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ОБЩАЯ И ФИЗИЧЕСКАЯ ХИМИЯ

HISTORY AND CHEMICAL CHARACTERIZATION OF A FOURTEENTH CENTURY ARMENIAN ILLUMINATED GOSPEL FROM THE AGHTAMAR ISLAND

YEGHIS KEHEYAN*[1], PIETRO BARALDI[2], GAYANE ELIAZIAN[3], STELLA NUNZIANTE CESARO[1] and DANIELA FERRO[1]

[1]CNR, c/o Dept. of Chemistry, University of Rome "La Sapienza"
p.le A. Moro, 5 Rome (Italy) E-mail::yeghis.keheyan@uniroma1.it
[2]Dept. of Chemical and Geological Sciences
University of Modena and Reggio Emilia, Via G. Campi, 183, Modena (Italy)
[3]Restoration Dept. of Matenadaran Museum of Yerevan
Yerevan, Mashtotsi Ave., 53 (Armenia)

This contribution presents results from the ongoing technical study of a fourteenth-century Armenian illuminated manuscript in the collection of the museum of Matenadaran (Yerevan, Armenia). A characterization of the manuscript components has been undertaken to create a preservation plan for the manuscript. Proceeding in the analysis of the painting materials and techniques of Armenian illuminated manuscripts we refer about a XIV century Gospel (Ms. 4915) from Aghtamar, Van, (Historical Armenia). Some microsamples were analyzed with micro-Raman, FT-IR, XRF, SEM-EDX spectroscopy and showed that traditional pigments were used, but some products and mixtures are typical of Armenia illumination, such as vergaut, a mixture of indigo and orpiment, a green suitable for foliage. Among the most frequently found pigments there are: carbon, white lead, gypsum, calcite, orpiment, lazurite, indigo, cinnabar, hematite, azurite, minium, etc. A pale green is antlerite, a basic copper sulfate characteristic of regions around Armenia.

Figs. 19, table 2, references 25.

Introduction

The manuscript n. 4915 is an Armenian illuminated manuscript written on paper and conserved at the Matenadaran. It is one of the survived manuscripts. Book illumination is one of the most important kinds of fine arts of the Middle Age [1]. Combining valuable things from neighboring countries: Assyria, Babylonia, Egypt, Greece and Byzantium and with its own high culture, Armenia has achieved great success in the field of the chemistry of dyes [1-4].

A brilliant example of that are artistically executed illuminated manuscripts, which have been preserved to our days due to high quality of paints.

At present only few analyses have been carried out in order to identify the nature the used dyes ~~(Orna).~~ A careful study of Armenian medieval recipes for obtaining pigments and paints reveals a variety of products [5-10].

The combination of different and independent methods of analysis, allows us to determine the identity of the materials used, provides an opportunity not only to determine the composition of the pigments, but also to reproduce them according to the recipes reported in the ancient manuscripts. The findings enlighten about the condition of the manuscript and also shed new light on technical aspects of medieval Armenian monastic art [11-16].

In this paper we studied manuscript n. 4915 (Aghtamar, Van). Some micro-samples were taken from different parts; sheets, inks, wood cover, leather and a range of pigments and were analyzed by using scanning electron microscope (SEM), energy dispersive x-ray spectrometry (EDS), Fourier Transform infrared spectroscopy (FTIR), micro Raman spectroscopy (Raman) and X-ray fluorescence (XRF). The data obtained with each technique is discussed. The samples were taken with a lancet on deteriorated portions of Armenian codex. Only small fragments were used, since spectroscopic techniques need amount down to the microgram. This is due to their high spatial resolution, also the overlapping layers of pigments and preparation to be studied and their molecular identity to be ascertained in a non-destructive way: the same samples could be subjected to other analyses with other techniques. The goal of the analysis of the manuscript lies in the lack of analytical information on the pictorial media used in medieval ages in this locality. Even though medieval illuminated manuscripts studied from the historical point of view rarely described in their material composition. Though the number of colors is limited, they are used in their pure combinations. Thanks to different degrees of saturation and the specific selection of hues, a very special range of colors is attained, unusual in its expressiveness and poetic mood.

Description of manuscript

The Aghtamar Gospels are a single bound manuscript (26.5-27×18.5-19 *cm*) of 288 leaves written in *bolorgir*, a medieval Armenian cursive script. While no binding is extant, sewing holes and trimmed edges show that it was bound at least twice previously. Notable are the full-page miniatures of the evangelists Matthew, Mark, Luke and John. Yellow, blue, green, magenta and red are lavishly employed in the miniatures in a range of shades.

White, black, grey and brown are used in discrete areas. The facing pages of the miniatures contain brightly decorated headpieces that signal the opening of the Gospel texts, plus stylized initials, zoomorphic writing and linear arabesque marginalia.

Most of the text is written with opaque black ink, with occasional rubrication (Rubrication was one of several steps in the medieval process of manuscript making)

and headings in orange-red or dark magenta. A faint grey color and strong indentations in the paper substrate show the ruling lines. The paper of the text block is surface sized, probably with starch, and has been burnished to give it a smooth, glazed appearance similar to parchment [9].

Writer: Grigor, Painter: Zakaria, Tuma priest, receiver: Murat

Material: Paper, 26.5-27×18.5-19 *cm*, Written in two column (2×12.5-13) Lines: 21

Cover is made of wood and brown leather. There are 35 miniatures including Canon Tables, headpieces and titles.

Materials and methods

A total of 29 samples were examined belonging to different parts of the manuscript n. 4915 (Aghtamar, Van): leaves, inks, wood cover and leather and a range of pigments from different illuminated folios. Most of them were recovered during the manuscript restoration and only few of them were extracted with a lancet.

The aim of the investigation was to obtain a comprehensive outline of the codex materials on the basis of the most current technologies. When possible all techniques were applied to the study of the same samples. However, in a few cases this extensive study was not possible due to the scarcity of the sample.

Micro-Raman spectroscopy

The Raman spectra were recorded with a Labram instrument (JobinYvon-Horiba). The laser used had wavelength of 632.8 *nm*; the Rayleigh radiation was eliminated with an edge filter. The Raman detector was a charge-coupled device (CCD)(254×1,024 pixels) cooled to −70 °C by the Peltier effect. The spot to be analyzed was focused with the chosen Olympus objective ×10, ×50 or ×100, and the laser, properly attenuated in order to avoid possible alteration of the material. The spectra were recorded in backscattering in several positions within a small area (down about 2×2 μm) the sample. The spectral resolution was about $2cm^{-1}$. The maximum power employed was 5 mW, and the recording time for a good signal-to-noise ratio varied between 10 and 100 *s*, according to the intrinsic intensity of the radiation. Subsequently, GRAMS/AI 7.02 software was used for the elaboration of spectra.

X-ray fluorescence spectroscopy

XRF analyses were carried out with a transportable instrument Artax 200 Bruker with a Molybden tube with an acceleration voltage of maximal 50 *kV* and a current 700μA measuring spot size with a diameter of ca~ 5 *mm* for 30 s.

Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS)

SEM-EDS micro-morphological and chemical investigations were carried out by a LEO 1450 VP -INCA 300 scanning electron microscope coupled with a system for X-ray microanalysis, resolution of 3,5*nm* with the possibility to analyze non conductive sample by operating in no-vacuum conditions. The interfacing with EDS gives the possibility to have qualitative and quantitative composition of elements into the area observed. For quantitative analysis this method is not sensible under 0.1% in weight. Electron beam energy is 20*keV* to allow the detection the most of the chemical elements. Under these experimental conditions the ancient samples have been analyzed without any treatment, by using the apparatus in low vacuum. The observations in back scattered electron mode allows to discriminate the various materials; pigments, ligands, fibers, wood on the basis of the "atomic number contrast" to individuate areas of different composition.

FT-IR spectroscopy

Diffuse Reflection Infrared (DRIFT) spectra of powdered samples were recorded using an Alpha FT-IR spectrometer (Bruker) equipped with the DRIFT module in the spectral range 7500 – 375 cm^{-1} at a resolution of 2 cm^{-1} cumulating at least 200 scans.

A few endband samples were studied in Attenuated Total Reflectance (ATR) spectroscopy using a Thermo Electron Nicolet 6700 FTIR spectrometer equipped with a Diamond cell detector in the spectral range 4.000 - 400 cm^{-1} at 4cm^{-1} resolution. Compounds have been recognized by comparison with spectra of pure minerals and/or databases (www.irug.org).

Results and discussions

Information available on the pigments used in Armenian manuscripts is rather poor if compared to manuscripts from other cultures. The scientific literature contains few studies, among which the most relevant are those by Orna *et al.* [5-9 and references therein]. With few exceptions [10] these studies date back to the '80 and early '90 and are entirely based on invasive methods, i.e. upon withdrawal of micro-samples. In Figure 1 the picture of some folios are reported with indication of the exact sampling point.

The whole palette and the techniques for their detection in the codex are reported in Table 1.

Table 1

Sample	Color	Raman	FT-IR	XRF	EDS[1]
01	red	cinnabar, carbon	silicate, $CaCO_3$		cinnabar, (Hg, S)
02	black ink	Carbon	cellulose	Fe	
03	dark ochre	carbon, (cinnabar)			
04	yellow halo	lazurite, orpiment, (cinnabar)	silicates, $CaCO_3$	As	
05	pink dress				
06	black thread	carbon, hematite	irongall ink		Ca, (Fe), (Cu), As, (S)
07	green leaves	orpiment, indigo, antlerite	silicate, $CaCO_3$ (indigo)		
08	white chaptel	indigo, hematite			
09	red ink	Cinnabar			(Hg, S)
10	dark blue desk	indigo, cinnabar	$CaCO_3$, Co and Sn oxides		
11	white in blue dress	orpiment, indigo		As	
12	brown stripe	Fiber	$CaCO_3$,		
13	dark blue decoration				Ca, Ti,Al, Si, (Mg), S
14	red ink	cinnabar, (azurite)			
15	yellow shade	lazurite, cinnabar, indigo			
16	black thread	Protein	black fibroin		
17	red thread	Protein			
18	blue thread	protein, Indigo	fibroin cellulose		
19	raw thread	Protein	fibroin		
20	leather cover	protein, (gypsum)			
21	blue paper	Carbon	cellulose		
22	red ink	Cinnabar			
23	black ink				
24	paper	indigo, quartz	cellulose		cellulose
25	wood plate		cellulose		wood
26	brown ink	Hematite	organic residues, water, silicates, (hematite, indigo)		
27	brown ink	carbon, hematite			partially decomposed old ink
28	black ink	hematite , carbon			
29	blue ink	Indigo	(indigo)		Ca, S (principal elements)

[1]Relatively minor quantity of the elements is reported in parentheses.

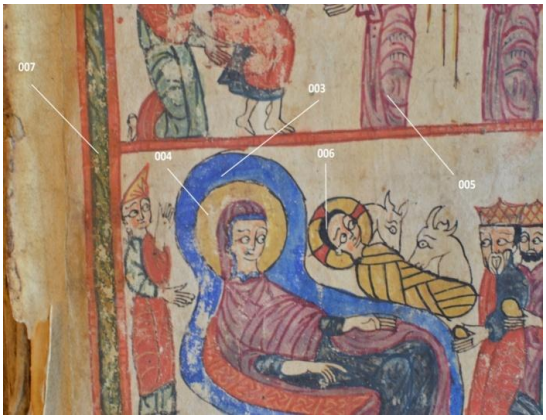
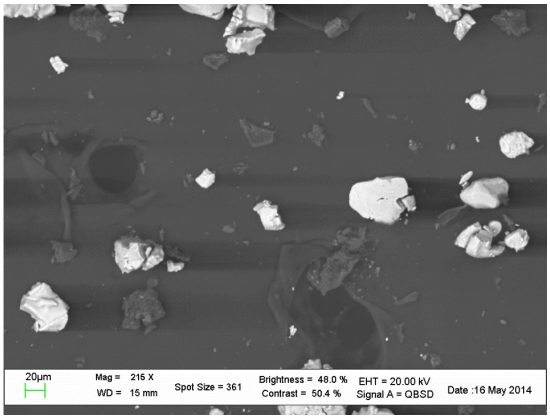


Fig.1. Presentation of Nativity, Folios 11r, 3v, 10v.



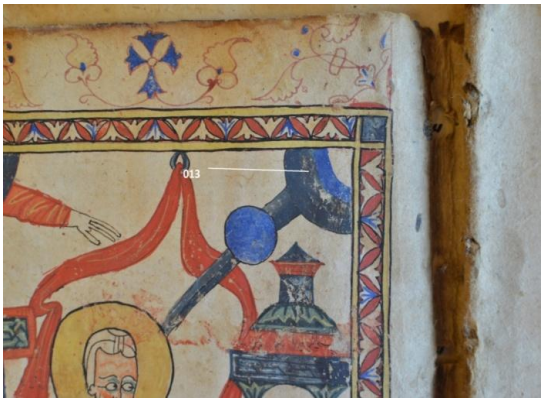


Fig.4. Sample 013.

SEM-EDS analysis

To characterize a manuscript, it is very important to be able to recognize all the minimal details either of the support, or of the artistic picture. The samples have been analyzed in order to detect either the morphological aspect or the chemical elements present in the different phases.

Table 2 is representative of the characteristic element useful for the identification of a pigment. In fact, C and O are not considered and the quantitative values (wt%) normalized to 100% are only indicative of a possible relation among chemical species.

Table 2

Sample n.	Mg	Al	Si	S	Cl	Ca	Ti	Fe	As	Hg
01	0.8		2.4	10.6		5.2				53.2
01 bis	1.3		2.4	13.1		5.3		1.3		61.4
06		2.8		9.0	1.4	39.2		7.3	35.0	
06 bis			1.3	3.1	1.9	31.3		10.8	32.9	
07										
09	4.3	15.0	30.6	4.03	2.4	24		9.5		
13		13.6	30.4	3.2		3.6	21.4	1.60		
13			16.3	6. 5.4	14	10.0	4.8			
24 light part 24 dark			21.5 0.8							
25		8.4	4.7			2.6		3.3		
29	4.4 4		11.2 0	11.3	8.4	36.1		3.9		
29	3.7 2		10.1	16.8	4..3	36		3.7	7.2	

The observation in back-scattered electrons (QBSD) allows distinguish elements through the contrast difference. A light contrast indicates the presence of element with high atomic weight. In the SEM picture it is possible to observe the complete integration with the fiber of the ink materials composed by a matrix in which small granules are dispersed with the function of pigments. The big cubic crystals are not pertinent with the original status of sample 1, the compactness of the layer of ink is observable and was in a thick layer and pressed into the fibrous matrix.

Concerning the sample 1 from the SEM back scattering image it is possible to observe that the fiber is swollen, perhaps due to interaction with the pigment (Fig.2). The EDS analyses reveal the presence of Hg and S referable to vermilion, the corresponding presence of Ca could induce to hypothesize the use of gypsum as substrate. The date is confirmed by other techniques (see Table 1).

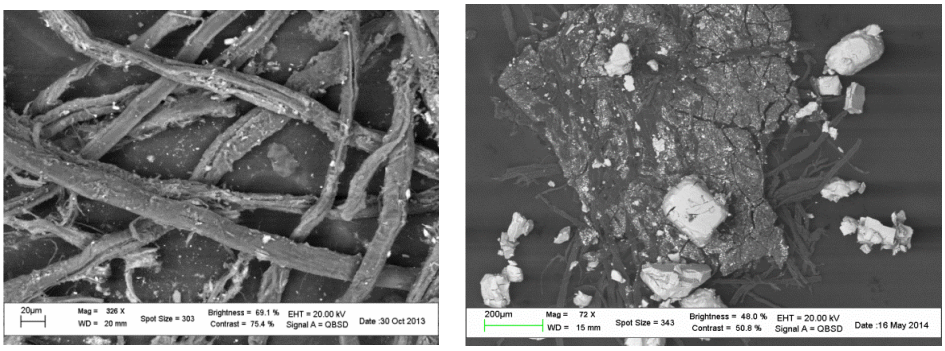


Fig.2. SEM-EDX of sample 01. Red color on paper, left: fibers morphology, right: pigment.

In the case of sample 006, the results have identified only few scattered fragments and not consistent with the fibers. This observation leads to consider the use of a support for the pigment labile in time and which therefore requires attention for its preservation. The micro areas analyzed reveal elements that lead to consider an overlapping of black pigment on orpiment.

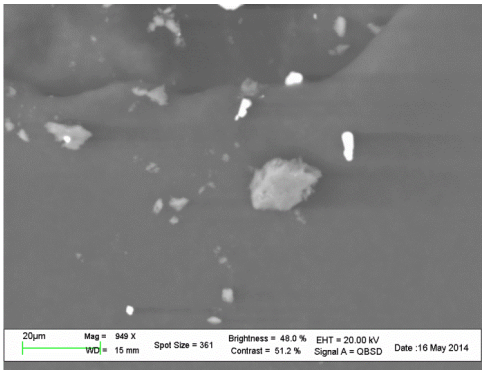


Fig.3. Sample ~~0~~06, dark pigment taken from the part of head.

Sample 013 presents decidedly a dark blue coloration. The few fragments available for an analysis allow to suppose the use of a pigment with cubic crystals: this excludes the use of an ink made as composite matrix/pigment, but can indicate the use of gypsum as support to a liquid solution or the use of two different materials for chromatic effects. The dispersion of very small grains, in white contrast allows identify the pigment absorbed by all the fibers. Big cubic crystal could have the original function to homogenize the surface.

In sample ~~0~~25, Fig. 5 the morphological aspect seems to identify the presence of wood, even if the observed anatomic detail is not sufficient to trace the tree species. The morphological details can be useful to compare the sample with others taken from other manuscripts. The clear particles on the surface consist in acicular crystals.

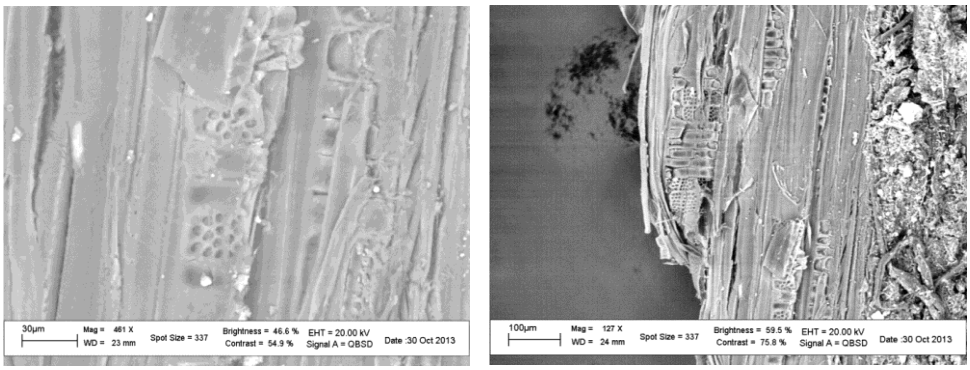


Fig. 5. SEM image of sample ϕ25 with analysis of the surface layer, anatomic details of wood, white crystals (acicular).

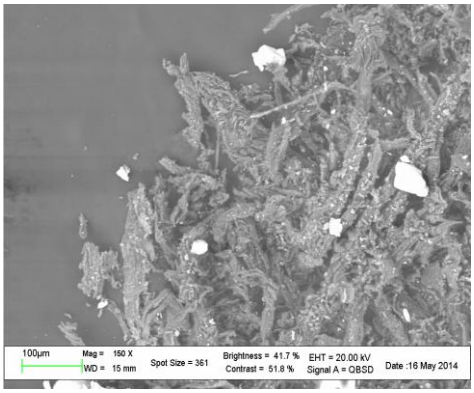


Fig. 6. SEM-EDX sample ϕ29 is a mixture of blue ink indigo, fiber, gypsum and different other mixtures.

FT-IR analysis

The spectra FT-IR ATR for samples 16, 18, 24 (from top to down) and sample 21 have been used.

ATR spectra of samples 16, 18 and 24 are compared in Fig 7.

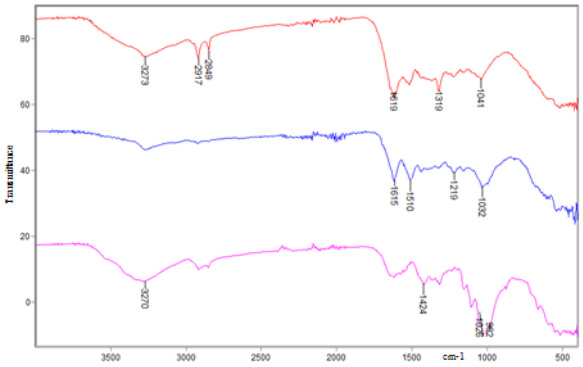


Fig. 7. From top to bottom: ATR spectra of sample 16, is fundamentally protein, sample 18 in the middle (blue) is only protein and in bottom (sample 24) is a cellullose.

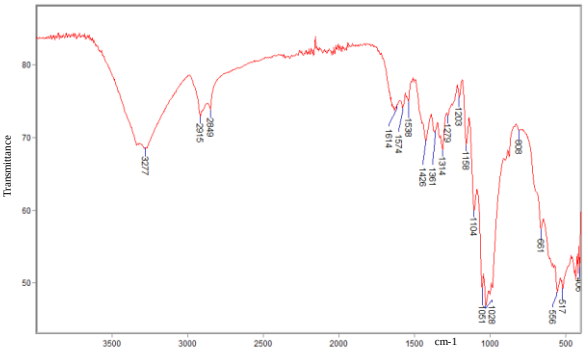


Fig.8. FTIR ATR spectrum of sample 21 (cellullose of paper).

A few pigments have been analyzed using the DRIFT spectroscopy. A strong absorption band at 1435 and a medium intensity peaks at 877 and 713 cm^{-1} have been observed in most of the spectra with constant intensity ratio depending on the concentration of the sample dispersed in potassium bromide. They indicate the presence of powdered calcium carbonate probably used for coating paper and/or as support of the pigment. The assignment is supported by the observation of two combination modes at 2516 and 1796 cm^{-1} respectively [17].

An additional absorption band was also detected around 1030 cm^{-1} in the spectra of all pigments analyzed together with broad features lying around 3600 and 1600 cm^{-1}, assigned to O-H stretching and H-O-H bending modes respectively, and a weak doublet at 2919 and 2884 cm^{-1} readily attributed to C-H stretching modes. The simultaneous observation of the mentioned spectral features suggested the presence of an organic component, probably Arabic gum often employed as binding medium [18]. For sake of example the DRIFT spectrum of pigment 12 is shown in Fig. 9. Only the spectral range of fundamental modes of the analyzed samples (4000-375 cm^{-1}) is reported in the DRIFT spectra, since overtones and/or combination modes lying at frequencies higher than 4000 cm^{-1} have not been detected.

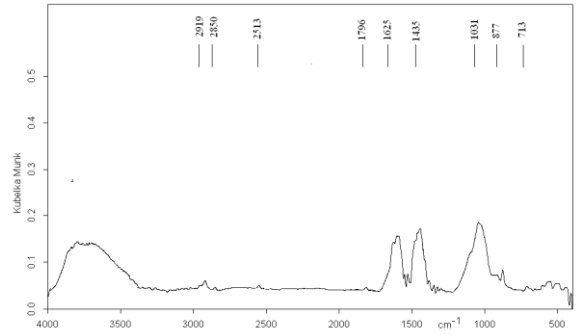


Fig 9. DRIFT spectrum of pigment 12.

It is evident that the presence of noticeable amount of calcium carbonate and/or binding media in the micro samples made difficult the detection of the pigments and

uncertain their assignment. However, in a few cases, hypotheses on the nature of the utilized pigment could be formulated.

The spectrum of pigment 07 is reported in figure 10. A high concentration of calcium carbonate is observed together with the binding medium peaks. Additional bands are detected at 1580, 1120, 1070 and 750 cm^{-1} suggesting the existence of natural indigo traces in the sample (IRUG database, [15]).

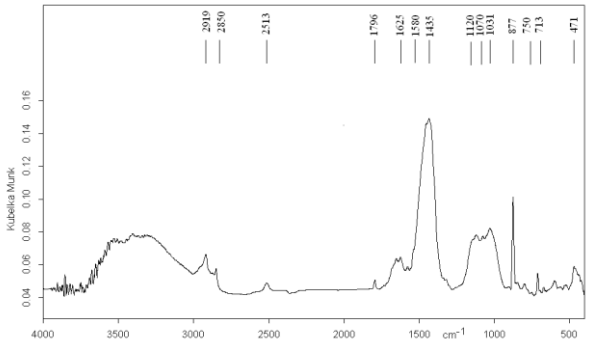


Fig. 10. DRIFT spectrum of pigment 07.

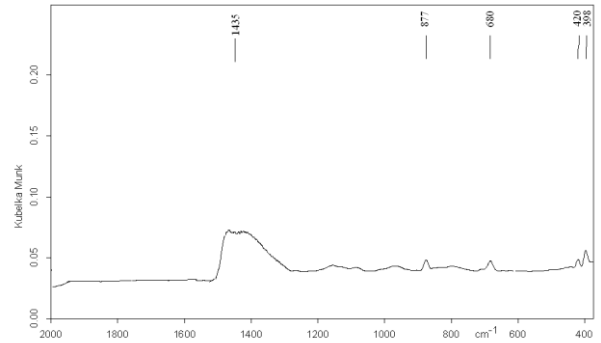


Fig. 11. DRIFT spectrum of pigment 10.

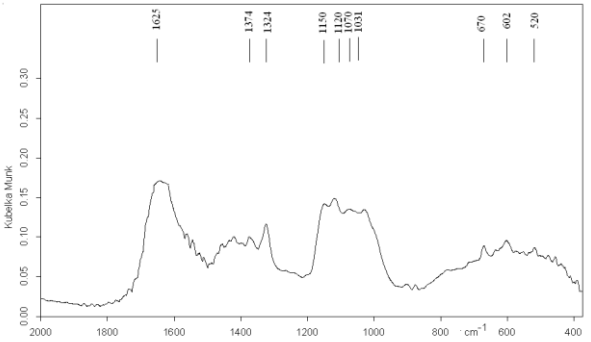


Fig. 12. DRIFT spectrum of pigment 26.

The very magnified DRIFT spectrum of pigment 10 is shown in figure 13 only in the 2000-375 cm^{-1} spectral range where active bands were detected. Some calcium carbonate is shown (1430 and 877 cm^{-1}). Very tiny additional peaks are seen at 680, 420 and 398 cm^{-1} in a spectral range where oxides are expected. The presence of

cerulean blue traces, a mixture of cobalt and tin oxides, can be only hypothesized [19].

In pigment 26 (Fig. 12) the binding medium is still present at 1030 cm^{-1} but calcium carbonate is nearly absent allowing a more accurate inspection of the 1450-1300 cm^{-1} range. Therefore, peaks at 1374 and 1324 cm^{-1} are observed. The spectral behavior of this sample in the 1100-1000 cm^{-1} region shows a close similarity with that of the pigment 7 suggesting indigo as component of the pigment. The aforementioned bands at 1374 and 1324 cm^{-1} seem to support the previous assignment. Few peaks lying at 680, 602 and 570 cm^{-1} suggest an additional constituent of the pigment and are tentatively attributed to hematite in traces [20-24].

Raman analysis

A research on some micro fragments from two Armenian manuscripts has been carried out. Raman spectroscopy was employed with a red laser. It is particularly useful as the laser may be directed, using microscope optics, even to single pigment grain, and using fiber optics it may be directed at paint samples */in situ/*. Among the most frequently found pigments following pigments have been found: carbon, white lead, gypsum, calcite, orpiment (with realgar), lazurite, indigo, vermilion, probably mosaic gold (purpurine), azurite, minium). A green pigment probably is a basic copper sulfate (antlerite) with a defined Raman spectrum.

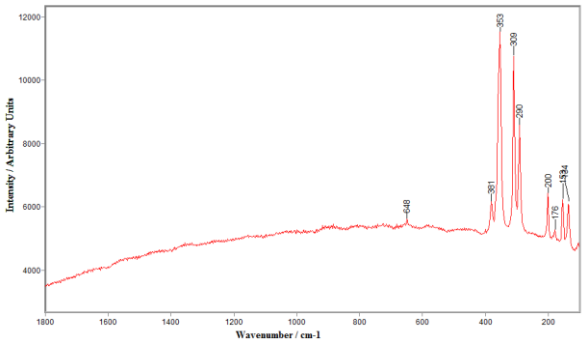


Fig.13. Sample 04, orpiment alterated

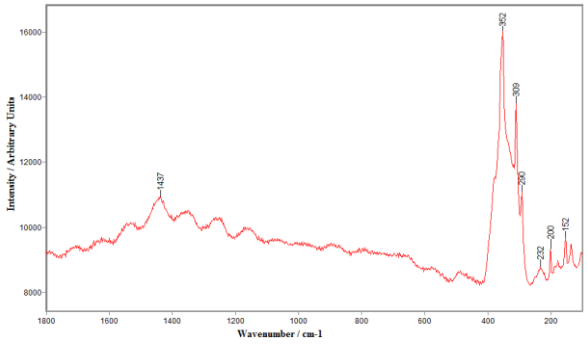


Fig.14. Sample ~~0~~04, yellow point in the miniature is orpiment

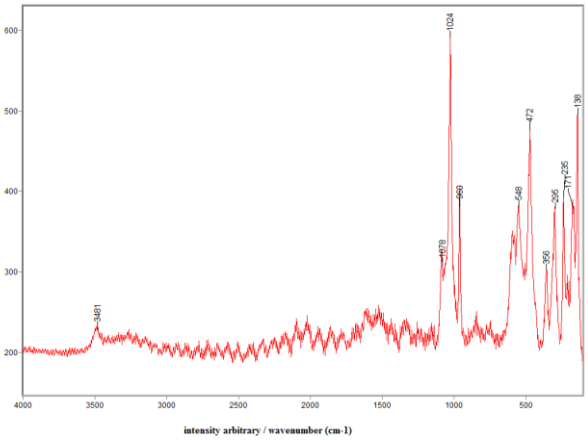


Fig.15. Sample 04 yellow-green point; sulfate e/o phosphate of iron?

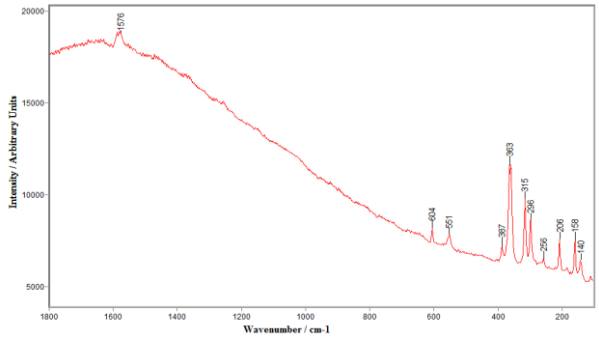


Fig.16. Sample 11; Indigo with orpiment (25)

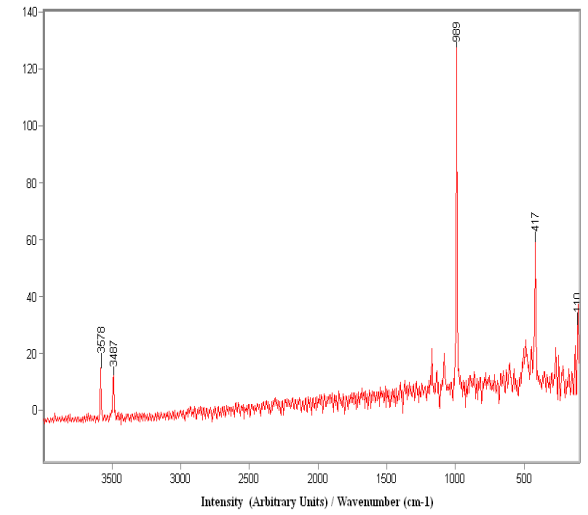


Fig. 17. Raman Spectrum of a pale green of the Gospel is antlerite; a basic sulfate mineral $CuSO_4*2Cu(OH)_2$, probably from the region around (see rruff database).

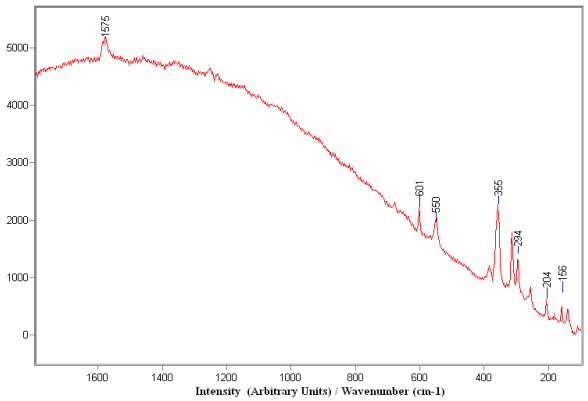


Fig.18. Vergaut is a mixture of indigotine and orpiment. It refers to samples with this material obtained from boiling indaco (indigo) with orpiment (samples 7,11).

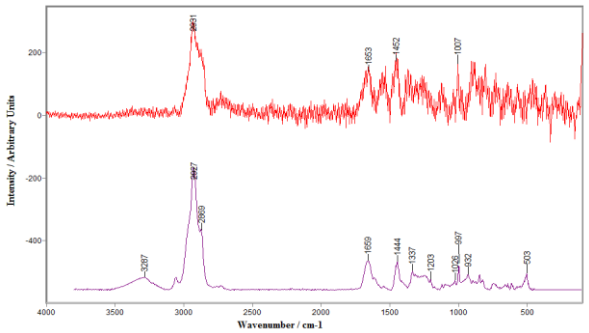


Fig.19. Raman spectrum of fiber (sample 19, raw thread) compared
with wool protein spectrum.

Armenian illuminators have left no written account of how they prepared their pigments. Six pigments are the staples of the Cilician palette: gold, white lead, vermilion, orpiment, ultramarine and red lake. The first four are ancient pigments, the last two medieval. In Cilician manuscripts, as in Byzantine, it served for backgrounds, highlights, halos, and other decorative purposes. White lead was one of the earliest artificially prepared pigments. It was the most widely used of all artists' pigments both in Europe and the East. Vermilion or cinnabar occurs in nature as the mineral cinnabar and its presence has been detected in samples 9, 22. In many cases, i.e. samples 1, 3,10, 14, 15 and 28, it was observed mixed to other pigments occurs in nature as the mineral cinnabar. China very early found methods to manufacture the red pigment from Hg and S. The natural and artificial pigments can be distinguished on the basis of their particle size. Red lake is a magenta red pigment. Natural green is missing from the Armenian palette (apart from the rare antlerite) this is made up of orpiment with small quantities of indigo or ultramarines. The organic yellow, which in some cases resembles saffron, is also used in mixture, sometimes to supply green by mixing with ultramarine, sometimes to add warmth to orpiment.

Conclusions

Twenty nine samples coming from the fourteenth-century Armenian illuminated manuscript belonging to the collection of the museum of Matenadaran (Yerevan, Armenia) have been studied in order to identify the pigments and the binding medium. To this aim few techniques that is micro-Raman, FT-IR, XRF and SEM-EDX spectroscopy have been adopted. All samples have been studied using Raman spectroscopy and the data obtained are supported by the results furnished by an independent technique.

It is worth observing that analyses showed the use of traditional pigments in illuminations such as cinnabar, orpiment, indigo, hematite, lazurite, azurite, iron gall. Analysis by micro-Raman, FT-IR, XRF, SEM-EDX spectroscopy showed the use of traditional pigments in illuminations. However, some products and mixtures are typical of Armenia illumination, such as vergaut, a mixture of indigo and orpiment suitable for foliage. An iron gall component was unambiguously found with SEM-EDS. The material was found as small particles rich in both iron and sulfur. The binding medium in the ink was determined by FTIR as a mixture of a gum and a resin, the same binding medium was also identified in the paints. Red ink was cinnabar identified by Raman and EDS. Dark blue was a mixture of indigo and cinnabar, yellow shade was mixture of lazurite and indigo mixture. In addition, threads are identified as proteins. Green leaves are orpiment and indigo as identified by Raman analysis.

ԱՂԹԱՄԱՐ ԿՂԶՈՒ ՀԱՅԿԱԿԱՆ 14-ՐԴ ԴԱՐԻ ՄԻ ԱՎԵՏԱՐԱՆԻ ՊԱՏՄՈՒԹՅՈՒՆԸ ԵՎ ՔԻՄԻԱԿԱՆ ԲՆՈՒԹԱԳՐՈՒՄԸ

ԵՂԻՍ ՔԵՀԵՅԱՆ, ՊԻԵՏՐՈ ԲԱՐԱԼԴԻ, ԳԱՅԱՆԵ ԷԼԻԱԶՅԱՆ, ՍՏԵԼԼԱ ՆՈՒՆՅԻԱՆՏԵ ՉԵՋԱՐՈ և ԴԱՆԻԵԼԱ ՓԵՌՈ

Հոդվածը նվիրված է միջնադարի հայկական ավետարաններից մեկի մանրանկարներում օգտագործված նյութերի անալիզին՝ որը հնարավոր է դարձել վերջին 1-2 տասնամյակում մշակված հիմնականում սպեկտրաչափական եղանակների շնորհիվ: Նմանատիպ հետազոտությունները մեծ պատմամշակութային արժեք են ներկայացնում: Միևնույն ժամանակ դրանք խիստ կարևոր են Մատենադարանում տարվող ռեստավրացիոն աշխատանքները պատշաճ մակարդակով իրականացնելու տեսանկյունից:

ИСТОРИЯ И ХИМИЧЕСКИЕ ХАРАКТЕРИСТИКИ АРМЯНСКОГО ЕВАНГЕЛИЯ ЧЕТЫРНАДЦАТОГО ВЕКА ОТ ОСТРОВА АХТАМАР

ЕГИС КЕГЕЯН, ПИЕТРО БАРАЛДИ, ГАЯНЕ ЭЛИАЗЯН, СТЕЛЛА НУНЦИАНТЕ ЧЕЗАРО и ДАНИЕЛА ФЕРРО

Статья посвящена анализу красителей, употребленных в миниатюрах одной из армянских средневековых рукописей. Анализ красок стал возможен благодаря изысканиям в области спектроскопии, проводимым за последние 10-20 лет. Вышеназванные исследования, несомненно, представляют собой историко-культурную ценность, в то же время являются очень важным фактором в работах Матенадарана по консервации и реставрации.

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