Original Work

Sayed Mohammadjavad Mousavi*, Hossein Ahmadi, Abbas Abed-Esfahani, Mohammad Mortazavi and Maurizio Aceto

Identification and Analytical Examination of Copper Alloy Pigments Applied as Golden Illuminations on Three Persian Manuscripts

Abstract: Golden pigments are among the most common colourants used in Persian illuminated manuscripts. In this research, golden pigments were investigated in three eighteenth- to nineteenth-century manuscripts. Initially, scanning electron microscopy–energy dispersive spectrometry analyses showed that different kinds of metallic pigments were present and some of them were ternary alloys made up of copper, zinc and tin, hence copper-based alloys were ascertained as cheap alternatives to gold. Discolouration of the pigment was observable through alteration of the metallic pigments to greenish residues in the manuscripts. Subsequently, the greenish products in the golden pigments were studied by Raman spectroscopy. Copper carboxylates were recognized as degradation products. We inferred that the alteration is a consequence of the interaction between copper alloy pigments and carboxylic acids in conditions of high humidity. Moreover, more progressive degradation has caused the discolouration, brittleness and gradually crumbling of the paper in the painted areas. Signs of damages in the paper were comparable with decomposition of the paper by green copper pigments such as verdigris in historical documents and miniatures.

DOI 10.1515/res-2014-0022
Received October 8, 2014; accepted November 5, 2014

***Corresponding author: Sayed Mohammadjavad Mousavi,** Faculty of Conservation, Art University of Isfahan, P.O. Box 1744 Isfahan, Iran, E-mail: j_mousavi83@yahoo.com
Hossein Ahmadi, Faculty of Conservation, Art University of Isfahan, P.O. Box 1744 Isfahan, Iran, E-mail: h.ahmadi@aui.ac.ir
Abbas Abed-Esfahani, Basic Sciences Department, Islamic Azad University-Khorasgan Branch, P.O. Box 81595–158 Isfahan, Iran, E-mail: aabed@khuisf.ac.ir
Mohammad Mortazavi, Faculty of Conservation, Art University of Isfahan, P.O. Box 1744 Isfahan, Iran, E-mail: m.mortazavy@aui.ac.ir
Maurizio Aceto, Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Università degli Studi del Piemonte Orientale, Viale Teresa Michel, 11–15121 Alessandria, Italy, E-mail: maurizio.aceto@mfn.unipmn.it

1 Introduction

Metallic pigments have constituted a large part of illuminations in Persian manuscripts and golden-based pigments are the most important among them. Metallic pigments crowned the precious palette of Persian miniature paintings, because Iran was rich in alluvial gold and copper ore (Purinton and Watters 1991). Golden pigments have been applied in different parts of decoration, but non-figurative illuminations are more usual in the layout of illuminated manuscripts. In most of the old Persian treatises, it has been mentioned that gold leaf is made of pure gold. Alternatively, high-carat gold alloys were used for preparation of golden powder (Mayel Heravi 1993).

Few analytical investigations have been performed on Persian manuscripts to identify the composition of golden pigments and the results revealed that gold was the main element, together with small amounts of other elements such as copper, silver and iron (Burgio et al. 2008; Purinton and Watters 1991). In other studies, researchers have been satiated to microscopic inspections of golden pigment (Clark and Mirabaud 2006) and/or essentially concluded that gold was used in the cases studied. Indeed, it must be considered that different pigments have been used in the course of history of painting art for the purpose of gilding. Pure gold could be used in powder form, i.e. the so-called *shell gold*, or in a leaf form, i.e. in very thin sheets. While gold leaf was usually of high purity, powder gold could be mixed with copper in order to ease its milling. However, cheaper alternatives were commonly used at least from Middle Ages. One common substitute, typical of Italian miniature, was *porporine* or *mosaic gold*, a synthetic tin (IV) sulphide used since thirteenth century. Before that, orpiment, its name derives from Latin *aurum pigmentum*, because of its resemblance to gold, and saffron were cited in ancient treatises, such as the Leyden Papyrus X, as cheaper substitutes of gold (Caffaro and Falanga 2004). Less information is available on the use of copper which once mixed with tin or zinc compounds in proper ratios will display a golden appearance; these alloys have been identified in some instances (Banik 1983; Aceto et al. 2006, 2010), but their use is most probably much more common than expected.

We have recently discovered astonishing alterations of golden paints on some of the illuminated manuscripts belonging to different museums in the course of our visual inspections. This alteration had been rarely realized before in archives of Persian heritage: It appeared generally as a chromatic change from the golden aspect to a greenish one and in some areas it caused discolouration and decomposition in the paper supports (Figure 1); discoloured illuminations are partly visually similar to corrosion products in corroded copper alloy artefacts. Generally, this alteration caused problems for the illuminated manuscripts in both aesthetic and conservative points of view. At first glimpse, it was possible to discard the hypothesis of the use of high-carat gold alloys for preparation of metallic pigments in the discoloured illuminations because of the known chemical resistance of gold.

In a similar study, Banik (1983) investigated degradation phenomena in two sixteenth- to eighteenth-century illuminated manuscripts caused by corrosion of brass alloy pigments applied as gilding imitations. On the other hand, besides the degradation of green pigments such as *Verdigris*, copper alloy – usually brass – that has been used in order to imitate gilding, causes similar destructive effects on paper and it could also be due to similar chemical mechanisms (Banik 1989, 1990). In more recent studies, Aceto and collaborators (2006, 2010) have found tarnishing of brass-like ink as an unusual substitution for gold pigments on some ninth- to tenth-century Italian manuscripts.

In this research, alteration of golden pigments was investigated on three eighteenth- to nineteenth-century Persian manuscripts. Emphasis was mainly confined on identification of the composition of the golden pigments and possible effective agents in their alterations. Later, degradation mechanisms of paper caused by altered metal pigments should be investigated in more specific studies. In experimental stages, at first, original composition of the golden

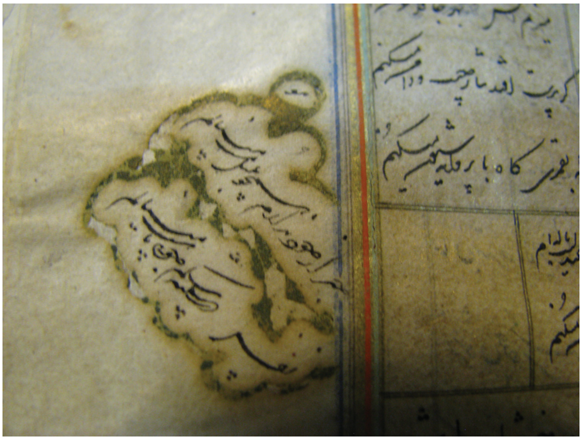

Figure 1: Alteration of golden illuminations as ornamental margin in an eighteenth-century Persian manuscript, Malek National Library and Museum Institution, Tehran (Iran)

pigments was identified by scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS). Then, analytical investigation on the discoloured parts of illuminations to inspect the green degradation products was carried out by Raman spectroscopy. Evidence of the chemical composition of the degradation products helps to identify the substantial alteration processes which are undeniably necessary for stopping further degradation. However, concerning the manuscripts, it is not accurately known whether the alteration occurred prior to its acquisition by the museum or at later periods. Obviously, diagnosis of the alteration processes can prevent similar pigments from degradation in illuminated manuscripts which can be used in preventive conservation issues.

2 Descriptions of the manuscripts

In this study, three illuminated manuscripts belonging to Soltanabad Museum of Arak (Iran) were selected in order to perform analytical investigations. The manuscripts had not been precisely dated, but their creation date might fall into the Qajar dynasty (1797–1925) by codicological data. The most important factor for the selection of the case studies was that the manuscripts are richly illuminated with golden metallic pigments and also the unusual alteration of the formerly golden pigments into greenish discolouration was observed.

The first manuscript is called *Bayāż* (Figure 2(a)). The illuminated elements consist of gilding between the lines of the text on the introductory pages and also golden frame around the text area on each page. *Bayāż* is a type of manuscript usually indicated as a small paper notepad opening lengthwise, with covers made of leather.

The second manuscript is called *Golšan-e rāz* (Figure 2(b)). The manuscript contains golden grids and frames that divide the poem lines on every page; also all papers have been gold-sprinkled by use of fine particles of gold leaf. These papers are known as *Kaghadh-e afshan* in Persian traditional artistic practices. *Kaghadh-e afshan* was a paper which was flecked with gold or silver powder. In most cases, the gold flecking was done before the text was written upon (Floor 2003).

The third manuscript is named *Qur'an* (Figure 2(c)). This manuscript is devoted to *Juz'* 22 (part 22) of Qur'an. The golden illuminations consist of the heading on the first page, the frame of gold with black, blue and red rules around the text area on each page and the small golden roundels that mark the end of each verse.

Figure 2: The manuscripts examined: (a) *Bayāż* manuscript, (b) *Golšan-e rāz* manuscript, (c) *Qur'an* manuscript

3 Experimental section

3.1 Initial observation

At first glance, the altered golden illuminations appeared uniform in their greenish colouration. Since in most discoloured parts, unchanged golden particles have not been observed with naked eye, it is probably suspected that green pigment had been originally used for illuminations. Initially, discoloured pigments were inspected through an optical microscopy before performing analyses. Microscopic observations were useful for preliminary survey of the colouration features in the altered golden pigments and with respect to the situation of the paper support.

Microscope images showed that most illuminations discoloured to greenish residues, while some unchanged particles are still observed which demonstrated an alteration in the appearance of the colour of the illuminations. In some details, the alteration has almost completely occurred and golden grains could rarely be observed among the alteration products (Figure 3(a) and (b)). Some of the unchanged golden particles seemed to be situated on top of the greenish parts and adhered less to the paper supports (Figure 3(c)). This could be interpreted as an alteration of golden pigments that started from the interface between the pigment powders and the paper support. In some parts, most of the pigment particles were removed from the paper support which is probably due to the loss of adhesive power while green traces of them remained on the painted areas of paper (Figure 3(d)).

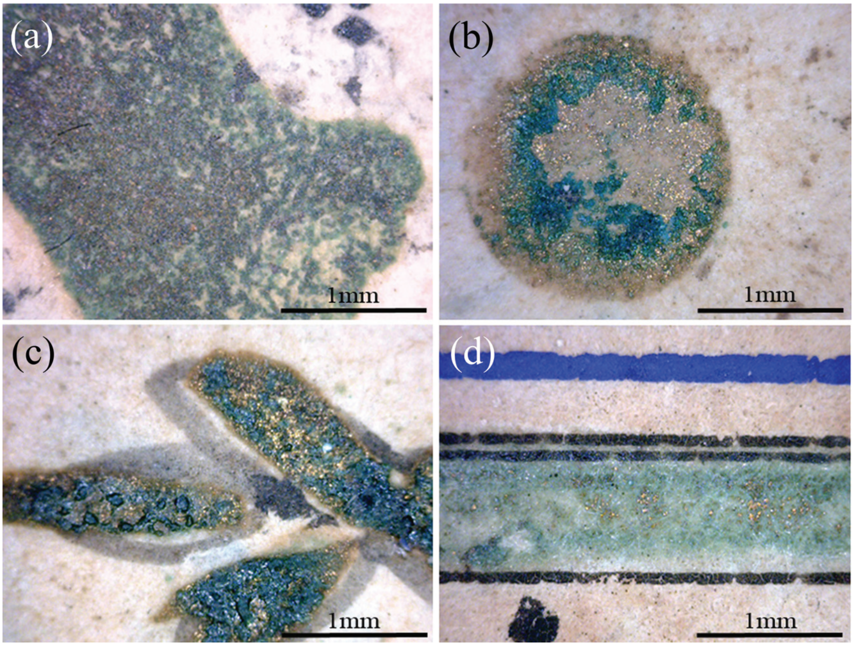

Figure 3: Microscopic views of altered golden illuminations: (a) the illumination between the lines of text in *Bayāż* manuscript, (b) small golden roundel, (c) the small part of the heading on the first page in *Qur'an* manuscript and (d) golden frame around the text in *Golšan-e rāz* manuscript

In the manuscripts, paper degraded specifically in the vicinity of the discoloured golden illuminations. Since the destruction process passes through several stages, paper degradation has been observed in different forms (Banik et al. 1981). In preliminary stages of degradation, paper has discoloured to green appearance and subsequently turned brownish underneath and around the illuminations. Some paper discolouration could be discerned in the surrounding paper of the golden fine particles, which have illuminated the whole surfaces of papers in *Golšan-e rāz* manuscript (Figure 4(a) and (b)). At first sight, it may be imagined that the discoloured particles would be foxing spots caused by corrosion of metal particles. In the following stages of degradation, paper support has become brittle and friable as a result of the alteration. Crumbling and losses are observed in the painted areas of papers, especially in *Bayāż* and *Golšan-e rāz* manuscripts (Figure 4(c) and (d)).

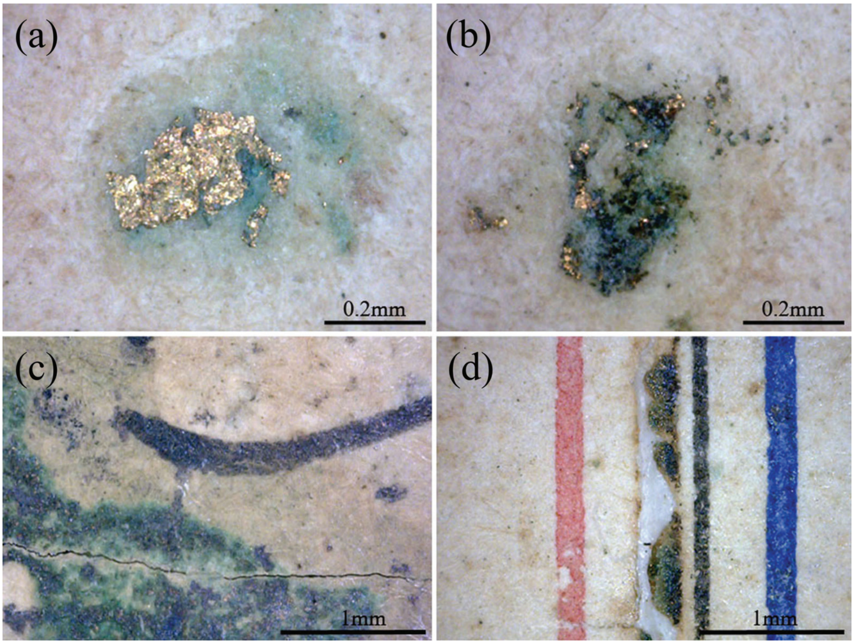

Figure 4: Microscopic views of paper degradation: (a, b) discolouration in surrounding paper of the fine particles of gold leaf in *Golšan-e rāz* manuscript, (c) tearing and discolouration of paper in illuminated area in *Bayāż* manuscript and (d) tearing and crumbling of paper in the frame around the text in *Qur'an* manuscript

3.2 Original composition of the golden pigment

In some areas, as the microscope images show, a few bright golden particles among greenish residues or altered golden particles can be seen. Therefore, SEM–EDS analysis was used to identify the chemical composition of unaltered golden particles (see Appendix). Although only small amounts of material were available, the samples were collected from various illuminations of the three manuscripts. SEM–EDS analyses showed that copper (Cu), zinc (Zn) and tin (Sn) are the main components in the pigments applied to the manuscripts (Table 1). Identified golden particles had an average of 81–90 wt% copper, 4–10 wt% zinc and 2–7 wt% tin. Also, small amounts of lead (1–3 wt%) in *Golšan-e rāz* and

Qur'an manuscripts and gold (up to 1 wt%) in *Qur'an* manuscript were present in addition to the main elements. According to SEM–EDS analyses, it can be presumed that a ternary alloy with a composition close to brass had been used instead of the expected gold pigment. Small amounts of lead and especially gold can be considered as impurities in the initial ore sources, even if the amount of lead in *Golšan-e rāz* manuscript (ca. 3 wt%) can be attributed to an intentional use of the metal in the alloy. A SEM image (Figure 5) of golden

Table 1: Results of the SEM–EDS analyses of golden illuminations on manuscripts

Manuscripts	Decorations	Cu (%)	Zn (%)	Sn (%)	Au (%)	Pb (%)	Total wt%
Bayāż	*Frame*	81.88	10.52	7.60	–	–	100.00
	Inter lines	86.47	7.29	6.24	–	–	100.00
Golšan-e rāz	*Frame*	90.12	4.88	2.01	–	2.99	100.00
	Gold-sprinkled	81.18	10.07	5.82	–	2.93	100.00
Qur'an	*Frame*	90.94	6.10	2.06	–	0.90	100.00
	Heading	83.16	9.08	4.84	1.02	1.90	100.00

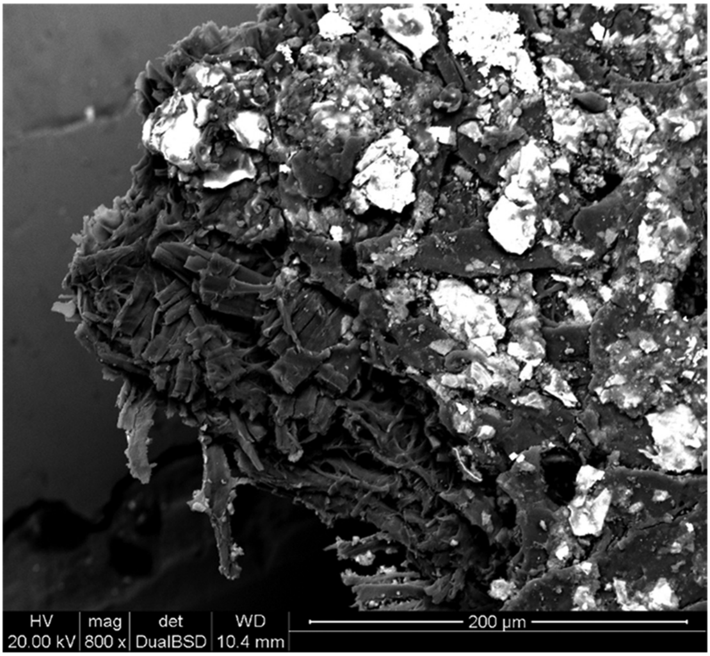

Figure 5: Backscattered electron (BSE-SEM) image of altered and unaltered golden metallic powders on the fibres of paper as a support

powder showed the original metal grains (lighter particles) and also altered metal grains (darker particles). Golden powders are seen as small pieces of metal leaf or metal chips that have been squeezed together.

3.3 Greenish compounds as alteration products

Raman spectroscopy was selected to recognize the nature of the greenish compounds present in the illuminated areas (for analytical details, see Appendix). Raman spectroscopy is highly applicable in the identification of pigments in paintings and illuminated manuscripts and also in the investigation of degradation of pigments (Stuart 2007). Therefore, microscopic samples of the altered illuminations in manuscripts were collected for Raman analysis. Initial results proved that the original nature of the greenish material is organic. The interpretation of the Raman spectra generally expressed the existence of organic salts of copper due to the possible conversion of metallic copper to copper carboxylates. Figure 6 shows the obtained Raman spectrum of the greenish product in *Bayāż* manuscript. Its spectral wave numbers and relative intensities have been assigned in Table 2.

At first, the organic nature of the compound is supported by two bands occurring at 2,850 and 2,896 cm^{-1} which are assigned to –CH stretching. A further band at 1,440 cm^{-1} is assigned to –CH bending and bands occurring at 1,299 and 1,582 cm^{-1} are assigned to $-COO^-$ groups. Another remarkable band occurs at 415 cm^{-1} and is assigned to –Cu–O bond. A weak band that occurs at 957 cm^{-1} and is assigned to –C–C bond; the low intensity of this band may suggest that formate could be the main carboxylate present. Therefore, the Raman spectrum of the greenish products in *Bayāż* suggests that the greenish product is mainly composed of copper formate ($HCOO^-Cu^+$), with minor contribution of copper acetate ($CH_3COO^-Cu^+$).

In another instance, a Raman spectrum from the greenish products on *Golšan-e rāz* (Figure 7) was obtained which was not as good as the spectrum of *Bayāż*, but at least the presence of copper formate could be hypothesized. A Raman spectrum from the greenish products on *Qur'an* (Figure 8) showed that we are facing a compound which is a mixture of copper formate/acetate, and hence, chemically, these greenish products are notably close to the greenish products in *Bayāż* manuscript. In Raman analyses it was observed that bands in the spectra are slightly broad, while usually Raman bands are sharp. This may be due to two main features in greenish compounds: firstly, we are facing scarcely crystalline compounds and/or secondly, there are varied/mixed organic compounds, so that the bands of the different compounds build up broad bands.

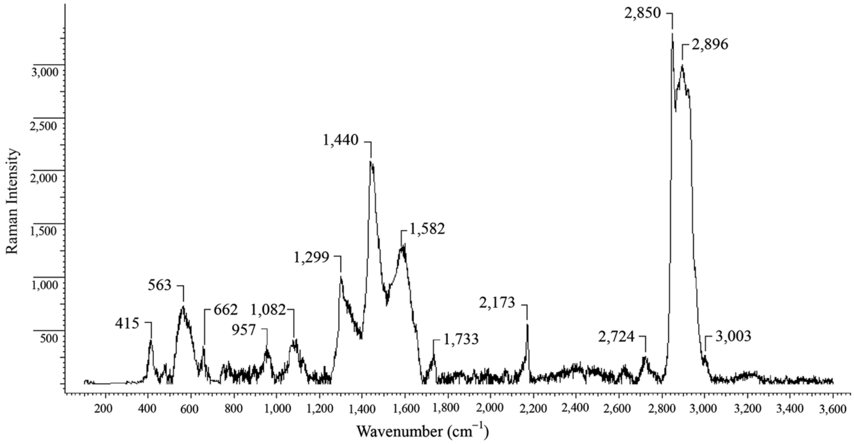

Figure 6: Raman spectrum of the greenish products in *Bayāż* manuscript

Table 2: Spectral wave numbers and relative intensities in the Raman spectrum of the altered pigment in *Bayāż* manuscript (W: weak, VW: very weak, M: medium, S: strong, VS: very strong and SH: shoulder)

No	cm^{-1}	Intensity	Vibrational mode assignment
1	415	W	Cu–O carboxylate stretching
2	563	W	Cu–water vibration
3	662	VW	Unassigned
4	957	VW	Possible acetate C–C symmetric Stretching
5	1082	W	Unassigned
6	1,299	M	Formate OCO symmetric stretching
7	1,440	S	Formate CH in-plane bending
8	1,582	M	Formate OCO asymmetric stretching
9	1,733	VW	Unassigned
10	2,173	W	Unassigned
11	2,724	VW	Formate 2 × OCO symmetric stretching
12	2,850	VS	Formate CH stretching
13	2,896	VS	Formate CH stretching
14	3,003	SH	Possible acetate CH stretching

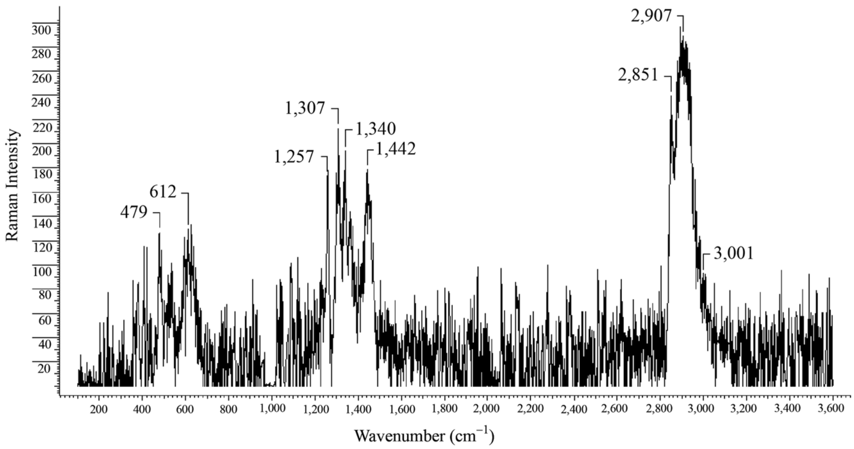

Figure 7: Raman spectrum of the greenish products in *Golšan-e rāz* manuscript

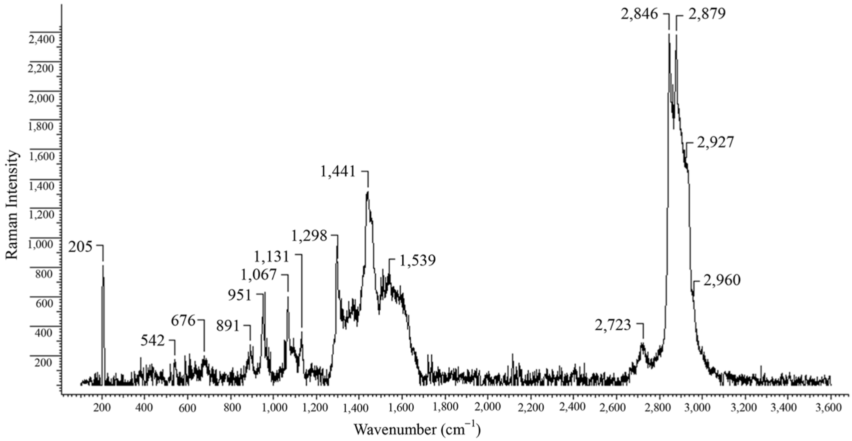

Figure 8: Raman spectrum of the greenish products in *Qur'an* manuscript

4 Discussion

4.1 Brass alloy as golden pigment (gilding imitation)

SEM–EDS analyses showed copper, zinc and tin as the main elements of golden metallic pigments. Accordingly, the use of a ternary alloy (Cu–Zn–Sn) with low amounts of lead and gold in some cases was identified. As suggested by their bad state of preservation, no significant amounts of gold were found in the studied illuminations. On the other hand, brass with appreciable quantities of tin was used for producing golden metallic pigments. Tin is one of the common alloying elements present in the composition of brasses: its presence improves mechanical properties of brasses in such a way that Cu–Zn–Sn alloys have an excellent cold workability (ASM Handbook 1992; Vilarinho et al. 2004).

By SEM–EDS, such discoloured illuminations based on brass alloy pigments as gilding imitations have been identified in Armenian and Persian–Turkish illuminated manuscripts belonging to the sixteenth and eighteenth centuries, respectively, (Banik 1983). The gilding material has been introduced as α-brass. Also, Aceto et al. 2006, 2010) found brass alloy pigments on some ninth- to tenth-century Italian manuscripts by inspecting tarnished gilding imitations. In their studies, X-ray fluorescence (XRF) spectroscopy revealed that the golden painted areas were actually made of copper–zinc alloy with traces of gold and lead in some cases. They believe that brass alloy pigments were used as a cheap substitute for gold pigments and were possibly a typical pigment of the ninth to tenth centuries among Italian illuminators. It is difficult to confirm how intensive the use of copper alloy pigments had been as a substitute for gold in Persian manuscripts due to the fact that few analytical studies on illuminated manuscripts have been done. Also in conservation studies, owing to luminosity and intactness of golden illuminations in many historic documents, there was possibly no reason to analyse them and therefore golden illuminations have been taken as genuine gold pigments in many cases. Hence, tarnishing of the golden illumination was the first reason why we have analysed the golden illuminations in the manuscripts.

Scott (2002) has mentioned that if brass alloy powder had been preserved and remained untarnished, such items could be only distinguished from gold by chemical analysis. In addition to gold and silver as prevalent metal pigments, very occasionally bronze and copper have been mentioned in old treatises on painting (Porter 2011). Also, preparation techniques of copper alloys as pigment have been described in the same procedure as for silver and gold powders. In one of the best known procedures for gold powder in old Persian treatises (Mayel Heravi 1993) it has been explained that first a piece of gold foil or a gold bar was placed between layers of animal skin and then it was beaten until it became very thin, obtaining a gold leaf. Subsequently, the gold leaf was ground with honey in a mortar for a while and then the honey was washed away by warm water. The acquired gold powder should be processed preferably with gelatine or gum Arabic as a binder. In general, zinc and tin in brass pigments have undeniable effects on the proper golden colour, on the malleability properties for leaf making and also with regard to better corrosion resistance. These features have been probably discerned by former colour makers. Scott (2002) has mentioned that gold-coloured brass alloys could be beaten into thin foils or leaves, which is often called by the misnomer "*bronze powder*". In other sources (Gettens and Stout 1966; Eastaugh et al. 2004) it has also been stated that brass powder was often named "*bronze powder*" by mistake. Nevertheless, in some cases, copper–tin alloys had been possibly used for bronze powder. In addition to their gold-like visual appearance, high malleability for preparing thin leaves and also economical reasons could justify the use of brass alloy as a low-cost, convenient alternative to gold.

4.2 Formation of copper carboxylates as degradation products

Raman analysis suggested the presence of two kinds of copper carboxylates: copper formate and possibly copper acetate. These compounds which mostly formed the greenish products are the result of an alteration of the metal pigment. Based on the alteration products, different agents can contribute to the alteration processes of the golden illuminations.

In a similar research, Aceto et al. (2010) have also recognized copper carboxylates as degradation residues on brass alloy pigments used in the illumination and in the text of a ninth-century Italian manuscript. These compounds were considered to be responsible for a greenish aspect of golden illuminations. It was hypothesized that these compounds are the results of the interaction of copper with carboxylic acids. In numerous studies, copper carboxylates, especially copper formate and copper acetate, have been identified as corrosion products of copper-based artefacts in museums and collections (Scott 2002).

The scientific examinations have proved that various levels of most common organic carbonyl pollutants such as formaldehyde, acetaldehyde, formic acid and acetic acid, collectively known as volatile organic compounds (VOCs), play a major role in the formation of copper carboxylates (Hatchfield 2005). Most of the pollutants have been identified in museum environments; they principally off-gas from man-made products applied in display and storage equipment. Consequently, inside museums these pollutants can be emitted from paints, board, carpets and cleaners, as well as many other materials and products. Grzywacz (2006) mentioned that formaldehyde has been identified in the highest concentration of four organic carbonyl pollutants in the majority of the sampled locations. It is usually used in adhesives and coating of wood products, most notably urea–formaldehyde resins. Formaldehyde and acetaldehyde (as aldehyde) are risks for collections because they are easily oxidized to carboxylic acids. For example, formaldehyde turns into formic acid in the presence of water; hence high relative humidity (RH) can substantially influence and ease the degradation processes by organic carbonyl pollutants (Grzywacz 2006).

Unfortunately, no certified reports are available concerning the previous condition of the manuscripts in the studied repository, so the pollutant sources which were in fact responsible for the expected VOCs cannot be distinguished. It should be noted that although many VOCs contain carbonyl groups, the organic carbonyl pollutants which are of primary concern to museums are formaldehyde, acetaldehyde, formic acid and acetic acid. Concerning the humidity – as an effective factor in alteration processes – it can be stated that wrinkles, distortions and also water stains on most of the paper support imply that the manuscripts have been possibly stored in an environmental condition with high humidity levels for an extended period of time.

A definite difference should be considered between the destructive effect of organic carbonyl pollutants on the alloy pigments and the other kinds of cultural materials, especially metal objects. For example, unlike a copper alloy object which has been directly exposed to polluted air, copper alloy pigments have been trapped among the paper leaves of the manuscripts. For this reason, the manuscripts can be considered as an absorbent for pollutants, and thus paper as support for pigment plays a significant role in the alteration process by trapping the organic carbonyl pollutants. High RH of the environment not only accelerates the reaction rate between the objects and the pollutants (Hatchfield 2005), but also can have a role in the transport of pollutants into the fibre (Banik and Brückle 2011). Accordingly, paper as support plays an important and undeniable role in alteration process of the copper alloy pigments; also, in a reciprocal interaction, paper has been decomposed by metal-catalysed degradation due to the migration of copper ions to paper matrix.

The cellulose chain breaking that can be triggered as a consequence of oxidation is the most direct effect of oxidative ageing which causes apparent damage as the so-called corrosion of paper by copper, iron or other oxidative catalysts in pigments and impurities. In addition, oxidation of cellulose has secondary effects on increase of the hydrolysis rate (Banik and Brückle 2011). Oxidation reactions of cellulose mainly form carbonyl groups from the hydroxyl groups (on the glucose units) and the carbonyls may then oxidize further to carboxylic acids (Banik and Brückle 2011; Hoshi and Kitada 2002). For this reason, formation of copper carboxylates may result from acids which had been produced in the cellulose by oxidation of the hydroxyl group.

De Bruin et al. (2008) have described that a variety of low molecular weight products are formed, several of which are volatile and thus have an increased mobility not only within the material, but also within a collection. They have summarized the numerous exogenous factors (such as humidity, temperature and pollution) and endogenous factors (such as pH, metal ions and degradation products) influencing cellulose degradation. As a consequence, volatile degradation products (VOCs) can be both emitted and absorbed by paper. However, since acidic carboxyl groups are formed during the oxidation of cellulose, the hydrolytic degradation of cellulose in the presence of acidic components of endogenous or exogenous origin could be a further damaging factor (Meyer and Neumann 2009).

5 Conclusions

The aim of this research was to study the unusual alteration in golden illuminations in some Persian manuscripts. In this study, the use of copper alloy pigments as gilding imitation has been proved in three eighteenth- to nineteenth-century illuminated manuscripts, a feature which had been previously recognized in only a few cases. Due to the lack of analyses on Persian manuscripts, it is not possible to estimate the prevalence of such alloy pigments in a single period. The peculiar characteristic in the manuscripts was the conversion of metallic copper pigments into greenish residues and in some areas degradation of papers could be seen in the form of brownish discolouration, brittleness and even perforation of the papers in the vicinity of the pigments. Therefore, the evidences of paper damages in these samples are remarkably similar to degradation of paper by green copper pigment (verdigris). Recognition of probable alteration processes assists in diminishing of rate of alteration. Reduction of pollution risk by decreasing sources of organic carbonyl pollutants and methodical monitoring of the indoor air quality in museum environments and also preparing proper RH can help to achieve the goals of preventive conservation. However, for further developments we will need to consider artificially ageing on model samples in the course of particular alteration conditions, by exposing the samples to organic carbonyl pollutants such as formaldehyde, formic acid and acetic acid, either separately or in combination, and also under the different RH and temperature.

Acknowledgements: The authors thank the Soltanabad museum of Arak (Iran) for providing the historical manuscripts that were studied in the present work. We would like to thank Maryam Karbasi, Material Engineering Faculty, Isfahan University of Technology (Iran), for SEM–EDS analyses. Our sincere thanks go to Professor Dr Gerhard Banik for his generosity in sending his useful articles relating to copper-based pigments.

Appendix: Analytical methodology

Microscopic examination (Optical microscope)

A digital microscope was used for preliminary, superficial inspection of the golden illuminations and visual features of altered pigments. Model of the digital microscope is *AM 313 T Dino-Lite Plus*. The AM 313 T hand-held digital microscope has variable magnification depending on distance and can view up to 200 $\times$.

SEM–EDS

Study of original composition of golden pigments was carried out with scanning electron microscope coupled with energy-dispersive spectroscopy analyser (SEM–EDS). Small flakes of each of the samples were mounted on carbon pads on aluminium stubs. The micrographs were obtained using SEM *LEO 1450VP* model, with an accelerating voltage of 20 keV, at high vacuum mode and backscattered electron detector. Microanalysis was performed to identify the weight percentage of elements using *Oxford INCA* EDS analyser. Carbon was used for coating of samples instead of gold because in EDS analysis the peaks from the gold coating may mask those of other available elements.

Raman spectroscopy

Raman spectra have been collected with a high-resolution dispersive *Jobin Yvon – Horiba (Villeneuved'Ascq, France) LABRAM HR* model Raman spectrophotometer. The instrument is equipped with 532, 633 and 785 nm excitation lasers; 600 and 1,800 lines/mm dispersive gratings; an 800 mm path monochromator and a Peltier-cooled charge-coupled device detector. In this work, 532 and 633 nm excitation lasers and 600 lines/mm grating were used. The optical arrangement on the instrument gave a spectral resolution of about 4 cm^{-1}. Spectra have been taken by placing the sample on the microscope stage and observed using long working distance 50 $\times$ and 80 $\times$ objectives. Laser power has been used with high filtering attenuation in order to avoid thermal ashing of the irradiated area on the sample. In particular, analysis on the green patinas was performed with 1% laser power. Spectra have been collected with long exposure times (120 s) with five replicates in order to improve the signal/noise ratio.

References

Aceto, M., A. Agostino, E. Boccaleri, F. Crivello, Cerutti Garlanda, A.: *Evidence for the degradation of an alloy pigment on an ancient Italian manuscript*. Journal of Raman Spectroscopy 37 (2006): 1160–1170.

Aceto, M., Agostino, A., Boccaleri, E., Crivello, F., Cerutti Garlanda, A.: *Identification of copper carboxylates as degradation residues on an ancient manuscript*. Journal of Raman Spectroscopy 41 (2010): 1434–1440.

ASM International Handbook Committee: *Vol. 2 of Properties and Selection: Nonferrous Alloys and Special-Purpose Materials*. Materials Park, OH: American Society for Metals (ASM) International, 1992.

Banik, G.: *Mikroanalytische Untersuchung von Vergoldungsmaterialien in der Buchmalerei*. Mikrochimica Acta I (1983): 23–28.

Banik, G.: *Discolouration of green copper pigments in manuscripts and works of graphic art*. Restaurator 10 (1989): 61–73.

Banik, G.: *Green Copper Pigments and their Alteration in Manuscripts or Works of Graphic Art*. In: Pigments et colourants de l' Antiquité et du Moyen Age, Editions du Centre national de la recherche scientifique, Paris: CRNS, 1990:89–102.

Banik, G., Brückle, I.: *Paper and Water: A Guide for Conservators*. Oxford: Butterworth-Heinemann, 2011.

Banik, G., Stachelberger, H., Mairinger, F., Vendl, A., Ponahlo, J.: *Analytical investigations of the problem of "Kupferfraß" in illuminated manuscripts*. Mikrochimica Acta 75 (1981): 49–55.

Burgio, L., Clark, R. J. H., Muralha, V. S. F., Stanley, T.: *Pigment analysis by Raman microscopy of the non-figurative illumination in 16th- to 18th-century Islamic manuscripts*. Journal of Raman Spectroscopy 39 (2008): 1482–1493.

Caffaro, A., Falanga, G.: *Il papiro di Leida. Un documento di tecnica artistica e artigianale del IV secolo d.C.* Salerno: ARCI Postiglione, 2004.

Clark, R. J. H., Mirabaud, S.: *Identification of the pigments on a sixteenth century Persian book of poetry by Raman microscopy*. Journal of Raman Spectroscopy 37 (2006): 235–239.

De Bruin, G., Steemers, T., Strlič, M., Kolar, J., Kralj Cigić, I.: *Knowledge transfer from a stakeholder perspective, research on organic volatiles in archival collections meets practice*. In: *Preprints*, 8th European conference on research for protection, conservation and enhancement of cultural heritage. Ljubljana: National and University Library, 2008.

Eastaugh, N., Walsh, V., Chaplin, T., Siddall, R.: *The Pigment Compendium*. London: Butterworth-Heinemann, 2004.

Floor, W.: *Traditional Crafts in Qajar Iran*. Santa Ana, CA: Mazda Publishers, 2003.

Gettens, R. J., Stout, G. L.: *Painting Materials: A Short Encyclopedia*. New York: Dover Publications, 1966.

Grzywacz, C. M.: *Monitoring for Gaseous Pollutants in Museum Environments*. Los Angeles, CA: The Getty Conservation Institute, 2006.

Hatchfield, P. B.: *Pollutants in the Museum Environment*. London: Archetype Publications, 2005.

Hoshi, E., Kitada, M.: *Effects of Copper on Degradation of Japanese Wood-Block Printing Paper of the Late Edo Era and Modern Japanese Paper*. In: Preprints, *Baltimore Congress*. London: IIC, 2002.

Mayel Heravi, N.: *Ketabara'I dar Tamaddon-e Eslami*. Mashhad (Iran): Astan-e Qods-e Razavi, 1993.
Meyer, F., Neumann, A.: *Recombinant Proteins: A new material for the chemical stabilization of copper pigment corrosion on paper*. Restaurator 30 (2009): 96–130.
Porter, Y.: *Painters, Paintings and Books: An Essay on Indo-Persian Technical Literature 12–19th Centuries*. Translated by Z. Rajabi. Tehran: Matn Publishers, 2011.
Purinton, N., Watters, M.: *A study of the materials used by medieval Persian painters*. Journal of the American Institute for Conservation 30 (1991): 125–144.
Scott, D. A.: *Copper and Bronze in Art- Corrosion, Colourants, Conservation*. Los Angeles, CA: The Getty Conservation Institute, 2002.
Stuart, B. H.: *Analytical Techniques in Materials Conservation*. New York: John Wiley & Sons, 2007.
Vilarinho, C., Soares, D., Castro, F.: *Contribution to the knowledge of the Cu-Sn-Zn system for compositions close to brass alloys*. Journal of Alloys and Compositions 379 (2004): 161–165.

Zusammenfassung

Identifikation und analytische Untersuchung von Kupferlegierungspigmenten, die in drei Persischen Manuskripten als goldene Illuminationen verwendet wurden

Goldfarbene Pigmente gehören zu den am meisten verwendeten Farbmitteln in illuminierten, persischen Handschriften. In dieser Untersuchung wurden die goldfarbenen Pigmente in drei persischen Manuskripten aus dem 18. und 19. Jahrhundert untersucht. In einem ersten Schritt wurden mittels Rasterelektronenmikroskopie (REM) mit energiedispersiver Spektrometrie (EDS) verschiedene Pigmente metallischen Ursprungs identifiziert. Einige davon sind tertiäre Legierungen, die aus Kupfer, Zink und Zinn bestehen, somit also Legierungen auf Kupferbasis sind, die als billige Alternativen zu Gold verwendet wurden. Die untersuchten Pigmente haben ihr metallisches Erscheinungsbild verloren und liegen nun als grünliche Überreste in den Manuskripten vor. Darüber hinaus wurden die grünlichen Partikel auf den vormals goldenen Illuminationen mittels Ramanspektroskopie untersucht. Kupfercarboxylate wurden als Abbauprodukte identifiziert. Wir sind zu der Schlussfolgerung gelangt, dass diese Veränderungen durch ein Zusammenwirken von Kupferlegierungspigmenten und Carboxylsäuren aus Celluloseabbaureaktionen bei erhöhter Luftfeuchtigkeit entstanden sein müssen. Darüber hinaus verursachte der Abbauprozess Verfärbungen, Versprödungen und ein langsames Zerfallen des Papiers in den illuminierten Bereichen. Diese Schadensphänomene im Papier sind vergleichbar mit jenen Abbauprozessen, wie sie auch durch Kupfergrünpigmente in historischen Dokumenten und Miniaturen beobachtet werden können.

Resumé

Identification et examen analytique des pigments faits d'alliages de cuivres appliqués comme enluminure dorée sur trois manuscrits persans

Les pigments dorés sont parmi les colorants les plus couramment utilisés dans les manuscrits enluminés persans. Au cours de ce projet de recherche, les pigments dorés de trois manuscrits du 18ème au 19ème siècle ont été étudiés. Initialement, l'observation par microscopie électronique à balayage-spectrométrie par dispersion d'énergie (SEM–EDS) a montré que différents types de pigments métalliques étaient présents et que certains d'entre eux étaient des alliages ternaires constitués de cuivre, de zinc et de l'étain; cela permet d'établir le fait que les alliages à base de cuivre représentaient certainement une alternative bon marché à l'or. La décoloration du pigment était visible dans les manuscrits à cause de l'altération des pigments métalliques en résidus verdâtre. Par la suite, les produits verdâtres contenus dans les pigments dorés ont été étudiés par spectroscopie Raman. Des carboxylates de cuivre ont été identifiés comme produits de dégradation. Il en a été déduit que cette dégradation est une conséquence de l'interaction entre les pigments de l'alliage de cuivre et les acides carboxyliques, ceux-ci étant les produits de dégradation de la cellulose dans des conditions de forte humidité. De plus, une dégradation plus avancée a progressivement causé une décoloration, une fragilité et un effritement du papier dans les zones peintes. Les signes de dégradation dans le papier étaient comparables à ceux de la décomposition du papier due à des pigments de cuivre verts tels que le vert-de-gris présents sur des documents historiques et des miniatures.

Authors

Sayed Mohammadjavad Mousavi received his BA in conservation and restoration of historic and artistic works at the Art University of Isfahan in Iran in 2008. In 2011 he obtained his MA degree from the Art University of Isfahan. His master thesis was focused on degradation process of gilding imitations and its effects on paper substrate in some of the illuminated manuscripts. He is specialized in paper conservation and interested in scientific studies on archival and graphic artworks. He has participated in several projects regarding the conservation–restoration of paper and parchment artefacts.

Hossein Ahmadi obtained his BA in conservation and restoration of cultural properties at the Art University of Tehran in Iran in 1994 and also obtained his

MA in Conservation of historic–cultural objects at the Art University of Tehran in 1997. In 2009 he received his PhD degree from Polytechnic University of Valencia in Spain for his studies on conservation and consolidation of mosaic tiles. He is currently an assistant professor and director of PhD group of Department for conservation of historic–cultural objects in Art University of Isfahan.

Abbas Abed-Esfahani obtained his BSc in chemistry in 1986 and his MSc in analytical chemistry from Isfahan University in Iran in 1990. Since 2008 he is studying as PhD candidate in conservation of historic and cultural properties at the Art University of Isfahan (Iran). Since 1991 he is lecturing chemistry and instrumental methods of analysis at the Isfahan Azad University (Khorasgan) and Art University of Isfahan. His interests focus on diagnosis in the field of cultural heritage conservation and chemical analysis of historic and artistic objects.

Mohammad Mortazavi received his BA in conservation and restoration of historic and artistic works at the Art University of Isfahan in Iran in 2004. During his studies, he worked as an intern in some World Heritage Sites in Iran. In 2006 he received his MA degree from the Art University of Isfahan for his diagnostic studies on tinned copper objects belong to the National Museum of Iran. In 2013 he received his PhD degree from the Art University of Isfahan for his studies on the original surface and conservation of archaeological copper-based artefacts. In 2013 he joined the Faculty of Conservation at the Art University of Isfahan. Besides teaching conservation of archaeological metal treatises he has worked for a number of major museums in Iran and contributed his expertise to research projects.

Maurizio Aceto graduated in chemistry in 1988 at the Università degli Studi di Torino (Italy), where afterwards he earned a doctoral degree in Scienze Chimiche in 1993. In 1997 he became research assistant at the Università degli Studi del Piemonte Orientale in Alessandria (Italy), where he teaches courses in the field of analytical chemistry. His main research interests deal with characterization of painting artworks, with particular concern to miniature painting, using non-invasive and non-destructive techniques such as Raman spectroscopy, FORS, spectrofluorimetry and XRF spectrometry; in this field he collaborates with several libraries and museums. He utilizes analytical information resulting from diagnostics to improve knowledge about the chronology of the use of pictorial materials in painting. He is author of more than 90 publications on national and international journals.