ATR/ FTIR INVESTIGATION INTO THE NATURE OF THE METAL THREADS FROM ROMANIAN MEDIEVAL TEXTILES

Zizi Ileana BALTA[1], Ioana DEMETRESCU[2], Ileana CRETU[3], Mihai LUPU[4]

In this paper, chemical and physical nature of the metal threads surfaces and their silk core yarns used in the Romanian religious embroideries and velvet brocades, dating from 15th to 16th century, have been investigated by using the Attenuated Total Reflectance/ Fourier Transform Infrared Spectroscopy (ATR/ FTIR). Results obtained may help decoding the history of some of the most valuable medieval metal thread textiles preserved in the Romanian museums and monasteries collections, and advancing diagnostic techniques for choosing appropriate conservation and restoration treatments and efficient monitoring of the deterioration processes.

Keywords: Attenuated Total Reflectance/ Fourier Transform Infrared Spectroscopy (ATR/ FTIR), metal threads, medieval textiles

1. Introduction

The ancient textiles decorated with precious metal threads are among the most valuable testimonies of the European cultural heritage and have a large geographical spreading in the world, marking actually the entire historical evolution of the humankind. Romanian museums and monasteries preserve one of the richest collections of archaeological and artistic metal threads textiles in the Southeastern Europe that reflect the triple influence of the Byzantine, Western and Oriental world, grafted on a deeply individual specificity.

The aim of our study described below was to bring new supplementary information on technological and manufacturing characteristics of the very thin and small, possibly multilayered, metal threads used for beautifully adorning the luxurious medieval metal threads textiles [1, 2]. We were particularly interested to identify the chemical nature of a possible organic material applied on the metal

[1] Researcher, Dept.of Scientific Investigation, National History Museum of Romania, Bucharest, Romania, e-mail: balta_z_i@yahoo.com

[2] Prof., Dept. of General Chemistry, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania

[3] PhD Senior Textiles Restorer, Dept. of Textiles Restoration, National Art Museum of Romania, Bucharest, Romania

[4] Prof., Dept. of Conservation and Restoration, Faculty of Art History and Theory, National University of Arts, Bucharest, Romania

threads surfaces and to determine the type, nature and the state of deterioration of the silk yarns on which the metal threads are wrapped around. Information acquired can be used not only by the restorers and conservators as an important and useful data when deciding and developing new appropriate restoration, preservation and conservation treatments, but also by art historians and curators for a correct interpretation of the function, significance, history and the degree of deterioration and degradation of the historical textiles.

2. Selection of the textiles

The metal threads samples were collected from the medieval gold brocaded velvets and religious embroideries preserved at the Putna Monastery Museum and the National Art Museum of Romania.

The embroideries, made in most cases for liturgical purposes, were worn by priests as church vestments or used during the religious services (epitrachelion, epimanikia, altar door curtain, nabedernita, etc.), most of them being produced locally in the Putna Monastery's embroidery school. They were worked in the traditional Byzantine technique using the cartoon models painted on religious themes, similar to those in the medieval mural paintings and icons.

The golden brocaded velvets were imported and produced abroad in the Italian workshops from Venice or Florence, or in the Ottoman Empire workshops, as appears mentioned in the historical literature [3]. Brocades were sumptuous silk velvet fabrics richly adorned with precious metal threads that were used in the articles of clothes of Italian and Oriental influence by the Moldavian and Wallachian princes, princesses and boyars. They were usually donated to churches and monasteries after being worn. With a simple cut, the gold clothes could be dismantled, the resulting fabric fragments being used during the religious services as temple veils, covers for the Communion Table or as tomb covers [3]. The selected textiles and the samples studied by ATR/ FTIR are shown in Figure 1 and listed in Table 1.

Fig. 1. Metal threads analyzed by μATR and ATR spectroscopy

3. Experimental

Materials

Five types of metal threads within the seven usually encountered in the medieval textiles were considered in this study: strips wrapped around a yellow or a white undyed silk yarn (I), organic strip membrane with gilded silver traces on surface wound around a yellow silk yarn (II), wires twisted on a dyed (red, green) silk yarn (III), and wires (IV) and strips (V) with no fiber core yarns. The length of the threads was of approximately 5 to 8 mm.

Table 1

Historical textiles and samples analyzed by ATR/ FTIR

Sample	Selected Textile	Description	Dating	Attribution
1m	**Prince Stephen the Great tomb cover**	Gold brocaded velvet	16th cent.	Venice? (Italy)/ Putna Monastery
2m				
E1	**Embroidery with eagles**	Byzantine religious embroidery	16th cent.	Putna Monastery
E2				
E4				
5d	**Red court vestment**	Gold brocaded velvet	15th / 16th cent.	Italy/ National Art Museum of Romania
5e				
F1	**Curtain veil "Virgin Mary's Assumption"**	Religious embroidery	15th cent.	Putna Monastery
F2				
F3				
B2	**Epitrachelion**	Religious embroidery	15th cent.	Putna Monastery
B4				
CB1	**Court vestment (red caftan)**	Gold brocaded velvet	15th cent.	Venice? (Italy)/ Bistrita Monastery
CC1	**Court vestment (blue caftan)**	Gold brocaded velvet	16th cent.	Venice? (Italy)/ Bistrita Monastery
CC2				
K1	**Princess Maria Voichita tomb cover**	Gold brocaded velvet "drappi d'oro"	15th / 16th cent.	Italy/ Putna Monastery
K2				
K4				
L1	**Court vestment fragment**	Gold brocaded velvet	16th cent.	Italy/ Putna Monastery
I1	**Archeological textile**	Turkish handkerchief with embroidery	15th cent.	Putna Monastery
V18.1	**Epitrachelion**	Religious embroidery	15th cent.	Putna Monastery
V18.2				
EG5	**Epitrachelion**	Religious embroidery	16th cent.	Govora Monastery
EG6				
ET20	**Epitrachelion**	Religious embroidery	16th cent.	Tismana Monastery
ET21				
S2	**Princess Maria de Mangop Nabederenita**	Religious embroidery	15th cent.	Putna Monastery
T16.6	**Epitrachelion**	Religious embroidery	15th cent.	Putna Monastery
T16.7				
T1a	**Court vestment fragment**	Gold brocaded velvet	15th / 16th cent.	Italy/ National Art Museum of Romania
T1b				
Mir1	**Archeological textile**	Brocaded velvet	15th cent.	Museum of Bucovina
Mir2				
Ept19.1	**Epitrachelion**	Religious embroidery	15th cent.	Putna Monastery
Ept19.5				

Instrumentation

Preliminary examinations in reflected and polarized light, at different magnifications, were carried out with a stereomicroscope Nikon SMZ1000 and an optical microscope Nikon Eclipse LV100D.

MicroATR and ATR investigations were perfomed on two different instruments. The μATR data was acquired using a Bruker Tensor 27 FTIR spectrometer with a Helios ATR microsampler equipped with a diamond single monolithic ATR objective and a video camera for accurate sample positioning. For the ATR measurements, a portable Bruker Alpha FTIR spectrometer with a diamond ATR sampling module was employed. The analysis area, in the μATR method, was of 20 μm – 250 μm and, in the ATR method, of about 1mm. Both μATR and ATR spectra were recorded over the range 4000 – 400 cm^{-1} with a resolution of 4 cm^{-1}, averaged over 32 scans for μATR and 64 scans for ATR. Both μATR and ATR spectra were evaluated using Opus 4.2 software.

For each sample, three measurements on three different areas, in both μATR and ATR method, were performed: on metallic surface of the strip or wire, on silk and on both silk and metallic surface.

3. Results and discussion

Preliminary optical microscopy measurements showed that the metal strips had a total width of 0.2–0.6 mm and a thickness of 0.01–0.05 mm, while the wires diameters are of approximately 0.1– 0.3 mm. Microscopical examinations in polarized light revealed that all wires and some of the strips have striations on the surface caused by drawing in the manufacturing process, and that all of them present traces of an organic material on the surface.

Initially, 4 samples of each of the three metal threads types: I, II, V, were analyzed by micro-ATR. Subsequently, 28 samples from all the five types were analyzed by ATR only. Both micro-ATR and ATR analysis were carried out on three different areas: on the metallic surface of the thread, on the silk yarn and on both silk and metallic surface. Samples were not subjected to any preparative treatment and were analyzed under ambient conditions.

Only by micro-ATR was possible to obtain information on the chemical nature of the organic coatings applied on metal threads surfaces. On some samples was identified beeswax and on others a gum (possibly, acacia or arabic gum) which is in accordance with the written historical sources [4,5]. The results and the assignments of the infrared characteristic bands are presented in Table 2.

Table 2

Infrared band assignments (ν, cm^{-1}) for samples analyzed by μATR/ FTIR

L1 (M+S)	**L1 (S)**	**I1 (M+S)**	**I1 (S)**	**V18.1 (M)**	**V18.2 (O+S)**	**Natural Silk** [6]	**Beeswax** [6]	**Acacia gum** [6]	**Assignment**
				3340				3386 (S)	ν OH
					3298				ν NH+ν OH
3284	3285		3283			3298			ν NH+ν OH
	3078					3076			ν (CH=CH)
		2955				2978	2950 (S)		ν CH
	2927			2928		2933		2931	ν_{as} CH_2
2920		2924			2919		2918 (S)		ν_{as} CH_2
2851		2856		2856	2850		2851 (S)		ν_{a} CH_2
1734		1740			1734		1736		ν C=O
1625	1629	1623	1627	1605	1646	1645 (S)		1607	Amide I
1542					1541				Amide II
1512	1511	1517	1514			1517 (S)			Amide II
							1472		δ CH_2
					1462		1464		δ_{as} CH_3
1448	1447	1448	1446	1437		1448		1421	δ_{s} CH_3
	1407		1400			1406			δ (CH_2, OH)
		1372		1384	1376	1373		1361	δ CH_2
1322					1312				ν_{a} (OCO^{-})
1230	1229	1235	1227		1262	1225 (S)			Amide III
					1198	1171	1184		ν_{a} (N-C)
1163	1164	1160	1162		1162				ν_{a} (N-C)
1062	1070	1066	1068	1060	1073			1057 (S)	ν(C-O), ν(N-C)
					1050	1053			ν(C-O),ν(C-OH)
		943	971			966			r CH_2
					720	704	719		ν CH_2
671		672	668	672	669			650	γ CH_2 + γ CH + γ NH
	634		629		601	607			
	547		549			545			

Symbols: δ, in-plane bending; ν, stretching; r, rocking; γ, out-of-plane bending.; M+S, metal strip on silk; M, metal strip; S, silk; O+S, organic strip on silk; (S), strong band.

Organic materials identification was done by comparison of the resulting data with the correspondent reference data from the IRUG database [6], a spectral library containing classes of compounds frequently encountered in the cultural heritage materials, and the assignments by using the general tables with the IR spectral data of the principal organic compounds [7,8] and results of FTIR spectra with specific absorbance wavelengths of the bonds which appeared in slk fibroin [9]. In Table 2, results indicated presence of the characteristic bands of beeswax on both I1 and L1 metallic surface. For I1, the IR band specific to the CH group valence vibrations at 2955 cm^{-1}, then strong bands at 2924 cm-1 related to CH2

asymmetrical valence vibrations, at 2856 cm^{-1} to CH2 symmetrical valence vibrations, and at 1740 cm^{-1} to the C=O stretching vibrations, were observed. On the L1 metallic surface, the IR bands in the region 2851-2920 cm^{-1} associated with the vibration of CH_2 groups and the band centered at 1734 cm^{-1} related to the carbonyl group (C=O), were also identified. Presence of the characteristic bands of an acacia gum was observed on sample V18.1 at 3340 cm^{-1} (ν OH), 2928 cm^{-1} (ν_{as} CH_2), 1605 cm^{-1} (Amide I), 1437 cm^{-1} (δ_s CH_3) and a strong band at 1060 cm-1 specific to the valence vibration of the functional groups C-O and N-C. For almost all the analyzed samples (exemption sample V18.1 with no silk core) was detected the presence of the IR bands of silk at 3298 cm-1 (ν NH + ν OH), 3076 cm^{-1} (ν (CH=CH), 2978 cm^{-1} (ν CH), 2933 cm^{-1} (ν_{as} CH_2), 1645 cm^{-1} (ν C=O Amide I), 1517 cm^{-1} (δ N-H Amide II), 1448 cm^{-1} (δ_s CH_3), 1406 cm^{-1} (δ (CH_2, OH)), 1225 cm^{-1} (ν C-N + δ N-H Amide III), 1171 cm^{-1} (ν_a (N-C)), 1053 cm^{-1} (ν (C-O), ν (C-OH)), 966 cm^{-1} (r CH_2), and 704 cm^{-1} (ν CH_2).

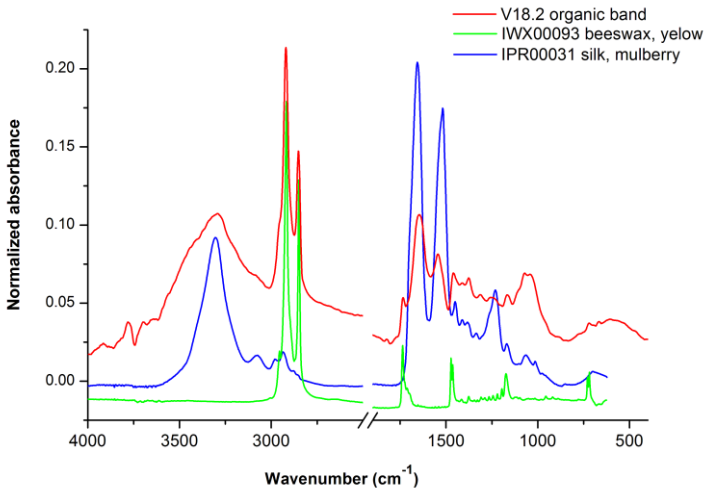

Fig. 2. μATR spectra of sample V18.2 compared with mulberry silk and beeswax (IRUG database)

No conclusive results were obtained by ATR for neither of the wires or strips analyzed. But interesting data resulted instead on the silk yarn cores of the metal threads and important differences between them related to the presence of sericin along with fibroin and the type of silk spun from different silkworms were observed, particularly in the wavelength range between 1800 and 800 cm^{-1} (Fig.3).

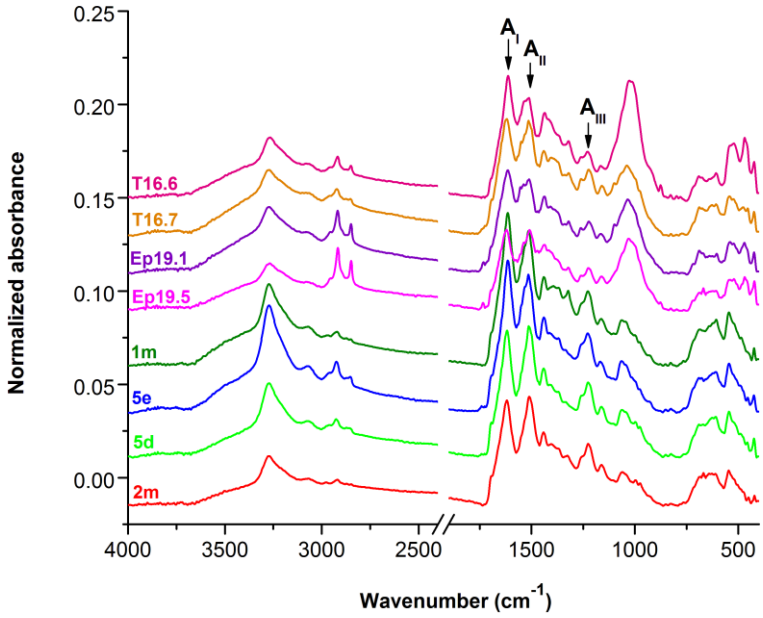

Fig. 3. ATR spectra of the silk cores of metal threads: 1m, 2m, 5d, 5e, Ep19.1, Ep19.5, T16.6 and T16.7.

Silk is a natural protein fiber having a chemical composition consisting essentially of 75-83 % by weight fibroin, 17-25 % sericin, 1,5 % fats and wax, and 1-2 % mineral salts. Wide variation in composition, mainly in the sericin and fibroin content, could result due to the different types of domesticated or wild silkworm species from which silk fibers are spun (ex. B. mori, A. panda, N. edulis, S. pavonia, A. luna etc.) [10]. Sericin gum acts as a protective coating for the silk fiber against heat and light damage, but over time, because it yellows easily, was selectively removed through the silk processing, especially for dying, to improve its color and texture. Removal of the sericin from silk fibroin is accomplished by a process called “degumming,” usually by one of three methods: (1) extraction with water at high temperatures, (2) extraction with dilute aqueous alkali or soap solutions, or (3) removal by proteolytic enzymes.

According to the literature [11,12], for evaluation of silk degradation and the sericin content in the silk fibers, the following estimators were considered: 1) Iamide l / Iamide ll ratio related to the hydrolysis processes; 2) $\Delta\nu$ (cm^{-1}), the difference between wavenumbers specific to amide I and amide II structures, related to chain degradation; and 3) the intensity ratios of the 1070/ 1164 and 1400/1444 IR wavenumbers for detecting the presence or absence of sericin in the silk fibers. All these results are presented in Table 3.

Table 3

Intensity ratios and Δν calculated for the silk cores from the metal threads samples

Sample code	Iamide l / Iamide ll	Δν (cm^{-1}) = νamide l - νamide lI	I_{1070} / I_{1164}	I_{1400} / I_{1444}
1m	1.07	101	0.87	0.89
2m	0.97	108	0.80	0.84
E1	1.14	100	1.08	0.83
E2	1.06	102	1.00	0.83
E4	1.14	98	1.18	0.87
5d	0.96	106	0.96	0.82
5e	1.10	99	1.00	0.82
CB1	1.15	101	1.07	0.83
CC1	0.89	115	0.79	0.82
CC2	1.10	103	1.21	0.84
K1	1.13	113	1.03	0.87
K2	1.14	98	1.15	0.91
K4	1.22	99	1.09	0.79
L1	1.16	106	0.88	0.88
I1	1.07	103	1.05	0.85
EG5	1.10	101	1.18	0.86
EG6	0.99	108	1.04	0.89
ET20	1.15	101	1.13	0.82
ET21	1.08	101	0.98	0.87
S2	1.16	107	1.00	0.79
T16.6	1.22	101	3.75	0.89
T16.7	1.01	105	1.38	0.92
T1a	0.98	107	1.01	0.79
T1b	1.05	101	0.90	0.79
Mir1	0.90	116	0.90	0.79
Mir2	1.06	102	0.97	0.82
Ept19.1	1.10	102	1.94	0.85
Ept19.5	1.01	112	2.17	0.88

The calculated data in Table 3 show that all samples were degraded by hydrolysis, Iamide l / Iamide ll ratios varying from 0.89 (CC1) to 1.22 (K4).
The deterioration degree Δν revealed highest values for samples: Mir1 (116 cm^{-1}), CC1 (115 cm^{-1}), K1 (113 cm^{-1}), Ept.19.5 (112 cm^{-1}), 2m (108 cm^{-1}) and EG6 (108 cm^{-1}).

In the ATR spectra, sericin has some fingerprint peaks at 1400 cm^{-1} and a much-enhanced absorbance peak at 1070 cm^{-1}, while for fibroin the specific peaks are at 1444 cm^{-1} and at 1164 cm^{-1}. The peak intensity ratios 1070/ 1164 and 1400/1444 are useful quantitative indicators of the sericin content of processed and unprocessed silks. In Table 3, the measured ratios 1070/ 1164 and 1400/1444 are all in the range 0.79 and 3.75 which, according to Zhang & Wyeth, indicates

intermediate sericin levels for almost all the silk samples, exemption making silks from the oldest 15th century two epitrachelions (T16.6, T16.7, Ept.19.1, Ept.19.5) on which a very high content of sericin was detected. The resulting data in Fig. 4 indicates that silks from the metal threads used in the brocaded textiles dating from 15th and 16th centuries were partially degummed, which is in accordance with the historical literature [5], while those in the metal threads from religious embroideries, especially those from 15th century, were raw silks (not degummed).

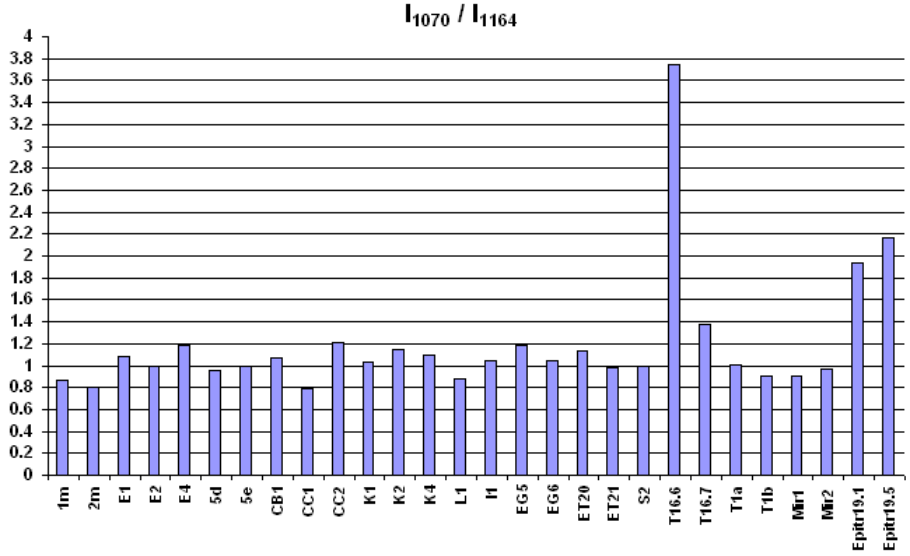

Fig. 4. Intensity ratio estimator 1070/ 1164 calculated for the silk yarns in the metal threads

It was also observed in the ATR spectra that some of the samples show a low intensity band in the region between 1690 and 1696 cm^{-1} suggesting the presence of the carboxylic compounds resulted from an oxidative deterioration process: Mir1 at 1696 cm^{-1}, Mir2 at 1693 cm^{-1}, 5d at 1693 cm^{-1}, T1b at 1696 cm^{-1}, CC1 at 1695 cm^{-1} and EG6 at 1690 cm^{-1}.

4. Conclusions

ATR spectroscopy proved to be a very useful and fast method for identifying the nature of the organic materials applied on the metal threads surfaces (μATR), for monitoring their structural and chemical changes over time, using a minimal amount of sample. ATR resulting data could give important information on the degradation of the metal threads silk cores, type of the silks

used: ungummed (with sericin) or degummed (only fibroin), their provenience and a possible classification of the historical silks.

In regards with the implications for preservation and conservation practice, metal threads coated with organic materials and wrapped on silk yarns rich in sericin, or even with some remnant sericin, would require different restoration and conservation protocols. So, results obtained could help restorers and conservators to decide to choose on appropriate treatments in order to bring the historical textiles closest to their originally intended appearance.

Data obtained on metal threads chemical and physical nature could contribute as reference and could constitute a preliminary database to further studies. Furthermore, accurate data obtained on the nature of the medieval textiles metal threads could contribute to a better understanding of their particularities and could be used in studies of provenience and authentication.

R E F E R E N C E S

[1]. *Z.I. Balta, L. Csedreki, E. Furu, I. Cretu, R. Huszank, M. Lupu, Z. Torok, Z. Kertesz, Z. Szikszai,* Ion beam analysis of golden threads from Romanian medieval textiles, Nuclear Instruments and Methods in Physics Research B, Vol. 348, 2015, pp. 285-290

[2]. *Z.I. Balta, I. Cretu, M. Lupu, L. Csedreki, Z. Szikszai, R. Huszank, I. Uzonyi, Z. Kertesz, E. Furu,* Analysis of golden threads from Romanian medieval textiles by IBA techniques (PIXE, RBS), Restitutio 7, Conservation – Restoration Bulletin of the ”Dimitrie Gusti” National Village Museum, 2013, pp. 162-171

[3]. *C. Nicolescu,* Costumul de Curte în Ţările Române (Sec. XIV-XVIII), Întreprinderea Poligrafică Arta Grafică, Bucureşti, 1970

[4]. *C.S. Smith and M. Teach Gnudi*, The Pirotechnia of Vannoccio Biringuccio. The Classic Sixteenth Century Treatise on Metals and Metallurgy, Dover Publications Inc., New York, 1990

[5]. *L. Mola,* The silk industry of Renaissance Venice, The Johns Hopkins University Press, Baltimore, 2000

[6]. *Price, Beth A., and Boris Pretzel*, eds. Infrared and Raman Users Group Spectral Database. 2007 ed. Vol. 1 & 2. Philadelphia: IRUG, 2009. Infrared and Raman Users Group Spectral Database. Web. 20 June 2014. <www.irug.org>

[7]. *M.R. Derrick, D. Stulik, J.M. Landry*, Infrared Spectroscopy in Conservation Science, The Getty Conservation Institute, Published by J. Paul Getty Trust, 1999

[8]. *M. Avram, G.D. Mateescu,* Spectroscopia in infrarosu. Aplicatii in chimia organica, Editura Tehnica, Bucuresti, 1966

[9]. *M.R. Tudora, C. Zaharia, I.C. Stancu, E. Vasile, R. Truşcă, C. Cincu,* Natural silk fibroin micro- and nanoparticles with potential uses in drug delivery systems, UPB Scientific Bulletin, Series B: Chemistry and Materials Science, vol.75, pp. 43-52

[10]. *M. Boulet-Audet., F. Vollrath, and C. Holland*, Identification and classification of silks using infrared spectroscopy, Journal of Experimental Biology, Published by The Company of Biologists Ltd., Vol. 218, 2015, pp. 3138-3149

[11]. *X. Zhang and P. Wyeth*, Using FTIR spectroscopy to detect sericin in historic silks, Science China Chemistry Journal, Vol. 53, No. 3, Springer Journals, 2010, pp. 626-631
[12]. *O. Marincas, M. Giurginca*, Conservation – restoration of textiles materials from Romanian medieval art collections, REV. CHIM., vol. 60, Nr. 1, 2009, pp. 9-14