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Material and Technical Analysis of Armenian Wall Paintings in New Julfa, Isfahan

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I shall build a boat,

I shall cast it in the water.

I shall sail away from this strange earth

Where no one awaken the heroes in the wood of love.

I shall continue sailing.

I shall continue singing.

Beyond the seas there is a town

Where the sun is as wide as the eyes of early risers.

Poets inherit water, wisdom and light.

Beyond the seas there is a town!

One must build a boat.

Sohrab Sepehri (1928 – 1980)

To my loving Mom, Soori

To my dear Dad, Majid

To my wonderful sisters

Spanta & Armita

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Anahita Sasani
Ferrara, 2015

Glossary of Terms

AD	Anno Domini
BC	Before Christ
BCE	Before the Common Era
BM	British Museum
CE	Common Era
EDX	Energy Dispersive X-ray
FT-IR	Fourier Transform Infrared
ICHHTO	Iranian Cultural Heritage, Handcrafts and Tourism Organization
IR	Infrared
IRUG	Infrared & Raman Users Group
PMA	Philadelphia Museum of Art
SEM	Scanning Electron Microscopy
SH	Solar Hijri
WACC	Williamstown Art Conservation Center
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

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CHAPTER ONE

1. Introduction

> *"We see not just painted surfaces, but are given a multi-disciplined information which brings the painting themselves to life." (Forester, 1990)*

1.1. Scope of study

Within the context of the conservation profession, technical study of all varieties of historical artefacts has become commonplace, especially for painting and polychromy (Nadolny, 2003, p. 39). "The desire to know more about the whole" wall painting and "to get behind the picture, and even through it, is very much a feature" of every cultural heritage study. "Finding the real information hiding behind" (Carlyle, 1995, p. 1) the appearance of artworks is one of the most important field of cultural heritage and artefacts.

On the other hand, "the definition of a painting technique is often based on macroscopic observations and on the experience of art historians, archaeologists and conservators, although in the past 20 years scientific approaches have been increasingly applied, including microtextural, microstratigraphic and chemical analyses" (Piovesan, Mazzoli, Maritan, & Cornale,2012, p.724).

Therefore, the focus of this thesis is the materials of Armenian wall paintings, especially their pigments in three churches and one house in New Julfa (Nor-Djulfa)-Isfahan in 17th century. According to the discussion, "New Julfa has been noted for its Armenian churches, which by the end of the seventeenth century numbered thirty. Thirteen of these edifices, built during the years of 1607-64, have survived to this day" (Sanjian, 1999, p. 42).

Also, there are some few Armenian houses in the New Julfa district which all of these buildings present image of a mixture of Armenian and Iranian styles. Therefore, they have an important rule for study about Armenian-Iranian art and architecture in Isfahan. The decorations and wall paintings of these buildings, also, are worthwhile proof of the combining Eastern and Western art in the seventeenth century.

The European style of 17th century paintings of Iran could be a result of trade connection between Armenian merchants of New Julfa with different countries and the role of Armenians as the deputies of Safavid court in European countries. Because the Julfan merchants "were arguably the only Eurasian community of merchants to operate simultaneously and successfully across all major empires of the early modern period[1]… [Furthermore], between all Asian communities of merchants operating across the Indian Ocean…the Julfans [were] possibly the only Asian community [that] left a trail of documentation…written by themselves [which still exists]" (Aslanian, 2011, pp. 3-4).

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[1] Including the three "gunpowder empires" of Islamicate Eurasia (Mughal, Ottoman and Safavid), Muscovite Russia, Qing China and all the major European seaborne empires (the Portuguese, Spanish, British, Dutch and French (Aslanian, 2011, p. 3).

The evidence of these international activities can be found in the European style wall paintings in the Armenian churches and houses in New Julfa. It must be considered that at the same time, "Persian painting did not try to reproduce a model from nature but to represent an archetype" (Porter, 2000, p.113).

The aim of this research, therefore, is to investigate the interaction of Iranian, Armenian, and European styles in the wall paintings of New Julfa, through pigment analysis. Because the absence of knowledge about material compounds makes problem for correlation of these painting styles. It is hoped that this study and others like it, will help to determine what Armenian-Iranian artists actually used by examining the art works with scientific analytical equipment.

1.2. Rational for the Studies and Reasons for Undertaking the Analysis

Studying of Armenian palette has been done numerously on their illuminated manuscripts but not about Armenian wall paintings. Also there are different sources which described Armenian palette since old ages by analysing the Armenian illuminated manuscripts. Therefore, the pigment analysis was carried out chiefly to:

- Provide a complete description of the 17th century Armenian wall paintings by identification of each pigment;

- Establish the palette of the Armenian wall paintings with respect to Iranian traditional palette based on two old treatises; Gulistan-i Hunar [Rose Garden of Art] by Qadi Ahmad (1596-1606 or 1608) and Qanun us-Suvar (Canons of Painting or forms) by "Sadiqi Bek Afshar (sometime between 1576 and 1602);

- Determine whether or not the collaboration between Armenian and European artists, through technical analysis to find different influences of European artists. This could be supported by examination of Armenian working methods and choice of materials;

- Gain more information about some wall paintings in different Armenian buildings by technical analysis rather than rely on only written or oral information of that period.

1.3. Experimental Procedure

1.3.1. Sampling

In the first step, taking samples and choosing sampling locations must be done by considering the ethical factors. During this project, samples from different buildings were collected by permission of Armenian Council of Churches in Isfahan. All samples were taken from accessible areas[2] of wall paintings. According to the Iranian Cultural Heritage, Handcrafts, and Tourism Organization (ICHHTO), the selected paintings were not previously restored in recent years and the pigments

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[2] Even by using a scaffold till the dome and dome-drum of the church, those area became accessible.

could be considered genuine.[3] There were some limitations for collecting samples from the buildings but an important point was that collecting specimens was done without further damaging the painting and they were taken from flaking zones. For this project, forty- one samples were collected from seven Armenian wall paintings.

1.3.2. Samples' preparation

Considering the size and form of the samples, cross sections were provided for those samples which had that possibility. All samples were studied by polarized microscope and numerous images with different magnifications were provided of them.

1.3.3. Techniques Applied to Samples

"The only possibility available to those interested in ancient technique, apart from the historical texts, [is] examination of the works of art themselves through…[analysis and] experimentation" (Nadolny, 2003, p. 39). The identification of the different pigments used in the historical wall paintings is one of the most valuable issues in the study of paintings and archaeometrical methodologies. Furthermore, "the accurate identification of pigments in artistic and historic works is of great importance for determining the construction, history, and future preservation of these works" (Trentelman, Stodulski, & Pavlosky, 1996, p.1755-1758).

"The analysis of the pigments contained in [wall paintings] can be approached in various ways. The final decision regarding approach must be made on the basis of availability of samples, the equipment at the disposal of the analyst, and the amount of information that can be gained" (Mathews & Sanjian, 1991, p. 48). Pigment identification was done through different analyses which it can be classified as follows:

X-ray fluorescence analysis (XRF); Micro Raman spectroscopy; Fourier Transform Infrared (FTIR) spectroscopy; some pigments which needed to be more studied were also analysed by using Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray spectrometer (EDX) and X-ray Diffraction (XRD).

1.4. Research Framework

The research presented here, organized into ten chapters that cover the previously mentioned issues. The framework of the thesis is outlined below:

A descriptive overview of the historical context of the study, mostly about Armenian history, presence of Armenian people in Iran, the Armenian great migration to New Julfa, and the role of Armenian merchants in the Safavid court is provided in second chapter.

Chapter 3 investigates the formation of Armenian architecture through shapes of buildings, most common masonry material in architecture, Armenian churches in Armenia and Iran, and Armenian houses in New Julfa.

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[3] However, more investigation about these wall paintings showed different interventions in them which had happened during several years.

Chapter 4 is about the Iranian and Armenian paintings and palettes of pigments. The information about Iranian wall paintings and Armenian pictures, mosaics and illuminated manuscripts helped to improve this part of the study. Persian palette based on historical treaties and Armenian palette trough documents about their illuminated manuscripts are presented.

In chapter 5, examination of wall paintings by scientific methods, classification of some important pigments, sample preparation, and analytical techniques are the main subjects. Furthermore, the experimental methods, details about the instruments and theirs settings are provided.

Chapters 6 to 9 dedicated to introduce the case studies, experimental approaches, results and discussions about each sample.

Chapter 10 contains the final conclusions from the data.

CHAPTER TWO

2. Historical Studies

2.1. Armenian History

According to Armenian History (1999):

> Contemporary scholarship suggests that the Armenians are descendants of various indigenous people who meld (10th through 7th century BC) with the Urarteans (Ararateans); while classical historians and geographers cite the tradition that the Armenians migrated into their homeland from Thrace and Phrygia, or even Thessaly. These views are not necessarily contradictory, since present-day Armenians are undoubtedly an amalgam of several peoples…and immigrants who emerged as one linguistic family around 600 B.C.…The first written records to mention the inhabitants of Armenia come from hieroglyphs of the Hittite Kingdom, inscribed from 1388 to 1347 B.C., in Asia Minor. The earliest inscription to be found directly upon Armenian lands, carved in 1114 B.C. by the Assyrians, describes a coalition of kings of the central Armenian region referring them as "the people of Nairi".
>
> By the 9th century B.C., a confederation of local tribes flourished as the unified state of Urartu. It grew to become one of the strongest kingdoms in the Near East and constituted a formidable rival to Assyria for supremacy in the region. The Urartians produced and exported wares of ceramic, stone and metal, building fortresses, temples, palaces and other large public works. (para. 1 & 3-4)

Gregorian's (1996) study shows that:

> Throughout history Armenia has been a battlefield for many invaders, contending empires, and a bridge for many cultures and civilizations. During the past…years, Armenia was conquered by the Persian Empire, Alexander the Great, the Roman Empire,

> Byzantium, the Arabs, Seljuqs, Mongols, Tatars, the Ottoman Empire, Safavid Persia, and the Russian Empire.
>
> Armenian kingdoms, principalities and even a short-lived empire (95-55 B.C.) managed to survive and thrive for some 1,700 years. Under various kings and princes, the Armenians developed a sophisticated culture, an original architecture and their own national alphabet….The Seljuq conquest of the last Armenian kingdom in the 11th century marked the beginning of an exodus of the Armenians from historical Armenia resulting in the advent of an Armenian Diaspora. As a result of this migration, an Armenian kingdom was established on the shores of the Mediterranean, in Cilicia[1]. This kingdom, often an ally to the West during the period of the Crusades, absorbed Frankish culture. The kingdom fell in 1375, ending the independence of the Armenian Statehood. (para. 1-2)

2.2. Armenian presence in Iran

A study by Garsoian (2004) found that:

> The appearance of Armenian literature in the second half of the fifth century CE, in the generation which followed the great revolt of the Armenian nobles in 450 against Yazdgird II's attempt to re-impose Zoroastrianism on their already Christian country, resulted in its almost total obliteration of Armenia's ties to the Iranian world. The ideology of its exclusively Christian, ecclesiastical authors reiterating that the Armenian self-image was Christian by definition, simultaneously obscured any memory of the country's earlier past. Consequently, Armenian sources, particularly in the case of Iran, must often be read as through a distorting mirror. Persian sources are all but non-existent except for brief

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[1] Cilicia, ancient district of southern Anatolia, bounded on the north and west by the Taurus Mountain Range, on the east by the Anti-Taurus, and on the south by the Mediterranean Sea.
(Cilicia | ancient district, Anatolia. (n.d.). Retrieved February 10, 2014, from http://www.britannica.com/EBchecked/topic/117794/Cilicia)

> references in early inscriptions, to which late Sasanian seals add occasional, mostly administrative, details. Chance references in classical sources are often inaccurate or hostile….Nevertheless, even in the face of such obstacles, no serious study can avoid recording the fundamental elements linking pre-Islamic Armenia to Iran, especially in the crucial, if occasionally subliminal, cultural aspects which were to survive the political vicissitudes of more than a millennium from the 6th century BCE to the mid-7th century of the Christian era. (para. 1-2)

2.2.1. Presence of Armenian in Iran before Islam

In Armenian history (1999), it has been mentioned that:

> In the 6th century Urartu[2] fell to the Medes[3], but not long after, the Persian conquest of the Medes, led by Cyrus the Great, displaced them. Persia ruled over Armenia from the 6th century until the 4th century B.C. Its culture and Zoroastrian religion greatly influenced the spiritual life of the Armenian people who absorbed features of Zoroastrianism into their polytheistic and animistic indigenous beliefs. (para. 4)

Also according to Garsoian (2004):

> The first written evidence for the name of the plateau at the easternmost edge of Anatolia, an area increasingly dominated by the Indo-European speakers whom Herodotus, would call "Armenioi," comes from the late 6th century BCE; Darius I's Bisotun

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[2] Urartu was one of several first millennium B.C. states that came into existence and prominence in Anatolia (modern Turkey) after the destruction of the Hittite state around 1200 B.C. (Retrieved February 10, 2014, from http://www.metmuseum.org/toah/hd/urar/hd_urar.htm)

[3] Mede, one of an Indo-European people, related to the Persians, who entered northeastern Iran probably as early as the 17th century bc and settled in the plateau land that came to be known as Media. (Retrieved February 10, 2014, from http://www.britannica.com/EBchecked/topic/372077/Mede)

> (Behistun) inscription refers to it as "Armina". According to Herodotus, Armenia was part of the Achaemenid Empire, of which it formed the satrapy XIII.

"It brought Armenia into the Iranian socio-politico-economic orbit, and it became a satrapy of the empire under the first semiautonomous Armenian dynasty, the Orontids (in Avestan, aurand, mighty hero, in Pahlevi, arvan, in Armenian, ervand), who were related to the Persian royal house" (Papazian, 2001, para. 7).

Also "Xenophon would mention a "palace of the satrap" in one of the villages he passed in the tribal, non-urban land crossed by his army in its retreat from Mesopotamia to the Black Sea" (Garsoian, 2004, para. 3). Therefore "as part of the Persian Empire, Armenia also was divided into provinces (satrapies), each with a local governing satrap (viceroy) supervised by a Persian" ("Armenian History," 1999, para. 5).

"The actual relationship of Armenia to Iran under the Achaemenids is not altogether clear, since Darius's inscription at Susa lists Armenia among the countries which "Ahuramazda bestowed upon me" (Garsoian, 2004, para. 3).

Figures 2.1 & 2.2. Apadana relief showing Armenian subjects representing their sovereign with their Gifts - Nowruz Ceremony at Persepolis, ceremonial capital of Achaemenid Empire 500 BCE. (Photo by: M.Koliaei)

Bournoutian's (1994) study found that:

> Prior to the third century A.D., Iran had more influence on Armenia's culture than any of its other neighbors. Intermarriage among the Iranian and Armenian nobility was common. The two peoples shared many religious, political, and linguistic elements and traditions and, at one time, even shared the same dynasty. Sasanian policies and the Armenian conversion to Christianity, in the fourth century, however, alienated the Armenians from Zoroastrian Iran and oriented them toward the West.

Actually, "After the fall of the Sasanian empire in the middle of the seventh century A.D the Armenians came for a long period under the influence of Islamic masters…but…[it] did not greatly affect Armenian culture and language since the Armenians remained firmly Christian" (Schmitt & Bailey, 2011) .

2.2.2. Presence of Armenian in Iran after Islam

Bournoutian (1994) mentioned that:

> The Arab conquests which ended the Iranian Empire and the conversion of Iran to Islam in the seventh century culturally separated the Armenians even further from their neighbor. In the eleventh century, the Seljuk Turks drove thousands of Armenians to Iranian Azerbaijan, where some were sold as slaves, while others worked as artisans and merchants. The Mongol conquest of Iran in the thirteenth century enabled the Armenians, who were treated favourably by the victors, to play a major role in the international trade among the Caspian, Black, and Mediterranean seas. Armenian merchants and artisans settled in the Iranian cities bordering historic Armenia. Sultanieh, Marand, Khoi, Saimas [Salmas], Maku, Maraghe, Urmia, and especially Tabriz, the Mongol center in Iranian Azerbaijan, all had, according to Marco Polo, large Armenian populations.

2.2.2.1. Depopulation of Armenia

> Tamerlane's invasion at the end of the fourteenth century and the wars between the "Qara Qoyunlu" Black and "Aq Qoyunlu" White Sheep Turkmen dynasties in the fifteenth century had a devastating effect on the population of historic Armenia. The latter part of the fifteenth century witnessed the weakening of the White Sheep and the attempts of the Ottoman sultan, Bayazid 11 (1481-1512), to take advantage of the situation and to extend his domains eastward into Armenia and northwestern Iran. At the dawn of the sixteenth century, however, Iran was unified under a new dynasty, the Safavids (1501-1732) and after some nine centuries once again acquired the sense of nationhood which has continued into the present.

"The Safavids assumed importance during the early fourteenth century when Sheikh Safi ad-Din established his Sufi order" (Bournoutian, 1994) "among Turkish speaking people of west of the Caspian Sea, at Ardabil. The Safavid order survived the invasion of Timur to that part of the Iran in the late 13th century. By 1500 the Safavids had adopted the Shi'a branch of Islam" (Ghasemi, 2012) "and began gathering support among the Turkmen tribes of northwestern Iran and eastern Anatolia. The order obtained the support of a number of major Turkic tribes, who called themselves the *kizil-bash*, or red heads (from the red caps that they wore)" (Bournoutian, 1994). "They had great devotion for their leader as a religious leader and perfect guide as well as a military chieftain" (Ghasemi, 2012).

According to Bournoutian (1994):

> By 1501 the Safavid leader…declared himself, shah. Ten years later he managed to gain control over Iran, historic Armenia, and much of eastern Transcaucasia….The emergence of the Safavids and the rise of Shi'ism in eastern Anatolia were major threats to the Ottomans, whose claim to the caliphate and the leadership of the Muslim world was challenged by the new Iranian dynasty.
>
> In 1514 Sultan Selim I (1512-1520) crossed the Euphrates River and for the first time entered historic Armenia. Shah lsma'il was not ready to fight the Ottomans and withdrew his forces, burning many villages en route to forestall the advancing Ottoman army. Thousands of Armenians were force to leave their land. The Ottomans pushed deep into Armenia and on August 23, 1514, at the Battle of Chaldiran, destroyed the Iranian army through superior numbers and artillery….[The battle between the Ottoman and the Safavids] repeated a several times, particularly during the reign of Shah Tahmasb I (1524-1576).
>
> The harsh Armenian climate and difficulties in transportation and in communications with Constantinople made it possible for the Safavids to repeatedly survive such defeat….[but] the first peace agreement between the two powers in 1555 left the western parts of historic Armenia in Ottoman bands, while the eastern parts ended up under Iranian control....But the uncertain situation over Tahmasb's succession

> encouraged the Ottomans to invade Armenia again in 1578….Caught in the middle of these warring powers, some Armenians were deported by the Ottomans to Constantinople from Tabriz, Karabagh, and Nakhichevan and others, by the Iranians, to Iranian Azerbaijan from Van.

2.2.2.2. The Great Migration

Around sixty years before, Haik Ajamian, one of the most famous Armenian researchers had found some Armenian headstones in Armenian cemetery in Shiraz which had the date of 1550 AD. Thus it shows that at least 50 years before the Armenian great immigration to Iran, the Armenian merchants had their community, houses and churches in Shiraz. Also they had great trade relations with India through Shiraz and the port of Gambrun (Bandar Abbas) (Ajamian, 1958, p. 30).

Bournoutian's (1994) study found that:

> It was Shah `Abbas the Great (1587-1629) who left the greatest imprint on modern Iran and the Iranian Armenian community. Recognizing the comparative weakness of the Iranian army, he quickly concluded a treaty with the Ottomans in 1590, Ceding eastern Armenia and parts of Iranian Azerbaijan. He then began the Formation of a new force, recruiting Georgian and Armenian mercenaries and Converts as sharpshooters, and, with European help, fashioned an artillery and the basis of a modem army. He moved his capital from Qazvin to Isfahan, a safer location. Isfahan was also closer to Baghdad, the soft underbelly of the Ottoman Empire.
>
> By the start of the seventeenth century `Abbas felt strong enough to break the peace he had made with the Ottomans in 1590. In the autumn of 1603 the shah advanced to retake Iranian Azerbaijan and to force the Ottomans out of Transcaucasia as well. He succeeded in taking the cities of Tabriz, Marand, Ordubad, Akulis, and the province of Nakhichevan, which included the town of Julfa. The shah was greeted as a liberator by the Armenians, who could no longer endure heavy Ottoman taxes, and the Shi`i Muslims, who

> were tired of religious persecutions. The Armenian merchants of Julfa, who had been engaged in international trade for some time, were especially happy with the Iranian capture of Julfa. On the other hand, some sources believe that the population was deported to Iran. According to one primary source, the Sunnis of Nakhichevan province were killed and their villages were razed by the Safavid army. The same source adds that `Abbas deported the Armenian merchants of Julfa to Iran at this time in order to prevent the region from regaining its economic viability.

Therefore, based on historical views, Hakhnazarian and Mehrabian (1991) mentioned that:

> The aims of this forced deportation of whole populations whose life for centuries had been trade and the production of semi-finished products in silk were to create a new trade route for the precious material, to make the Persian Gulf the new center of transit, and to deprive the Ottoman Empire of its primacy over trade between East and West. A further aim [as it mentioned] was to weaken that empire economically by snatching away part of taxes and levies that poured into its coffers year after year. (p. 8)

Figure 2.3. Armenian great emigration from Julfa to Isfahan (Hakhnazarian & Mehrabian, 1991, p. 6).

> [Also]….the attention of Shah Abbas was focused on the population of the city of Djulfa in Armenia. As early as the 16th century, it was a prosperous city, a commercial center of international importance. Situated on the Silk Route, with the surrounding towns and villages it controlled the flow of goods both from the adjacent regions and from the Far East toward the South and Europe. (p. 6)
>
> [Hence it is clear that]….Shah Abbas fully supported the idea of concentrating the Armenians in Iranian territory, ordering the inhabitants of entire towns on the border between the Ottoman and Iranian Empires to be deported. The reasons for this were mainly strategic, the objective being to create a belt of desolation between the empires so as to make it difficult to get supplies to the Ottoman army. Furthermore, it was rather advantageous in economic terms to concentrate in Iranian territory, a people with an age-old tradition of craftsmanship – capable, therefore, of passing on the skills and knowledge required to make articles of prestige – and a people with a great deal of experience in regional and international commerce. (ibid)

At that time, most of Armenians were settled in Isfhan, Fereydan, Chaharmahal and Bakhtiari villages, Soltan Abad (Arak) and Kharraqan. Sources tell that most of the artisans were grouped together in Isfahan and they also started to build their churches, monasteries, community, and church councils in Isfahan (Pashayan, 1969; Houyan, 2004). As it has been documented "in 1610, to strengthen the link of community to the royal court, Shah Abbas gave permission to build a church in Isfahan, for the Christian community in general and the Armenian community in particular" (Hakhnazarian & Mehrabian, 1991, pp. 8-9).

Figure 2.4. Isfahan and New Julfa territory (source: google maps)

It has been mentioned that these Armenian "met a luckier fate, they were granted farming land by the Iranian government; they had direct relations with the state and paid taxes in proportion to their harvests; they were "free citizens" who had no arbab, or master (ibid, p.8). [But] "the worst fate lay in store for the silk workers: moved to Guilan and Mazandaran, two regions south of the Caspian Sea, they soon perished as a result of epidemics of cholera and malaria" (ibid).

Also Hakhnazarian and Mehrabian (1991) found that:

> Later in 1615, with a new edict, Shah Abbas donated to the community a vast stretch of land belonging to the royal court and located south of the River Zayandeh-Rud and the city of Isfahan. On this land, where non- Christians were not allowed to buy immovable goods or to obtain residence permits; the Armenian district of Nor-Djulfa was to stand. (p.9)

2.2.2.3. Different Groups of Armenians in the Capital city of Isfahan

McCabe (2005) investigated different groups of Armenian in Isfahan and mentioned:

> The principal differences among Armenians of the capital were based on distinctions of class, wealth and regional origins prior to deportation. A study of three groups – the Julfan silk merchants, the ghulams and the artisans – shows

> how these seemingly distinct groups, who did not initially share the same urban space, are in actual fact closely tied to one another. The determining factors of social distinction at the beginning of the 17th century were class and wealth, not as one might suppose, place of residence within the capital city, religion or ethnicity. (para. 4)
>
> ….The town of old Julfa on the bank of the river Aras was internationally renowned for its silk trade. (para. 5)….Following settlement in Iran, the Julfan silk trade benefited from unprecedented growth. As a result of their success, Armenian merchants acquired high rank. As Halil Inalcık explained, the European demand for Iranian silk could not be overestimated because it was the determining factor in the organization of both the Iranian and the Ottoman economies. The competition between the Ottomans and the Safavids in the silk trade was fierce. The silk-weaving industry in the Ottoman Empire, as well as in Italy, depended on exports of raw silk from Iran. The Safavids wanted control of the trade to support their State-building and war efforts. Because they were indispensable to Iran's new international trade, Julfa's silk traders were given magnificent lodgings and a neighborhood of their own in a suburb of Isfahan: New Julfa. (para. 6)

The second group is that of Caucasian prisoners of war at first under Tahmasb and subsequently, half a century later, under Abbas I. The Julfans were not prisoners of war and were not required to convert to Islam as many Armenians and Georgians had been during the Safavid Ottoman wars. Among Caucasian prisoners of war however, many converted and became royal slaves – ghulams. These Caucasian ghulams entered Abbas' administration and army and many achieved the highest ranks….The highest ranking

> members of the New Julfan merchants and the ghulams, together with their dependents were members of the Royal Household and housed in a wing in the Safavid palace. The ghulams were involved in the mint and with the internal organization of the silk trade, many became extremely wealthy. They participated directly in the building of the new capital and a number are recognized as sponsors of the splendid monuments that adorned the new parts of the city. (para. 7)
>
> The third Armenian group is that of the artisans who settled and lived in old Isfahan, outside of the new neighborhoods built by Abbas I. Arakel, a seventeenth century Armenian priest and historian who wrote around 1657, mentioned two groups of Armenian artisans in the city. Both groups were composed of artisans who lived in the center of Isfahan: one group had a chief named Murad, the other a chief named Yosip; both leaders were appointed by the Shah. Unlike the Julfans, these Armenians were craftsmen, and extremely poor when they arrived in Isfahan….The Shahs understood that the Armenian merchants' Christian faith was instrumental to international trade between the Safavids and the European States, particularly with the king of Spain and Rome. To attract business, the Persian king sent ambassadors, many of whom were Europeans or Armenians residing in Isfahan, with bales of Iranian silk. (para. 8)

In the large canvas painting by Carlo and Gabriele Caliari (figure 2.5) has been shown *Doge Marino Grimani receiving the Persian ambassadors* (1603) therefore this painting "illustrates the excellent diplomatic relations in modern times between the Serenissima and Safavid Persia at the time of Shah Abbas the Great (1587-1629), at a time when both nations were intent on countering the threatening Ottoman expansion" ("Fondazione Musei Civici di Venezia- Palazzo Ducale," 2013).

Figure 2.5. Gifts by Shah Abbas the Great to the Serenissima which shows Diplomatic relations between the Republic of Venice and Safavid Persia ("Fondazione Musei Civici di Venezia- Palazzo Ducale," 2013).

According to MacCabe (2005):

> The Armenian artisans living in Isfahan, did not own their houses or land; they owned a lease on property that belonged to the royal domain. A Jesuit source reported that Armenians living in the city of Isfahan could sell their lease to people outside their own community. After the sale, the buyer would have to pay rent to the shah. The land remained the shah's property at the rate of 25 abbasis per jarib (10 000 square meters). Unlike artisans, silk merchants of New Julfa owned the suburb they lived in as it had been granted by Abbas I in October 1619, following a September silk auction in which the Armenians officially assumed responsibility for exporting Iranian silk. The land in New Julfa was given as a royal gift to the autonomous Armenian merchant oligarchy who ruled the suburb. (para. 10)

2.2.2.4. Brief description of Armenians' benefits in New Julfa

Research by Hakhnazarian and Mehrabian (1991) mentions that:

> In 1606, Armenian residents in Iran were granted the status of “royal privileged persons”. Juridically, the populations and towns came under the royal court and were not obliged to pay many of the tolls and duties. The civil rights of the Armenians were made equivalent to those of the Persians, and the court issued laws imposing heavy sanctions for crimes committed by the Persians against members of the Armenian community. Administrative independence was one of the most important concessions gained by the community. An elected *Kalantar*, or mayor, ran the community according to Armenian laws and customs and handled problems of defense and relations with the Armenian civil authorities. The mayors were selected among the most prominent merchants and they often held important positions at the royal court, where they dealt above all with economics and finance. Within the community, a *Katkhoda*, or judge, [resolved or addressed] controversies independently of Persian jurisdiction. The autonomy granted to Nor-Djulfa in religious administration soon made it the cultural and spiritual center for the whole community.
>
> ….Shah Abbas lavished large sums of money in the form of interest-free financing and tax facilitation on Armenian companies operating in international trade. Later, he granted the Nor-Djulfa merchants the right to concentrate and monopolize goods imported and exported into and from the empire. In 1617, he stripped the East India Company of its monopoly in the silk trade and granted it to the Armenians of Nor-Djulfa (p. 9).

2.3. Conclusion

By permission of royal court of Iran, the Armenian merchants of Nor-Djulfa started their own real commercial activities. As political and commercial deputies, they were well known in different European and Eastern countries. The trading system of Armenian merchants was very valuable and substantial in that historical era which leads to describe the period of its maximum development as the "region of the Armenian merchants of Nor-Djulfa" (Hakhnazarian & Mehrabian, 1991).

Nevertheless, the Armenian merchants lost their powerful position in the royal court of Iran and their "privileged relationship with the Safavid court" did not continue in the later time. Their number was reduced because many families moved to India and Europe. "After the 1660s, the court randomly and heavily taxed New Julfa, a practice unheard of in the years when the Julfans were members of the royal household" (MacCabe, 2005, para. 45).

However, it is undeniable that the Armenians were one of the primary channels for the introduction of Western art and culture to Iran. Artefacts and objects in Armenian houses and churches in new julfa/Isfahan are considered to be one of the most important cultural heritages in Iran and great relationships with Europe since 17th and 18th century made Armenian one of the most effective factors in birth of different art in Iran which was different with Iranian traditional art.

CHAPTER THREE

3. Armenian architecture

3.1. Introduction

"Historic buildings provide the most tangible legacy of our past civilization and in some cases they speak clearer than any remaining manuscripts" (Gavrilovič, Kelley, & Šendova, 2003, p. 63). "In the realm of Armenian art, architecture….was the first of the arts…to be seriously studied, and to this day Armenian architecture receives more scholarly attention than all of the other arts combined" (Kouymjian, 2002, para. 2). "Buildings are natural vehicles for decoration, they differ from other art objects by often incorporating in themselves the two most important of the other arts: painting and sculpture" (ibid).

3.2. Shapes of buildings

Kouymjian (1992) studied about Armenian architecture and he found that:

> In the study of architecture, however, primary attention is not given to the decoration, but to the structural forms of buildings and their evolution. Thus, monuments are analyzed by their architectural aspects -- the general design or look of the interior and exterior of buildings -- and architectonic considerations -- the methods used to construct them. Classes of buildings are studied by their plans.
>
> Everyone is familiar with certain common types of structures; their names immediately evoke specific images: skyscraper, lighthouse, pyramid, windmill, stadium, [and] Greek temple. Other types of buildings are less precisely visualized, because their forms are diverse: houses and churches, for instance, vary greatly in different parts of the world. They are differentiated architectonically by materials and methods of construction, architecturally by their shape. The form of a building is expressed by its ground plan.

"The history of Armenian architecture is in reality the history of the development of a single type of building: the church….[But it does not mean that there is no] architecture in Armenia before Christianity. The very sophisticated building techniques were in use in Armenia and a strong architectural tradition in stone was exercised for more than a thousand years before the first church was built" (ibid).

3.3. Armenian architecture as church architecture in Armenia

Tuohy (1969) argued that:

> The history of Armenian ecclesiastical architecture begins with Armenia's conversion to Christianity, and almost simultaneously the construction of the Cathedral of Holy Etchmiadzin at the beginning of the fourth century. Although the church has since undergone at least two major reconstructions, its foundations indicate the centralized plan, crowned with a conical dome, that later became the classic design of Armenian church architecture.
>
> The triumph of Armenian architecture, nonetheless, is at Ani, an ancient city which, during the tenth century, became a royal capital, and, consequently, the largest and richest city in Armenia. The Cathedral of Ani (figures 3.1 and 3.2), completed in 1001, was the masterpiece of the architect Trdat, the same architect who repaired the dome of the Hagia Sophia in Constantinople after a devastating earthquake. (as cited in "Armenian Church Architecture," n.d.)

Inscription on the southern facade of the Cathedral shows that the church was built in the year 450 (AD 1001) of the Armenians ("The Cathedral of Ani," 2005).

Figures 3.1 & 3.2. The cathedral of Ani after earthquake damage in 1988 and a model which is showing what the dome looked like ("The Cathedral of Ani," 2005)

According to Tuohy (1969), "Armenian architecture, and particularly the Cathedral of Ani, holds an important place in medieval architecture, suggesting in many ways what was to come later in Romanesque and Gothic styles of western Europe". Some other important Armenian buildings "are the Holy Cross Church on the island of Aghtamar, St. Hripsime Church in Vagharshapat, the Cathedral of Marmashen near Gyumri, as well as the monasteries at Keghart, Sanahin, and Haghbat" (as cited in "Armenian Church Architecture," n.d.).

Figure 3.3. Southwest view from the Marmashen Monastery, 10th-11th Century ("Index of Armenian Art: Armenian Architecture, Marmashen," n.d.)

Kouymjian (2002) found the following:

> Thousands of Armenian churches were built during the long history of Christianity. They varied in size from very small to large, though there were no giant structures like St. Peters in Rome or Hagia Sophia in Constantinople or the large cathedrals of Europe. Some churches were intended to stand alone, while others were parts of monasteries. A large

> number of types were developed, providing a great variety of exterior shapes and interior volumes. Some types are found in adjoining Christian areas, but in Armenia their plans were usually modified to conform to local conditions. A number of unique church forms were invented by Armenian architects in their pursuit of ever more efficiently built and aesthetically conceived houses of worship.

3.4. Formation of an Armenian style

Kouymjian's (1992) study shows that:

> Despite the large diversity in the types of early churches, Armenian architecture achieved a distinctive style through the combination of a number of common characteristics and materials. The compositional employment of these traits was unique to Armenia, though its northern neighboring Georgia was also to benefit by a flourishing of building activity. By the late sixth or early seventh century a unique national style of church architecture came into being. Some scholars have called this phenomenon the first national style in Christian architecture. It had been achieved long before the Byzantine, Romanesque, and Gothic or the less known Ethiopian, Scandinavian, and Slavic styles were concretely formed.

There are some important features that make an Armenian church instantly recognizable:

> First, all churches are built entirely in stone. The scarcity of wood prevented its architectural use in medieval Armenia. With rare exceptions, the stone used is a volcanic tufa abundant in Armenia in many colours and shades: pink, red, orange and black. Dark basalt was also used for more sturdy foundation work.[1] Only in outlying regions of Armenia, where tufa is not readily available, was another stone substituted….Second,

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[1] A more important reason for the care devoted to the tufa walls was protection against earthquakes.

> ceilings were always vaulted. Since wood was not available for making simple flat roofs, stones were employed, but their weight demanded they be arranged in arcs so that the thrust of their mass could be directed to robust stone walls and thence to the ground. This, at first, produced buildings with thick walls, and few and small openings to comfortably accommodate the pressure from above.
>
> Third, the Armenian preference or weakness for the dome manifested itself very early. By the end of the sixth century, a church without a dome was unthinkable. Other than a few early exceptions, the dome or cupola was elevated above the other vaulted ceilings by a cylindrical drum (usually polygonal on the outside). The prevalence of the dome forced architects to think in terms of centrally planned buildings.
>
> Fourth, roofs were composite in their appearance because they had to cover the vaults and domes of a complex, though symmetric, group of inner spaces. Like the inner and outer walls and the drum, they too were made of tufa thinly cut into uniform shingles.
>
> These are not all the features common to Armenian architecture….Each church is, however, an individual creation, distinguished by its inner and outer form, its size, and its decoration. Most belong to a certain class of building, though some are unique. Almost all monuments of whatever period have a ground plan elaborated during the first three hundred years of Christianity in Armenia (fourth to seventh centuries) when the creative energies of Armenian architects seemed to overcome all obstacles engendered by construction in stone that sought ever more inner space and less massive structures.

3.5. Other kinds of Armenian architecture

Kurkjian (2014) mentioned that:

> [Besides of] the architecture of worship in Armenia, [there is] the architecture of defense, buildings for military and strategic purposes. There are hundreds of strongholds, among the most ancient works of the constructive art,…[in] inaccessible…heights of this mountainous country.
>
> [Also], there is funerary architecture like cemeteries full of memorials for the departed and ornamented tombstones…[The architecture of public utility buildings is another kind of Armenian architecture] which includes hostelries for the accommodations of caravans and travellers, and bridges…Finally, the architecture of man's residence, royal palaces, dwellings of princes, citizens [and so on], of which we can say little, lack archaeological evidence. The architecture of the peasant's abode in Armenia, continues to be unchanged and of the same type as described by Xenophon in his *Cyropaedia*, fourth century B.C. (p. 353)

3.6. Armenian architecture as church architecture in Iran

"**T**he majority of churches in Iran that possess historical and artistic value were built around the 14th century AD, and the period thereafter. Of course, this does not mean that there were no churches existing in the country before that period" ("Iranian Architecture and Monuments," n.d.).

"Azerbaijan is host to the oldest churches in Iran. Among the most significant are the Tatavous Vank (St. Tatavous Cathedral), which is also called the Ghara Kelissa (the black monastery).[2] There is also the church known as Saint Stepanous" (ibid).[3]

The section of historical churches in Iran, in Iranian architecture and monuments study (n.d.) found the following:

> Generally, each church has a large hall for congregational prayers; its foremost part is raised like a dais, adorned with the pictures or images of religious figures and it also serves as an altar....On the foreground is the praying congregation, which face the platform

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[2] This is located at the Siahcheshmeh (Ghara-Eini) border area south of Makou.

[3] It stands 24 kilometres south of Azerbaijan's Julfa town.

> where the priest is leading the rites in the church; this is similar to the Muslim practice of praying facing the niche in the mosque….The structure of churches in Iran follows more or less the pattern of Iranian architecture, or they are a mixture of Iranian and non-Iranian designs.

3.6.1. Saint Stepanous Church

This church is located in Julfa, East Azerbaijan. According to Hayk Ajimian, an Armenian scholar and historian, it dates back to the ninth century AD, but a lot of earthquakes in Azerbaijan destroyed the previous construction and "the church was rebuilt during the rule of Shah Abbas the Second". The significant features of this church are its "beautiful paintings by Honatanian, a renowned Armenian artist", decorated façade, and pyramidal dome (ibid).

Figure 3.4. The Church of Saint Stephanus, Julfa. The monument is also known under the name of the church of Darreh Sham. (Photo by: M. Mishmast)

3.6.2. Saint Mary's Church in Tabriz

Iranian Cultural Heritage Organization (2008), has mentioned the following description in its report: From the earliest day of Christianity there has been a sizable Armenian community in Tabriz, and the city boasts of a number of churches, including one mentioned by Marco Polo on his travels. Probably, the most interesting and the oldest but substantially rebuilt is the Church of St Mary (*Kelisa-ye Maryam-e Moghaddas*) which was completed in 1785. "This church was built in the sixth century A.H. (12th century AD) and in his travel chronicles, Marco Polo, the famous Venetian traveler who lived during the eight century A.H. (14th century AD), referred to this church on his way to China" ("Iranian Architecture and Monuments," n.d.).

3.6.3. The Saint Tatavous Monastery or the Qara Kelissa

The same source found that:

> Initially, this church comprised of a small hall with a pyramid- shaped dome on the top and 12 crevices similar to the Islamic dome-shaped buildings from the Mongol era. The difference was that the church dome was made of a stone. The main part of this pyramid structure followed Byzantine (Eastern Roman) architecture, including the horizontal and parallel fringes made of white and black stones in the interior and black stones on the exterior facing. Since the facade is dominated by black stones, the church was formerly called Qara Kelissa (or black monastery) by the natives.

3.6.4. Historical Churches at New Julfa of Isfahan

The most important historical church in Iran is the old cathedral, commonly referred to as the Vank or the church of Surb Amenaprkitc (Savior of All or All Healing). The first church was a small one which was built in 1606. "The present cathedral was built on the site of this church some 50 years later. Work started in 1655 C.E. and the cathedral was completed in 1664 C.E ("Jolfa: The Vank Cathedral," 1998).

This building "completely reflects Iranian architecture. It has a double-layer brick dome that is very much similar to those built by the Safavids. The interior of the church is decorated with glorious and beautiful paintings and miniature works" ("Iranian Architecture and Monuments," n.d.) that "were paid for by the Armenian merchant, Avedic Stepanusian, and were executed by three monks, Havans, Stepanus and Minas" ("Jolfa: The Vank Cathedral," 1998). "The wall paintings represent biblical traditions and the image of angels and apostles, all of which have been [painted] in a mixture of Iranian and Italian styles. The ceiling and walls are coated with tiles from the Safavid epoch" ("Iranian Architecture and Monuments," n.d.).

Figure 3.5. View of Vank Cathedral (1655-64). (Photo by: M. Mishmast)

Figure 3.6. Wall paintings under the dome (Photo by: M. Mishmast)

Figure 3.7. Interior wall paintings of the Vank cathedral. (Photo by: M. Mishmast)

Figure 3.8 Wall painting in the arc of the church. (Photo by: M. Mishmast)

There are some other historical churches in New Julfa like the Church of Surb Betghehem, the Church of Surb Astvatzatzin church (Holy Mother of God), the church of Surb Stepanos (St. Stephen) and so on. Since the specimens for analytical studies have been taken from these churches, they will be described separately.

3.6.5. The Armenian Church in Shiraz

Also, there is an Armenian church in Shiraz which according to Iranian Architecture and Monuments study (n.d.) it is "from the era of Shah Abbas the Second". It is located in a district which is called "*Sare Jouye Aramaneh*". This building has "a prayer hall with a lofty flat ceiling and several cells flanking the two side of the building. The ceiling is decorated with original paintings from the Safavid era and the adjoining cells are adorned with niches and arches and plaster molding, also in the Safavid style".

Figures 3.9 & 3.10. The Armenian Church in Shiraz called: "Sare Jouye Aramaneh" Church (Shiraz Cultural Heritage Organization, 2013)

Further, based on the same source, there are some other old churches from the Qajar period like the Saint Simon's Church and the church of the Glory of Christ in Shiraz and villages around it, Saint Tatavous Church – the oldest church in Tehran which was built during the reign of the Qajar king, Fathali Shah. "Meanwhile in Bushehr, there is a church from the Qajar period that is a good specimen of Iranian architecture. All the windows are modeled after old Iranian buildings and the coloured panes are purely Iranian art work (ibid).

There are also many other churches in Ourumieh, Arasbaran, Ardabil, Maragheh, Naqadeh, Qazvin, Hamedan, Khuzestan, Chaharmahal, Arak, in the old Vanak village north of Tehran, etc. These churches, though, are all deserted and are of little artistic significance ("Iranian Architecture and Monuments," n.d.).

3.7. New Julfa and its churches

"New Julfa stood out as a magnificent and prosperous neighborhood [in Isfahan] and was described by many, including Jean Thévenot, as the wealthiest quarter" (MacCabe, 2005, para. 21).

Also Hakhnazarian and Mehrabian's (1991) study about New Julfa found the following:

> Construction of the district of New Julfa began in 1605. A road was laid running east to west parallel to the river [Zayandeh-Rud] and half a kilometer from its bank. It took the name Nazar from Khodja Nazar, first mayor of the district.
>
> ….The district was soon fitted out with all the services a residential area needed, along with places of worship (only 13 of the original 24 survive today) and other

> infrastructures…..Schools, built later than the religious complexes, were erected at strategic points of the district and some of them still survive. Buildings at the service of the public included the orphanage, hospital, hospice and various public baths which completed the district's services. (pp. 12-13 passive)

"These churches represent a mixture of Armenian and Persian styles...[and] their interior decoration, provides valuable evidence of the interaction of ideas and artistic concepts between East and West in the seventeenth century" (Sanjian, 1999, p. 43).

Hakhnazarian and Mehrabian (1991) mentioned that based on "climatic conditions and a non-Christian urban environment", Armenian needed to change their masonry material of architecture-stone- and begin to use brick in their buildings (p.13). In their study, they found that the "characteristic ground plan" of Armenian churches in New Julfa is based on Armenian tradition, "a hall with four free-standing pillars in the central area surmounted by a dome [but] at times, there are no pillars and the dome rests directly on the main walls. [Therefore], just the ground plan reflects traditional Armenian architecture. The rest is of Iranian-Safavid inspiration" (ibid). The exteriors of churches usually are not "heavily decorated with tiles", unlike the Islamic buildings and monuments of the same period.

Also in some Armenian churches, "if the domes are large –as in Surb Astvatzatzin and Surb Betghehem, for instance- they have a double spherical vault; if they are smaller, they have a single one"(p. 13). The arches are the important feature of the Safavid architectural tradition.

3.8. Armenian Houses in New Julfa

According to Christopher (1979), "The identity of old buildings comes from each of their parts being united with their environment and, can recognize the forces around it and obeys the principle of environment and human nature" (as cited in Karimi & Hosseini, 2012, p. 81).

Aside religious buildings in New Julfa, the Armenian houses are significant too. Cornelis de Bruijn[4] (1652 – 1726/7) in his itinerary described districts, churches and houses of New Julfa with details (Tajyryan, 1993). Also Diba et al. (2001) described that "according to travelers, the most beautiful and grandest houses of the entire capital were in New Julfa" (as cited in MacCabe, 2005, para. 21).

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[4] He was a Dutch artist and traveler who made two large tours and published illustrated books with his observations of people, buildings, plants and animals also he made drawings of towns like Isfahan and Persepolis (1704–1705). He knew an Armenian merchants from Isfahan whose name he recorded as Jacob Daviedof.

Armenian houses in New Julfa have the same pattern like Iranian traditional houses and it means "all those who could afford it, from prosperous artisans upwards, built inward-facing houses with between one and three courtyards. With no windows facing outwards and only one door to the outside world" (Loosley, 2011, p. 618) which could provide the maximum privacy.

"Just as the [Iranian] palace complex, houses had the *biruni* and the *anderuni*, so the courtyard houses of the upper- and middle-ranking residents of Isfahan had a clearly defined sense of gendered space" (Ibid, p.621).

"Houses in traditional architecture of Iran were all based on special principles…All these buildings were built in order to fulfill people's requirements....The physical feature of traditional Iranian houses reflects natural, cultural needs and occupant's requirements" (Nabavi, Ahmad, & Goh, 2012). Those houses contained some special parts like *Biruni* (exterior) and *Andaruni* (interior) parts; *Hashti* which is the small enclosed transitional space between entrance door and corridor that was connected to the courtyard and the small central pool or *howz* with gardens around it. "The idea of garden and courtyard, complements to the hot, arid plateau of Iran, remain as significant forms in the concept of paradise during the Islamic era" (Ibid).

Between historic Armenian houses in New Julfa, most of them have been effected by urban development projects during years but there are some few samples which could be recognized and they have been used by Art University of Isfahan as its different departments (Karapetian, 1974).[5]

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[5] More information can be found in: Karapetian, K. (1974). *Isfahan, New Julfa- The Houses of the Armenians*. IsMEO.

CHAPTER FOUR

4. Iranian- Armenian Wall paintings and Historical Pigments in 17th Century

> *"By virtue of its beauty, each work opens the door to paradise. One may truthfully say that the painters, armed with Mani's pen, have let their imagination and thoughts gallop with Rakhsh (Rustam's steed)." (Abdi).*

4.1. Iranian Wall Paintings

4.1.1. Iranian Painting before Islam

Wall painting was utilized throughout Persian history to convey the power of the Persian court in the public sphere and to serve as an erotic stimulus in the private spaces of palace complexes. "Figured wall paintings are documented in Iran from at least the fourth century B.C., but few wall paintings of the Parthian and Sasanian periods have survived…[, but they usually] are badly fragmented" (Kawami, Becker, & Koestler, 1987, p. 25).

To Āyatollāhi and Haghshenās (2003), "painting was considered the most important art of the Parthian period. Unfortunately with the passing of time and may be due to the Sasanian's reluctance to preserve Parthian artworks, not many of the murals created in this period have survived today" (p. 106).

According to Diba's (2001) study:

> In more recent periods, it was also found in popular contexts such as bath-houses, coffee-houses, and bazaars. The memory of such imagery was preserved through oral tradition, popular sayings, and historical and literary texts, and was perpetuated through philosophical and ontological beliefs in the power of images.

"Of the numerous palaces and buildings of antiquity embellished with figural wall painting", there are some sites that have been mentioned more often; Kuh-i Khwajah from third-fourth centuries A.D. (figures 4.1 and 4.2), Panjakent from seventh century A.D. (ibid) (figure 4.3), the Sasanian Manor House at Hajiabad, and the city of Ardashir-Khurrah in Fars which some of their wall paintings have survived (Azarnoush, 1994). "In the site of Kuh-i Khwajah, there were excavations by Aurel Stein (in 1915-1916), and then Ernst Herzfeld, and then Giorgio Gullini (in a short expedition in 1960)" (Mawer, n.d.).

"Herzfeld tentatively dated the palace complex to the 1st century CE, that is, within the Arsacid period…He later revised his estimate to a later date and today the Sassanid period (224-651 CE) is usually considered to be more likely" (ibid).

Figure 4.1. The view of Kuh-i Khwajah

Figure 4.2. Wall painting from Lake Hamun's Kuh-i Khwajah, Eastern Iran, circa 200-800 A.D. (Ramazan-nia, 1997)

Also as Diba (2001) described:

> The principal subjects of palace decoration-enthronement, battle, and feasting-were described by Arab geographers of the medieval period. For instance, the thirteenth-century author Yaqut-i Mustacsimi, described a painting of the Sasanian ruler Khusraw Anushirwan (531-579) triumphing over the Turks, the Roman Emperor, and the King of Sind, that decorated the audience hall of the palace of Dukkan in Western Iran. (pp. 5-6).

Following Herzfeld studies, Kawami et al. (1987) also described some old Iranian wall paintings that can be the hints for further researches. Based on their report; the murals of Kuh-e Khwaja provide an unexpectedly complex picture of artistic activity in Sistan and form the largest corpus of painting in ancient Iran. The evidences confirmed that:

> Fragments of wall paintings had a smooth ground of the reddish-brown clay or [prepared plaster] laid over a base or scratch coat of coarse clay mixed with chopped straw….The [paintings] were first sketched with brown iron oxide pigment; then [in figural paintings,] the skin areas were painted with various iron oxide and gypsum mixtures. Finally, the black hair and details of eyes, ears and costumes were added with carbon-based paint. The image was finished with a thin black outline, and a whitewash of gypsum was applied to the ground.

In addition, various colours like yellow, green, purple and blue have been used since Achaemenid period (late sixth through fourth century B.C.) to the seventh and eighth century wall paintings. Most of the pigments dissolved in water and perhaps they were with some organic binders. There is rare physical evidence of painters' tools in the ancient Near East, but studies show that the pigments were applied with a thin brush that was made of hair rather than vegetable fiber (Kawami et al., 1987, pp. 48-49).

Research by L'Historien Errant (2012) illustrated that:

> In c. 740 A.D., a reception hall in a private house in Panjakent was decorated with an extensive cycle of mural paintings. Panjakent is located in what is now Tajikistan, but in the 8th century it was part of the Sogdian Empire, one of the last remnants of pre-islamic Persia, soon to be conquered, though, by the Samanids. (In between, the area was also part of the Soviet Union which is why the wall paintings ended up being detached and brought to the Hermitage Museum in St. Petersburg where they can still be found today.) Some of the scenes in the murals can clearly be identified as the Seven Labours of Rostam, the greatest hero of Persian literature and mythology.

Figure 4.3. The Seven Labours of Rostam, mural paintings from Panjakent, 740 A.D., Hermitage, St. Petersburg ("L'Historien Errant," 2012)

4.1.2. Iranian Painting in Islamic era

According to Diba (2001), "in the majority of Islamic countries, the art of painting has been restricted to non-figural and geometric designs in the public sphere, and strictly limited to small scale narrative illustrations of manuscripts in the private sphere" (p. 5). "Rows of standing figures have occurred frequently in both Parthian and Sasanian art, as well as in Kushan art of Afghanistan and Pakistan" (Kawami et al., 1987, p. 26). But based on evidences, since Safavid era, "Iran witnessed the development of large-scale figural painting. Such a decisive break with Islamic tradition where religious and social beliefs were primarily expressed through textual and calligraphic means… "(Diba, 2001, p. 4).

The life-size figure was popular before Islam and even after that, especially in Samanid and Ghaznavid era. Also the same source found that "Imagery continued in use for palace decoration during the Seljuk period" (p. 9). The significant role of imaginary in Persian life reveals "the persistence of this tradition despite Islamic strictures against imagery" (p. 10).

A description about wall paintings in Iran by Diba (2001) found that:

> According to contemporary sources, wall painting under the Timurids and their contemporaries, the Turcoman rulers of western Iran, functioned as visual equivalents of the state's ideological programs and the pleasures of the princely life, celebrating and the confirmations and prerogatives of Timurid power.
>
> ….In the sixteenth and seventeenth centuries, monumental mural paintings were commissioned by Safavid rulers (1501-1722) for their palaces in the capitals of Qazvin, Isfahan, and elsewhere….The appearance of early sixteenth-century mural painting is also reflected in contemporary illustrated manuscripts. (pp. 11-13)
>
> "It is the seventeenth-century palaces, bazaars, and residences of Isfahan… that provided" opportunity for the architects and painters to produce the stunning decorations for their rulers and embellish the interior-exterior of the important buildings. Safavid and Qajarid architects and craftsmen used "the garden pavilion structures", often with "deep columned porches", "the pools", "the stone carvings", "the painted decoration of the interiors", "the tile work", and "the floral and figural designs of the facades" (ibid, p. 13).

Figures 4.4 & 4.5 Figural wall paintings of Chehel Sotoun Palace in Isfahan from Safavid dynasty
(Photo by: M. Mishmast)

Also, the battle and hunt scenes are stylistically and thematically recognizable from the repertoire of Persian paintings"(Leoni & Natif, 2013, p.131). The notable case is the martial themes of battle, and hunts also were popular in the Armenian houses in New Julfa. In this period, "the life-size, multi-figural scene in a Europeanizing style of painting depicting a veritable European fete", could be found: "men and women with European physiognomies and dress[es], people seated at a dining table…and musicians playing European instruments"…(ibid). One of the important elements which could be seen in the paintings of the Safavid period and also appears in the Herat and Isfahan schools, is described as a "bird's eye view" of various scenes and objects. In these scenes, "the different stages of each event [were] presented in a succession of images that [were] all seen from above" (Ayatollahi, 2003, pp. 147-148). The evidences of such decorations are significant in The Chihil Sutun palace, the pavilion of Ali Qapu on the Royal Square, the Hasht Bihisht, Qaysariyya bazaar- the royal sponsored principal marketplace in Isfahan and as Karapetian mentioned even in the house of Khoja Petros Veliginian[1], one of the richest and most famous Armenian merchants in New Julfa (as cited in Leoni & Natif, 2013, p. 140).

"The innovative style introduced by the late Safavid court artists…–a not always successful but nevertheless intriguing blend of European post-Renaissance tradition, Mughal interpretations thereof and traditional Persian values– continued to be the predominant style in the eighteenth century" (Diba, 1989, p. 148).

4.2. Armenian Paintings

4.2.1. Pictures and mosaics

According to Kurkjian (2008):

> The interior of churches in Armenia were adorned with figures, even some mosaics and some specimens from those ornaments have remained in ruins of Zwartnots (Zvartnots). In Armenia…, many of the paintings have been destroyed but their existence is obvious. Vrtanes Kertogh (the poet) has mentioned representations of the Virgin with the Child, St. Gregory as tortured and Ste. Gayaneh…[in different churches]. The church of Aghtamar was rich in pictures of Gospel miracles…and Byzantine examples are noticeable in them.

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[1] Minas, the famous Armenian painter, restored the hunt scene in the house of Khoja Petros in 1668, according to an inscription (Leoni & Natif, 2013, p. 140).

> Also Syrian and Persian influences [could be found clearly] in the specimen of the Gospel of the Walters Art Gallery in Baltimore.
>
> At certain periods, Byzantine touch is seen more than the oriental, especially in miniature decorations. Painting received impetus under Armenian rule in Cilicia. (p. 356)

Figure 4.6. The Armenian Bird Mosaic, Jerusalem- The Church of St. Polictos; a pavement mosaic from the sixth century. At the upper part of the mosaic, the following inscription has been preserved "in memory and salvation of all the Armenians whose names are known by the Lord." ("Армянские святые архитектурные сооружения в Иерусалиме ," n.d.)

4.2.2. Illuminated Manuscripts

The most important Armenian paintings have been presented in their manuscripts. "The earliest Armenian illuminations date from about the 7th century, and surviving manuscripts indicate that the format and traditions of the Armenian Gospel Book were well established by the 10th century" (Merian, 1994, p.4).

Furthermore, Merian (1994) illustrated that during 12th to 14th centuries:

> [Armenian] Cilician illumination reflects manifold contacts with Western and neighboring cultures. The Byzantine tradition is most apparent in evangelist portraits, and elements of Western illumination were also adopted. The concept of twisting images of animals, birds, and men into letters of the Armenian alphabet were borrowed from the West, where such letters had been used in Latin manuscripts since the 8th century. (p. 7)

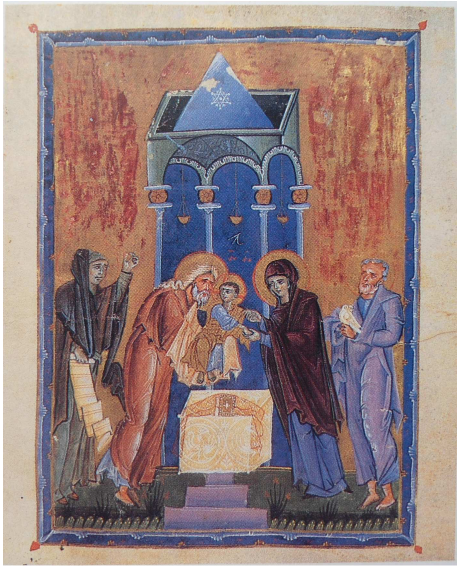

Figure 4.7. The Armenian illumination, "Presentation in the Temple" by T'oros Roslin, 1262. Roslin is renowned for his graceful and delicate images, brilliant colouring, and his ability to incorporate artistic influences from the Latin West into his traditional Armenian style. Baltimore, Walters Art Gallery, MS W.539, Fol.211 (Merian, 1994, p.6).

Between the 14th and early 17th centuries, there are almost 1000 manuscripts which are "coherent in style and iconography. Figures are boldly outlined and enlivened with a limited palette of bright [colours]" (ibid, p.10).

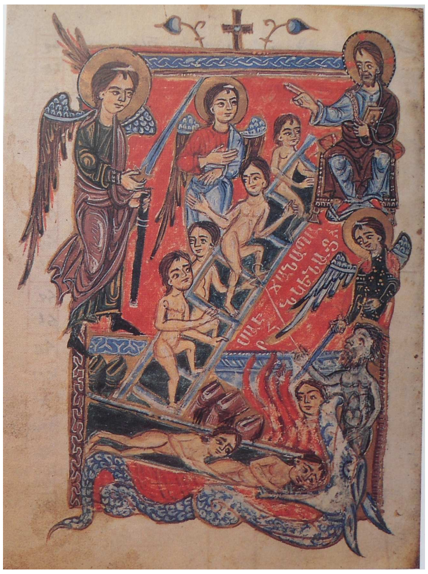

Figure 4.8. The Armenian illumination from 1350, by Sargis Pitsak. Michigan, K. P. Sogoian, fol. 170v (Ibid, p.7).

During that period, "the subjects and compositions of Gospel illumination at Lake Van region changed". For instance, Khach'atur of Khizan, one of the "most innovative Armenian artists" used "vivid, energetic figures", and "vibrant floral motifs" which had borrowed "from Islamic Timurid art" (ibid).

"Khach'atur's influence is evident in the work of later painters, such as Mesrop of Khizan, who became popular with the 17th century Armenian community in New Julfa (Isfahan)". He was the painter who used "brilliant colours with dramatic, pulsating outlines and backgrounds" (ibid, pp.10-11). Further, there were some Armenian miniature paintings in New Julfa which according to Sirarpie Der Nersessian, "the painters who worked in New Julfa, during the first decade of the seventeenth century were originally from different provinces of Armenia and for this reason, heirs to different traditions" but even in the artworks of the new generation of painters, "the influence of the masters who had trained [them], is felt" (Sanjian, 1999, p. 44).

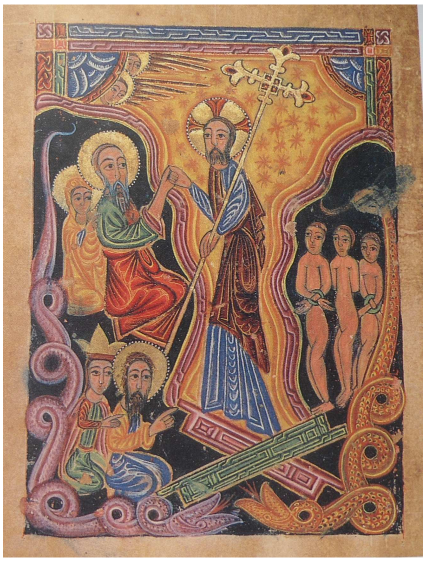

Figure 4.9. This illuminated manuscript has been painted in New Julfa by Mesrop, 1618-22. The miniature is typical of Mesrop's use of rhythmic line and vivid colour. Private Collection I, MS 48, fol. 17v (Merian, 1994, p.11).

"A distinctively Iranian cultural background, a theological separateness studiously cultivated, a self-conscious literature of great richness, ancient Christian rituals jealously guarded for centuries; these involved distinct patterns of thought and behavior in Armenia that gave shape to Armenian art" (Sanjian, 1999, p. 59). In the many of Armenian miniatures and illuminated manuscripts, "fine lines of black ink underline the vibrant painting in rose, blue, yellow, and orange" (ibid, p. 127) and the faces are tinted with a light orange, lined with a darker shade of the same pigment (ibid, p. 172).

4.3. Persian Pigments palette and Artist's technique

4.3.1. Persian palette based on historical treatises

Some introductory remarks about the Persian art and paintings have been explained in the Persian literatures. Although some of these texts have been translated into western languages, others have not and therefore remained out of reach of the majority of scholars.

As it has been mentioned in Dickson and Welch's (1981) study, "only two translations into English of technical treatises on Persian painting exist" (as cited in Purinton & Waiters, 1991). One of them was Qadi Ahmad's *Gulistan-i Hunar* [Rose Garden of Art] (1596-1606 or 1608). This biographical account of calligraphers and painters…can be considered fundamental to the history of the arts of Safavid times" (Porter, 2000, p. 109).[2]

Another one is Qanun us-Suvar (Canons of Painting or forms) by "Sadiqi Bek Afshar, a royal painter in the 16th-century Safavid Iran". According to Dickson and Welch's (1981), "He wrote the Qanun sometime between 1576 and 1602.[3] …In his treatise, Sadiqi Bek discussed theoretical aspects of painting such as the basic categories of decorative art and its different idioms, including animal and decorative drawing (as cited in Purinton & Waiters, 1991).

Purinton and Waiters' (1991) study found the following:

> Sadiqi Bek also has described the manufacture of some of the colours used in a painting. The only white pigment he mentioned was [lead white] produced by melting lead in a closed vessel and then, after it had cooled, alternately washing it with a saline solution and pounding it with sal-am-moniac and vinegar. To make red lead, the [lead white] was roasted. The green pigment, verdigris, was made by burying copper plates, immersed in vinegar, in a pit two meters deep for one month. Sadiqi Bek also explained a red lake that was made from boiling lac in a soda solution to which possibly lime was added. He instructed the artist to make vermilion by pounding mercury and sulfur in a mortar and then heating it for several hours.

The Gulistan-i Hunar appendix covers some different topics in comparison with Sadiqi Bek studies. For instance, "it includes instructions for ruling framework, or drawing decorative margin lines around calligraphy" (ibid).

Research by Minorsky (1959) showed that:

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[2] As the great Iranian scholar M. T. Danish-Pazhuh has shown, however, some parts of Qadi Ahmad's text were in fact taken from the works of Abdi Beg Shirazi (Porter, 2000, p. 109).

[3] To the present day, the only known Persian technical treatise devoted entirely to painting and in any way comparable to Cennini's artist handbook is Sadiqi Beg Afshar's Qanin al-suvar (most probably 1597). (ibid, p. 112).

> The author [also] explained how to grind and dilute the pigments made of lapis lazuli and gold. Gum arabic was the only medium mentioned, and artists were advised to add it to colours. The pigments included in this section of the treatise are cinnabar, lapis lazuli (ultramarine), orpiment, and [lead white]. All these colours would be washed as a final preparation step by adding water to the pigment in a vessel, allowing it to settle; and then decanting the liquid. Gum arabic was added to the colours before they were ground. At one point the artisan is advised to add vinegar to lapis lazuli (a blue stone) and grind it until it turned green. In another the artisan is instructed to mix verdigris (a green) with white lead to make pink. Such instructions suggest that at least some information in this treatise is inaccurate. This appendix also described four methods of preparing a black ink: one from lampblack, another from baked wheat starch paste, another with gallnuts and lampblack, and the last with tin and mercury. (as cited in Purinton & Waiters, 1991)

Most of the information in the both treatises give directions about paintings on paper, but the explanation for making pigments is the same or similar for different paintings' techniques including wall paintings. Table 4.1 shows the brief description of Iranian palette based on old treatises: Canons of painting and Rose garden of art.

Table 4.1. The brief description of Iranian palette based on old treatises

Iranian Palette ***Canons of painting*** **by Sadiqi Bek Afshar- 16th century &** ***Rose garden of art*** **by Qadi Ahmad- 16th century**	
Colour	**Pigment/Dye**
White	Lead white
Blue	Ultramarine, indigo, smalt (especially in glassmaking, painting, and pottery).
Red-Orange	Red lead, ochre, vermilion, red lake
Green	Verdigris
Yellow	Orpiment

Not only the walls but also the ceilings are often part of the artwork. Among all of Iranian artworks, murals had a very important place because they were the most common method for decorating buildings such as palaces, churches and houses. Iranian artists have used a variety of methods for the preparation and creation of murals such as water colour painting, tempera and oil painting, but sometimes they mixed all of these methods with a special technique which is called gilding or *Tala Chasban*. This method also have been used by Armenian artists in their precious art works and wall paintings.

Figure 4.10. Wall painting of the Chehel Sotoun Palace with Tala Chasban.

Figure 4.11. Wall painting under the dome of the Betghehem church with Tala Chasban (Photo by: Y. Hamzavi)

4.3.2. Persian Artist's techniques and methods

Because of the climatic condition and availability of materials, a lot of murals in Iran have been done with the specific materials. In many cases, different layers of murals include:

- **Support layer:** The most common masonry for support layer in Iranian wall paintings are clay, brick, stone and sometimes wood.
- **Brown coat:** a layer of rough plaster covering the support. In Iran this layer is made up of earthen plaster.

Figure 4.12. Preparation of brown coat, finish coat and white ground.

- **Finish coat:** It is the final smoothest coat of plaster. In Persian it is called *Koshteh*, meaning very soft gypsum.

- **White ground layer:** Usually the finish coat layer is covered by a smooth white ground. Based on availability, artist's choice and experience, many different kinds of materials and mediums are applied as this layer. Ground can be kaolinite, chalk or gypsum and medium which must be mixed with ground, can be diluted gum arabic[4], animal glue (Serishom), herbal glue (Serish), sugar syrup and tragacanth gum, albumen and yolk. After the finish coat the next step is transference the cartoon.

  "Sadiqi Bek stated that a painting would have a two-layer ground. The bottom layer would be a mixture of glue, plaster, and grape treacle; on top of that would be a layer of lead white] and oil-varnish". Nevertheless, based on Dickson and Welch (1981) "this type of ground was probably intended for book bindings or paintings on stiff layered paper (like cardboard) surfaces (as cited in Purinton & Waiters, 1991), seems it also was used for a lot of old Iranian wall paintings.

- **Paint layer:** This layer consists of dyes or pigments, medium and some additional materials. "Different types of colourants can be distinguished by their solubility in the paint medium. Pigments are (almost) insoluble, whereas dyes are soluble. Although the vast majority of the historical pigments are inorganic, some are organic; they can be synthetic as well as from natural sources" (Edwards & Chalmers, 2005, p. 71). Medium that has binding properties can be gum arabic, egg yolks, albumen and linseed oil.

- **Varnish layer:** Iranian artists used diluted animal glue (Serishom), mixture of sugar syrup and tragacanth (Shiraz gum) and Kaman oil (Arch oil) for varnish (Sasani, 2007).

4.3.3 Gypsum plaster as a main masonry

The important thing about Iranian wall paintings is that the support and coating soft layer in Iranian mural painting is not like European fresco technique. The most popular masonry for Iranian artists was gypsum plaster rather than lime (hydrated lime or slaked lime) and they painted on dry support layer.

Gypsum plaster is one of the oldest materials for decorating buildings and the Iranian artists used this material in different forms. Stucco mortar consists of dry plaster of Paris and water mixed together. The primary setting process takes about 4 or 5 minutes and by 7 to 30 minutes, it would finish and gypsum minerals would appear.

Plaster hardens quickly, so craftsmen cannot cover the great surfaces with it. In Iran for covering with gypsum plaster, especially for coating the exterior surfaces, craftsmen applied two layers of

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[4] Gum arabic is a binder made from acacia trees.

plaster. First layer or priming is the rough plaster and the next layer for fulfilling is the very smooth-textured gypsum. Addition of some materials to the plaster makes mortar hardening late or soon. "The set is accelerated by adding gypsum dust, salt (NaCl) [and powder of slaked lime ($Ca(OH)_2$)] and is retarded when organic materials like glue or starch are present" (Torraca, 1982, p. 66). However amount of these additional materials is very important in acceleration process. For instance, even though adding 2 percent of salt behaves as an accelerator; additional salt around 10 percent, causes the hardness to take longer than usual, about 12 minutes.

In Iran, for long lasting of the plaster mortar formation, craftsmen add some clay to the plaster of Paris because during the mixing process, the clay absorbs some of the water first and then it will give water back to the compound slowly so the mortar hardening will take longer (Abbasian, 1992).

4.4. Armenian Palette and techniques

4.4.1. Armenian palette

Studying of Armenian palette has been done numerously on their illuminated manuscripts but not about Armenian wall paintings. Also there are different sources which described Armenian palette since old ages. Merian, Mathews, and Orna (1994) mentioned that the Armenian palette in manuscripts from 1200 to 1348 does not include more than six pigments. These pigments are the main colours of the Cilician palette: gold, lead white, vermilion, orpiment, ultramarine, and red lake. The first four are ancient pigments and the last two medieval (p. 129).

Based on more literature reviews, it has been mentioned that the palette of miniatures in 13th century was "composed of yellow, light green, pale lilac and blue, and shades supporting the basic combination of reds and dark blues. Also there was lavish use of gold leaf" in some manuscripts (Nersessian, 2001, p. 165). Artists especially in late 14th century had a limited palette, composed mainly of green and red with occasional additions of black, brown and yellow (ibid, p. 170).

In the later time around 1455, one of the most famous Armenian palette is the palette of Khatchatur of Khizan. Khatchatur was a priest and "the leading [painter and] artist of the Khizan School" (ibid, p. 226).

The range of Khatchatur's pigments is impressive. Cabelli and Mathews (1982) found that "the red was found in his artworks is vermilion (red mercuric sulphide, HgS), a pigment which was available naturally and synthetically throughout the Middle Ages" and very early, probably in China. "This is one of truly ubiquitous Armenian pigments", occurring in different Armenian manuscripts (p. 38).

Also another most characteristic colour in Armenian paintings is magenta. "The magenta was found to be an organic lake pigment" from the lac (secretion) of the *laccifer* or *lacca*, an insect of India and the Far East. "In Armenian practice this magenta is frequently used in monochrome, but

Khatchatur enlivens his monochrome with passages of light green, blue, and yellow" (ibid; Merian et al., 1994, p. 129).

About green colour, "a true green pigment seems to have been unknown in the Cilician tradition. Generally, Armenian painters mixed their green from a mineral yellow, orpiment, and blue; the blue may be ultramarine or an organic blue (Khatchatur uses the latter)" (ibid).

To Merian et al. (1994):

> Orpiment is a mineral pigment available close at hand to the Armenians, mined in the Lake Van region and elsewhere in Asia Minor [and]….natural ultramarine is a blue pigment extracted from the semiprecious stone, lapis lazuli…It was mined in Badakshan in Afghanistan where its use as a pigment was pioneered in the sixth century….It was always more readily available in Armenia than in Byzantium and the West, where it was regarded as a substance of great value. (p. 129)

Gold as a painter's pigment was used since old ages probably since second century. In Armenian artworks and "manuscripts, as in Byzantine, it served for backgrounds, highlights, halos, and other decorative purposes. [Lead white] was the most widely used of all artist's pigment in Europe and the East…It is a toxic substance [and] one of the earliest artificially prepared pigments" (ibid).

With respect to these colours it is evident that Khatchatur is following time-honored Armenian painting traditions (Cabelli & Mathews, 1982, p. 38). Also there were two more organic pigments into Armenian palette which are indigo and an organic yellow, both of oriental origin.[5] Table 4.2 shows the brief description of Armenian palette.

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[5] As its name implies, indigo derives from a plant grown in India, and its use in Europe was extremely limited before the sixteenth century. The organic yellow, which in some cases resembles saffron, is used in mixtures, sometimes to supply green by mixing with ultramarine, sometimes to add warmth to orpiment. The use of this organic pigments have been mentioned especially in Armenian illuminated manuscripts (Merian et al., 1994).

Table 4.2. The brief description of Armenian palette

Armenian Palette **Based on analyses of Armenian illuminated manuscripts**	
Colour	**Pigment/Dye**
White	Lead white
Blue	Ultramarine, indigo
Red-Orange	Vermilion, red lake
Green	Orpiment+ ultramarine- organic blue
Yellow	Orpiment, organic yellow

4.4.2. Armenian Artist's techniques and method

Merian et al. (1994) illustrated that "the knowledge and techniques necessary to create precious Armenian paintings were handed down from master to student, sometimes father to son" (p. 125) and like "contemporary Byzantine workshops, it was not uncommon for assistants to do backgrounds or figures, leaving more important features and faces to be completed by the master" (p. 128). Also in their study they found that "Painters generally began with a sketch, and flaking paint sometimes offers a glimpse of this preparatory stage. The drawing is usually light brown"…and in gilded parts, there is an undercoat of "red bole which offered a smooth surface for the metal" (ibid). About gilded parts of Armenian paintings, it was found that the surface of gold leaves were often polished or burnished, probably with a smooth stone or shell, to give the gold leaf a smooth shiny surface.

Furthermore, Merian et al. (1994) mentioned:

> The black which was used over the gold leaf was Carbon ink, usually made of soot suspended in a glue or gum solution such as gum Arabic. This type of ink does not really penetrate the support, although it sometimes flakes off. It can also be spoiled by contact with water.
>
> Another type of ink was iron-gall ink, which was developed later than carbon inks. This ink was made by mixing a tannin-containing product (oak galls are a common source)

> and a metallic salt (such ha vitriol, or iron sulfate) with gum Arabic. This ink is often acidic. (p. 128)

Since seventeenth-century imagery often relied on European sources, it has been mentioned that the pigments in Armenian palette are probably also Western. As it was discussed before; Armenian merchants and representatives had a strong trade connection with Europe, especially Venice and Amsterdam. Therefore importing and exporting different goods, artefacts and pigments could be happened during that era. So beside the effects of European style which are definitely obvious in the topics and presentation of Iranian- Armenian wall paintings, cognition of European palette at around the same time would be considered as well.

4.5. European Palette

"Until the 18th century artists made their own paint from raw pigments ground into a binder; the colours available would be dependent on the artist's contacts in major trading areas or the latest developments in chemistry" ("Winsor & Newton," 2013).

In Italy, Venetian painters took great delight in experimenting with the new colours that entered through the trade connection with different parts of the world. One of "the greatest painter of 16th-century Venice, was Titian (c. 1490-1576). He was the first painter to have a mainly international clientele. During his long career, he experimented with many different styles of painting which embody the development of art during his epoch" ("The National Gallery," n.d.).

"Titian was active in the period which Venice was the supreme European trading area, importing goods, including pigments, from around the world" ("Winsor & Newton," 2013). "Titian used an unusually wide range of pigments, including orpiment, [the highly toxic arsenic sulphide] the only true orange of the Renaissance, realgar available in Venice from around 1490, vermilion and ultramarine. The greens in his paintings include malachite, verdigris and copper resinate (Ball, 2001, p. 123).

In Les Élémens de Peinture Pratique (1684), Roger de Piles[6] discusses oil painting technique with an emphasis on the layout of the artist's palette. He explained that:

> In oil painting are usually used eight principal colours: almost all others are derived and are composed of a mixture of these. They are arranged in a range roughly this way. 1.

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[6] Roger de Piles was a French painter, engraver, art critic and diplomat who lived in the latter part of the 17th century. He was the French ambassador to Venice, Portugal and Spain. While in Venice (1682–1685), he started a famous collection of prints, drawings and paintings of Giorgione, Correggio, Rembrandt, Claude Lorrain, Rubens, Antoine Coypel and Jean-Baptiste Forest.

> [Lead white]. 2. Yellow ochre. 3. Brown red. 4. Lake. 5. Stil de grain. 6. Green earth. 7. Umber. 8. Bone or ivory black. [These colours have been reproduced in later time and even in recent years and they have been named] as 1. Lead White. 2. Lemon Ocher. 3. Venetian Red. 4. Madder Lake. 5. Italian Sienna. 6. Verona Green Earth. 7. Cyprus Umber Medium. 8. Bone Black. ("17th Century Flesh Tone Palette," 2014)

And finally the important artist's palette in Netherlands -which was a major manufacturer of pigments- was the palette of Rembrandt who "had easy access to lead white, smalt, lead tin yellow, and vermilion" ("Winsor & Newton," 2013). "Also lake pigments were an essential constituent of the 17th-century Dutch artist's palette, despite being light-sensitive and liable to fade" ("The National Gallery," n.d.). Table 4.3 shows the brief description of European palette (especially Venetian and Dutch palette).

Table 4.3.The brief description of European palette

European Palette **(Especially Venetian and Dutch palette)**	
Colour	**Pigment/Dye**
White	lead white
Blue	ultramarine, smalt
Red-Orange	Venetian red (feric oxide +manganese oxide-Sinopia), realgar (arsenic sulfide), vermilion, red lake
Green	verdigris, malachite, copper resinate, green earth (hydrosilicate of Fe, Mg, Al, K)
Yellow	orpiment, yellow ochre, lead tin yellow

4.6. Conclusion

It has been mentioned in different sources that the Persian painters in pre-Safavid dynasty did not try to "reproduce nature and did not show shadows, but a bright, pure, luminous world, beyond the reach of terrestrial sight" (Porter, 2000, p. 113).

But in Safavid dynasty, artists' started to show different forms and styles in their paintings. The Safavid shahs of Isfahan supported various kinds of arts in different styles. "The attitude of Isfahan artists and patrons toward European art was similar. Painters came to Isfahan from Europe, and local mural painters sometimes emulated their works, even as others produced large-scale paintings very similar to Isfahan Style miniatures" (Taylor & Walsh, 1995, p. 25). "Shah 'Abbas II himself studied drawing with Dutch painters, and his son, Shah Sulaiman, supported Muslim painters whose work features so many European elements that scholars once commonly assumed that they must have studied in Italy" (ibid, p. 28).

As a result, "The development and significance of *farangi-sazi* (or Europeanized mode) is very obvious at the Persian court and in the Armenian suburb of New Julfa during the seventeenth century" (Leoni & Natif, 2013, p. xiv). Furthermore, the school of realistic and historical paintings which was close to European style were developed "in the course of eighteenth century based on trends that began in the Safavid period" (Diba, 1989, p. 147).

About palette of pigments in Armenian and Iranian paintings, it was studied that the Armenian palette before their presence in Iran, represents a tradition somehow similar to painting in Islamic lands. Nevertheless, there are some differences between two palettes and must be considered. For instance, natural green, which is missing in Armenia, is copper green in Iran. Red lead and red earth supplemented the Armenian red lake. Despite of explanation of producing red lake in Sadiqi Bek's treatise, there is no evidence of using such a red lake in Iranian wall paintings. It seems both Iranian and Armenian artists used the red lake for their manuscripts and not for the wall paintings. In case of blue colour ultramarine, smalt, and indigo were used in Iranian paintings. Vermilion, lead white, and orpiment existed in both Armenian and Iranian palette.

The similarity between Armenian and European palettes (especially the palette of Venice and Amsterdam) has been discovered about the following pigments: orpiment, ultramarine, lake pigments, lead white, and black bone.

CHAPTER FIVE

5. Examination of Wall paintings by Scientific Methods

5.1. Introduction

"Throughout history, paint has been used as a medium to express the artist's ideas, applied with distinct techniques on different substrates" (Edwards & Chalmers, 2005, p.72).

Artists and painters from the different historical periods have left a valuable archive of special artist's material and different methods and techniques in their artworks. The study of artist's materials, therefore, could be very important to get more information about their techniques.
Also chemical and technical analysis of pigments may describe the interrelationships of artists and schools.

According to Nadolny (2003), the "early analytical work on paintings", appears to start since 1780. Furthermore, "analyses of pigments in mural paintings" were done by "Haslam in 1800 and "Humphrey Davy in 1815" (as cited in Scientific examination of art, 2005, p. 6).

There are different techniques and analytical methods for study about the materials of wall paintings. Any information about "elemental composition" and "physical properties" can help researchers for identification of painting materials. The important factor for "choosing an analytical technique" is to minimise damages to the wall painting, therefore application of "non-destructive techniques" always are more necessary. In cases which just destructive techniques can be applied, very tiny amount of material from the locations with minimum aesthetic damages must be taken (Stuart, 2007, p. 1).

"In archaeometry, it is important to identify the colouring materials and, depending on the nature of the colorants, different analytical techniques might be more useful to identify the different colorants" (Edwards & Vandenabeele, 2012, p. 349).

According to Edwards and Chalmers (2005) "paint is the recurring subject of many investigations in the field of art analysis and consists of three major compounds: the colourant, the binding medium and the solvent" (p. 72).

Also "Different types of colourants can be distinguished by their solubility in the paint medium. Pigments are (almost) insoluble, whereas dyes are soluble" (ibid). An overview of the classification of some pigments is given in the table 5.1.

Table 5.1. Classification of some important pigments[1]
(Edwards & Chalmers, 2005, p. 72)

Insoluble colourants: **Pigments**	**Inorganic**	**Organic**
Natural	Lapis lazuli[1]	Natural indigo
	Cinnabar[2]	Natural Indian yellow
	Malachite	
	Azurite	
	Ochre	
	Chalk	
Synthetic	Egyptian blue	Synthetic indigo[3]
	Prussian blue	Modern organic pigments, such as Hansa Yellow, Copper phthalocyanine, Naphthol AS pigments, Anthraquinone pigments, etc.
	Verdigris	
	Lead-tin yellow	
	Synthetic titanium white	
	Ultramarine	
	Naples yellow	
	Lithopone	

1. Lapis lazuli is the mineral form of ultramarine, which is a synthetic pigment.
2. Cinnabar (HgS) is a mineral pigment that could be used as such after milling. Often the mineral was purified by sublimation before using it. In this case the pigment is dubbed vermilion.
3. Indigo can be used as an insoluble compound in a binding medium (pigment), but often it is used as a dye. The natural form is extracted from different plant sources; from woad (Isatis tinctoria) and from the indigo plant (Indigofera tinctoria).

"A comparison of commonly used chemical analysis techniques" is given in table 5.2. "Each technique has its own advantages, and when techniques are used together, they can supply complementary information on a sample" (Derrick, Stulik, & Landry, 2000, p.17).

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[1] The vast majority of the historical pigments are inorganic, some are organic; they can be synthetic as well as from natural sources (Edwards and Chalmers, 2005, p. 71).

Table 5.2. A comparison of commonly used chemical analysis techniques
(Derrick, Stulik, & Landry, 2000, p.17)

Technique	**Acronym**	**Description**	**Minimum Sample size**	**Sample preparation**	**Specificity**
Polarized light microscopy	PLM	Identification of material Identification of material	5 µm	easy	none
IR spectroscopy	IR	Compositional analysis of organic and inorganic compounds	10 µg	easy	none
X-ray fluorescence	XRF	Elemental analysis	non-destructive 1 mm spot	none	elements only (heavier than potassium)
Energy dispersive spectroscopy	EDS	Elemental analysis (similar to XRF but attached to scanning electron microscope)	1 µm spot	easy	elements only heavier than carbon)
X-ray diffraction	XRD	Compositional analysis of crystalline materials	10 µg	easy	crystalline materials

In this chapter a brief description of scientific techniques which were applied during this research are presented.

5.2. Sample Preparation and Analytical Techniques

5.2.1. Cross section

The majority of wall paintings were created with multiple layers but, usually, only the top paint layer is accessible for visual observation and the under layers are hidden. Sometimes in case of damages, flaking paints, and detached layers; the under paint layers could be seen.

Therefore, information about layer structure can only be obtained by collecting samples from the wall painting and preparing paint cross sections. Taking samples and choosing sampling locations must be done by considering the "ethical factors". A paint cross section is made by embedding the paint sample in a resin or polyester. Then resin must be polished, till the different paint layers will be exposed. Then Paint cross sections must be viewed through a microscope (Weerd, Veen, Heeren, & Boon, 2003, p. 716; DeGhetaldi, 2014).

5.2.2. X-ray Fluorescence Spectroscopy

One of the most popular instrumental techniques for pigment analysis is X-ray fluorescence spectrometry (XRF). This technique "provides an elemental analysis of selected colour areas of each painting but is reliable only for those pigments containing elements with atomic numbers above that of potassium" (Purinton & Waiters, 1991). Even though this method only identifies pigments through the elements; "It is often amongst the first tools used because sometimes elemental data is sufficient for pigment characterization….[but] pigments with similar elemental compositions or different crystal structures cannot be differentiated" by XRF (McGlinchey, 2012, p. 131).

"Unfortunately, the method is not specific to the analysis of the upper pigment layer since it ambiguously incorporates the ground layer and even the support" (Claes, Van Ham, Janssens, & Van Grieken, 1999, p. 263). However, it is very important to remember that no single instrument can answer every question.

For reporting the XRF results, "identification of most bilk elements is easily achieved by using the instrument manufacturer's peak identification tools to identify the elements via K and or L lines present from the raw data" (McGlinchey, 2012, p. 151).[2]

Table 5.3 gives an overview of some pigments, and their corresponding key-elements.

Table 5.3. Overview of some important pigments, along with the corresponding key-elements (Edwards & Vandenabeele, 2012, p. 350)

Pigment	**Colour**	**Chemical formula**	**Key-element (XRF)**
Vermilion	Red	HgS	Hg
Azurite	Blue	$2CuCO_3.Cu(OH)_2$	Cu
Lapis Lazuli	Blue	$Na_{8..10}Al_6Si_6O_{24}S_{2..4}$	_
Carbon black	Black	C	_
Realgar	Orange	As_4S_4	As
Orpiment	Yellow	As_2S_3	As
Red lead	Red	Pb_3O_4	Pb
Lead white	White	$2PbCO_3.Pb(OH)_2$	Pb
Massicot	Yellow	PbO	Pb
Titanium white	White	TiO_2	Ti
Zinc white	White	ZnO	Zn
Verdigris	Green	$Cu(CH_3COO)_2.nCu(OH)_2$	Cu
Malachite	Green	$CuCO_3.Cu(OH)_2$	Cu
Posnjakite	Green	$Cu_4SO_4(OH)_6.H_2O$	Cu
Lead-tin yellow (type I)	Yellow	Pb_2SnO_4	Pb, Sn
Lead-tin yellow (type II)	Yellow	$PbSn_2SiO_7$	Pb, Sn
Chalk	White	$CaCO_3$	Ca
Gypsum	White	$CaSO_4.2H_2O$	Ca
Prussian blue	Blue	$Fe_4[Fe(CN)_6]_3$	Fe
Haematite	Red	Fe_2O_3	Fe

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[2] For more information see: Shugar, A. N., & Mass, J. L. (Eds.). (2012). *Handheld XRF for Art and Archaeology* (Vol. 3). Leuven University Press.

5.2.3. X-ray Diffraction (XRD)

According to Jenkins and Snyder (1996) "The main purpose of the XRD-measurements is to achieve information on the compositional properties of the pigments by crystallographic phase analysis (as cited in Hochleitner, Desnica, Mantler, & Schreiner, 2003, p. 644).

In Stuart's (2007) study, it was mentioned that "XRD has been widely used to identify inorganic pigments used in paintings. This technique is particularly useful for differentiating pigments of the same chemical structure but with different crystalline phases" (p. 232).

5.2.4. Micro Raman Spectroscopy

According to Burrafato et al. (2004) "Raman spectroscopy has been used successfully in the investigation of the chemical composition of materials employed in various types of artefact of artistic–historical interest….The results obtained from investigations of paint pigments seem, at present, by far the most promising" (p. 879). In fact "Raman spectroscopy is an excellent tool for the characterisation of paintings and has been used to examine easel, panel and wall paintings, as well as rock art, from a range of periods" (Stuart, 2007, p. 139).

A major advantage for the application of Raman spectroscopy, in study of wall paintings, is the minimal size of the sample which can be used for Raman analysis; without "prior chemical or mechanical pre-treatment". It is often enough to remove dust from the sample surface, but in some selected samples in this study, it was necessary to remove the thick layer of varnish before starting the analysis by micro Raman spectroscopy. However, it could be the major disadvantage of Raman spectroscopy, since the majority of wall paintings have been coated with varnishes and resins which can produce much fluorescence and can hide the Raman spectrum (Edwards & Chalmers, 2005, pp. 41-42), "but the use of a larger excitation wavelength can avoid this problem" (Stuart, 2007, p. 140). On the other hand, "Inorganic pigments produce good quality Raman spectra as they are crystalline materials – such materials show sharp Raman bands with lattice vibrations appearing in the low wave number region of the spectrum" (ibid, p.139).

5.2.5. Fourier transform infrared (FTIR) spectroscopy

"Infrared spectroscopy has the distinct advantage of providing information about both the organic and inorganic components in paint. FTIR databases containing the spectra of painting components are available and pigments, fillers and binders may all be identified using infrared spectroscopy" (Stuart, 2007, p. 126).

"A spectral pattern, sometimes called a fingerprint, is used to identify an unknown material when the absorptions in its spectrum are matched with the absorptions in the spectrum of a known material" (Derrick et al., 2000, p.14).

Table 5.4 shows "The infrared bands of some common inorganic pigments found in paintings" (Stuart, 2007, p. 126).

Table 5.4 Major mid-infrared bands of some common inorganic pigments and fillers
(Stuart, 2007, p. 127)

Compound	***Wave number cm*−1**
Azurite	3425,1490, 1415, 1090, 952, 837
Barium sulphate	1185, 1128–1120, 1082, 639, 614, 200
Cadmium sulphide	250
Calcite	1492–1429, 879, 706
Calcium sulphate	1140–1080, 620, 3700–3200
Chrome yellow	887
Chromium oxide	632, 566
Cinnabar	347, 285, 130
Gypsum	3500–3400, 1700–1600, 1150–1100, 700–600
Indigo	3400–3200, 3100-2800, 1700–1550, 1620–1420
Kaolinite	3700–3200, 1100–1000, 910–830
Lead chromate	905, 860, 830
Lead white	3535–3530, 1400, 1047–1045, 693–683
Litharge	375, 295
Malachite	3400, 3320, 1500, 1400, 1095, 1045
Naples yellow	666, 408
Orpiment	305, 183, 139
Prussian blue	3500–3000, 2083
Realgar	373, 367, 343, 225, 170
Red lead	530, 455, 320, 152, 132
Silica	1100–1000
Ultramarine	1150–950
Viridian	3500–3000, 1600, 555, 481
Zinc sulphide	290
Zinc white	400–500

Also in the following table (table 5.5) the brief description of the distinctive bands of the common functional bands in IR Spectroscopy has been given (University of Colorado-IR Spectroscopy Tutorial, n.d.).

Table 5.5. Distinctive bands of the common functional bands in IR spectroscopy

frequency, cm^{-1}	**bond**	**functional group**
3500-3300 cm^{-1}	N–H stretch	amines
3500-3200 cm^{-1}	O–H stretch	alcohols, a broad, strong band
3100-3000 cm^{-1}	C–H stretch	alkenes
3000-2850 cm^{-1}	C–H stretch	alkanes
1760-1665 cm^{-1}	C=O stretch	ketones, aldehydes, esters
1680-1640 cm^{-1}	C=C stretch	alkenes

Derrick et al. (2000) concluded that "samples from paintings contain many materials….These variations can produce a reflectance spectrum that…looks different from the spectra collected by transmission from the same components because of the dissimilar reflection and absorption characteristics of each material" (p.34).

5.2.6. Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometry (SEM-EDX)

"In scanning electron microscopy (SEM) the image of an object is created using a beam of electrons rather than traditional visible light" (Stuart, 2007, p. 91). "A scanning electron microscope can magnify objects of the order of 100 000 times and detailed three-dimensional images can be produced" (ibid, p. 92).

This technique can be used with EDS to detect elements in very small amounts of samples. Actually, "elements can be detected in quantities as low as 0.1 weight per cent" (Caddy, 2002, p. 244). "SEM/EDS has the ability to simultaneously detect a wide range of elements on the periodic chart. When used properly, the technique will enhance discrimination potential by revealing the identity of various elements in the coating" (ibid).

5.3. Equipment and Experimental Methods

During this study, the cross sections were prepared from many samples. The size and form of some samples (very powdery and sometimes a small amount) did not provide any possibility to make cross sections or do some analyses. The samples were embedded in liquid synthetic resin Bio-Plastic that hardens with the addition of a catalyst.

5.3.1. X-Ray Fluorescence (XRF)

A portable Bruker ARTAX™ 200 µEDXRF spectrometer was used as the XRF spectrometer which consisted of an X-ray tube with a Mo target placed at 6˚ and a beryllium window. Analyses were carried out by using a collimator with diameter from 200 µm to 650 µm and a helium flow.
The excitation conditions was 30 KeV which has been proved to be optimal for analysing the various elements. Nevertheless, in case of using different excitation energy beam, it has been mentioned in the part of XRF analysis of each sample. The collecting time (time of acquisition) for each spectrum was 100 s. The system was controlled by ARTAXControl 7.2 software. The peaks Mo-Kα and Mo-Kβ in each spectra, are related to the Rayleigh and Compton effect.

5.3.2. Micro- Raman Spectroscopy

The micro-Raman instrument which was used in this research was a LabRam HR800 spectrometer (Horiba Jobin Yvon, France) with a focal length of 80 mm, fitted with an air-cooled CCD detector (1024 x 256 pixels) at -70°C. The acquisitions were performed with a 600 grooves/mm grating. The excitation source was a He–Ne laser (632.8 nm line) with a maximum laser power of 20 mW. Spectra were recorded by placing the samples on the XeY motorised stage and observing them with 50x and 100x objectives.

The spectrometer was calibrated with silicon at 520 cm^{-1} and the recorded spectra were handled with LabSpec 5 software.

5.3.3. Fourier Transform Infrared (FTIR) Spectroscopy

Transmission work carried out on a Nicolet Avatar 320 FT-IR spectrometer, attenuated total reflectance (ATR) accessory- Golden Gate. Sample held in a diamond cell and 32 scans were averaged at 4 cm^{-1} resolution. The peaks' positions have been specified by using the GRAMS/32 software package. The resulting spectrum represents the molecular transmission which creates a molecular fingerprint of the sample.

5.3.4. X-ray Diffraction (XRD)

The instrument employed in this study is a Bruker AXS D8 Advanced X-ray Powder Diffractometer for. The instrument parameters used in this study are the following:

Type: Locked Coupled, Step: 0.020°, Step time 10s, Anode: Cu, WL1: 1.5406

5.3.5. SEM-EDX

In this project, analyses were performed with a ZEISS EVO MA15HR scanning electron microscope equipped with OXFORD Smatmap EDS INCA for EDS chemical microanalysis (University of Ferrara, Italy); electron source LaB6 cathode, with accelerating voltage 20 kV, and 8-10 mm working distance. Elemental data were prepared using the INCA Energy 300 software. Sample preparation (coating) was not applied for the samples.

5.4. Conclusion

This chapter presented an introduction about samples preparation and analytical techniques which were used in this study.

Apart from the historical texts and literature review about artists' pigments, examination of the wall paintings themselves through different analyses can provide lots of information. Pigments analysis can be done in various ways but the availability of samples, instruments, and equipment has the very important rule in the study of wall paintings or any other archaeometrical studies.

CHAPTER SIX

6. The House of Sukas (Sokiasian)

6.1. Introduction

One of the most famous Armenian houses in New Jolfa is called Sukas or Sokiasian (figures 6.1 and 6.2). This house, and especially its paintings (figures 6.3 and 6.4), have been described by Carswell. There is the proposed date of 1655 for this house. Also, Carswell stated that the date was communicated to him verbally by the owner. Karapetian's study (1974) found the following:

> In the absence of historical documents, an approximate, indirect dating may be attempted in the following way. In the central room a sovereign is portrayed who may be recognized as Shah Abbabs I (1586-1628) and in any case, the painting bears his name. To be allowed to have the King's portrait painted and to keep it in the house was a privilege which could be granted only by the King himself. This would lead one to believe that, in the first place, permission had been asked to portray the reigning monarch and not one of his predecessors; secondly, that the owner of the house enjoyed a high prestige, and that perhaps the King himself had honoured him with a visit. For these reasons, the house may be considered to have been built and, at least partly, painted during the reign of Shah Abbas I (pp. 124-125).

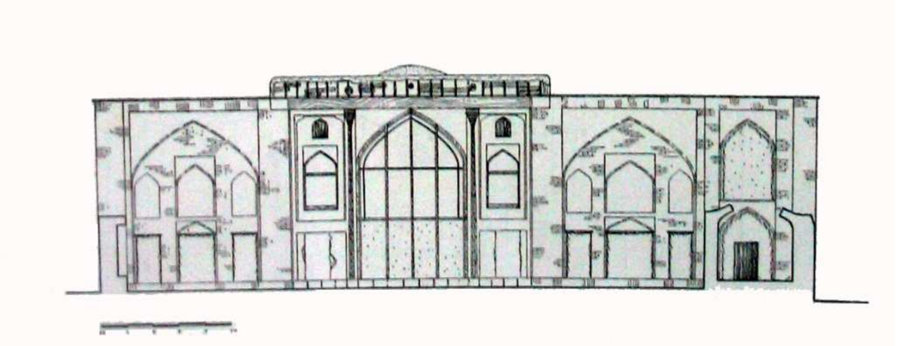


Figure 6.1. Main façade (north), scale 1:200 (Karapetian, 1974, p. 130).

Figure 6.2. The house of Sukas, north façade

Figures 6.3 & 6.4. The wall paintings of the house in exterior parts which are blends techniques of Iranian and European styles.

6.2. Experimental Approaches

6.2.1. Samples

In this building samples were collected from three different wall paintings inside the house. The following figures show the sampling spots on the wall paintings (figures 6.5-6.7).

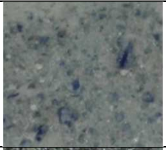
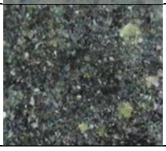
Figure 6.5. Samples S1 and S8 from the first wall painting in house of Sukas

Figure 6.6. Samples S3, S4, S5, and S9 from the second wall painting in house of Sukas

Figure 6.7. Samples S2, S6, and S7 from the third wall painting in house of Sukas

Table 6.1 shows the samples, the visual colours of the samples, and image of the samples. Each sample is denoted with the letter S for house of Sukas and the number describes different area sampled from the mural:

Table 6.1. Samples and their description

Samples from house of Sukas	Visual Colours of the Samples	Sample Images- Magnification 40X
S1	Light green	
S2	Green	
S3	Light green	
S4	Gold leaf over red layer	
S5	Orange- Red	
S6	Dark yellow	
S7	Dark red	
S8	Blue	
S9	Dark green	

6.2.2. Techniques and Analysis

A comprehensive analytical survey was undertaken to identify the painting materials used in these wall paintings. Table 6.2 gives the sample preparation and analytical techniques applied.

Table 6.2. Techniques applied to samples[1]

Samples	Cross section	XRF	Micro Raman	FTIR
S1	-	✓	✓	✓
S2	-	✓	✓	✓
S3	✓	✓	✓	✓
S4	✓	✓	-	✓
S5	✓	✓	✓	✓
S6	✓	✓	✓	✓
S7	✓	✓	✓	✓
S8	✓	✓	✓	✓
S9	✓	✓	✓	✓

1. The size and form of some samples (very powdery and sometimes a small amount) did not provide any possibility to make cross sections or do some analyses.

6.3. Results and Discussion

6.3.1. Sample S1

Due to the size and form of this sample, cross section was not provided. XRF analysis for sample S1 showed lead as the main constituent of the sample while copper, calcium, and iron were detected in the composition too (figure 6.8), therefore sample could be green copper pigment.

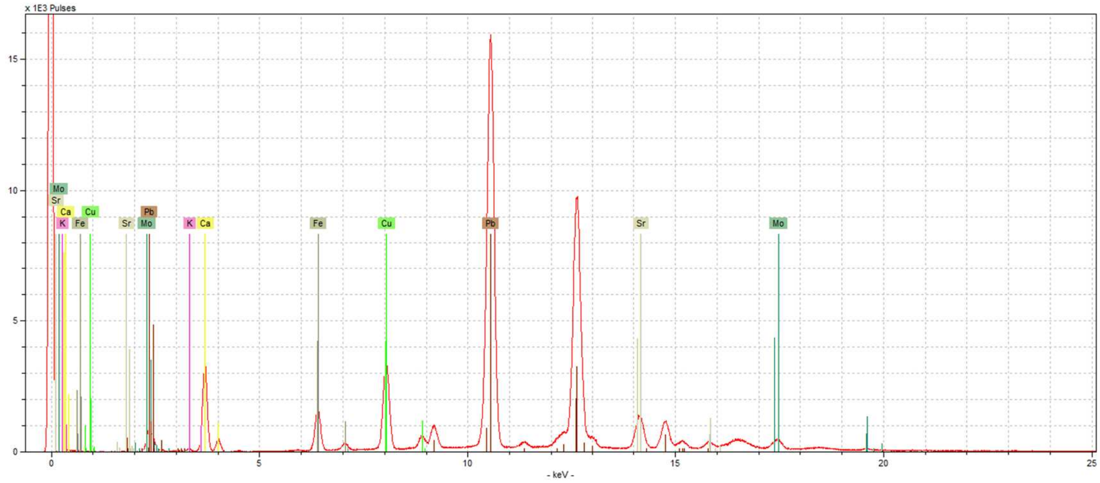


Figure 6.8. XRF spectrum on light green sample

The XRF analysis also was carried out on underside of this sample which showed that calcium is the main element and iron, sulphur and strontium are other elements in this composition (figure 6.9). This sample can be identified as a gypsum layer. The presence of iron in gypsum from Isfahan area is very common.

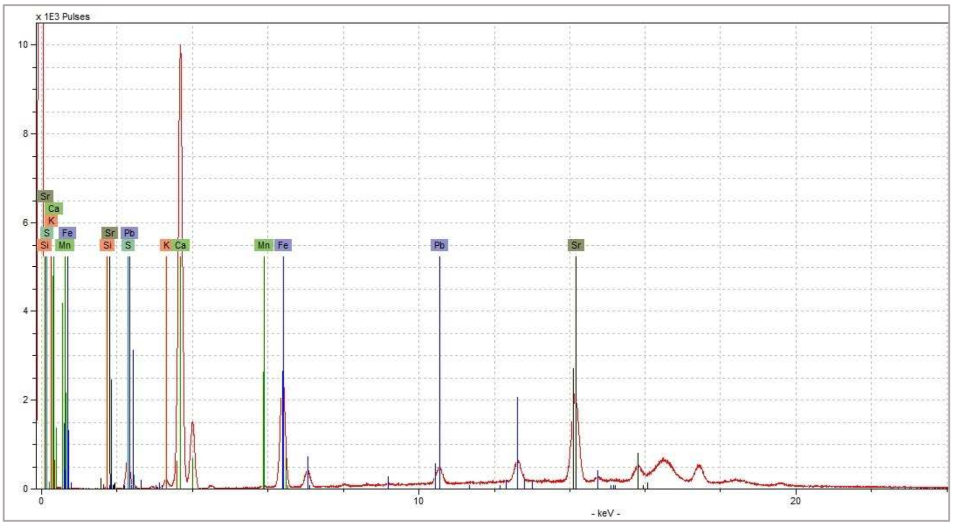


Figure 6.9. XRF spectrum of white side of the sample S1

This sample burned under the micro Raman analysis even with very low energy. Therefore, through Raman analysis, more information could not be gained about this sample.

6.3.2. Sample S2

Due to the size and form of this sample, cross section was not provided. The XRF examination of sample S2 showed copper as the main constituent and lead, calcium, and sulphur in minor amounts (figure 6.10).

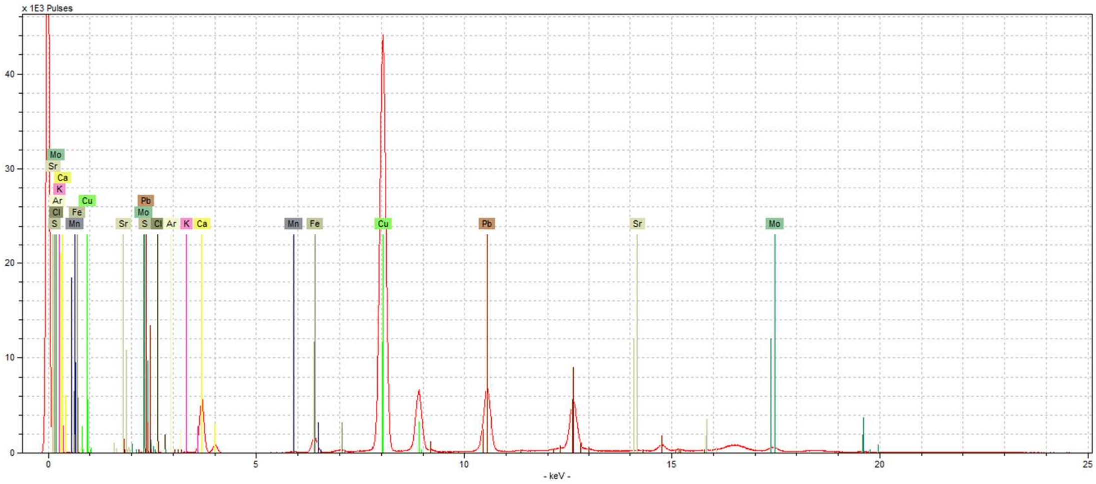


Figure 6.10. XRF analysis of the sample S2

During micro Raman analysis, the sample burned because of the high amount of binder mixed with pigment. Even after trying to extract the binder from the pigment, the residue did not provide reliable results and the high amount of binder brought much fluorescence. In the following spectrum (figure 6.11) the characteristic bands could be assigned to huntite but presence of magnesium was not confirmed by XRF analysis. The study of characteristic bands identified gypsum by its characteristic sulphate band at 1008 cm^{-1} (Burgio et al., 2010, p.5726).

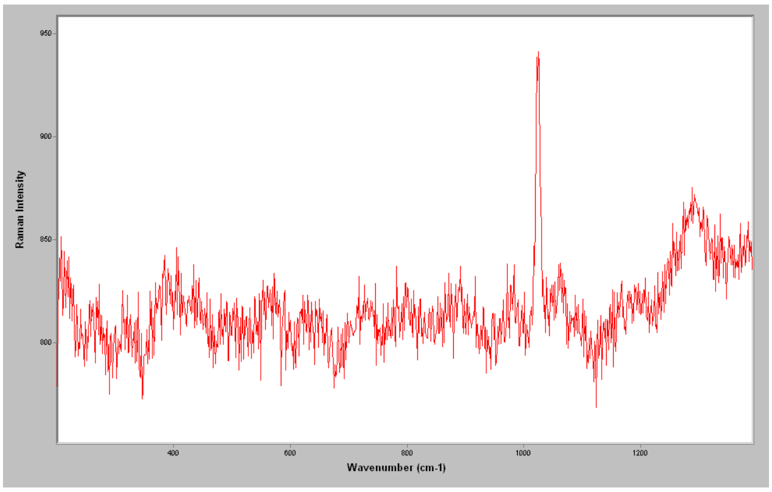


Figure 6.11. Raman spectrum of the sample S2 showed gypsum by its characteristic band at 1008 cm^{-1}.

6.3.3. Sample S3

The paint cross-section was viewed through a microscope. The microscopic image of sample's cross section (figure 6.12) showed different layers. The schematic sketch of the sample's layers (figure 6.13) contains: 1) light green paint, 2) dark or black layer, and 3) finish coat.

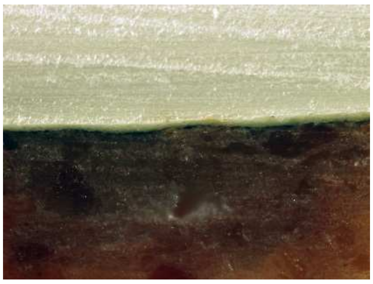


Figure 6.12. Cross section image of the sample S3, magnification 200X

Figure 6.13. Schematic sketch of the sample's layers

The XRF examination of sample S3 showed lead and copper as the main constituents of the material and calcium, and iron in minor amounts (figure 6.14).

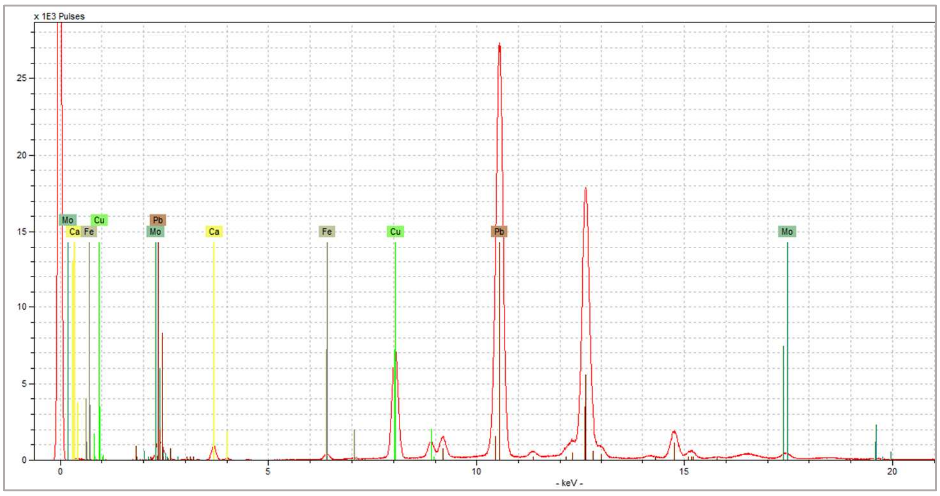


Figure 6.14. XRF spectrum of the sample S3

Presence of high amounts of lead can indicate lead white pigment. This would have been mixed to create a light green colour.

In the following Raman spectrum of sample S3 (figure 6.15) the characteristic band at about "1026 cm^{-1} could be assigned to γ-$CaSO_4$ (soluble anhydrite) which is the low-temperature dehydration product of gypsum" (Prasad, Pradhan, & Gowd, 2001, p. 1203).

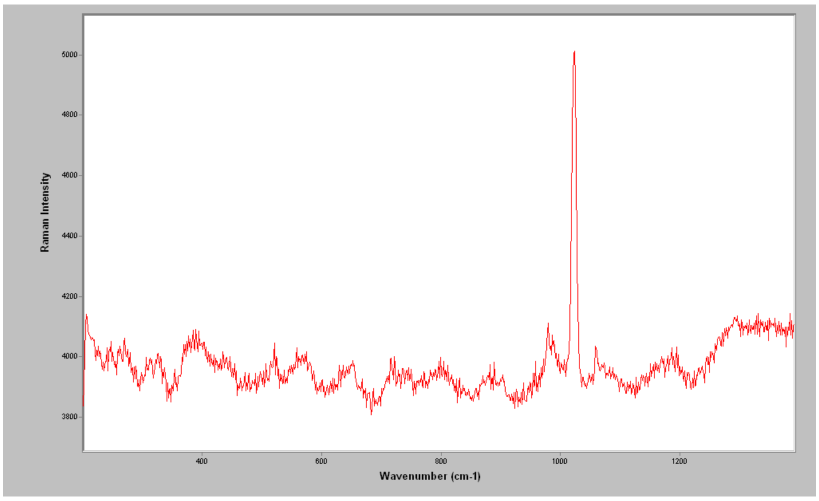


Figure 6.15. Raman spectrum of the sample S3

6.3.4. Sample S4

The microscopic image of sample's cross section (figure 6.16) showed different layers. The schematic sketch of the sample's layers (figure 6.17) contains: 1) very thin layer of gold leaf, 2) varnish or oily layer, 3) red ground layer, and 4) finish coat.

Figure 6.16. Cross section image of the sample S4, magnification 200X

Figure 6.17. Schematic sketch of the sample's layers

Sample S4 contains very tiny amount of gold leaf over the red layer. The XRF analysis of this sample was carried out with a 45 KeV energy beam. The result is shown in figure 6.18 and it confirms the presence of calcium, iron, lead, and gold. Copper is a minor amount in this sample. Calcium and sulphur could be from a gypsum layer used as a ground layer for this sample. The presence of iron could be from Armenian bole (Fe_2O_3) which was usually used under the gold leaf.

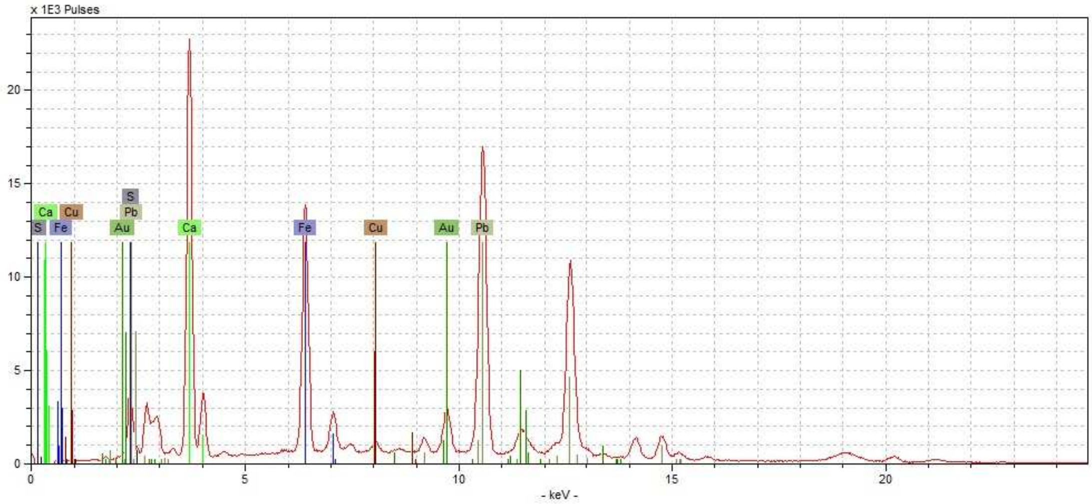


Figure 6.18. XRF spectrum of the sample S4

6.3.5. Sample S5

The paint cross-section of the sample S5 was viewed through a microscope. The microscopic image of this sample (figure 6.19) showed the presence of orange-red paint and finish coat layer.

Figure 6.19. Cross section image of the sample S5, magnification 200X

The XRF analysis on sample S5 (figure 6.20) showed that lead is the greatest amount, followed by calcium which is also main constituent in this sample. Other elements like iron, mercury, and sulphur exist in minor amounts.

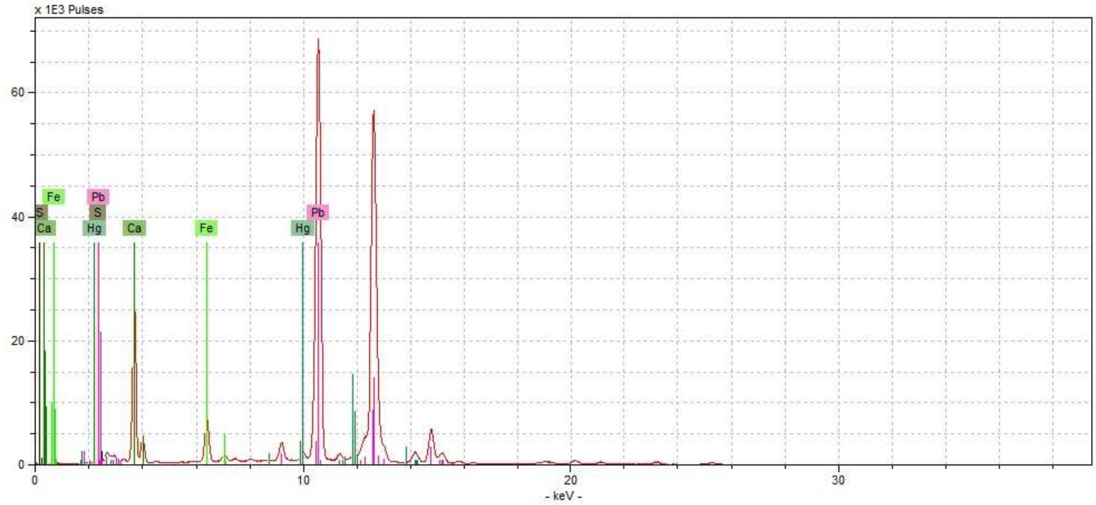


Figure 6.20. XRF spectrum of the sample S5

The Raman spectrum of this sample (figure 6.21) shows a very strong characteristic band at 252, a shoulder at 282 and a medium peak at 343 wave number/cm^{-1}, which could all indicate vermillion; however, there was no sign of litharge peak in Raman spectrum or mercury peak in XRF spectrum. This could be a mixture of vermilion and litharge together as two colours can be seen in the microscopic photo (figure 6.22).

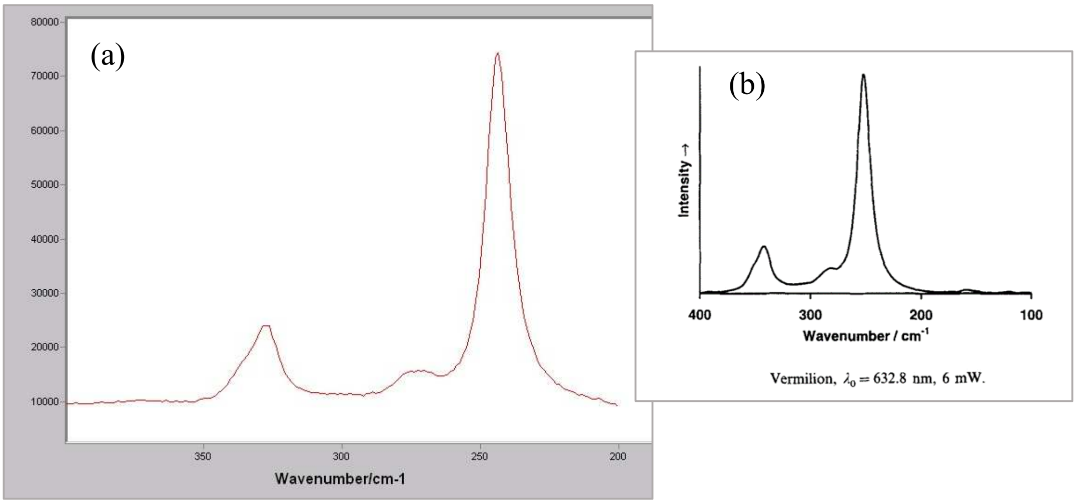


Figure 6.21. Micro Raman spectrum (a) from the orange-red sample in comparison with Raman database spectrum of vermilion (b) (Bell, Clark, & Gibbs, 1997, p. 2165).

Figure 6.22. Microscopic detail of the sample S5 which shows two different orange-red colours, magnification 40X

6.3.6. Sample S6

The microscopic image of sample's cross section (figure 6.23) showed different layers. The schematic sketch of the sample's layers (figure 6.24) contains: 1) yellow paint, 2) varnish or oily layer, 3) red paint layer, and 4) finish coat.

Figure 6.23. Cross section image of the sample S6, magnification 200X

Figure 6.24. Schematic sketch of the sample's layers

Sample S6 shows the high presence of lead in XRF examination (figure 6.25). Other elements like calcium, iron, and zinc are in minors in this sample. The presence of arsenic also was investigated from its Kα line at 10.54 KeV and its Kβ line at 11.73 KeV. As there was no peak at 11.73 KeV, the sample does not contain arsenic.

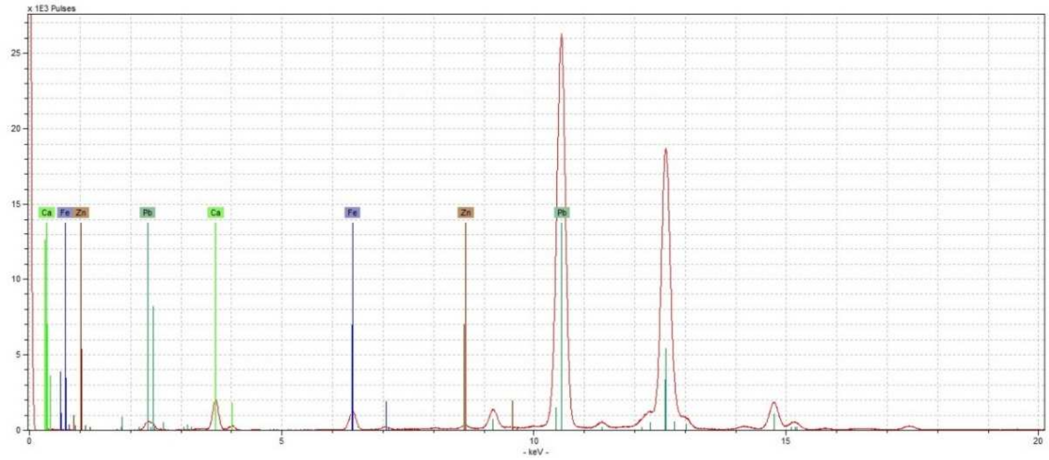


Figure 6.25. XRF spectrum of the sample S6

Micro Raman result did not provide a very clear spectrum but it shows that the sample contains vermilion (figure 6.26). "Cinnabar has primary peaks at 254, 277, and 340 cm^{-1} in the Raman fingerprint region" (Liritzis & Katsaros, n.d., p. 1).

The characteristic band at 385 wavenumber/cm^{-1} could be assigned to massicot (UCL Chemistry, 2010). The weak peak at 230 wavenumber/cm^{-1} could be assigned to orpiment, As_2S_3 (ibid), but arsenic was not detected in XRF analysis. This sample, therefore, is a mixture of vermilion and massicot.

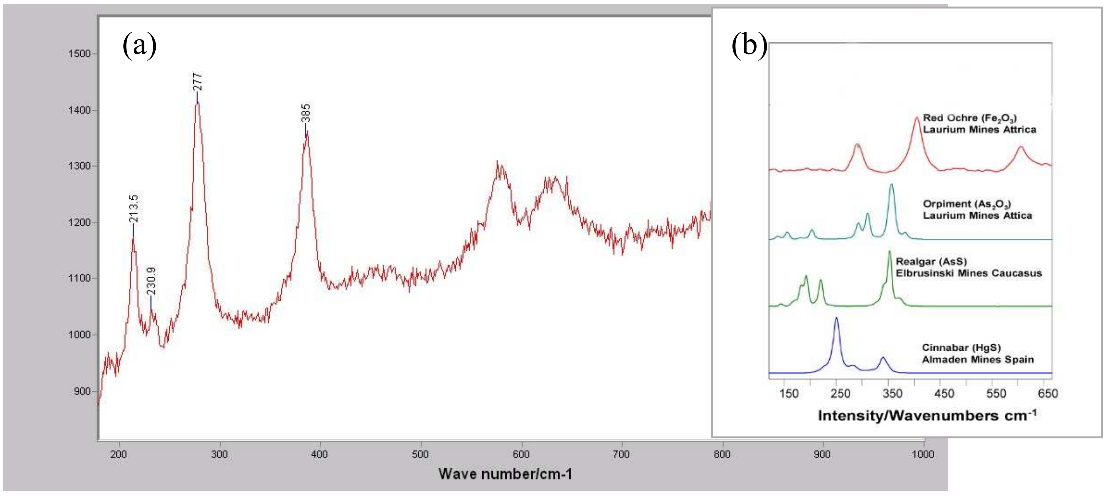


Figure 6.26. Micro Raman spectrum from the sample S6 (a) in comparison with "some databases" (b) (Liritzis & Katsaros, n.d., p.2)

6.3.7. Sample S7

The microscopic image of sample's cross section (figure 6.27) showed different layers. The schematic sketch of the sample's layers (figure 6.28) contains: 1) red paint, 2) mixture of dark blue-black with light colours, 3) oily layer, and 4) finish coat.

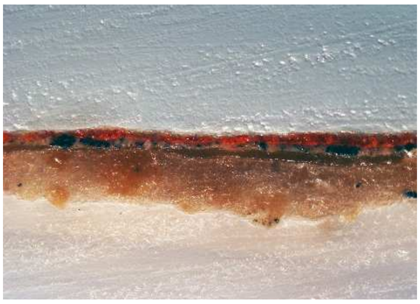


Figure 6.27. Cross section image of the sample S7, magnification 200X

Figure 6.28. Schematic sketch of the sample's layers

XRF analysis for sample S7 (figure 6.29) showed lead and mercury as the main constituents of the pigment while calcium and iron are in minor amounts.

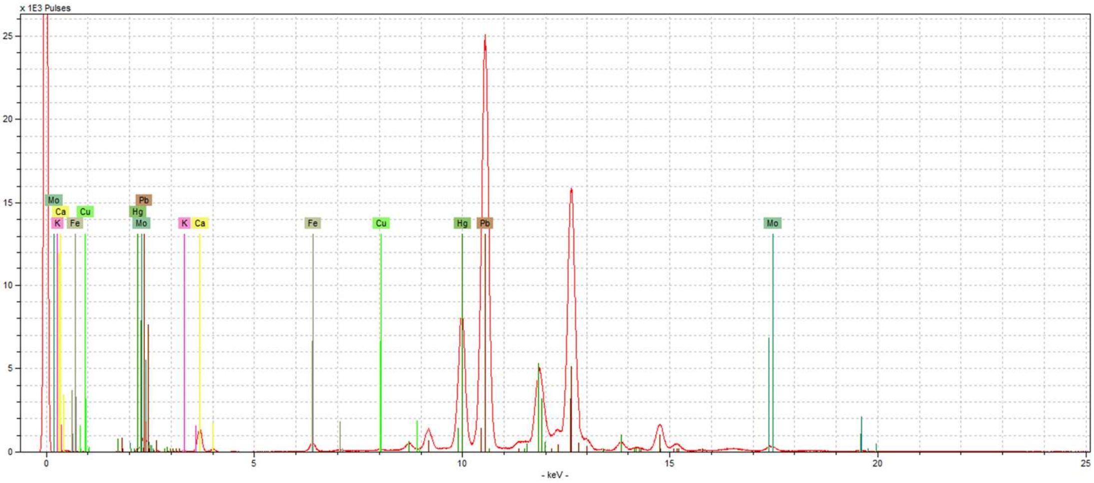


Figure 6.29. XRF spectrum of sample S7

Micro Raman analysis results, in comparison with a spectrum from a Raman database (figure 6.30), confirmed that the sample contains vermilion.

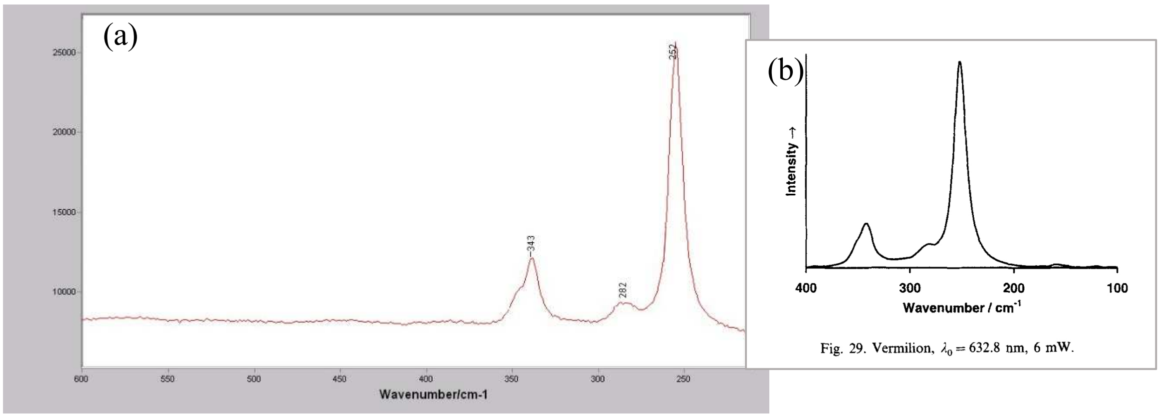


Figure 6.30. Micro Raman spectrum from the dark red sample (a) in comparison with Raman database spectrum (b) (Bell et al., 1997, p. 2165).

6.3.8. Sample S8

The paint cross-section of the sample S8 was viewed through a microscope. The microscopic image and schematic sketch of this sample (figures 6.31 and 6.32) showed the presence of 1) blue paint, 2) thin white ground layer, and 3) finish coat.

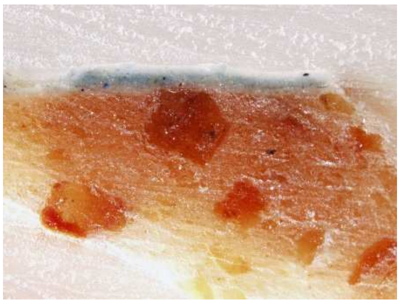


Figure 6.31. Cross section image of the sample S8, magnification 200X

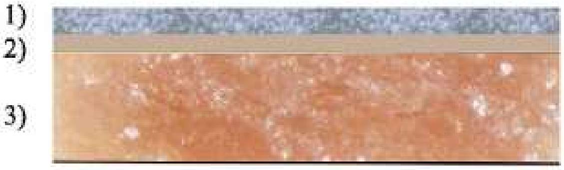


Figure 6.32. Schematic sketch of the sample's layers

The XRF analysis of this sample was carried out with a 15 KeV energy beam and it showed calcium, iron, cobalt and lead as the main constituents (figure 6.33). High presence of lead could indicate lead white which would usually be mixed with different colours to provide a light tonality.

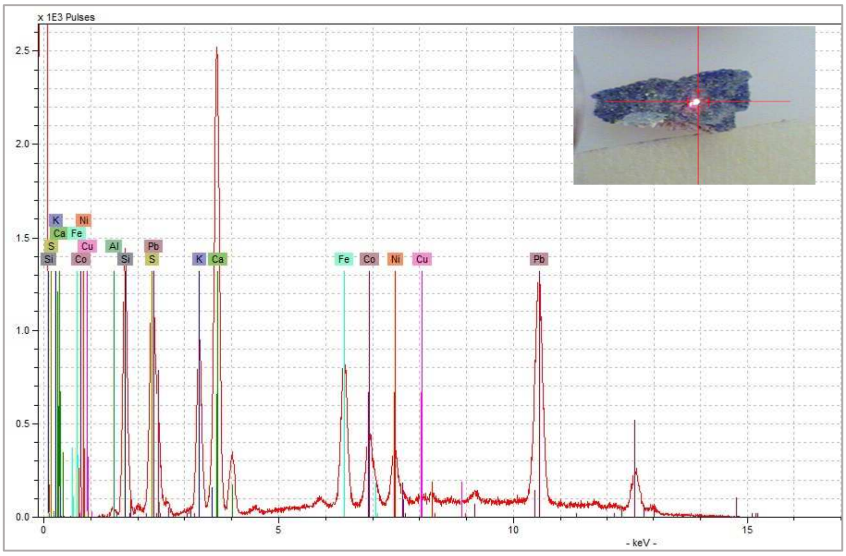


Figure 6.33. XRF spectrum of the sample S8

Figure 6.34 shows the micro Raman spectrum of this sample which is a very tiny and small grain of blue pigment (see figure 6.34-b). The strong bands at 548 and 1096 cm^{-1}, and weaker bands at 808, 583 and 259 cm^{-1} can be assigned to lazurite with general formula $(Na,Ca)_8[(Al,Si)_{12}O_{24}]Sn$ (Burgio, Clark, & Hark, 2010, p. 5727; Muralha, Burgio, & Clark, 2012, p. 24).

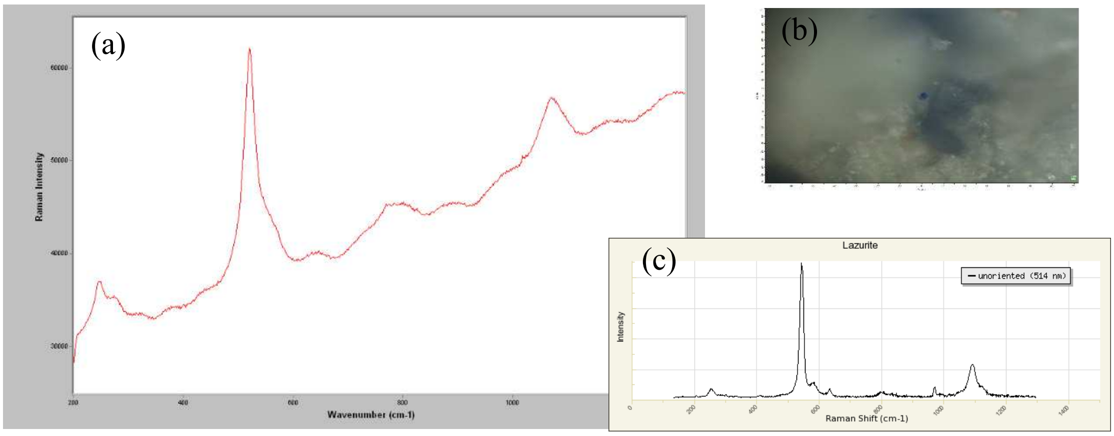


Figure 6.34. Micro Raman spectrum of blue specimen (a) in comparison with reference micro Raman spectrum of lazurite (b) (RRUFF database); the characteristic bands show that the sample contains lazurite.

Also micro Raman analysis was carried out for a different glassy blue of another part of this sample (figure 6.35) but the spectrum showed a fluorescence signal and no Raman peak could be observed. Therefore micro Raman spectroscopy did not show any result for this part of sample S8.

Based on XRF analysis, the presence of Si, K, and Co in the composition of the blue pigment was confirmed. Cobalt could provide a blue shade and other elements detected in the XRF analysis could be due to the glassy form of the blue smalt "either as flux (i.e. Pb and Ca) or colouring agent (i.e. Fe and Cu)" (Holakooei & Karimy, 2014, p. 425). Therefore it could be assumed that the blue with a glassy appearance is smalt.

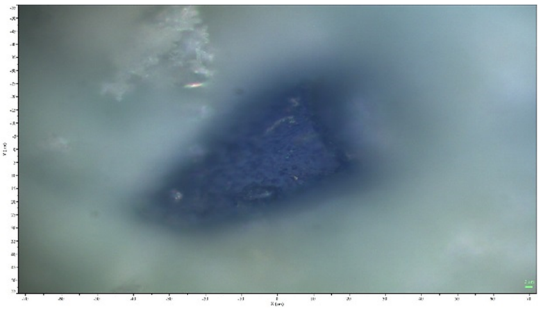


Figure 6.35. Detail of another part of sample S8, photo taken using the micro Raman spectrophotometer.

XRF and micro Raman analyses were carried out on the underside of sample S8 (figures 6.36 and 6.37). The XRF spectrum shows the presence of calcium, sulphur, and iron. Also micro Raman spectrum identified gypsum by its characteristic sulphate band at 1008 cm^{-1} (Burgio et al., 2010, p.5726). This part of the sample therefore contains gypsum as the main masonry material.

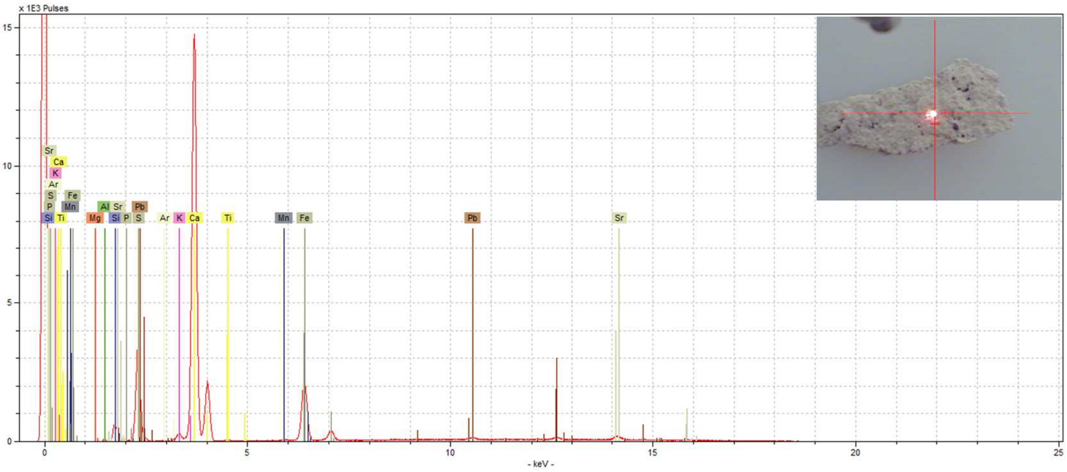


Figure 6.36. XRF spectrum of underside of sample S8

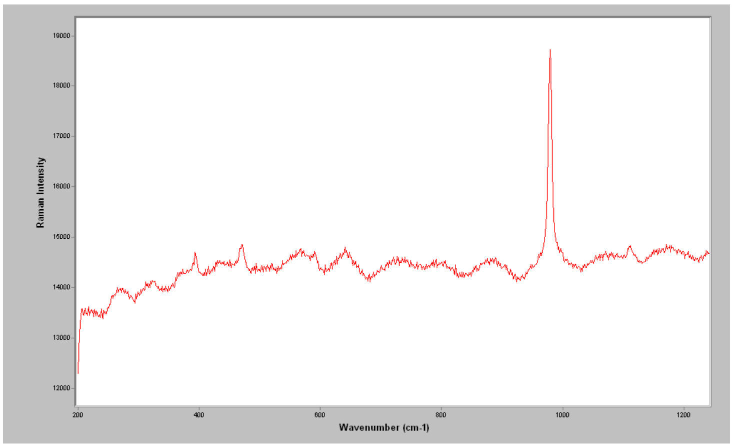


Figure 6.37. Micro Raman spectrum of underside of the specimen showed gypsum by its characteristic sulphate band at 1008 cm^{-1} (Burgio et al., 2010, p.5726).

6.3.9. Sample S9

The paint cross-section of the sample S9 was viewed through a microscope. The microscopic image and schematic sketch of this sample (figures 6.38 and 6.39) shows the presence of 1) dark green paint and 2) finish coat. From microscopic examination, it is obvious that this sample contains some yellow paints in dark green paint layer.

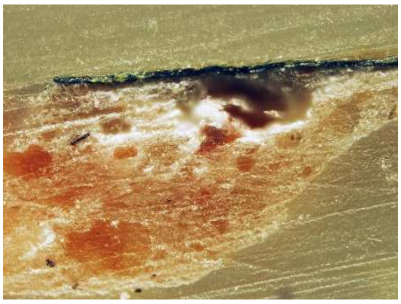


Figure 6.38. Cross section image of the sample S9, magnification 200X

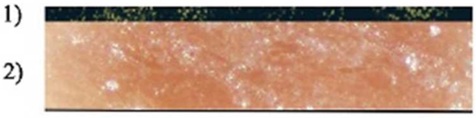


Figure 6.39. Schematic sketch of the sample's layers

XRF analysis for this sample (figure 6.40) showed that calcium, lead, arsenic, sulphur, and iron are the main constituents of this sample.

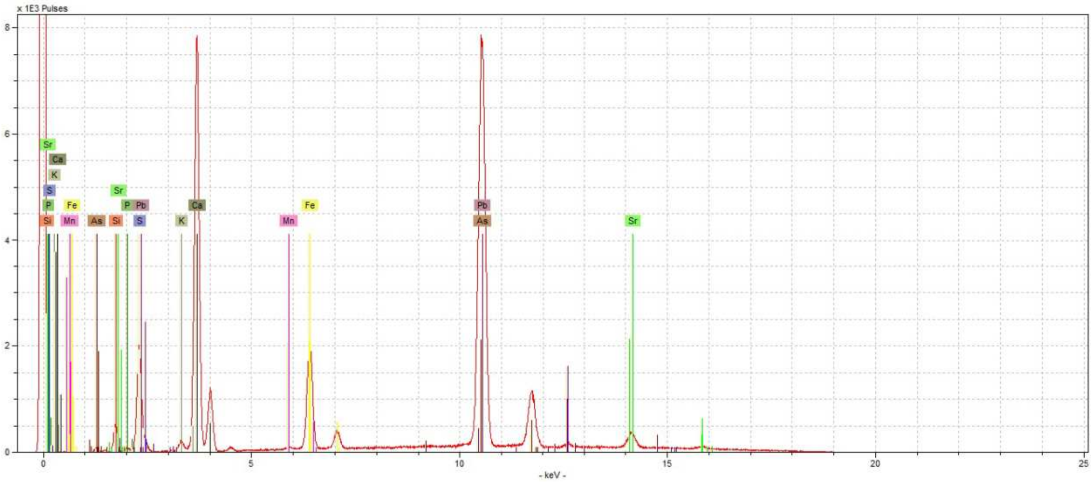


Figure 6.40. XRF spectrum of the sample S9

From micro Raman analysis of this sample (figure 6.41), the weak characteristic band at 336 cm^{-1} could be assigned to litharge (UCL Chemistry, 2010) and another "peak around 292 to 294 cm^{-1}" could show the presence of orpiment (Muralha et al., 2012, p. 25; Burgio et al., 2010, p. 5728). "The weak peak around 278 cm^{-1} could show the mixture of α-As_4S_4, β-As_4S_4, and χ-As_4S_4. Orange realgar (α-As_4S_4), its yellow photo-induced degradation product pararealgar (β-As_4S_4), their intermediate phase (χ -As_4S_4), and mixtures thereof were encountered only rarely" (Burgio et al., 2010, pp. 5727 & 5728).

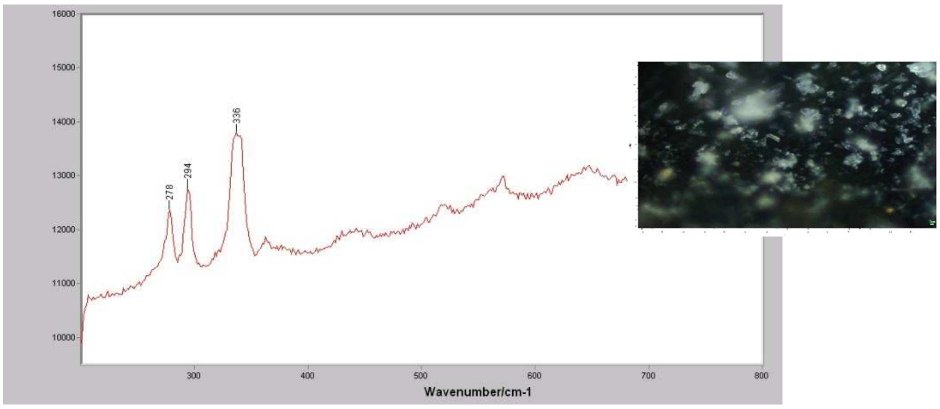


Figure 6.41. Raman spectrum of the sample S9

Another micro Raman analysis of this sample on the very small blue spot showed the presence of lazurite (figure 6.42).

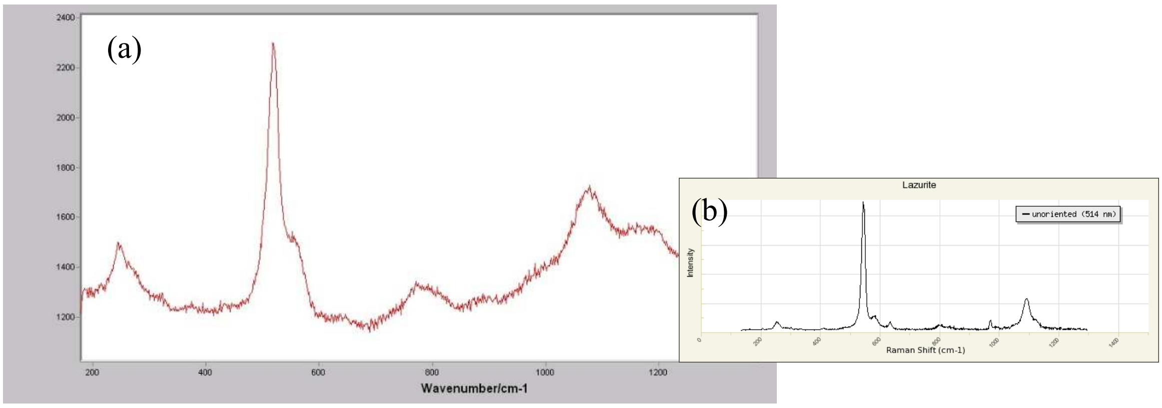


Figure 6.42. Raman spectrum of blue spot in the sample S9 (a) compared to reference micro Raman spectrum of lazurite (b) (RRUFF database).

The Raman spectra of the green portions revealed a complex mixture of products including orpiment and lazurite. Also this sample could contain a mixture of realgar and pararealgar. As it mentioned in chapter four, for the Armenian palette, Armenian painters generally mixed their green from a yellow mineral, orpiment, and a blue; the blue may be lazurite or an organic blue. For this wall painting, they chose lazurite.

6.3.10. FTIR Analysis

Another analysis which was carried out for these samples was Fourier transform infrared (FTIR) spectrometry. It is a popular technique for identifying unknown material in the conservation field. The results of FTIR analyses of samples are in the following figures (figures 6.43-6.46). The spectra show that all samples contain mainly $CaSO_4.2H_2O$ (gypsum). Peaks marked with x and y are due to organic compounds (Shurvell, 2002).

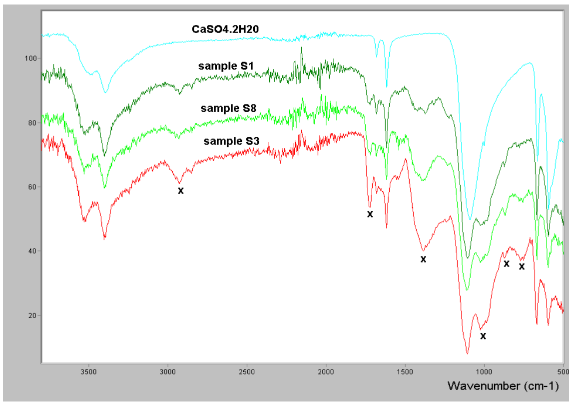


Figure 6.43. FTIR spectra of samples S1, S3, and S8 compared to the IR spectrum of gypsum (Shurvell, n.d.)

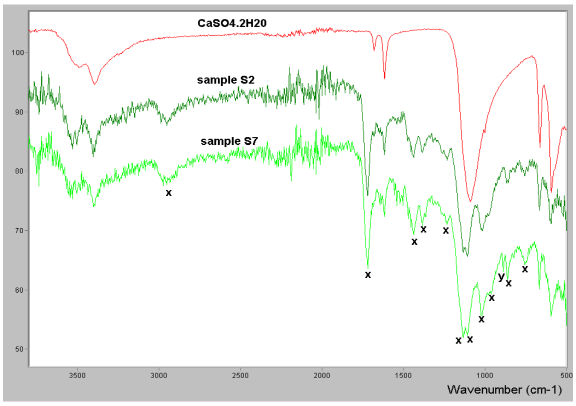


Figure 6.44. FTIR spectra of samples S2 and S7 compared to the IR spectrum of gypsum (Shurvell, n.d.)

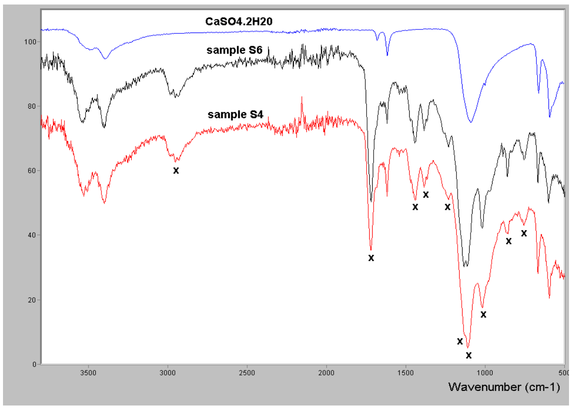


Figure 6.45. FTIR spectra of samples S4 and S6 compared to the IR spectrum of gypsum (Shurvell, n.d.)

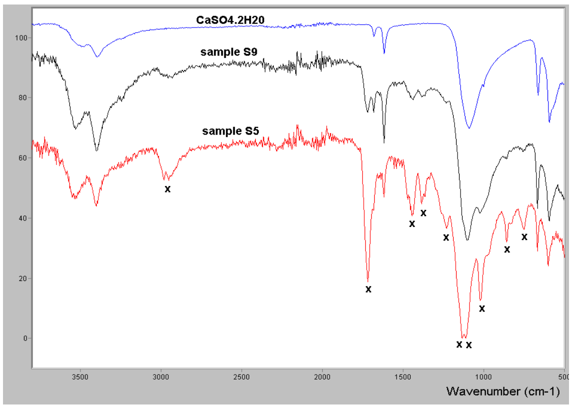


Figure 6.46. FTIR spectra of samples S5 and S9 compared to the IR spectrum of gypsum (Shurvell, n.d.)

Usually in every sample, "there are so many IR bands that it is not feasible to assign every band in an IR spectrum. Instead,…the region from 4000-1300 cm^{-1} is particularly useful for determining the presence of specific functional groups" (University of Colorado-IR Spectroscopy Tutorial, n.d.).

6.4. Conclusion

The finish coat layer of the samples was recognized as gypsum. Also some samples were a mixture of different pigments or contained different layers. In these wall paintings, the presence of two different green colours was confirmed through different analyses:

a) Copper green pigments
b) A mixed green colour from a yellow mineral, orpiment, and a blue mineral, lazurite.

Orpiment is yellow and is often found associated with realgar which is red to red-orange. Realgar under the sunlight, changes to a yellow powdery material which had generally been taken as orpiment. However, it has been determined that this material is pararealgar that was popular for the Renaissance masters, especially Tintoretto. The characteristic Raman bands of pararealgar are near 230 cm^{-1} and a group of four peaks at about 330 cm^{-1} (Trentelman, Stodulski, & Pavlosky, 1996, p.1755-1758).

Raman spectrum of the sample S9 did not show these peaks. Therefore, based on the analyses, the yellow paint is orpiment. Consequently painters used both Armenian and Iranian palettes to provide green colours.

CHAPTER SEVEN

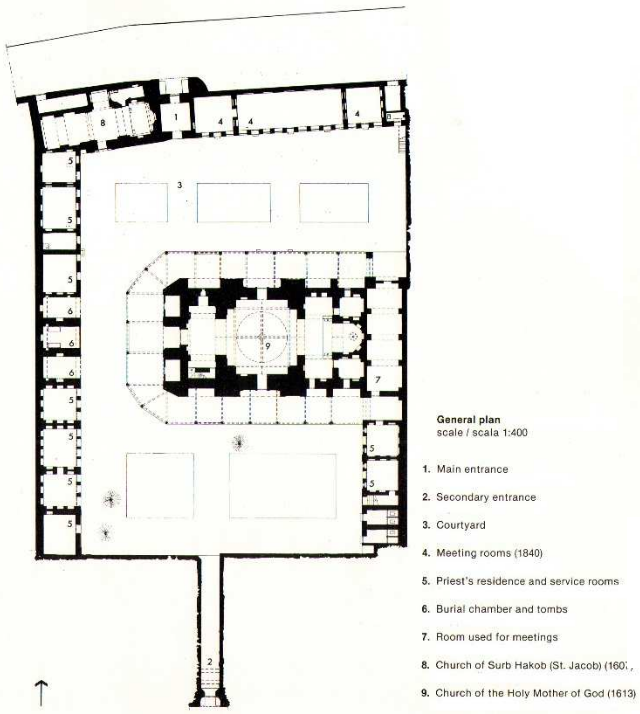
7. The Complex of Surb Astvatzatzin (Holy Mother of God)

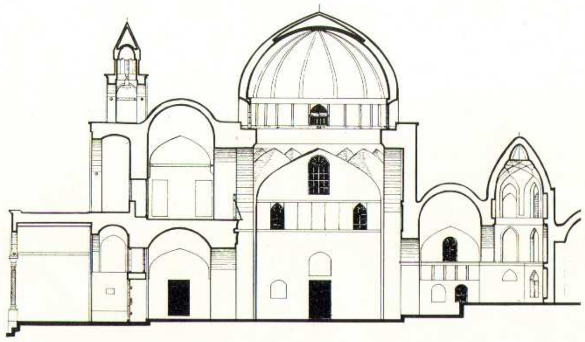
7.1. Introduction

"The church…was built in 1613 by Khodja Avetik and it encompasses other buildings already existing on the site, including the single-nave church of Surb Hakob…, which dates back to 1607 and can be regarded as the oldest church still standing in Julfa" (Hakhnazarian & Mehrabian, 1991, p.37) .

"In the course of time and because of the increasing the Armenian population in Isfahan, the Surb Hakob church didn't have enough capacity for the people who came to church for praying. Also it did not have any kind of decorations" (Yaghoubi & Beheshti, 2004, p.129). According to Hakhnazarian and Mehrabian (1991):

> Another chapel from the same period, the chapel of Surb Stepanos (St. Stephen), was demolished during construction work on the church of Holy Mother of God. According to a custom observed in all of the Julfa complexes, this courtyard is fully paved in brick and houses numerous tombs of religious and lay people from various epochs (Figures 7.1 and 7.2).
>
> The interior of the church of St. Jakob is rather simple, sombre and completely plastered. It features round arches that are different from those in all the other churches in Julfa, which usually have pointed or broken arches.
>
> The church of Holy Mother of God has been completely built in brickwork but it has its own special features and its pediments have been decorated with motifs in ceramic tiles (figure 7.3.). (pp. 37-41 passive)





Figures 7.1 & 7.2. South elevation, longitudinal section of the church of Surb Astvatzatzin, and plan of the whole complex, (Hakhnazarian and Mehrabian, 1991, pp. 36 & 40).

Figure 7.3. The church of Surb Astvatzatzin, the columns are decorated in the traditional Iranian style with bricks and polychrome tiles (The Armenians Community from Isfahan and South of Iran, 2014)

"The church contains European style wall paintings with biblical subjects and bands bearing inscriptions in Armenian, alongside exquisite Iranian decorations" (figure 7.4). The female figure with wings is similar to the figure in Iranian traditional, "Khurshid Khanum", or typical angels of the Zoroastrian tradition (Hakhnazarian & Mehrabian, 1991, p.41).

Figure 7.4. Interior designs and wall paintings in the church of Surb Astvatzatzin

7.2. Experimental Approaches

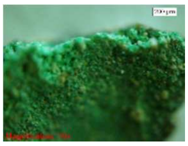
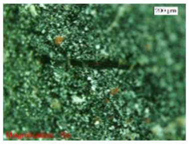
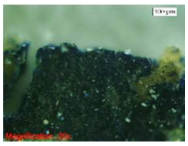
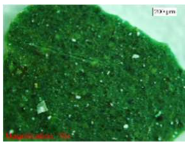
7.2.1. Samples

Some samples were taken from accessible areas of one of wall paintings. According to the Iranian Cultural Heritage, Handcrafts, and Tourism Organization (ICHHTO), the painting was not previously restored and the pigments could be considered genuine. As mentioned before, there were some limitations for collecting samples from the churches but an important point was that collecting specimens was done without further damaging the painting and they were taken from flaking zones. In figure 7.5, sampling areas on the painting are shown.

Figure 7.5. Sampling points on the selected wall painting, the church of Surb Astvatzatzin

The table 7.1 shows the samples, the visual colours of the samples, and an image. Each sample comes from the church of Surb Astvatzatzin, denoted by the letters MA, and the number describes different area sampled from the mural.

Table 7.1. Samples and their description

Samples from the church of Surb Astvatzatzin	**Visual Colours of the Samples**	**Sample Images- Magnification 10X and 20X ***
MA1	Red-Brown	
MA2	Green	
MA3	Black-Dark green	
MA4	Blue	 *
MA5	Green	

7.2.2. Techniques and Analysis

First, all samples were studied under the optical microscope to determine the probable layers of each sample. After that, different analyses were performed on the samples to identify the painting materials used in these wall paintings. Table 7.2 gives the sample preparation and analytical techniques applied.

Table 7.2. Techniques Applied to Samples

Samples	**Cross section**	**XRF[1]**	**Micro Raman[2]**	**FTIR**
MA1	✓	✓	✓	-
MA2	✓	✓	✓	✓
MA3	✓	✓	✓	✓
MA4	✓	✓	✓	✓
MA5	✓	✓	✓	✓

7.3. Results and Discussion

7.3.1. Sample MA1

The paint cross-section was viewed through a microscope. The microscopic image of this sample (figure 7.6) did not show too much information of the painting layers, since the sample's amount was too little and its structure was very powdery.

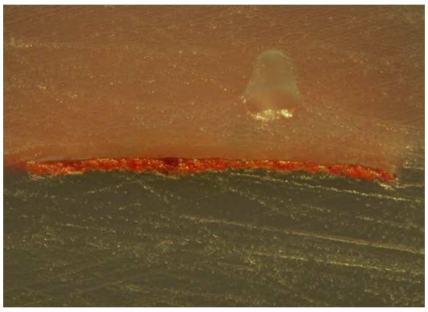


Figure 7.6. Cross section image of the sample MA1, magnification 200X

The XRF examination results of the red-brown sample (figure 7.7) showed lead as the main constituent of the pigment while sulphur, calcium, iron and mercury were detected in minor amounts in the composition.

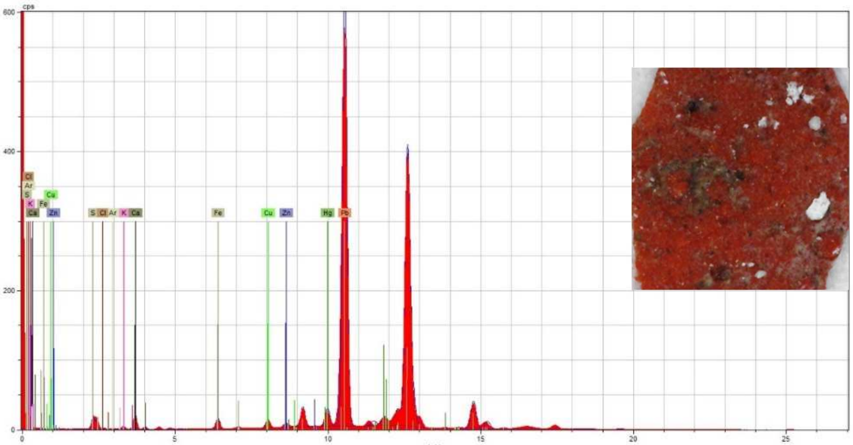


Figure 7.7. XRF spectrum on red-brown pigment

Micro Raman analysis of this sample confirmed the XRF result. With very low energy (2 mW)[1], the characteristic bands can be assigned to massicot. Figures 7.8 and 7.9 show the micro Raman spectrum from red-brown sample in comparison with "Raman database peaks which are Raman spectra of (a) orthorhombic massicot, (b) tetragonal litharge (both PbO), and (c) red lead or minium (Pb3O4). The spectra were acquired using the 632.8 nm (15,803 cm^{-1}) output of a He–Ne laser with 350 mW of power at the sample" (Smith & Clark, 2004, p. 1139).

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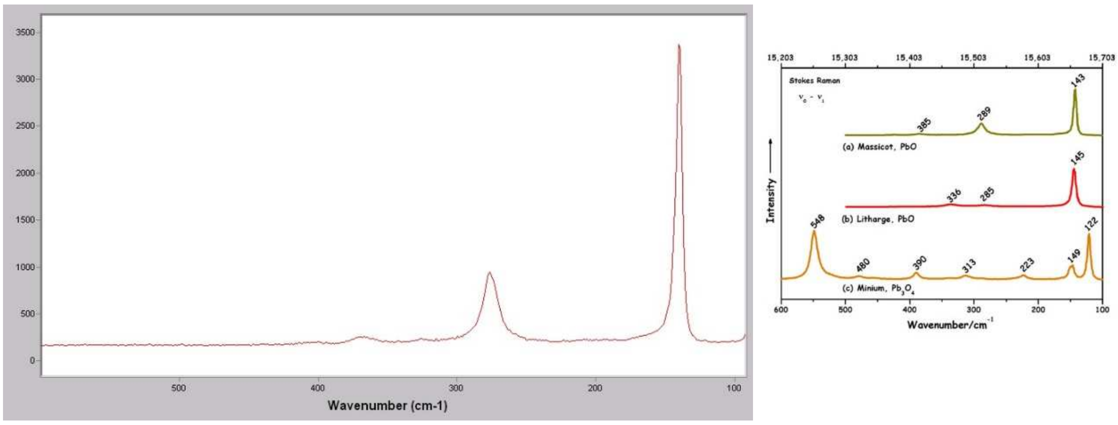
[1] Usage of low energy was for avoiding of sample burning.



Figures 7.8 & 7.9. Micro Raman spectrum from red-brown sample in comparison with Raman database (Smith & Clark, 2004, p. 1139).

Considering these analyses, the chemical compound of red-brown sample is probably massicot. "Both massicot and litharge often terms used for the same pigment, but more correctly they are lead monoxides derived from different sources. Massicot is the unfused monoxide of lead made by the gentle roasting of white lead at 300°C. The white lead reacts upon heating and gives off carbon monoxide and water. Massicot, the soft, sulphurous yellow powder is left….Litharge is more orange in comparison to massicot due to the content of some red lead….The manufacture of yellow monoxide has been known since ancient times" and was found in Egypt, across Europe in general (for example in Italy, and Germany), and in North and South America (McBride, 2002, p.19).

In this sample, there was also a white layer on the underside of the paint which was studied by micro Raman spectroscopy. The spectrum (figure 7.10a) shows the presence of huntite ($CaMg_3(CO_3)_4$) in this sample.

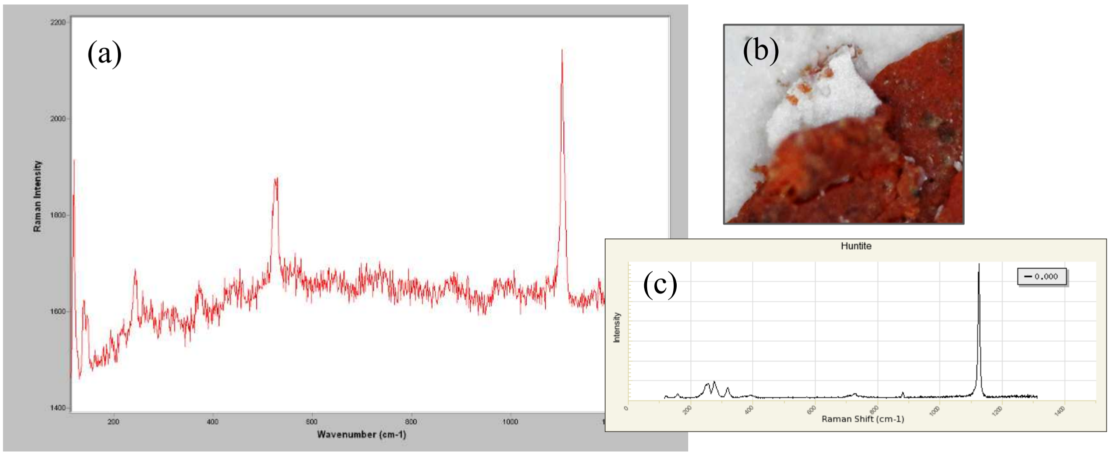


Figure 7.10. Micro Raman spectrum of white side (a) in comparison with reference micro Raman spectrum of huntite (c) (RUFF database).

According to Scheetz and White (1977), the Raman bands at 704, 726, 744, and 1123 cm^{-1} could be assigned to the mineral huntite (as cited in Holakooei & Karimi, 2014, p.422) which can confirm our hypothesis about Iranian traditional method for wall painting which were using the white ground layer of huntite, kaolinite and gypsum mixed with diluted gum Arabic, animal glue (Serishom), herbal glue (Serish), sugar syrup and tragacanth gum, albumen and yolk under the paint layer.

"As a mineral, huntite [has] been reported in various zones of Iran[,] including [the] southern coast of the Persian Gulf, [and] eastern and central Iran. In Iran it is called 'Gil-i sifıd' which means white mud. The evidences of the use of huntite for painting walls can also be found in the descriptions of historical texts of painting materials. There are some historical Persian treatises which mention clearly the term 'Gil-i sifıd' for describing a white pigment for whitening walls of buildings" (Holakooei & Karimi, 2014, p. 422).

Some Raman bands in this spectrum at 143, 252, 289, 385, and 553 cm^{-1} could be due to lead compound on the other side of the sample which affected the white side (Burgio, Clark, & Hark, 2010, 5728; Smith & Clark, 2004, p. 1139; UCL Chemistry, 2010).

7.3.2. Sample MA2

The microscopic image of sample's cross section (figure 7.11) showed different layers. The schematic sketch of the sample's layers (figure 7.12) contains: 1) green paint, 2) varnish or oily layer, 3) dark green, 4) white ground layer, and 5) finish coat.

Figure 7.11. Cross section image of the sample MA2, magnification 200X

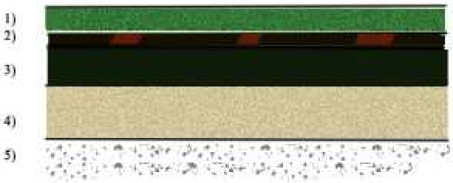


Figure 7.12. Schematic sketch of the sample's layers

The XRF examination results (figure 7.13) showed arsenic, copper, and lead as the main constituents of the sample while sulphur, calcium and iron were detected in minor amounts in the composition.

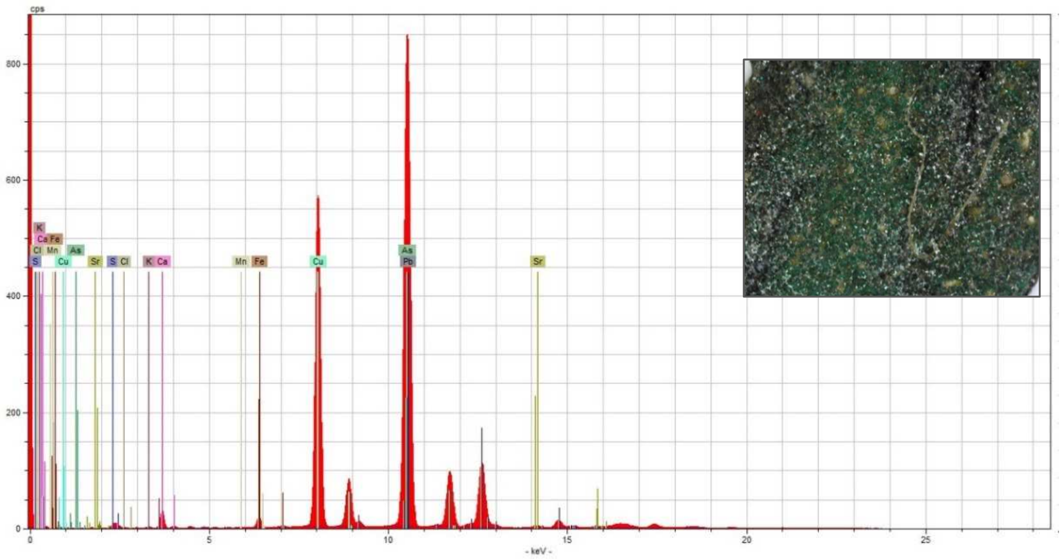


Figure 7.13. XRF spectrum on green pigment

The presence of arsenic and copper in this green specimen could indicate the presence of emerald green but micro Raman examination was carried out on the sample to confirm the XRF results.

This sample contained a medium which caused some noise in this spectrum but the characteristic Raman bands of emerald green, a copper acetoarsenite ($Cu[C_2H_3O_2]\cdot 3Cu[AsO_2]_2$), could still be found at 951, 539, 492, 371, 242, 217, and 154 cm^{-1} (Muralha, Burgio, & Clark, 2012, p. 27).

"Emerald green is a synthetic pigment introduced into Europe between 1800 and 1814 and discovered while trying to improve another popular green, Scheele's green (a copper arsenite of varying composition). There is no naturally occurring copper acetoarsenite, and so it is presumed that this pigment must have been added to the [wall painting] at some early stage[s] by way of restoration", as there is no record of such intervention during recent years….Emerald green was a very popular green pigment due to its brilliant colour" (ibid) but "use of the material as an artist's pigment had a short life span due to its rapid blackening upon reaction with hydrogen sulphides in the atmosphere" (McBride, 2002, p. 28).

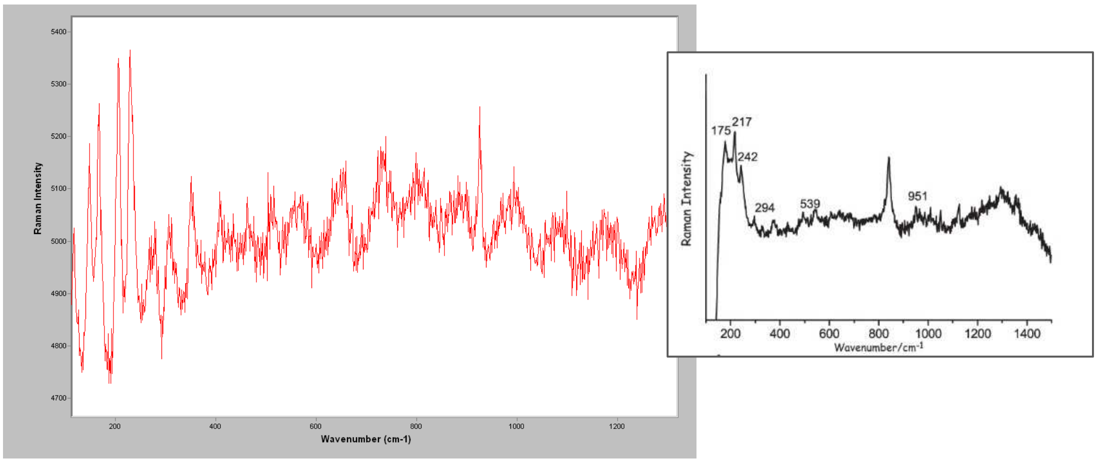


Figure 7.14. Micro Raman spectrum of green specimen in comparison with micro Raman spectrum of Emerald green in 16–17th c. Persian manuscripts in the Victoria and Albert Museum (V&A) (Muralha, Burgio, & Clark, 2012, p. 27).

The FTIR examination of the sample MA2 (figure 7.15) shows this sample contains calcium carbonate (broad absorption centred near 1400 cm^{-1} and the sharp peak at 875 cm^{-1}) and gypsum (absorptions at 3500, 3400, 1620, 670 and 600 cm^{-1}). Evidence of hydrocarbon groups is seen near 2900 and 1440 cm^{-1}, marked with an X. The absorptions marked Y may be due to an amide group from a protein-based paint. The strong broad band near 1000 cm^{-1} is probably due to clay or silica (Shurvell, 2002).

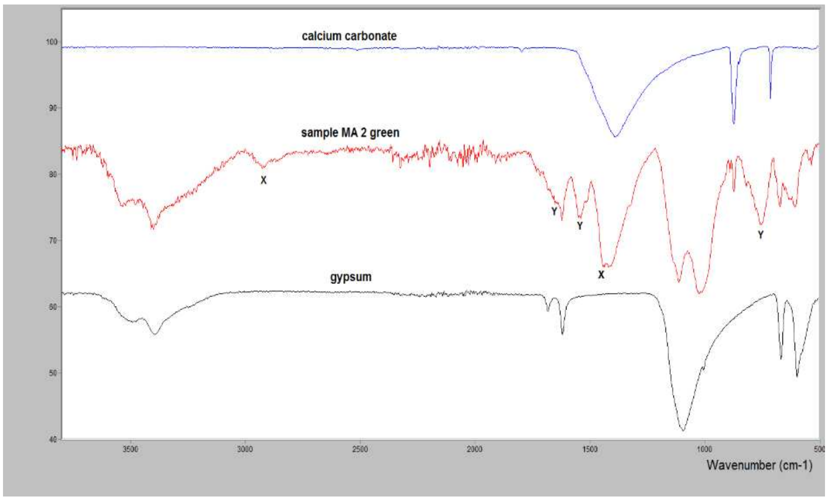


Figure 7.15. The infrared spectrum of sample MA2 compared with "reference spectra of calcium carbonate and gypsum" (Shurvell, n.d.).

7.3.3. Sample MA3

The microscopic cross section image of this sample (figure 7.16) showed different layers. The schematic sketch of the sample's layers (figure 7.17) contains: 1) green and black paints, 2) red paint layer, 3) varnish or oil layer, 4) black layer, and 5) finish coat.

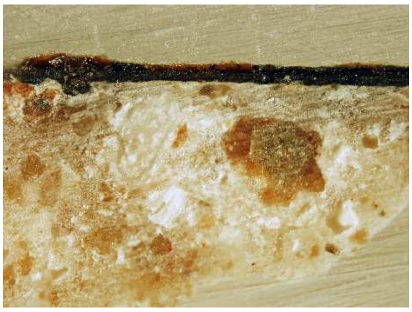


Figure 7.16. Cross section image of the sample MA3, magnification 100X

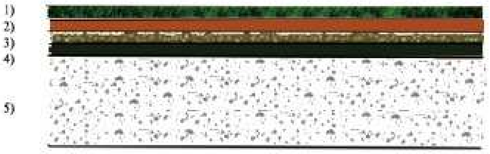


Figure 7.17. Schematic sketch of the sample's layers

This sample was similar to the previous sample, MA2, in XRF analysis. It showed the characteristic chemical elements of the dark-green or black pigments are copper and arsenic, but presence of iron and calcium is significant too.

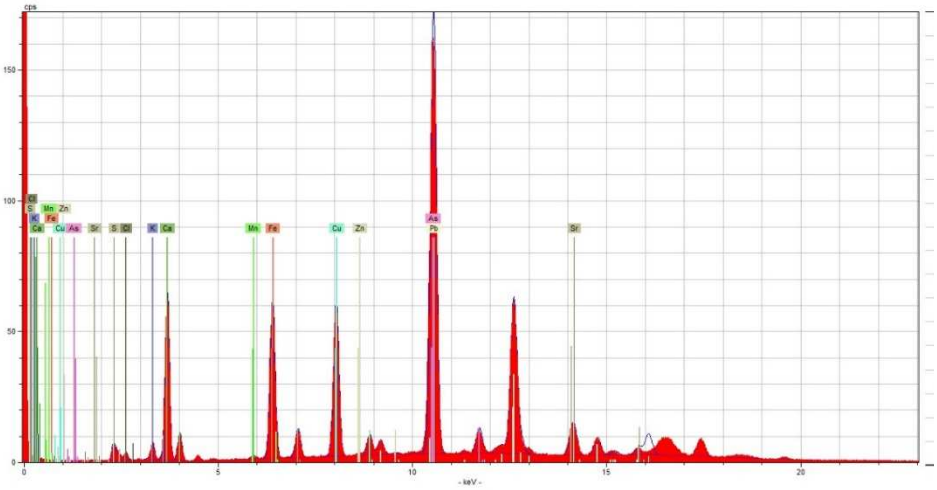


Figure 7.18. XRF spectrum on green pigment

Similar result has been obtained also by Raman analysis and the spectrum is shown in figure 7.19. The characteristic bands confirm the presence of emerald green in this sample. From visual examination, it is obvious that this sample contains several colours like green, black and red, therefore micro Raman was used on these specific colours.

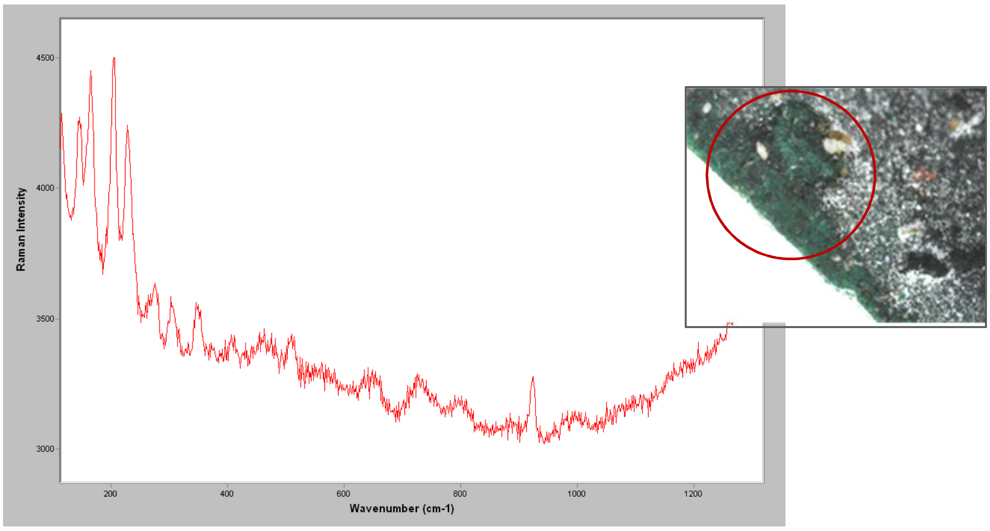


Figure 7.19. Micro Raman spectrum of green specimen

The micro Raman spectrum from the black area showed bands at ~1325, 1341, ~1580, and 1584 cm^{-1} which are characteristic of carbon black (Bell, Clark, & Gibbs, 1997, p. 2170; Smith & Clark, 2004, p. 1146).

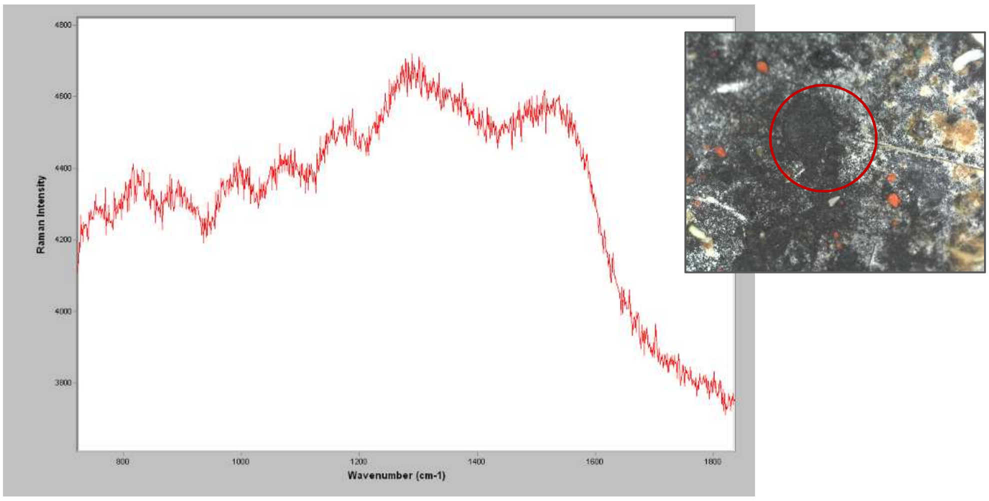


Figure 7.20. Micro Raman spectrum of black parts of the specimen

The colour of the sampling area was close to brown in some parts and in the microscopic photo of the sample, the presence of small red-brown points were obvious. It could be considered a mixture of green pigments with red ones to produce a brown appearance or maybe the pigments were accidentally mixed by the painter. Micro Raman analysis was carried out on these points to get more information. The characteristic bands at 143 and 289 cm^{-1} confirmed the existence of massicot (Smith & Clark, 2004, p. 1139).

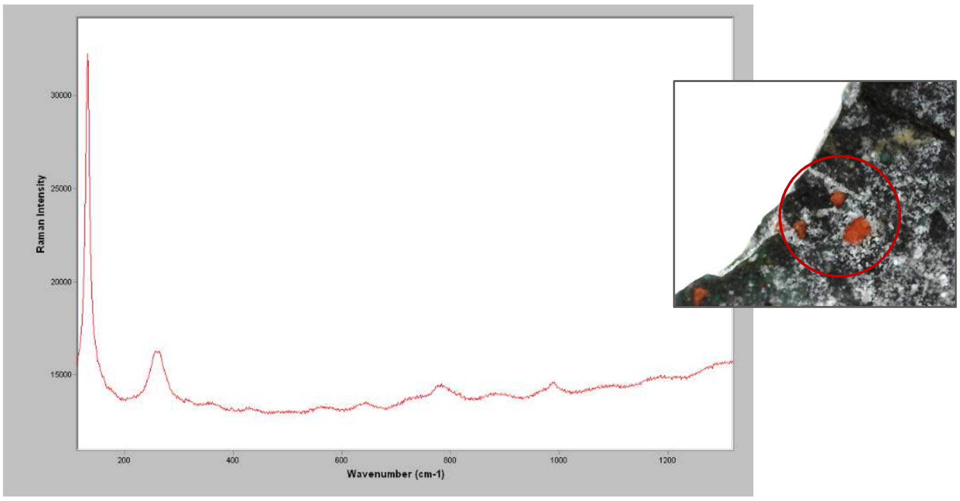


Figure 7.21. Micro Raman spectrum of red-brown parts of specimen

For examination of the underside of the sample, the micro Raman analysis was used. The Raman spectrum (figure 7.22) showed the presence of gypsum ($CaSO_4 \cdot 2H_2O$), identified by its characteristic sulphate band at around 1008 cm^{-1} (Burgio et al., 2010, p.5726).

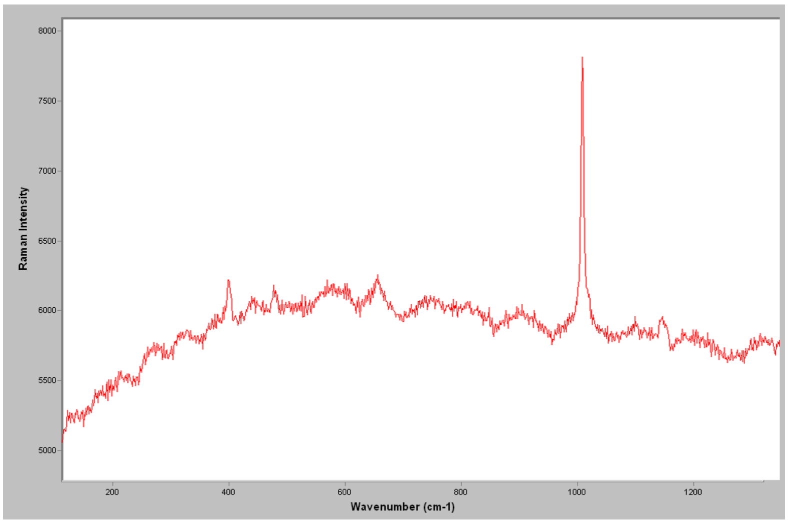


Figure 7.22. Micro Raman spectrum of underside of the, the characteristic bands shows that the sample contains gypsum.

Because of the similar results between sample MA3 and MA5, FTIR examination of the sample MA3 has been shown in figure 7.36 compared with FTIR spectrum of the sample MA5 and reference spectra of calcium carbonate and gypsum.

7.3.4. Sample MA4

The paint cross-section of the sample MA4 was viewed through a microscope. The microscopic image of this sample (figure 7.23) showed the presence of blue paint and finish coat layer. From microscopic examination, it is obvious that this sample contains some impurities in blue paint layer which could be seen as shiny golden colour.

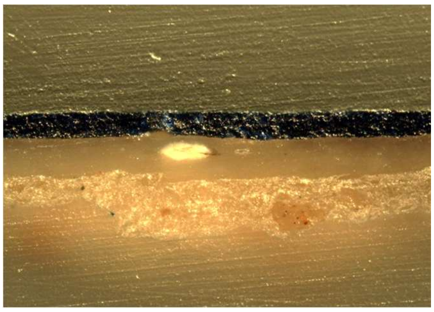


Figure 7.23. Cross section image of the sample MA4, magnification 200X

The XRF examination of blue sample (figure 7.24) confirmed the presence of calcium, iron, sulphur and lead as the main elements with other elements in minor concentrations.

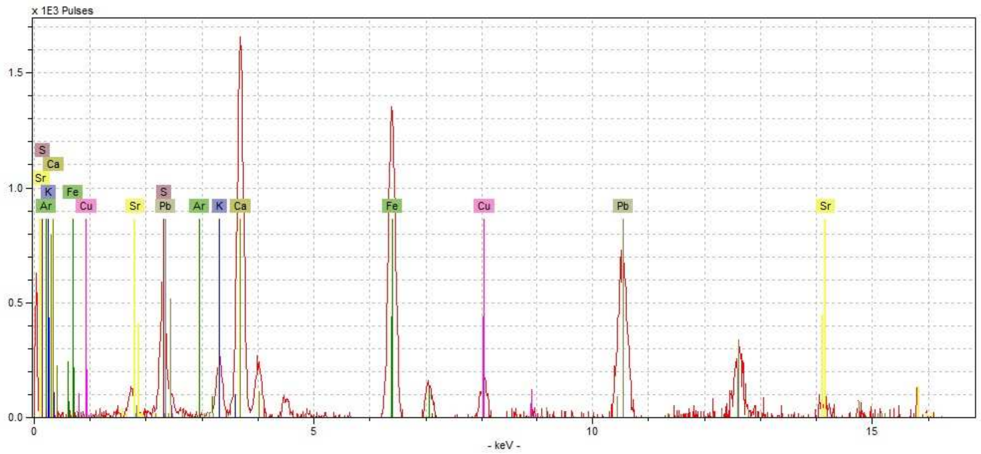


Figure 7.24. XRF spectrum on blue pigment

Further information about this sample was obtained through micro Raman analysis. The strong bands at 548 and 1096 cm^{-1}, and weaker bands at 808, 583 and 259 cm^{-1} could be assigned to lazurite (Burgio et al., 2010, p.5727; Muralha et al., 2012, p.24).

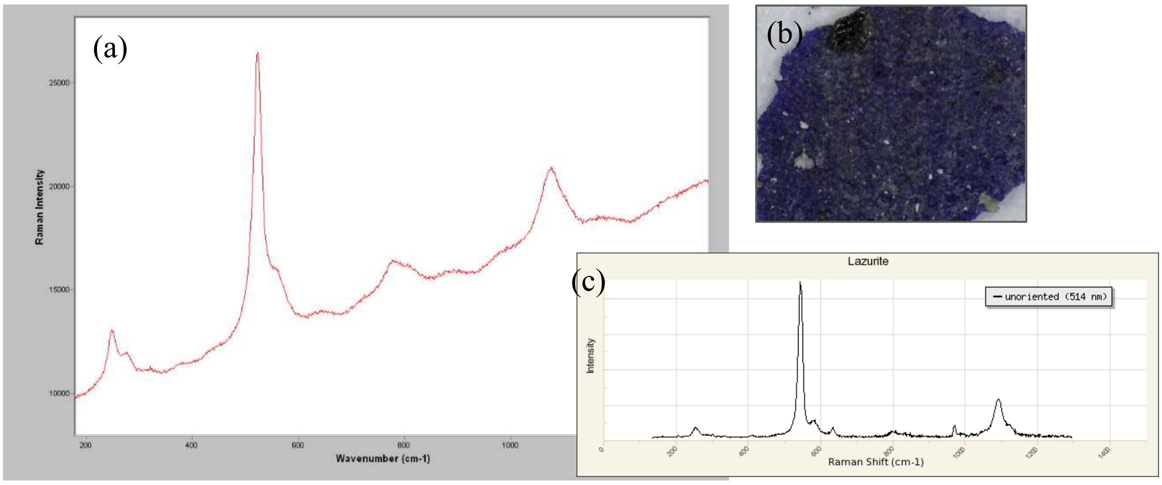


Figure 7.25. Micro Raman spectrum of blue specimen (a) in comparison with reference Micro Raman spectrum of lazurite (c) (RRUFF database); the characteristic bands show that the sample contains lazurite.

"Lazurite is the geological and chemical name of the blue crystalline component of the mineral lapis lazuli, a sulphur-containing sodium aluminium silicate mineral with [the] general formula $(Na,Ca)_8[(Al,Si)_{12}O_{24}]Sn$. The blue colour is due to [the] entrapped sulphur radical anions; lazurite may contain minor impurities, [for example] pyrite, calcite and other trace minerals" (Muralha et al., 2012, p.24) which in the sample MA4, presence of these impurities, especially pyrite, was obvious as shiny golden colour.

The FTIR result of sample MA4 shows that the sample could possibly be ultramarine. Also the FTIR spectrum (figure 7.26) shows this sample contains calcium carbonate (broad absorption centred near 1400 cm^{-1} and the sharp peak at 875 cm^{-1}) and a little amount of gypsum (absorptions at

1620, 670, and 600 cm^{-1}). Evidence of hydrocarbon groups is seen near 1440 cm^{-1}. The strong broad band near 1000 cm^{-1} is probably due to clay or silica (Shurvell, 2002; Stuart, 2007, p. 127).

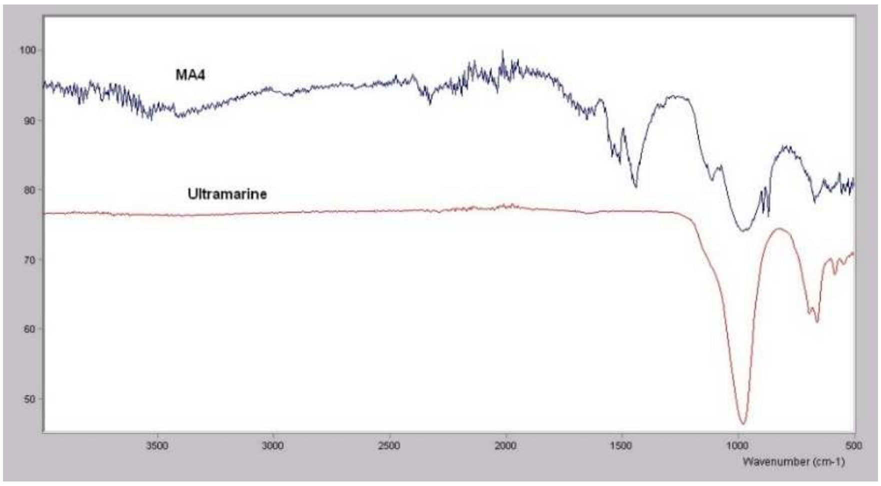


Figure 7.26. FTIR spectrum of the sample MA4 compared with reference spectrum of ultramarine (IRUG, 2007, IMP00075).

7.3.5. Sample MA5

The microscopic image of sample's cross section (figure 7.27) showed different layers. The schematic sketch of the sample's layers (figure 7.28) contains: 1) green paint, 2) varnish or oily layer, 3) green paint, 4) white ground layer, and 5) finish coat.

Figure 7.27. Cross section image of the sample MA5, magnification 100X

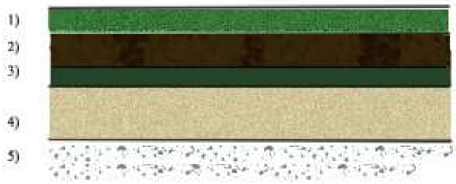


Figure 7.28. Schematic sketch of the sample's layers

For this green sample, XRF analysis was carried out (figure 7.29) and it showed arsenic, copper and lead as the main constituents of the sample while sulphur, calcium, and iron were detected in minor amounts in the composition.

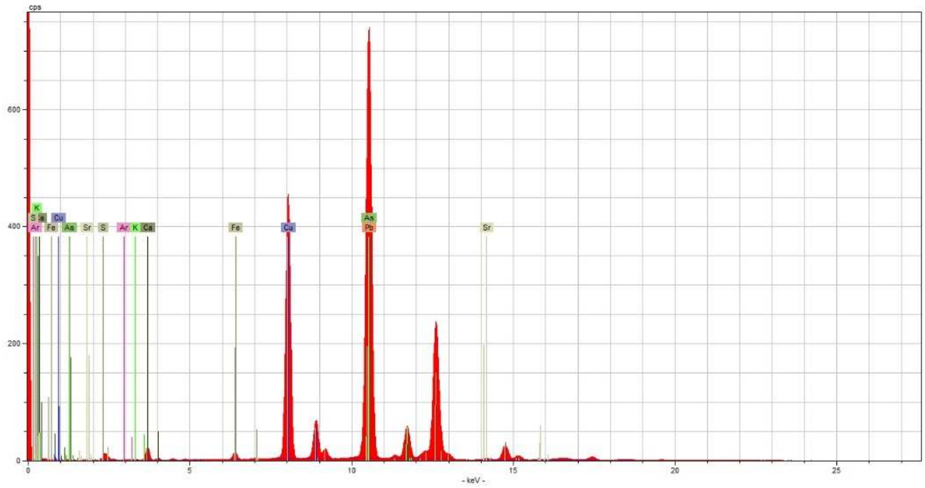


Figure 7.29. XRF spectrum on green pigment

The characteristic Raman bands at around 951, 835, 539, 492, 371, 242, 217, 154, and 122 cm^{-1} (figure 7.30) could be assigned to emerald green. Also litharge could be identified by its Raman band at ~145 cm^{-1}.In this case, Raman results confirmed XRF results (Muralha, Burgio, & Clark, 2012, p. 27; UCL Chemistry, 2010).

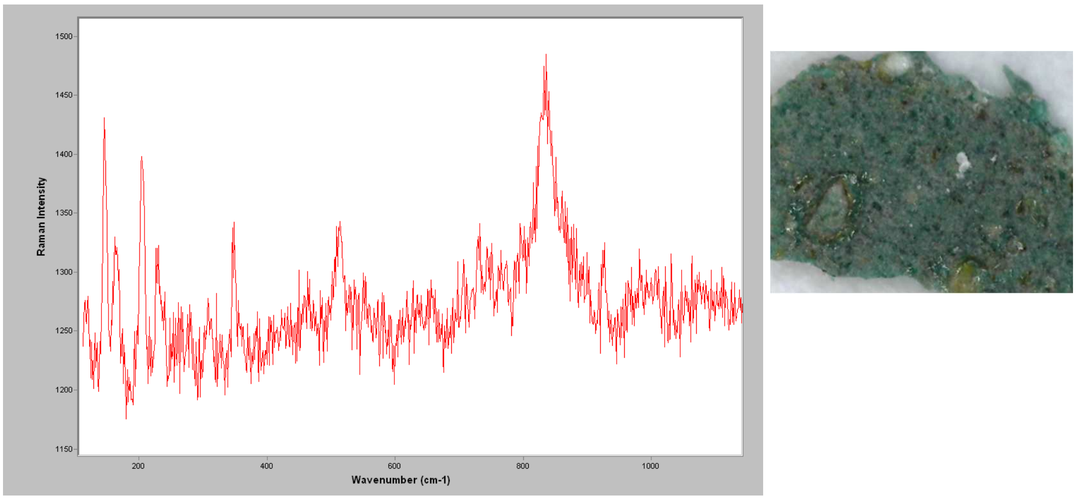


Figure 7.30. Very noisy micro Raman spectrum of the green sample; the characteristic bands show that the sample contains emerald green and litharge.

Figure 7.31 shows the infrared spectra of samples MA3 black-dark green and MA5 green compared with reference spectra of calcium carbonate and gypsum (Shurvell, n.d.). Sample MA5 contains some calcium carbonate (broad absorption centred near 1400 cm^{-1} and the sharp peak at 875 cm^{-1}), but no gypsum. Sample MA3 is mainly gypsum (absorptions at 3500, 3400, 1620, 1100, 670 and 600 cm^{-1}). Evidence of hydrocarbon groups is seen in both samples (near 2900 and 1440 cm^{-1} marked with an X). The absorptions marked Y may be due to an amide group from a protein-based paint. The strong broad band near 1000 cm^{-1} is probably due to clay or silica. The assignment of the additional peaks marked Z is uncertain (Shurvell, 2002).

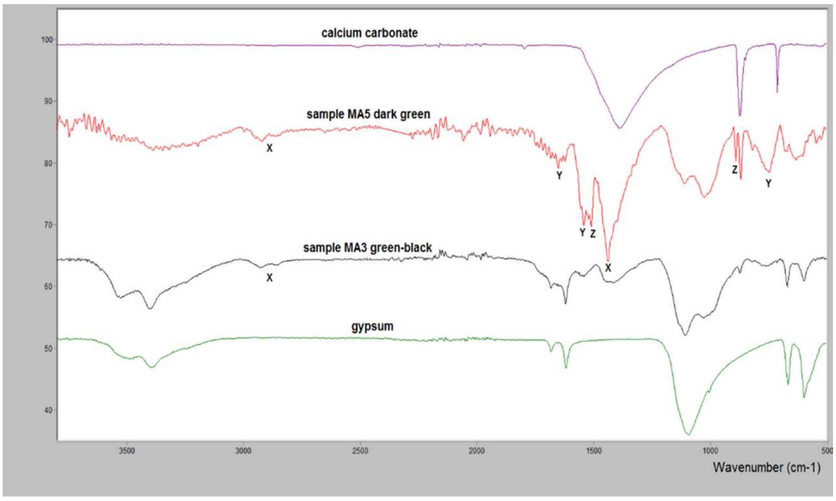


Figure 7.31. The infrared spectra of samples MA3 and MA5 compared with reference spectra of calcium carbonate and gypsum (Shurvell, n.d.).

7.4. Conclusion

Different analyses of the materials from the wall painting show the small range of colours. Several of these primary pigments were, however, mixed to obtain the different ranges of colour observed. The following pigments were identified on this wall painting analysed: massicot, litharge, lazurite, huntite, emerald green, and a carbon-based black pigment.

It is not surprising to find lazurite as the blue pigment in the Persian palette, since it is almost the most common blue pigment mentioned in the treatises.

According to the treatises, the preferred green pigment for Persian artists was verdigris, a copper ethanoate, $Cu(CH_3COO)_2$, of various chemical compositions. This is called ‘raw’ verdigris and several recipes exist for the preparation of such greens with different chemical compositions (Muralha et al., 2012, p.28). There was no sign of this green pigment in the wall painting and the emerald green pigment seems to have been added to the wall painting during an early restoration.

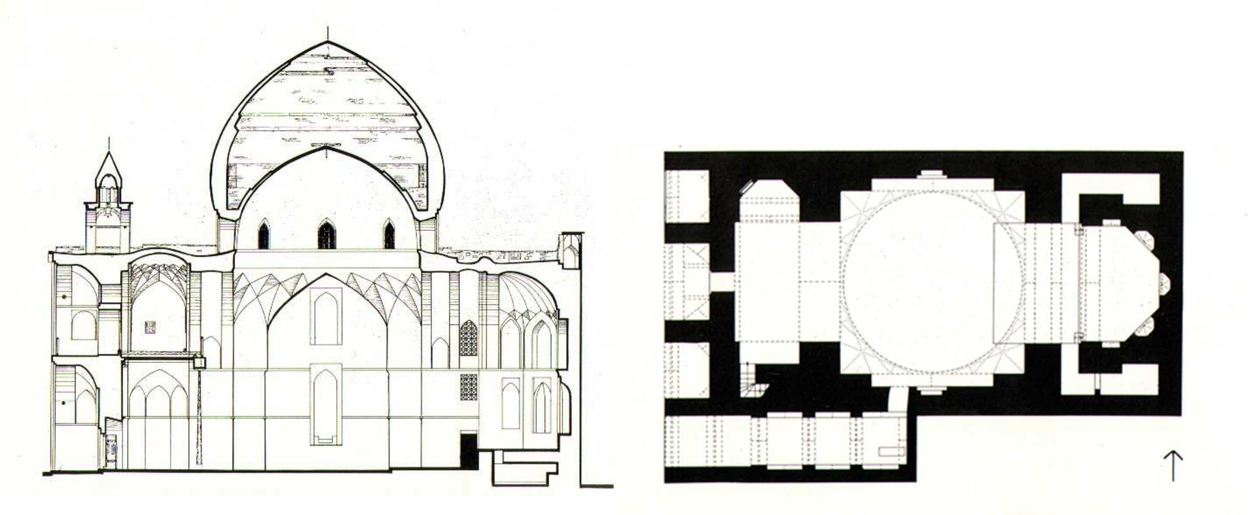
CHAPTER EIGHT

8. The Church of Surb Betghehem (Church of Holy Bethlehem)

8.1. Introduction

This church is situated in the square of the same name, near the complex of Holy Mother of God. "Built in 1628 with contributions from Khodja Petros Velidjanian, the church of Holy Bethlehem has greatly suffered from urban development projects" (Hakhnazarian & Mehrabian, 1991, p. 45). It has a rectangular plan and is completely built in brickwork (figures 8.1 and 8.2).

"In spite of the rectangular plan, the central quadrangular body repeats the classic model of the Armenian "domed hall". The dome above rests on four half-columns built into the perimeter walls and is the largest of all Armenian churches in Julfa" (ibid).



Figures 8.1 & 8.2. Longitudinal section, plan and west elevation of the church of Surb Betghehem, scale 1:400 (Hakhnazarian & Mehrabian, 1991, p. 46)

Hakhnazarian and Mehrabian (1991) mentioned that:

> The interior of Holy Bethlehem is richly decorated: a fascia in ceramics covers the lower part of the entire perimeter and reflects the local style of the 17th-century (figure 8.3). The remaining wall surface area is copiously frescoed. The paintings are extremely valuable due to the beauty and originality of their topics and also because, unlike other architectural treasures in a state of neglect, they are rather well conserved. Well worthy of note are the frescoes of the altar, which reiterate the style of the "Vaspurakan" school of Armenian miniatures (figures 8.3-8.5).

Also in this church, European-style paintings exist which are blended with Armenian and Iranian paintings styles (figure 8.6). "The church of Holy Bethlehem was extensively restored in 1870 and 1899; consolidation work began in 1984" (ibid).

Figures 8.3 & 8.4. The blend of Iranian, Armenian and European art style in wall paintings and decorations of the church of Surb Betghehem.

Figures 8.5 & 8.6. Decorated interior in the church of Surb Betghehem.

8.2. Experimental Approaches

8.2.1. Samples

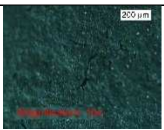
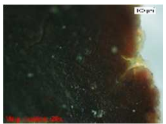
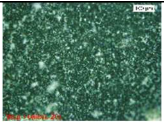
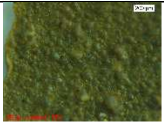
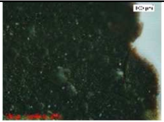
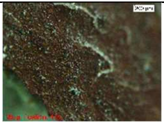
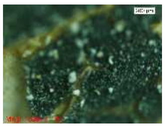
In this building samples were collected from two different wall paintings which were located at the dome drum, inside the church. The following figures show the sampling spots on the wall paintings (figures 8.7-8.8).

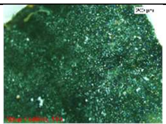
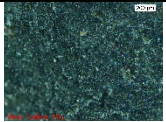
Figure 8.7. Samples B1-B5 and B13-B15 from the first wall painting in the church of Surb Betghehem (Photo by: Y. Hamzavi).

Figure 8.8. Samples B6-B12 and B13-B15 from the second wall painting in the church of Surb Betghehem (Photo by: Y. Hamzavi).

The table 8.1 shows each sample, its visual colour, and an image. Each sample is denoted with the letter B for the church of Surb Betghehem and the number locates the sample area.

Table 8.1. Samples and their description

Samples from the church of Surb Betghehem	**Visual Colours of the Samples**	**Sample Images- Magnification 10X and 20X ***
B1	Blue	
B2	Purple, Dark red	
B3	Dark red, red-brown	 *
B4	Gold leaf over red layer	
B5	Red-brown	 *
B6	Green	 *
B7	Yellow	
B8	Brown	 *
B9	Red-brown	
B10	Blue	
B11	Gold leaf	

B12	Red-brown	
B13	Green	
B14	Blue	
B15	Gold leaf over red layer	

8.2.2. Techniques and Analysis

A comprehensive analytical survey was undertaken to identify the painting materials used in these wall paintings. Table 8.2 gives the sample preparation and analytical techniques used.

Table 8.2. Techniques Applied to Samples

Samples	Cross section	XRF	Micro Raman	FTIR
B1	✓	✓	✓	✓
B2	✓	✓	-	✓
B3	✓	✓	✓	✓
B4	✓	✓	-	✓
B5	✓	✓	✓	✓
B6	✓	✓	✓	✓
B7	✓	✓	✓	✓
B8	✓	✓	✓	✓
B9	✓	✓	✓	✓
B10	✓	✓	✓	✓
B11	✓	✓	✓	✓
B12	✓	✓	✓	-
B13	✓	✓	✓	✓
B14	✓	✓	✓	✓
B15	✓	✓	-	✓

8.3. Results and Discussion

8.3.1. Sample B1

The paint cross-section was viewed through a microscope. The microscopic image of this sample (figure 8.9) shows different layers. The schematic sketch of the sample's layers (figure 8.10) contains: 1) blue paint, 2) thin white layer, 3) red paint, and 4) white ground layer.

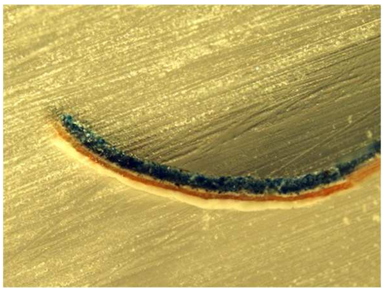


Figure 8.9. Cross section image of the sample B1, magnification 100X

Figure 8.10. Schematic sketch of the layers

The XRF analysis for sample B1 showed lead as the main constituent of the sample while sulphur, iron, cobalt, and calcium were detected in minor amounts in the composition (figure 11). Since the lead cannot provide blue colour then the sample need to be studied more by other analyses.

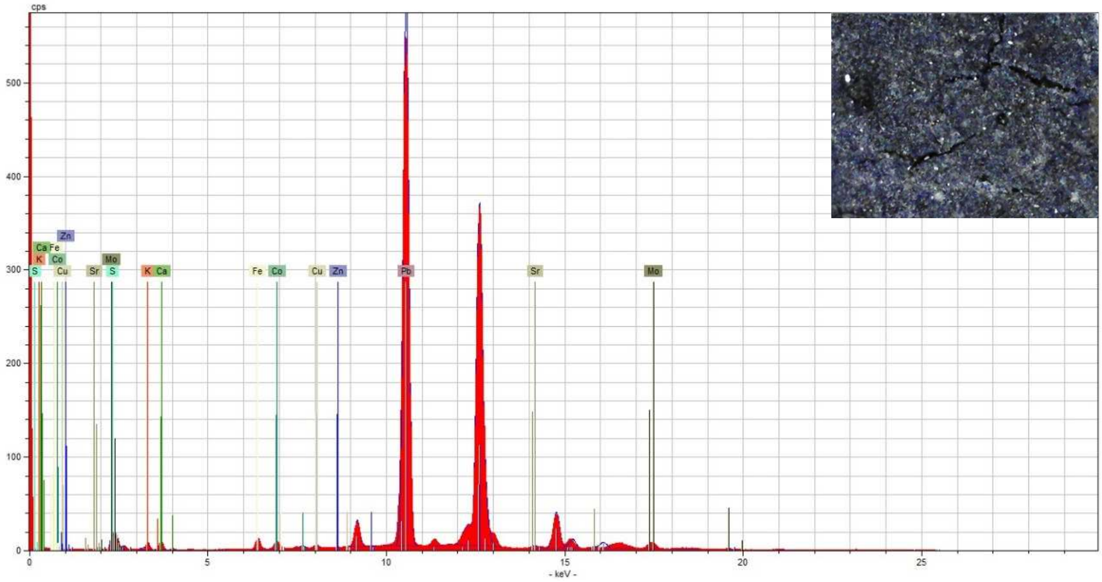


Figure 8.11. XRF spectrum of blue sample

Also Micro Raman analysis was carried out for this sample (figure 8.12). The strong bands at "548 and 1096 cm^{-1}, and weaker bands at 808, 583 and 259 cm^{-1} could indicate lazurite" (Burgio, Clark, & Hark, 2010, p. 5727; Muralha, Burgio, & Clark, 2012, p. 24).

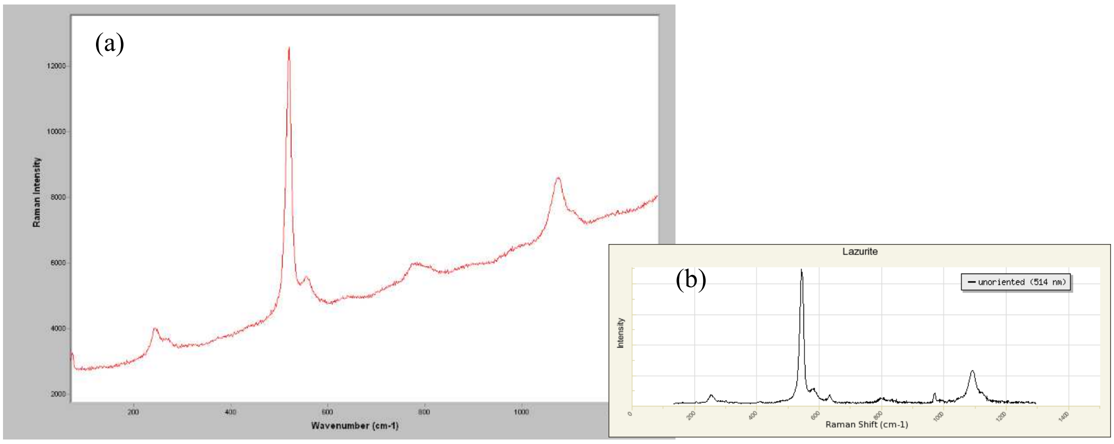


Figure 8.12. Micro Raman spectrum of blue specimen (a) compared to reference micro Raman spectrum of lazurite (b) (RRUFF database), the characteristic bands show that the sample contains lazurite (RRUFF database).

Figure 8.13 shows the infrared spectrum of the sample B1 compared with reference spectra of calcium carbonate (Shurvell, n.d.) and ultramarine (IRUG database, 2007, IMP00075). The FTIR result showed that the sample could possibly be ultramarine. Also sample B1 contains some calcium carbonate (broad absorption centred near 1400 cm^{-1} and the sharp peak at 875 cm^{-1}). The broad band near 1000 cm^{-1} is probably due to clay or silica (Shurvell, 2002).

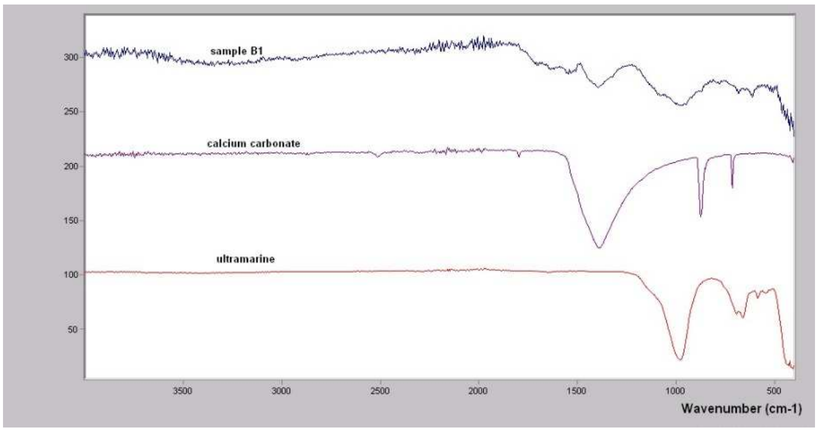


Figure 8.13. The infrared spectra of sample B1 compared with reference spectra of calcium carbonate (Shurvell, n.d.) and ultramarine (IRUG database, 2007, IMP00075).

8.3.2. Sample B2

The microscopic cross section image of the sample (figure 8.14) showed different layers. The schematic sketch of the sample's layers (figure 8.15) contains: 1) oily dark red paint, 2) mixture of dark-black colour with light colour, 3) oily layer, and 4) white ground layer.

Figure 8.14. Cross section image of the sample B2, magnification 200X

Figure 8.15. Schematic sketch of the layers

The XRF examination of the sample B2 (figure 8.16) showed lead as the main constituent of the sample and calcium, potassium, and iron are in minor amounts. Therefore the sample could possibly be red lead.

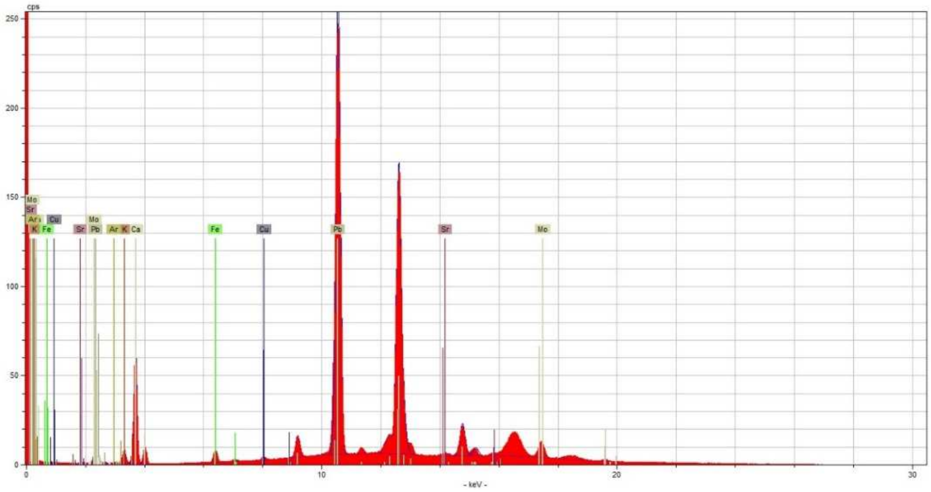


Figure 8.16. XRF spectrum of the sample B2

During micro Raman analysis, the sample burned because of the high amount of binder mixed with pigment. Even after trying to extract the binder from the pigment, the residue did not provide reliable results and the high amount of binder brought much fluorescence. Therefore more information could not be gained about this sample through Raman analysis.

Figure 8.17 shows the infrared spectrum of the sample B2 compared with reference spectrum of gypsum (Shurvell, n.d.). The result indicates mainly gypsum (absorptions at 3500, 3400, 1620, 1100, 670 and 600 cm^{-1}) (ibid) which could come from the underside of the sample.

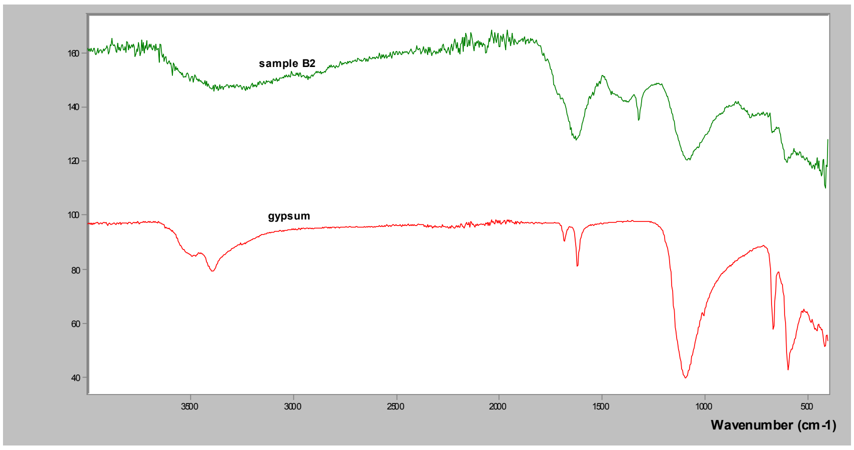


Figure 8.17. The infrared spectrum of sample B2 compared with reference spectrum of gypsum (Shurvell, n.d.).

8.3.3. Sample B3

This sample was similar to the previous sample, B2. The microscopic cross section image and the schematic sketch of the layers of the sample (figures 8.18-8.19) showed different layers which are: 1) oily layer or varnish, 2) red-brown paint, 3) mixture of dark-black colour with light colour, 4) oily red layer, and 5) white ground layer.

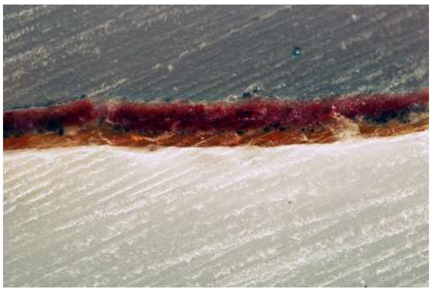


Figure 8.18. Cross section image of the sample B3, magnification 200X

Figure 8.19. Schematic sketch of the layers

The XRF examination of the sample B3 (figure 8.20) showed lead and mercury as the main constituents of the sample and calcium and iron were detected in minor amounts.

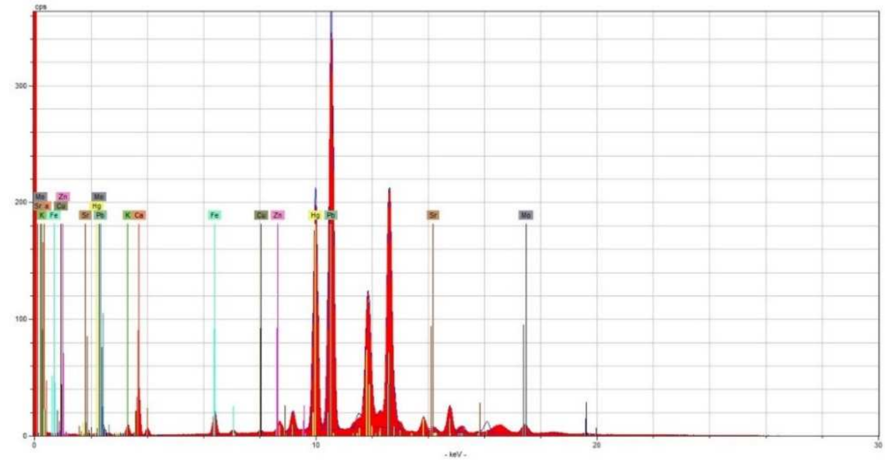


Figure 8.20. XRF spectrum of the sample B3

The high amount of binder mixed with pigment did not provide reliable results in micro Raman examination and brought much fluorescence. Evidence of a characteristic Raman band at about 250 cm^{-1} marked with an X (figure 8.21) which could be assigned to vermilion.

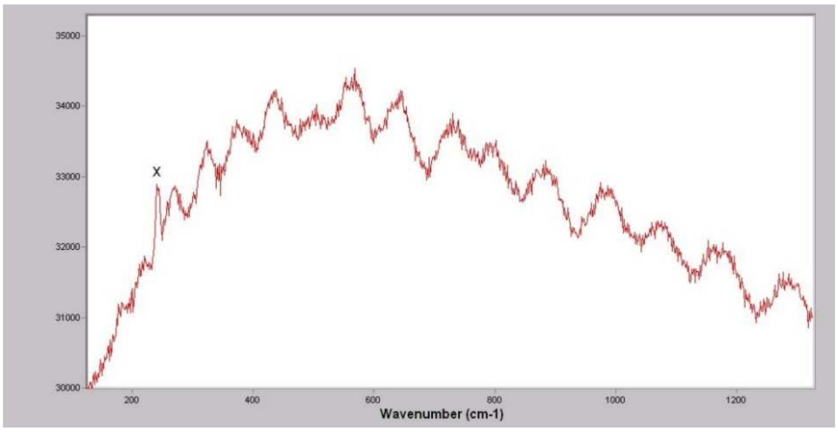


Figure 8.21. Micro Raman spectrum of the sample B3

The FTIR examination of the sample B3 (figure 8.22) compared to reference spectrum of gypsum shows this sample contains gypsum (Shurvell, 2002).

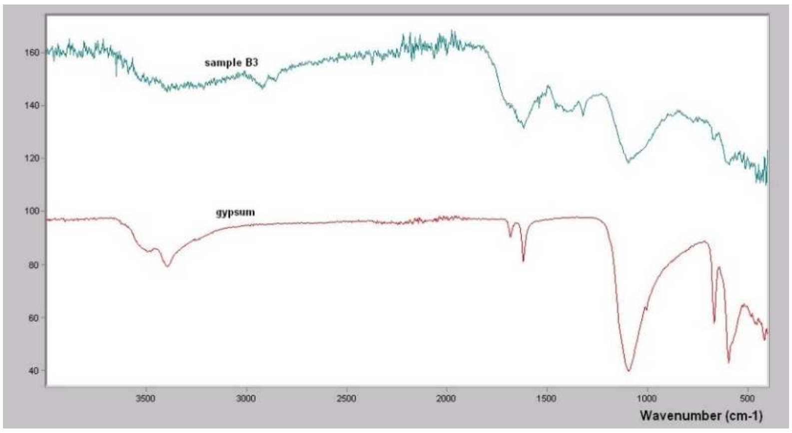


Figure 8.22. The infrared spectrum of sample B3 compared with reference spectrum of gypsum (Shurvell, n.d.).

8.3.4. Sample B4

The microscopic cross section image of the sample (figure 8.23) showed different layers. The schematic sketch of the layers of the sample (figure 8.24) contains: 1) thin gold leaf, 2) oily red layer, 3) mixture of dark-black colour with light colour, 4) oily red layer, and 5) finish coat.

Figure 8.23. Cross section image of the sample B4, magnification 200X

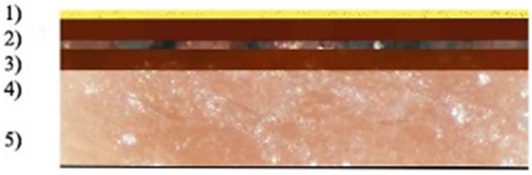


Figure 8.24. Schematic sketch of the layers

The XRF analysis for this sample (figure 8.25) showed that lead and gold are the main constituents of this sample while iron and calcium were detected in minor amounts in the composition.

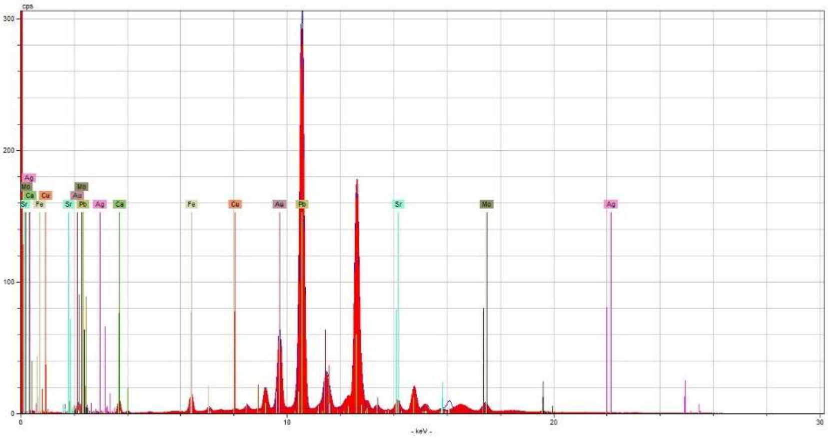


Figure 8.25. XRF spectrum on the sample B4

The FTIR examination of the sample B4 (figure 8.26) compared to reference spectra of gypsum (Shurvell, n.d.) and polymerized linseed oil (Gettens Raw Material Collection, n.d., C28). Absorption near 2900 cm^{-1} is due to hydrocarbon groups of organic compounds and absorption near 1720 cm^{-1} is due to carbonyl groups (Shurvell, 2002). The result shows this sample contains gypsum and old or polymerized linseed oil which was very common painting medium in Iranian oil paintings.

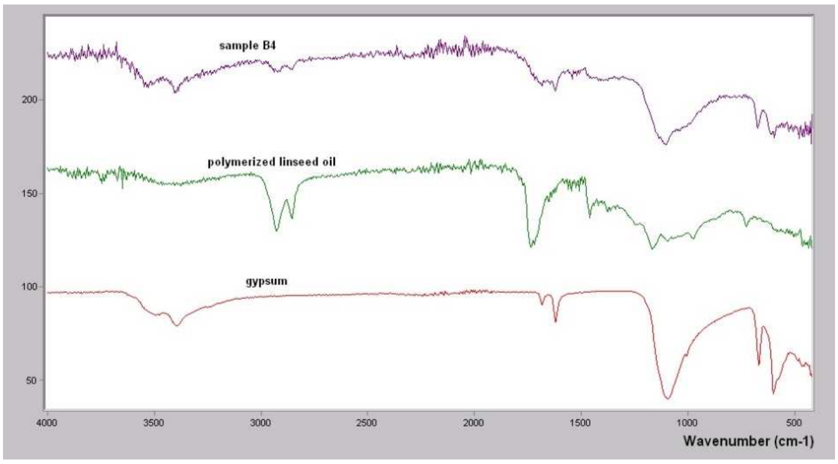


Figure 8.26. The infrared spectrum of sample B4 compared with reference spectrum of gypsum (Shurvell, n.d.) and polymerized linseed oil (Gettens Raw Material Collection, n.d., C28).

8.3.5. Sample B5

First, the microscopic cross section image of the sample (figure 8.27) showed different layers. The schematic sketch of the layers of the sample (figure 8.28) contains: 1) mixture of dark-black colour with light colour, 2) dark-brown layer, 3) dark red layer, and 4) red layer.

Figure 8.27. Cross section image of the sample B5, magnification 200X

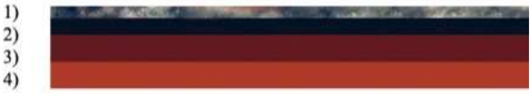


Figure 8.28. Schematic sketch of the layers

By polishing more, the presence of a very thin gold leaf appeared under the dark-brown layer (figure 8.29).

Figure 8.29. Cross section image of the sample B5, presence of gold leaf, magnification 200X

Sample B5 shows the high presence of lead in XRF examination (figure 8.30). Other elements like iron and calcium are in minor amounts in this sample.

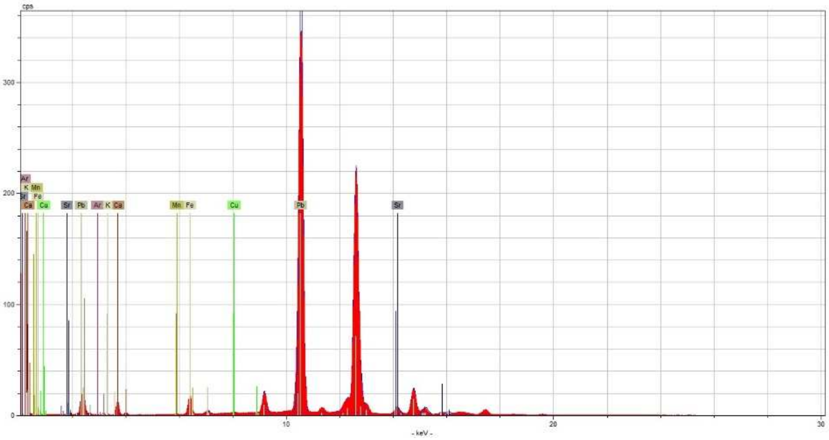


Figure 8.30. XRF spectrum on the sample B5

The Raman spectrum of this sample (figure 8.31) shows a characteristic band at about 145 wave number/cm^{-1} which could indicate litharge (Bell, Clark, & Gibbs, 1997, p. 2174) and some other characteristic bands at about 122, 199, 223, and 548 wave number/cm^{-1}, which could all indicate minium (red lead) (ibid; Muralha et al., 2012, p. 25). This could be a mixture of red lead and litharge together. In this case, Raman results confirmed XRF results.

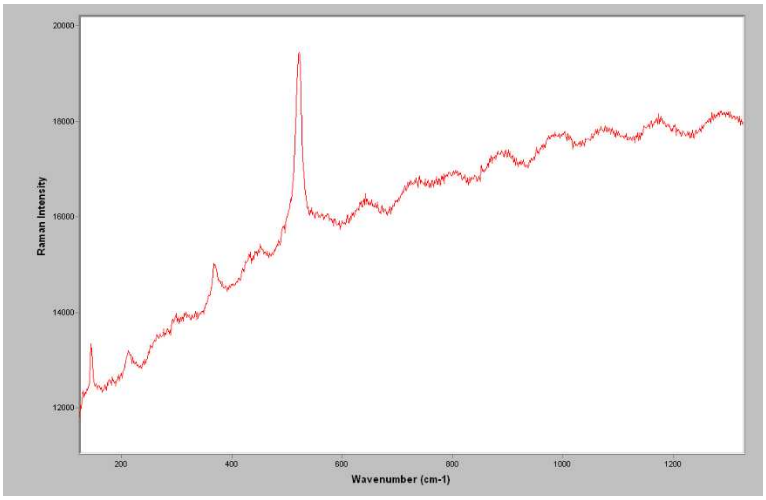


Figure 8.31. Micro Raman spectrum of the sample B5

The colour of the sampling area was close to brown in some parts and in the cross section image of the sample, the presence of the thin dark layer was obvious. Micro Raman analysis was carried out on these points to get more information. In figure 8.32, the characteristic bands at about 133 and 258 cm^{-1} confirmed the existence of lead compounds (Burgio & Clark, 2001, p. 1504; Burgio et al., 2010, p. 5728; & Burgio et al., 1997, p. 2174). The dark layer, therefore, could be considered a degradation product of lead compounds.

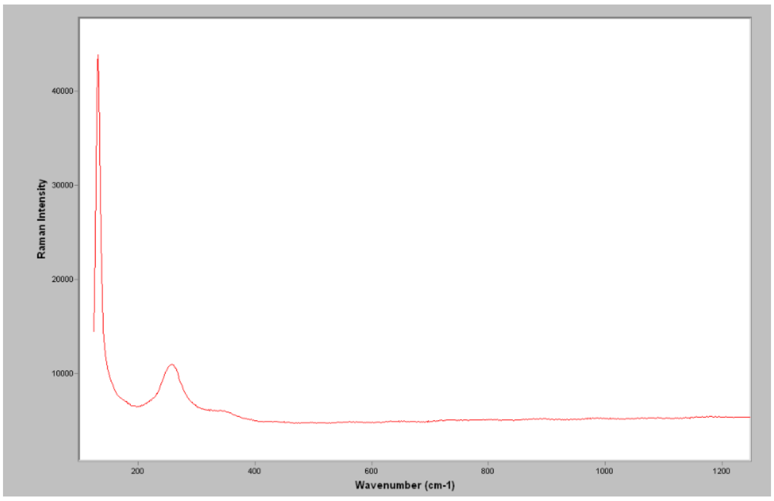


Figure 8.32. Micro Raman spectrum of dark colour parts of the sample

Figure 8.33 shows the infrared spectrum of sample B5 compared with reference spectra of gypsum (Shurvell, n.d.) and mastic (IRUG database, 2007, INR00067). The results show the sample contains gypsum (absorptions at 3500, 3400, 1620, 1100, 670 and 600 cm^{-1}) and mastic. The presence of silica (sand, dirt etc.) is indicated by the broad absorption near 1000 cm^{-1}. Absorption near 2900 cm^{-1} is due to hydrocarbon groups of organic compounds and absorption near 1720 cm^{-1} is due to carbonyl groups (Shurvell, 2002).

Mastic is so brittle and could be solved in boiling alcohol or turpentine. It could provide a semi-gloss varnish layer which increases lustre of the paintings and it usually employed as a protection layer for oil painting. "This varnish yellows with age, and becomes fragile and fissured" (Church, 1915, p. 76).

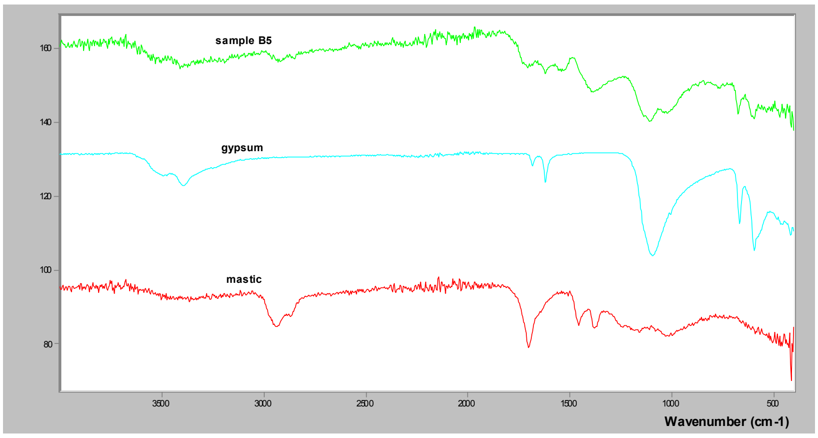


Figure 8.33. The infrared spectrum of sample B5 compared with reference spectrum of gypsum (Shurvell, n.d.) and mastic (IRUG database, 2007, INR00067).

8.3.6. Sample B6

The microscopic cross section image of the sample (figure 8.34) showed different layers. The schematic sketch of the layers of the sample (figure 8.35) contains: 1) green paint, 2) white ground layer, 3) oily red layer, and 4) finish coat.

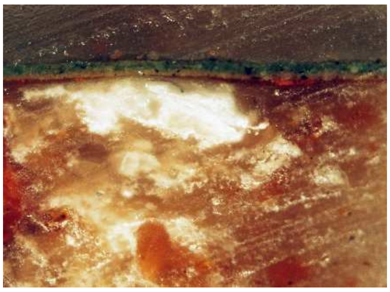


Figure 8.34. Cross section image of the sample B6, magnification 200X

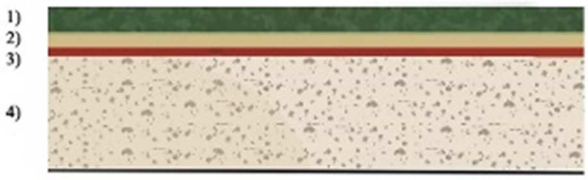


Figure 8.35. Schematic sketch of the layers

The XRF examination of sample B6 showed copper and lead as the main constituents of the material and calcium, and iron are in minor amounts (figure 8.36). Presence of high amounts of lead can indicate lead white pigment. This would have been mixed with green to create a light green colour.

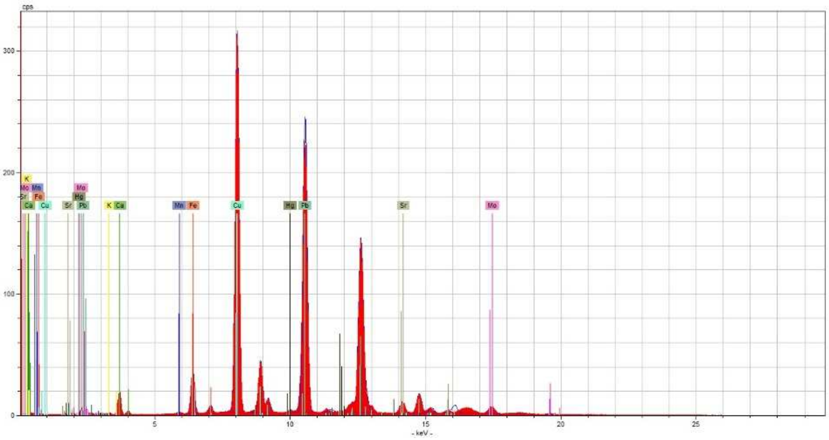


Figure 8.36. XRF spectrum of the sample B6

The high amount of binder mixed with pigment did not provide reliable results in micro Raman examination and brought much fluorescence.

Sample B6 was studied by FTIR to get more information for identification. The FTIR examination of the sample B6 (figure 8.37) compared with reference spectra of gypsum (Shurvell, n.d.) and polymerized linseed oil (Gettens Raw Material Collection, n.d., C28). The results show the sample contains gypsum (absorptions at 3500, 3400, 1620, 1100, 670 and 600 cm^{-1}) and possibly a drying oil (peaks at ~2900 and ~1720 cm^{-1}). The band near 1000 cm^{-1} is probably due to silica (Shurvell, 2002).

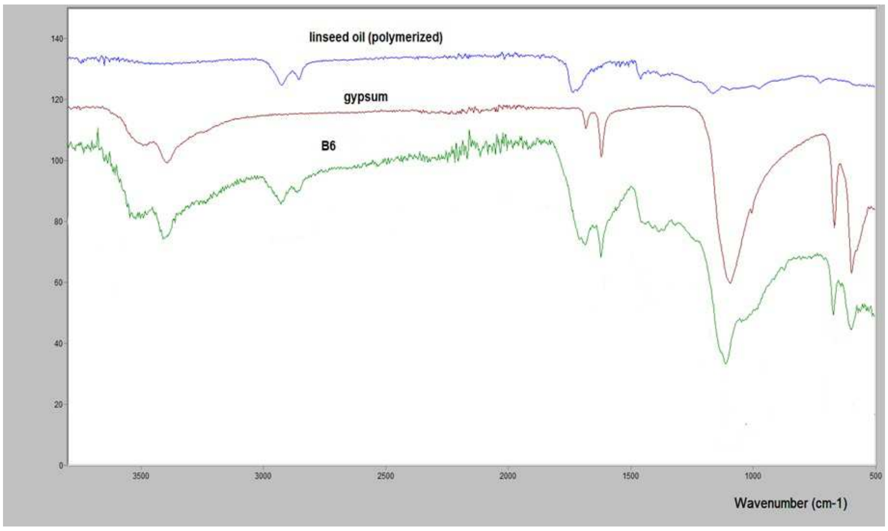


Figure 8.37. The infrared spectrum of sample B6 compared with reference spectra of gypsum (Shurvell, n.d.) and polymerized linseed oil (Gettens Raw Material Collection, n.d., C28).

8.3.7. Sample B7

The microscopic cross section image of the sample B7 (figure 8.38) showed different layers. The schematic sketch of the layers of the sample (figure 8.39) contains: 1) yellow paint layer, 2) dark orange- brown layer, 3) thin white layer, and 4) oily red layer.

Figure 8.38. Cross section image of the sample B7, magnification 200X

Figure 8.39. Schematic sketch of the layers

The XRF analysis for this sample (figure 8.40) showed that lead and iron are the main constituents of this sample while copper and calcium were detected in the composition too. The yellow paint could possibly be from lead or iron compounds.

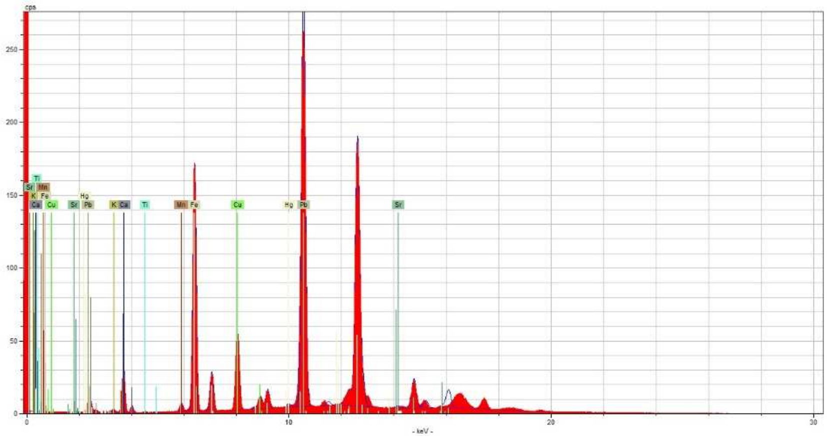


Figure 8.40. XRF spectrum of the sample B7

This sample burned under the micro Raman analysis even with very low energy. Therefore, through Raman analysis, more information could not be gained about this sample.

The FTIR examination of the sample B7 (figure 8.41) shows this sample contains calcium carbonate (broad absorption centred near 1400 cm^{-1} and a peak at 875 cm^{-1}) and possibly a drying oil (peaks at ~2900 and ~1720 cm-1). The strong broad band near 1000 cm^{-1} is probably due to clay or silica (ibid).

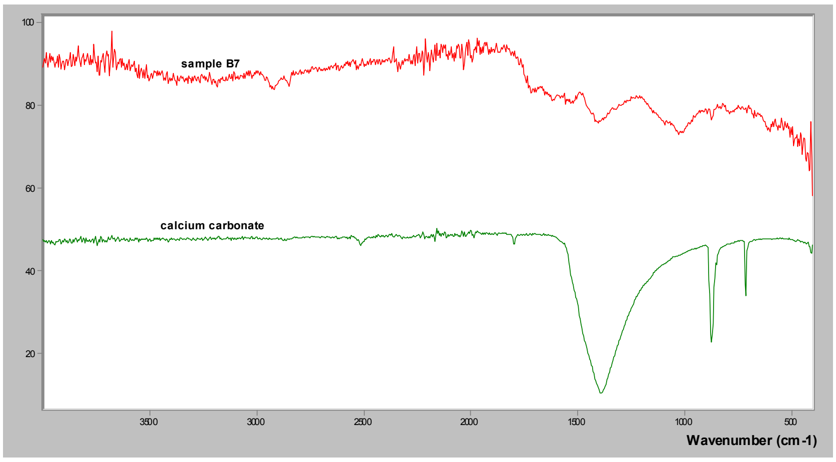


Figure 8.41. The infrared spectrum of sample B7 compared with reference spectrum of calcium carbonate (Shurvell, n.d.).

8.3.8. Sample B8

The microscopic cross section image of the sample B8 (figure 8.42) showed different layers. The schematic sketch of the layers of the sample (figure 8.43) contains: 1) gold leaf, 2) dark brown paint, 3) bulging oily brown layer, and 4) oily red layer.

Figure 8.42. Cross section image of the sample B8, magnification 200X

Figure 8.43. Schematic sketch of the layers

The XRF examination (figure 8.44) showed lead as the main constituent of the sample while iron, mercury, and calcium were detected in minor amounts in the composition.

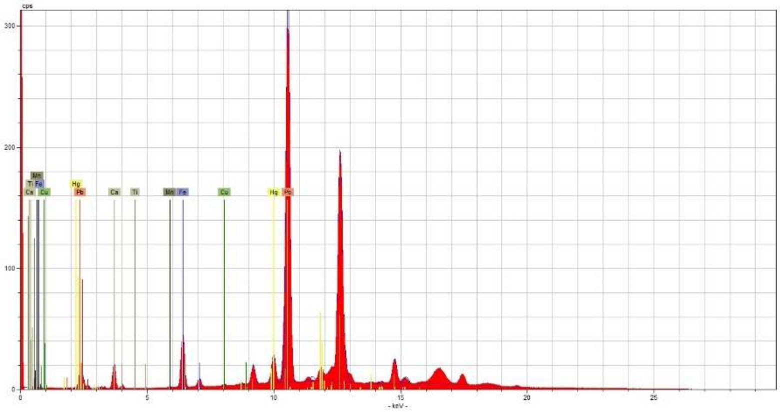


Figure 8.44. XRF spectrum of the sample B8

Micro Raman analysis shows that the sample contains vermilion (figure 8.45). "Cinnabar has primary peaks at 254, 277, and 340 cm^{-1} in the Raman fingerprint region" (Liritzis & Katsaros, n.d., p. 1). According to XRF and Raman results, this sample could be a mixture of vermilion and the lead compounds.

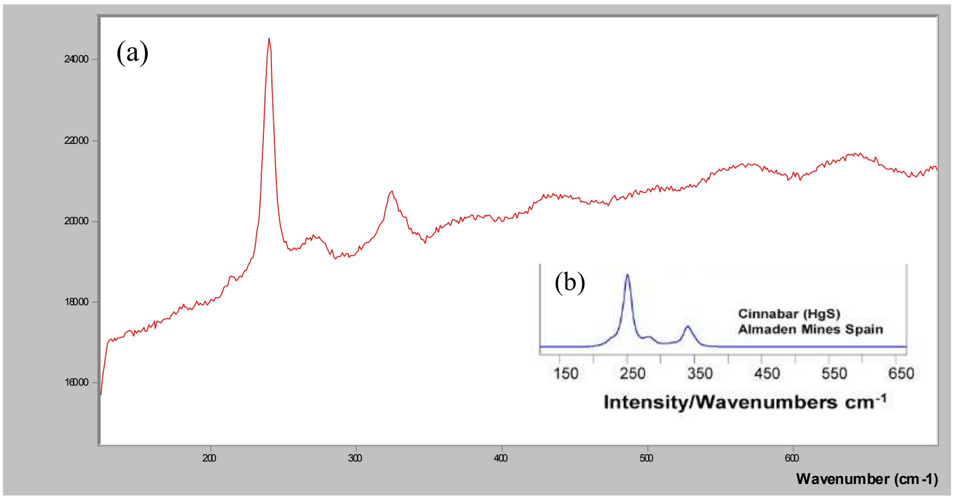


Figure 8.45. Micro Raman spectrum (a) from the sample B8 in comparison with Raman database spectrum of cinnabar (b) (Liritzis & Katsaros, n.d., p. 2).

The FTIR examination of the sample B8 (figure 8.46) shows this sample could contain calcium carbonate and mastic.

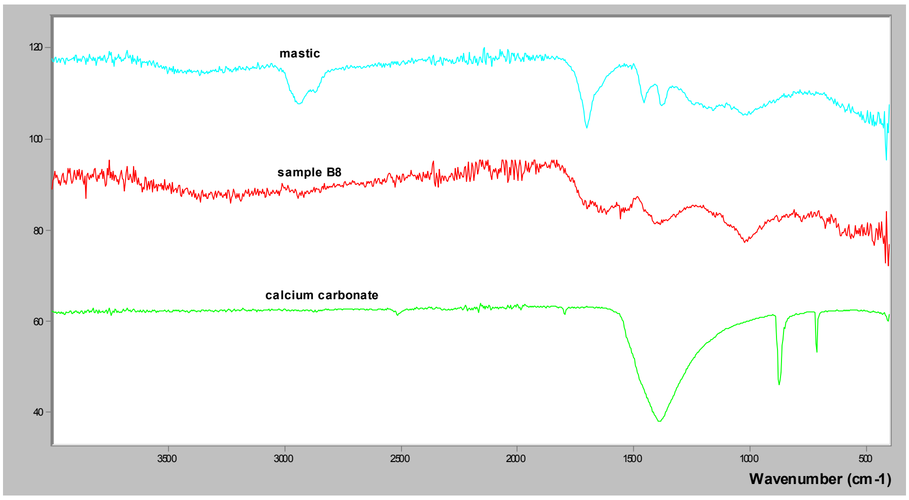


Figure 8.46. The infrared spectrum of sample B8 compared with reference spectra of mastic (IRUG, 2007, INR00067) and calcium carbonate (Shurvell, n.d.).

8.3.9. Sample B9

The microscopic cross section image of the sample B9 (figure 8.47) showed different layers. The layers schematic sketch of the sample (figure 8.48) contains: 1) red paint, 2) oily brown layer, and 3) finish coat layer.

Figure 8.47. Cross section image of the sample B9, magnification 200X

Figure 8.48. Schematic sketch of the layers

Sample B9 shows the high presence of mercury in XRF examination (figure 8.49). Other elements like iron and calcium are in minor amounts in this sample.

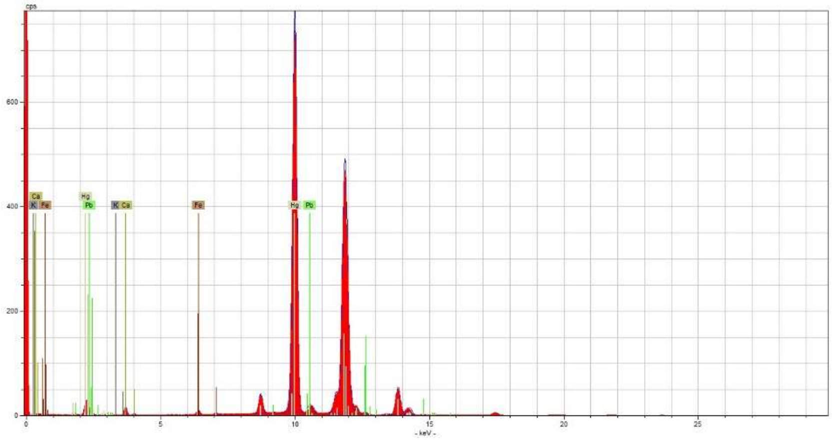


Figure 8.49. XRF spectrum of sample B9

Further information about this sample was obtained through micro Raman analysis. This sample was similar to the previous sample, B8, in Raman analysis. The Raman spectrum showed the presence of vermilion (figure 8.50).

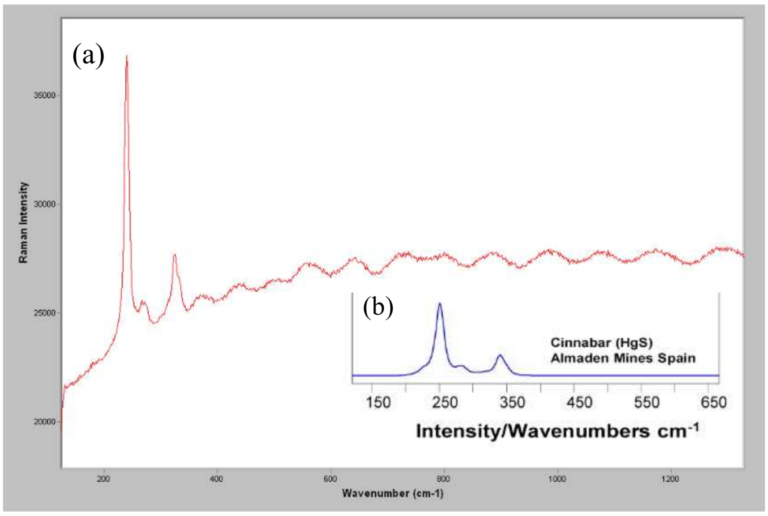


Figure 8.50. Micro Raman spectrum (a) from the sample B9 in comparison with Raman database spectrum of cinnabar (b) (Liritzis & Katsaros, n.d., p. 2).

The FTIR examination of the sample B9 (figure 8.51) shows this sample contains gypsum (absorptions at 3500, 3400, 1620, 1100, 670 and 600 cm^{-1}) (Shurvell, 2002).

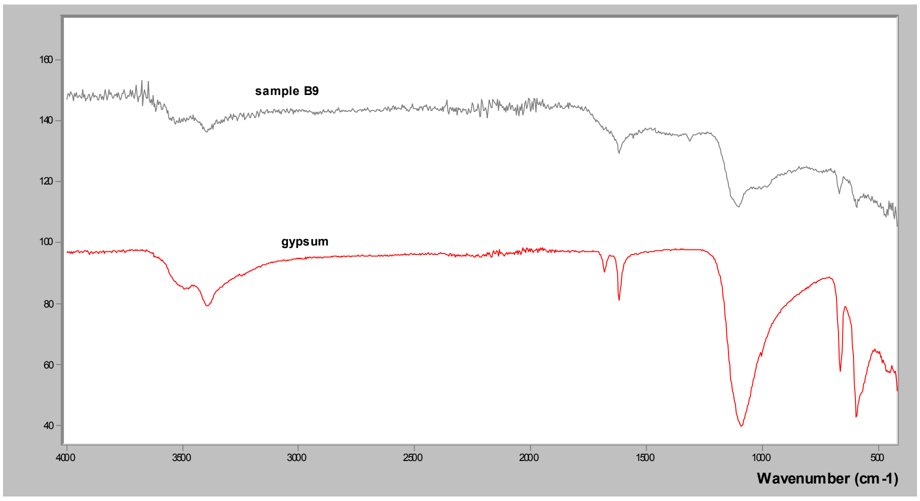


Figure 8.51. The infrared spectrum of sample B9 compared with reference spectrum of gypsum (Shurvell, n.d.).

8.3.10. Sample B10

The microscopic cross section image of the sample B10 (figure 8.52) showed two different layers. The layers schematic sketch of the sample (figure 8.53) contains: 1) blue paint and 2) white ground layer.

Figure 8.52. Cross section image of the sample B10, magnification 200X

Figure 8.53. Schematic sketch of the layers

For this sample, XRF analysis showed lead as the main constituent of the sample while other elements like calcium, iron, and copper are in minor amounts (figure 8.54).

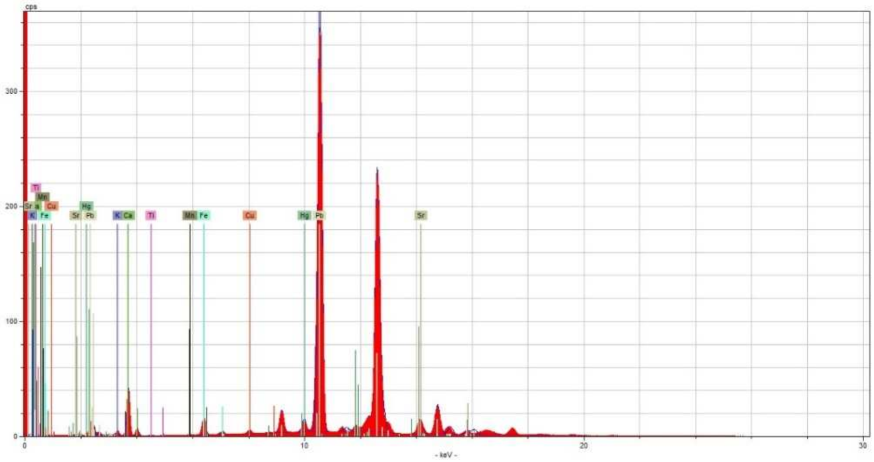


Figure 8.54. XRF spectrum of sample B10

Another XRF analysis was carried out on the underside of sample B10 (figure 8.55). The XRF spectrum shows the presence of calcium, iron, and sulphur. This part of the sample therefore contains gypsum as the main masonry material.

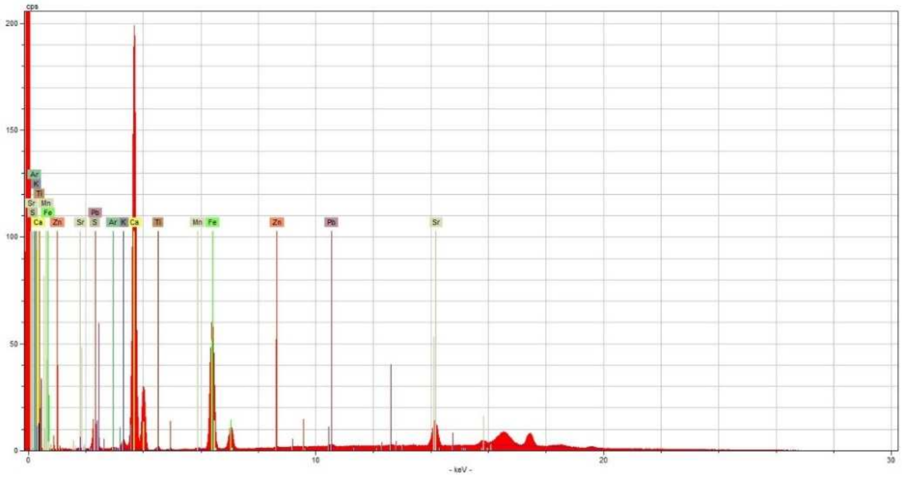


Figure 8.55. XRF spectrum of underside of sample B10

During micro Raman analysis, the high amount of binder brought much fluorescence and no Raman peak could be observed. Therefore micro Raman spectroscopy did not show any result for the sample B10.

The FTIR result of Sample B10 shows that the sample could possibly be ultramarine. The FTIR spectrum (figure 8.56) shows this sample, also, contains gypsum (absorptions at 3500, 3400, 1620, 1100, 670, and 600 cm^{-1}) (Shurvell, 2002).

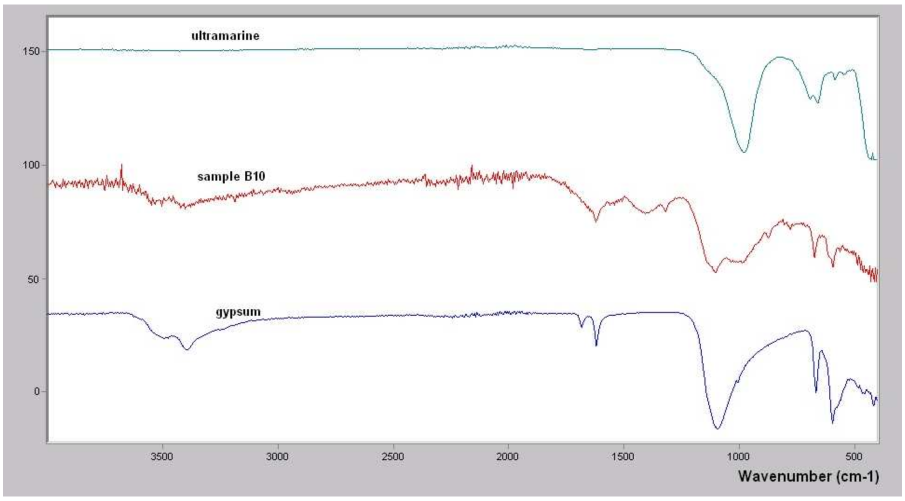


Figure 8.56. The infrared spectrum of sample B10 compared with reference spectra of gypsum (Shurvell, n.d.) and ultramarine (IRUG, 2007, IMP00075).

8.3.11. Sample B11

The microscopic cross section image of sample B11 (figure 8.57) showed different layers. The schematic sketch of the layers of the sample (figure 8.58) contains: 1) thin gold leaf, 2) dark oily layer, 3) red oily layer, and 4) red ground layer.

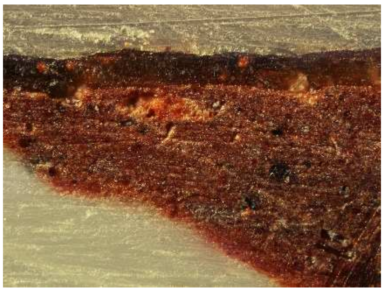


Figure 8.57. Cross section image of the sample B11, magnification 200X

Figure 8.58. Schematic sketch of the layers

The XRF analysis confirms the presence of lead, iron, and gold (figure 8.59). Calcium is a minor amount in this sample. The presence of iron could be from Armenian bole (Fe_2O_3) which was usually used under the gold leaf.

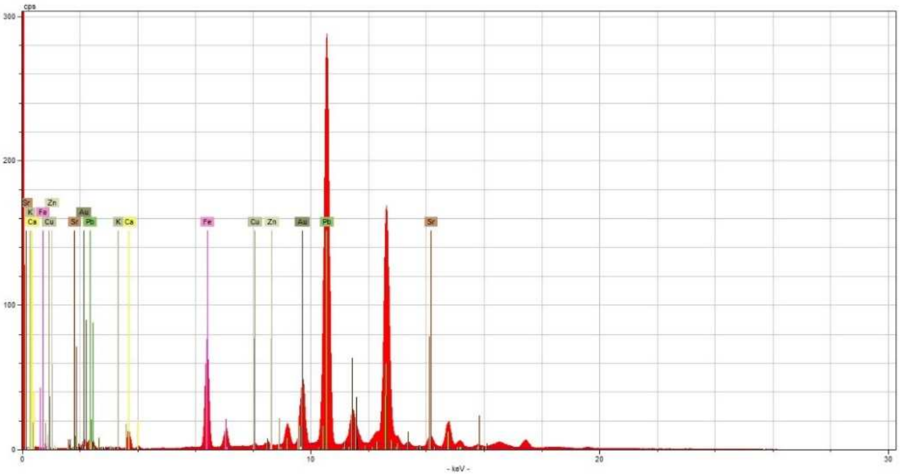


Figure 8.59. XRF spectrum on gold leaf of the sample B11

Another XRF analysis was carried out on the underside of sample B11 (figure 8.60). The XRF spectrum shows the presence of iron, lead, calcium, and gold as the main constituents of this sample. This part of the sample, therefore, could contain hematite or Armenian bole.

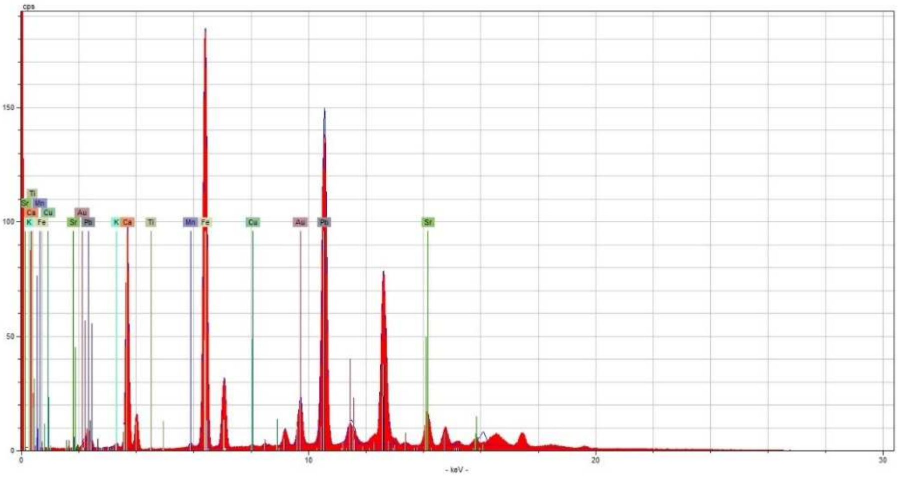


Figure 8.60. XRF spectrum on red layer of the sample B11

In Raman analysis, the characteristic Raman bands at 220, 286, 402, 491, and 601 cm^{-1} (figure 8.61) could be assigned to red ochre or hematite (Bell et al., 1997, p. 2174). Also Raman bands at 280, 406, and 608 cm^{-1} have been mentioned as characteristic Raman bands for red ochre (Liritzis & Katsaros, n.d., p. 2). In this case, Raman results confirmed XRF results.

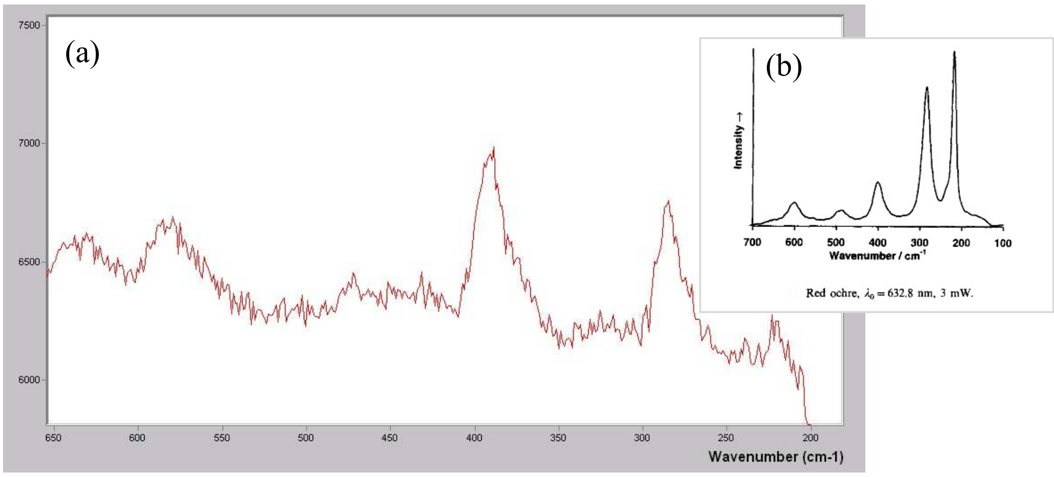


Figure 8.61. Micro Raman spectrum (a) from the sample B11 in comparison with Raman database spectrum of red ochre (b) (Bell et al., 1997, p. 2164).

Figure 8.62 shows the infrared spectrum of samples B11 compared with reference spectrum of gypsum (Shurvell, n.d.). The results show that the sample is mainly gypsum (absorptions at 3500, 3400, 1620, 1100, 670 and 600 cm^{-1}) (Shurvell, 2002).

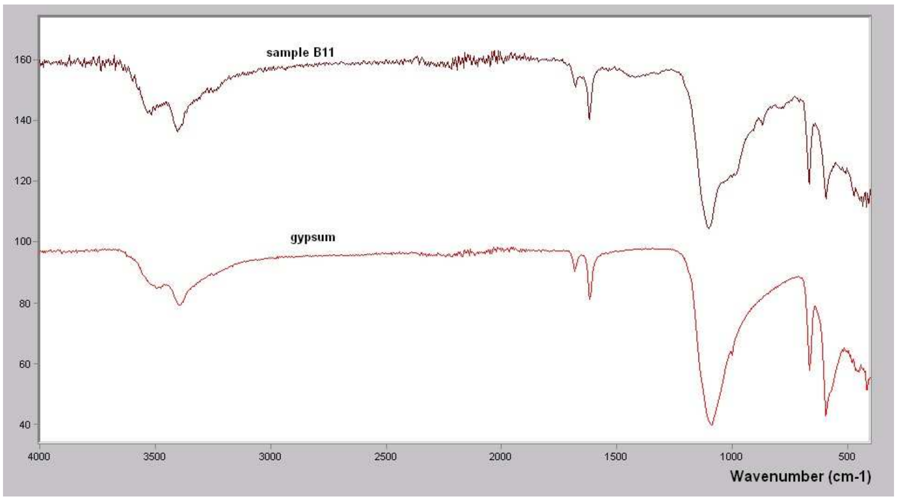


Figure 8.62. The infrared spectrum of sample B11 compared with reference spectrum of gypsum (Shurvell, n.d.).

8.3.12. Sample B12

The microscopic cross section image of sample B12 (figure 8.63) showed different layers. The schematic sketch of the layers of the sample (figure 8.64) contains: 1) oily red layer, 2) dark red-brown paint, and 3) ground layer.

Figure 8.63. Cross section image of the sample B12, magnification 200X

Figure 8.64. Schematic sketch of the layers

The XRF analysis confirms the presence of lead and barium as the main constituents while calcium, iron, zinc, and mercury are in minor amounts in this sample (figure 8.65).

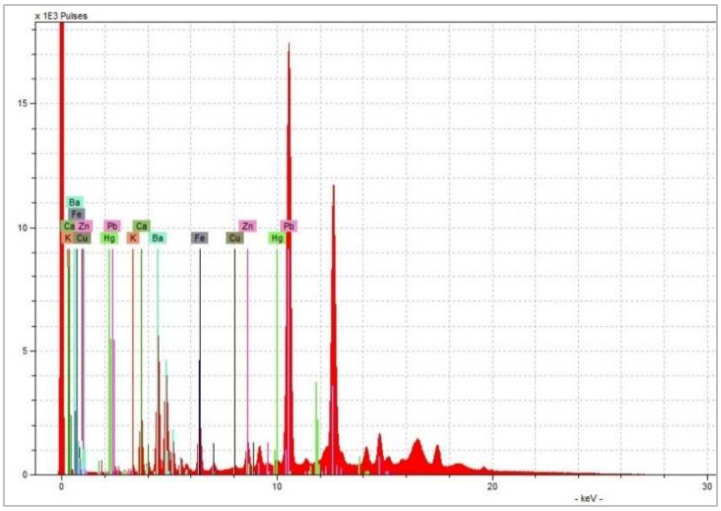


Figure 8.65. XRF spectrum of the sample B12

The Raman spectrum of this sample (figure 8.66) shows a characteristic band at 223 and a strong Raman band at around 530 wave number/cm^{-1} which could possibly indicate red lead. Therefore, about lead compound, Raman results confirmed XRF results but there was no sign of any barium compounds in Raman results.

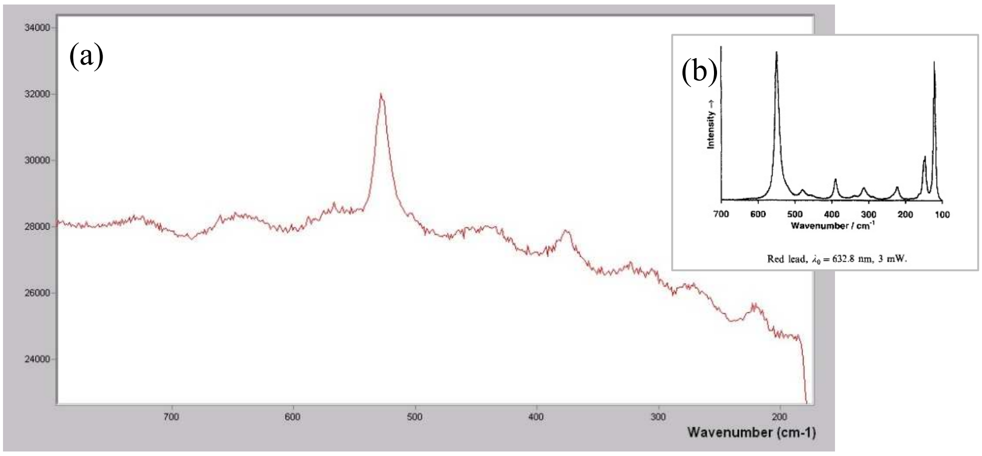


Figure 8.66. Micro Raman spectrum (a) from the sample B12 in comparison with Raman database spectrum of red lead (b) (Bell et al., 1997, p. 2165).

8.3.13. Sample B13

The microscopic cross section image of the sample B13 (figure 8.67) showed three different layers. The layers schematic sketch of the sample (figure 8.68) contains: 1) oily light red layer, 2) green paint and 3) ground layer.

Figure 8.67. Cross section image of the sample B13, magnification 100X

Figure 8.68. Schematic sketch of the layers

The XRF analysis confirms the presence of copper as the main constituent of this sample (figure 8.69). Other elements like lead, iron, and calcium are in minor amounts in the composition. The sample, therefore, could be a copper green pigment.

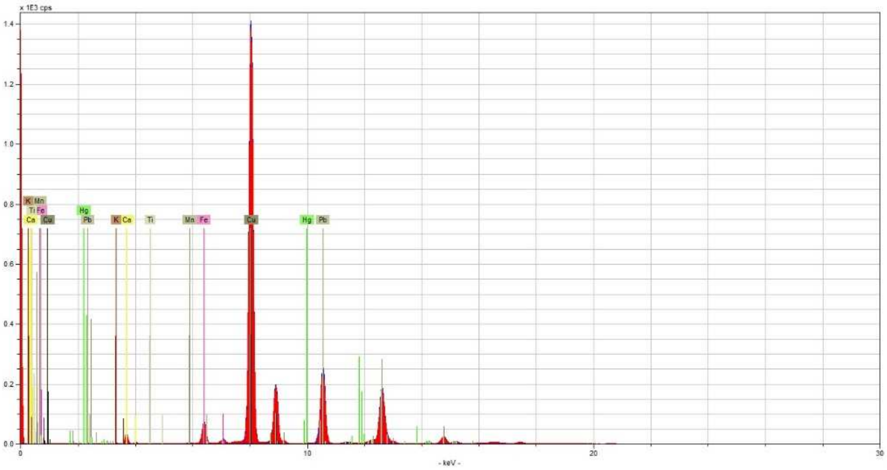


Figure 8.69. XRF spectrum of the sample B13

During micro Raman analysis, the sample did not provide reliable results because of the high amount of varnish and binder mixed with pigment and the high amount of binder brought much fluorescence. In the following spectra (figure 8.70), Raman analysis revealed the presence of moolooite, $CuC_2O_4nH_2O$, in sample B13 through the detection of its characteristic band at about 920 wave number/cm^{-1} (Zoppi, Lofrumento, Mendes, & Castellucci, 2010).

"Moolooite (copper oxalate), a very rare compound, was found as a degradation product from the decay of malachite in several specimens of Cultural Heritage" (Castro et al., 2008, p. 4103).[1]

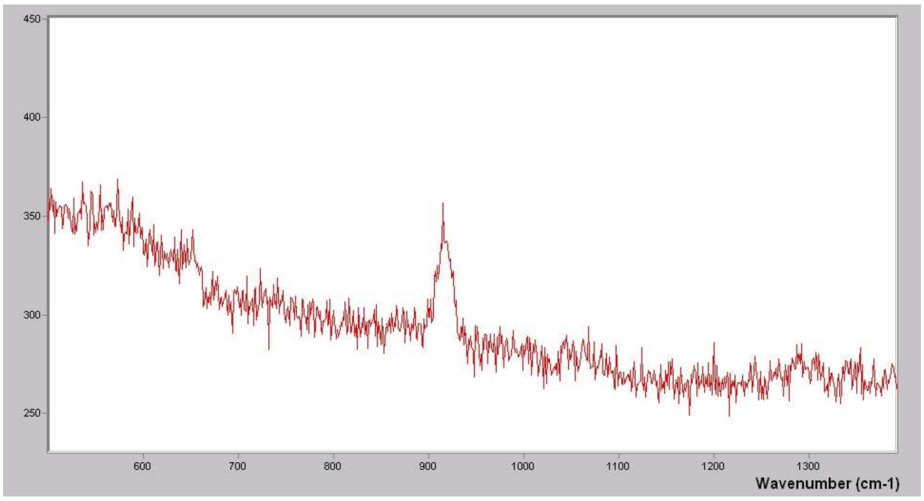


Figure 8.70. Micro Raman spectrum of the sample B13

Figure 8.71 shows the infrared spectrum of underside of sample B13 compared with reference spectrum of gypsum (Shurvell, n.d.). The results show that the sample is mainly gypsum (absorptions at 3500, 3400, 1620, 1100, 670 and 600 cm^{-1}).

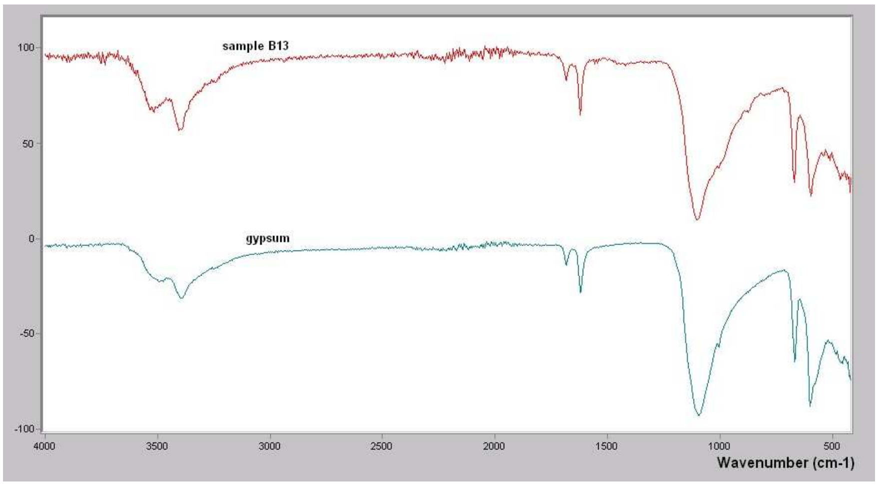


Figure 8.71. The infrared spectrum of sample B13 compared with reference spectrum of gypsum (Shurvell, n.d.).

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[1] Castro et al. (2008) mentioned that copper pigments are very sensitive to environmental pollutants. They studied the degradation mechanism of green copper pigments due to the presence of microorganisms excreting oxalic acid.

8.3.14. Sample B14

This paint cross-section, also, was viewed through a microscope. The microscopic image of this sample (figure 8.72) showed different layers. The layers schematic sketch of the sample (figure 8.73) contains: 1) blue paint, 2) oily red layer, and 3) red ground layer.

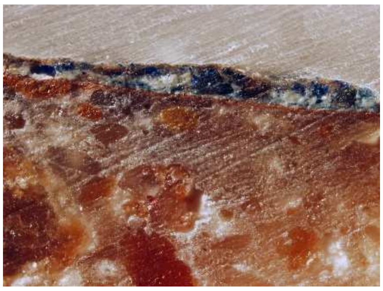


Figure 8.72. Cross section image of the sample B14, magnification 200X

Figure 8.73. Schematic sketch of the layers

XRF analysis for this sample showed that lead is the main constituent while calcium and iron were detected in the composition too (figure 8.74).

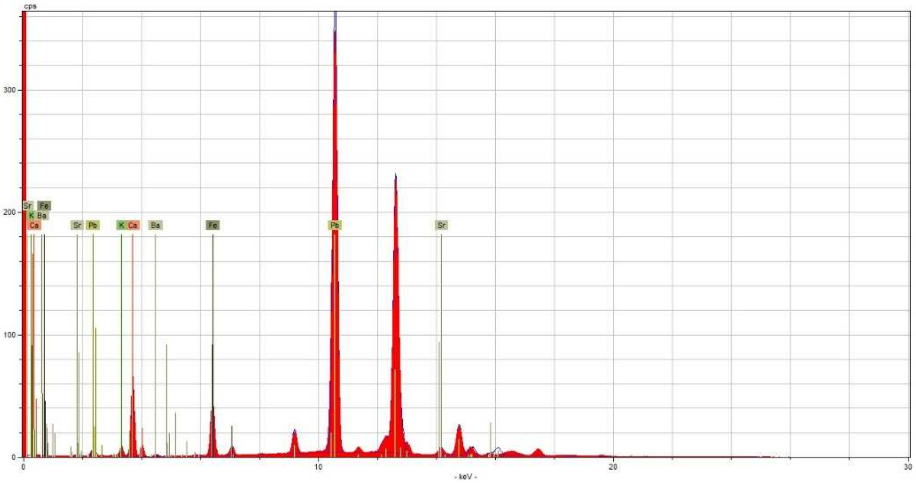


Figure 8.74. XRF spectrum of the sample B14

Presence of high amounts of lead could indicate lead white pigment. This would have been mixed to create a light blue colour which is obvious in the microscopic cross section image.

Figure 8.75 shows the micro Raman spectrum of this sample. The characteristic bands at 548 and 1096 cm^{-1} can be assigned to lazurite (Burgio et al., 2010, p. 5727; Muralha et al., 2012, p. 24).

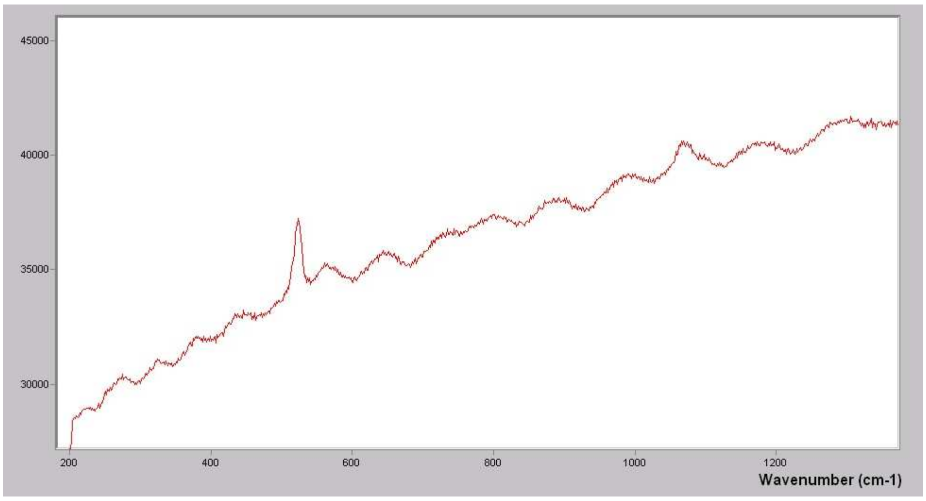


Figure 8.75. Micro Raman spectrum of the sample B14

In this sample, there was also a red ground layer which was studied by micro Raman spectroscopy. The characteristic Raman bands at 220, 280, 293 and around 402 cm^{-1} (figure 8.76) could be assigned to red ochre or hematite (Bell et al., 1997, p. 2174; Liritzis & Katsaros, n.d., p. 2).

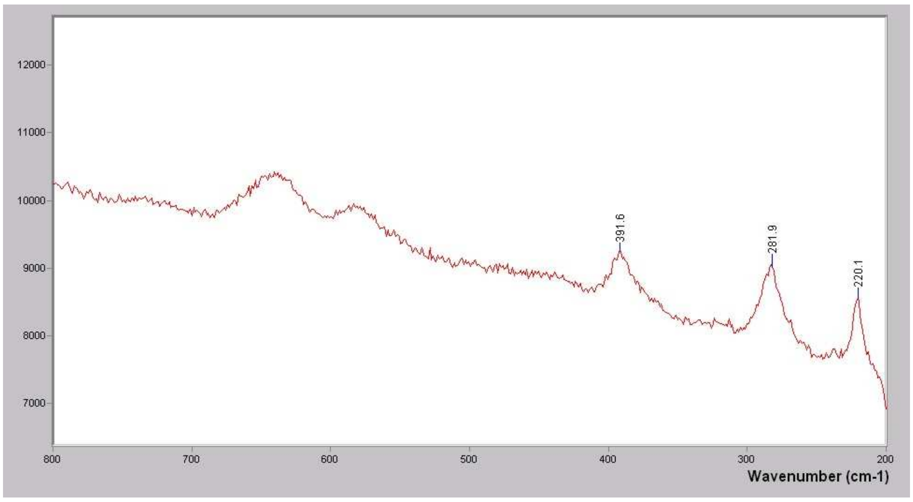


Figure 8.76. Micro Raman spectrum of underside of the sample B14

The FTIR results of sample B14 show that the sample could possibly be ultramarine. The FTIR spectrum (figure 8.77) shows this sample also contains a little amount of gypsum. Evidence of hydrocarbon groups is seen near 1440 cm^{-1}. The strong broad band near 1000 cm^{-1} is probably due to clay or silica (Shurvell, 2002).

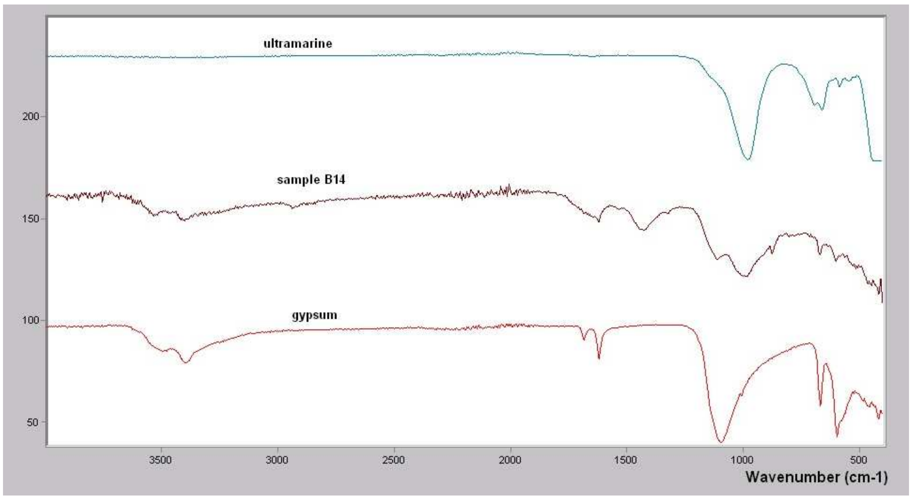


Figure 8.77. FTIR spectrum of the sample B14 compared with reference spectra of ultramarine (IRUG database, 2007, IMP00075) and gypsum (Shurvell, n.d.).

8.3.15. Sample B15

The paint cross-section images of this sample (figure 8.78-8.79) showed very interesting layers. The layers schematic sketch of the sample (figure 8.80) contains: 1) oily red layer, 2) gold leaf, 3) oily dark layer, 4) ground layer, 5) oily dark layer, 6) gold leaf, 7) oily dark layer, and red ground layer.

Figure 8.78. Cross section image of the sample B15, magnification 200X

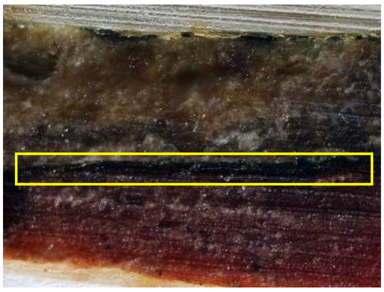


Figure 8.79. Cross section image of the sample B15, presence of gold leaf between layers, magnification 200X

Figure 8.80. Schematic sketch of the layers

Sample B15 contains a thin gold leaf over the red layer. The XRF analysis of this sample shown in figure 8.81 and it confirms the presence of copper as the main constituent of the sample while zinc, iron, and calcium are in minor amounts. The results could confirm presence of brass leaf behalf of gold leaf in the wall painting. The presence of iron could be from Armenian bole (Fe_2O_3) which was usually used under the gold leaf.

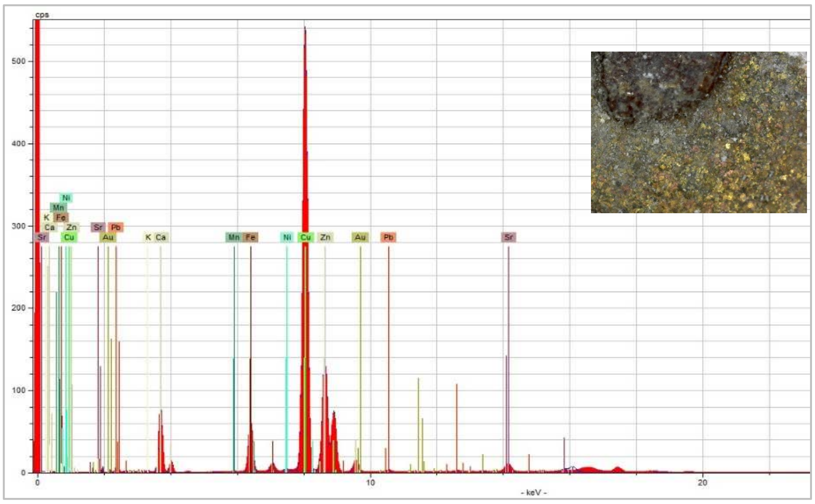


Figure 8.81. XRF spectrum of the sample B15 shows existence of copper and zinc behalf of gold that can cause more corrosion.

The results of Raman analysis for this sample brought much fluorescence, therefore, more information could not be gained about this sample.

Figure 8.82 shows the infrared spectrum of white ground layer of samples B15 compared with reference spectrum of gypsum (Shurvell, n.d.). The results show that the sample is mainly gypsum. Evidence of hydrocarbon groups is seen near 1440 cm^{-1}. The strong broad band near 1000 cm^{-1} is probably due to clay or silica (ibid).

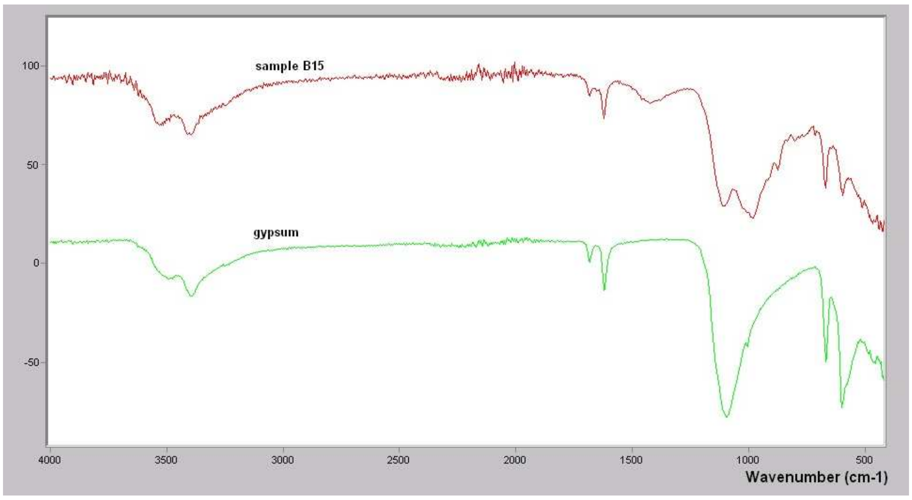


Figure 8.82. The infrared spectrum of sample B15 compared with reference spectrum of gypsum (Shurvell, n.d.).

8.4. Conclusion

The following pigments were identified on these wall paintings analysed: Lazurite, lead white, minium (red lead), litharge, red ochre, vermilion, and copper green pigments. Calcium carbonate, gypsum, and red ochre also were used as ground layers for the paint.

According to the Iranian Cultural Heritage, Handcrafts, and Tourism Organization (ICHHTO), the painting was not previously restored and the pigments could be considered genuine. Nevertheless, study of microscopic cross section images of different samples showed different layers, which were used on top of another layer. For instance, it is not very common to cover the gold leaf under the dark layers, since the purpose of the gilded parts of wall paintings was to provide a bright and luxurious appearance for the buildings.

Therefore, it is presumed that these layers must have been added to the wall paintings at some early stages by way of restoration, as there is no record of such intervention during recent years. The Raman results showed presence of moolooite in the sample B13. This material cannot be original compound and its occurrence could be because of the changes in the original pigment. According to Castro et al. (2008) "this material is a very rare natural mineral first reported in 1985 in Australia" (p. 4105).

FTIR analysis showed the probable presence of mastic resin as the main component of the varnish and linseed oil in some samples. According to the painter William Dyce, "mastic varnish would yellow, but not to the same extent as a varnish containing oil" (as cited in White & Kirby, 2001, p. 64). Usually in every sample, there are so many IR bands that it is not feasible to assign all of them, but the main goal of this study was to gain more information about each sample.

CHAPTER NINE

9. The Church of Surb Stepanos (1614)

9.1. Introduction

"The church of St. Stephen is the largest church in New-Julfa. It was built in the second decade of the 17th century" (Hakhnazarian & Mehrabian, 1991, p. 65). In 1848, the church was repaired under the supervision of priest Gregorian (Restoration report, Cultural Heritage Organization of Isfahan, 1391 SH/2012, p. 2).

Hakhnazarian and Mehrabian (1991) described the church:

> This church has the form of a parallelepiped. The architectural structure is a classic "domed hall", with its interior articulated by four large free-standing pillars that support the vault (figure 9.1). The pentagonal apse contains the altar and is flanked by rooms at the two sides. The room in the north contains a font and opens to the outside. Built in to the west wall is a staircase leading to the upper floor, traditionally reserved for women (p. 65) (figures 9.2- 9.3).

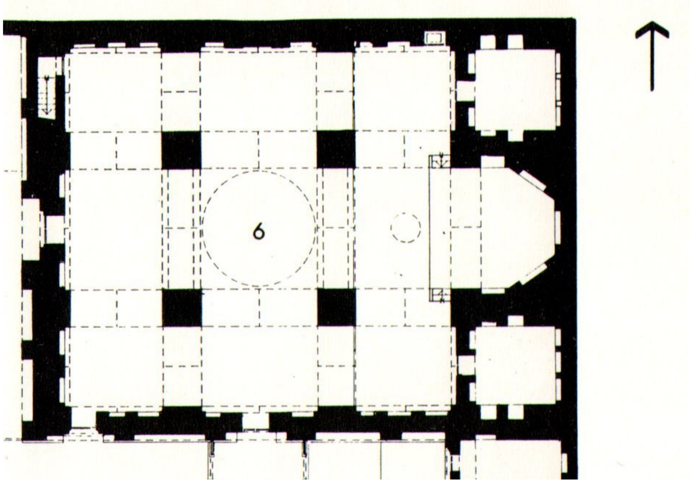


Figure 9.1. Apse position in the church of Surb Stepanos (Hakhnazarian & Mehrabian, 1991, p. 68)

"The walls inside are plastered and a very fine decorative fascia in ceramic tiles [that] runs around the lower perimeter. […] A profusion of sacred ornaments decorates the interior, partly hiding the damage caused by a series of poor restoration efforts" (ibid).

During years, this church underwent inappropriate restoration on several occasions. Many of the wall paintings disappeared or covered by a gypsum layer, with the exception of the lower decorative bands and a few reliefs (ibid, p. 66).

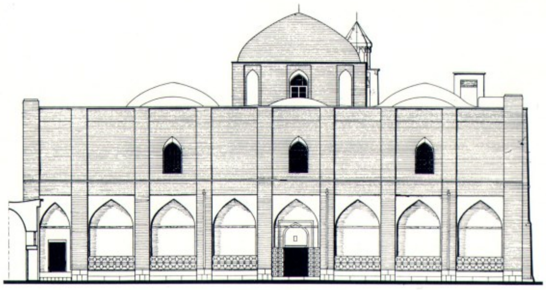


Figure 9.2.The north elevation of the church of Surb Stepanos, scale 1:250 (ibid, p. 66).

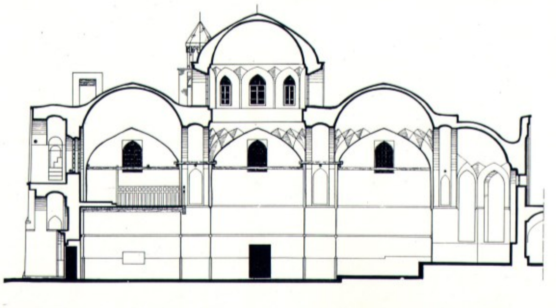


Figure 9.3. The longitudinal section of the church of Surb Stepanos, scale 1:250 (ibid).

The decoration and ornaments in the church of Surb Stepanos include: figurative wall paintings, canvas paintings which have been hung over the walls, water-colour paintings with arabesque motifs, Laye-chini decoration (pastiglia), and TalaChasban (gilded substrate).

Wall paintings inside the apse of the church of Surb Stepanos were covered under the gypsum layer until 2009 when they were accidentally found. Through the restoration projects in 2010-2011, under the supervision of Iranian Cultural Heritage Organization, all the wall paintings were recovered (figures 9.4- 9.5).

Figures 9.4 & 9.5. Apse of the church after recovering its wall paintings.

9.2. Experimental Approaches

9.2.1. Samples

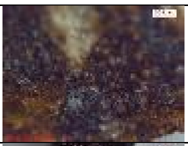
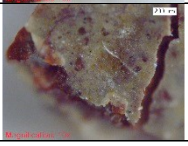
One of the major challenges of the project was how to deal with the sheer volume and diversity of data that wanted to collect. Because there were some limitations for collecting samples based on the importance of these wall paintings, during this project, an opportunity was provided to acquire historical material from one wall painting which is located in the apse. In figures 9.6 and 9.7 sampling areas on the painting are shown.

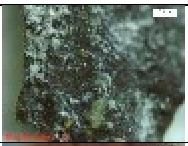
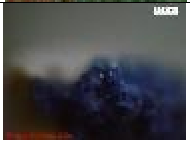
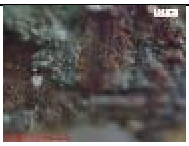
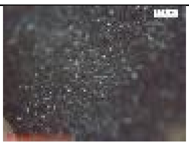
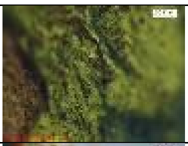
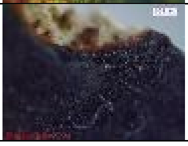
Figures 9.6 & 9.7. Sampling points on the selected wall painting, the church of Surb Stepanos

In order to perform analysis, samples of different colours were taken from the parts where the paint was flaking. Thirteen micro samples were collected to investigate composition of the polychromy.

The table 9.1 shows each sample, its visual colour, and an image. Each sample comes from the church of Surb Stepanos, denoted by the letters SA, and the number describes different area sampled from the mural.

Table 9.1. Samples and their description

Samples from the church of Surb Stepanos	**Visual Colours of the Samples**	**Sample Images- Magnification 10X and 20X ***
SA1	Dark orange-brown	
SA2	Dark blue	
SA3	Dark green	
SA4	White over orange	

SA5	Green	
SA6	Red under the gold leaf	
SA7	Light green	
SA8	Blue	 *
SA9	Brown over green	 *
SA10	Dark brown- black	 *
SA11	Gold leaf	
SA12	Dark green or black	

9.2.2. Techniques and Analysis

Different analyses were performed on the samples to identify the painting materials used in this wall painting. Table 9.2 gives the sample preparation and analytical techniques used.

Table 9.2. Techniques applied to samples

Samples	Cross section	XRF	Micro Raman	FTIR	XRD	SEM-EDS
SA1	-	✓	✓	✓	-	-
SA2	✓	✓	✓	✓	✓	✓
SA3	✓	✓	✓	✓	✓	✓
SA4	✓	✓	✓	✓	-	✓
SA5	✓	✓	✓	-	✓	✓
SA6	-	✓	✓	✓	-	-
SA7	-	✓	✓	-	-	-
SA8	✓	✓	✓	✓	✓	✓
SA9	-	✓	✓	✓	-	-
SA10	✓	✓	✓	✓	-	✓
SA11	-	✓	✓	✓	-	-
SA12	✓	✓	✓	✓	✓	✓

9.3. Results and Discussion

9.3.1. Sample SA1

Due to the size and form of this sample, cross section was not provided. XRF analysis for sample SA1 showed lead as the main constituent of the sample while calcium, sulphur, and iron were detected in minor amounts in the composition (figure 9.8).

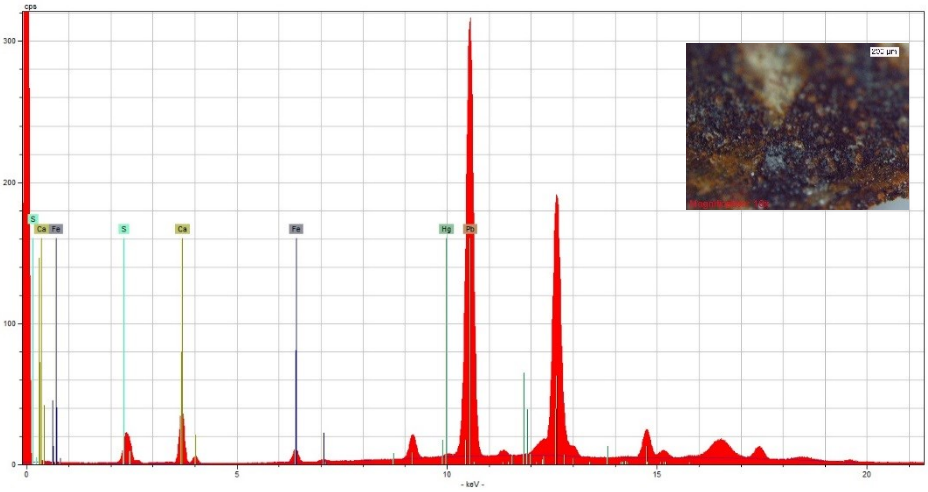


Figure 9.8. XRF spectrum of sample SA1

The Raman spectrum of this sample (figure 9.9) shows the characteristic bands at 220, 375 and a very strong Raman band at 525 wave number/cm^{-1} which could not exactly be identified. At first step, it could be considered as red lead but there was no sign of red lead characteristic bands especially at 122, 149, and 548 wave number/cm^{-1}.

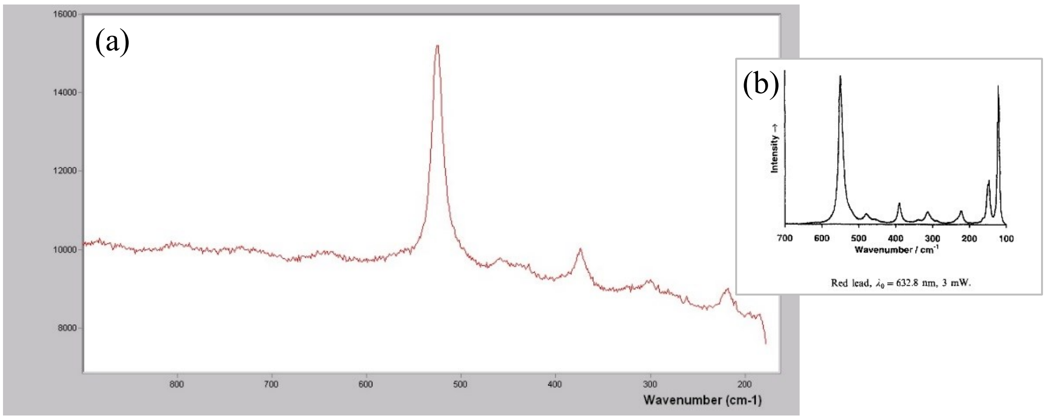


Figure 9.9. Micro Raman spectrum (a) from the sample SA1 in comparison with Raman database spectrum of red lead (b) (Bell et al., 1997, p. 2165).

Figure 9.10 shows the infrared spectrum of sample SA1 compared with reference spectra of gypsum and calcium carbonate (Shurvell, n.d.). The results show this sample contains calcium carbonate (broad absorption centred near 1400 cm^{-1} and the sharp peak at 875 cm^{-1}) and gypsum (absorptions at 3500, 3400, 1620, 670 and 600 cm^{-1}) (Shurvell, 2002).

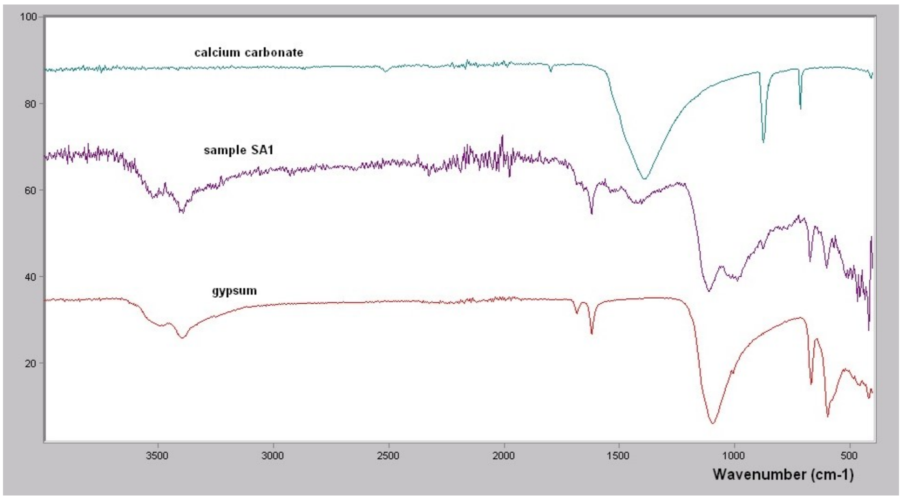


Figure 9.10. The infrared spectrum of sample SA1 compared with reference spectra of calcium carbonate and gypsum (Shurvell, n.d.).

By consideration of XRF results, the dark orange- brown sample could be a lead compound.

9.3.2. Sample SA2

The microscopic cross section image of the sample (figure 9.11) showed different layers. The schematic sketch of the layers of the sample (figure 9.12) contains: 1) thin gold leaf, 2) blue paint layer, 3) thin dark layer, and 4) white ground layer.

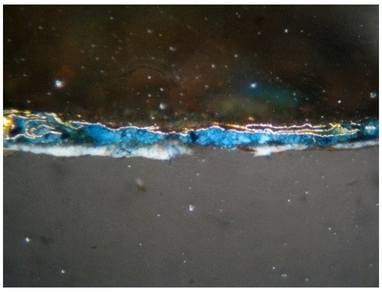


Figure 9.11. Cross section image of the sample SA2, magnification 180X

Figure 9.12. Schematic sketch of the layers

The XRF analysis for this sample (figure 9.13) showed that lead is the main constituent of this sample while iron, calcium, sulphur, cobalt, and copper were detected in minor amounts in the composition.

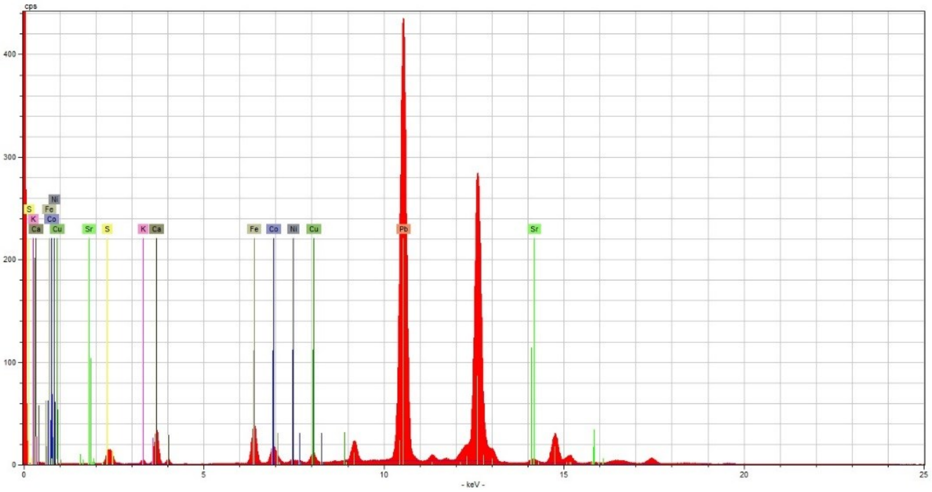


Figure 9.13. XRF spectrum on the sample SA2

The micro Raman spectrum from this sample (figure 9.14) showed a strong band at ~1030 cm^{-1}, which could be characteristic of lead white, cerussite - $PbCO_3$ (Martens, Rintoul, Kloprogge, & Frost, 2004, p. 8; Burrafato et al, 2004, p. 884). Also Raman band at ~ 1048-1052 cm^{-1} could be assigned to lead white (Burgio, Clark, & Hark, 2010, p.5727). The characteristic bands at 268 and around 509 cm^{-1} could possibly indicate the presence of malachite, basic copper(II) carbonate $CuCO_3.Cu(OH)_2$, in this sample (Bell, Clark, & Gibbs, 1997, p. 2172).

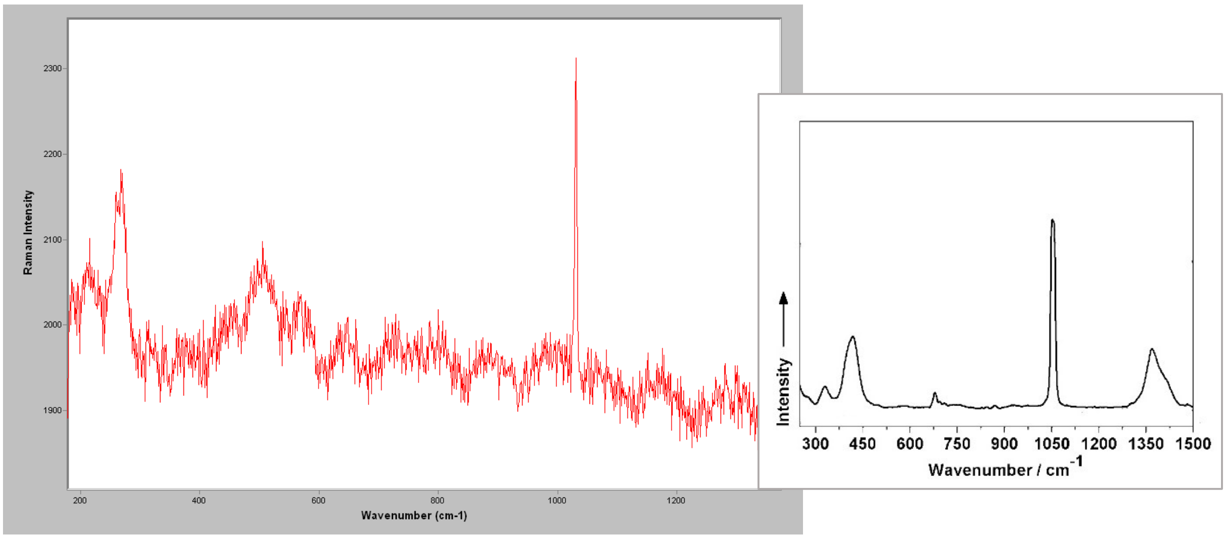


Figure 9.14. Raman spectrum of the sample SA2 in comparison with reference micro Raman Spectroscopy of lead white-dry pigment (Burrafato et al, 2004, p. 884)

Furthermore, X-ray diffraction (XRD) analysis was carried out on this sample to get more information. In the XRD spectrum of the sample SA2 (figure 9.15) the diffraction lines from gypsum, calcium carbonate, cerussite, and quartz could be identified.

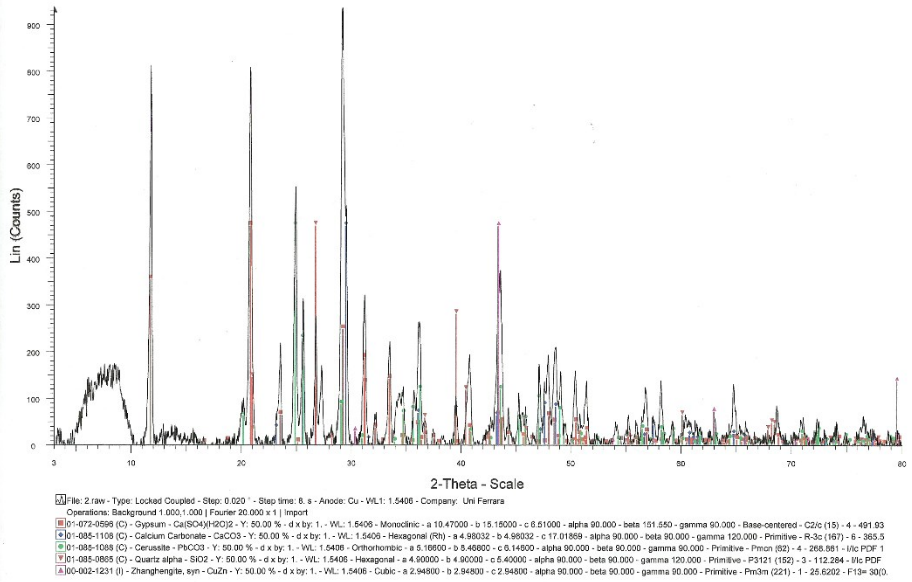


Figure 9.15. XRD spectrum of the sample SA2

Also scanning electron microscopy- energy dispersive X-ray spectroscopy (SEM-EDX) was employed for pigment analysis and on different layers of the sample SA2. Figure 9.16 shows the selected points and areas for SEM-EDX analysis. The results revealed that the white layer observed under all layers in the cross-section is lead white (figure 9.17).

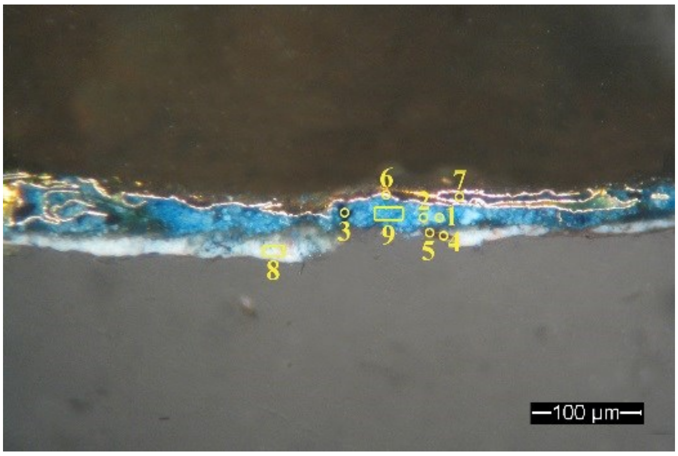


Figure 9.16. The selected points for the SEM-EDX analysis, sample SA2, magnification 180X

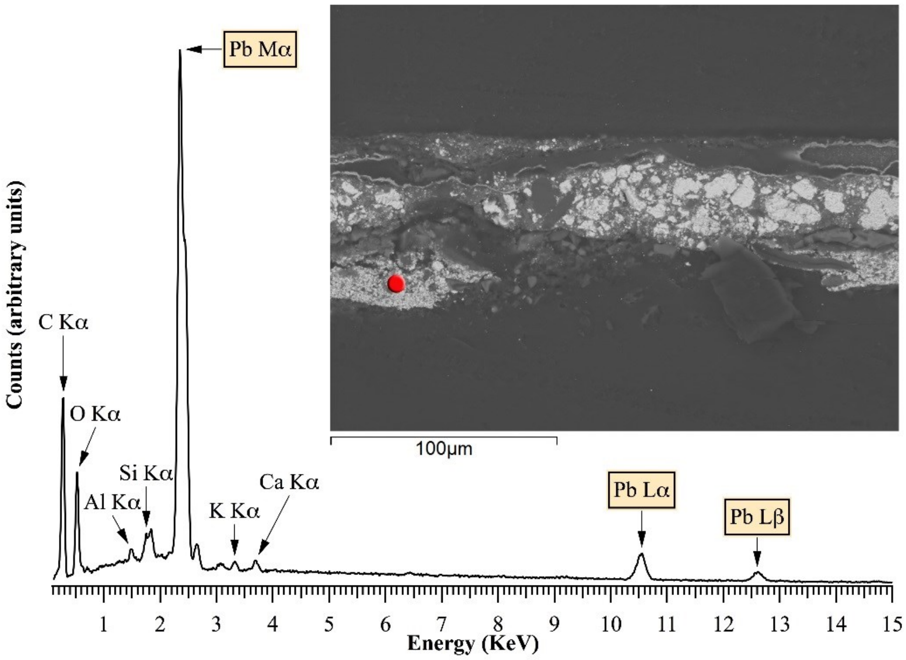


Figure 9.17. Backscattered electron SEM image of the sample SA2 and the SEM spectrum of the white ground layer

Other SEM-EDX analyses were carried out on the blue paint layer and both blue and white parts were examined (figures 9.18 and 9.19). The results show that this layer contains carbon and lead as the main constituents and copper is in minor amounts in the composition.

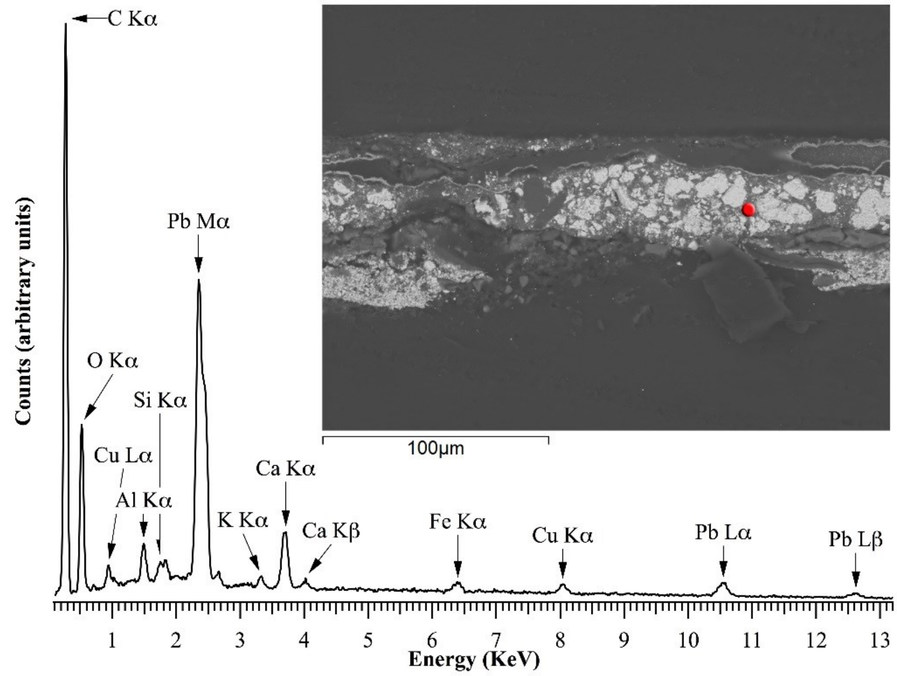


Figure 9.18. Backscattered electron SEM image of the sample SA2 shows the selected blue point for the analysis and SEM spectrum of the blue paint layer

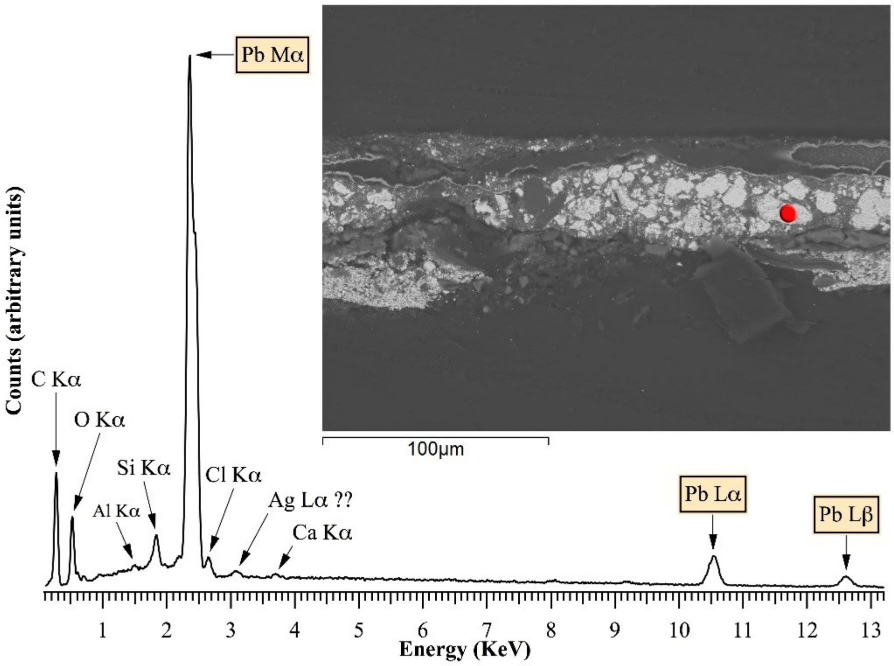


Figure 9.19. Backscattered electron SEM image of the sample SA2 shows the selected white point for the analysis and its SEM spectrum

Another SEM-EDX analysis was carried out on the thin dark layer under the blue paint layer (figure 9.20). The results show that this layer, also, contains lead and carbon as the main constituents and copper is in minor amounts in the composition. Therefore, the main compound of this layer is lead white.

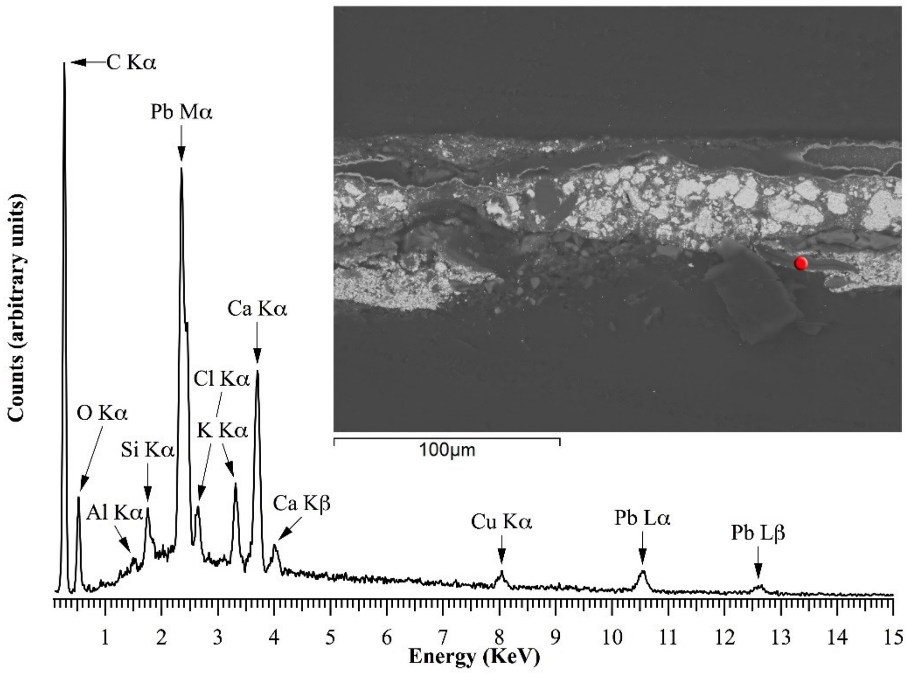


Figure 9.20. Backscattered electron SEM image of the sample SA2 shows the selected point for analysis and SEM spectrum of the thin dark layer

Figure 9.21 shows the selected area of gold leaf and its SEM spectrum. The result showed high amount of copper and presence of zinc. Therefore, it could confirm presence of brass leaf behalf of gold leaf in the wall painting.

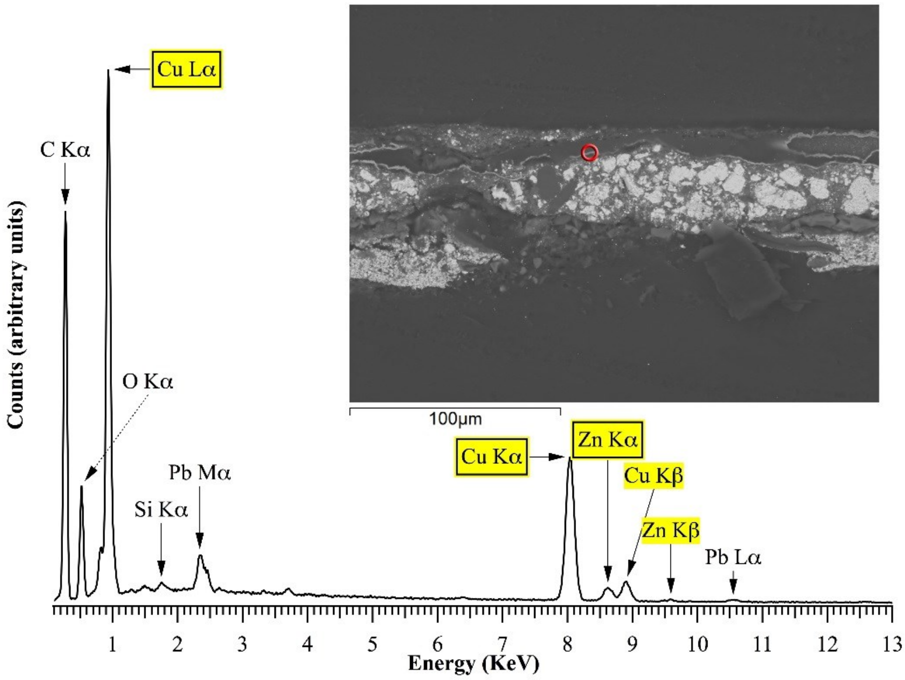


Figure 9.21. Backscattered electron SEM image of the sample SA2 shows the selected area for the analysis and its SEM spectrum

The FTIR examination of the sample SA2 (figure 9.22) shows this sample contains gypsum (absorptions at 3500, 3400, 1620, 670 and 600 cm^{-1}) and possibly a drying oil (peaks at ~2900 and ~1720 cm-1). Also the IR spectrum was investigated for the mid-infrared bands of indigo (at 3400–3200, 3100-2800, 1700–1550, 1620–1420 cm^{-1}) (Stuart, 2007, p. 127), the bands at 3400, 2850, 1620, 1420 cm^{-1}, marked with an X, could slightly indicate the presence of indigo in this sample. "Indigo (chemical formula: $C_{16}H_{10}N_2O_2$) is an organic dye extracted from a plant leaf called Lancao…" (Cheng, Xia, Ma, & Lei, 2007, p. 1277). The strong broad band near 1000 cm^{-1} is probably due to silica (ibid; Shurvell, 2002).

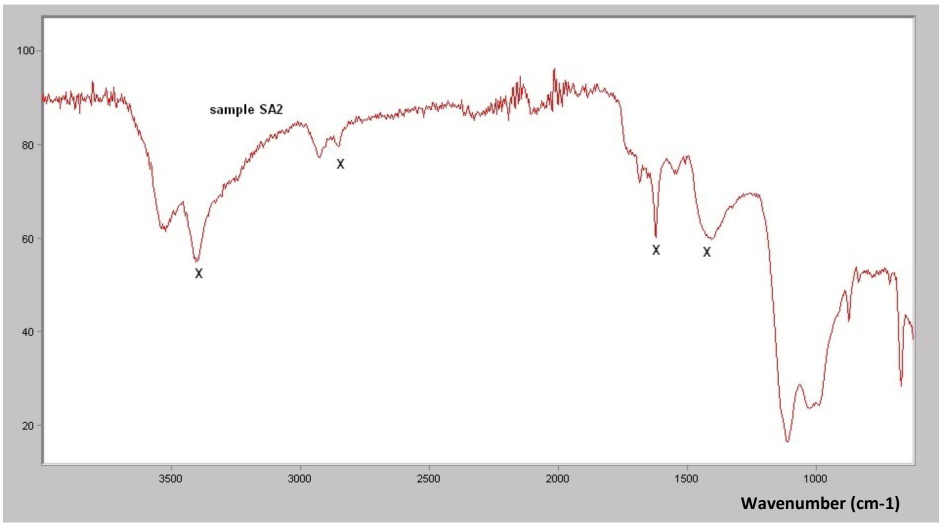


Figure 9.22. The infrared spectrum of sample SA2

9.3.3. Sample SA3

The microscopic cross section image and the schematic sketch of the layers of this sample (figures 9.23-9.24) show different layers which are: 1) oily dark layer, 2) green paint, 3) reddish orange layer, and 4) finish coat layer.

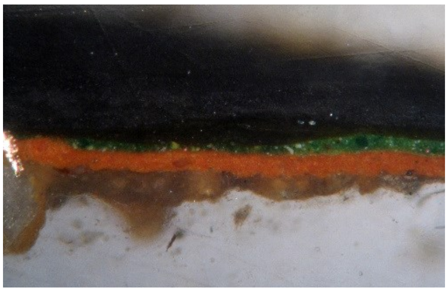


Figure 9.23.Cross section image of the sample SA3, magnification 180X

Figure 9.24. Schematic sketch of the sample's layers

The XRF examination was carried out for this sample and the results (figure 9.25) showed copper, iron, lead, and calcium as the main constituents of the sample while sulphur was detected in minor amounts, therefore sample could be copper-based green pigment.

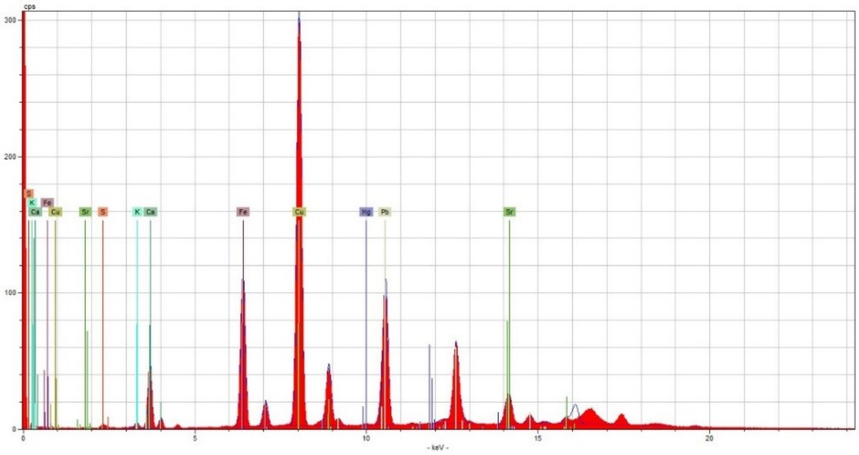


Figure 9.25 XRF spectrum on dark green pigment

Figure 9.26 shows the Raman spectrum of the sample. The results showed a strong band at ~1030 cm^{-1}, which could be characteristic of lead white, cerussite- $PbCO_3$ (Martens et al., 2004, p. 8; Burrafato et al, 2004, p. 884).

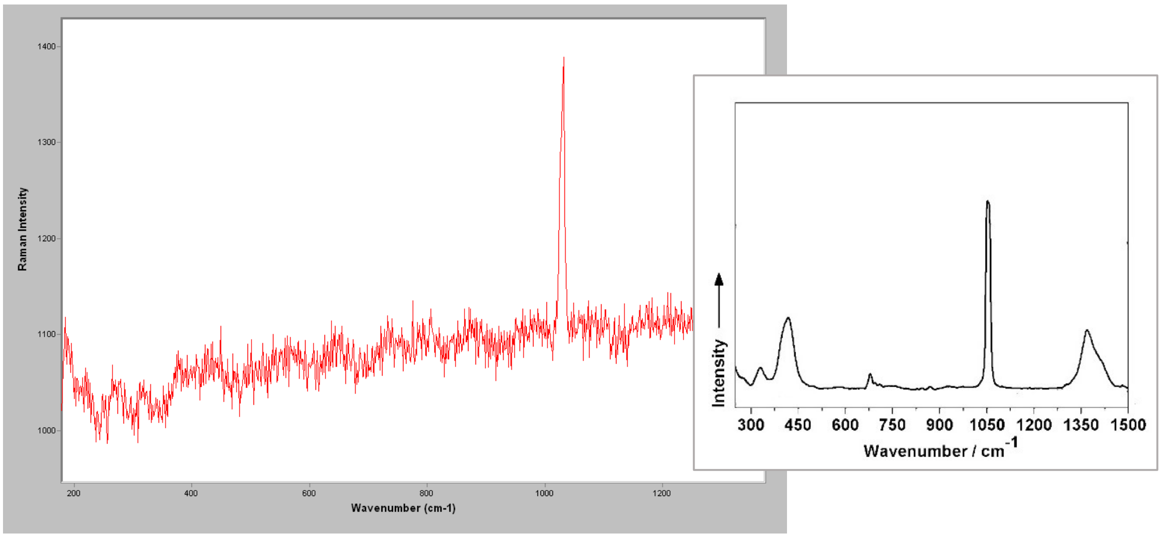


Figure 9.26. Raman spectrum of the sample SA3 in comparison with reference micro Raman Spectroscopy of lead white-dry pigment (Burrafato et al, 2004, p. 884)

Figure 9.27 shows the infrared spectrum of the sample SA3 compared with reference spectra of gypsum (Shurvell, n.d). Based on the results, sample SA3 contains gypsum (absorptions at 3500, 3400, 1620, 1100, 670 and 600 cm^{-1}). Evidence of hydrocarbon groups is seen in this sample (near 2900 and 1440 cm^{-1} marked with an X) (Shurvell, 2002).

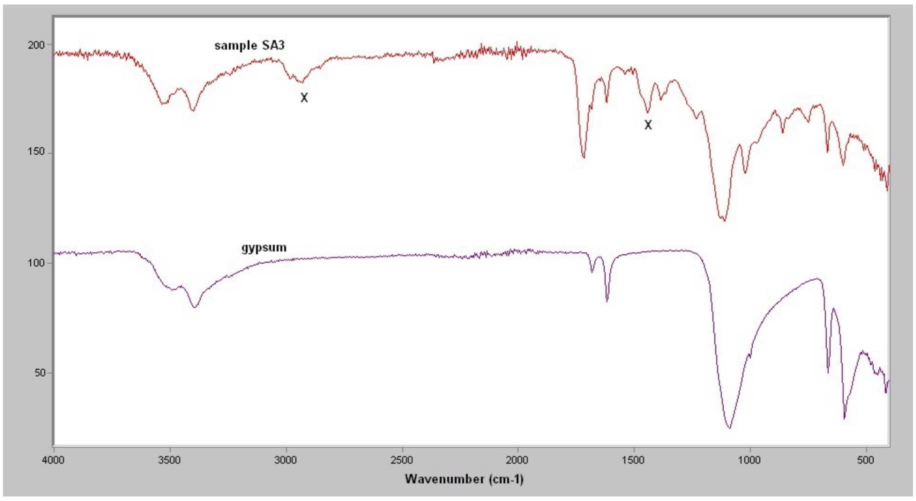


Figure 9.27. The infrared spectrum of sample SA3 compared with reference spectra of gypsum (Shurvell, n.d.)

XRD analysis was carried out on the underside of the sample SA3 (figure 9.28). The results showed the diffraction lines from gypsum and quartz.

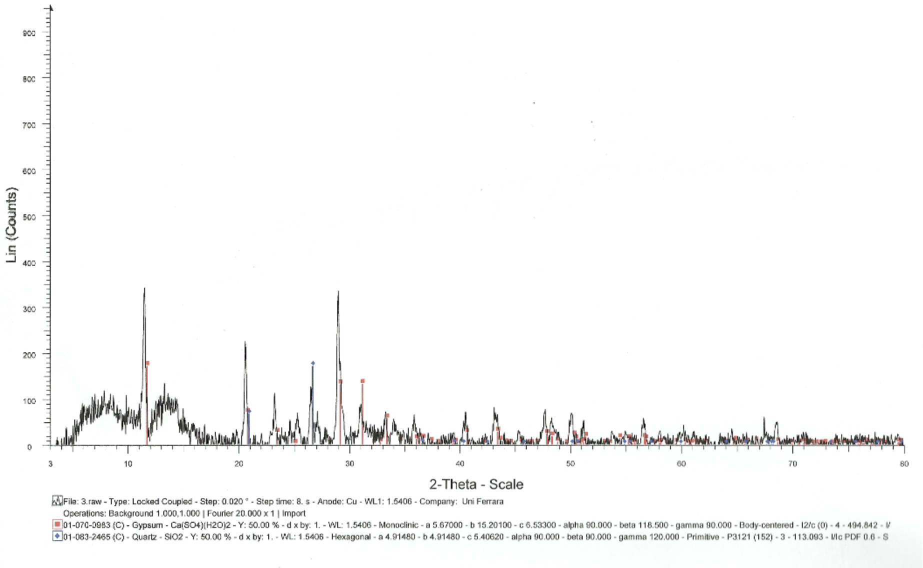


Figure 9.28. XRD spectrum of the sample SA3

SEM-EDX analysis was carried out on different layers of the sample SA3. Figure 9.29 shows the selected points and areas for SEM-EDX analysis.

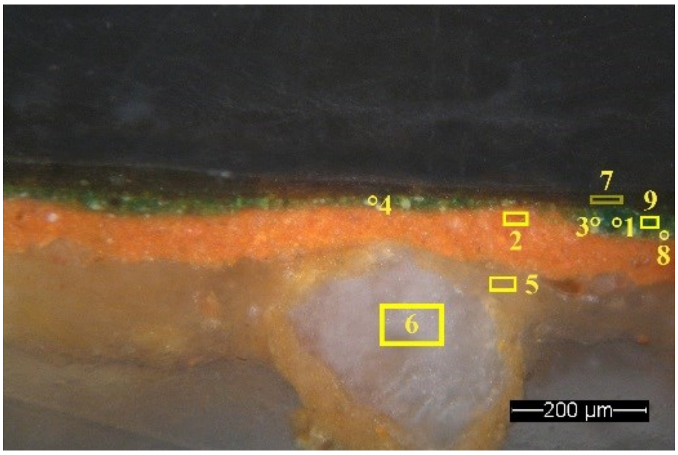


Figure 9.29. The selected points for SEM-EDX analysis, sample SA3, magnification 110X[1]

The results revealed that the dark green point contains high amount of copper (figure 9.30). Also there are some light green (white-green) points in the green paint layer which were analysed and they contain lead and copper (figure 9.31).

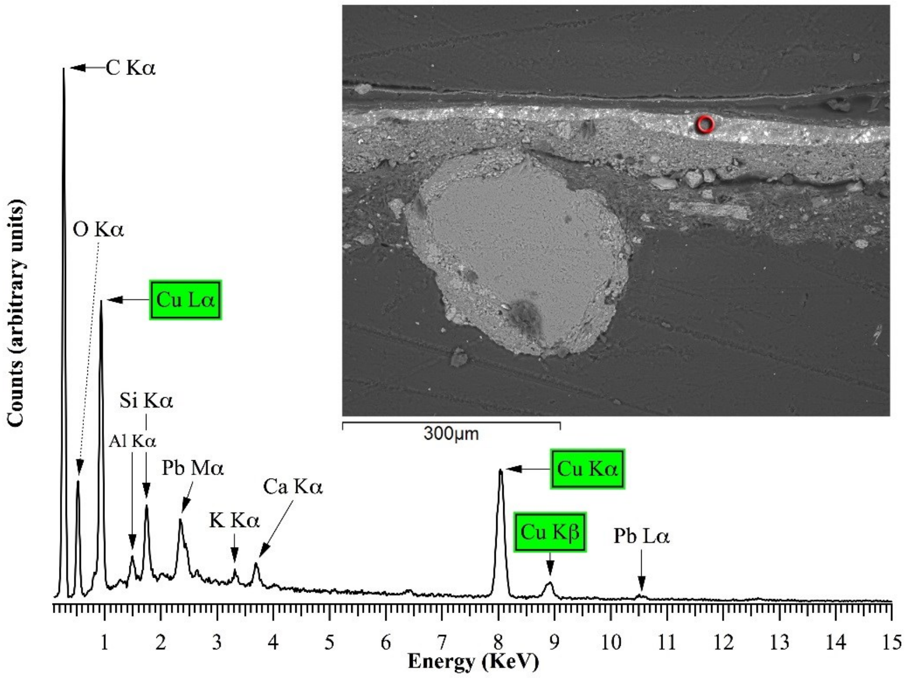


Figure 9.30. Backscattered electron SEM image of the sample SA3 shows the selected green point for the analysis and its SEM spectrum

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[1] The area 7 was from the resin, not a part of the sample.

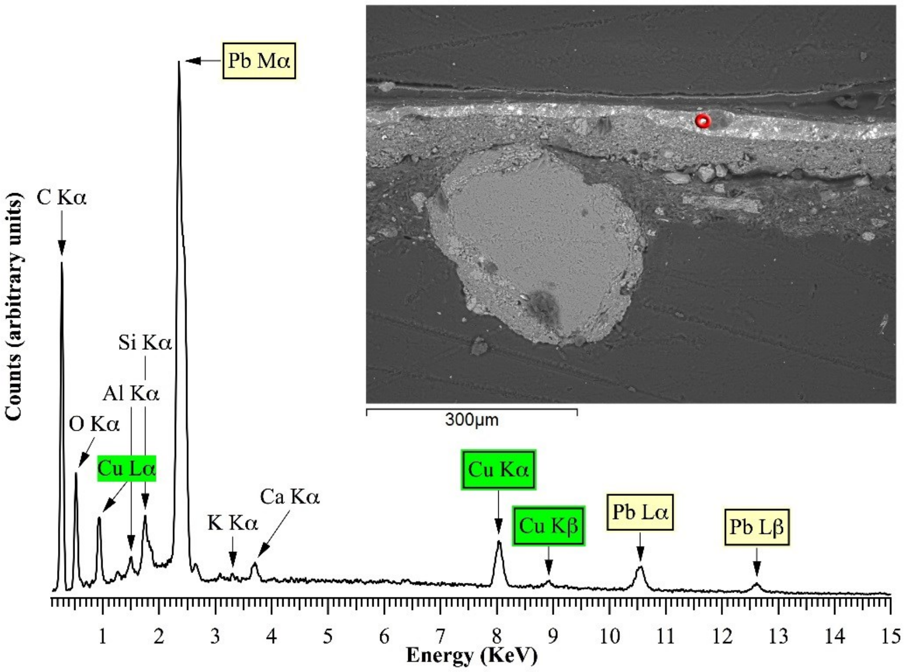


Figure 9.31. Backscattered electron SEM image of the sample SA3 shows the selected white-green point for the analysis and its SEM spectrum

The SEM-EDX analysis of the white point in the green layer shows high amount of lead which can confirm presence of lead white (figures 9.32). Therefore, SEM-EDX results confirmed Raman results.

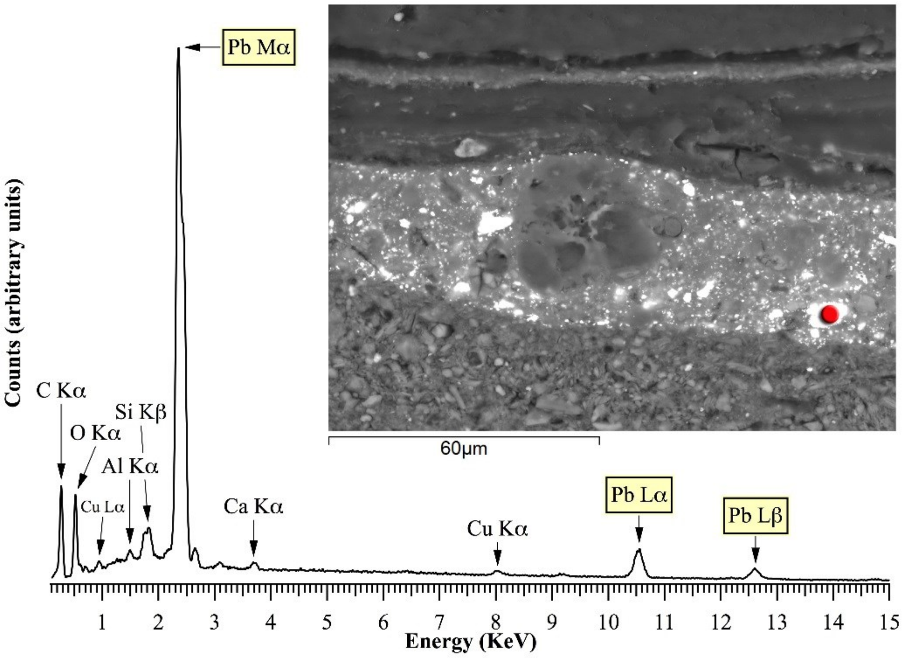


Figure 9.32. Backscattered electron SEM image of the sample SA3 shows the selected white point for the analysis and its SEM spectrum

Figure 9.33 shows the selected area for the SEM analysis. The results confirmed the presence of a copper-based green pigment mixed with lead white.

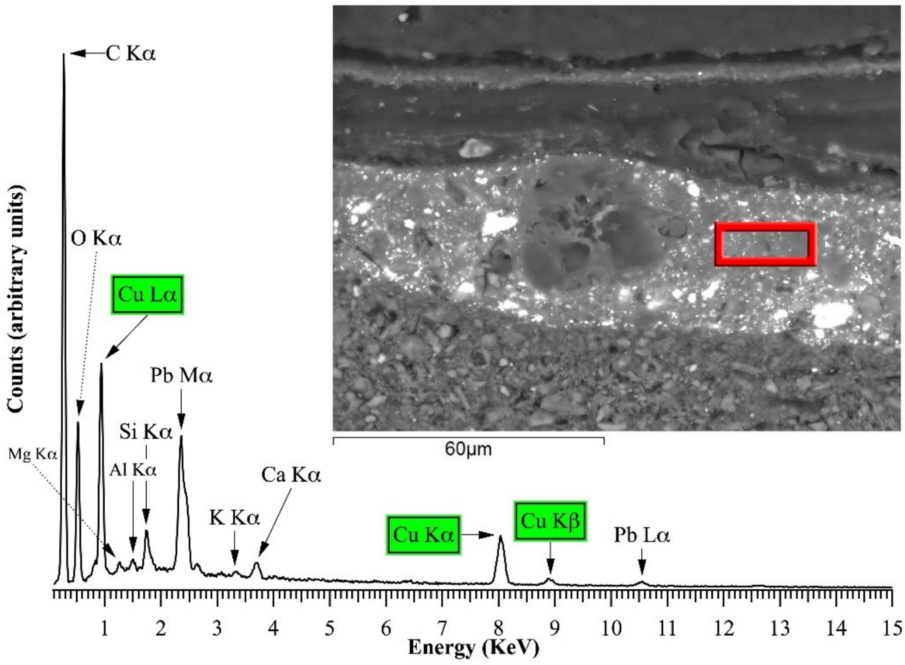


Figure 9.33. Backscattered electron SEM image of the sample SA3 shows the selected area for the analysis and its SEM spectrum

Figure 9.34 shows the selected area of reddish orange layer for analysis and its SEM spectrum. The results confirmed that this layer could contain red ochre (iron(III) oxide chromophore, Fe_2O_3 + clay + silica) (UCL Chemistry, 2010) or hematite.

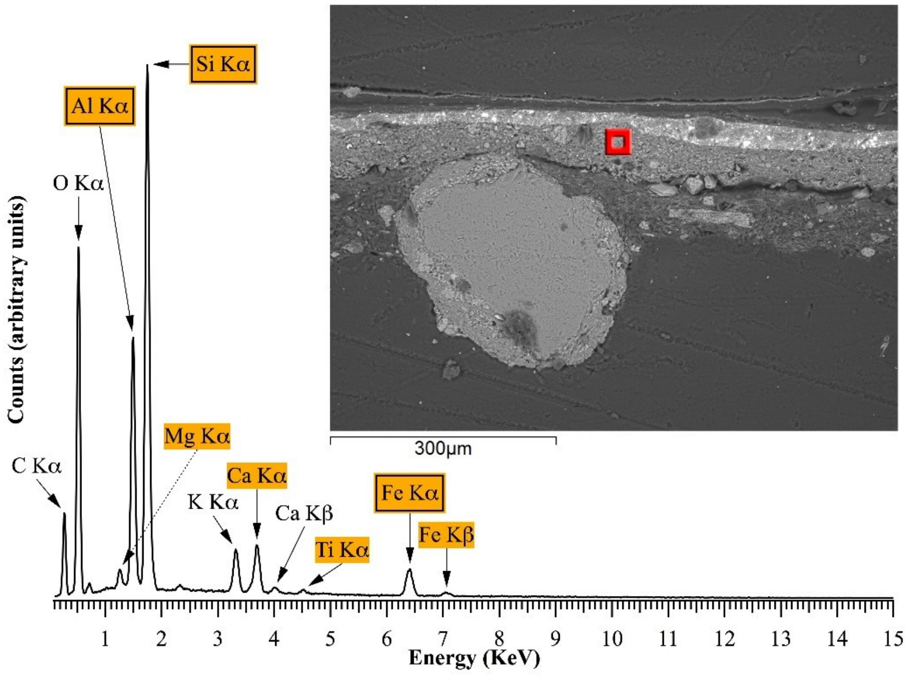


Figure 9.34. Backscattered electron SEM image of sample SA3 shows the selected area for the analysis and SEM spectrum of the reddish orange layer

SEM-EDX analysis was also carried out on the finish coat layer. The results show that this layer contains gypsum (figure 9.35).

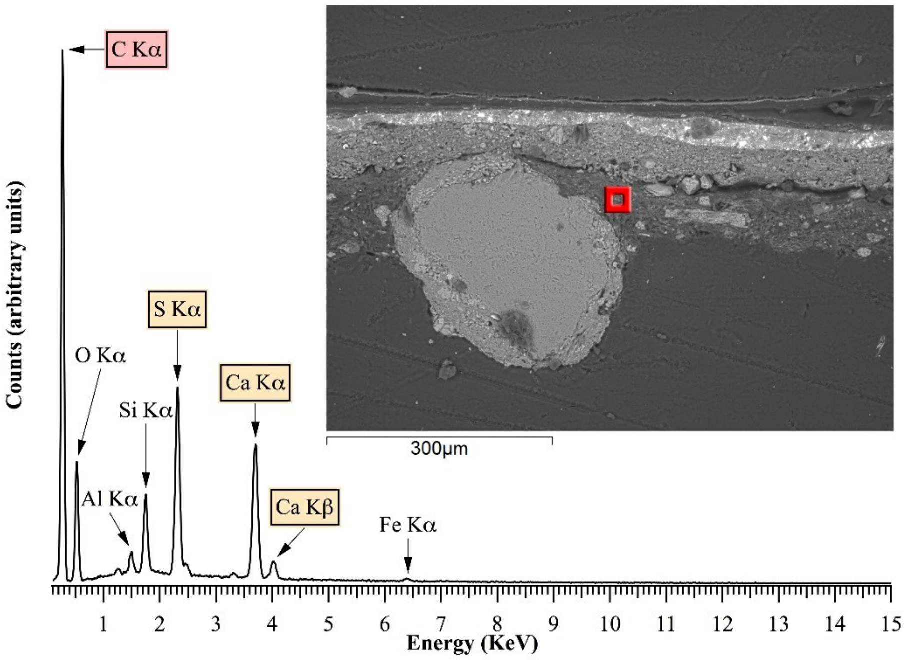


Figure 9.35. Backscattered electron SEM image of the sample SA3 shows the selected area for analysis and SEM spectrum of the finish coat layer

There is a white material in the finish coat layer. SEM-EDX analysis was carried out on this part to get more information for identification (figure 9.36). The results revealed that this part of the finish coat contains quartz. Therefore SEM-EDX results confirmed XRD results.

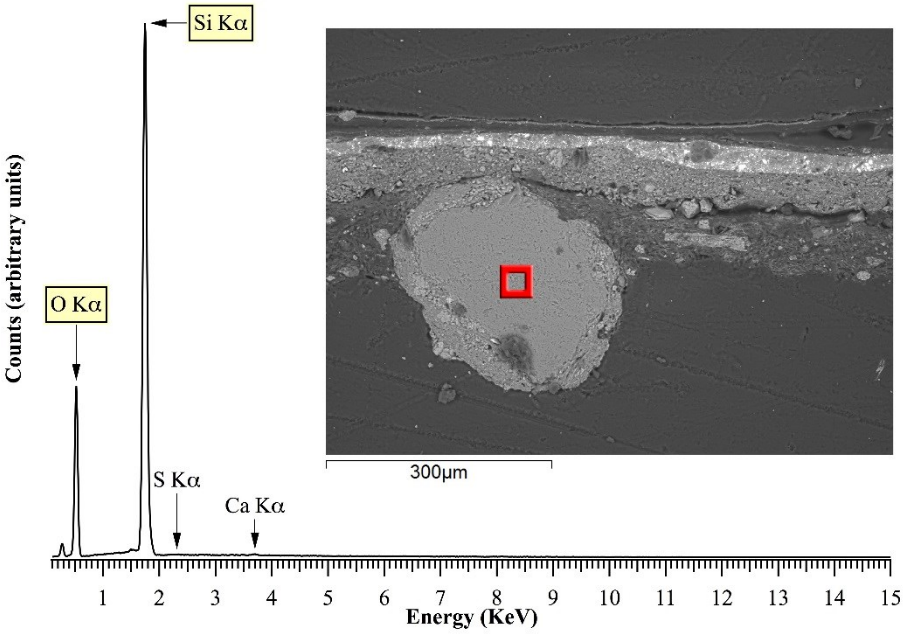


Figure 9.36. Backscattered electron SEM image of the sample SA3 shows the selected area for analysis and SEM spectrum of the white material in the finish coat layer

The results confirmed presence of lead white, a copper green pigment, red ochre, and gypsum in this sample.

9.3.4. Sample SA4

The microscopic cross section image of this sample (figure 9.37) showed different layers. The schematic sketch of the layers (figure 9.38) contains: 1) dark oily layer, 2) white paint, 3) oily dark layer, 4) orange ground layer, and 5) finish coat.

Figure 9.37. Cross section image of the sample SA4, magnification 180X

Figure 9.38. Schematic sketch of the layers

The XRF examination of the white sample (figure 9.39) showed lead as the main constituent of the pigment. Therefore, the white paint layer could be lead white. Iron, calcium, and sulphur are other elements in this composition.

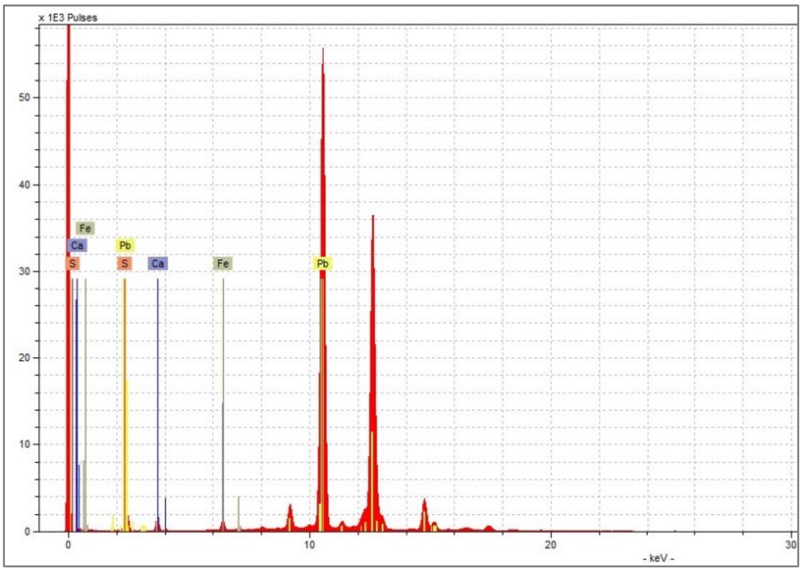


Figure 9.39. XRF spectrum on white pigment

In this sample, there was also an orange layer on the underside of the paint which was studied by XRF. The spectrum (figure 9.40) shows the presence of lead as the main constituent of the sample. Also the mercury peaks are at 9.99 and 11.82. Other elements like iron, calcium, and copper are in minor amounts in the composition.

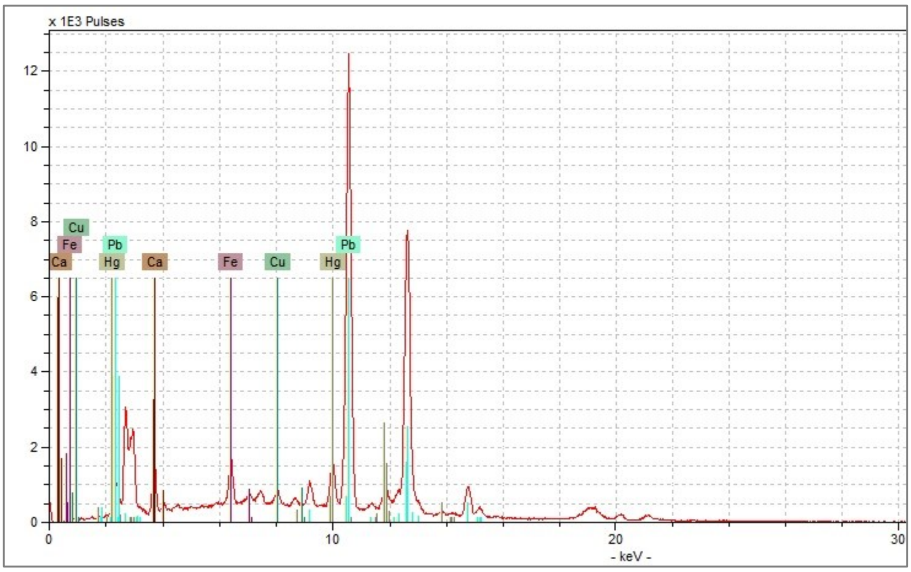


Figure 9.40. XRF spectrum on orange side of the sample

Micro Raman analysis was carried out on the orange layer to get more information for identification. The Raman spectrum of this sample (figure 9.41) shows a very strong characteristic band at 252, a shoulder at 277 and a medium peak at about 340 wave number/cm^{-1}, which could all indicate vermillion. Therefore, XRF and Raman results showed the presence of two different materials, vermilion and lead compound, in this sample

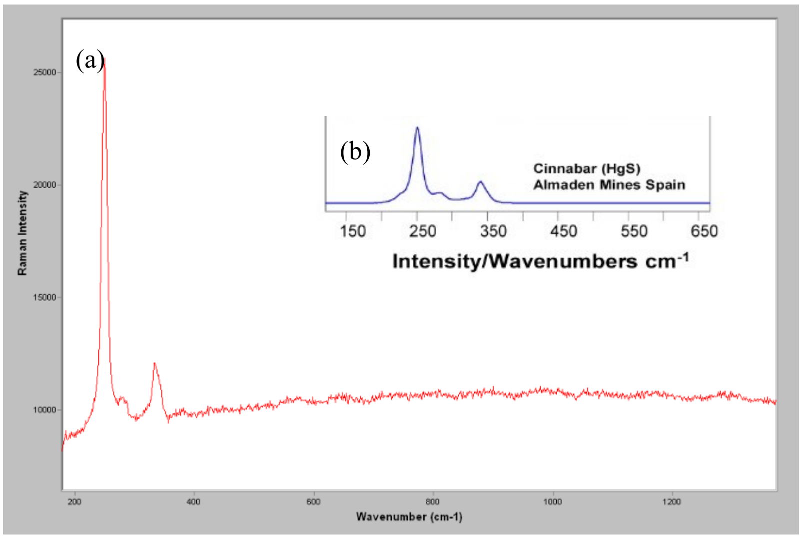


Figure 9.41. Micro Raman spectrum on orange part of the sample SA4 (a) in comparison with Raman database spectrum of cinnabar (b) (Liritzis & Katsaros, n.d., p.2)

The infrared spectrum of sample SA4 compared to a spectrum of gypsum (Shurvell, n.d.) (figure 9.42). The CH stretching and bending absorption near 2900 and 1400 cm^{-1} and the carbonyl peak at 1720 cm^{-1} indicate the possible presence of a drying oil such as linseed oil. The three weak unassigned absorptions marked X are probably also due to organic material (Shurvell, 2002).

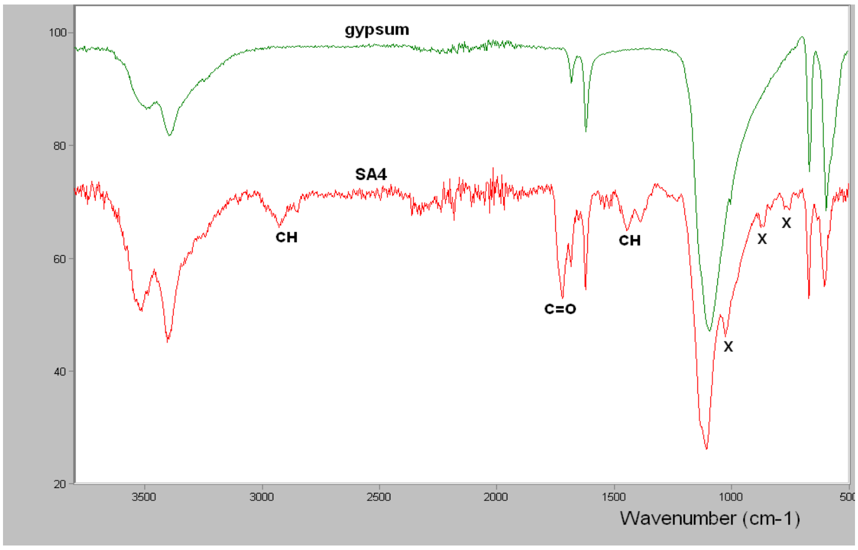


Figure 9.42. FTIR spectrum of the sample SA4 compared with reference spectrum of gypsum (Shurvell, n.d).

XRD analysis was carried out on this sample to get more information. In the XRD spectrum of the sample SA4 (figure 9.43) the diffraction lines from gypsum, litharge, cinnabar, hydrocerussite, and quartz could be identified.

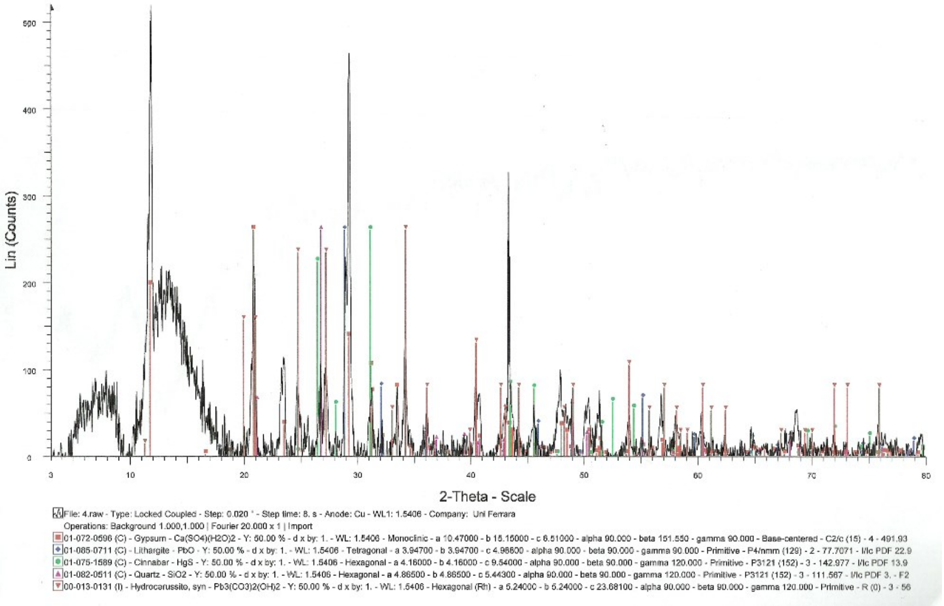


Figure 9.43. XRD spectrum of the sample SA4

Figure 9.44 shows the selected points and areas for SEM-EDX analysis. SEM-EDX analysis (figure 9.46) revealed that the white layer observed under all layers in the cross-section is gypsum. According Doner and Warren (1989), "gypsum is a common component and the most common sulfate mineral in soils of arid and semi-arid areas" (as cited in Toomanian, Jalalian, & Eghbal, 2001, p. 200).

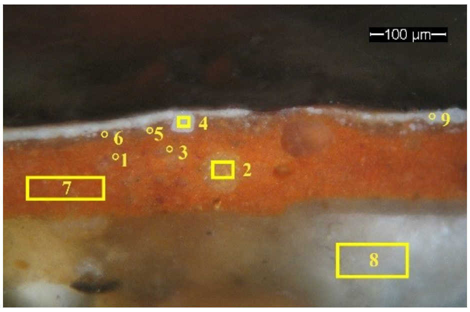


Figure 9.44. The selected points for SEM-EDX analysis, sample SA4, magnification 180X

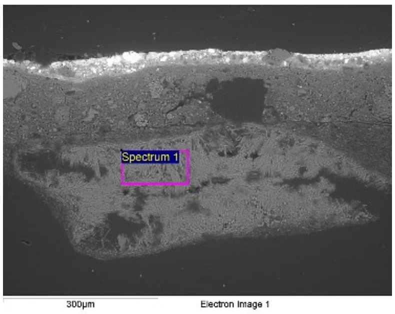


Figure 9.45. Backscattered electron SEM image of the sample SA4 shows the selected area for analysis

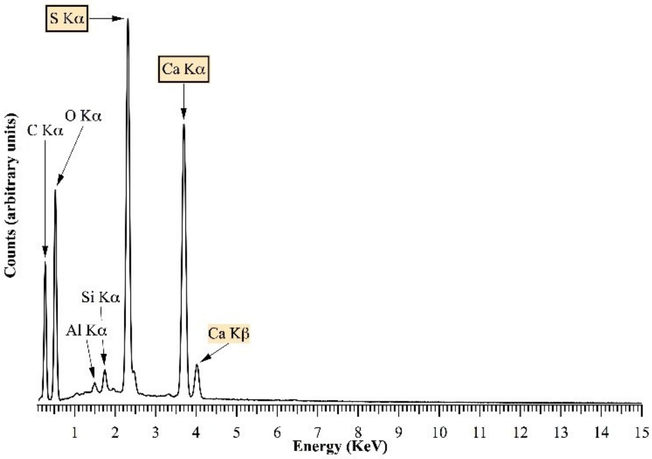


Figure 9.46. SEM spectrum of the finish coat layer

SEM-EDX analysis (figures 9.47-9.48) showed that above the gypsum layer in the cross-section of sample contains clay or Armenian bole which also known as bole Armenic and is native to Armenia. Its colour usually is red, although based on Hill historical review (1748), the true Armenian bole also exists in yellow colour (p.10).

The bole layer serves as an underpainting and a basic colour for some areas of this wall painting.

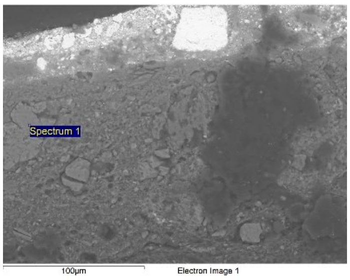


Figure 9.47. Backscattered electron SEM image of the sample SA4 shows the selected point for analysis

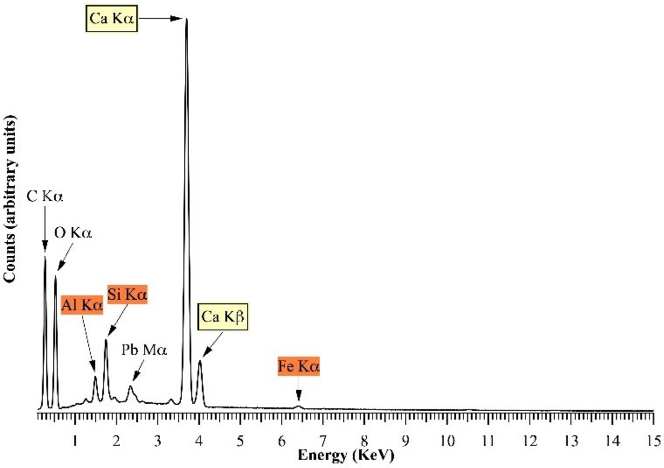


Figure 9.48. SEM spectrum of the selected point

Also another SEM-EDX analysis of the orange layer of the sample showed the presence of lead in this layer (figures 9.49-9.50). The results, therefore, confirmed a mixture of clay and lead compound. There was no sign of mercury in this analysis.

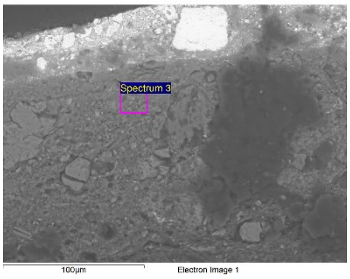


Figure 9.49. Backscattered electron SEM image of the sample SA4 shows the selected point for analysis

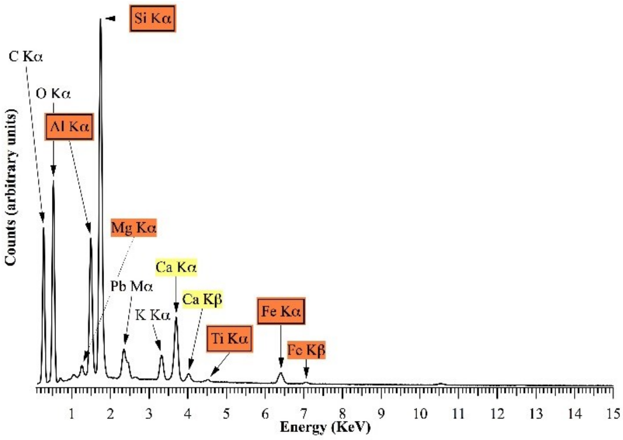


Figure 9.50. SEM spectrum of the selected point

SEM-EDX examination of oily dark layer over the orange part, showed the mixture of clay and a lead compound (figures 9.51-9.52).

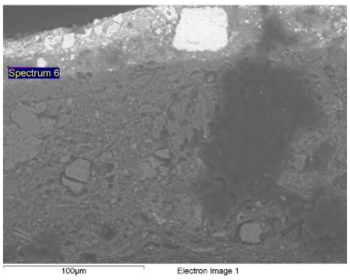


Figure 9.51. Backscattered electron SEM image of the sample SA4 shows the selected point for analysis

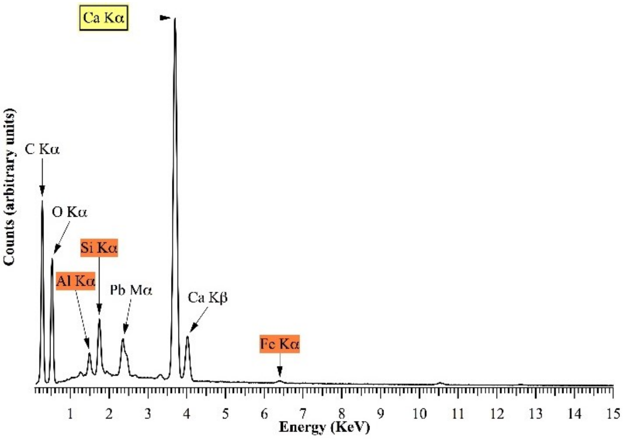


Figure 9.52. SEM spectrum of the selected point

SEM-EDX analysis was carried out for the upper white paint layer. The results (figures 9.53-9.54) revealed that the white paint layer observed over the layers in the cross-section is lead white.

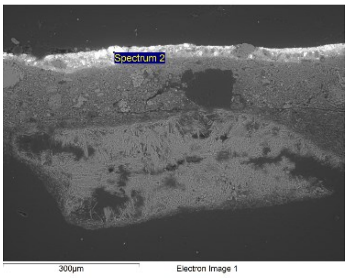


Figure 9.53. Backscattered electron SEM image of the sample SA4 shows the selected area for analysis

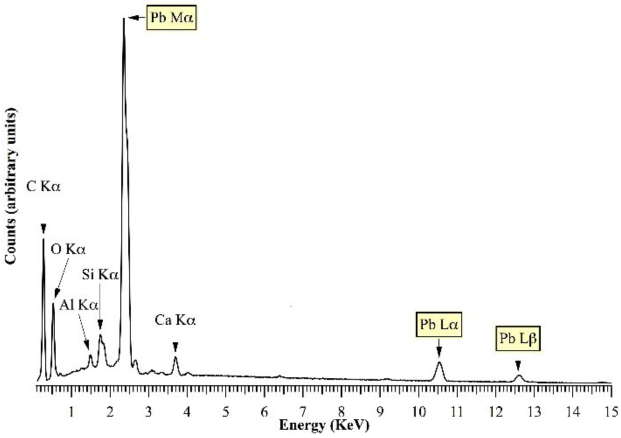


Figure 9.54. SEM spectrum of the upper white layer

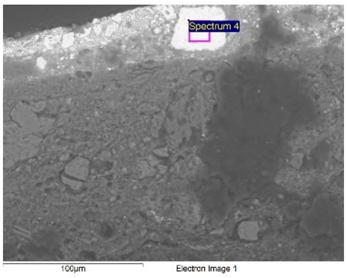


Figure 9.55. Backscattered electron SEM image of the sample SA4 shows the selected area for analysis

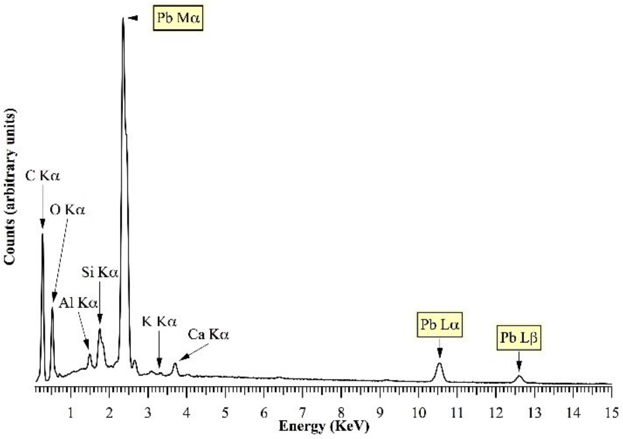


Figure 9.56. SEM spectrum of the selected area

Sample SA4 contains different layers which from top to bottom mainly are as following; lead white, the mixture of clay and a lead compound, mixture of litharge and vermilion, and gypsum.

9.3.5. Sample SA5

The paint cross-section was viewed through a microscope. Cross-section images (figure 9.57) show the occasional green particles in the layer of white paint which makes the green colour.

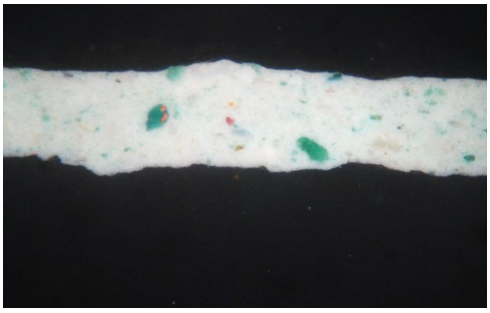


Figure 9.57. Cross section images of the sample SA5, magnification 180X

In XRF analysis, this specimen shows copper and lead peaks, which may indicate a mixture of lead white or lead yellow and copper green pigments (figure 9.58). The combination of verdigris as a copper-based pigment and lead tin yellow has been found in several paintings. For tin (Sn) there should be peaks at 3.44 and 3.66; however, there is nothing at 3.44 and the peak at 3.66 is from the calcium. This result, therefore, indicates that there is no tin at the special point which was studied by XRF.

On the other hand some artists "would glaze verdigris over lead white. Verdigris was most commonly used in the 15th and 17th centuries because of its transparent abilities as a glaze on paintings" (Douma, 2008). However, Cennini and Thompson (1954) suggested the painters never use verdigris near to lead white since "they are mortal enemies in every respect" (p. 33).

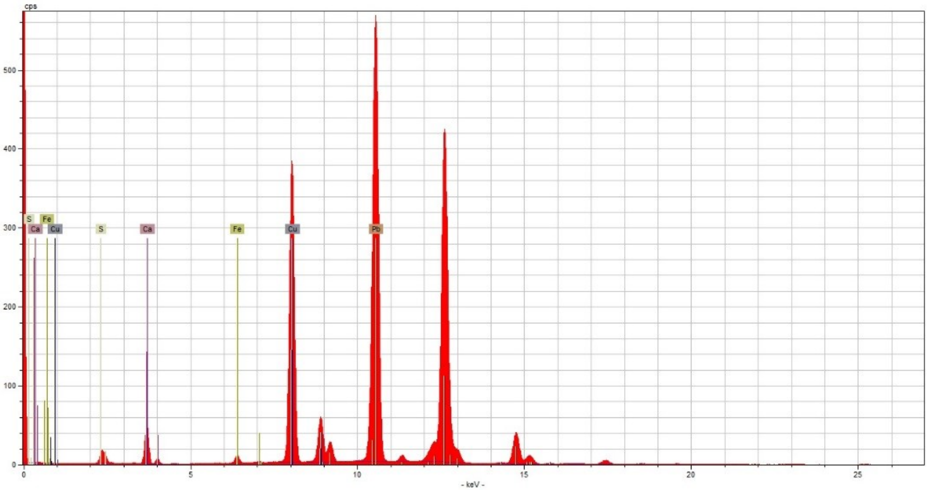


Figure 9.58. XRF spectrum of the sample SA5

In the following Raman spectrum of sample SA5 (figure 9.59) the strong characteristic band at 129 cm^{-1} could be assigned to lead tin yellow- type I, Lead(II) stannate Pb_2SnO_4, (Chaplin, Clark, Jacobs, Jensen, & Smith, 2005, p. 3617). Another characteristic band for lead tin yellow-type I at 195 cm^{-1} was not found. However, the presence of lead tin yellow could be very interesting as it has not been reported in the Iranian and Armenian palettes of pigments.

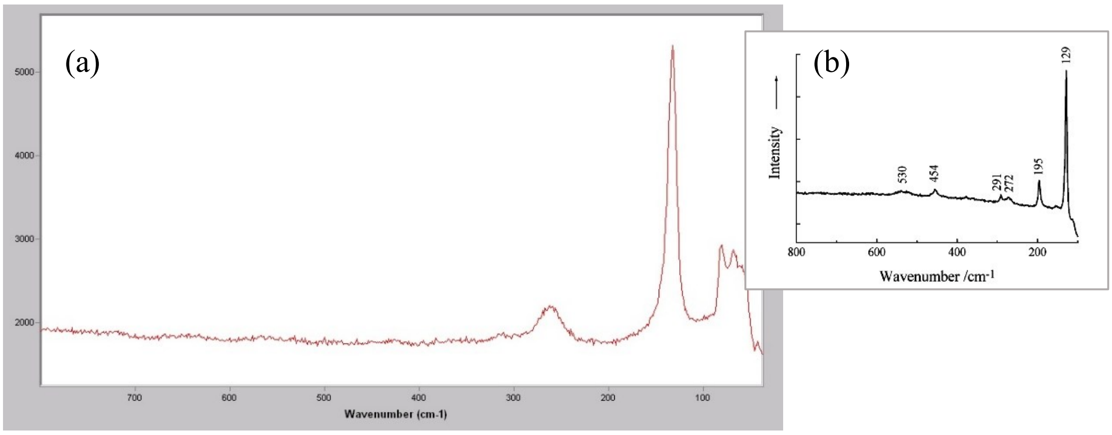


Figure 9.59. Raman spectrum of sample SA5 (a) in comparison with Raman database spectrum of lead tin yellow- type 1 (b) (Chaplin et al., 2005, p. 3616)

In the XRD spectrum of the sample SA5 (figure 9.60) the diffraction lines from hydrocerussite, quartz, gypsum, and massicot could be identified.

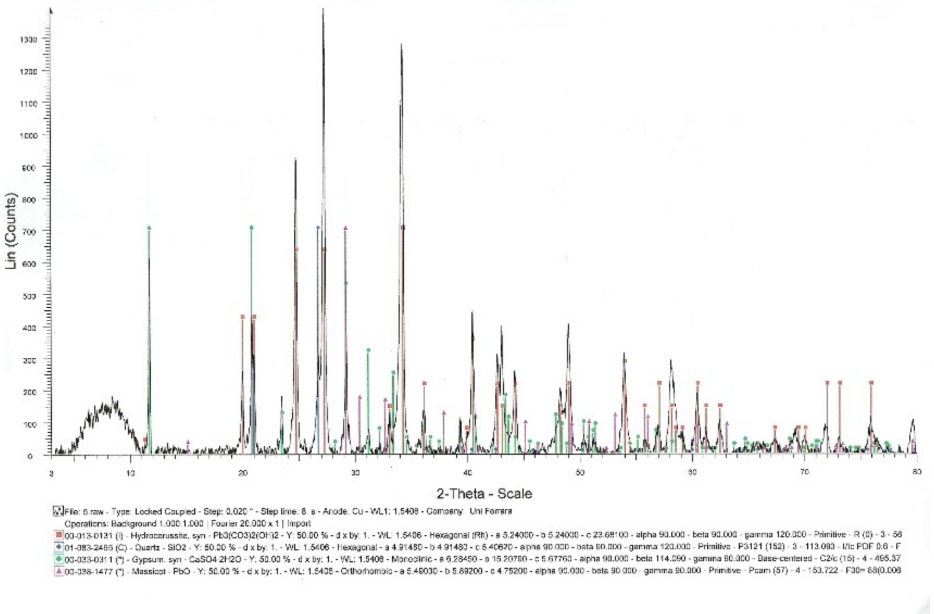


Figure 9.60. XRD spectrum of the sample SA5

Also SEM-EDX analysis was carried out for the sample SA5. Figure 9.61 shows the selected points for SEM-EDX analysis. The results of SEM-EDX analysis on green particles showed high presence of copper which revealed that the green paint observed in the cross-section is a copper-based green pigment (figures 9.62-9.65).

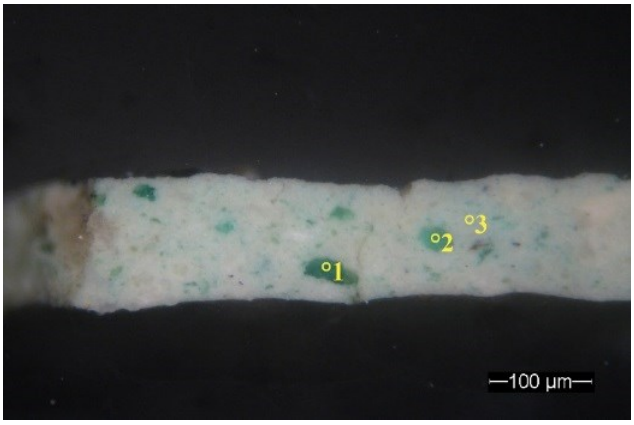
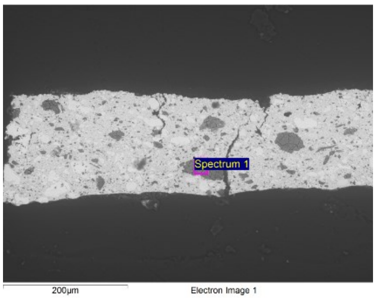


Figure 9.61. The selected points for SEM-EDX analysis, sample SA5, magnification 180X



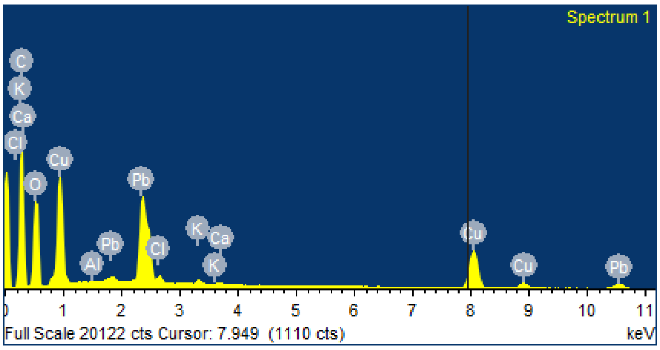
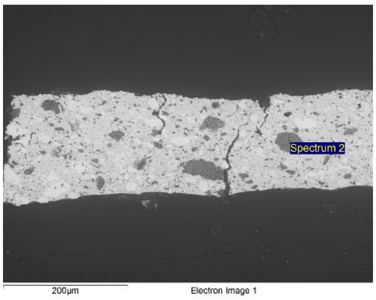


Figure 9.62. Backscattered electron SEM image of the sample SA5 shows the selected point for analysis

Figure 9.63. SEM-EDX spectrum of the green particle



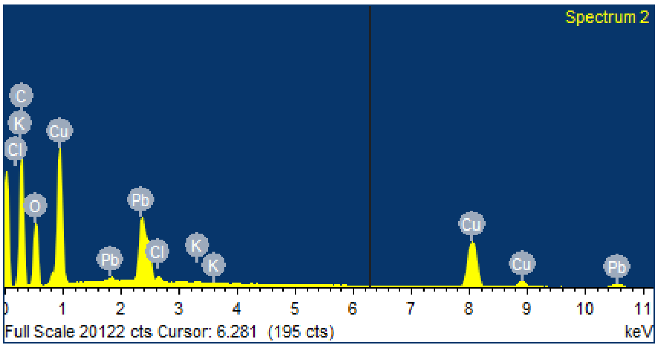
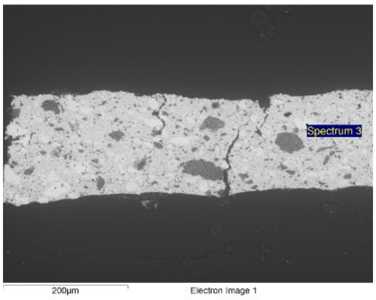


Figure 9.64. Backscattered electron SEM image of the sample SA5 shows the selected point for analysis

Figure 9.65. SEM-EDX spectrum of the green particle

Also SEM- EDX was run for the white area of the sample (figure 9.66) and the results shows high amount of lead which can confirm the previous results that is lead white (figure 9.67).



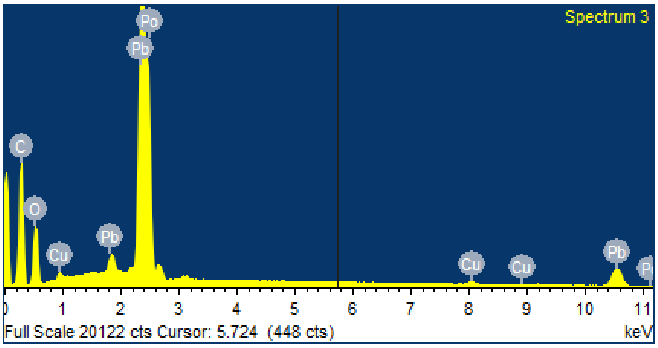


Figure 9.66. Backscattered electron SEM image of the sample SA5 shows the selected point for analysis

Figure 9.67. SEM spectrum of the white point

Consequently, the presence of a copper-based pigment was confirmed through analyses, also the results represented the existence of lead white in the majority parts of the sample. The presence of one characteristic Raman band for lead tin yellow, type I, could be very interesting because both Iranian and Armenian palettes had orpiment as yellow pigments and lead tin yellow just has been reported in the European palette. Nevertheless, the other analyses did not show the presence of tin in the sample. Therefore, sample SA5 could be considered a mixture of lead white and a copper-based green pigment.

9.3.6. Sample SA6

Due to the size and form of this sample, cross section was not provided. The XRF examination of sample SA6 showed iron and calcium as the main constituents (figure 9.68). This sample also contains lead because of its Lα line at 10.55 KeV and its Lβ line at 12.61 KeV and arsenic because of its Kα line at 10.54 KeV and its Kβ line at 11.73 KeV; but they are in minor amounts.

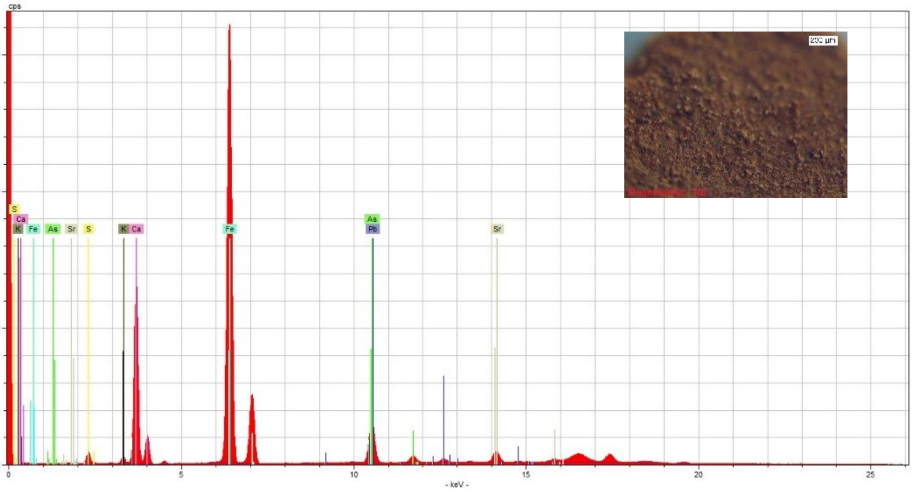


Figure 9.68. XRF spectrum of the sample SA6

In Raman analysis (figure 9.69) the characteristic Raman bands (marked with X) at 220 and 280 cm^{-1} could be assigned to red ochre or hematite (Bell et al., 1997, p. 2174; Liritzis & Katsaros, n.d., p.2). In this case, Raman results confirmed XRF results. Also micro Raman spectrum identified goethite, $FeO(OH)$, by its characteristic medium band at 299 cm^{-1} and strong band at 385 cm^{-1} (marked with Y) (Edwards & Chalmers, 2005, p. 254). Hradil, Grygar, Hradilová, and Bezdička's (2003) study found the following:

> Earthy pigments varying from dull yellow to red and brown are commonly called ochres in the economic geology, mining industry, and painting. Ochres are defined by Mayer (1991) as clays used to make the earth colours; in pigment terminology, the word ochre is predominantly used as a synonym for yellow ochre. Its colour is given by a presence of

different iron oxyhydroxides and oxides, mainly goethite and hematite; sometimes the colour is brownish due to manganese oxides. (p.227)

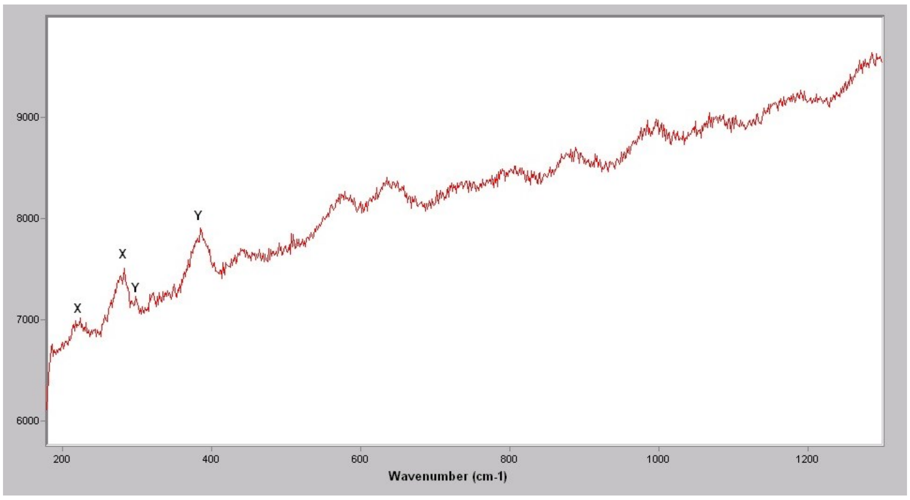


Figure 9.69. Micro Raman spectrum of the sample SA6

The FTIR results of sample SA6 (figure 9.70) show that the sample contains gypsum. The strong broad band near 1000 cm^{-1} is probably due to clay or silica (Shurvell, 2002).

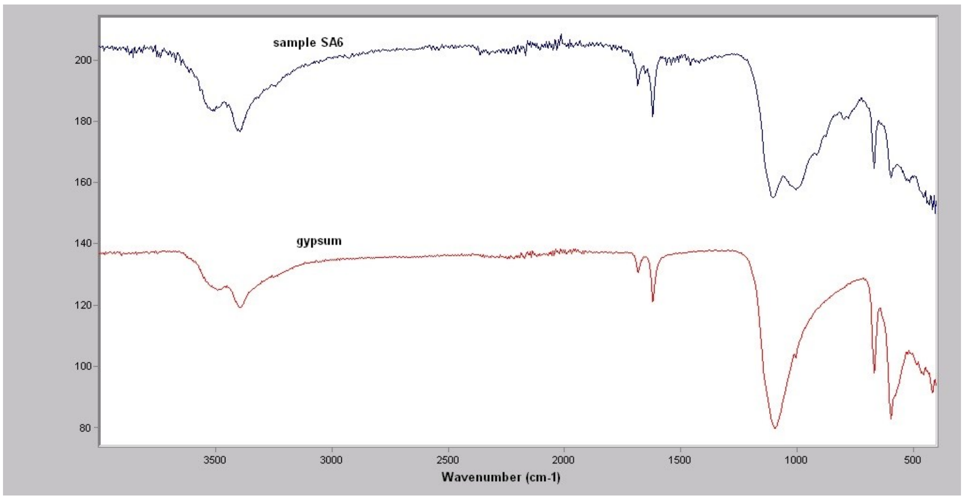


Figure 9.70. The infrared spectrum of sample SA6 compared with reference spectrum of gypsum (Shurvell, n.d.).

9.3.7. Sample SA7

Due to the size and form of this sample, cross section was not provided. The XRF examination of sample SA7 (figure 9.71) showed lead and copper as the main elements while calcium, sulphur, and iron are in minor amounts. Therefore, the green sample is a copper-based green pigment.

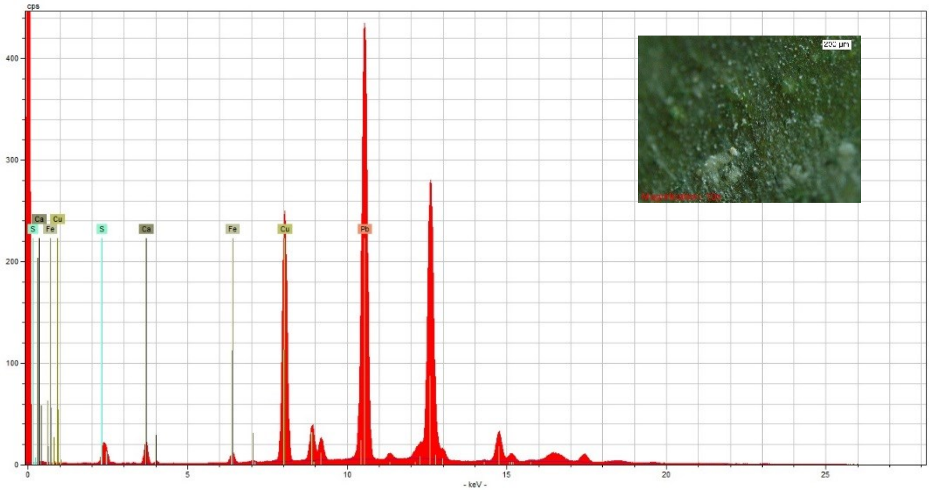


Figure 9.71. XRF spectrum of the sample SA7

Further information about this sample was obtained through micro Raman analysis. In this sample, there was also a red layer on the underside of the paint which was studied by micro Raman spectroscopy. The spectrum (figure 9.72) shows the strong characteristic band at about 129 cm^{-1} which could be assigned to lead tin yellow- type I, (Chaplin et al., 2005, p. 3617) but there was no tin in XRF results. In every sample, there are some bands that it is not always possible to assign or identify all of them in a spectrum. Nevertheless, this strong Raman band could possibly show the presence of a lead compound in this sample.

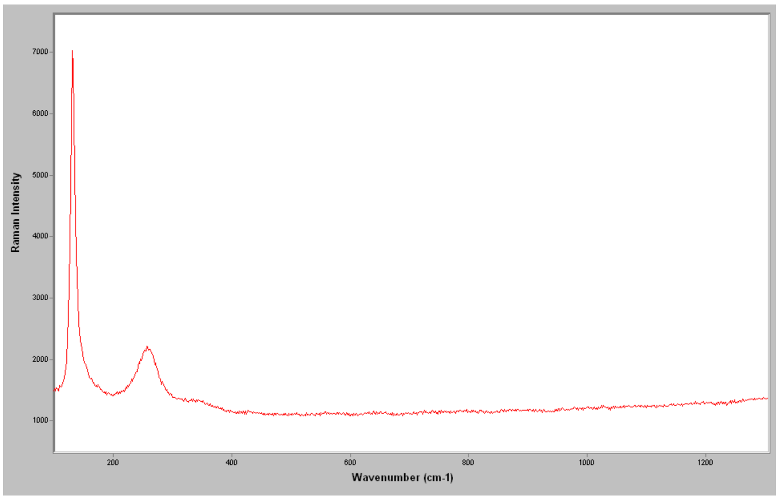


Figure 9.72. Micro Raman spectrum of the sample SA7

9.3.8. Sample SA8

The paint cross-section was viewed through a microscope. The microscopic image of the sample (figure 9.73) showed two different layers. The schematic sketch of the layers (figure 9.74) contains: 1) blue paint and 2) finish coat.

Figure 9.73. Cross section image of the sample SA8, magnification 110X

Figure 9.74. Schematic sketch of the layers

The XRF examination of the blue sample (figure 9.75) showed lead, arsenic, cobalt, and iron as the main constituents of the sample while potassium, calcium, and copper were detected in minor amounts in the composition.

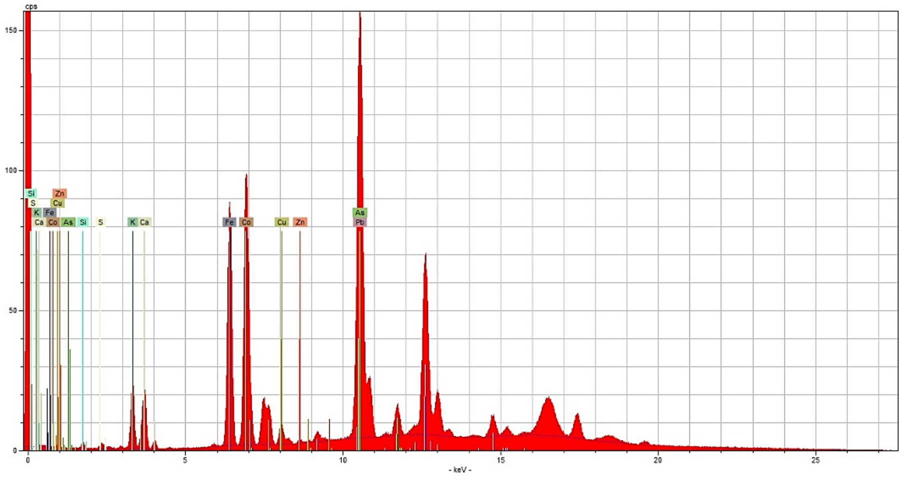


Figure 9.75. XRF spectrum on the sample SA8

During micro Raman analysis, the sample did not provide any result and just brought much fluorescence. Also no information was gained through XRD analysis. The sample SA8 was not an appropriate specimen for Raman and XRD analyses since it possibly is a glass based pigment (figure 9.76). Therefore, since some of "cobalt-containing pigments" are "amorphous glasses", "crystallographic methods" may not always provide the suitable result but SEM-EDX analysis could be a better method for study about this kind of samples (McGlinchey, 2012, p. 141).

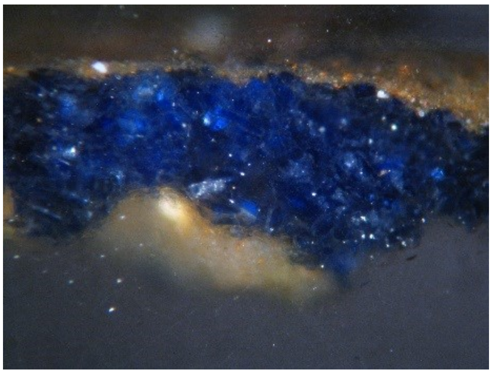


Figure 9.76. Sample SA8, blue glass based pigment, magnification 180X

Figure 9.77 shows the FTIR spectrum of the sample SA8 compared to reference spectrum of smalt (IRUG database, 2007, IMP00096). "Amorphous silica produces a strong Si-O stretching band near 1050 cm^{-1}....Nearly all types of glass (including smalt) produce an absorption band that is similar in appearance, even though glass is composed of a wide range and mixture of materials" (Derrick, , Stulik, & Landry, 2000, p. 117). Therefore, this sample could possibly contain smalt.

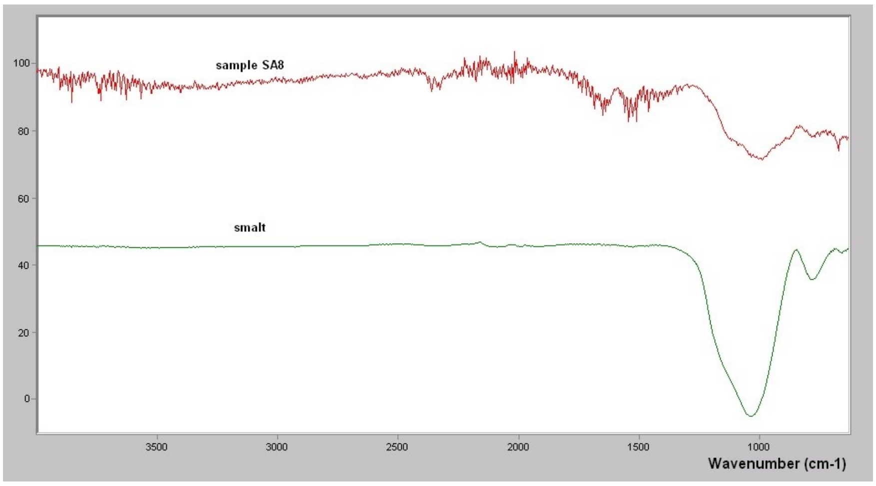
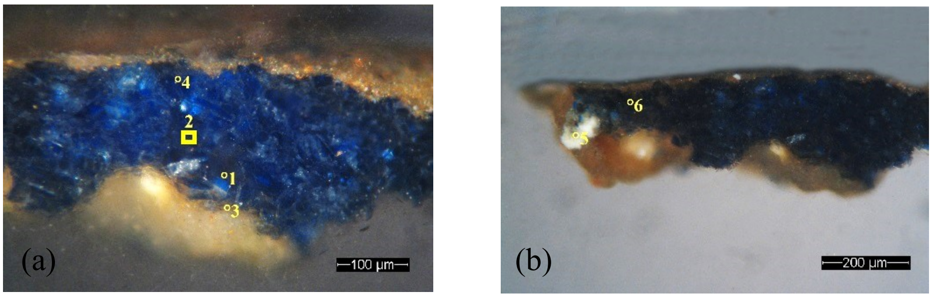


Figure 9.77. FTIR spectrum of the sample SA8 compared with reference spectrum of smalt (IRUG).

Also SEM-EDX analysis was employed for different layers of the sample SA8. Figures 9.78 and 9.79 show the selected points and areas for SEM-EDX analysis.



Figures 9.78 & 9.79. The selected points and areas for SEM-EDX analysis, sample SA8, magnification (a) 180X and (b) 110X

SEM-EDX spectrum of blue areas of this ample revealed presence of glass-based material (potassium and silicon), cobalt, and iron (figures 9.80 and 9.81).

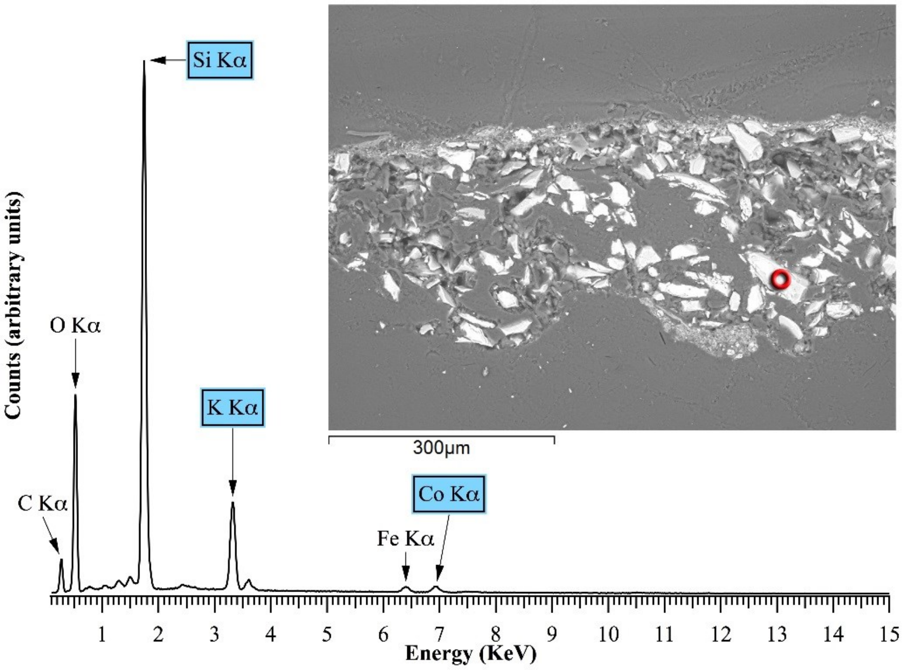


Figure 9.80. Backscattered electron SEM image of the sample SA8 shows the selected blue point for analysis and its SEM spectrum

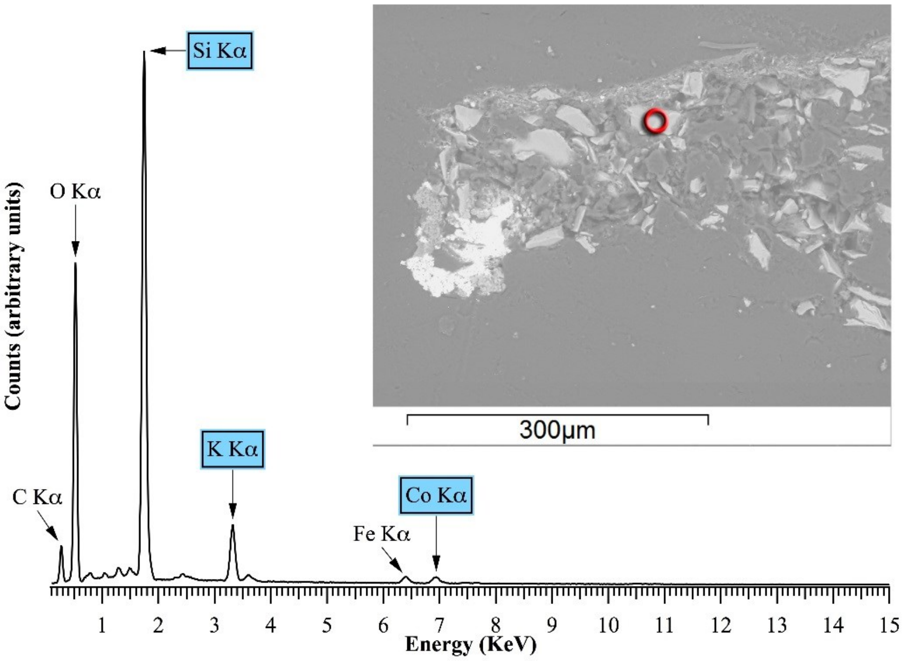


Figure 9.81. Backscattered electron SEM image of the sample SA8 shows the selected blue point for analysis and its SEM spectrum

SEM-EDX analysis was carried out on the white particle of sample SA8. The results showed that lead is the main constituent of this part of the sample (figure 9.82). The sample, therefore, contains lead white.

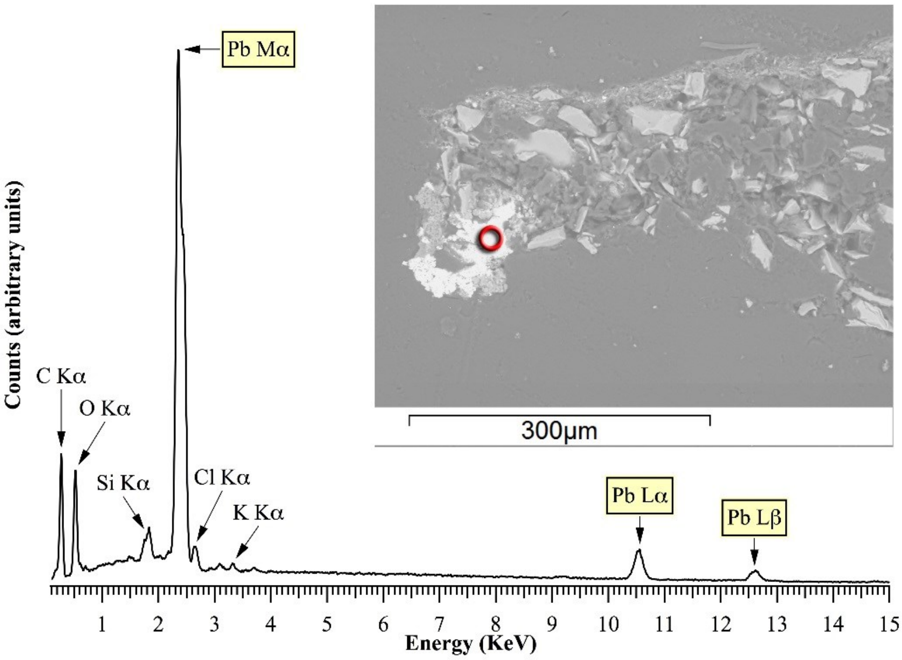


Figure 9.82. Backscattered electron SEM image of the sample SA8 shows the selected point for analysis and the SEM spectrum of the white particle

SEM-EDX analysis of the finish coat of this sample (figures 9.83) confirmed presence of gypsum and also some amounts of clay.

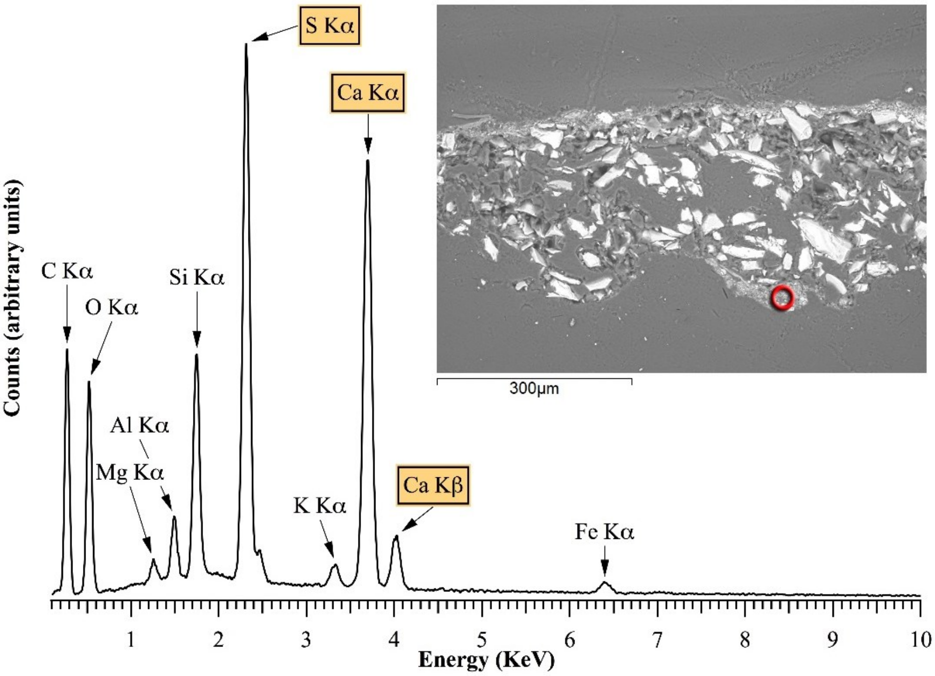


Figure 9.83. Backscattered electron SEM image of the sample SA8 shows the selected point for analysis and the SEM spectrum of the finish coat

The widespread use of smalt in European paintings started since the second half of the 16th century. Painters preferred to use an inexpensive substitute for azurite and ultramarine; and smalt was an available blue pigment for them (Eikema Hommes, 2004). Nevertheless in Iran and most eastern country reaching ultramarine was much easier than European countries but as it was mentioned in old treaties (chapter four), Iranian artist had different kinds of blue colour (ultramarine, indigo, and smalt) in his palette.

9.3.9. Sample SA9

Due to the size and form of this sample, cross section was not provided. The XRF examination of sample SA9 showed lead and copper as the main constituents (figure 9.84). This sample also contains sulphur, calcium, and iron in minor amounts. Presence of high amounts of lead can indicate lead white pigment. "Mixing the colours to a lighter shade, for instance by adding extra lead white was a method which used to overcome the effect of the oil's tendency to darken" (ibid, p. 24).

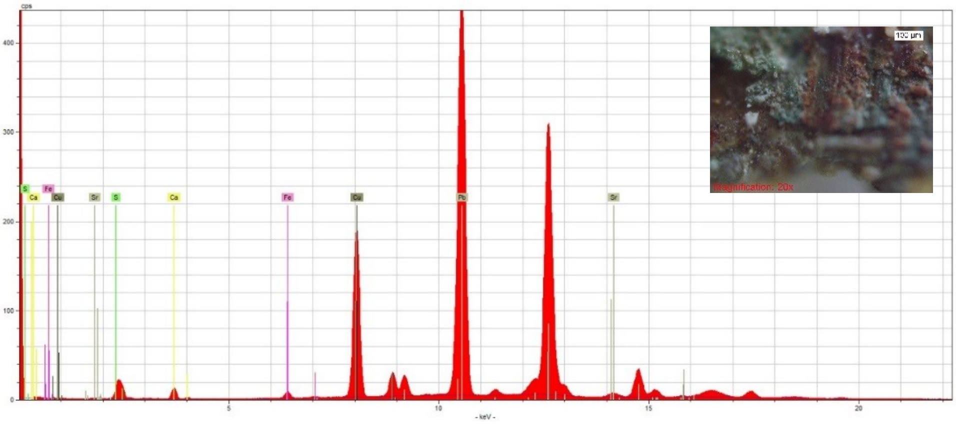


Figure 9.84. XRF spectrum of sample SA9

Also micro Raman analysis was carried out for this sample but the spectrum showed a fluorescence signal and no Raman peak could be observed. Therefore micro Raman spectroscopy did not show any result for the sample SA9.

Figure 9.85 shows the infrared spectrum of sample SA9 compared with reference spectra of calcium carbonate and gypsum (Shurvell, n.d.). The results showed this sample contains some calcium carbonate (broad absorption centred near 1400 cm^{-1} and the sharp peak at 875 cm^{-1}) and gypsum (absorptions at 3500, 3400, 1620, 1100, 670 and 600 cm^{-1}). Evidence of hydrocarbon groups is seen near 2900 cm^{-1} (Shurvell, 2002).

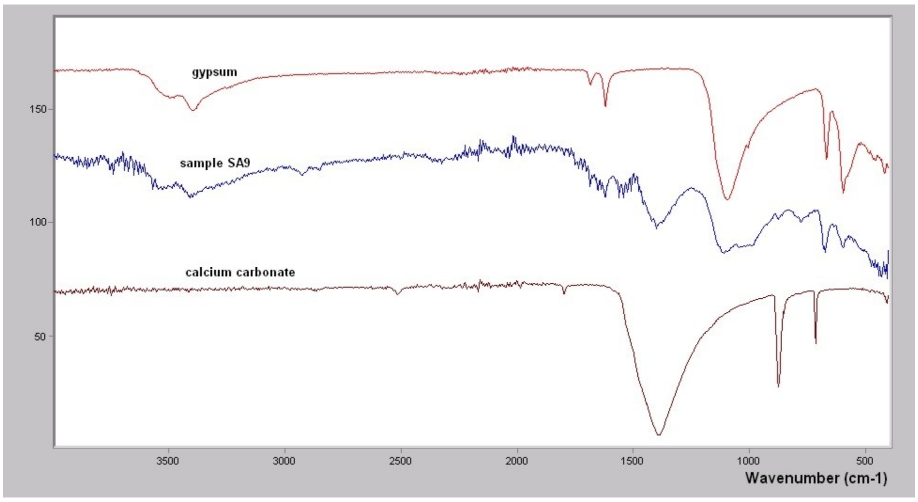


Figure 9.85. The infrared spectrum of sample SA9 compared with reference spectra of calcium carbonate and gypsum (Shurvell, n.d.).

9.3.10. Sample SA10

This sample is from the Armenian handwriting that has been written over the gold leaf, around the wall painting. The paint cross-section was viewed through a microscope. The microscopic image of sample's cross section (figure 9.86) showed different layers. The schematic sketch of the sample's layers (figure 9.87) contains: 1) gold leaf, 2) dark or black layer, 3) light green paint, 4) orange paint, 5) oily dark red, 6) red-orange layer, and 7) finish coat layer.

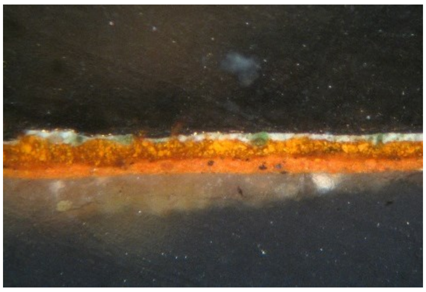


Figure 9.86. Cross section image of the sample SA10, magnification 180X

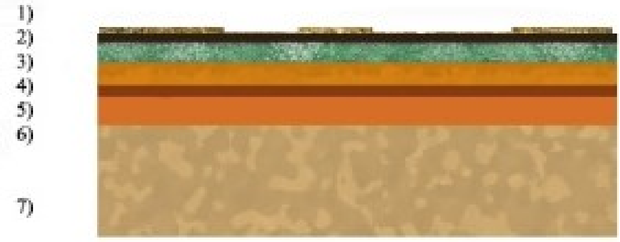


Figure 9.87. Schematic sketch of the layers

XRF analysis for this sample showed that lead is the main constituent while calcium, iron, and sulphur were detected in the composition too (figure 9.88). The presence of calcium, iron, and sulphur found in the XRF analysis may refer to Isfahan gypsum which covered these wall paintings for many years.

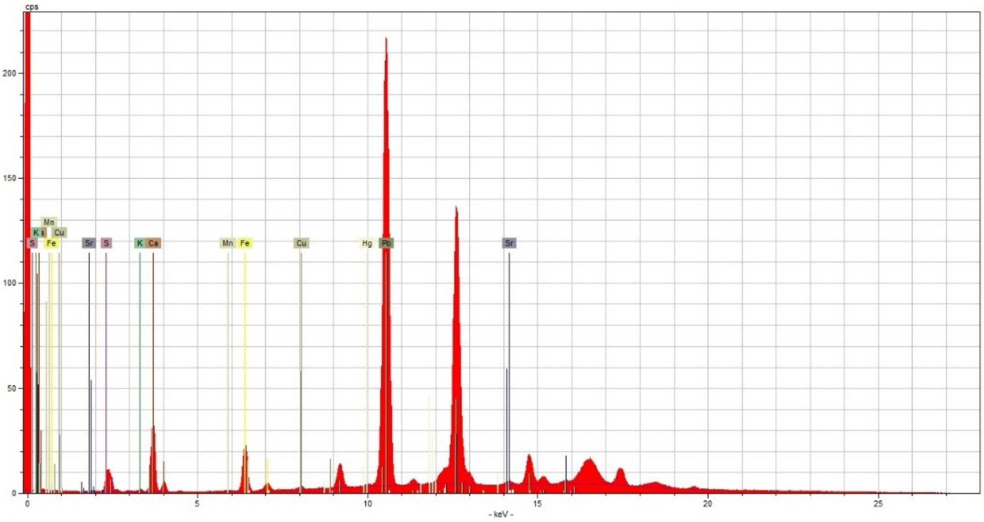


Figure 9.88. XRF spectrum of the sample SA10

In the cross-section image, the presence of green layer under the black outer layer has also been found. Micro Raman result for this sample was not appropriate because the high amount of varnish and binder in the sample caused the specimen to burn. Even after trying to extract the binder from the pigment, the residue did not provide reliable results.

Sample SA10 was studied by FTIR to get more information for identification. The FTIR examination of the underside of sample (figure 9.89) compared with reference spectrum of gypsum (Shurvell, n.d.). The results show the sample contains gypsum.

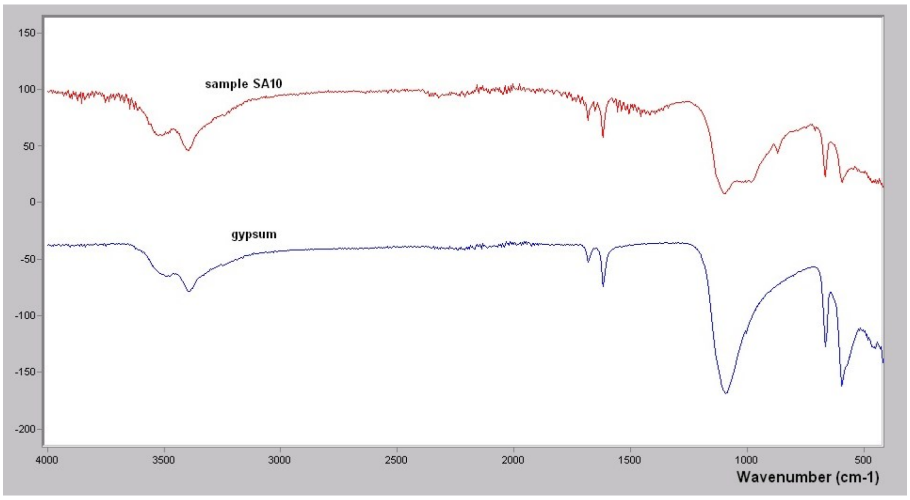


Figure 9.89. The infrared spectrum of sample SA10 compared with reference spectrum of gypsum (Shurvell, n.d.).

Figure 9.90 shows the selected points and areas for SEM-EDX analysis. SEM-EDX analysis was carried out on the gold leaf (figure 9.91). The results revealed the presence of gold, in this layer (figure 9.92).

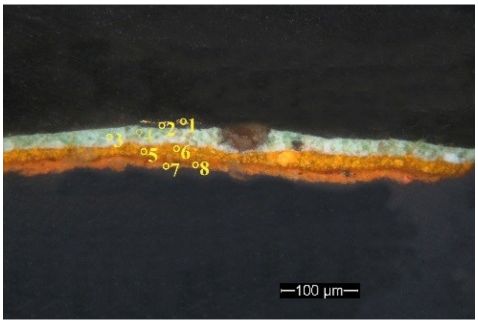


Figure 9.90. The selected points for SEM-EDX analysis, sample SA10, magnification 180X

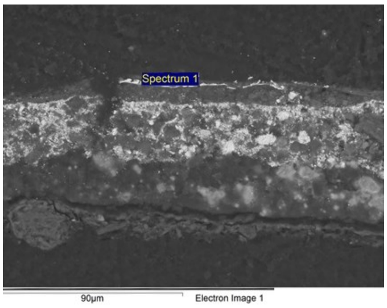


Figure 9.91. Backscattered electron SEM image of the sample SA10 shows the selected point for analysis

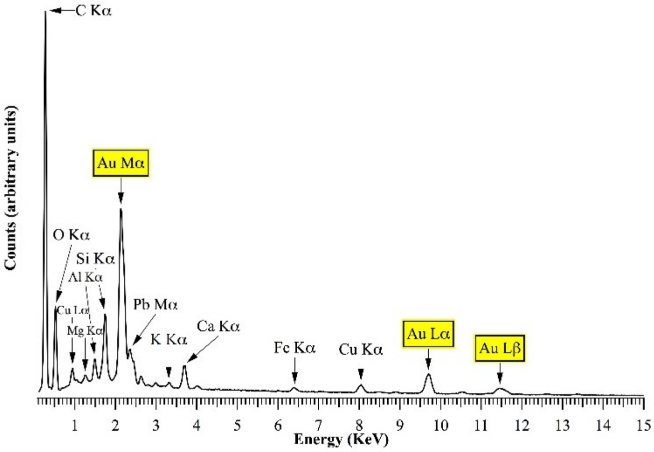


Figure 9.92. SEM spectrum of the gold leaf

SEM-EDX analysis was carried out on the dark layer under the gold leaf (figure 9.93). The results showed that this layer could possibly contain Armenian bole (figure 9.94).

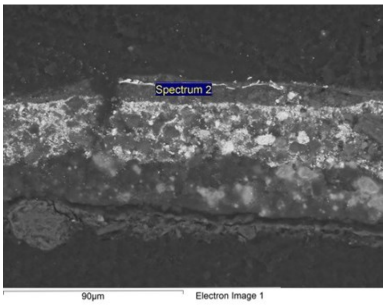


Figure 9.93. Backscattered electron SEM image of the sample SA10 shows the selected point for analysis

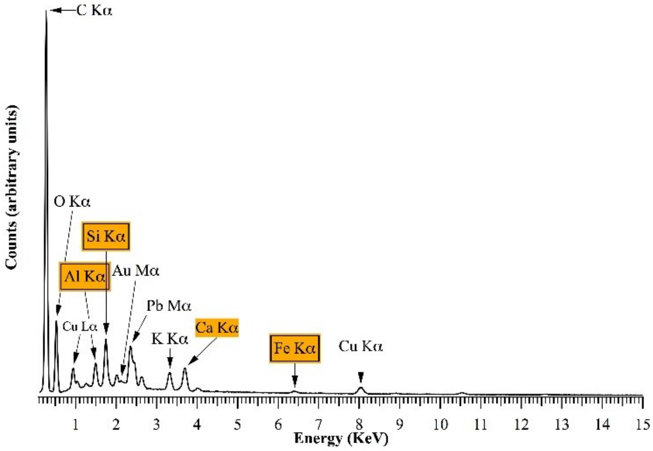


Figure 9.94. SEM spectrum of the dark layer

Figures 9.95 to 9.98 show the SEM-EDX spectra of the green layer. The results confirmed the presence of lead and copper. Presence of high amounts of lead can indicate lead white pigment. This would have been mixed with copper-based pigment to create a light green colour.

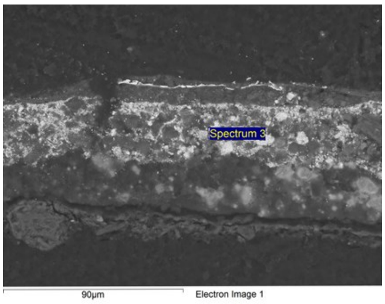


Figure 9.95. Backscattered electron SEM image of the sample SA10 shows the selected point for analysis

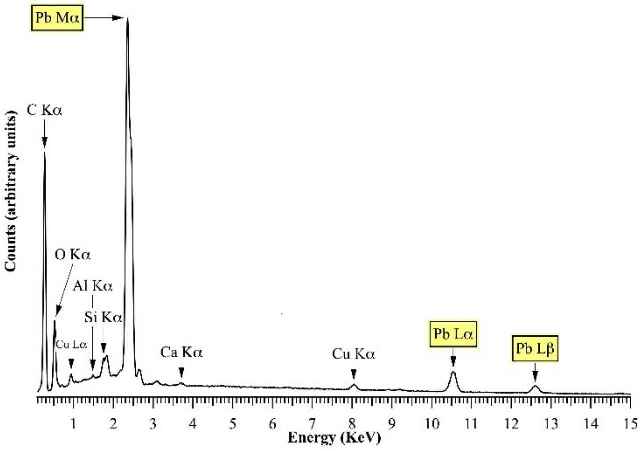


Figure 9.96. SEM spectrum of the white point in green layer

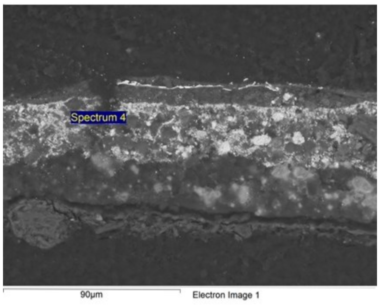


Figure 9.97. Backscattered electron SEM image of the sample SA10 shows the selected point for analysis

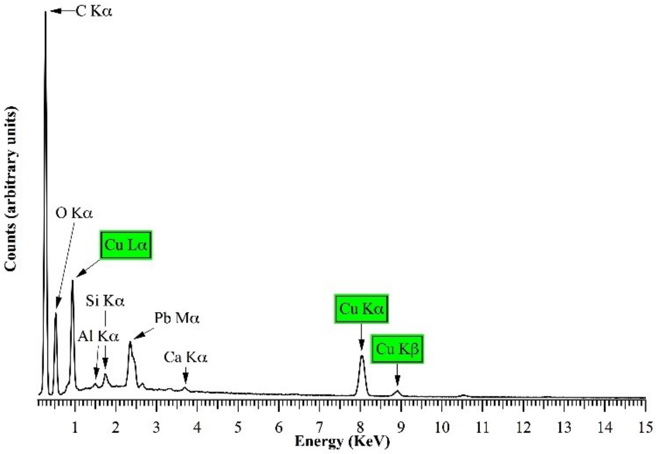


Figure 9.98. SEM spectrum of the green point

Figure 9.99 also shows the selected points and areas for SEM-EDX analysis. In some parts of this sample, gold leaf was used directly over the orange layer. SEM-EDX analysis of this layer showed presence of a lead compound and clay or Armenian bole (figures 9.100 and 9.101).

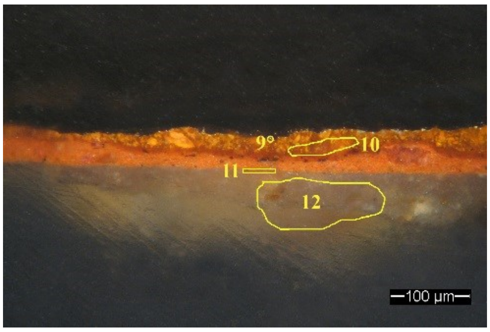


Figure 9.99. The selected points and areas for SEM-EDX analysis, sample SA10, magnification 180X

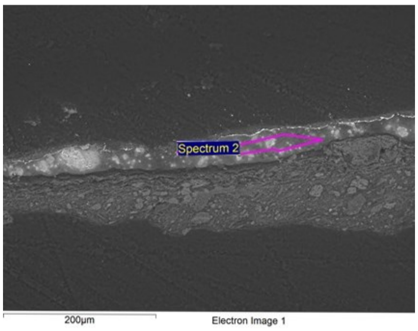


Figure 9.100. Backscattered electron SEM image of the sample SA10 shows the selected area for analysis

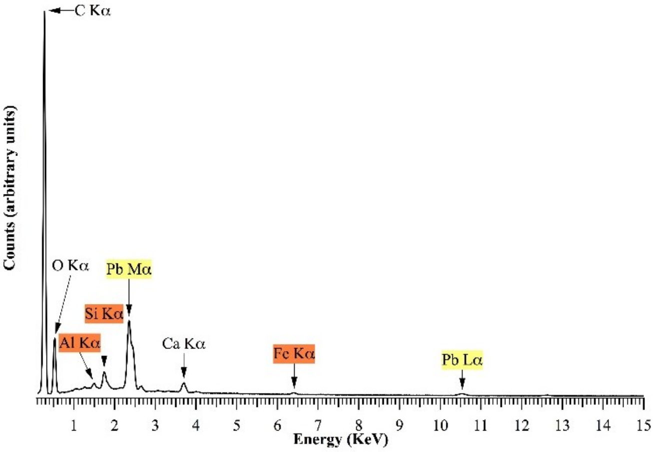


Figure 9.101. SEM spectrum of the orange layer

SEM-EDX spectra of oily dark red and red-orange layer (figures 9.102-9.105) confirmed the presence of Armenian bole in both of these layers.

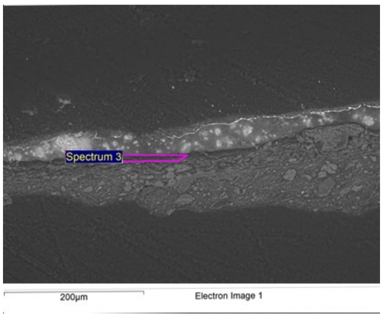


Figure 9.102. Backscattered electron SEM image of the sample SA10 shows the selected area for analysis

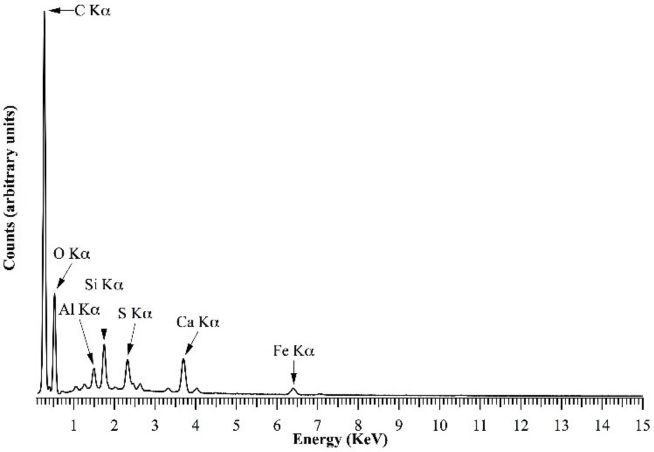


Figure 9.103. SEM spectrum of the dark red area

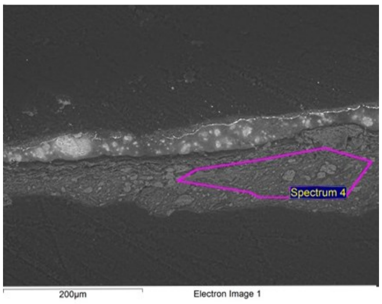


Figure 9.104. Backscattered electron SEM image of the sample SA10 shows the selected areas for analysis

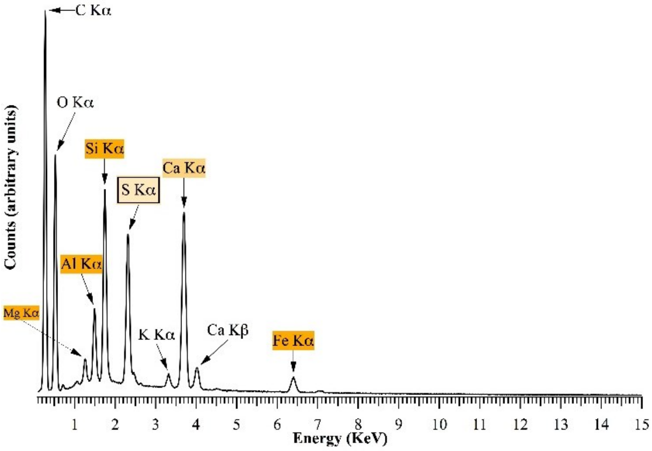


Figure 9.105. SEM spectrum of the red-orange layer

This leads to the conclusion that the painter or master provided different layers of Armenian bole, at least three layers, then he applied a layer of green and finally he put the gold leaf on top in some locations. Also Cennini and Thompson (1954) had mentioned about usage of Armenian bole under the gold leaf (p. 101).

9.3.11. Sample SA11

Due to the size and form of this sample, cross section was not provided. The XRF analysis confirms the presence of iron, lead, copper, and gold (figure 9.106). Calcium, sulphur, and zinc are in minor amounts in this sample. The presence of iron could be from Armenian bole which was usually used under the gold leaf. The results could confirm presence of brass leaf behalf of gold leaf in the wall painting which could cause more corrosion and damage.

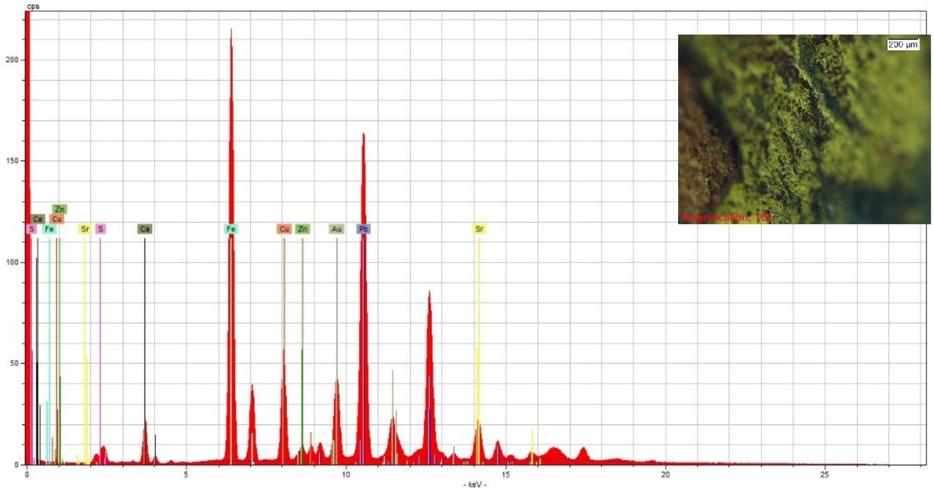


Figure 9.106. XRF spectrum of the sample SA11

In Raman analysis of red ground layer, the characteristic Raman bands at 220, 286 cm^{-1} (figure 9.107) could be assigned to red ochre or hematite (Bell et al., 1997, p. 2174). In this case, Raman results confirmed XRF results. The band at ~983 cm^{-1} could be assigned to posnjakite (basic copper(II) sulphate), $CuSO_4.3Cu(OH)_2.H_2O$ (ibid, p. 2171). This material could be a corrosion product of the brass leaf, especially when the humidity and the sulphate concentration is high enough.[2] "Posnjakite may result from the oxidation of Cu(I) to Cu(II) species, which, in the presence of SO_4^{2-} ions, leads to:

$$2Cu_2O + SO_4^{2-} + 4H_2O + 1/2\ O_2 \longrightarrow Cu_4(SO_4)(OH)_6.\ H_2O$$

" (Bastos et al., 2008, p. 633)

Also posnjakite is one of the important compounds that can be found in the patina constituents of the copper alloys (Vasant & Bansal, 2013, p. 9).[3]

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[2] For many years, the wall painting was covered by a gypsum layer which could cause the high concentration of sulphate in the samples' area.

[3] For more information about Posnjakite see: Scott, D. (2002). *Copper and bronze in art: Corrosion, colorants, conservation*. Los Angeles: Getty Conservation Institute.

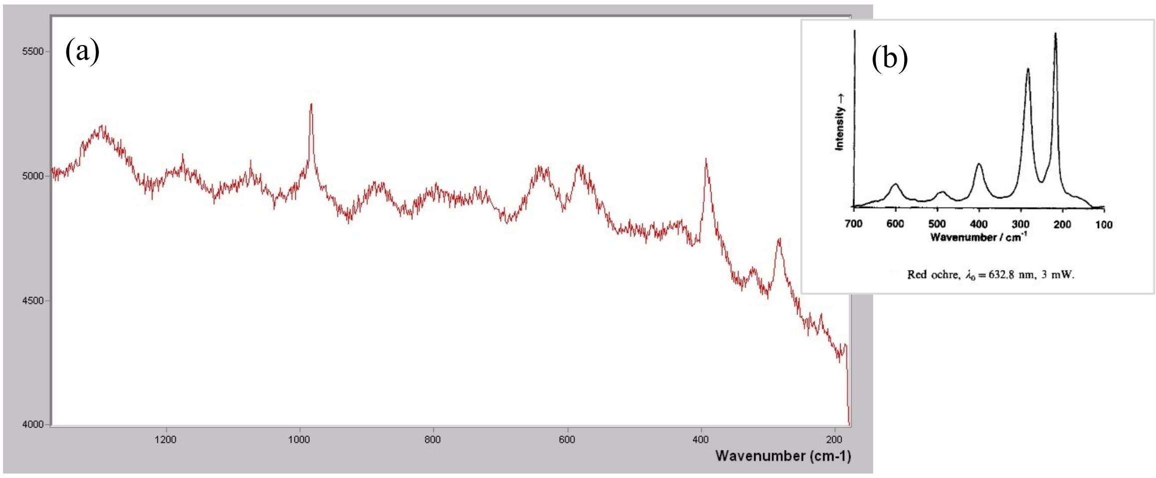


Figure 9.107. Micro Raman spectrum (a) from the sample SA11 in comparison with Raman database spectrum of red ochre (b) (Bell et al., 1997, p. 2164).

The FTIR examination of the underside of sample (figure 9.108) in comparison with reference spectrum of gypsum (Shurvell, n.d.) showed the sample contains gypsum (absorptions at 3500, 3400, 1620, 1100, 670 and 600 cm^{-1}) (Shurvell, 2002).

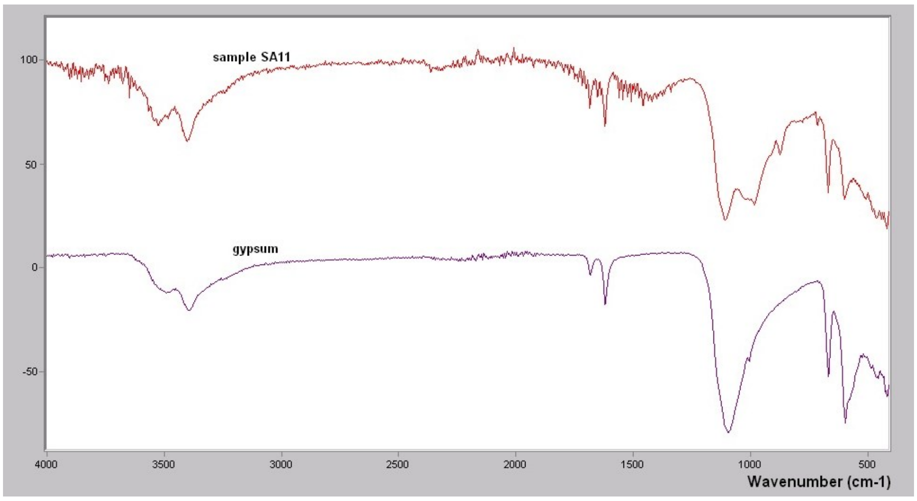


Figure 9.108. The infrared spectrum of sample SA11 compared with reference spectrum of gypsum (Shurvell, n.d.).

9.3.12. Sample SA12

The microscopic image of the cross section of the sample (figure 9.109) showed different layers. The schematic sketch of the layers (figure 9.110) contains: 1) oily dark green, 2) green paint layer, 3) orange ground layer, and 4) finish coat layer.

Figure 9.109. Cross section image of the sample SA12, magnification 180X

Figure 9.110. Schematic sketch of the layers

The XRF examination of the green sample (figure 9.111) showed copper and lead as the main constituents of the sample while iron and calcium were detected in minor amounts in the composition.

The copper peak could be from copper-based green like verdigris, but because of lead peak, the green could be mixed with lead white, lead tin yellow, or other lead compounds. There is no tin in XRF spectrum so it means lead tin yellow does not exist in this sample. Presence of calcium and iron can indicate Isfahan gypsum which had covered the surface of this wall painting.

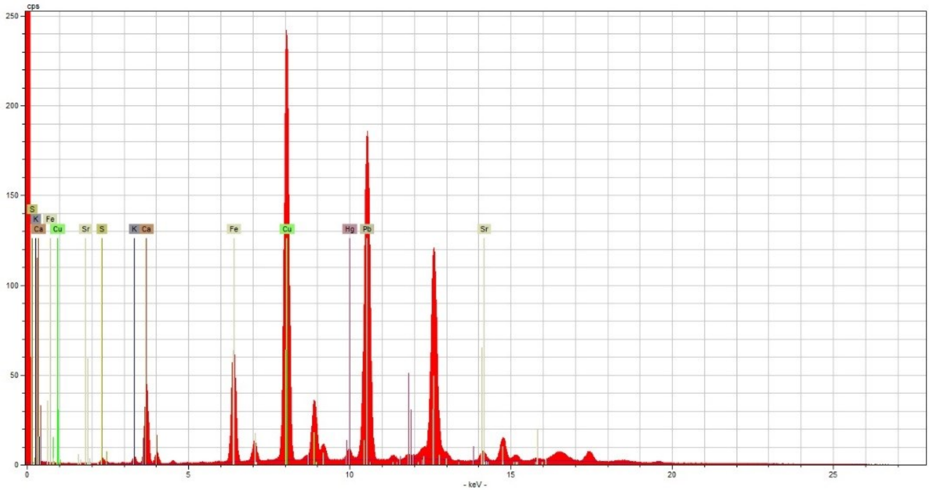


Figure 9.111. XRF spectrum of the sample SA12

In Raman spectrum from green part, the result was not clear and it was full of fluorescence. The specimen may contain copper resinate. Also the sample burned under micro Raman analysis because it contains varnish or binder that even after trying to clean, it did not give the exact results or peaks.

The infrared spectrum of sample SA12 compared to a reference spectrum of gypsum (Shurvell, n.d.) (figure 9.112). The CH stretching and bending absorption near 2900 and 1400 cm^{-1} and the carbonyl peak at 1720 cm^{-1} indicate the possible presence of a drying oil such as linseed oil. The three weak unassigned absorptions marked X are probably also due to organic material (Shurvell, 2002).

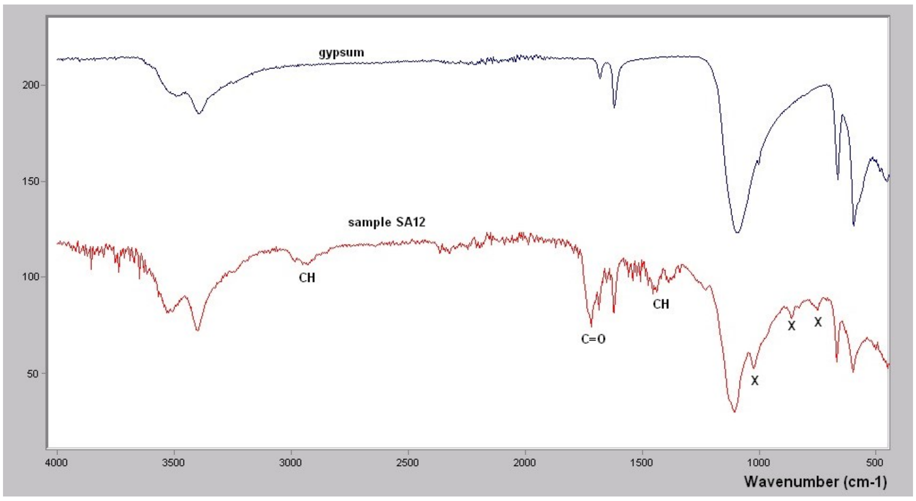


Figure 9.112. FTIR spectrum of the sample SA12 compared with reference spectrum of gypsum (Shurvell, n.d.).

Furthermore, XRD analysis was carried out on this sample to get more information. In the XRD spectrum of the sample SA12 (figure 9.113) the diffraction lines from gypsum, quartz, minium, and hydrocerussite could be identified.

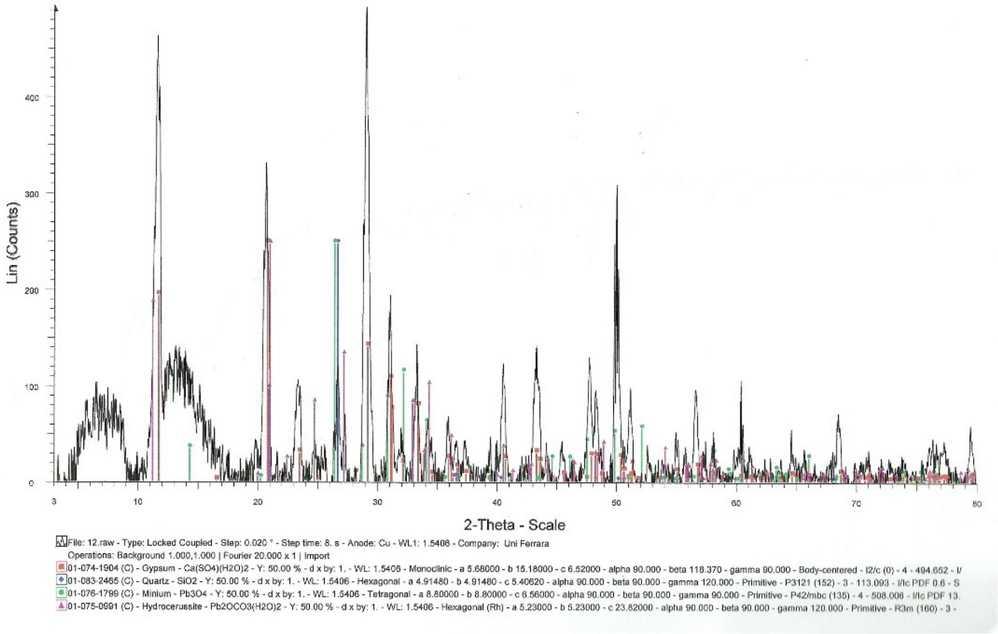


Figure 9.113. XRD spectrum of the sample SA12

Figure 9.114 shows the selected points and areas for SEM-EDX analysis. SEM-EDX analysis was carried out on the white particles of the green layer (figure 9.115). The results revealed the presence of lead in this part of the sample which could be from lead white (figure 9.116).

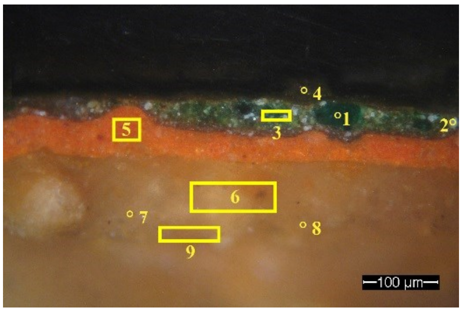


Figure 9.114. The selected points and areas for SEM-EDX analysis, sample SA12, magnification 180X

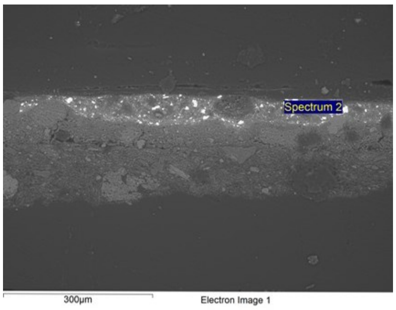


Figure 9.115. Backscattered electron SEM image of the sample SA12 shows the selected point for analysis

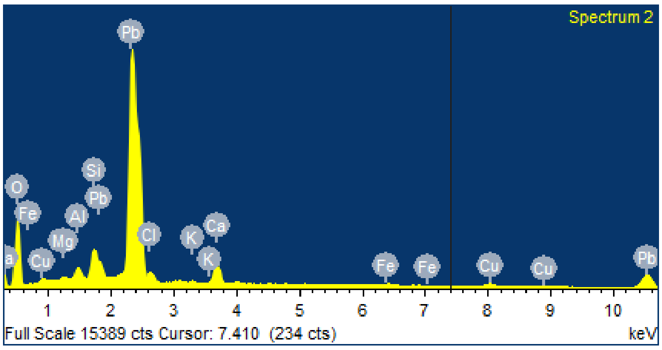
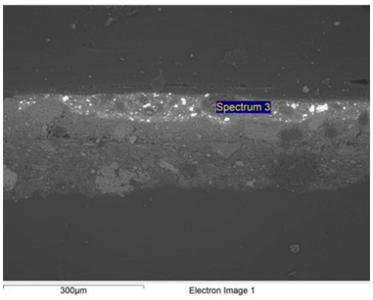


Figure 9.116. SEM spectrum of the white particle

SEM-EDX analysis was carried out on the green layer (figure 9.117). The results showed that this layer contains lead and copper which may indicate a mixture of lead white and copper green pigments (figure 9.118).



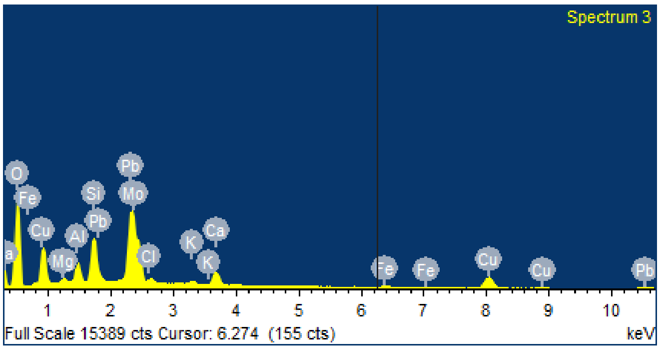


Figure 9.117. Backscattered electron SEM image of the sample SA12 shows the selected area for analysis

Figure 9.118. SEM spectrum of the green layer

SEM-EDX analysis was also carried out on the orange layer under the green paint (figure 9.119). The results showed that this layer could possibly contain clay or Armenian bole (figure 9.120).

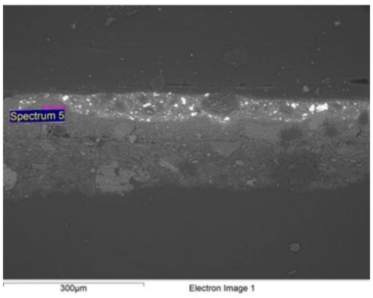


Figure 9.119. Backscattered electron SEM image of the sample SA12 shows the selected area for analysis

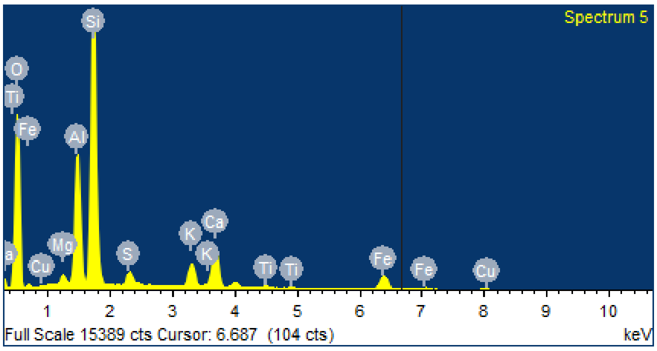


Figure 9.120. SEM spectrum of the orange layer

Figure 9.121 shows the selected area for SEM-EDX analysis. SEM-EDX analysis was carried out on the finish coat layer of the sample. The results revealed the presence of gypsum. The iron found in this SEM-EDX analysis may refer to Isfahan gypsum (figure 9.122).

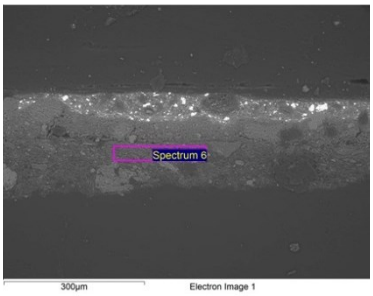


Figure 9.121. Backscattered electron SEM image of the sample SA12 shows the selected area for analysis

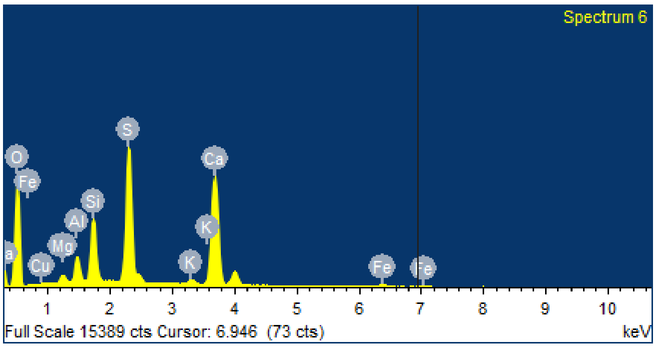


Figure 9.122. SEM spectrum of the finish coat layer

9.4. Conclusion

According to the analyses and observations, the artists rarely used the pure colours and preferred to mix different pigments to provide more various colour effects. Also study of microscopic cross section images showed different layers, which were used on top of each other.

It could be assumed that during the painting process, the artist would change his mind or choice by himself or the master of the studio could ask or suggest different colours for the wall painting. On the other hand, during years, this church underwent inappropriate restoration on several occasions. Therefore, presence of several different layers could be the sign of those inappropriate interventions.

In the church of Surb Stepanos, different pigments and materials were identified such as lead white, vermilion/cinnabar, red lead/minium, massicot, litharge, smalt, indigo, malachite, hematite or red ochre, gypsum, and calcium carbonate.

Also the presence of a copper-based green pigment mixed with a lead compound was confirmed through analyses. According to Roy (1977), "it was very common to use verdigris mixed to lead white for providing more suitable surface covering, especially when the artist wanted to use verdigris in oil paintings" (p. 132). Furthermore, Eikema Hommes (2004) mentioned that "mixing the colours to a lighter shade, for instance by adding extra lead white was a method which used to overcome the effect of the oil's tendency to darken" (p. 24); but it is very important to remember for some pigments, the presence of specific element may provide a whole range of pigments; for instance copper which by presence of it in green pigment, the pigment cannot be definitely identified.

Goethite is another pigment in this wall painting. It is an earthy pigment which usually has a brownish yellow colour.[4] "Because the colour strength of hematite is greater than…goethite,…a few percent of hematite admixtures change the hue of goethitic yellow earths to brownish or reddish" (Hradil et al., 2003, p. 229).

About blue pigment, the widespread use of smalt in European paintings started since the second half of the 16th century. Painters preferred to use an inexpensive substitute for azurite and ultramarine; and smalt was an available blue pigment for them (Eikema Hommes, 2004). Nevertheless in Iran and most eastern country reaching ultramarine was much easier than European countries but as it was mentioned in old treaties (chapter four), Iranian artist had different blue colours (ultramarine, indigo, and smalt) in his palette.

The analyses showed that the bole layer serves as an underpainting and a basic colour for some areas of this wall painting. Especially in gilding parts of the wall painting, the painter or master provided different layers of Armenian bole.

The analyses of the gold leaf or golden colour leaf could confirm presence of brass behalf of gold in some parts of the wall painting which could cause more corrosion and damage. Also presence of posnjakite (basic copper II sulphate) along with brass leaf was confirmed through Raman analysis. As it was mentioned; this material is one of the important compounds that can be found in the patina constituents of the copper alloys (Vasant & Bansal, 2013, p. 9). "The corrosion of copper alloys occurs in the form of tarnishing of the surface without a voluminous corrosion product, significant loss of mass or other serious corrosion form" (Dillmann, Watkinson, Angelini, & Adriaens, 2013, p.328).

The FTIR analysis showed the possible presence of a drying oil such as linseed oil. Also presence of indigo in the sample SA2 was confirmed through FTIR analysis.

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[4] The hue of goethite is affected by its crystallinity and elemental purity. Finely particulate (poorly crystalline) goethite, commonly called limonite in the past, is brownish yellow (Hradil et al., 2003, p. 229).

CHAPTER TEN

10. Conclusion

In this chapter, a brief description of all conclusions which made through this research project has been provided.

As it was mentioned by permission of royal court of Iran, the Armenian merchants of Nor-Djulfa started their own real commercial activities. As political and commercial deputies, they were well known in different European and Eastern countries. The trading system of Armenian merchants was very valuable and substantial in that historical era which leads to describe the period of its maximum development as the "region of the Armenian merchants of Nor-Djulfa" (Hakhnazarian & Mehrabian, 1991). During these times, Armenians were one of the most effective factors in the birth of different styles in Iranian art which was bound to its Islamic and local traditions.

Nevertheless, the Armenian merchants lost their powerful position in the royal court of Iran and their "privileged relationship with the Safavid court" did not continue in the later time. Also their number was reduced because many families moved to India and Europe (MacCabe, 2005, para. 45).

However, it is undeniable that the Armenians were one of the primary channels for the introduction of Western art and culture to Iran. Artefacts and objects in Armenian houses and churches in new julfa/Isfahan are considered to be one of the most important cultural heritages in Iran and great relationships with Europe since 17th and 18th century made Armenian one of the most effective factors in birth of different art in Iran which was different with Iranian traditional art.

Different sources illustrated that the Persian painters in pre-Safavid dynasty did not try to "reproduce nature and did not show shadows, but a bright, pure, luminous world, beyond the reach of terrestrial sight" (Porter, 2000, p. 113). But in Safavid dynasty, artists' started to show different forms and styles in their paintings. The Safavid shahs of Isfahan supported various kinds of arts in different styles. As a result, "The development and significance of *farangi-sazi* (or Europeanized mode) is very obvious at the Persian court and in the Armenian suburb of New Julfa during the seventeenth century" (Leoni & Natif, 2013, p. xiv). Furthermore, the school of realistic and historical paintings which was close to European style were developed "in the course of eighteenth century based on trends that began in the Safavid period" (Diba, 1989, p. 147).

About palette of pigments in Armenian and Iranian paintings, it was studied that the Armenian palette before their presence in Iran, represents a tradition somehow similar to painting in Islamic lands.

It would be considerable to remember that studying of Armenian palette has been done on their illuminated manuscripts but not about Armenian wall paintings. Merian, Mathews, and Orna (1994) mentioned that the Armenian palette in the 13th and 14th centuries, contained six pigments. These pigments are the main colours of the old Armenian palette for the manuscripts: gold, lead white, vermilion, orpiment, ultramarine, and red lake (p. 129). In a later time other pigments and dyes like indigo were added to their palette.

There were some similarities between the Armenian and Iranian traditional palettes, with the lead white, gold, orpiment, ultramarine, indigo, and vermilion. Nevertheless, there are some differences between the Iranian and Armenian palettes and must be considered. For instance, natural green, which is missing in Armenia, is copper green in Iran. Red lead and red earth supplemented the Armenian red lake. Despite of explanation of producing red lake in Sadiqi Bek's treatise, there is no evidence of using such a red lake in Iranian wall paintings. It seems both Iranian and Armenian artists used the red lake for their manuscripts and not for the wall paintings. In case of blue colour ultramarine, smalt, and indigo were used in Iranian paintings. Vermilion, lead white, and orpiment existed in both Armenian and Iranian palette.

On the other hand, the similarity between Armenian and European palettes (especially the palette of Venice and Amsterdam) has been discovered about the following pigments: orpiment, ultramarine, lake pigments, lead white, and black bone.

Since one of the major aims of this study was to gain more information about some wall paintings in different Armenian buildings by technical analyses rather than rely on only written or oral information of that period, forty-one samples of paint and ground layers were taken from different Armenian wall paintings and were subjected to instrumental analyses.

Samples were analysed by X-ray fluorescence analysis (XRF), Micro Raman spectroscopy, and Fourier Transform Infrared (FTIR) spectroscopy. Some pigments which needed to be more studied were also analysed by using Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray spectrometer (EDX) and X-ray Diffraction (XRD). According to the analyses and observations, the artists rarely used the pure colours and preferred to mix different pigments to obtain more various colour effects. Also some samples contained different layers. According to the Iranian Cultural Heritage, Handcrafts, and Tourism Organization (ICHHTO), the wall paintings were not previously restored and the pigments could be considered genuine. Nevertheless, study of microscopic cross section images of different samples showed different layers, which were used on top of each other. For instance, it is not very common to cover the gold leaf under the dark layers, since the purpose of the gilded parts of wall paintings were to provide a bright and luxurious appearance for the buildings.

Therefore, it is presumed that these layers must have been added to the wall paintings at some early stages by way of restoration, as there is no record of such intervention during recent years.

According to the different analyses, the results could be classified as follows:

- The finish coat layer of the majority of samples was recognized as gypsum.
- White ground layer was identified as huntite or magnesium calcium carbonate.
- Red ochre was used for the paint layer and also as a ground layer. The analyses showed that the Armenian bole or hematite serves as an underpainting and a basic colour for some areas of some wall paintings. Especially in gilding parts of the wall paintings, the painters or masters provided different layers of Armenian bole.

- The analyses of the gold leaves could confirm presence of both gold and brass leaves in the wall paintings. The application of brass leaf behalf of gold leaf in some parts of the wall paintings could cause more corrosion and damage. Also presence of posnjakite (basic copper II sulphate) along with brass leaf was confirmed through Raman analysis. As it was mentioned; this material is one of the important compounds that can be found in the patina constituents of the copper alloys (Vasant & Bansal, 2013, p. 9).

- Goethite is another pigment in the Armenian wall paintings. "While red earth pigments are generally coloured by hematite, most of the yellow or yellow-brown earths are coloured primarily by goethite" (Helwig, 1998, p. 87). "Because the colour strength of hematite is greater than…goethite,…a few percent of hematite admixtures change the hue of goethitic yellow earths to brownish or reddish" (Hradil et al., 2003, p. 229).

- The presence of different green colours was confirmed through the analyses:

a) Copper green pigments, especially malachite.
b) A mixed green colour from a yellow mineral, orpiment, and a blue mineral, lazurite. Consequently painters used both Armenian and Iranian palettes to provide green colours and
c) Emerald green;
Emerald green is a synthetic pigment introduced into Europe between 1800 and 1814 and there is no naturally occurring copper acetoarsenite, therefore, it is presumed that this pigment must has been added to the wall painting by way of restoration.
d) The Raman results showed presence of moolooite in the sample B13. This material cannot be original compound and its occurrence could be because of the changes in the original pigment. "Moolooite (copper oxalate), a very rare compound, was found as a degradation product from the decay of malachite in several specimens of Cultural Heritage" (Castro et al., 2008, p. 4103).[1]

- Lead pigments like lead white, massicot, litharge, and minium (red lead) were found in these Armenian wall paintings.

- For the black colour, presence of a carbon-based black pigment was confirmed through analyses.

- For the blue colour, it is not surprising to find lazurite as the blue pigment in the Persian and Armenian palettes, since it is almost the most common blue pigment mentioned in the treatises.

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[1] The colour change happens because of the decomposition of the pigment. Some different factors like high UV, relative humidity, and temperature levels would accelerate the degradation process (Augusto, Casanova, Sequeira, & Cabrita, 2008). About the green copper pigments, the presence of microorganisms excreting oxalic acid could cause degradation mechanism too (Castro et al., 2008).

Also smalt and indigo were identified in these wall paintings. Sometimes the artists mixed different blue colours together for instance; lazurite and smalt. Furthermore, treaties often advise adding smalt to indigo to achieve a brighter blue colour (Eikema Hommes, 2004, p. 141). The widespread use of smalt in European paintings started since the second half of the 16th century. Painters preferred to use an inexpensive substitute for azurite and ultramarine; and smalt was an available blue pigment for them (ibid, 2004). Nevertheless in Iran and most eastern country reaching ultramarine was much easier than European countries but as it was mentioned in old treaties (chapter four), Iranian artist had different blue colours (ultramarine, indigo, and smalt) in his palette.

- Vermilion, mercury(II) sulphide-HgS, is another pigment which was found. The mercury sulphide compounds are very important between the mercury group pigments and "they include the red mineral cinnabar (HgS) and its synthetic analogue mercury(II) sulphide, commonly known as vermilion"(Eastaugh, Walsh, Chaplin, & Siddall, 2004, p. 259).
  "Vermilion is, largely, a permanent pigment....However in the presence of hydrogen sulphides and sunlight the pigment reacts chemically darkening to a black…" (McBride, 2002, p. 13).

- Also orpiment and a mixture of realgar and pararealgar were used by the artist in the Armenian wall paintings in New Julfa. Orpiment is the common pigment in both Armenian and Iranian palettes. It is yellow and is often found associated with realgar which is red to red-orange. Realgar under the sunlight, changes to a yellow powdery material which had generally been taken as orpiment. However, it has been determined that this material is pararealgar that was popular for the Renaissance masters, especially Tintoretto (Trentelman, Stodulski, & Pavlosky, 1996, p.1755).

- FTIR analysis confirmed the presence of mastic resin as the main component of the varnish and the possible presence of a drying oil such as linseed oil in some samples.[2] Usually in every sample, there are so many IR bands that it is not feasible to assign all of them, but the main goal of this study was to gain more information about each sample.

As the main result, the effects of European style is completely obvious in the topics of the wall paintings that showed perspective, and light and shadow, but in this study, it has been found that artists in these Armenian buildings did not necessarily follow an European palette. Furthermore, this research project showed the application techniques and material compositions of the selected Armenian wall paintings in New Julfa.

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[2] In different European painters' manual it has been mentioned that usually, the oil for oil painting, was washed with water wherein water-soluble components dissolved. In order to absorb mucilaginous material, painters used to add sawdust, snow, powdered chalk, breadcrumbs or alum to the water. Painters also tried to obtain more permanent colours by bleaching the oil in sunlight. The result was an oil with a much lighter colour. Instructions suggest that blue and white paints that were particularly susceptible to yellowing should not be made with linseed oil but with a medium that did not discolour to the same extent (Eikema Hommes, 2004, p. 20).

The results of the analyses showed material differences and similarities between Iranian and Armenian palettes. Also they even could be useful to introduce these art works as examples of joint Armenian-Iranian cultural heritage.

Finally, for every field of the cultural heritage especially these wall paintings, the specialists in art, history of art, restoration, and conservation science investigate different aspects and through their study, they provide valuable information about the techniques, art historical period or special school and style. Therefore to provide the real understanding of the wall paintings' technique, it is very important to establish a multidisciplinary collaboration between different fields and groups. The results of this collaboration and the obtained information contribute to a better understanding of Armenian wall paintings techniques and, ultimately, may aid conservators in their efforts to preserve these art works.

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