Between West and East: a non-invasive study of colourants on Syriac manuscripts

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Abstract

Syriac manuscripts represent an important treasure as they document the spread of early Christian iconography throughout the Eastern Mediterranean. While they are well-known from the historical, artistic and religious literary points of view, the knowledge of the pictorial materials with which they were produced is only in its infancy. Few of them have been subjected to diagnostic analysis, the most important being the 6th century *Rabbula Gospels* kept in Florence at Biblioteca Medicea Laurenziana (cod. Plut. I, 56). The present contribution reports on the results obtained from the identification of colourants in two important groups of Syriac manuscripts, the first one kept in Paris at Bibliothèque nationale de France (BnF) and the second one kept in Rome at Biblioteca Apostolica Vaticana (BAV). As a whole set, the manuscripts date from the 6th to the 14th century.
The diagnostic study has been carried out in totally non-invasive way. The techniques used were UV-visible diffuse reflectance spectrophotometry with optic fibres (FORS), X-ray Fluorescence Spectrometry (XRF), Fibre Optic Molecular Fluorimetry (FOMF) and Optical Microscopy (OM). The FORS technique was systematically applied to have a preliminary identification of the colourants and in most of the cases allowed having a reliable identification. FOMF analysis was used to confirm some uncertain results. XRF spectrometry was used to support FORS identification and to have information on the metal pigments. Optical microscopy, finally, was used to have a view under the micro scale, useful to aid the identification obtained by the spectroscopic techniques.
The results obtained show that precious colourants, such as lapis lazuli, cinnabar and insect dyes, were widely used, apart from the oldest manuscript (ms. Syriaque 33 - BnF). One remarkable group of manuscripts is the one formed by the 12th-13th century manuscripts Syriaque 30, 40, 41, 54, 355, 356 (BnF) and Vat. Sir. 559 (BAV): these manuscripts contain miniatures decorated with lapis lazuli, pararealgar (an unusual yellow pigment, possibly produced by alteration of realgar), iron gall ink (a pigment of Western tradition, very unusual in Asian countries) and an insect dye, most probably derived from the Indian scale insect *Kerria lacca*. This set of colourants appears to be a synthesis between Asian and European cultures and it is quite different from the palette used in the oldest manuscripts.
Despite being only a small fraction of the existing Syriac manuscripts, the results here presented can be considered a preliminary view of the colourants used by the early and late medieval artists of this cultural area. It is advisable that further analyses will be carried out to have a more complete view of the Syriac miniature painting art.
This contribution is in loving memory of Prof. Guido Frison, colleague and friend as well as a source of inspiration for this and a thousand other projects.

Keywords: Syriac, manuscripts, non-invasive, colourants, FORS, XRF.

Introduction

Syriac manuscripts represent an important treasure as they document the spread of early Christian iconography throughout the Eastern Mediterranean. While they are well-known from the historical, artistic and religious literary points of view, the knowledge of the pictorial materials with which they were produced is only in its infancy. Very few of them have been subjected to diagnostic analysis, the most important being the 6th century *Rabbula Gospels* (cod. Plut. I, 56) kept in Florence at Biblioteca Medicea Laurenziana which was analysed by Lanterna *et al.* (Lanterna, Picollo and Radicati, 2008). Another manuscript, dated to the first half of 13th century, is ms. Add. 7170 kept at British Library in London, analysed by Clark and Gibbs by means of Raman spectroscopy (Clark and Gibbs, 1997).

The present contribution reports on the results obtained from the identification of colourants in two important groups of Syriac manuscripts, the first one kept in Paris at Bibliothèque nationale de France (BnF) and the second one kept in Rome at Biblioteca Apostolica Vaticana (BAV). As a whole set, the manuscripts date from the 6th to the 14th century.

The diagnostic study has been carried out in totally non-invasive way. The techniques used were UV-visible diffuse reflectance spectrophotometry with optic fibres (FORS), X-ray Fluorescence Spectrometry (XRF), Fibre Optic Molecular Fluorimetry (FOMF) and Optical Microscopy (OM). The FORS technique was systematically applied to have a preliminary identification of the colourants and in most of the cases allowed having a reliable identification. FOMF analysis was used to confirm some uncertain results. XRF spectrometry was used to support FORS identification and to have information on the metal pigments. Optical microscopy, finally, was used to have a view under the micro scale, useful to aid the identification obtained by the spectroscopic techniques.

Materials and methods

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 with a wavelength range of 360–2500 nm; the detector and light source were connected with fibre optic cables to an Avantes FCR-7UV200-2-1,5x100 reflection probe. In this configuration, light is sent and retrieved with a unique fibre bundle positioned at 45° from the surface normal, in order not to include specular reflectance. The spectral range of the detector was 200–1160 nm; depending on the features of the monochromator (slit width 50 µm, grating of UA type with 300 lines/mm) and of the detector (2048 pixels), the best spectra resolution was 2.4 nm calculated as FWHM. The diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile provided by Avantes and guaranteed to be reflective at 98% or more in the spectral range investigated. The investigated area on the sample had a 1 mm diameter. In all measurements the distance between the probe and the sample was kept constant at 2 mm, corresponding to the focal length; the probe was inserted into a small aluminium block. To visualise the investigated area on the sample, the block contained a USB endoscope. The instrumental parameters were as follows: 10 ms integration time, 100 scans for a total acquisition time of 1.0 s for each spectrum. The system was managed with AvaSoft v. 8 dedicated software running under Windows 7.

X-ray Fluorescence Spectrometry (XRF): XRF measurements were performed with an EDXRF Thermo (Waltham, MA, USA) NITON spectrometer XL3T-900 GOLDD model, equipped with a Ag tube (max. 50 kV, 100 µA, 2 W), a large area SDD detector and an energy resolution of about 136 eV at 5.9 keV. The analysed spot had an average diameter of 3 or 8 mm and was focused by a CCD camera, with a working distance of 2 mm. The total time of analysis was 240 s. The instrument was held in position with a moving stage allowing micrometric shifts, in order to reach the desired probe-to-sample distance; the stage was laid on a tripod. The obtained spectra were processed with the commercial software bAxil, derived by the ac-ademic software QXAS from IAEA.

Fibre Optic Molecular Fluorimetry (FOMF): an Ocean Optics (Dunedin, FL, USA) Jaz model spectrophotometer was employed to measure the molecular fluorescence spectra. The instrument was equipped with a 365 nm Jaz-LED internal light source and an Avantes FCR-7UV200-2-

1,5x100 reflection probe used to drive excitation light on the sample and to recover emitted light. The spectrophotometer was working in the range 191–886 nm; according to the features of the monochromator (200 µm slit width) and the 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 distance between the probe and the sample was kept constant at 1.2 mm, corresponding to the focal length; the probe was inserted into a small aluminium block in order to exclude contributions from ex-ternal light. To visualise the investigated area on the sample, the block contained a USB endoscope. Instrumental parameters were as follows: 3 s integration time, 3 scans for a total acquisition time of 9 s for every spectrum. The system was managed with Spec-traSuite software running under Windows 7.

Optical Microscopy (OM): a Dino-Lite (Naarden, The Netherlands) AM413TL-FVW model optical microscope was employed to record digital images from the parchment. The microscope allows magnification in the range 20x–90x.

Results and discussion

Most of the colourants were identified by means of FORS analysis and confirmed by means of FOMF and XRF. While for most of them the identification can be considered as reliable, according to the minima and/or the inflection points present in the spectrum that fit well those reported by the scientific literature (Aceto *et al.*, 2014), in a few cases a certain grade of uncertainty must be declared. In particular, two cases must be cited:

- the identification of lac dye relies on the absorption features in the FORS spectrum of purple, pink and violet paints, typical of anthraquinone dyes. As it is well known, it is relatively easy to distinguish between vegetal (madder) and animal (kermes, Armenian cochineal, Mexican cochineal, Polish cochineal and lac dye) anthraquinone dyes according to the spectral features of the FORS responses: the typical absorption bands occur at 510 and 540 nm for madder and at 520-535 and 560-575 nm for the animal dyes. Among the animal dyes, it was recently noted (Aceto *et al.*, 2019) that the absorption bands of lac dye occur at longer wavelengths, typically 530-535 and 565-575 nm. This hypothesis has been reinforced by means of a few micro-invasive measurements by means of HPLC-MS analysis, that confirmed the exclusive presence of laccaic acids in samples where the presence of lac dye was suggested by FORS.
- the identification of the yellow pigment pararealgar is suggested by the inflection point in the FORS spectrum, occurring between 500 and 515 nm, by the presence of As and S in the XRF spectrum and by the strong emission peak in the FOMF spectrum, occurring between 545 and 560 nm; these features suggest that the pigment is pararealgar and not orpiment, nor any other yellow pigment or dye. The identification, however, could not be unequivocally confirmed by means of Raman analysis.

The list of the manuscripts analysed is reported in Tab. 1.

Source	Signature	Period	Provenance
Bibliothèque nationale de France	Syriaque 33	6th	Turkey
Bibliothèque nationale de France	Syriaque 341	6th-7th	Iraq
Bibliothèque nationale de France	Syriaque 27	8th	Syria
Biblioteca Apostolica Vaticana	Vat. Sir. 13	8th	
Biblioteca Apostolica Vaticana	Vat. Sir. 529	9th-11th	
Biblioteca Apostolica Vaticana	Barb. Or. 118	10th-11th	
Biblioteca Apostolica Vaticana	Vat. Sir. 94	11th	Turkey
Biblioteca Apostolica Vaticana	Vat. Sir. 118	12th	

Bibliothèque nationale de France	Syriaque 30	12th	Turkey
Bibliothèque nationale de France	Syriaque 40	12th	Syria
Bibliothèque nationale de France	Syriaque 41	12th	Turkey
Bibliothèque nationale de France	Syriaque 54	12th	Syria
Bibliothèque nationale de France	Syriaque 355	12th	Turkey
Bibliothèque nationale de France	Syriaque 356	12th-13th	Turkey
Bibliothèque nationale de France	Syriaque 112	13th	Turkey
Biblioteca Apostolica Vaticana	Vat. Sir. 559	13th	Mosul (Iraq)
Biblioteca Apostolica Vaticana	Vat. Sir. 622	13th	Iraq

Tab. 1 – List of manuscripts analysed in this study

In particular, two groups of manuscripts were taken into consideration:

- the oldest ones, BnF Syriaque 33 and 341, dated to 6th-7th centuries;
- an homogeneous group of 12-13th centuries manuscripts (BAV Vat. Sir. 559 and BfN Syriaque 30, 40, 41, 54, 355 and 356) produced between Syria, Turkey and Iraq.

The oldest manuscripts. Ms. BnF Syriaque 33 or *Tétraévangile syriaque*, produced in Syria or Turkey, is dated to 6th century; ms. BnF Syriaque 341 or *Bible syriaque*, most probably produced in Iraq, is dated to 6th-7th centuries. Though very close in time, they have a remarkably different palette. One common feature is the use of irongall ink for the text, which is unusual for manuscripts written in Asian areas where the use of carbon inks was much more common. The introduction of irongall ink is uncertain both from the historical and the geographical point of view, but the first analytical evidence of the use is reported to be in the Western part of the Mediterranean Basin, with reference to the *Vercelli Gospels* (Aceto *et al.*, 2008) and the *Codex Sinaiticus* (Moorhead *et al.*, 2015), respectively produced in Italy and in Egypt.

Ms Syriaque 33 was decorated with indigo, indigo/orpiment mixture (for the green hues), cinnabar, red lead, madder and orpiment. As cited above, the text was written with an irongall ink. The palette seems to be close to those of the late antique manuscripts *Ilias picta*, *Vergilius Romanus*, *Vergilius Vaticanus* (Aceto *et al.*, unpublished results) which recall the Roman tradition.

The palette of ms. BnF Syriaque 341 is richer and more variegate. In fact, it contains ultramarine blue, azurite and indigo, gold, verdigris and indigo/orpiment mixture, cinnabar, red lead, madder and yellow ochre. The text was written with an irongall ink. Of particular interest is the use of ultramarine blue, the pigment obtained from the semiprecious stone lapis lazuli, here used in one of the earliest occurrences ever recorded, surely favoured by the proximity of Iraq to the lapis lazuli mines of Badakshan (present-day northeastern Afghanistan). The use of gold is remarkable as well and suggests that this set of colourants is closer to those of the early medieval manuscripts and in particular of the three 6th century purple codices *Vienna Genesis*, *Rossano Gospels* and *Codex Sinopensis*.

The group of 12th-13th centuries manuscripts. These manuscripts, produced in an area between Syria, Turkey and Iraq, show a very homogeneous and characteristic palette. It is composed by ultramarine blue and indigo; verdigris and a mixture of indigo and a yellow colourant; gold; cinnabar; a scale insect dye, most probably lac dye; pararealgar. As for the older manuscripts, the text was written with an irongall ink. The most remarkable points of this palette are the following:

- the systematic use of ultramarine blue: this is a feature typical of all the Near Eastern and Middle Eastern Asian painting schools (Persian, Ottoman, Turkish, etc.). Again, this must be favoured by the proximity of the Badakshan mines, but it is nevertheless a clear sign of richness.

- the use of lac dye, a dye obtained from the *Kerria lacca* scale insect, typical of the Indian subcontinent. This seems to suggest a link between the Syriac-speaking area and India. Interestingly, the Syriac church has a long history in India that is traditionally dated to the 1st century AD, when St. Thomas the Apostle is believed to have landed in Kerala (Perczel, 2019).
- the uncommon use of pararealgar, a yellow arsenic sulphide - As_4S_4 – naturally occurring as light-induced alteration phase of the orange mineral realgar – same formula – or artificially produced by photodegradation of realgar itself. It is interesting to note that in nearly all instances where pararealgar was found, the yellow colour was coherent from the iconographic point of view, so to suggest that the Syriac artisans were able to exploit the photodegradation of realgar to obtain a new yellow pigment. Pararealgar was known to ancient Egyptians (Burgio and Clark, 2000; Daniels and Leach, 2004) but it has rarely been reported on medieval manuscripts, and only in paintings from Middle Eastern Asia. Clark and Gibbs identified it on the manuscript Add. 7170 kept at British Library in London (Clark and Gibbs, 1997), not by chance produced near Mosul (Iraq) and showing a strong relationship with ms. Vat. Sir. 559 of Biblioteca Apostolica Vaticana. Knipe et al. identified pararealgar in manuscripts from Iraq and Iran dated respectively to 13th and 14th centuries (Knipe *et al.*, 2018). Later identification from nearby geographic areas was reported by Muralha *et al.* in a 16th century Persian manuscript (Muralha, Burgio and Clark, 2012), by Burgio *et al.* in two 16th century Ottoman manuscript (Burgio *et al.*, 2008) and by Jurado-López *et al.* in a 16th century Turkish manuscript (Jurado-López *et al.*, 2004). The exclusive occurrence of pararealgar on these Syriac manuscripts and in all other evidence cited can be explained by the wide availability of realgar mines in the area between Turkey and Iran.
- the use of irongall inks for the text: while nearly all of the Islamic documents were written in carbon inks, most of the medieval Western documents were written with irongall inks, so this seems to suggest a strong "Western" influence on the scribes who wrote these Syriac manuscripts.

In the end, it is interesting to compare the palette of the group of 12-13th centuries Syriac manuscripts with typical late medieval "Western" and "Oriental" palettes (Tab. 2).

Colour	12th-13th century Syriac	Oriental	Western
black	irongall ink	carbon	irongall ink
blue	ultramarine blue	ultramarine blue	ultramarine blue azurite indigo
gold	gold	gold	gold mosaic gold
green	verdigris indigo/yellow colourant	verdigris indigo/yellow colourant	verdigris indigo/yellow colourant
orange	cinnabar	red lead	red lead
pink/purple/violet	scale insect dye (lac dye)	scale insect dye	scale insect dye
red	cinnabar	cinnabar red lead	cinnabar red lead
yellow	pararealgar	orpiment	orpiment yellow ochre

Tab. 2 – Comparison of palettes

In the end, the palette of the Syriac manuscripts seems to be influenced both by the Western (irongall ink) and the Oriental (lapis lazuli, lac dye) traditions.

Conclusions

Despite being only a small fraction of the existing Syriac manuscripts, the results here presented can be considered a preliminary view of the colourants used by the early and late medieval artists of this cultural area. It is advisable that further analyses will be carried out to have a more complete view of the Syriac miniature painting art.

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