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FULL PAPER

CHARACTERISATION OF COLOURANTS ON A 15TH CENTURY ARMENIAN MANUSCRIPT BY MEANS OF DIFFERENT SPECTROSCOPIC TECHNIQUES

Yeghis Keheyan[1*], Maurizio Aceto[2], Elisa Cala[2], Monica Gulmini[3], Ambra Idone[3]

1. CNR, c/o Dipartimento di Chimica, piazzale Aldo Moro, 5 - Rome, Italy

2. Dipartimento di Scienze e Innovazione Tecnologica, Università degli Studi del Piemonte Orientale, viale T. Michel, 11 – 15121 Alessandria, Italy

3. Dipartimento di Chimica, Università degli Studi di Torino, via P. Giuria, 7 - 10125 Torino, Italy

* corresponding author:
yeghis.keheyan@uniroma1.it

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Abstract

This contribution illustrates the results from the technical study of a 15th century Armenian illuminated manuscript produced at Aghtamar Island (Vaspurakan region, historic Armenia), presently kept in the collection of Matenadaran ancient manuscript museum, in Yerevan. Fifteen fragments taken from different miniatures in the manuscript were analysed by means of UV-Visible diffuse reflectance spectrophotometry with optic fibres (FORS), fluorimetry, Raman spectroscopy, SERS and SEM-EDX. The combination of molecular and elemental techniques allowed the characterisation and identification of colourants used in miniatures; these were carbon, cinnabar, indigo, iron-gall ink, orpiment, red lead, ultramarine blue, vergaut and white lead. A pink dye was assigned to lac dye according to preliminary measurements. The goal was to compare the results with a previously analysed 14th century manuscript coming from the same region: were the same colourants used or not?

1 Introduction

Illuminated manuscripts are among the most valuable artworks and the comprehension of their value can be only improved by the knowledge concerning the pictorial materials involved in the decoration. They also are among the most fragile artworks, so that their preservation is a challenging task for conservators and curators. A major contribution to both aspects can be given by chemical analysis, which allows obtaining different kinds of information.

In a recent paper[1], results of detailed analyses of the 14th century manuscript n. 4915, belonging to the Matenadaran collection in Yerevan (Armenia), were given. In this paper we have reported the results of analyses of the miniatures of a 15th century manuscript 1448 from the same collection, in order to compare the differences of palettes and to evaluate changes after one century in miniature painting in the same region, that is Aghtamar Island, Vaspurakan region, historic Armenia. The manuscript is written on paper with 324 pages and has a wood binding covered in leather and decorated with silver crosses and three fragments of talismans. The size of the manuscript is 18.5x27x 8.5 cm. According to the tradition, this manuscript is considered as good-luck charm. It contains 13 thematic miniatures at ff. 1b, 2, 2b, 3, 3b, 4, 4b, 5, 5b, 6, 6b, 7 and 7b; 10 representations of altars at ff. 8b, 9, 9b, 10, 10b, 11, 11b, 12, 12b and 13; the figures of Evangelists at ff. 13b, 103b, 158b and 251b; 4 frontispieces at ff. 13, 104, 159 and 252.

The rhythm of line and light, characteristic for Vaspurakan miniatures, and even more evident when placed on background of white paper, can be linked to the direct influence of folk art techniques. Though the number of colours is limited, they are used by means of skilful combination. Thanks to different degrees of saturation and the specific selection of hues, a very special range of colours is attained, unusual in its expressiveness and poetic mood. In works by miniature painters of the 14th-15th centuries, line and colour acquire more and more obvious functional significance, helping to express themes, to reveal their essence. Painters exploit more resources of plastic line and half-tints of colour which, of course, is the result of the influence of other schools of Armenian miniatures.

2 Experimental

2.1 Discussion of Analytical Techniques

In order to characterise the whole palette of the manuscript, so being able to compare it with ms. n. 4915 from the same collection and more extensively with known data on Armenian miniature painting, some micro samples were taken from the manuscript during a restoration intervention. From the analytical point of view, the availability of micro-samples is an enormous advantage over pure non-invasive analysis because a wide range of measurements can be carried out. Among those that can work on a micro-scale, Raman analysis and Scanning Electron Microscopy - Energy Dispersive X-ray spectroscopy (SEM-EDX) are examples of techniques yielding respectively molecular and elemental information, with a diagnostic power far higher than non-invasive techniques. The combination of Raman and SEM-EDX spectroscopies seems to be suitable to provide the information needed for the characterisation of colourants on a manuscript.

In particular, the use of Surface Enhanced Raman Spectroscopy (SERS) is highly specific and efficient in the identification of organic colourants (dyes and lakes) which is usually hard to be achieved with conventional Raman spectroscopy as well as with other spectroscopic techniques; the identification of dyes, in fact, is generally carried out with high efficiency with chromatographic techniques, but this usually involves a larger amount of sample, a condition which is rarely available as far as manuscripts are concerned. Indeed, HPLC-PDA-MS analysis can be performed on very tiny samples, even smaller than 1 mm^2, but it requests more manipulation to put the sample in proper analytical conditions. SERS analysis can be performed on samples smaller than 1 mm^2 and usually it just requests pouring a drop of silver nanoparticle colloid on the sample. In the last years several publications have been devoted to SERS analysis of dyes and lakes on cultural heritage items, so that a large amount of information is available[2-5].

The analysis of ms. 1448 from Aghtamar Island was therefore carried out on micro-samples detached from the miniatures, choosing areas in which the withdrawal of coloured matter had minimal visual impact. A total of 15 samples were taken, covering the different hues present in the palette. In cases where the samples were large enough ($\geq$ 1 mm^2), UV-Visible diffuse reflectance spectrophotometry with optic fibres (FORS) and fluorimetry were used to yield preliminary diagnostic information.

2.2 Sampling of the Manuscript

In order to determine the palette used in the decoration of this manuscript, micro-samples were taken from painted areas. A total of 15 samples were analysed, covering all hues represented in the miniatures. Micro-samples of paint were taken from the manuscript by means of a scalpel. The diameter of the samples ranged from 0.2 to 1 mm. The list of samples is reported in Table 1.

Sample n.	Folio	Colour
001	front binding	silver
002	1b	dark blue
003	1b	red
004	1b	yellow
005	2	dark blue
006	2	orange
007	1b	black
008	3	grey-blue
009	6	yellow
010	3b	black
011	5	pink
012	4b	red
013	6	pink
014	8b	pink
015	3	violet

Table 1: List of samples taken from ms. 1448

2.3 Raman Spectroscopy

Raman spectra were collected with a high-resolution dispersive Horiba (Villeneuve d'Ascq, France) LabRAM HR model spectrophotometer coupled with a confocal microscope. The instrument is equipped with a 633 nm excitation laser, two (600 and 1800 lines/mm) dispersive gratings, an 800 mm path monochromator and a Peltier cooled CCD detector. The optical arrangement gave a spectral resolution of about 2cm^{-1}. Spectra were taken placing samples on the microscope stage and observing them with long working distance 20x, 50x and 80x objectives. The sampled area was identified and focused using either a video camera or the microscope binoculars. Laser power at the sample was initially kept low (< 100μW) by means of a series of neutral density filters, in order to prevent any thermal degradation of the molecules, then gradually increased up to the optimal signal-to-noise ratio. Exposure time was 1-120 seconds according to needs. The system was managed with LabSpec 5 software running under Windows XP.

2.4 Preparation of SERS Substrates

For SERS analysis, a colloidal paste of silver nanoparticles was prepared. Reagents and solvents (nitric acid, hydrochloric acid, methanol, silver nitrate and sodium citrate dihydrate) were purchased from Carlo Erba reagents (Arese, Italy); Ultra high quality (UHQ) water was obtained by means of a Millipore (Darmstadt, Germany) Direct-q 3 system. The preparation of Ag colloidal pastes was carried out following the procedure described elsewhere[6] which is based on the Lee and Meisel reduction of silver nitrate[7]. The analysis of the fragments from the manuscript was performed directly on the sample, by pouring on it 1 μl of Ag colloidal paste and allowing to dry before exposing the sample to the laser beam.

2.5 UV-Visible Diffuse Reflectance Spectrophotometry with Optic Fibres (FORS)

FORS analysis was performed with an Avantes (Apeldoorn, The Netherlands) AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light source; detector and light source are connected with fibre optic cables to a 1.5 mm diameter FCR-7UV200-2-1,5x100 probe. Incident and detecting angles were 45° from the surface normal, in order to exclude specular reflectance. The spectral range of the detector was 200-1160 nm. The best spectra resolution of the system, calculated as FWHM, was 2.4 nm. Diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile, guaranteed to be reflective at 98% or more in the spectral range investigated. The investigated area on the sample was 1 mm diameter. In all measurements the distance between probe and sample was 1 mm. To visualise the investigated area on the sample, the probe contained a USB endoscope. The instrumental parameters were as follows: 10 ms integration time, 100 scans for a total acquisition time of 1 s for each spectrum. The system was managed by means of AvaSoft™ 8 software running under Windows 7™.

2.6 Fluorimetry

An Ocean Optics (Dunedin, Florida, USA) Jaz model spectrophotometer was employed to record molecular fluorescence spectra. The instrument was equipped with a 365 nm Jaz-LED internal light source; fibre optic cables to an FCR-7UV200-2-1,5x100 probe were used to drive excitation light on the sample and to recover the emitted light. The spectrophotometer worked in the range 191-886 nm; according to the features of the monochromator (200 μm slit width) and detector (2048 elements), the spectral resolution available was 7.6 nm calculated as FWHM. The investigated area on the sample was 1 mm in diameter. In all measurements the sample-to-probe distance was kept constant to 12 mm, corresponding to the focal length of the probe. To visualise the samples, the probe was equipped with a USB endoscope. Instrumental parameters were as follows: 2 s integration time, 3 scans for a total acquisition time of 6 s for every spectrum. The system was managed with SpectraSuite™ software under Windows 7™.

2.7 SEM-EDX Spectrometry

SEM images at different magnification were recorded on a Quanta 200 FEI (Hillsboro, Oregon) Scanning Electron Microscope equipped with EDAX (Mahwah, New Jersey) EDS attachment, using a tungsten filament as electron source at 20 KeV. The instrument was used in E-SEM mode (90 mbar of water pressure in chamber) in order to avoid samples metallisation.

3 Results and Discussions

Most of the colourants were identified by means of conventional Raman spectroscopy; in the case of dyes, instead, SERS analysis was successful in identifying the exact type. One relevant feature given by the availability of micro-samples is that it is possible to characterise selectively all or most of the phases present in a sample. This is usually not possible when non-invasive techniques are used, such as UV-visible diffuse reflectance spectrophotometry, since in this case the response given is comprehensive of all the compounds present in a sample and it is hard to single out individual contributions. With Raman spectroscopy applied on a micro-sample, on the contrary, it is possible identifying the single phases yielding a large view on the paints used: in each sample, besides the main colourant, minor phases or contaminants can be identified. The same consideration holds for SEM-EDX analysis: different phases can be characterised from the elemental point of view, obtaining information on contaminants that can be useful, as an example, for the identification of the geographic provenance of the colourants.

In the following of the discussion, the palette identified will be detailed colour by colour.

3.1 Black Colourants

Two samples, n.007 taken from the hair of Holy Archangel Gabriel in the *Annunciation* scene at f. 1 and n.010 taken from the beard of Saint Jacob in the *Transfiguration* scene at f. 3b, were from black areas. Unexpectedly, both samples yielded a Raman spectrum that can be attributed to iron-gall ink rather than to a carbon-based pigment, according to the peaks occurring at 567, 1342, 1485 and 1574 cm^{-1} (Figure 1); these spectral features are in good agreement with those reported by Lee *et al.*[8,9] and by Aceto *et al.*[10].

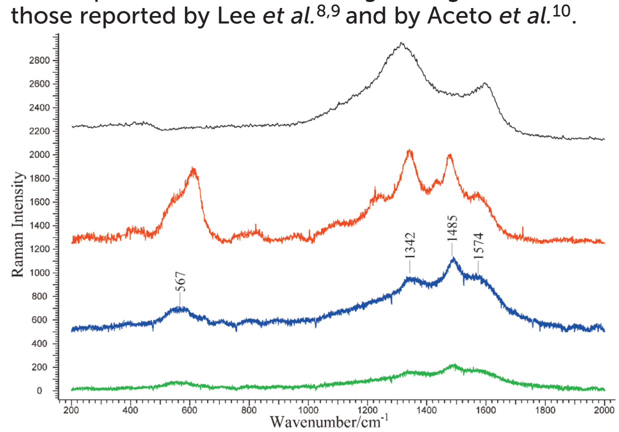

Figure 1: Raman spectra of sample n.007 (blue line), sample n.010 (green line), a standard iron-gall ink (red line) and a carbon-based pigment (black line).

This identification was confirmed by means of FORS analysis on sample n.007 that was large enough to perform such measurement: the reflectance spectrum showed the typical rising in the NIR region[11]. In addition, SEM-EDX analysis identified the presence of iron, sulphur and a small amount of copper.

While the use of iron-gall ink is quite common as material for writing, its use as a black pigment in the illumination of manuscripts was less reported and only recently[11] it has been demonstrated that it was used more commonly than previously known. At any rate it was hardly, if ever, attested in Armenian manuscripts: to the authors' knowledge, in fact, the only other instance ever recorded has been on ms. n. 4915 from Aghtamar Island[1], while in other pictorial schools it has been identified, among others, by Aceto *et al.*[12] in a 12th century Italian illuminated manuscript, by Burgio *et al.*[13] in medieval and Renaissance Italian manuscript cuttings and by Nastova *et al.*[14] in medieval old-Slavonic manuscripts. The limited occurrence of certified evidences in Armenian manuscripts could be possibly due to the relative difficulty in the identification. In fact, most of the analyses carried out in the past on manuscripts of the Armenian school identified only carbon-based pigments[15-18], but it is reasonable to think that those based on elemental techniques could be not specific enough in order to discriminate between carbon pigments and iron-gall ink; the same holds for polarized light microscopy and X-ray diffraction, two techniques that were frequently used in the '80s, as iron gallotannate normally shows amorphous character when attached to parchment.

It is not possible to establish whether iron-gall ink was used as exclusive black pigment in the manuscript, due to the limited number of samples; indeed, in other samples, e.g. n. 009 taken from folio 6 showing the *Crucifixion* scene (Figure 2), the presence of a carbon-based pigment was identified as a contamination in a yellow area set just below a black area (both representing the Holy Cross), so that we can hypothesise that a carbon-based pigment has been used along the manuscript in some instances, as it is usual in Armenian miniatures.

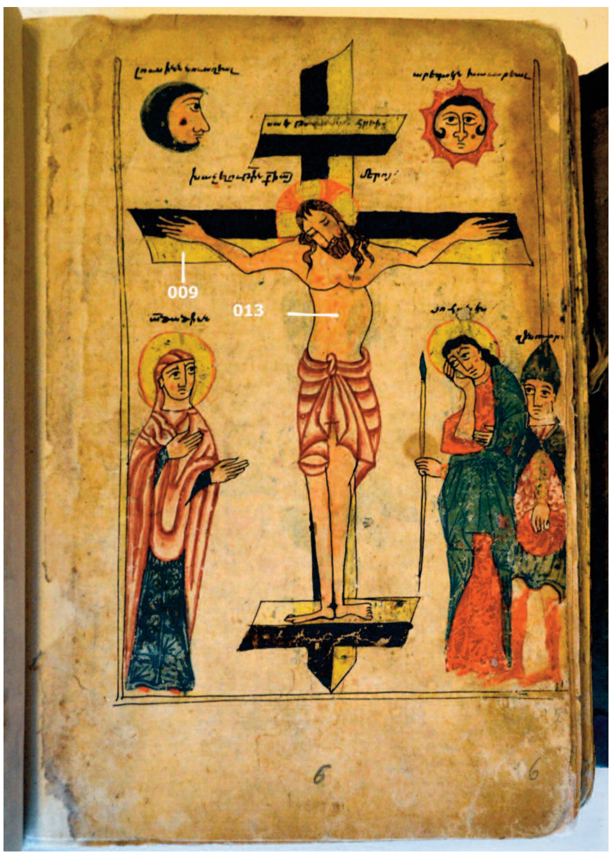

Figure 2: Crucifixion scene (folio 3b).

3.2 Blue Colourants

The role of blue colour in the palette is critical in defining the value of a manuscript from the material point of view. The use of lapis lazuli in place of less expensive pigments such as indigo, azurite or smalt, clearly establishes the richness of the commitments of the artwork. In sample n.002, taken from the dress of the Virgin on the right in the *Annunciation* scene at f. 1b (Figure 3), the painter used lapis lazuli, according to the typical Raman spectrum obtained (Figure 4, middle) and considering the relatively large size of the blue grains, so that the pigment can be definitely identified as *natural ultramarine blue*.

Figure 3: Annunciation scene (folio 1b).

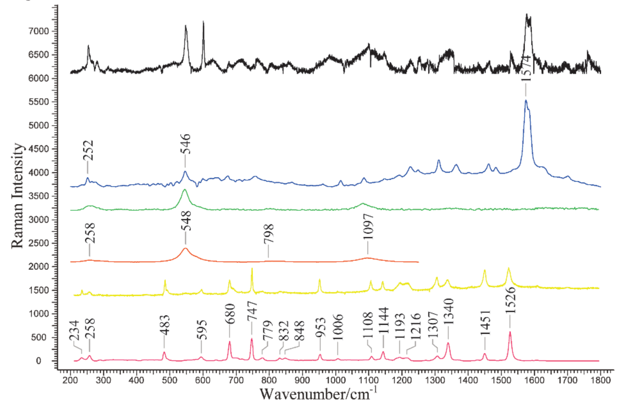

Figure 4: Raman spectra of a blue particle in sample n.005 (black line), standard indigo (blue line), a blue particle in sample n.002 (green line), standard ultramarine blue (red line), a blue particle in sample n.002 (yellow line) and standard phthalocyanine blue (purple line).

Nevertheless, in other instances the artist used indigo (see Raman spectrum in Figure 4, top), as for the garments of the *Magi* in the *Adoration* scene at f. 2 (Figure 5) and for other features with a darker blue hue. In general, it seems like the painter chose to set aside the most precious pigment for the most important features in the images.

Figure 5: *Adoration of the Magi* scene (folio 2).

It must be noted that the dress of the Virgin at folio 1b revealed a very recent restoration intervention. In fact, in the blue area of the dress Raman analysis (spectrum in Figure 4, bottom) yielded the identification of phthalocyanine blue, an organic pigment firstly patented in 1935.

3.3 Green Colourants

The green hues were rendered with a mixture of indigo and orpiment, the so-called *vergaut* very common in Middle Ages in several pictorial schools. Though the lack of pure green colourants may sound strange in a palette, it must be considered that the mixing of a blue and a yellow colourant allowed reaching a wider range of green hues.

3.4 Red, Orange and Pink Colourants

According to spectral features, two pigments seemed to have been used for hues ranging from dark red to orange: cinnabar and red lead (Raman spectra in Figure 6). While the latter, considered of lesser value, was used mainly for the flesh of the characters, the former and more valuable cinnabar was used in many and different instances, i.e. curtains, painted walls or garments; there seems to be no clear scheme in the intention of the painter regarding the hierarchy of the use of these pigments. Both pigments, indeed, are definitely of common use in Armenian manuscripts. Cinnabar is also used in mixture with indigo to render a dark violet hue as in the robe of Saint John Baptist in the miniature at f. 3 (sample n.015) shown in Figure 7.

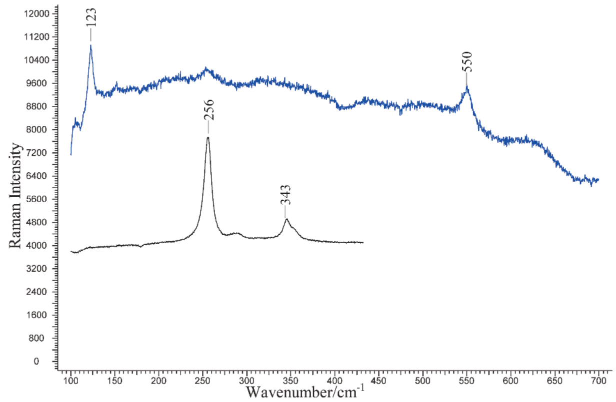

Figure 6: Raman spectra of a red particle in sample n.006 (black line) and an orange particle in sample n.011 (blue line).

Figure 7: Baptism of Saint John.

A pink colourant was present in samples n.011 and 014 that did not yield any spectrum in conventional Raman analysis, therefore suggesting that it could be an organic colourant, i.e. a dye or a lake. As the samples were large enough (~ 1 mm), preliminary measurements by means of FORS and fluorimetry were carried out that revealed the main colourant being a coccid dye, i.e. an anthraquinonic dye obtained from scale insects, according to the absorption maxima at 528 and 561 nm as determined by means of FORS[19,20] (Figure 8) and to the emission maxima at 607 and 622 nm as determined by means of fluorimetry[21] (Figure 9).

The use of such dyes in miniature painting is well known and documented, but it is difficult to distinguish among the different possible substrates due to the difficulty in a specific characterisation that can be

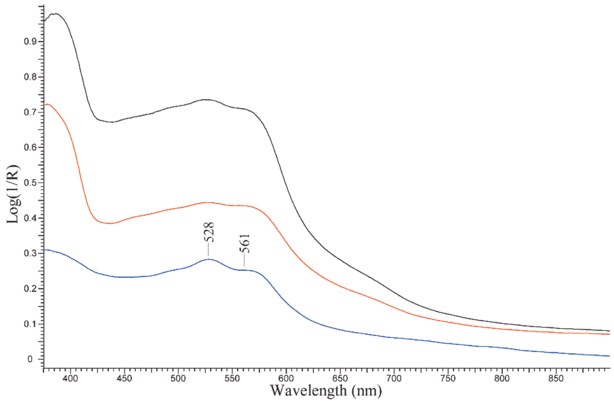

Figure 8: FORS spectra of sample n.011 (black line), sample n.014 (red line) and standard cochineal (blue line).

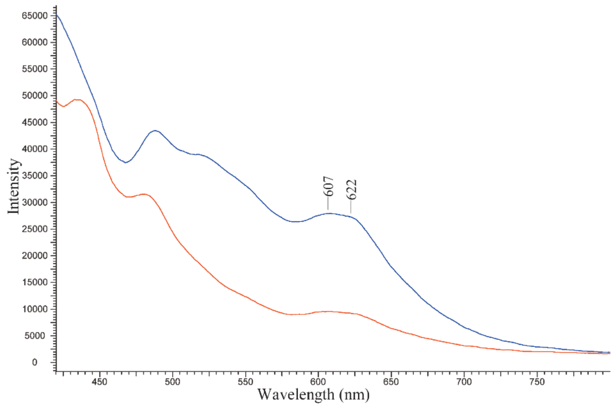

Figure 9: Fluorimetry emission spectra of sample n.014 (red line) and standard cochineal (blue line).

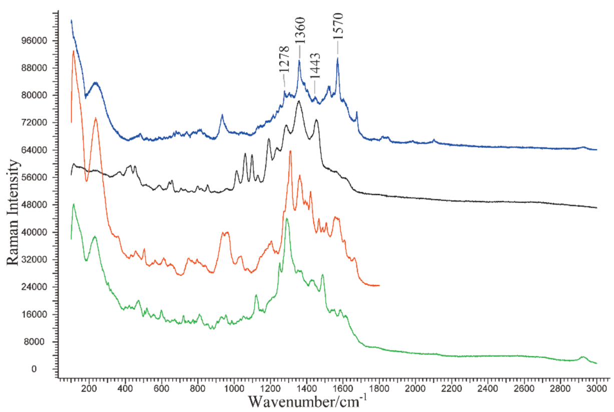

Figure 10: SER spectra of sample n.014 (blue line), standard lac dye (black line), standard kermes (red line) and standard Armenian cochineal (green line).

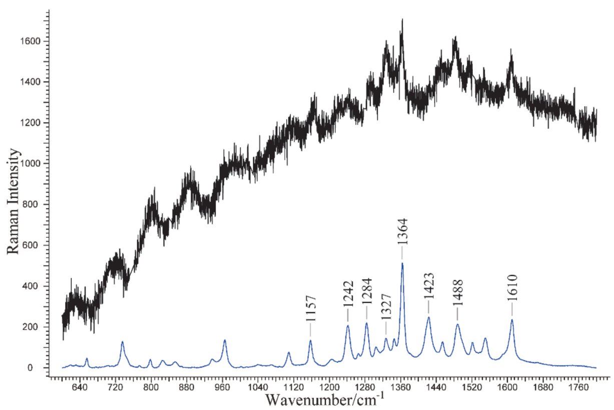

Figure 11: Raman spectra of sample n.002 (black line) and standard PR8 (blue line).

guaranteed by chromatographic techniques at the expense of a larger sample or of more sample preparation manipulation[22]. Considering the colour (pink), the epoch (late Middle Ages) and the geographic area in which the manuscript was composed (Central Asia, Anatolia), it can be hypothesised that the dye be inside this group: Armenian cochineal, extracted from *Porphyrophora hameli*; Polish cochineal, extracted from *Porphyrophora polonica*; lac dye, extracted from *Kerria lacca*; and kermes, extracted from *Kermes vermilio*. Mexican cochineal, extracted from *Dactylopius coccus*, can be safely excluded since it was introduced in the Old World only after the Spanish conquest of Mexico in 1521. Madder, the anthraquinonic dye extracted from the roots of *Rubiaceae* plants, can be excluded as well since its absorption bands occur at slightly lower wavelengths than those of coccid dyes. In this case, the application of SERS analysis with silver nanoparticles colloid was useful in suggesting a specific dyestuff. Surprisingly, the dye under study seemed to be lac dye, according to the comparison of the SER spectrum of sample n.014 with that obtained from standard lac dye, kermes and Armenian cochineal (Figure 10).

The peak at 1570 cm^{-1} could be due to another component of the dyeing mixture, at present unidentified.

Finally, a further red colourant was found in few instances, among which the already cited sample n.002 (the dress of the Virgin in the *Annunciation* scene at f. 1b). In this case also it is possible to assign this colourant to a restoration intervention: in fact, despite the poor quality of the Raman spectrum obtained (Figure 11), spectral features at 1157, 1242, 1284, 1364, 1423, 1488 and 1610 cm^{-1} allow identifying the synthetic pigment PR8 or Permanent Red F4R, patented in 1911[23].

3.5 Yellow Colourants

In all instances the yellow colour is rendered with orpiment, the arsenic sulphide As_2S_3 used since Egyptian times and all through Middle Ages. The identification is relatively easy due to the fact that orpiment is a very good Raman scatterer (spectrum not reported). While orpiment is usually considered more valuable than yellow iron oxide-based pigments, its use was diffuse in all pictorial schools, including the Armenian one.

3.6 Metal Pigments

A single sample, n.001 taken from the front binding, was of metallic nature as confirmed by the absence of any Raman signal. SEM-EDX analysis allowed identifying the material as pure silver. It must be considered that this information pertains to the binding and not necessarily to the manuscript itself.

3.7 Comparison among the Palettes

As the main aim of this study was to compare the colourants used in ms. 4915 (14th century) and ms. 1448 (15th century), both produced in Aghtamar Island, the results of the characterisation of the corresponding palettes are shown in Table 2.

Colour	ms. 4915	ms. 1448
black	iron-gall ink carbon	iron-gall ink carbon
blue	ultramarine blue indigo	ultramarine blue indigo
green	vergaut	vergaut
orange	red lead	red lead
pink	*	lac dye**
red	cinnabar	cinnabar
violet	indigo/cinnabar	indigo/cinnabar
white	white lead	white lead
yellow	orpiment	orpiment

Table 2: Comparison between the Palettes of ms. 4915 and 1448
* unidentified
** to be confirmed

It appears clearly that the palettes are quite similar, not only for what concerns pure hues but also for mixture, e.g. green obtained with indigo/orpiment or violet obtained with indigo/cinnabar. The only difference occurred in the identification of a coccid dye, most probably lac dye, in ms. 1448 while no pink dyes were identified in the study on ms. 4915, but this difference must be ascribed to lack of diagnostic information rather than to a different choice of colourants by the artists.

4 Conclusions

The analysis of ms. 1448 from Aghtamar Island was carried out on micro-samples detached from the miniatures, choosing areas in which the withdrawal of coloured matter had minimal visual impact. The results of analyses of the miniatures of the 15th century ms. 1448 were compared with those obtained from the 14th century ms. 4915 from the same collection and changes were evaluated after one century in miniature painting in the same region, that is Aghtamar Island, Vaspurakan region, historic Armenia. Iron-gall ink was used as a black pigment as well as on ms. 4915 from Aghtamar Island[1]. This presence has never been recorded before on Armenian manuscripts. The blue pigment was definitely identified as *natural ultramarine blue*. Two pigments were used for hues ranging from dark red to orange, according to the typical spectral features: cinnabar and red lead. The presence of lac dye for pink hues has been hypothesised according to the results of SERS analysis.

The comparison among the palettes has demonstrated that they were identical, confirming the continuity in the choice of colourants by the artists working at Aghtamar Island.

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Yeghis Keheyan dedicates this paper to the memory of John Havermans, great friend, who had introduced many people in the world to the field of cultural heritage.

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