinnabar and ocher have been used as the three main colour to create red, orange, and brown tones in different cities (schools) and at different times.

The two colours red lead and cinnabar have been used to produce red and orange or orange-red in most cities (schools) at different times. In addition to these two colours, only some painters in Herat and Shiraz have used cochineal to create dark red tones in very small dimensions (Fig. 5-186).

As you can see in the figure 5-186, ocher has been used to create brown colour in most cities (schools), although in Herat, in addition to ocher, two combinations of cinnabar + orpiment and cinnabar + red lead is also used as a brown colour (Fig. 5-186). In the city of Shiraz, only one case of using the colour combination red lead + orpiment to create a brown colour has been identified. As you can see, the colours used for the red, orange, and brown tones have changed the least over time (Fig. 5-186).

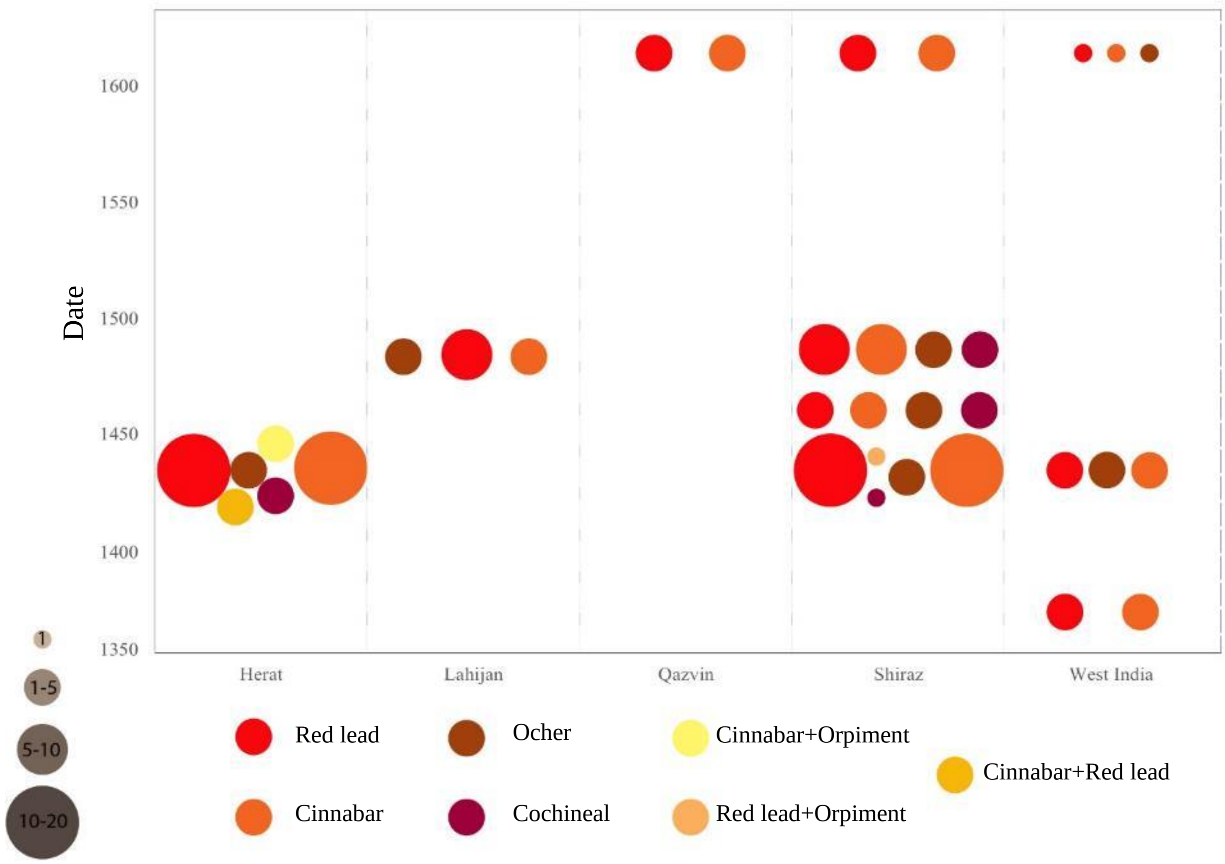


Figure 5-186: Geographical and time distribution of red, orange, and brown colour

As you can see in figure 5-187, different combinations have been used in different cities (schools) and at different times to create pink, violet, purple, and peach tones. It seems that in different cities (schools) and workshops, according to the desired colour tonality, different combinations have been used to create these colour tones. For these colour tones finding commonalities between the colours used in different cities (schools) is not easy, but for each city (school) and workshop, several and more colour combinations can be identified.

As you can see in figure 5-187, the colour combination red lead + white lead has been used the most to create pink and violet colour tones in Herat. In Herat paintings Indian lac has also been used to create pink and violet tones, and cochineal has been used in only one case. In the paintings of Shiraz and West India, Indian lac has been used repeatedly to create pink and violet colour tones. The pure cochineal has been identified on the paintings of Lahijan, Qazvin, Herat (only in one case) and Shiraz to create pink and violet tones (Fig. 5-187).

As you can see in figure 5-187, in Herat, three colour combinations, ultramarine + cochineal, ultramarine + indigo, and ultramarine + red lead, have been used to create the colour tonality of the purple. Among these three colour combinations, only ultramarine + cochineal colour combination has been identified in Shiraz and Lahijan (only in one case) paintings and the other two colour combinations have been used only in Herat (Fig. 5-187). The two colour combinations of red lead + indigo and red lead + copper green are also used as purple colour only in Herat. As you can see in figure 5-187, the city of Herat has the greatest variety of colour materials for these colour tonalities.

In Lahijan, cochineal and red lead + white lead has been used to create pink and purple tones (Fig. 5-187). And in Qazvin, cochineal and cochineal + yellow dye is the only colour materials that have been used to create pink and purple tones (Fig. 5-187). Among these, the colour combination of cochineal + yellow dye has not been seen in any of the other paintings except Qazvin paintings. As you can see in figure 5-187, in Shiraz before the first half of the 15th century, colour combinations based on cochineal and ultramarine were used to create pink and purple tones.

Therefore, cochineal has been used for pink and purple tones, and ultramarine + cochineal and cochineal + indigo colour combinations have been used to create purple tones (Fig. 5-187). But from the Middle of the 15th century, cochineal gave way to Indian lac, and Indian lac was used purely to create pink and violet tones, and in combination with ultramarine and indigo to create purple tones. The colour combination of ultramarine + Indian lac has been identified only in Shiraz paintings of the late 15th century and a similar example has not been observed in this study (Fig. 5-187).

Also, the colour combination of cinnabar + ultramarine has been used to a significant extent to create purple and peach colour tones in Shiraz paintings. As you can see in figure 5-187, in the Inju Shiraz style paintings of the late 16th century, in addition to cochineal, which is used for pure pink and purple tones, two combinations of cinnabar + white lead and cinnabar + yellow dye have also been used.

As shown in figure 5-187, in late 14th century in Indian paintings, simple colour combinations such as ultramarine + white lead and cinnabar + white lead was used for pink, peach, and purple tones. But as continued in Indian paintings since the Middle of the 15th century, the variety of colours used has improved significantly.

Therefore, in addition to the two colour combinations mentioned, Indian lac has been used for pink and violet tones, and for peach and purpol tones cochineal + indigo, indigo + Indian lac, cinnabar + orpiment, cinnabar + ultramarine have been used. Among these compounds, the colour combination cinnabar + orpiment has only been identified in Indian paintings of the Mid-15th century, and a similar case has not been seen in any of the other paintings. Mughal Indian painters in the late 16th century used Indian lac and red lead + white lead for pink and purple tones.

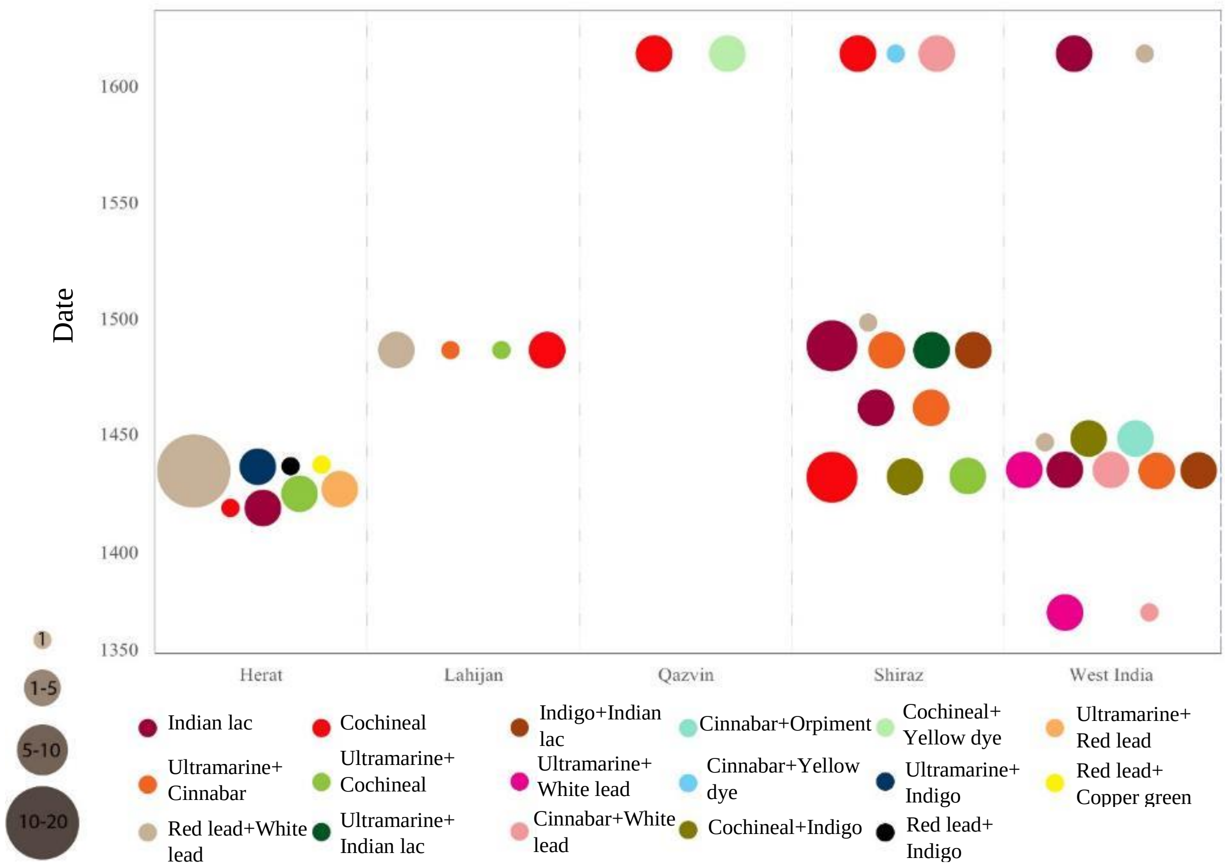


Figure 5-187: Geographical and time distribution of pink, violet, purple, and peach colour

As you can see in figure 8-188, in different cities (schools) and over time, orpiment has been used as the main material for yellow tones. This pigment has been used in pure form or in combination with other pigments to create different shades of yellow. In the paintings of the cities (schools) of Herat, Shiraz, and in Indian paintings, orpiment has been used repeatedly (Fig. 5-188). But in Lahijan paintings, orpiment is mostly used in combination with yellow dye and is used only in one case in its pure form. In Herat, the combination of orpiment with yellow dye and gold has been identified in two cases, although one case of pure yellow dye has also been identified (Fig. 5-188).

In Shiraz, in addition to using orpiment in its purest form, the combination of orpiment with other coloured materials such as gold, yellow dye and red lead has also been used (Fig. 5-188). The colour combination of orpiment + red lead has been identified only in Shiraz paintings of the late 15th century and a similar example has not been seen in any of the paintings studied in this study. Also, as you can see in figure 5-188, the colour combination of gold + yellow dye, which creates a kind of dark yellow tonality (earth yellow), has been used in the paintings of the late 15th century in Shiraz.

However, the use of yellow dye alone and without combining with gold has been identified in one case in Shiraz paintings (Fig. 5-188). Injou style painter of Shiraz in the late 16th century used only the combination of orpiment + yellow dye to create a yellow tone.

As shown in figure 5-188, in Qazvin paintings of the late 16th century, orpiment and compounds containing orpiment are much less used. In Qazvin paintings, Indian yellow has been used, a similar example of which has been identified only in Mughal Indian paintings belonging to the late 16th century. However, as you can see in figure 5-188, other Indian paintings use more orpiment and its combinations to create yellow tones. In Mughal Indian paintings, the combination of gold + yellow dye is also used, although in one case yellow dye without gold has been identified (Fig. 5-188).

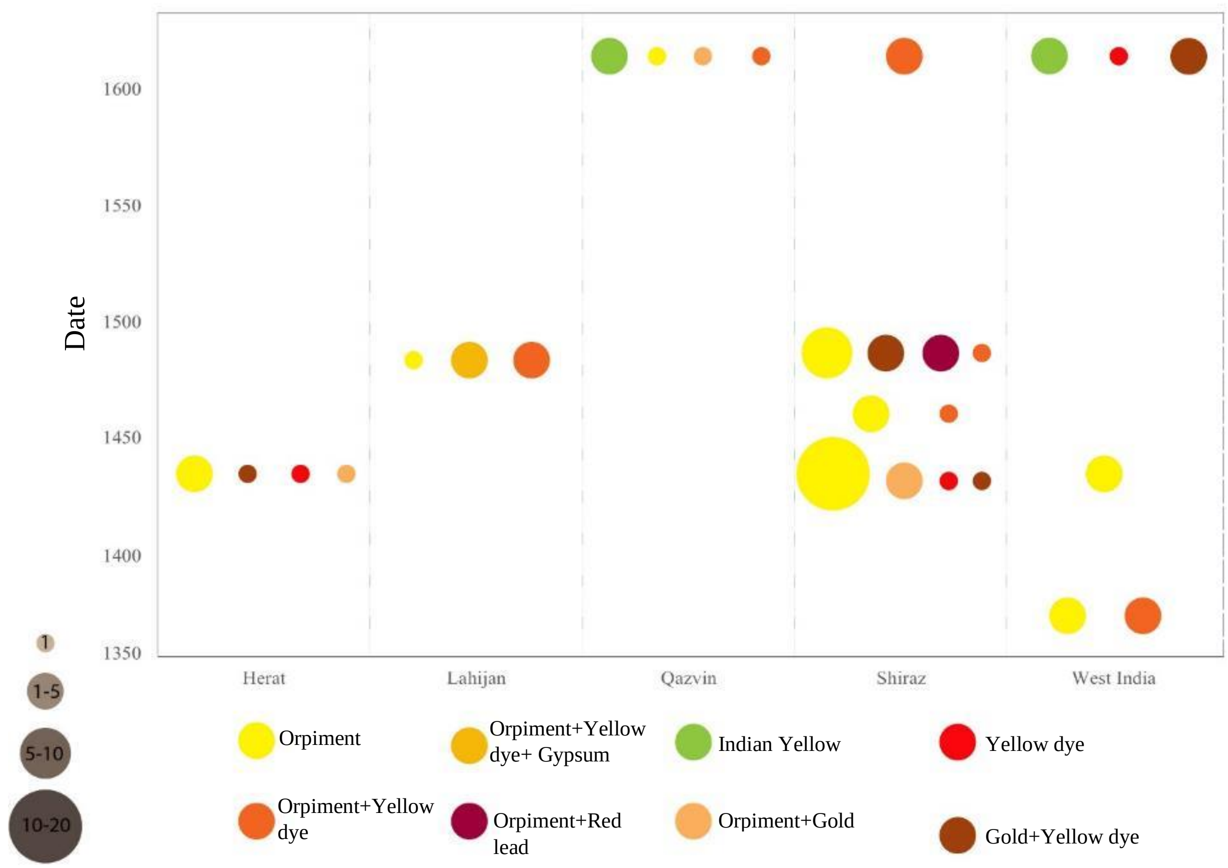


Figure 5-188: Geographical and time distribution of yellow colour

As shown in figure 5-189, the dark and light tones of gray in all cities (schools) and at different times have been created by silver (degraded silver) and indigo + white lead colour combination. In the city of Herat, in addition to these two materials, a colour combination based on cinnabar or red lead has also been used (Fig. 5-189). This compound, which produces a very dark gray colour (close to black), appears to be a combination of cinnabar + red lead, in which at least one of its components has corroded and changed colour to dark gray. This colour combination has been identified in one case in paintings after the Middle of the 15th century in Shiraz. As you can see in figure 5-189, the colour combination of ultramarine + white lead has also been used as a kind of light gray (light blue) in Herat, Shiraz and Indian paintings to a very small extent (single case). The two colour combinations of indigo + red lead and ocher + red lead have also been used in Shiraz as a dark gray colour as a single case (Fig. 5-189). These two colour combinations appear to have been initially dark in colour other than dark gray, and probably changed to dark gray due to red lead corrosion.

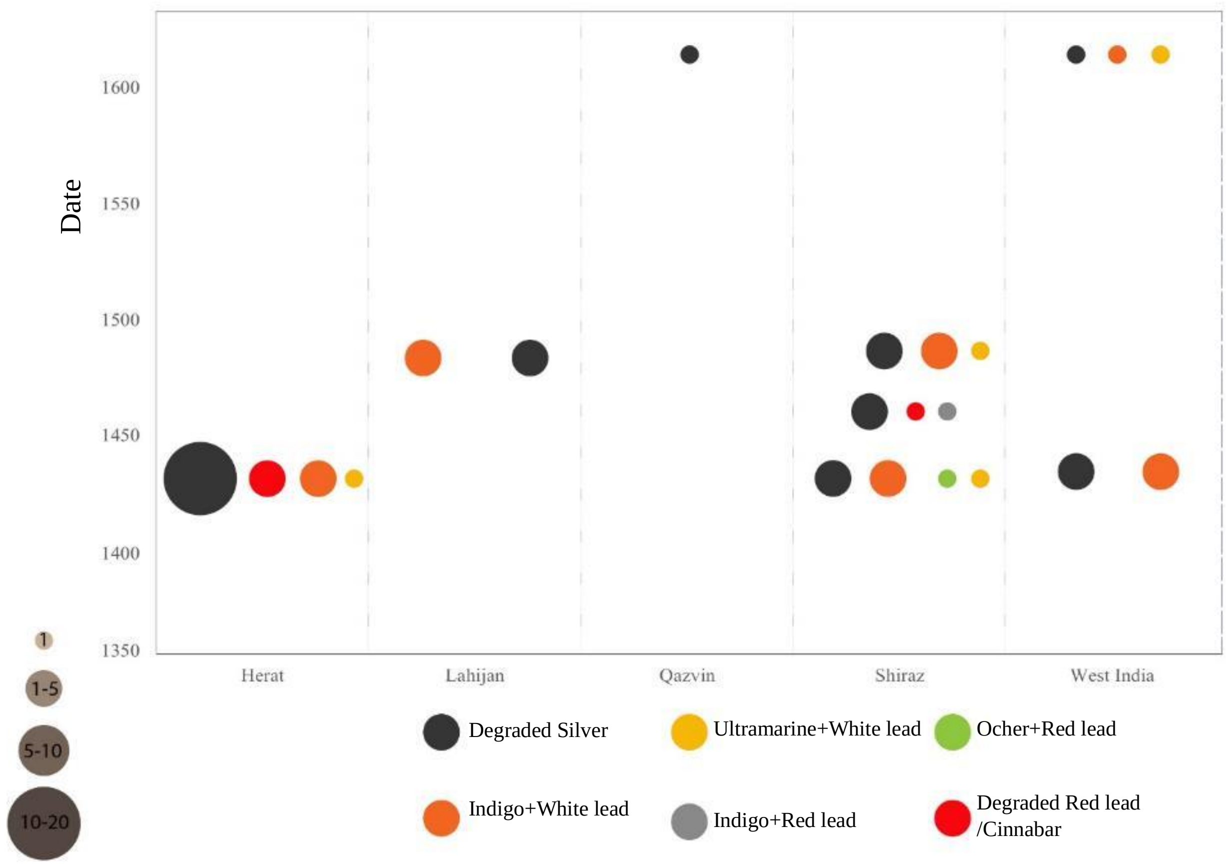


Figure 5-189: Geographical and time distribution of gray colour

In the classification of metal pigments, two pigments of gold and silver were examined in this study. But since silver pigment has been corroded in all paintings and has lost its metallic luster, we will only examine gold pigment in the study of metal pigments. As you can see in figure 5-190, gold pigment has been used in all the cities (schools) studied in this study over time. Regardless of the importance of the manuscript and the workshop in which the manuscripts were produced, gold pigment was used. Only in some Indian and Shiraz and Qazvin paintings, painters have combined and used gold or orpiment to achieve different colour tones or reduce costs (Fig. 5-190). As you can see in figure 5-190, pure gold pigment is less used in Indian paintings than other paintings, and more gold pigment combined with silver or orpiment is used. Gold pigment along with ultramarine is one of the most widely used colour materials used in Persian illustrated manuscripts. Although these two pigments are considered expensive colour materials, they have been widely used in Persian manuscripts.

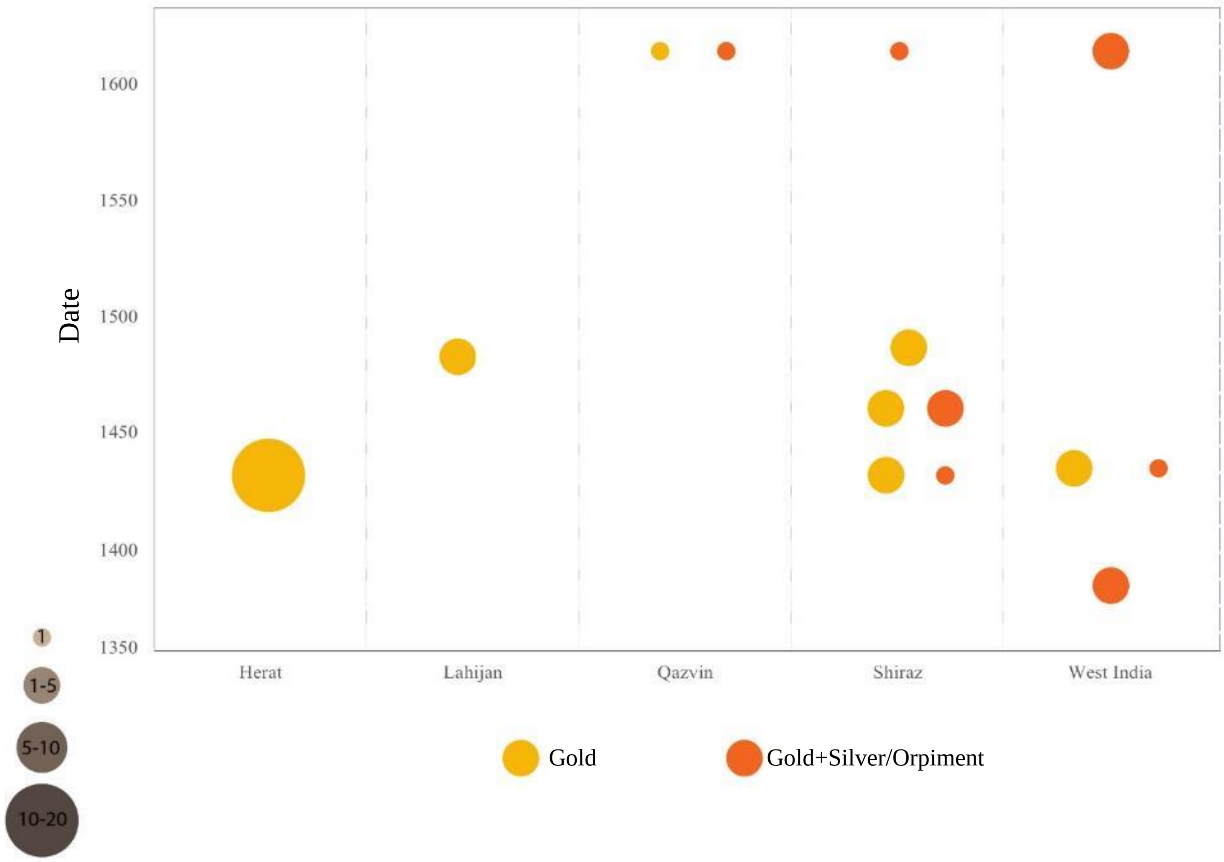


Figure 5-190: Geographical and time distribution of metallic colour

CHAPTER 6: Discussion and interpretation of data

6-1 Introduction

In this section, we will have an overview of the analysis performed in this study, and also the results of comparing the colours used in the paintings of different cities (schools) at different times. These colour comparisons are reviewed to answer the questions posed in this study, and at the end, new questions are raised as a result of these colour comparisons. As explained in Chapter One, presenting a colour palette of Persian paintings and comparing the colour materials used in paintings of different cities (schools)[45] are the two main objectives of this study.

Therefore, in Section 6-2, while presenting a coherent palette of colour materials used in Persian paintings, a summary of the results obtained by comparing the colour materials used in paintings of different cities (schools) at different times is presented. In this section, to better comprehension of colour analysis and comparisons, a system based on the main colour and sub-colour materials for each colour tonality has been designed. In this system, in addition to introducing the colour materials used for each colour tonality, it is also possible to detect variable colour materials in the paintings of different cities (schools).

As explained in Chapter One, another objective of this study is to investigate the capabilities of the FORS, FOMF, and XRF combined analysis methods to identify the pigments and dyes used in illustrated manuscripts. Therefore, in Section 6-3, the capabilities of this combined analysis method to identify the pigments and dyes used in illustrated manuscripts are presented. In the second chapter, the characteristics of this method of combined analysis are explained, in section 6-3 of this chapter, the capabilities of this method of combined analysis are studied in more detail.

In the last part of this chapter, in the section 6-4, a general conclusion of the study has been conducted. Further was attempts to answer the questions that have been arisen during the course of this study.

[45] This method of naming and dividing Persian styles of painting has been popularized by Western scholars. In This naming method, Persian painting schools are based on the name of the capital city of the empire (Tavoosi 2016, p.7).

6-2 Summary of the colour palette of Persian paintings

In order to conclude correctly from the colour analysis and comparisons performed in this study, it is necessary to at first, have a correct understanding of how to make Persian illustrated manuscripts and their paintings. According to historical evidence, the main tradition of writing and producing paintings in the Middle Islamic period (from the Ilkhanid period 13th Century) was in the form of workshops (teamwork), and most painters were usually male and worked in groups on manuscripts (Pakbaz 2006, p.60; Roxburgh 200, p.6; Kargar and Sarikhani 2012, p.109)[46]. Painters usually worked in the city's bazaar workshops or family workshop (Mayil Haravi 1993, p.12).

Leading figures, usually the most talented and professional artists, were selected as royal painters and worked in royal workshops. These people sometimes gained a special place in the court of the rulers (sultans) (Mayil Haravi 1993, p.11). For example, according to some of the surviving works, we find out that some rulers took artists with them when traveling to different cities, and some of them were able to work in a more personal environment (Roxburgh 2000, p.6-8; Mayil Haravi 1993, p.11).

Usually in each royal workshop, an experienced supervisor was appointed, whose main task was to supervise the works in production, and sometimes even wrote on her own products (Pakbaz 2006, p.65). According to the available documents, the painters prepared and used the colours they needed with great difficulty. Only in the royal workshops the colour producers help the painters in this field. For this reason, painters were very experienced and knowledgeable in the field of material science and colour combination (Kargar and Sarikhani 2012, p.196).

At first glance, it may seem that the colour materials used in illustrated manuscripts are common in different cities (schools) and different times. But if these pigments are examined more carefully and in detail, some differences will be revealed. It will also be seen that the colour materials that are the same in different cities are sometimes so different in the techniques of preparation and combination with other colour materials that they have created completely different colour tonalities.

In this study, different methods were performed for correct conclusions from colour analysis and comparisons. An attempt was made to make these comparisons by considering the principles of statistical science. Therefore, in the one-to-one review of each manuscript, the percentage is used.

For example, it was stated that the sum of the analysis performed on green colours in a particular manuscript, what percentages of them are copper green and what percentages are indigo + orpiment (see

[46] There are some evidence from the Safavid period that in Isfahan some people produced manuscripts as family and women in the family also played a role in the production of manuscripts (Mihan 2016).

Chapter 5). But this method (percentages) could not be applied to compare two different manuscript or to compare the analysed manuscripts in different cities.

Because the number of analysis performed on different manuscripts and the number of manuscripts analysed from different cities (schools) were not equal, and therefore the percentages provided could be misleading. Therefore, to compare the colour materials used in two different manuscripts or in two different cities (schools), the number of identified samples of each colour in a particular city (school) or a specific manuscript was presented without percentage and only based on the number of identified samples (see Chapter 5).

But in this section, for correct conclusions from the analysis and comparisons made to present the colour palette of Persian paintings and also to identify common and variable colour materials used in each city (school), the colour materials used for each colour tonality in the four groups of colour materials were classified and presented. In this model, reviewing and displaying information is according to Figure 6-1. The main material/s used for a colour tonality is considered as the first main colour and is placed in the centre of the circle (Fig. 6-1).

In fact, the first main colours are the colour materials for each the colour tonality has been used the most and is common in different cities (schools) and manuscripts, such as orpiment for yellow. The first sub-colour/s, which is shown in Figure 6-1 in the second ring. These colour materials are colour combination containing the first main colours + another colour material/s, for example the combination of orpiment + gold for yellow. In fact, these colour materials have been used in different ways in different cities and different manuscripts.

The second main colour/s, which is shown in Figure 6-1 in the third ring, is/are usually a colour material that has been used but to a lesser extent than the first main colour materials and has only been used in some cities (schools) or manuscripts. This colour materials are one of the differences in the use of colour materials in different manuscripts and cities (schools).

The second sub-colour/s in Figure 6-1 in the fourth ring are actually a colour combination that includes the second main colour materials + another colour materials. These colour materials are often used only in a specific manuscript or city (school), and in a way they can be considered as a specific colour materials for a specific city (school) or manuscript or time.

It must be considered all colour tonalities does not have all these four groups. Some colour tonality like green has only the first main colour and the first sub-colour because colour materials used for this colour tonality do not have much complexity and variety.

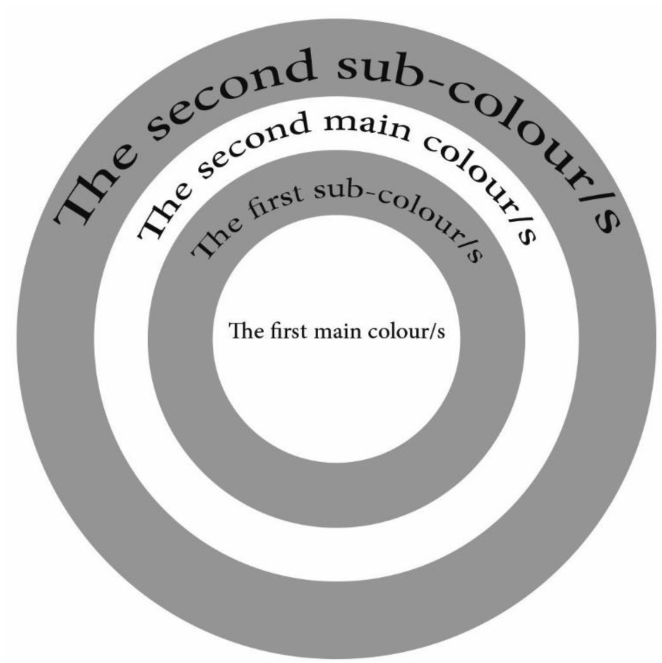


Figure 6-1: The classification and presentation system used in this study to display main and subsidiary colour materials for each colour tonality

According to the comparisons made, the greatest difference in the colour materials used in each city (school) should be sought in the second main colour materials and the second sub-colour materials. The second sub-colour materials should be considered as special items for a particular manuscript or painter. In other words, in this study, after performing more than 1000 analysis of nine different manuscripts, it can be concluded that the painters had certain raw colour materials available for the production of each colour (the first main colour material).

These raw colour materials was in complete accordance with their taste and technically had desirable properties. Therefore, painters have used these colour materials (the first main colour material) the most. The desire to create specific colour tonalities has been the only place where painters have gone beyond the framework of designated colour materials and experimented with different colour combinations. On the other hand, it can be said that the person ordering the manuscript and the workshop in which the manuscript was produced had a direct relationship with the quality and variety of colour materials used in each manuscript.

This means that the painters who worked in the royal workshops and were supported by the rulers and courtiers had access to more colour materials than the painters of the other workshops. Indeed, the description of the higher quality of colour materials is also related to the methods of preparation and usage of colour materials. In other words, the technique of preparing and using colour materials in royal workshops is much more advanced than bazaar or family workshops.

As it is clear in historical documents that in royal workshops, people specialized in the process of preparing colour materials for painters (Kargar and Sarikhani 2012, p.109). For example, in the two manuscripts Or 420 and Ms 22-1948, which were produced in almost at the same time in the city of Shiraz in two different workshops.

There are major differences in terms of preparation techniques of colour and how to use them. In manuscript Or 420, ultramarine is faded and the paper is corroded in the places where copper green is used, while in the Ms 22-1948 manuscript, the same colour materials are used without causing corrosion and destruction of the paper. Therefore, from the sum of these evidence and analysis, it can be concluded that due to the large commonalities of the colour used in these two manuscripts, the quality of the preparation of colour and the technique of its use in the Ms 22-1948 manuscript is much higher.

Also, based on the analysis performed in this study, it can be stated that the manuscripts produced in Herat are in a higher position in terms of the quality of the colour used and the technique of their application, and the manuscripts produced in India have the lowest quality in this field. In other words, with the exception of two Indian paintings were produced in the late 16th century at the Mughal court and were added to the RAS 239 manuscript, the other Indian paintings studied in this study are significantly inferior in the way they are prepared and used.

6-2-1 Blue

Below you can see the classification of colour materials used for each colour. For example, for blue, as shown in figure 6-2, ultramarine is the first main colour to be used in various cities (schools) over time. The first sub-colour contains a combination of ultramarine with lead white, which has been used to produce light blue tones[47]. As you can see in figure 6-2, the second main colour material category includes indigo and azurite, and the second sub-colour material includes a combination of these two colour materials with white lead or ultramarine + azurite combination, which is only identified in Lahijan manuscripts.

It should be noted that the colour used for blue have the least possible change in different cities and at different times, and ultramarine has been used in almost all paintings. The only differences in the colour materials used for the blue colour tonality can be seen in the use or not use of indigo in wide area. Obviously, indigo has been used as a colour in almost all paintings to blend the figures, but here we mean to use indigo in larger dimensions and independently as a blue colour. Another noteworthy point is the use of azurite pigment, which is used only in Herat.

[47] some researchers believe that the light blue tones obtained from ultramarine are not the result of combining ultramarine with white lead. they belive Persian painters by changing the preparation processing of ultramarine pigments from its ore lapis lazuli have created different tonality of blue (Jokar 2011, p.109).

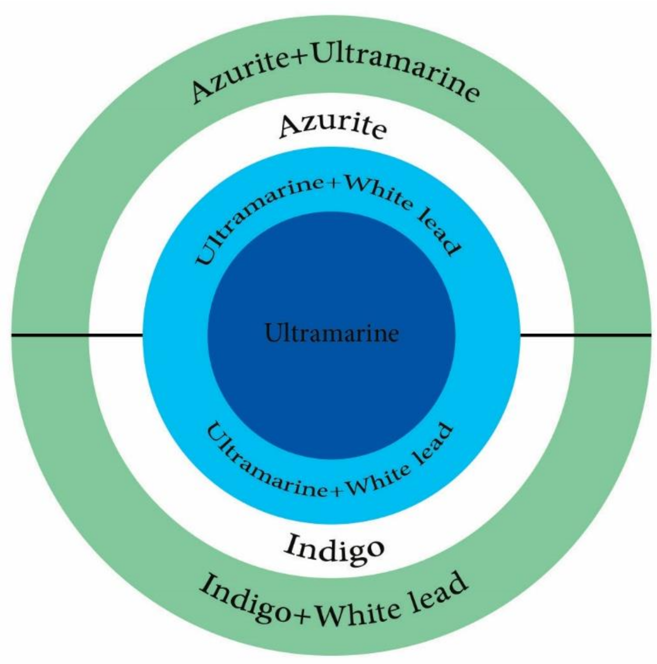


Figure 6-2: The classification of blue colour materials in this study

6-2-2 Green

As you can see in figure 6-3, there are two main colours for green, orpiment + indigo and copper green, which are used simultaneously in most cities (schools). As you can see in the figure 6-3, the first sub-colour materials for green colour include two colour combinations indigo + yellow dye and orpiment + ultramarine, which are rarely used and only in some paintings of Shiraz. Another sub-colour is the pigment, which contains two minerals, azurite and malachite, which are used only in Lahijan. It should be noted that one of the painters in Herat also used this pigment.

Copper green, which has a light green tint, has been used to paint armor, helmets, and barding, while the combination of indigo + orpiment has been used more to paint the leaves of trees, shrubs, and shrubs. Another noteworthy point about green colour tonality is the corrosion or non-corrosion of paper by copper green, which is directly related to the use or non-use of saffron to neutralize the corrosive effect of copper. In other words, corrosion or non-corrosion of paper due to copper-based green pigments can be one of the specific criteria for measuring colour preparation techniques and as a result, the importance of manuscripts and workshop rolls in which manuscripts have been produced.

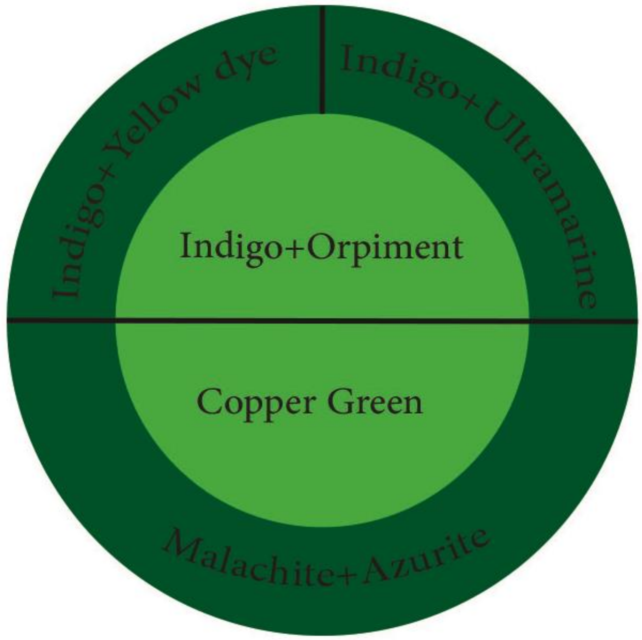


Figure 6-3: The classification of green colour materials in this study

6-2-3 Red, orange, and brown

As you can see in figure 6-4, the two colours red lead and cinnabar are the first main colour for red, orange, and brown tones. These two colours have been used in almost equal proportions in all cities (schools) to create red and orange tones. The three colour combinations of cinnabar + orpiment and red lead + orpiment and red lead + cinnabar are the first sub-colours of this colour tonality (Fig. 6-4).

These three colour combinations have been used to create different shades of brown. The second main colour material is ocher and cochineal, which are used to create brown and dark red tones, respectively (Fig. 6-4).

As you can see, the colour materials used for the red, orange, and brown tones are the least different in different cities (schools). The only difference observed is the use of pure cochineal as a dark red colour that has only been used in Herat and Shiraz. This use refers to shapes with very small dimensions such as small background flowers and sometimes blood stains.

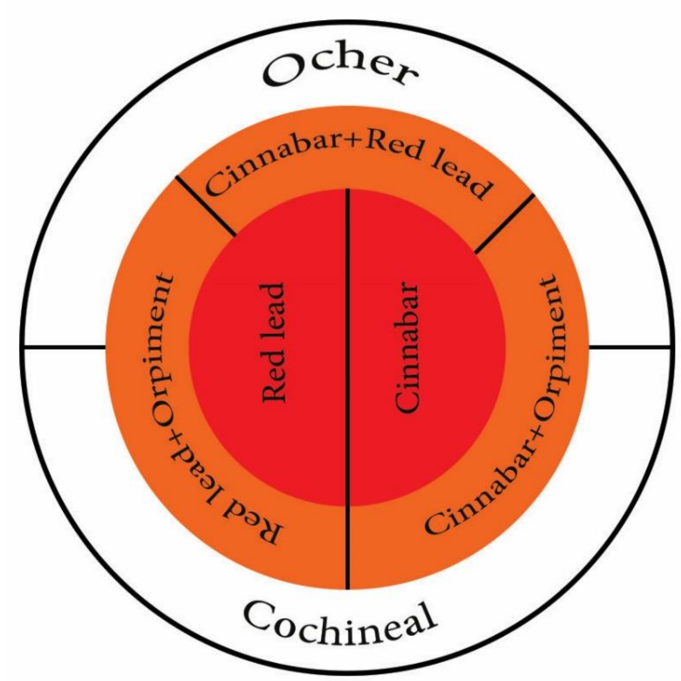


Figure 6-4: The classification of red, orange, and brown colour materials in this study

6-2-4 Pink, violet, purple, peach

Since different painters in different cities (Schools) have used a variety of colour materials to create pink, violet, purple, and peach colour tones, it is very important to compare and study these colour tones. Perhaps the use of complex colour combinations for these colour tonalities has led to the fact that in the limited studies that have been done on Persian manuscript paintings, the colour materials used for these colour tonalities have been less carefully studied.

Due to the high variety of colour materials used for this colour tonalities, an attempt was made to carefully divide and present its main and subsidiary colours.

As you can see in figure 6-5, the three colours of Indian lac, cochineal, and red lead + white lead are considered as the first main colour materials for this colour tonalities. These three colour, along with ultramarine, are most used in the colour combinations used for these colour tones. Since ultramarine has never been used in its purest form to create these colour tonalities, these three pigments have been considered as the first main colour.

As you can see in figure 6-5, the first sub-colour materials include seven colour combinations; Indian lac + indigo, Indian lac + ultramarine, red lead + copper green, red lead + indigo, cochineal + ultramarine, cochineal + indigo, and cochineal + yellow dye (Fig. 6-5). Some of these seven colour combinations have been used repeatedly, but others, such as red lead + copper green and red lead + indigo, have been identified in only one case. The second main colour include ultramarine and cinnabar (Fig. 6-5).

These two pigments have never been used in pure form to create these colour tones but have been used repeatedly in combination with other colour materials. Therefore, these two pigments are considered as the second main colour. As you can see in figure 6-5, the second sub-colour materials include four colour combinations: ultramarine + indigo, ultramarine + cinnabar, cinnabar + orpiment, and cinnabar + yellow dye (Fig. 6-5).

As you can see in figure 6-5, the colour materials used for pink, violet, purple, peach tones have a high variety, which often includes a combination of several colour materials. The only pure materials used are cochineal and Indian lac, which are used for pink and violet.

It seems that the brilliant manuscripts which have been produced in royal workshops, a wide range of colour materials used for these colour tonalities. For example, the manuscript RAS 239 produced at the royal workshop of Herat has a higher diversity of colour materials used for these colour tones among all the manuscripts examined in this study. Indian paintings also have a great variety in terms of both the materials used and the colour tones created.

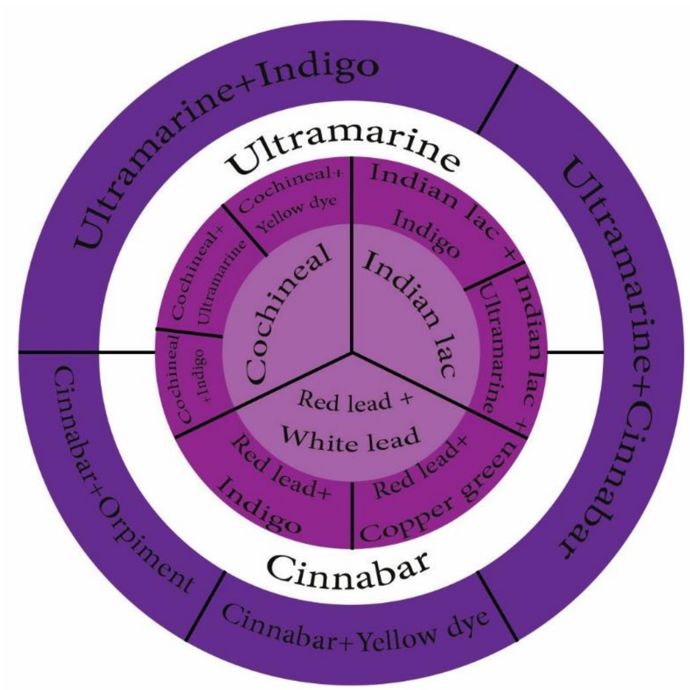


Figure 6-5: The classification of pink, violet, purple, and peach colour materials in this study

6-2-5 Yellow

As you can see in figure 6-6, orpiment is considered as the first main colour material for the yellow. This pigment has been used many times in different cities (schools) over time. Four colour combinations including orpiment are considered as the first sub-colour materials (Fig. 6-6).

These four colour combinations include orpiment + yellow dye, orpiment + gold, orpiment + red lead, orpiment + yellow dye and gypsum, which have been used many times in different cities (schools). As you can see in figure 6-6, the two dyes Indian yellow and yellow dye are considered as the second main colour materials.

As you can see, orpiment has been used as a yellow colour many times in pure form and in combination with other coloured materials. Indian yellow is another colour that, obviously, was used only in Indian and Qazvin paintings in the late 16th century.

The use of Indian yellow in manuscript paintings seems to have been common since the late 16th century and was not common before. Another dye used for yellow tones is yellow dye. As previously explained, due to the limitations of the analytical methods used in this study, it was not possible to recognize between saffron and turmeric.

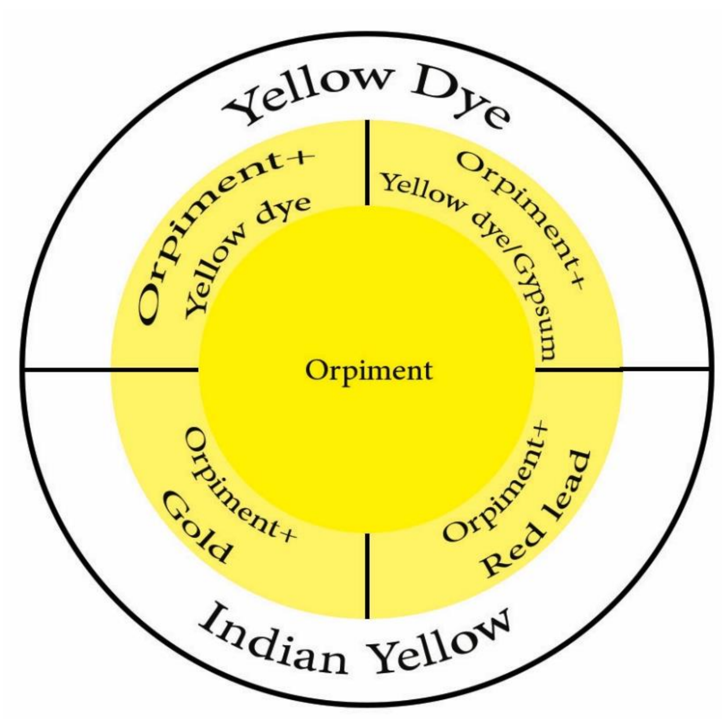


Figure 6-6: The classification of yellow colour materials in this study

6-2-6 Gray

As you can see in figure 6-7, the silver pigment and the colour combination of indigo + white lead is considered as the main colour materials for the gray colour tonality. The colour combination of indigo + red lead is considered as the first sub-colour material (Fig. 6-7).

Since there was no other colour materials for the gray colour tonality that has the necessary properties to be in the category of the main materials, no material was considered as the second main material for the gray colour. But as you can see in figure 6-7, the three colour combinations of ultramarine + white lead, ocher + red lead and degraded red lead or cinnabar had the necessary properties to be considered as a second sub-colour materials (Fig. 6-7).

It should be noted that the silver pigment has lost its metallic luster due to its current corrosion and has turned dark gray. Instead of being in the category of metallic pigments, it has been placed in a gray tint. Also, the colour combinations of indigo + red lead, ocher + red lead and degrade red lead / cinnabar seem to have had a colour other than gray at first.

These colour compounds have changed to gray due to corrosion of its components. Also, in many cases, in lower quality manuscripts, we see that some colours (especially ultramarine) have fallen off and as a result of the fall, they have left a light gray colour that should not be confused with the gray colour.

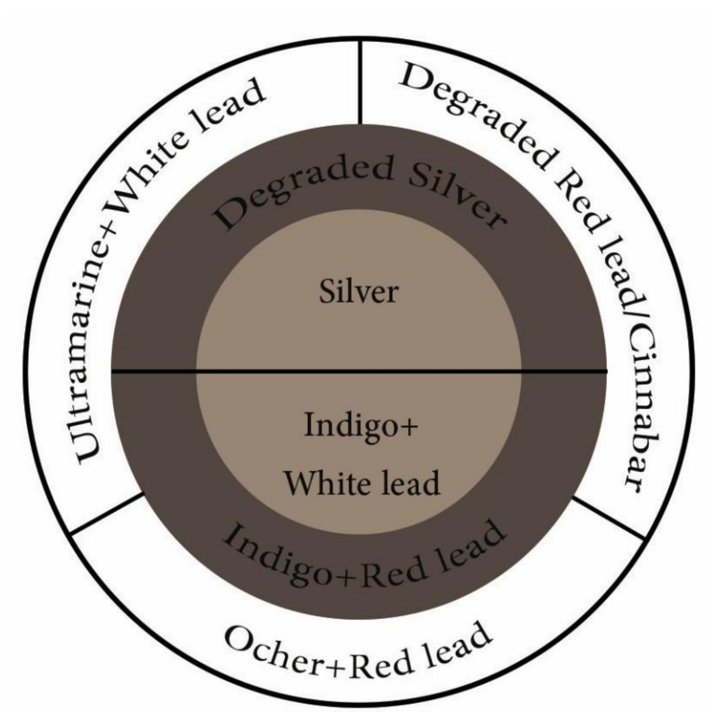


Figure 6-7: The classification of gray colour materials in this study

6-2-7 Metallic pigments

As shown in figure 6-8, gold pigment is considered as the main colour material for metallic pigment (golden). And the three colour combinations of gold + silver, gold + orpiment, gold + silver and orpiment are considered as the first sub-colour material for gold colour.

It should be noted that according to traditional instructions, gold colour was used in most cases along with saffron dye. It should also be noted that Persian painters used two methods to change the metallic luster of gold colour. In the first method, as mentioned above, it was combined with other coloured materials such as saffron or silver and orpiment to reduce its metallic luster. In the second method, by rubbing the surface of the gold pigment with marble, the metal polish was made more or less, and it was called raw or baked gold.

Figure 6-7: The classification of metallic colour materials in this study

6-3 Capabilities of the combination method of FORS, FOMF, and XRF

As mentioned in Chapter One, one of the important objectives of this study is to investigate the colour palette used in Persian manuscripts. To achieve this goal, a strategy was considered based on which it is possible to analyze more manuscripts. As explained in detail in the second chapter, in this study, to identify the colour materials used in the Persian manuscript, the combined analysis method of FORS, FOMF, and XRF techniques was used. SERS-Raman and HPLC-MS as micro-destructive analysis techniques were also performed on ten small samples prepared from manuscripts RAS 239, Persian 9, and Persian 933. These two techniques are micro-destructive and cannot be considered as a permanent solution that can be applied in different situations for manuscripts. And the formation of a large statistical community for colour comparison was inconsistent.

Therefore, only the capabilities of FORS, FOMF, XRF analysis methods to identify the pigments and dyes used in Persian manuscripts have been investigated in this section. According to the objectives of this study, three main criteria were considered in selecting the analysis methods which were: Non-destructive, portable, and fast. Since the aim of this study was to compare the pigments used in different cities (schools), we needed rapid and portable analysis techniques to give us a larger statistical set to compare colour materials.

Among these three analysis methods selected, since the XRF analysis method is very well known and its capabilities have been proven many times, in this section, most of the capabilities of the other two analysis techniques will be examined. Between FORS and FOMF analysis methods, FORS analysis method has recently been used as a preliminary analysis method to obtain the initial idea for the colour materials used in manuscripts, but FOMF method has been used less. In the following, we will take a closer look at the ability to combine these two methods and their ability to detect pigments and dyes.

It is true that for example the results of Raman or FTIR or SERS Raman analysis are much more reliable than FORS and FOMF, but my experience after analyzing more than 25 Persian manuscripts during my master's thesis and this study has proven FORS to be one of the best methods for manuscript analysis if it combined with XRF and FOMF. Due to the fact that manuscripts are very fragile and vulnerable and there are many limitations to their analysis, FORS is very suitable and useful as a fast and simple analysis method. On the other hand, in the combined analysis method considered in this study, FORS weaknesses are covered by two methods of XRF and FOMF analysis.

In the following, is presented a fast overview of some capabilities of the combination analytical method used in this study.

- Ultramarine and Indigo, which are among the most widely used colour materials in Persian manuscripts and cannot be easily identified by portable XRF technique. These two colour are easily identified by FORS. Identifying ultramarine is very challenging due to its light element and indigo due to its organic nature, but in this study, we easily identified both of these colour by FORS.
- XRF is not able to distinguish between copper-based pigments such as Azurite, Malachite and Verdigris, but FORS is able to recognize Azurite from Malachite and verdigris.
- In the case of yellow dye, the FORS and FOMF techniques are not able to distinguish saffron from turmeric and Indian yellow and can only confirm the use of yellow dye. It must be noted that these yellow dyes can be identified only with a proper combination of FORS and FOMF, because FORS alone is not enough to identify yellow dyes. Since, due to the fact that in the FORS spectrum yellow dyes have an inflection point and the inflection point (IP) changes with the concentration of the chromophore; as the concentration increases, the IP moves towards higher wavelengths. So, when we hypothesise the presence of a yellow dye (e.g. Indian yellow, orpiment, turmeric, etc.), it is always check whether the FOMF response is coherent with that identification.
- Identifying gold-based colour combinations in Persian manuscripts was very challenging. Compounds obtained by mixing gold with orpiment or silver or yellow dye. These compounds were identified through the participation of all three of these techniques. Gold, Silver and Orpiment, these compounds were detected by XRF. Gold, orpiment, and yellow dye were identified by FORS. Also, FOMF was used to confirm the presence of yellow dye in these compounds.
- One of the most important results obtained in this study was the identification of red dyes and their different types from each other. As previously mentioned, in this study we had the chance to analyze a number of colour samples with dark red, pink and purple tones by SERS and HPLC-MS analysis methods. As described in Chapter Two, these two techniques are micro-destructive and complex, but much more reliable than the FORS and FOMF techniques used to identify dyes. The samples analyzed by these two techniques were previously identified by FORS and FOMF as cochineal dye. But after analyzing these samples by SERS and HPLC-MS, we found that the colour samples of manuscript Persian 9 and 933 are actually Indian lac and not cochineal. As a result, with a closer look, we found out how we can recognize cochineal from Indian lac by FORS technique (see chapter four).
- As you have seen in previous sections, in Persian manuscripts, a variety of colour combinations have been used to create pink, violet, and purple tones. Some of these compounds contained two or more pigments, most of which contained the three pigments ultramarine, cinnabar, and red lead. XRF and FORS were used to identify the components of these colour compounds. Other compounds included a dye and a pigment. In such combinations, the pigment part was

identified by XRF and FORS, and the dye part, which mostly included cochineal or Indian lac or Indigo, was identified by a combination of FORS and FOMF methods.

- Almost all XRF spectra taken from the manuscripts studied in this study contain the element Pb. This is due to the use of white lead on paper. Also, Persian painters in many cases have combined any colour with white lead to change the tonality of a colour. Therefore, recognizing the substance used for some red tones was very challenging. Because in their XRF peak, there was Pb, which indicates the presence of Red lead or white lead pigment, and at the same time, in their XRF peak, there was the element Hg, which indicates the presence of another red pigment, Cinnabar. So, the big challenge was whether to use cinnabar + white lead or red lead at this colour point. In such cases, the FORS technique was very useful for distinguishing these two colour combinations. Infact when we have cinnabar and lead white, we will see Hg and Pb in the XRF spectrum, but only one inflection point (IP) in the FORS spectrum. If this IP is around 600 nm and the red hue is saturated, it is definitely cinnabar. If this IP is around 580 nm and the red hue is slightly saturated because it is diluted with lead white, it can be diluted cinnabar. If this IP is around 580 nm and the red hue is saturated, it is definitely NOT cinnabar but rather red ochre (but check that there is iron) or concentrated red lead (difficult). It should be noted that since in some cases red lead and cinnabar pigments have been combined and used, this issue needs to be further investigated to identify red colour materials.

- In the case of the pigment mixture of red lead with cinnabar the same problem mentioned above happened. In the presence of Hg and Pb together in XRF spectra is confusing distinguish between red lead, cinnabar, cinnabar + white lead, and red lead + cinnabar. In this situation, once again, FORS can be helpful to identify pigment mixture red lead + cinnabar. In fact, when red lead and cinnabar are present simultaneously, in FORS spectra two inflection points can be seen when we perform the first derivative of the curve.

- This combination method has often been useful for detecting different colour combinations. Especially for colour combinations including a pigment part and a dye part. In such samples as indigo + orpiment for green or indigo + white lead for gray, the pigment component was identified by XRF and FORS and the dye component by FORS and FOMF. In general, this method of combination analysis was very useful for identifying colour compounds and samples of many colour compounds were identified by these methods, two examples of which were mentioned above.

- In this study, three different types of FORS configurations were used, the full explanation of which is given in Chapter two. But my personal experience has shown that the configurations developed at the University of Turin in Italy by Dr. Aceto, which were also used in my master's thesis and this study, have the best results. In this configuration, a special handle designed to keep reflectance probe in a completely dark area to illuminate samples and to recover diffused light by sample (Fig. 6-8). This handle can also be used for FOMF to improve the quality of spectra. This handle by holding the reflectance probe angle constant relative to the folio of the manuscript. As well as creating an enclosed and dark compartment for the irradiation folio and recording of the light which is diffused by the folio. Therefore, this handle is very useful to register much more accurate FORS and FOMF spectra with very little noise. On the other hand, this handle has a kind of micro-camera, which is very helpful to makes sure that the fiber optic is in the right place before recording the spectra. Perhaps the biggest weakness of this configuration is the need for the handle to contact surface of manuscript's folio to create a completely dark space for recording the spectra. Although this weakness is compensated by covering the contact surface with inert and soft polymers (Fig. 6-8).

- FOMF analysis technique is one of the techniques used in this project that is less known and less used than the other two techniques. This technique can be very useful in identifying dyes used in manuscripts. It is true that the information obtained from this technique is not completely reliable compared to other dyes detection techniques such as SERS Raman and HPLC-MS or FTIR. But since these techniques are complex and micro/semi-destructive, they cannot be permanent options for identifying dyes used in manuscripts. As a result, the FOMF technique can be useful for identifying dyes if used in combination with the FORS technique. Perhaps The biggest (huge indeed) problem of FOMF is that the fluorescence peak moves according to the concentration of the dyes (more precisely, of the fluorophore) i.e. the functional group in the molecule that generates fluorescence: as the concentration of the dyes increases, the fluorescence peak moves towards the infrared region. So, we have the same problems as those generated by the movement of the IP in the FORS spectra of reds and yellows. Therefore, FOMF cannot be used alone but only as complementary technique.
- The other problem with the FOMF technique is the lack of standard spectra of dyes. To solve this problem, in a part of this study I tried to complete the bank of FOMF spectrum of different dyes used in Persian manuscripts. This bank of standard dyes samples was established by me in my master's degree in the university of Turin (Italy) and was completed in this study and its results are described in detail in Chapter Three of this dissertation. In general, it should be noted that in this study, the FOMF technique was helpful in identifying yellow dyes, cochineal, Indian yellow, and indigo, but this technique needs to be used more and more studies developed. It is also necessary to complete its standard sample bank.

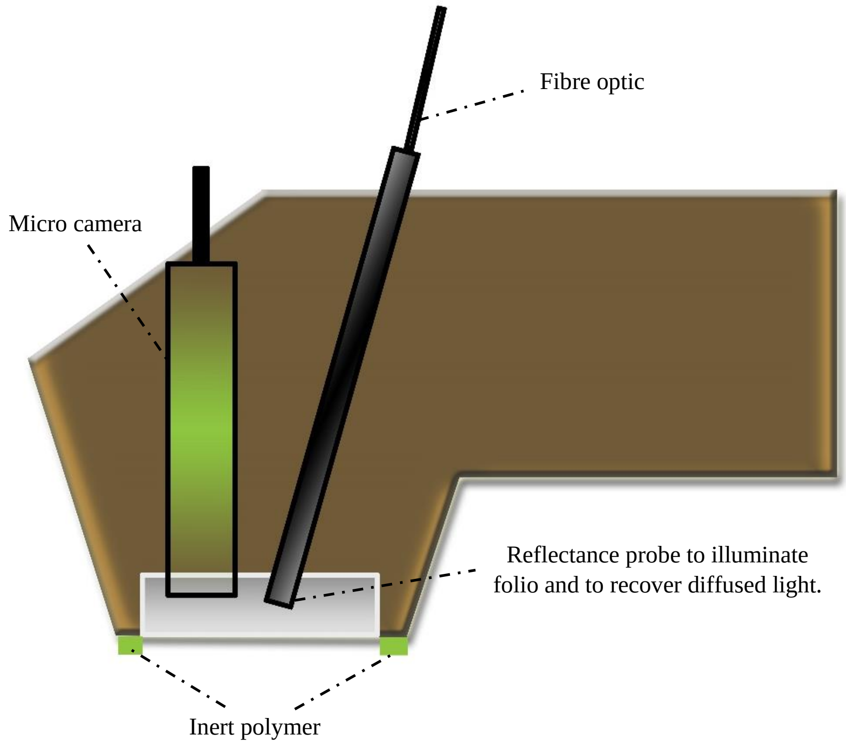


Figure 6-8: Special handle designed to improvement FORS and FOMF spectra

6-4 Discussion

Preparing and using colour is one of the most important topics in Persian painting and bookmaking. Painting colours are usually made by combining at least two materials: colour material and glue. Obviously, in many cases in addition to these two main components, improving materials have been added to colour compounds. Sometimes improver materials, filler or viscous materials, softener materials, disinfectant materials, etc. have been used in the Persian manuscripts (Kargar and Sarikhani 2012, p.196).

In bookmaking workshops the process of preparing colours was sometimes done by the painter himself or a pupil of the workshop and sometimes a professional craftsman who was only engaged in colour preperation (Kargar and Sarikhani 2012, p.196). This was directly related to the importance of the workshop in which the manuscripts were prepared. In private workshops it is likely that the painter or his apprentice was in the charge of preparing the colours, while in royal workshops a professional craftsman was only engaged in preparing the colours. This person had knowledge of materials comprehension and was familiar with the principles of chemical application of his time.

The sum of historical information on bookmaking in Persian civilization, the available information of artists who are still working with traditional methods, and the scientific analysis performed on Persian manuscripts by me in this study and my master's thesis and other similar studies caused many questions in my mind, such as: Were the painters who worked in manuscript workshops recognized as artists or craftsmen by the court and ordinary people of the society? The answer to this question is important because it can be the key to answer many other questions on the subject of colour materials used for illustrated Persian manuscripts as well as the style of painting. Were they craftsmen who had to carry out the demands of the clients in details, or were they stylized artists who independently chose to creat their artwork? Were the painters who worked in private workshops able to decide independently about the style of their paintings and the colour materials they used? Did the painters in royal workshops have any control over the colours they used and the style of their paintings? In royal workshops, were the colour and style of the painting determined by the head of the workshop, or did the painters themselves have the ability to make decisions in this regard?

To answer these questions we need to consider historical information to interpret the performed analysis. In the following, an attempt has been made to answer these questions based on the analyses performed by myself well as the existing historical documents, and new questions have also been raised.

According to the analysis, it is clear that the colour materials used in different cities and different workshops are similar. As explained above, the main materials used are similar and the differences are related to the sub-colours and the type of colour preparation and usage. Due to the vastness of the land of Persia and having various mineral resources, most of the frequently used colour materials were obtained from sources within Iran, with the exception of cochineal and Indian lac.

Therefore, in many cases, the colour materials used in the illustrated manuscripts in different cities and workshops were obtained from local sources and workshops or markets in the city. It is clear that usually the highest quality colour materials that were more expensive ended up in royal workshops. The higher quality of the colour materials used in some manuscripts can be attributed to the higher quality of the raw materials or of a better preparing process of raw colour materials.

The two colour materials, ultramarine and copper greens are the best examples to check the quality of preparation and use of colour materials by a painter. Because if the ultramarine is not prepared properly, it will fall off after a while, and also if a painter is not aware of the anti-corrosion effect of saffron and uses copper greens without saffron, after a while copper will cause corrosion on the paper. Therefore, falling the ultramarine and corrosion of the paper by copper pigments (mostly green) could consider as indication of preparing process of colour.

To answer the question of which of the two had the greatest impact on the final quality of the paintings, we return to the comparison of the two manuscripts Or 420 and Ms 22-1948. These two manuscripts have been produced in two different workshops in Shiraz at the same time. Manuscript Ms 22-1948 have been produced in the royal workshop (Ibrahim Sultan's workshop) but manuscript Or 420 have been produced in a family or Bazaar workshop[48]. Therefore, the final colour quality of the manuscript Or 420 is much lower than the manuscript Ms 22-1948.

Considering that the colour materials used for both of these manuscripts are very similar, but in the manuscript Or 420, in many cases, the colours have been damaged and fallen. It can be concluded that the painters of this manuscript are not fully acquainted with how to prepare and use colours. Also, maybe they did not have access to the high quality of raw colour materials. Obviously, it should not be overlooked that inappropriate storage conditions of a manuscript can also be the cause of damage to the colours of that manuscript. The same pattern can be attributed to the manuscript Persian 9. Where the colour materials used in the paintings of two Indian painters from two different workshops have suffered varying degrees of corrosion. But in the manuscript Ras 239, which was prepared by nine different painters in the royal workshop of Herat.

In this manuscript the colour materials used by all the painters remained without the slightest damage. This can be a confirmation of the fact that in the royal workshops there were experts whose job was only to prepare the colour materials, so they were fully aware of how to properly prepare the colour materials. The same subject can be seen in three Turkman style manuscripts (AKM 4, 5, 269) that were made in a period of time under Turkman workshops in Shiraz[49]. Putting together the results of all the comparisons made on different manuscripts, we can answer the question that both the quality of the raw materials and the process of preparation and use of colour materials have affected the final quality of the manuscript. However, because of the similarity of used colour materials, it seems the process of the preparation and use of colour materials has played a more decisive role in the final quality of the work.

Hence, the process of producing an illustrated manuscript relies more on the workshop in which the manuscript was produced than on a particular person or painter or even city. In other words, the process of producing a manuscript is based on teamwork. The group is headed by the workshop supervisor who oversees the process of producing the manuscript (Fig. 6-9). It is because of this group work, as well as the

[48] Some scholars such as "Norihito Hayashi 2012" considered this manuscript as an example of pre-Turkmen commercial-style.
[49] These manuscripts are known as Turkmen commercial style.

mystical vision of the painters, that the paintings have less signatures, and if a work was signed, the masters of painting used pseudonyms[50].

Manuscript RAS 239 is the best possible example to answer the question of whether Persian manuscript painters are artists or craftsmen. Because this manuscript was painted by seven different painters in the royal workshop of Herat. studying the painting style and colour materials used by each of these painters will help us to understand the prevailing atmosphere in the bookmaking workshops. Studying and comparing the colour materials used by each of these painters reveals that they have many similarities in the colour materials usage, but there are also obvious differences.

These differences are mostly related to the colour materials that we have placed them in the second main material category (see Fig. 6-1). The painter A, for example, is the only painter to have used indigo extensively for blue. Or Painter C is the only painter who has used Ocher. Barbara Brand In her book "Muhammad Juki's Shahnamah of Firdausi" (2010) describes the paintings of all these painters in great detail.

By combining this information with the scientific analyses performed in this study, we can get an overview of the workshop space in which this manuscript was produced. From all these data, it can be concluded that in the process of making this manuscript, two painters, B and C, have been considered as the main painters of this manuscript by the workshop supervisor.

In the meantime, Painter C, who was a master and an experienced painter, had a higher position and supervised the paintings of other painters. The effects of his paintings can be seen in the paintings of painters E and F who were probably his pupils. It seems that painters B and C had more choice in combining colour materials to achieve the desired tonality because the variety of colour tones and colour materials used by these two painters is much higher than other painters. And the interesting thing is that the colour materials used by these two painters are very similar.

Therefore, these two painters had good knowledge of different combinations of colour materials. The wider range of colour tonalities and colour materials used by these two painters can be due to the higher position that the greater choice of these two painters is due to their mastery of painting that they had gained in the Herat workshop. Putting together the scientific study done in this project and the codicology research done by Barbara Brand (2010) on this manuscript as well as the available historical information from the hierarchy of manuscript production workshops.

[50] One of the first manuscripts bearing the signature of the painter is the Jalayirid Divan of Khajavi Kermani (BL, Add. 18113) dated 1396, in which Junaid Baghdadi mentioned himself.

From all this information we can conclude that in the manuscript production workshops over time, the painters could achieve a higher position in the workshops due to their mastery.

This higher position allowed them to have more choice in choosing their painting style as well as the desired colour tones by combining different type of colour materials. In fact, because of the skill that these people gained in painting and also the knowledge that they gained from coloured materials. They were trusted by the workshop supervisor, so probably they were less controlled by the workshop supervisor. Some of the painters' pupils helped them along the way in illustrating a manuscript.

Depending on the level of each pupil, these aids could range from colour preparation to participation in drawing parts of a painting or even drawing an entire painting, as seen in this manuscript. For example, in this manuscript painters E and F were influenced by the paintings of painter C and were probably two of the painter's senior pupils. Also, Painter G, who has a painting in this manuscript, was clearly a novice painter, given the type of painting and the colour materials he used.

On the other hand, the workshop supervisor for a particular painting sometimes chooses a painter outside this cycle of the senior painters and their pupils. This happened to painters who were proficient in a particular type of painting, such as drawing battle scenes or nature, and so on. For example, in this manuscript, Painter A, who was a skilled painter himself and also worked on the *Shāhnāma* of Bāysunghuri, used scenes with many mountains and cliffs for three paintings. Therefore, for royal manuscript production workshops, the workshop hierarchy can be considered by placing the workshop supervisor at the top of the workshop management chart as shown to figure 6-9.

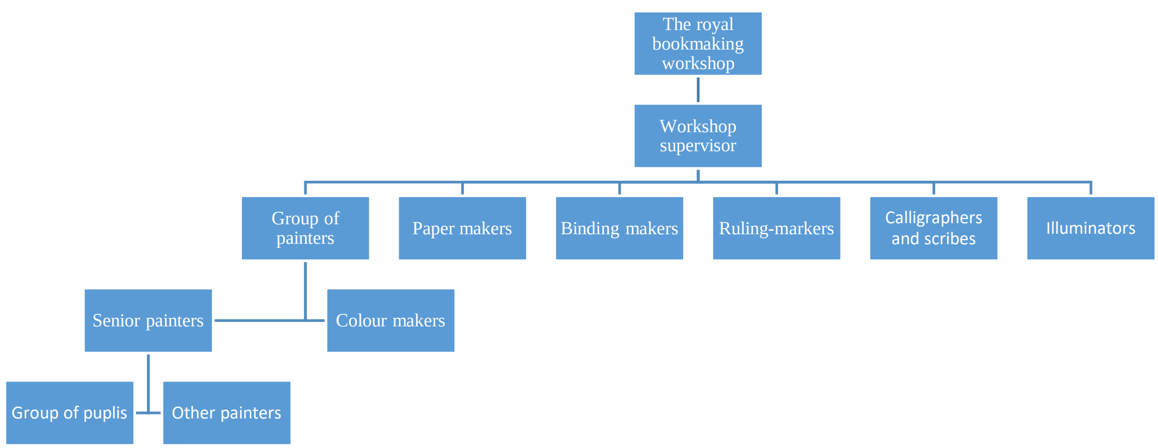


Figure 6-9: Manuscripts production in Royal workshop

On the other hand, comparing and studying the colours of the Turkman style manuscript also contains a lot of information to clarify the issue and answer the questions raised. Especially the manuscript AKM 6, which belongs to Lahijan. Three manuscripts AKM 4, 5, 269 are the Turkman commercial style manuscripts belong to Shiraz. All three manuscripts were made in between 1482 to 1492 CE. Although no information is available from the artists of the manuscript or the workshop in which the manuscripts were made. They are very similar in both the style of painting and the colour materials used.

Meanwhile, the two manuscripts AKM5 and AKM4, which were produced ten years apart, are very likely to have been made by a group of painters or in a workshop due to their similarity in painting style and colour usage. On the other hand, the manuscript AKM 269, which was made at the same time as the manuscript AKM 5, was commissioned by Sultan Abu'l-Nasr Qasim Khan and most likely produced in a high-level workshop or attached to the King's court in Shiraz. Due to the high quality of the colours and paintings of this manuscript, it seems that all three of these manuscripts have been created by skilled artists and produced in high-level workshops.

A review and comparison of these three manuscripts shows that the colours used in these manuscripts are very similar and differ only in some details. Could this similarity in style and colour materials be due to the fact that these manuscripts were made in the same workshop? or maybe it is because the Turkman artists of Shiraz have reached a common style of using colour materials by using the experiences from the past. This becomes more interesting when we compare these three manuscripts with the manuscript AKM 6, which was produced at the same time and in the same style, but in a different city in Lahijan. From the comparison of these manuscripts, it is clear that although the main materials used in all four manuscripts are common. However, the manuscript AKM 6 paintings are markedly different from the other three versions in both the style of painting and the colour materials used. In general, all these four manuscripts belong to the Turkman style but the colours of manuscript AKM 6 are brighter than the other three manuscripts.

Are these differences in colour tones, painting styles, and colour materials used in the AKM 6 manuscript due to different geographies in which these manuscripts were produced? Did the painters in Lahijan have access to different sources of raw materials than the painters in Shiraz? or is it because of the different tastes of the painters of this manuscript that they created different colour tonalities from different colour combinations? Or maybe it was the personal taste of Sultan "Ali Mirza" who commissioned this manuscript. In the following, based on the available historical information and analyses performed in this study, an attempt will be made to answer these questions.

As the comparison of the paintings drawn by seven different painters who worked on the manuscript RAS 239 in the royal workshop of Timurid Herat gave us a relative picture of the situation in the royal workshops of Timurid Herat. Comparison of the manuscripts produced in the same historical period and a well-known art style. As well comparing it with the manuscript of the same period and art style but in a different city will help us a lot to better understand the prevailing atmosphere in the manuscript workshops. All four manuscripts are categorized in the Turkman commercial style. In this style of manuscripts, who were the customers and supporters of producing manuscripts were mostly local rulers or some rich people.

Therefore, in terms of the structure of manuscript production and the workshops, probably they were at a lower level than the Timurid Herat workshop, where MS RAS 239 was produced. For this reason, it can be assumed that the order and classification that existed in the workshop of Timurid Herat probably did not exist in the production of these manuscripts. However, according to existing historical documents, the Turkman set up manuscript production workshops in imitation of the Timurids.

The phrase “Turkman Commercial Style” alone represents some of the characteristics of this style. The phrase “Turkman Commercial Style” was used by B.W. Robinson in the 1950s to categorize a specific style of Persian painting in the late 15th century from an elegant style belong to the contemporary Timurid and Turkman courts (Norihito Hayashi 2012, p.169). Robinson believes the purpose of this style was the production of manuscripts on a commercial scale. Therefore, the aim of the workshops was to produce a large number of manuscripts. However, the terms “Turkman Commercial Style” has been accepted and used by many scholars but recently some scholars like Norihito Hayashi have questioned about attribution of this style to Tabriz and its commercial nature.

The paintings of this style are simple with a simple composition consisting of two or three main figures. So, it can be said that due to its commercial nature and high production, was it considered as a suitable style for this purpose? As mentioned above colour materials used in the manuscripts AKM 4, 5, and 269 (belong to Turkman commercial style) are very similar. Was the approach to the high production of manuscripts (commercial nature) can be the reason for this high similarity?

The high similarity of colour materials used in this style can be matched with the high production of manuscripts. But on the other hand, the good quality of manuscripts is contrary to the high production of the manuscripts. Based on the theories about “Turkman commercial style” and analyses performed in this study it can be concluded that the features considered for this style are acceptable although more research is needed to discuss whether the production was for the commercial purposes or not.

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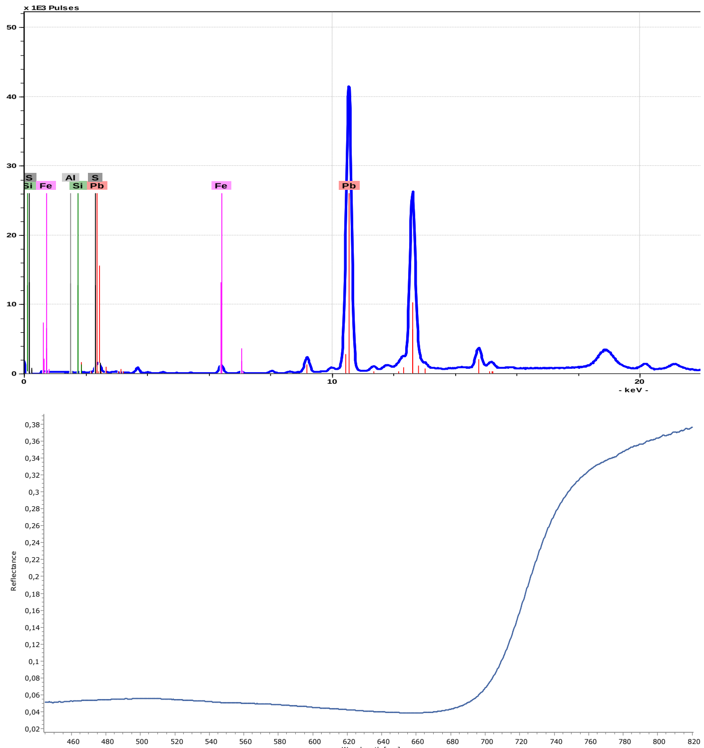
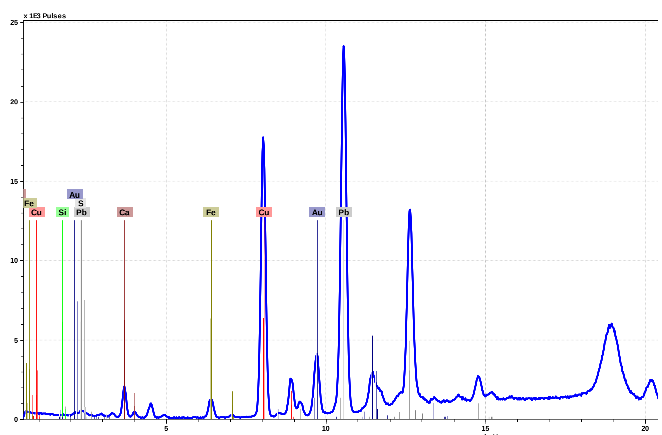
Appendixes

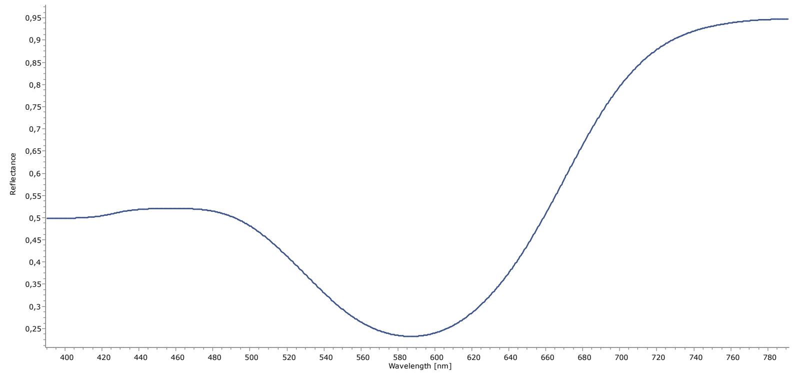
Appendix 1: the light grey colour used to paint the background decoration of manuscript AKM 4 (folio 47) is a combination of indigo with red lead, which is not a common colour combination to create a grey colour. this coloured spot may have actually been purple (indigo + red lead), which red lead pigment of colour mixture probably has been corroded and became black.



XRF and FORS spectrums of indigo + red lead

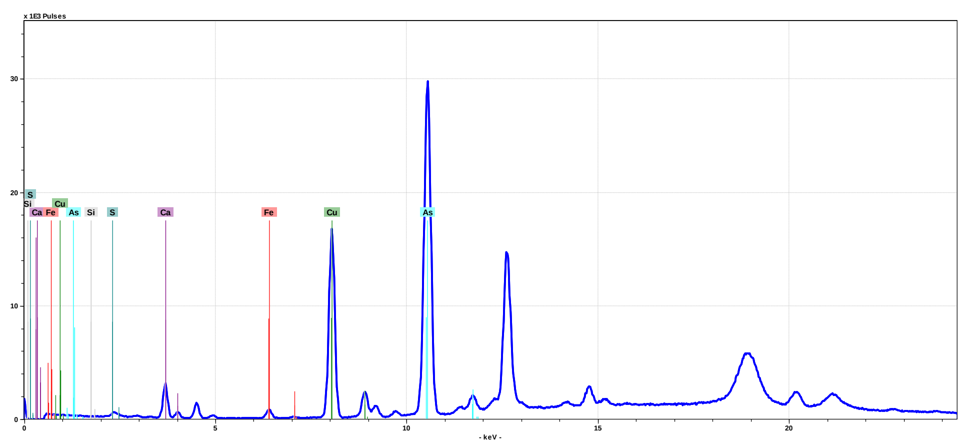
Appendix 2: Some blue spots on folio 63 of this manuscript AKM 6, which have a kind of very dark blue colour. According to the XRF and FORS spectra taken from this spot, it has been created through a combination of azurite and ultramarine.





XRF and FORS spectrums of mixture azurite and ultramarine
used to create dip blue Manuscript AKM 6 folio 63.

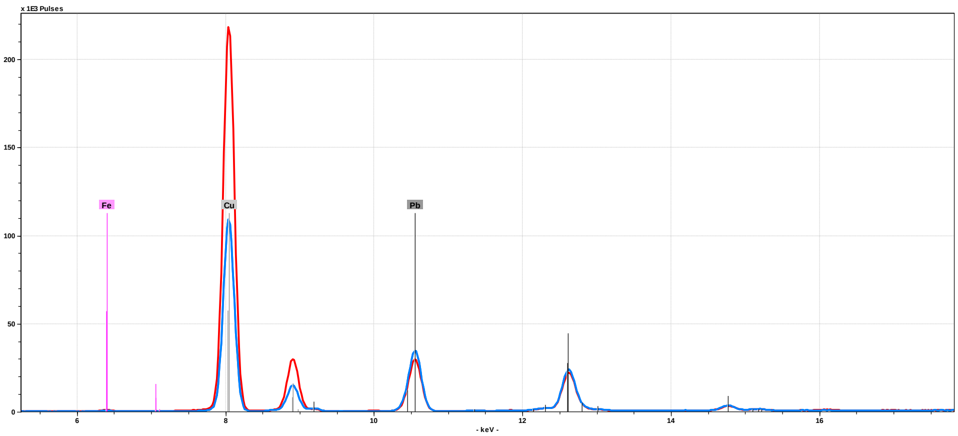
Appendix 3: In manuscript AKM 6 in folio 63 in the XRF spectrum of the yellow spots, in addition to the amount of AS (Orpiment) has been seen a certain peak of Ca and S, which can be a reason for claiming that the painters of this manuscript have combined and used orpiment with gypsum as white colour in order to produce a very bright and pale-yellow colour.



XRF spectrum of pale-yellow colour used in manuscript AKM 6

Appendix 4: In manuscript AKM 6 on folio 64, a copper-based green alone has been used to colour the horse barding. In same manuscript in folios 63, 64, and 92 a colour combining azurite with malachite is used for green.

The interesting point after comparing the XRF peaks of these two colour samples is that the copper peak related to the sample colour combining azurite with malachite (red) is much more intense than the peak of the sample made of copper-based green alone (blue).



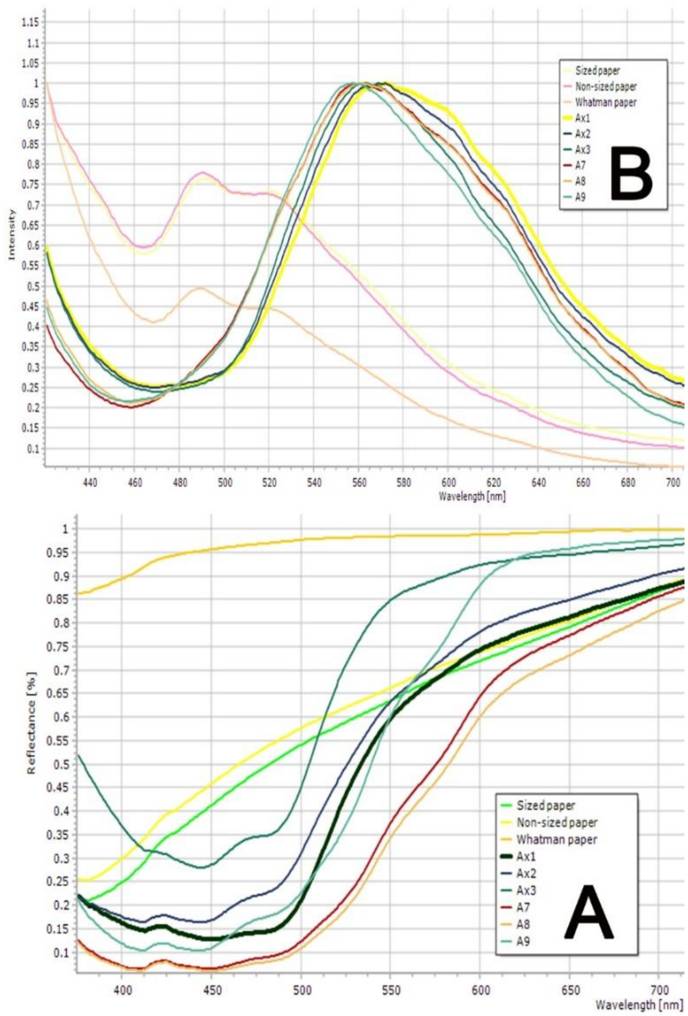
Differences in the amount of Cu in XRF spectrum of two green colour in manuscript AKM 6. Mixture of azurite with malachite (red), copper-based green (blue).

Appendix 5: Hence, for each dye, at least six samples were produced (three dyed samples and three painted samples). After measuring the samples, it became clear that there is no significant difference in FORS and FOMF spectra of the different dyed and painted samples. Therefore, to avoid the presence of spurious signals (noises) in the FORS and FOMF spectra for each dye one spectra have been presented in the main text and her you could see more spectra of each dye samples.

Saffron samples:

Sample name	Dyed	Painted	Sized paper	Non-sized paper	Whatman paper
$A^{x}1$	⁕		⁕		
$A^{x}2$	⁕			⁕	
$A^{x}3$	⁕				⁕
A7		⁕	⁕		
A8		⁕		⁕	
A9		⁕			⁕

List of the reference samples of Saffron analysed by FORS & FOMF

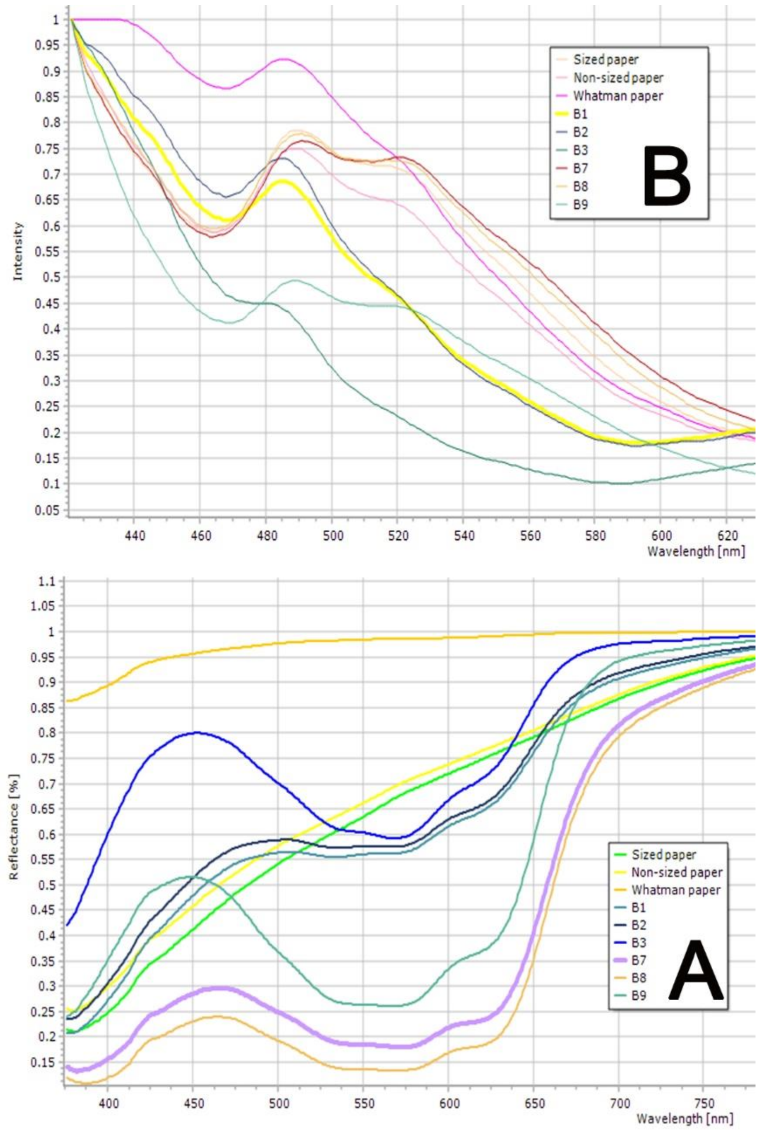


FORS(A) and FOMF(B) spectra obtained of reference samples of Saffron

Mallow samples:

Sample name	Dyed	Painted	Sized paper	Non-sized paper	Whatman paper
B^y1-B1	⁕		⁕		
B2	⁕			⁕	
B3	⁕				⁕
B4		⁕	⁕		
B7		⁕	⁕		
B8		⁕		⁕	
B9		⁕			⁕

List of the reference samples of Mallow analysed by FORS & FOMF



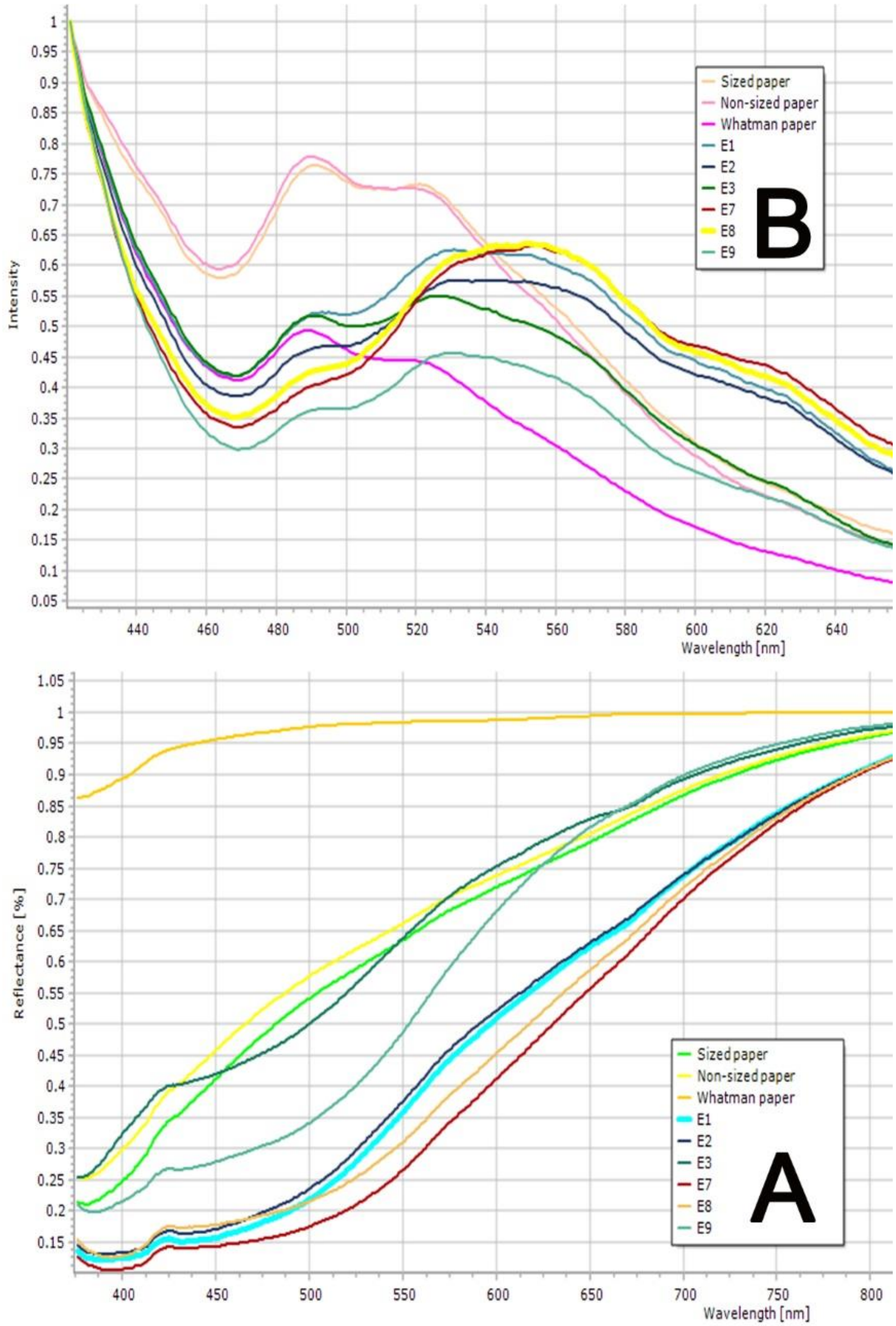
FORS(A) and FOMF(B) spectra obtained of reference samples of Mallow

Henna samples:

Sample name	Dyed	Painted	Sized paper	Non-sized paper	Whatman paper
E1	⁕		⁕		
E2	⁕			⁕	
E3	⁕				⁕
E7		⁕	⁕		

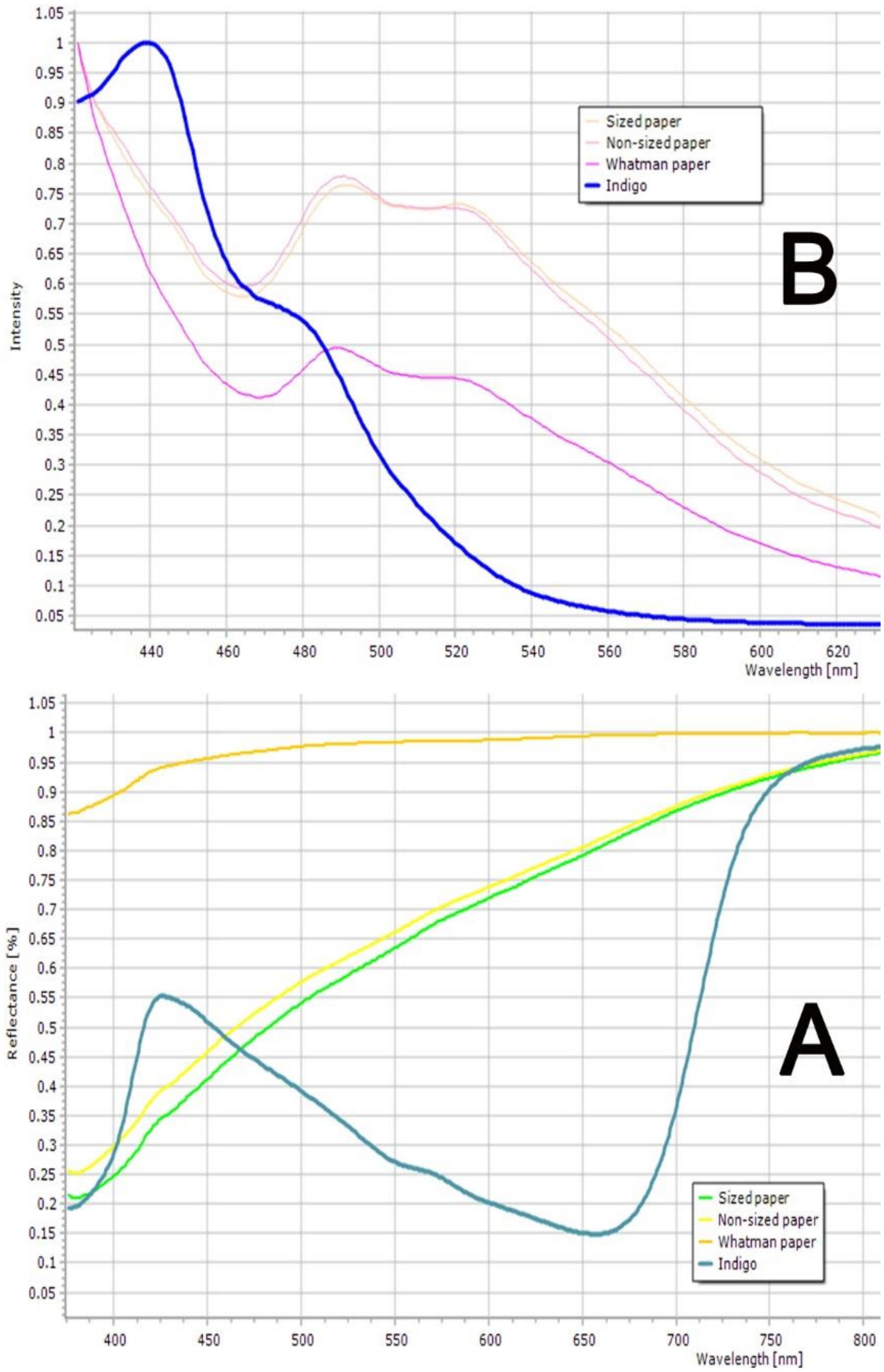
E8		⁕		⁕	
E9		⁕			⁕

List of the reference samples of Henna analysed by FORS & FOMF



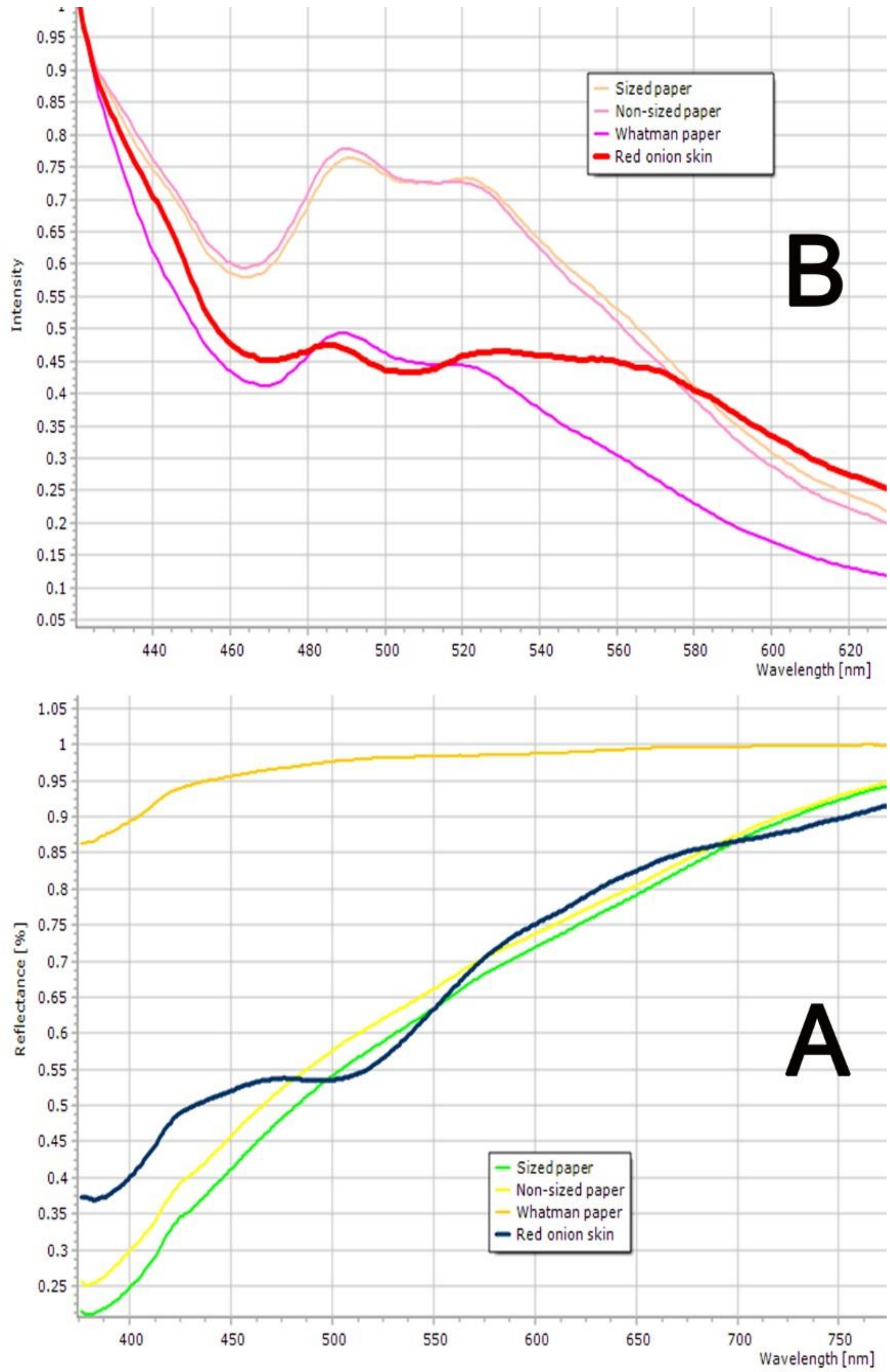
FORS(A) and FOMF(B) spectra obtained of reference samples of Henna

Indigo Sample:



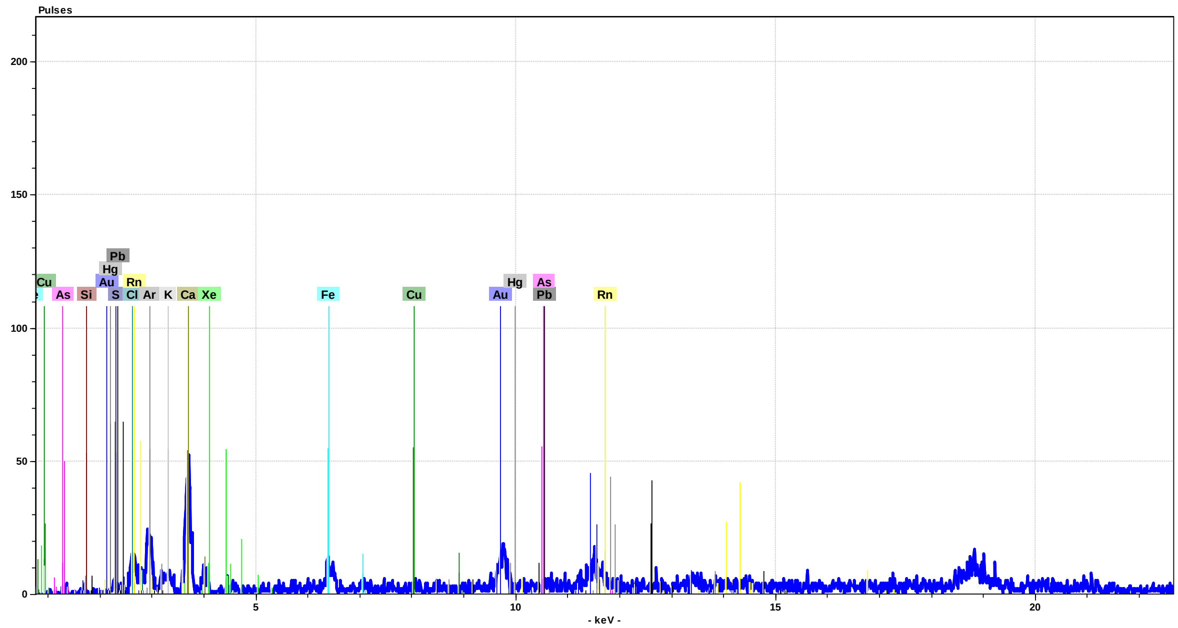
FORS(A) and FOMF(B) spectra obtained of reference samples of Indigo

Red onion skin Sample:

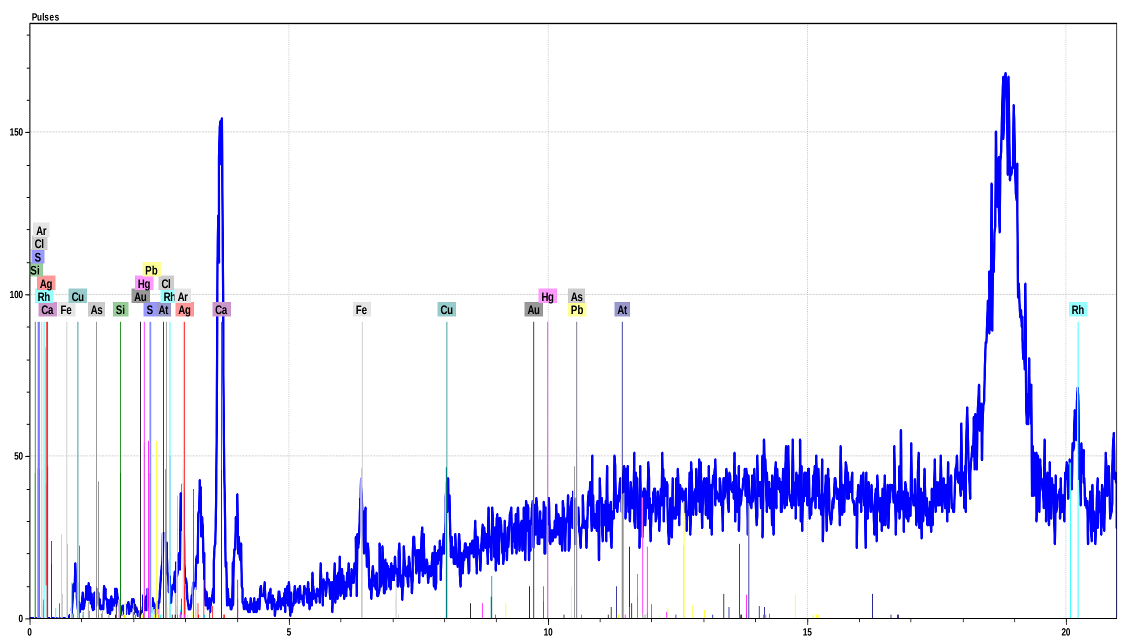


FORS(A) and FOMF(B) spectra obtained of reference samples of Red onion skin

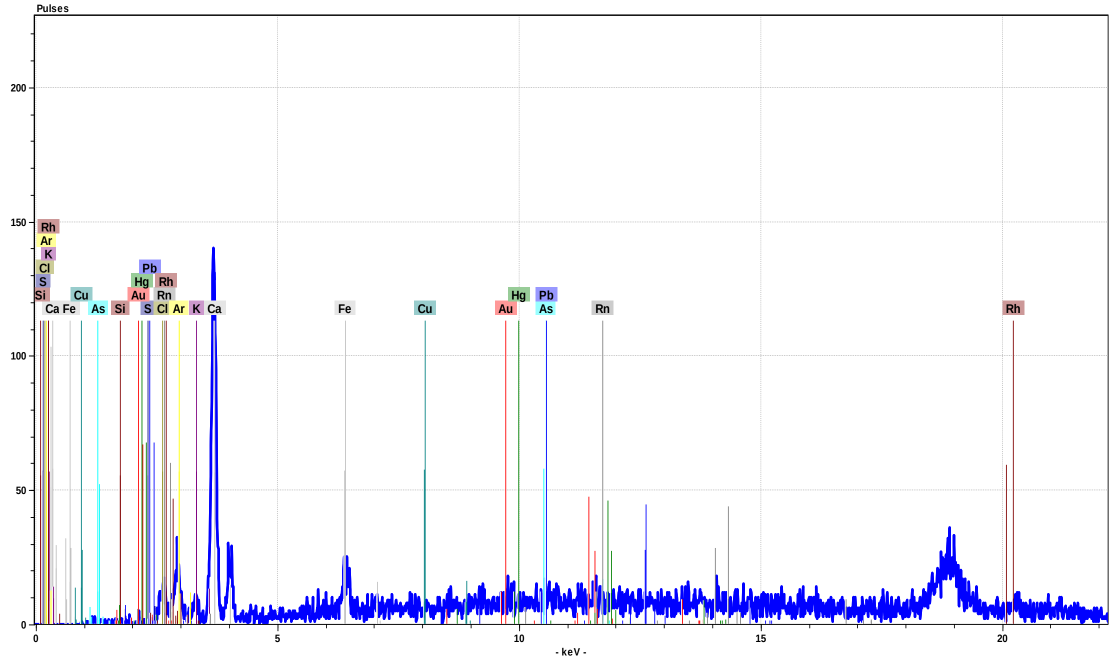
Appendix 6: XRF spectra of paper substrate of manuscripts under studied.



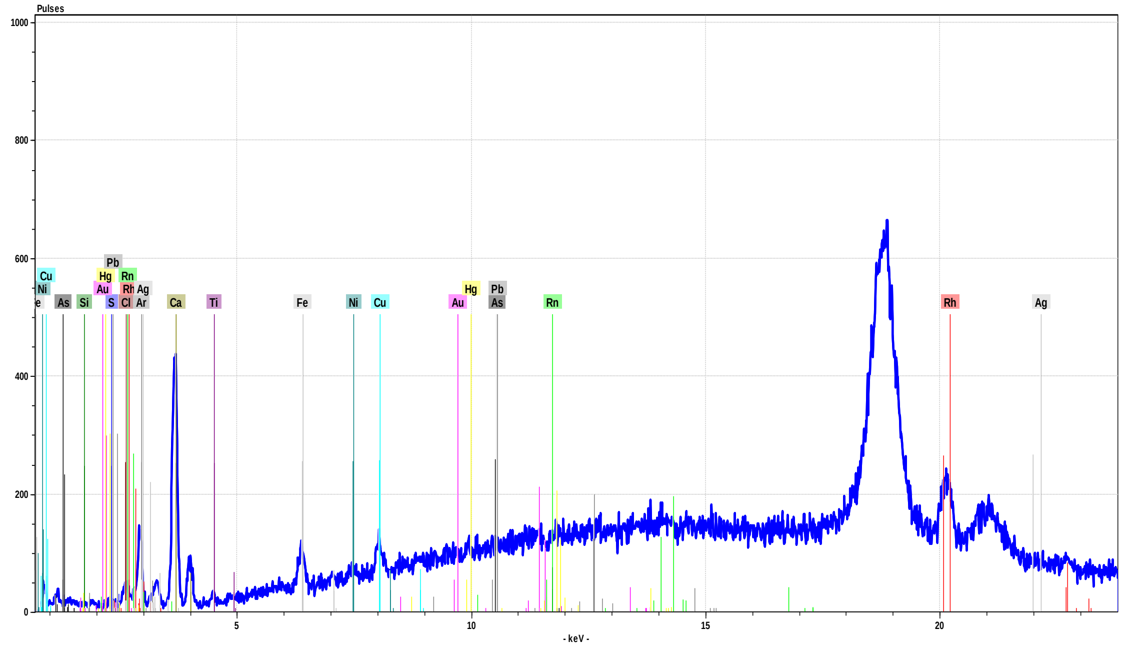
XRF spectra of paper substrate of manuscript RAS 239



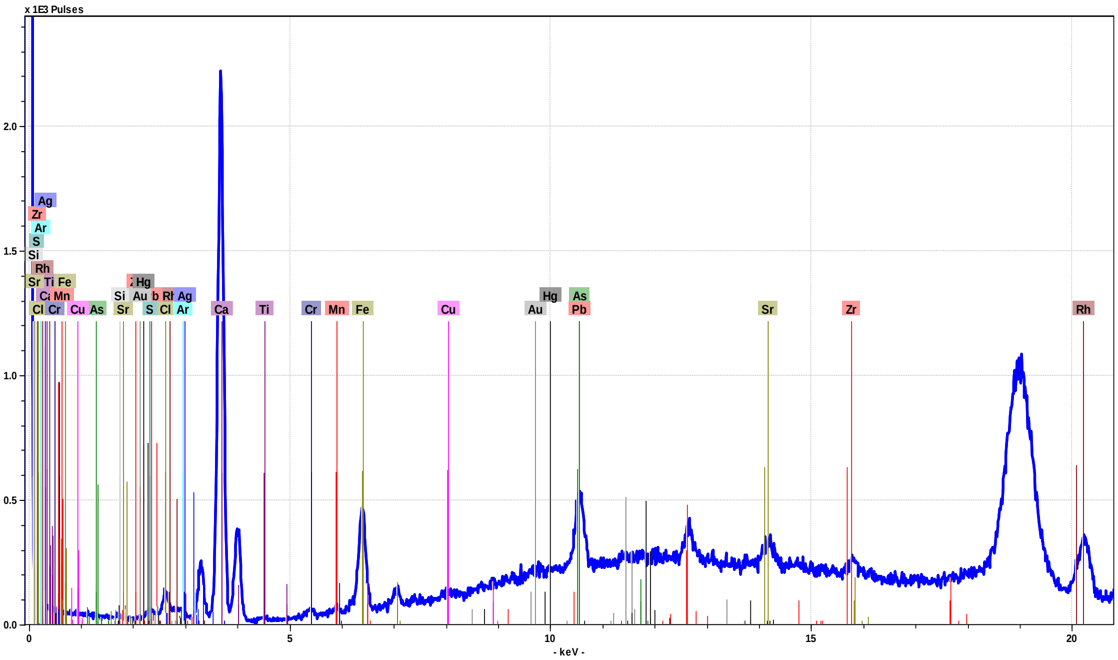
XRF spectra of paper substrate of manuscript Persian 9



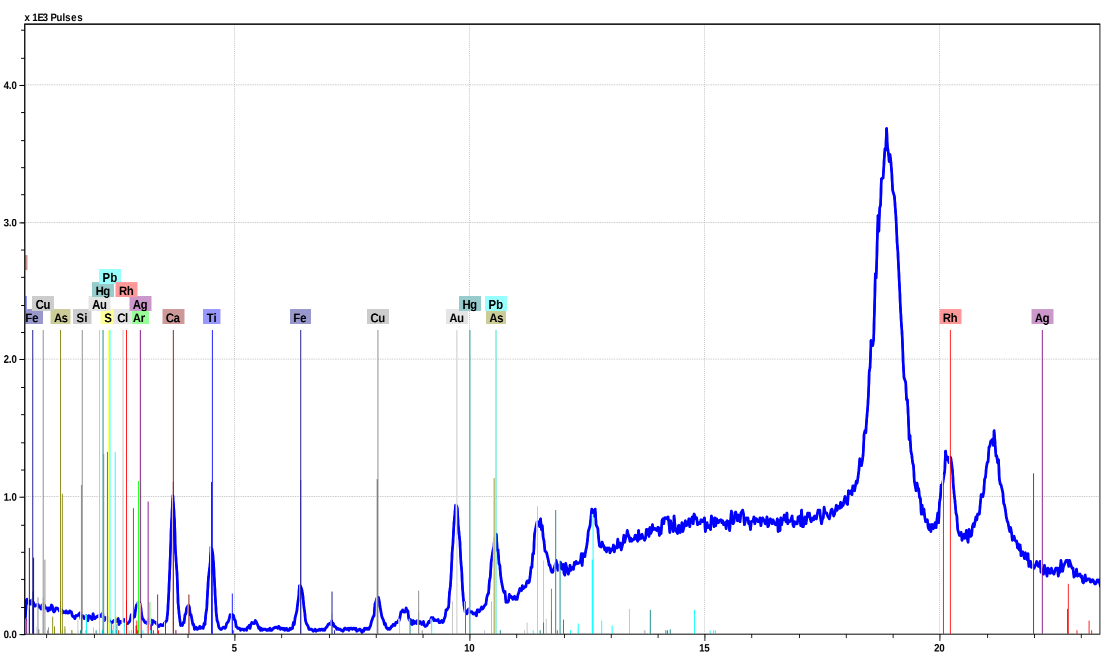
XRF spectra of paper substrate of manuscript Or 420



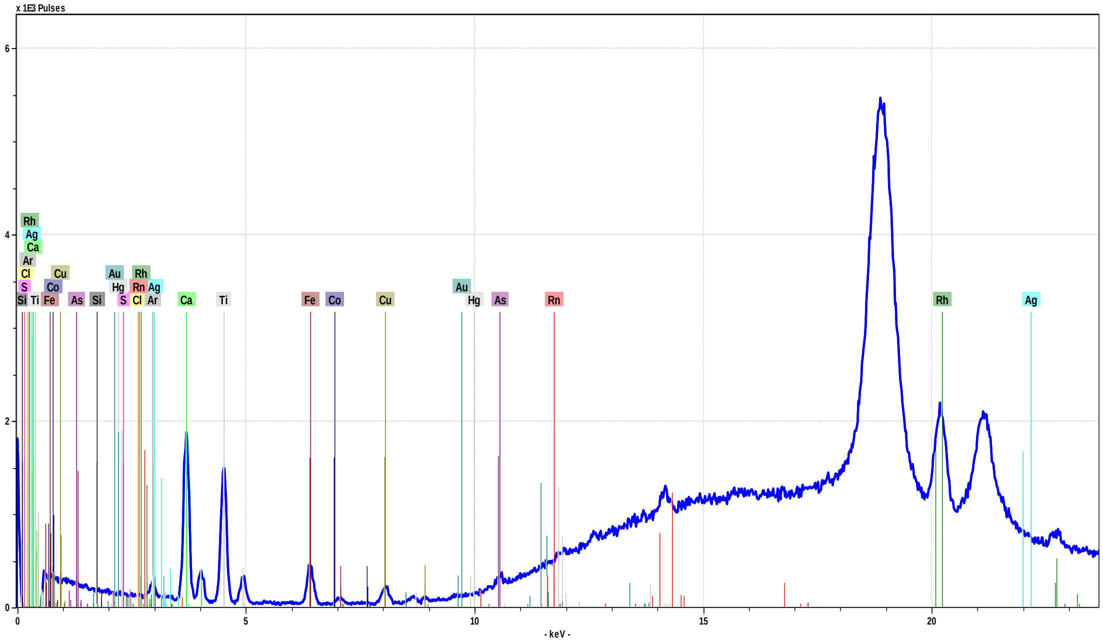
XRF spectra of paper substrate of manuscript Persian 933



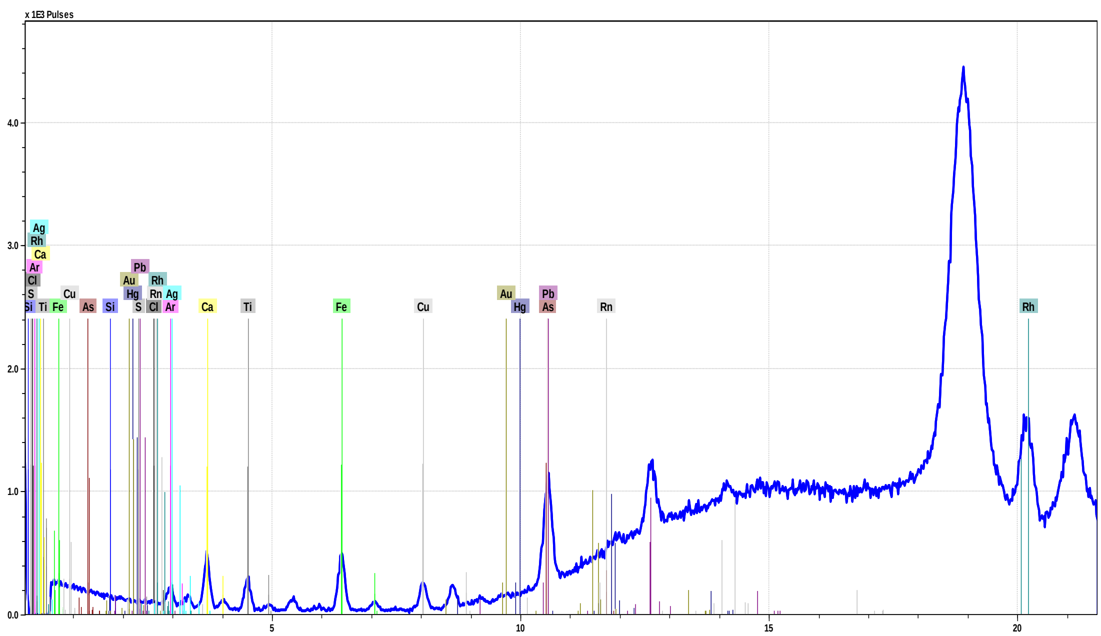
XRF spectra of paper substrate of manuscript MS 22-1948



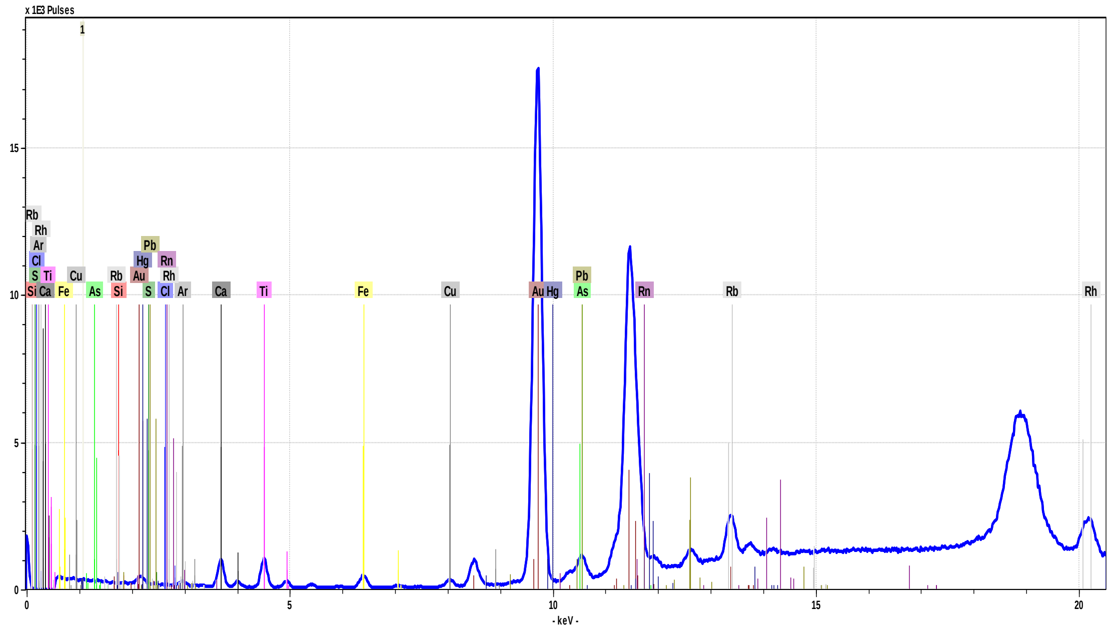
XRF spectra of paper substrate of manuscript AKM 4



XRF spectra of paper substrate of manuscript AKM 5



XRF spectra of paper substrate of manuscript AKM 6



XRF spectra of paper substrate of manuscript AKM 269

Kurzfassung der Ergebnisse der Dissertation

Illustrierte Persische Handschriften gehören zu den wertvollsten Objekten der Islamischen Welt. Eine der wichtigsten Perioden der Entwicklung solcher Handschriften ist das 15. Jahrhundert.

Die Persischen Handschriften des 15. Jahrhunderts wurden im Rahmen kunsthistorischer Studien in verschiedene Kategorien unterteilt. Diese vorhandenen Kategorisierungen ziehen dabei nicht die verwendeten Farbmaterialien der Illustrationen in Betracht, da diese bisher nicht Gegenstand der Untersuchungen waren. Diese Lücke in den Forschungsdaten über die illustrierten Persischen Handschriften des 15. Jahrhunderts aus dem Iran führte bisher zu einer deutlich spürbaren Einschränkung der Forschungsarbeiten. Die Bestimmung und der Vergleich der verwendeten Farbmaterialien in den verschiedenen Städten und Werkstätten offenbart zahlreiche Daten und Schlussfolgerungen auf den Gebieten der Persische und Islamische Kunst, der Kulturwissenschaften, der Kunstgeschichte und verwandter Disziplinen. Weiterhin sind diese Informationen von großer Relevanz für den Erhalt und die Restauration dieser Handschriften. Die vorliegende Arbeit kann als eine Pionierarbeit auf dem Gebiet der Bestimmung und des Vergleiches der Farbmaterialien Persischer Handschriften verschiedener Städte und Werkstätten dieses spezifischen Zeitrahmens angesehen werden.

Basierend auf den genannten Fakten waren die Hauptziele dieser Arbeit die Stoffe der Farbpalette der illustrierten Persischen Handschriften des 15. Jahrhunderts zu bestimmen, und einen Vergleich zwischen den Städten anzustellen, insbesondere der Städte Herat und Shiraz. Weiterhin sollten auch verschiedene Werkstätten des 15. Jahrhunderts verglichen werden.

Zum Erreichen der genannten Ziele der Arbeit mussten geeignete Handschriften zur Untersuchung ausgewählt werden, wobei der Herstellungszeitpunkt, der Herstellungsort und die Herstellungswerkstatt als Kriterien in Betracht gezogen wurden. Die Wahl fiel auf neun Handschriften des Schāhnāme, da diese alle erforderlichen Kriterien erfüllen.

Es muss angemerkt werden, dass die untersuchten Handschriften allesamt aus dem 15. Jahrhundert stammen, aber auch Illustrationen aus dem 14. und 16. Jahrhundert enthalten, welche ebenfalls untersucht wurden. Weiterhin wurden neben Illustrationen aus den Städten Herat und Shiraz auch Bilder aus Qazvin und Lahidschan, sowieso einige Indische Illustrationen untersucht (siehe Tabelle 1-1).

Die Methoden zur Bestimmung der Farbmaterialien mussten nicht nur nicht-invasiv und portabel sein, sondern auch eine ausreichende Geschwindigkeit aufweisen um statistisch signifikante Datenmengen zum Vergleich verschiedener Farbmaterialien erheben zu können. Hierzu fiel die Wahl auf eine Kombination aus nicht-invasiven FORS, FOMF und p-XRF (siehe Kapitel 3).

Als Teil dieser Arbeit wurde das Potential dieser kombinierten Analysemethode zur Bestimmung von Pigmenten und organischer Farbstoffe untersucht, diese Ergebnisse werden in Kapitel 6 erläutert (Abschnitt 6-3). Da Röntgenfluoreszenz (XRF) eine bereits etablierte Methode ist, wird dabei besonders auf den gemeinsamen Einsatz von FORS und FOMF eingegangen. Im Anschluss wird die Nachweisbarkeit einiger Farbmaterialien mittels dieser kombinierten Methoden im Abschnitt 6-3 detailliert ausgeführt.

Derzeitige Untersuchungen der Farbmaterialien Persischer Handschriften konzentrieren sich auf Farbpigmente, wohingegen nur wenige Untersuchungen organische Farbstoffe bestimmen. Dies ist damit zu begründen, dass organische Farbstoffe nur sehr schwierig mit nicht-invasiven Methoden nachweisbar sind.

Eine mögliche, aber eingeschränkte Methode zur Bestimmung von organischen Farbstoffen in Handschriften ist die Kombination von FORS und FOMF. Diese Methode wird allerdings nur selten angewendet, da Referenzspektren für die verwendeten Farbstoffe nicht verfügbar sind. Um diesen Mangel zu beheben wurde eine Datenbank mit FORS und FOMF Referenzspektren möglicher Farbstoffe angelegt. Die Referenzfarbstoffe wurden gemäß traditioneller Rezepturen hergestellt (siehe Kapitel 4).

Im fünften Kapitel dieser Arbeit werden die Ergebnisse der durchgeführten Messungen dargelegt. Zunächst werden die Messdaten der untersuchten Handschriften individuell ausgewertet und interpretiert, diese Resultate werden in Kuchen- und Säulendiagrammen präsentiert. Im Anschluss werden diese Ergebnisse zwischen den Städten verglichen. Am Ende des Kapitels werden in einer Zusammenfassung auch Vergleiche basierend auf dem Farbton der Farbstoffe angestellt.

Im sechsten Kapitel wird eine umfassende Palette der in Persischen Illustrationen verwendeten Farbmaterialien präsentiert und in einem der Vergleich der verschiedenen Städte, Werkstätten und Zeiträume zusammengefasst. Hierzu wurde, um alle relevanten Aspekte zu repräsentieren, ein Darstellungssystem für die Ergebnisse dieser Arbeit entworfen. In diesem System werden Kuchendiagramme für jeden Farbton erstellt um die gemeinsamen und variablen Farbmaterialien der verschiedenen historischen und regionalen Klassen einfach darzustellen (Abbildung 6-1).

Anschließend wurde anhand der aus dem Vergleich der Farbmaterialien gewonnenen sowie anhand von historischer und kodikologischer Informationen die Wichtigkeit und Stellung der Werkstätten untersucht. Hierbei wurde auch ein Versuch unternommen, die hauptsächlichen Unterschiedliche zwischen königlichen und anderen Werkstätten festzustellen.

Weiterhin wurden Messungen an vier turkmenischen Handschriften durchgeführt, welche zusammen mit kunsthistorischen Informationen zu turkmenischen Handschriften zur Untersuchung der Konzepte turkmenischer Handelsschriften dienen.

Summary of the results of this dissertation

Illustrated Persian manuscripts are among the most precious artistic objects in the Islamic world and one of the most important periods for the development of Illustrated Persian manuscripts is the 15^{th} century.

Persian manuscripts produced in the 15^{th} century have been studied and classified into different categories by art historians. However, the paintings included in different categories have never been studied in terms of the colour materials used. Obviously, the vacancy of such a study on illustrated Persian manuscripts of the 15^{th} century in Iran was very felt. Identifying and comparing the colour materials used in different cities as well as various workshops includes very useful information for the Persian/Islamic arts, cultures studies, art history, and related disciplines. In addition, this information is very fruitful in the protection and restoration of these manuscripts. This study can be considered as the first study to investigate and compare the colour materials used in Persian manuscripts of different cities and workshops in a specified timeframe.

Based on mentioned points the main aims of this study were identifying the colour palette of 15^{th} century illustrated Persian manuscripts, compare the colour materials used in manuscripts of different cities, especially the cities of Herat and Shiraz, and compare the colour materials used in different manuscripts production workshops in the 15^{th} century.

According to the objectives of this study, for selecting the manuscripts understudy, the place of production of these manuscripts, the date of their production, and the workshop of production of manuscripts was considered. Since Shāhnāma manuscripts have all the required features to achieve the aims of this study all nine analysed manuscripts are Shāhnāma manuscripts.

It should be noted that all the manuscripts analysed in this study belonged to the 15th century. Some of these manuscripts had paintings from the late 14th and 16th centuries, which were also studied. On the other hand, except for paintings related to the cities of Herat and Shiraz, paintings belonging to Qazvin and Lahijan, as well as several Indian paintings were also studied (see table 1-1).

To identify colour materials used in the manuscripts under study it was needed non-invasive rapid and portable analysis techniques to give us a larger statistical set to compare colour materials. Therefore, to identify colour materials, non-invasive combined analytical method of FORS, FOMF and p-XRF was used (see chapter 3).

During this study, the capabilities of this combined analytical method to identification pigments and dyes were examined and the result of this study are presented in chapter 6 (section 6-3). Since XRF technique is very well known, the capabilities of FORS and FOMF methods are further described when used together. Then, the capabilities of this combined analysis technique for the detection of some colour materials are explained in detail in sections 6-3.

Is quite obvious in studies on colour materials used in Persian manuscripts, less work has been done on the identification of dyes. Because identifying dyes with non-destructive methods is very difficult.

One of the limited non-destructive methods available for identifying dyes in manuscripts is the combination of FORS and FOMF methods. However, the lack of spectrum reference samples for dyes used in Persian manuscripts has caused these methods to be used less in the diagnosis of dyes. Therefore, to compensate for this lack the FORS & FOMF spectral database of some dyes possibly employed in Persian manuscripts is created in this study based on dyes recipes indicated in the traditional treatise (see chapter 4).

In the fifth chapter of this thesis, the results of the analysis performed in this study on manuscripts have been investigated. Firstly, the results of each manuscript analysis have been studied separately and the result of interpretation of the analysis performed on each manuscript has been presented in a percentage chart (Pie chart) as well as in a column chart. Then, the results of the colour material analysis used in each city are compared with other cities. At the end of this chapter, the results of the comparisons made in the form of a Summery are expressed. In this summary, comparisons have been made based on different colour tonalities and a diagram is displayed for each colour tonality.

In chapter 6 while presenting a coherent palette of colour materials used in Persian paintings, a summary of the results obtained by comparing the colour materials used in paintings of different cities (schools) at different times is presented. Therefore, considering all aspects, a system was designed to represent the results obtained in this study. In this system, a pie chart is considered for each colour tonality to provide a clear understanding of common and variable colour materials used in different historical and regional classifications (see Figure 6-1).

Then, based on information obtained from the comparison of colour materials in this study and historical and codicological information on the status of manuscript production workshops, the importance of manuscript production workshops was investigated. It was also tried to express the major differences between royal workshops of manuscript production and other workshops.

Furthermore, based on the analyses performed in this study on four Turkman manuscripts and the information of art history in the field of Turkman manuscripts, the concept of Turkman and Turkman commercial style manuscripts has been investigated.