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SPECTROSCOPIC STUDY OF AN ARMENIAN MANUSCRIPT FROM BIBLIOTECA UNIVERSITARIA DI BOLOGNA

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Abstract

The *manuscript of Edessa* or ms. 3290, a XVIII century Armenian manuscript kept at Biblioteca Universitaria di Bologna, has been thoroughly studied from the religious, artistic, historical and diagnostic point of view. Non-invasive measurements on the miniatures have been carried out *in situ* with portable instruments in order to evaluate the pictorial materials used to decorate this beautiful codex, lavishly illuminated with full-page miniatures. The results of the diagnostic study suggested that at least three different painters, each one with its own characteristic palette, contributed to the illumination of the manuscript. Precious colorants were employed for painting, among which of particular interest is the combined use of ultramarine blue and gold, considered the most valuable pictorial materials available to painters. Such a study could be a starting point for a larger research on the heritage of Armenian manuscripts held in Italian institutions.

Keywords: Armenian manuscripts, spectroscopy, colorants, non-invasive analysis, Raman

1. Introduction

Italy was for centuries a destination, a place of passage and sometimes adoptive land of Armenians: soldiers, pilgrims, monks, merchants, princes have always lived in the Italian cities. Traces of this secular presence, discreet but tenacious, remain in archival documents, inscriptions, monuments, place names, traditions [1]. In this work we want to help enhancing a particular expression of the Armenian culture that, through more different modes, became heritage of the Italian state: the Armenian codices kept in public libraries. It is known that Italy owns a significant part of Armenian manuscripts that survived after centuries of

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difficult and often tragic history (other large collections are in Yerevan Museum of Ancient manuscripts). The most remarkable collections are at San Lazzaro (Venice), at Biblioteca Apostolica Vaticana and Pontificio Collegio Armeno in Rome, while several minor collections are present in other cities. As for the dating, most of the manuscripts are in the range XVI-XVIII centuries, but other are datable down to the XIIIth century. The themes are mostly religious: Bibles, rituals, etc. Many codices from XIII-XIV centuries are related to the passage or permanent presence of religious Armenians in Italy. The first religious Armenians in Italian cities had a church and domus and are known under various denominations: *Basilian monks* or *bartolomiti*. In the early 30's of XIVth century, the Dominican Order founded the *Societas Fratrum Peregrinantium*, with the specific purpose of bringing the Catholic doctrine to the East. Religious Armenians who joined the union with Rome took various names (*Friars of Unity of Saint Gregory the Illuminator*) and took the dress and the rules of Saint Dominic. So a remarkable activity was started in Armenian translation of works of Theology and scholastic philosophy. The Dominican Order had one of the main scriptoria, so in Italian libraries there are codices containing works of Catholic doctrine in Armenian language.

In Biblioteca Universitaria di Bologna (BUB), three manuscripts of different origin are kept: mss. 3290, 3291 and 3292 [2]. These manuscripts are from the personal collection of Pope Benedict XIV (1740-1758), the Bolognese Cardinal Lambertini, who gifted them to his hometown. The three codices, particularly valuable for running and thumbnails, are linked to an important historical moment for the Armenian Church. In fact, after a long internal turmoil, in XVIIIth century it emerged in a part of Armenian people the will of an official recognition of the current Catholic Church who had, consequently, its own hierarchy directly dependent on the Holy See. This aspiration became reality in 1742 when the archbishop Ardzivian from Lebanon came to Rome to receive his investiture from the Pope. With that occasion, he brought with him some codices, more or less valuable, to pay homage to important personalities, not realising that these items were important assets. Pope Benedict XIV, who consecrated him with a lavish ceremony, received as a gift three among the most valuable codes, which are now among the treasures of BUB. In particular, the Gospel ms. 3290 deserves attention because of the motifs in embossed *niello* and a cross on a gold background on its binding, and its rich decoration on the pages: it is an extraordinary example, for the profusion of colours and the accuracy of the performance, of the Armenian miniature of XVI-XVII centuries. The codex lacks a true imprint; after the ritual formula "ended on the Gospel John", a date "a. 1144" was added by a different hand and several inks; this date is absolutely inconsistent with the constitutive elements of the manuscript, suggesting that it was added on purpose of increasing the value of the codex by backdating it.

1.1. Religion

Christianity was firstly introduced in Armenia by the apostles Bartholomew and Thaddeus in I century AD. As first nation to designate Christianity as state religion in 301 AD, the Armenians have a long and rich history with the Christian Church. Throughout all the hardship, forced migration and persecution faced by the Armenian people over the centuries, the Church has consistently been a place of refuge and community. The central role played by the Church has strongly combined it with the Armenian tradition and culture. Although Armenian traditions are similar to those of other Orthodox Christian faiths, they have a distinctly Armenian element that is a source of great pride for the people. The Armenian Church representatives did not agree with the Nestorian belief in the dual nature of Christ [3]. The Armenians then founded their Monophysite Church. While most Christian denominations believe in the dual human and divine nature of Christ, the Armenians believe that Christ was a purely divine being.

Following this split, the Catholicos (religious leader) moved the Armenian religious center to the city of Ejmiadzin, a city close to the capital of modern-day Armenia, Yerevan. Traditionally the Catholicos has held the role of religious and moral leader of Armenian Christians worldwide. Despite the split, the Armenian Church has held onto many traditions that closely resemble those practiced by the Greek and Syrian Orthodox Christian Churches. For example, all three denominations place great importance on the 7 sacraments (Baptism, Confirmation, Eucharist, Penance, Anointing of the sick, Matrimony and Holy Orders). Armenians also believe in *transubstantiation*, the idea that the bread and wine of communion actually becomes the body and blood of Christ once it is blessed by the priest. Armenians also pray to the Virgin and to saints. The calendar of the Armenian Church is also very similar to those of the other Orthodox Christian denominations, observing both Saints feasts and fast days. However, Armenians celebrate Christmas and Epiphany on January 6th, a practice of early Christians that other Orthodox denominations have discontinued. The last main similarity between the Armenian Church and the other Orthodox Christian Churches is the hierarchy system. The most important function of the Armenian Church is to preserve Armenian identity throughout all the relocations, wars and persecutions that have plagued the Armenian people. Armenian communities may be found around the world, from Turkey to India to the United States. There are many cultural differences between these communities, but the religious traditions and faith have remained a source of pride and ethnic association for Armenians worldwide. The Armenian Christian Church has consistently been the ‘chief agency to keep the people alive’.

1.2. Decoration

The Gospel ms. 3290 is lavishly illuminated, with great profusion of gold in the background of the full-page miniatures, framed in architectural profiles;

also, in the margins of the figures characters are brightened by gold contours. Striped mirror: 80x50 mm; 23 lines, in two columns (mm 23+4+23), parchment; red ink on vertical lines of justification. At the beginning of the book there are seventeen scenes from Christ's life as the Resurrection and the Ascension (ff. 23v and 24r). The Magi and stars are represented in the right margin of f. 33.

1.3. Scripture

Bolorgir (ancient lowercase writing used since the XIth century) in black ink by hand only; *erkatagir* (ancient uppercase letters) of different colours for initial words.

1.4. History of the manuscript

It is usually known as *manuscript of Edessa*. Its origin is not known specifically but one colophon states that it was done in *Armenorum* year 593 and Christian year 1144 (593 + 1144 = 1737) in the Ephraim Syri monastery at Edessa (Armenian Mesopotamia, presently belonging to Turkey) and given to Pope Benedictus XIV in 1743.

1.5. Analysis of the manuscript

The interest in analysing Armenian manuscripts lies in the fact that a wide diversity of pictorial materials may be expected. The Armenian world, in fact, at different periods in its history has been in close contact with Latin, Byzantine, Islamic and even further eastern civilizations. In addition, Armenian manuscripts are dated and located by colophons in a much larger percentage than those of other cultures. Therefore through the analysis of colorants they offer a greater chance of establishing chronological and geographical distribution patterns.

Figure 1. XRF analysis on ms. 3290.

Ms. 3290 has been studied with non-invasive techniques to identify the colorants used in its decoration. This information is relevant for appreciating the value of the artwork and for identifying the various hands that worked at it. Three spectroscopic techniques were used: UV-Visible diffuse reflectance spectrophotometry with optic fibres (FORS), Raman spectroscopy and X-ray fluorescence spectrometry (XRF, Figure 1). All measurements were performed in situ with portable instrumentations, in order not to cause any damage to the manuscript.

2. Experimental

2.1. 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.

2.2. Raman spectroscopy

A Horiba (Villeneuve d'Ascq, France) MicroHR model portable spectrometer was used for Raman analysis. The modular system was composed by a MicroHR spectrometer with 1200 gr/mm grating, a Synapse model CCD detector with 1024x256 pixels, a Modular Head model analytical probe head containing an edge filter and a video camera for visualisation of samples, microscope objectives (20x, 50x and 80x), a He-Ne laser (λ = 632.8 nm) with an output power of 20mW (reduced by attenuation filters to less than 1 mW on the sample) and two optical fibre bundles to convey laser radiation on the sample and Raman scattered light from sample to the detector. The spectral resolution was about 4 cm^{-1}.

2.3. XRF spectrometry

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

3. Results and Discussions

3.1. Role of the three techniques used

In the study on ms. 3290 three analytical techniques were applied according to the complementary information they can yield [4]. FORS and Raman spectroscopy are *superficial* techniques, i.e. they yield a response from the superficial part of the sample, while XRF spectrometry is an *in-depth* technique, so that it can investigate also underlying layers. In details, FORS analysis allows to perform a fast survey on a large number of painted areas and to identify most of the colorants present. Raman spectroscopy can give further insight in the identifications, this technique having a much higher diagnostic power; in addition, as it works at the microscopic scale, it allows analysing very small details (less than 100 μm of diameter). Finally XRF spectrometry, apart from complementing the overall identifications, adds qualitative and semiquantitative information on metal pigments (gold, silver, etc.), which are not detectable with the previous two techniques, and on inks; moreover, it can give information on underlying layers thanks to its penetration depth.

3.2. Previous studies on Armenian manuscripts

The information available on the colorants used on Armenian manuscripts is poor if compared to manuscripts from other cultures, e.g. Persian, Byzantine or Western. Among the few studies, the most relevant are those by Orna *et al.* [5-8] and by Cabelli *et al.* [9, 10]. With few exceptions [11] these studies date back to the ’80 and early ’90 and are entirely based on invasive methods, i.e. upon withdrawal of microsamples and subsequent analyses carried out in laboratory. Such procedures are usually harmless for the sampled artworks (samples of less than 1 mm are taken with a surgical scalpel) and have been applied also recently by Baraldi *et al.* [12, 13] on manuscripts held in Armenia, but are not allowed at present in Italy, so that only non-invasive, *in situ* analysis can be performed on manuscripts kept in Italian museums or libraries.

(a) (b)

Figure 2. (a) The binding of ms. 3290 and (b) side miniatures at ff. 126r and 266r.

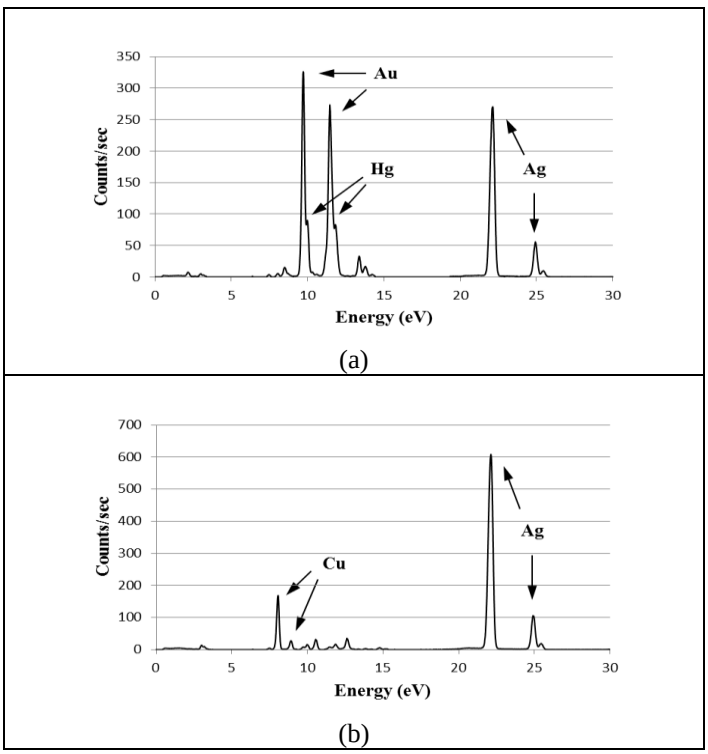


Figure 3. XRF spectra from the binding of ms. 3290: (a) background gilded silver and (b) black *niello* decorations.

3.3. Results of the non-invasive investigation on the manuscript of Edessa

The results of non-invasive analysis on ms. 3290 are described in the following. First at all, the book shows a peculiar binding (Figure 2a) in which, according to XRF analysis (Figure 3), the background was made of gilded silver with the well-known *fire gilding* technique, i.e. by means of a gold/mercury amalgam spread on the silver plate; the presence of mercury (Hg) is a clear clue for this procedure [14]. *Fire gilding* was definitely the main technique for

gilding of metals in both Europe and the Middle East, at least until the invention of electroplating in XIXth century.

The embossed black decorations on the binding were made according to the *niello* technique, a mixture of Ag_2S and CuS widely used in goldsmithry artworks for adding black details to a metallic surface. *Niello* was commonly found on silver jewellery in Eastern and Western Armenia [15]. The stoichiometry suggested by the semiquantitative XRF result is $2Ag_2S + Cu_2S$, compatible with the medieval recipes, e.g. in the XIIth century *Mappae clavicula* text [16].

As to the colorants used in the manuscript, some folios with no writing were thoroughly dyed, a yellow one with saffron and some purple ones with brazilwood (Figure 4, FORS spectra in Log(1/R) coordinates).

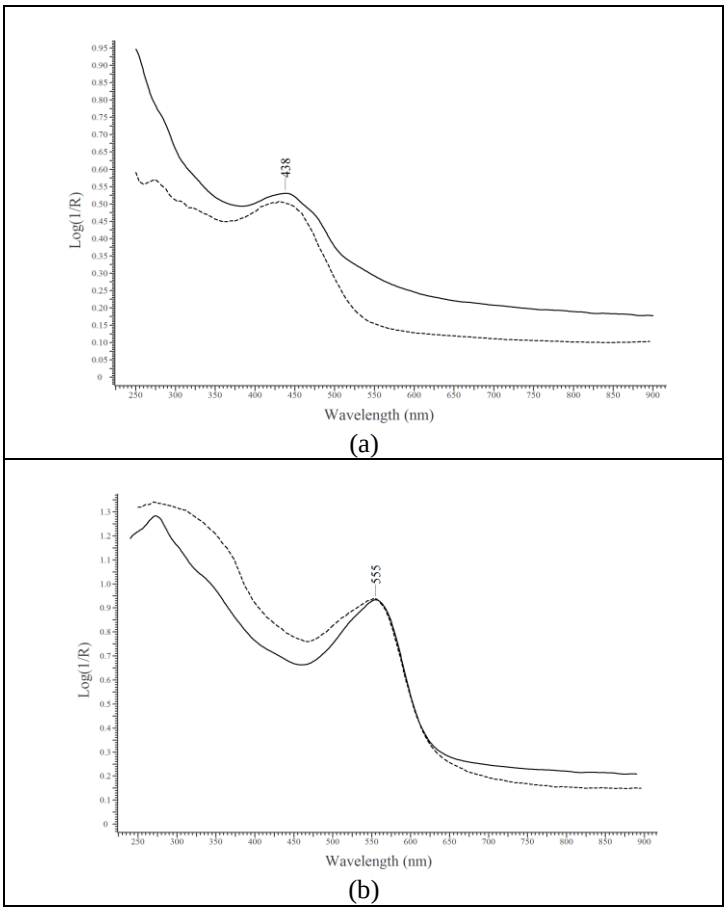


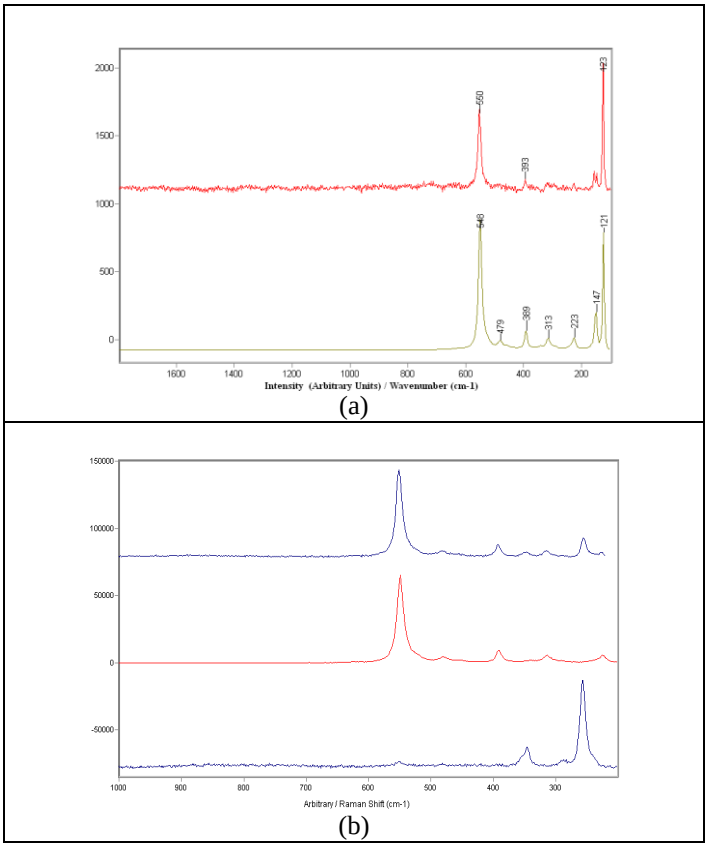
Figure 4. FORS spectra of non-written folios: (a) saffron (dashed line) and (b) brazilwood (dashed line) against their respective standards (solid line).

As both these dyes do not belong to the palette used by the painters who worked at the decorations (as shown in the following table), it is highly possible that these folios had been inserted later, maybe in a restoration intervention; in

addition, while the use of saffron could be ascribed to cultural influences from Persia or India, that of brazilwood is harder to be justified, being this dye more characteristic of Western painting art.

Table 1. List of the colorants identified.

Colours	I painter	II painter	III painter
Black	carbon black	carbon black	carbon black
Blue	indigo	ultramarine blue	smalt
Gold	gold leaf on glue	gold leaf on lead white	gold shell
Green	indigo + orpiment	verdigris	malachite
Orange	minium	minium	minium
Pink	Armenian cochineal	Armenian cochineal	Armenian cochineal
Red	cinnabar	cinnabar	cinnabar
White	lead white	lead white	lead white
Yellow	orpiment	yellow ochre	-



(a)

(b)

Figure 5. Raman spectra of: (a) minium at f. 8r (bottom: minium standard, top: sample); (b) a mixture minium/cinnabar at f. 266r (bottom: cinnabar standard, middle: minium standard, top: sample).

The list of the colorants identified in the miniatures by means of FORS, Raman and XRF analyses is resumed in Table 1. On the basis of the colorants present and according to stylistic considerations, it is possible to hypothesise that at least three different painters worked at the decoration of the manuscript.

All artists used lead white and carbon black for respectively white and black areas, cinnabar for red areas and minium for orange areas; the last two were sometimes used in mixture. A selection of Raman spectra with identifications of these colorants is shown in Figure 5.

For violet and pink areas an insect dye was used, sometimes highlighted with cinnabar; as to this dye, we can safely attribute it to the variety known as *Armenian cochineal* (FORS spectrum in Figure 6) considering the geographical provenance of the manuscript.

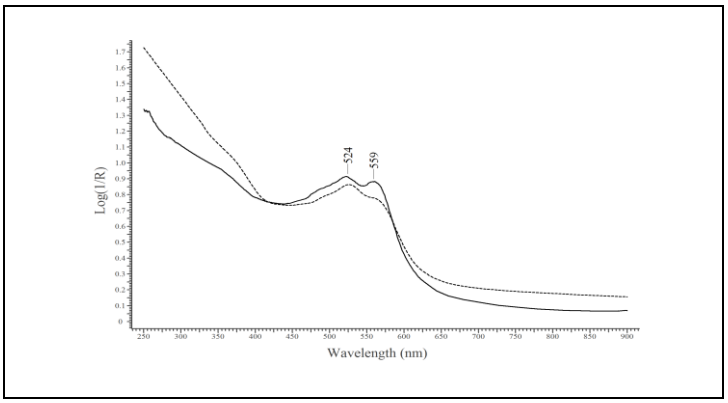


Figure 6. FORS spectrum of a purple area at f. 24r (dashed line) and of a standard Armenian cochineal (solid line).

Gold is widely used throughout the manuscript both as *gold leaf* and as *gold shell*. For what concerns gold leaf, two different preparations seem to be present: at f. 3r it is an Au/Ag alloy above an organic glue, similarly to the tradition of Eastern miniature schools, while at f. 163r it could be Au with traces of Cu on a lead white substrate, more similar to the Western miniature school, therefore indicating that different artists worked at those folios for gilding.

3.4. The first painter

A first painter, working on the miniatures of the first folios (1r-8r), used indigo for blue, vergaut (i.e. indigo + orpiment) for green and orpiment for yellow. This is a rather classical palette, typical of artists working in Early Middle Ages Europe. Particularly characteristic is the use of the mixture blue + yellow to obtain a green pigment.

3.5. The second painter

A second painter, who was at work on the subsequent miniatures (e.g. 16v-18r), used ultramarine blue for blue, verdigris for green and yellow ochre for yellow. The use of ultramarine blue indicates a wealthy commissioner and it is certainly favoured by the relative proximity to the source of the pigment, the precious stone lapis lazuli whose mines were at Badakshan in modern Eastern Afghanistan; in fact, the occurrence of ultramarine blue in miniature painting is much more common on manuscripts from nearby cultures (e.g. Persian, Ottoman) than on European manuscripts.

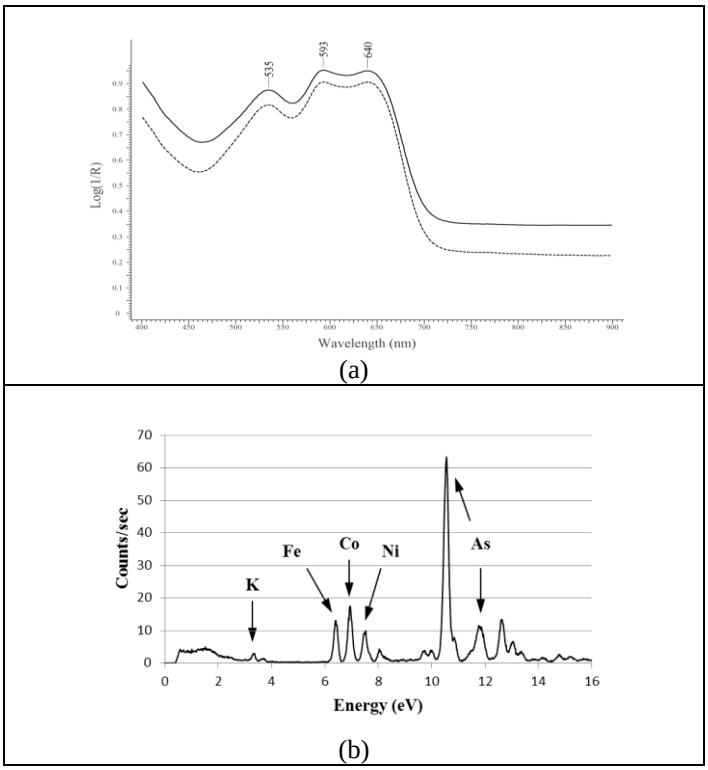


Figure 7. Spectra from analysis of blue areas at f. 126r: (a) FORS (smalt standard: solid line, sample: dashed line) and (b) XRF.

3.6. The third painter

A third artist worked on the side decorations present in several instances, e.g. at ff. 126r, 266r, 304r (examples were shown in Figure 2b). This painter used smalt for the blue and malachite for the green areas. The presence of smalt, a cobalt/potash glass pigment, is not unusual when compared with the palettes identified in earlier Armenian manuscripts [9-11] but its use in miniature painting is notwithstanding peculiar because it was more typically employed in easel and mural paintings. At any rate, more data on Armenian manuscripts

should be gathered in order to evaluate whether this pigment was characteristic or not of this pictorial school. Smalt was identified according to its typical FORS spectrum (Figure 7a) and to the presence of Co, Ni, Fe, As and K as revealed by means of XRF (Figure 7b). These elements allow to hypothesise that *skutterudite*, a mineral with formula $(Co,Ni,Fe)As_3$, was the source of cobalt for the preparation of the glass pigment; the amount of As is unusually high, perhaps due to incomplete roasting of the mineral.

4. Conclusions

Non-invasive analysis allowed to gain information on the pictorial materials used to decorate ms. 3290. The manuscript is illustrated with plenty of precious colorants (ultramarine blue, gold, cinnabar, orpiment, Armenian cochineal, etc.). Three different painters can be recognised all through the artwork, and every painter chose his own palette, with concern mainly to blue and green colorants, maybe according to the possibilities given by the commissioners.

In order to better appreciate the information obtained in this analytical research, it is obvious that many more Armenian manuscripts might be studied and characterised. The present study aims at becoming a reference point for a wider research on the Armenian manuscripts held in Italian institutions.

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