Universitatea "Alexandru Ioan Cuza"- Iaşi
Facultatea de Geografie şi Geologie
Școala doctorală de geostatistică
Specializarea Știința Mediului

The Studying of Historical Textiles by Using Multidisciplinary Analytical Techniques

PhD Candidate Nidal AL SHARAIRI

Supervisor Prof. Dr. Ion SANDU

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Content

Introduction

The approach of using analytical and instrumental techniques to study archaeological and historical textiles has emerged about three decades ago. Since that time scientist succeeded to use develop and innovate multi analytical techniques to study these old textiles objects. These analytical techniques have contributed in deciphering important information about the status and level of chemical and physical situation and changes of the examined textiles, to provide accordingly conclusions and recommendations as well as providing pivotal information to the examined samples.

This study investigated historical Ottoman and Romanian textiles that belong to 19th century and to 17th -18th century respectively, and succeeded to identify types of fibers, dyes and mordants. Contemporary natural textiles samples were prepared and dyed according to old documented dyeing recipes, using different types of natural dyes, fibers and mordants, to be used as reference samples for matching and comparing.

An overall elaboration of the study was described in **Chapter 1**, which included historical background for the textiles components (fibers, dyes and mordants) as well as full details on the approach, purpose and importance of the study, concluded the chapter with bibliographical review on the latest current state of knowledge in the field related.

In **chapter 2**, the natural components and constituents that are considered essential parts through the history of textiles making industry was described, including origin types of natural fibers which generally divided into either plant or animal source with each has its own morphological, physical and chemical characteristics. The second important constituent is the natural colorants dyes. The third component that has been described is mordants; their types, historical use and also their chemical and physical effect on fibers and on dyes.

Since samples understudy belong to Ottoman and Romanian historical era, there was necessity to include historical briefing in **chapter 3** about the dyed-textiles industry making during the times the samples belong to.

The experimental part starts from **chapter 4**, where a demonstration for the instrumental and analytical methods that were utilized for analysing the new- referenced dyed samples and the historical samples that comprised of Optical Microscope (OM) and Scanning electron Microscope (SEM), Fourier Transmission Infra-Red spectroscopy (FTIR, and high Performance

Liquid Chromatography equipped with UV-Vis unit (HPLC-PDA UV-Vis). These multidisciplinary methodologies have been subjected to study 16 historical samples taken from Ottoman costumes and Romanian fragments.

The analytical data resulted from the complementary use of microscopic, spectral and chromatographic devices allowed the recognition of several traded European and Ottoman fibers, dyes with metallic mordants (Alum) on the collected samples (**chapter 5**), highlighting several important conclusions on traditional dyes used during 17^{th}, 18^{th} and 19^{th} century as well as signalling on some unusual rarely- used colorants, also the results helped in providing approximate dating period according to the dyestuffs analyzed in the Ottoman (Prussians blue and Scheele's green) and Romanian yarns (Cochineal and lac).

Chapter One

INTRODUCTORY OVERVIEW

1.1. General overview of textiles making history

1.1.1. History of textiles

The use of textiles and dyes reaches back into history, they represent one of the earliest human craft technologies, some scholars say it's for certain older than metallurgy, and they have been a fundamental part of subsistence, economy, and exchange [Gleba, 2014]. The earliest dyes or coloring substances were undoubtedly discovered by accident through serendipitous staining by berries, fruits, nuts, blossoms, leaves, steams, roots, bark, twigs, etc [Weigle, 1974].

It is undoubtedly that after the technique of weaving had been discovered, it was inevitable that attempts would have been made to color fabric in a simple dyeing process. Though dyeing or coloring textiles may have taken place thousands of years earlier, but it has been lost in the depth of unrecorded history [Lambert, 1998].

1.1.2. History of natural dyes

The largest classes of organic dyes are produced from diverse types of plants. Three different types of vegetable dye can be segmented: plants, lichens and seaweeds. Dyes of animal origin are limited to two main types: shellfish dye and insect staining.

The use of protein fibers was the beginning of the use of natural dyes, since animal fibers can be dyed much easier than flax. It is known that from around 3000 B.C. dyeing techniques were well established in China. However, scientists still cannot determine when exactly the dyeing of textiles began [Cybulska and Maik, 2007].

1.1.3. Mordants

Many dyes don't penetrate into fibers, so the textile won't likely take on color. Plant fibers are difficult to dye than animal fibers because they need an alkaline medium to take on dye. Thus the dyer must have discovered the function of mordants at a rather early stage in textile history [Boertien, 2013]. The word "mordant" comes from the Latin word "*mordere*" which means "bite." The mordant bites into the fabric, allowing the dye to penetrate the cloth more intensely [Baliarsingh *et al.,* 2015].

Chapter Two

NATURAL CONSTITUENTS OF TEXTILES AND DYES

2.1 Natural fibers

2.1.1. Animal fibers

Animal fibers are naturally occurring fibers which consist mainly of specific proteins. Wool, silk, Kemp and mohair (a silk-like fiber) are the most famous examples of this fibre. During the moult, early methods of acquiring wool came from dragging it out; in ancient times, wool and hair were obtained by plucking or clipping [Boertien, 2013; Chandramohan and Marimuthu, 2011].

2.1.2. Plant fibres

Many plants may be used as the input ingredient for textile production, such as cotton, hemp, and flax. Cotton is fuzzy and spreads among cotton flower seeds. Bast fiber such as linen and hemp is harvested from the plants' bast.

2.2. Natural dyes

Natural dyes have been used to paint or stain a fiber. It is useful to distinguish between dyes and pigments depending on their solubility in the material used to spread the color; dyes are normally organic compounds that are soluble in a solvent, while pigments, used in painting, are typically inorganic compounds or minerals that are insoluble in the paint medium and scattered in the matrix. There are a variety of ways to classify natural dyes. They may be categorized in various ways, e.g. based on hue, chemical constitution, mode of implementation and roots [Samanta and Agrawal, 2009**].**

2.3. Mordants

Mordants are chemical intermediates that are able to bind to the substrate. They contain metal atoms such as aluminum (Al), iron (Fe), and chrome (Cr). Mordant can be placed on the fabric before dyeing, in the dye bath or after the dyeing process. The chemical bonding is usually very stable leading to the enhancement of the fastness of the mordanted dye [Lambert, 1998; Joseph, 1986].

The relative amount of the mordant to the amount of dye and size of textiles play an important role in confirming many shades for each color even for the same natural dye different types of mordants yield different colors [Bently and Turner, 1987]. Mordants can be classified namely metal salts, oil mordants, and tannins [Indi *et al.*, 2016; Prabhu and Bhute, 2012; Samanta and Agrawal, 2009].

Chapter Three

BRIEFING ON OTTOMAN AND ROMANIAN TEXTILES

3.1. History of dyed textiles in the Ottoman period

In the Ottoman period, textiles dyeing, weaving dyestuffs trading was one of the main economic activities that the state depended on. It witnessed manufacturing and imports at variable rates. At the end of the 19th century the most remarkable developments in the manufacture of Ottoman textiles were produced by the independent enterprises and the artisan manufacturing, not the large factories[Faroqhi *et al*, 1994].

3.3. Romanian Textiles

Romanian museums and monasteries maintain large collections of textiles representing heritage, strategic location at the intersection of the main old trade routes from East to West, and Romanians ' coexistence with other ethnic groups. For example, trade routes from the Ottoman Empire to Moldavia passed through Wallachia and close relations existed between the two Romanian provinces. This can be witnessed from textiles appeared to have oriental/ Ottoman origin from monasteries in Wallachia [Petroviciu *et al*., 2006].

Colored yarns and fabrics are mentioned among the imported goods in the history of Romanian trade. For instance, combinations of dye sources with an eastern origin, such as lac dye and madder, were used in religious embroideries, while others – for example redwood and tannins, kermes and cochineal, weld and young fustic, were all of western origin [Petroviciu *et al.*, 2009; Petroviciu *et al.*, 2017].

Chapter four

METHODS AND SAMPLES

4.1. Instrumental Methods for characterization of historical textiles

A number of analytical methods employed to analyse and identify the dyes, fibers and mordants to reconstruct the dyeing and weaving techniques used from the historical textiles samples understudied. Microscopic devices like optical microscopy and SEM will be used to study the type and surface morphology of the fibers. EDX attached with SEM will be used for elemental analysis to detect metallic presence used as mordants. Chromatography devices like HPLC and GC-MS will be used molecular identification and observing the chemical changes and differences before and after ageing process. Infrared spectroscopy like FT-IR will be used for fiber identification as well as observing functional groups changes after ageing process.

4.2. Materials and Sampling

Two sets of samples, for each Ottoman and Romanian separately, were studied, analyzed and compared; with the newly prepared dyed textiles as reference samples.

a. Ottoman textiles samples from Jordan

Small portions or few fibers were taken from costumes belonging to the late Ottoman period 19th Century. They are exhibited in the museum of Jordanian Heritage. The samples were taken from already badly damaged parts, from the shoulders, end of the clothes and from the linings. The costumes which had been sampled are described as follows:

These are some of the costumes, (Figs. 4.3 and 4.4):

Fig 4.3. Damaged part of the brown cloak

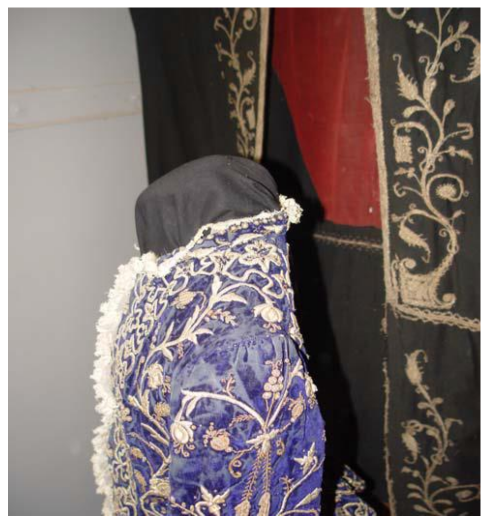

Fig 4.4. The blue dress and the black cloak with the red lining

b. Romanian textiles Samples

The textile samples under research are composed of eight fragments from the 17th-18th century era. All the collections are parts of debris that after restoration action could not be assembled into objects, or segregated from their initial artefacts due to human and environmental factors. All specimens have brownish-orange shades (Fig.4.5). The specimens were found in three monasteries in Northern Romania (Moldova).

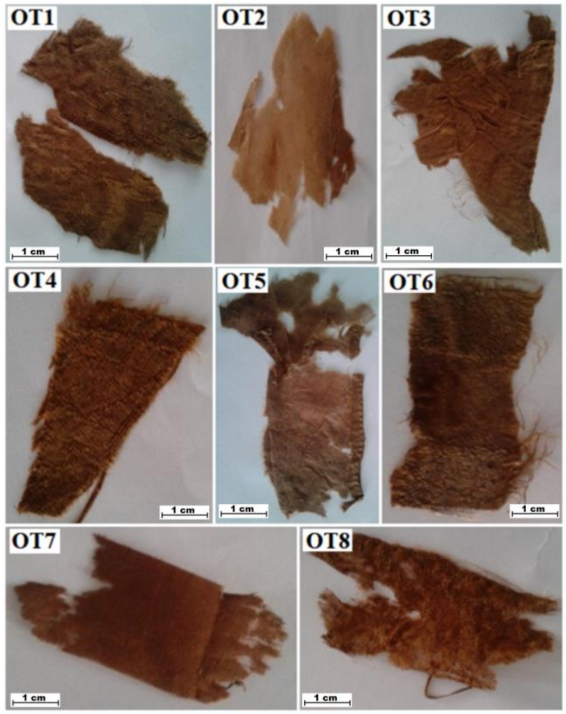

Fig. 4.5. Images for old textile samples from Romania

c. New dyed samples

For Ottoman samples to be compared, new wool, silk, and cotton fibers were selected after defining the types of the original threads, dyed with several commercial natural dyes, corresponded to the expected dyes that might be presented in the historical samples.

Reference samples (RT) were prepared using natural silk fabrics (bought from local market) and the following natural dyes to compare with historical Romanian samples.

Chapter Five

RESULTS AND DISCUSSIONS

5.1. Ottoman textiles results and discussion

5.1.3. Experimental

The identification procedure was carried out in two stages. Firstly, chemical analysis was carried out for historical and contemporary samples. Then, the data recorded was compared and matched. Energy Dispersive X-ray diffraction (EDX), Fourier Transform Infrared Spectroscopy (FT-IR) and High Performance Liquid Chromatography (HPLC) techniques were used for elemental and chemical analysis as an integrated technique.

5.1.4. Results and Discussion

Regarding the black cloak sample, there were significant matches between FTIR spectra between it and the cotton tannin-indigo dyed sample (Fig. 5.1). This result was confirmed by analysing the sample after extraction by DMF (Fig. 5.2). Tannins are believed to play as organic mordant, which increases the fastness of the dye towards light and impart deeper shade.

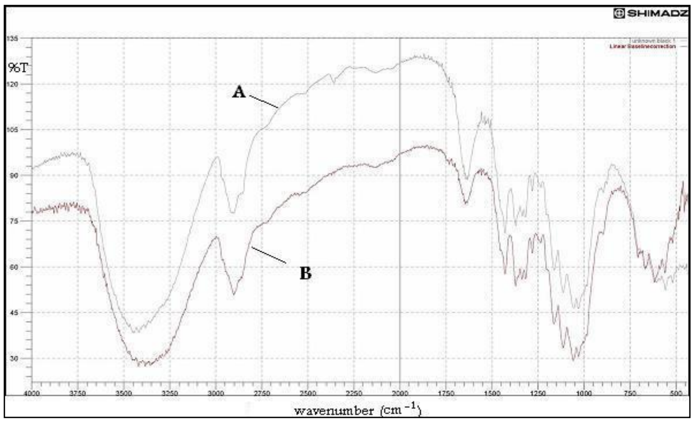

Fig. 5.1. A-FTIR spectrum for black cloack fibers sample;
B- FTIR spectrum for new cotton indigo –tannin dyed sample

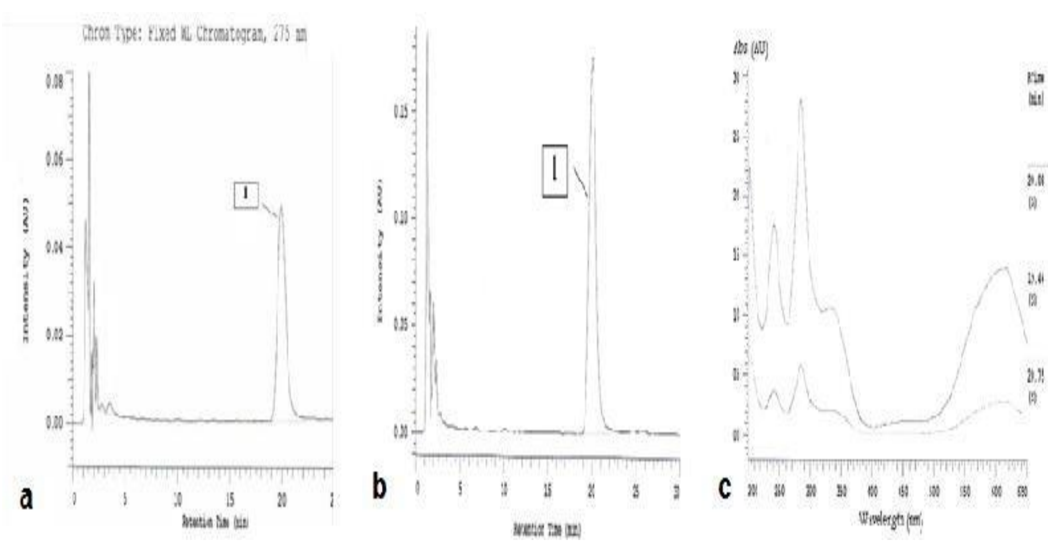

Fig. 5.2. Chromatograms: a **-** new indigo dye extract; b **-** sample 7; **c**, UV-vis spectrum of indigo

FT-IR spectrum of the sample belongs to the brown cloak showed it to be made of protein fibers, more specific sheep wool. This result was obtained after comparison with five different reference samples and based on literature [Fasoohi, 1994; Forbes, 1964.

Surprising results were obtained from the analysis of the blue and green woman dresses. Prussian blue was detected by FT-IR with a characteristic fingerprint at about 2085 cm^{-1} as shown in (Fig. 5.4). This peak is characteristic peak and considered as a clear fingerprint of Prussian blue pigment [Mathe, 2006].

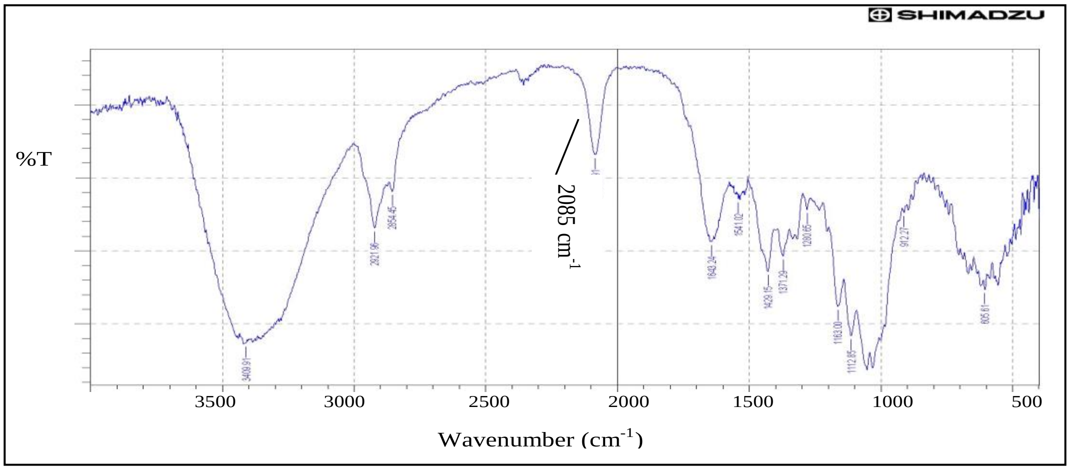

Fig. 5.4. FTIR spectrum for blue woman cotton sample dyed with Prussian blue

Lead and chrome were detected by EDX in the green lining in proportion of 0.1 and 5.55 (wt %) respectively (Fig. 5.5); this is may be to the presence of the pigment lead white ($PbCrO_4$). Mixing lead white with Prussian blue can yield a green color called "Chrome green".

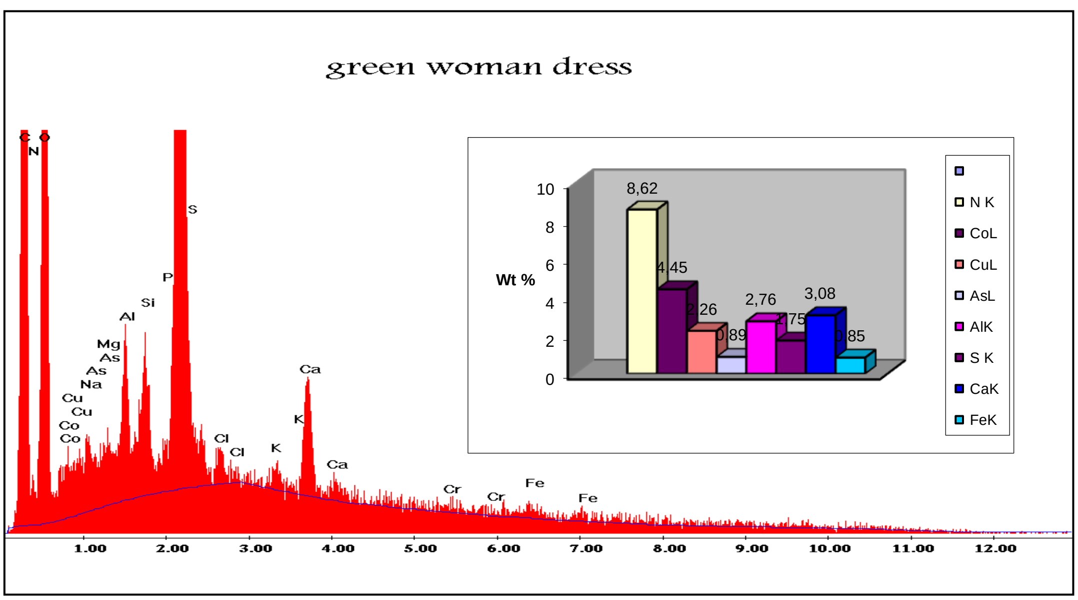

Fig. 5.5. EDX result of the green woman dress

Another unexpected result was the unknown green of the woman dress. It appears that the fabric consist of two kinds of dyes/pigments. The horizontal fibers (weft) contain about 0.44 (Wt %) chrome, while the vertical fibers (wrap) do not. In addition, the whole fragment contains appreciable amounts of cobalt, copper and arsenic. The mean amounts are 4.47, 2.19 and 0.85 (Wt %) respectively (Fig. 5.6). Recognition of arsenic and copper elements in appreciable amounts in the green dress was a clue of using copper- arsenic based dye. One of the main and earliest copper-arsenic pigments that were used to dye textiles in the 19th century is called "Scheele’s Green". "Scheele's Green" was discovered in 1775 called, which is chemically cupric hydrogen arsenite $CuHAsO_3$ [Mathe, 2006].

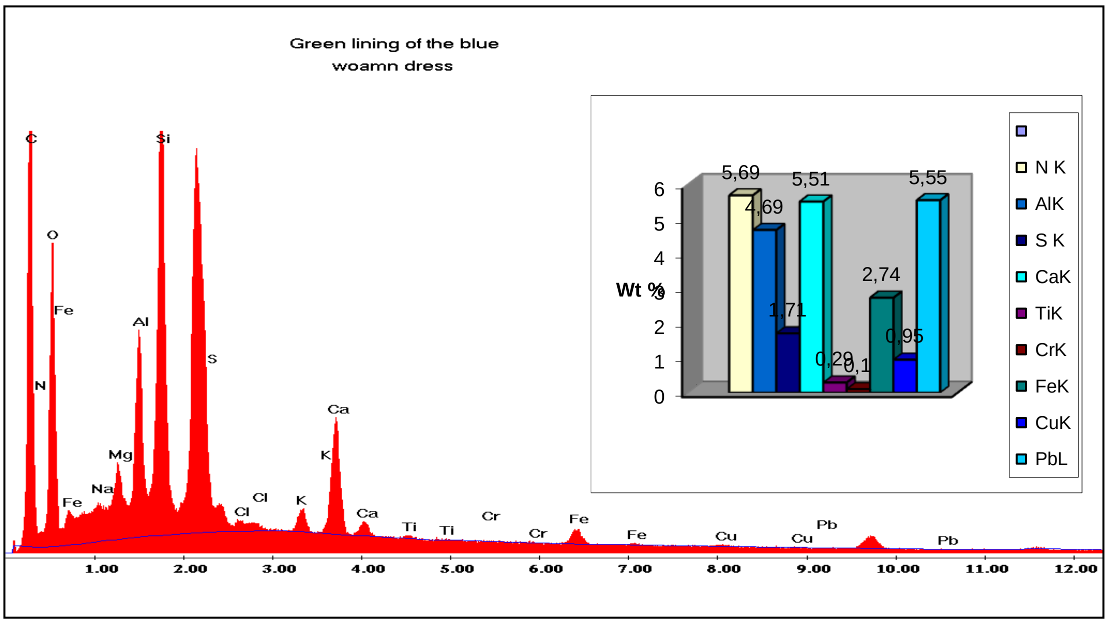

Fig.5.6 EDX result of green lining of the blue woman dress.

The red madder dye was identified in preliminary in the red lining of the gren dress-sample no. 8 by FTIR analysis (Fig. 5.7), and was confirmed by HPLC by detecting alizarin. The high intensity signal of the chromatographic result of Alizarin in sample 8 might suggest that cultivated madder has been used to provide the red color of the lining dress (Fig. 5.8b). Madder dye was also characterized in the extracts of sample no. 4 of the yellowish- brown cloak chest decoration (Fig. 5.8c), the yellowish shade is due to effect of mordant.

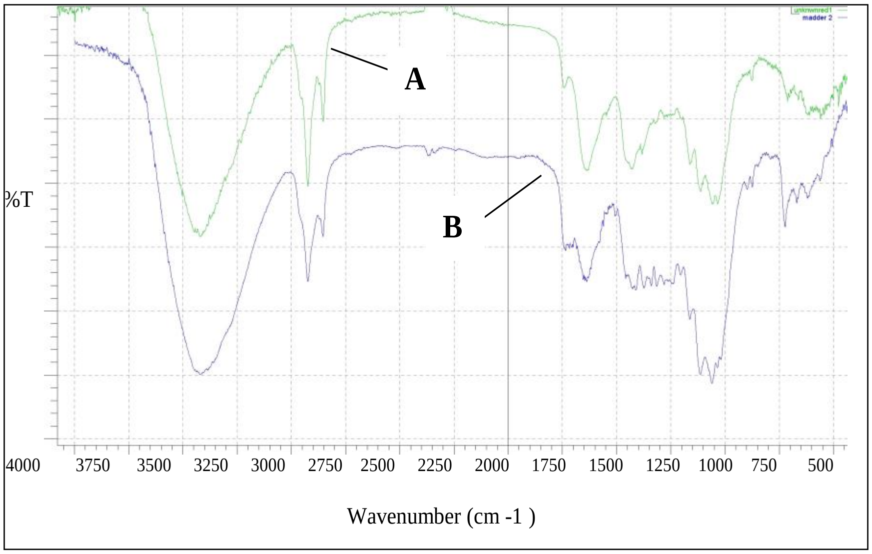

Fig.5.8. FTIR Spectrum: **A** – red lining of sample no.8; **B -** new cotton sample dyed with madder

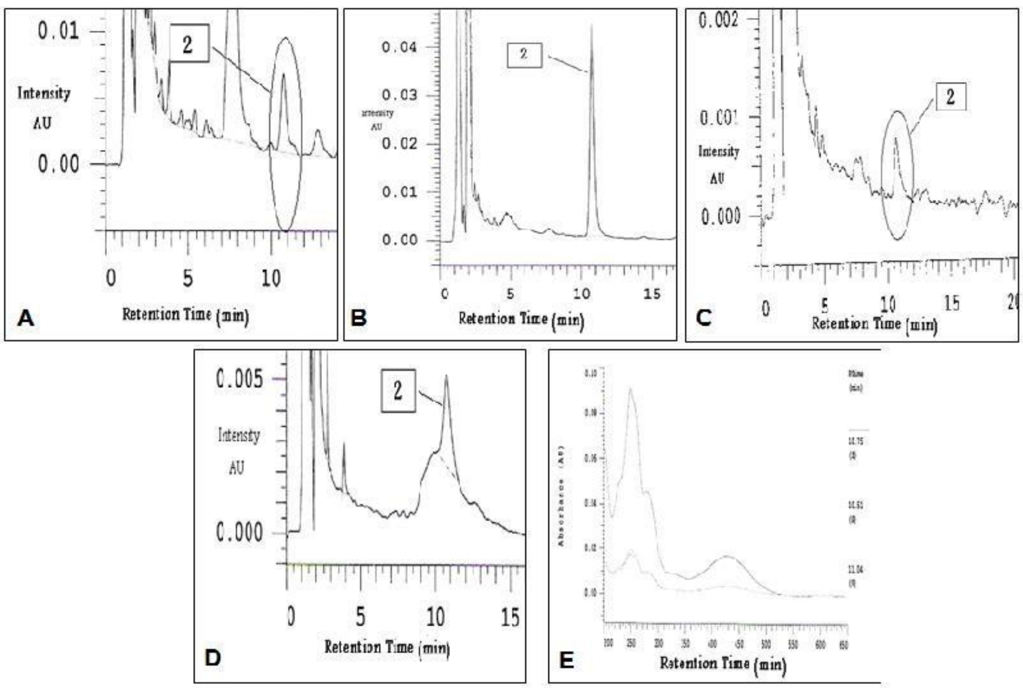

Fig. 5.8. Chromatograms of the samples: **A -** new madder extract; **B -** sample 8; **C -** sample 4; D - sample 2; E - UV-vis spectrum of alizarin

Table 5.2. Chromatographic results and maximum absorption for major examined dyes in Ottoman cotumes

Uural source	Chemical compound	Retention time (Second)	Absorption Maximum (nm)
Indigo	Indigotin	20.08	240, 285, 609
Madder	Alizarin	10.77	245, 285 (sh) *, 425
Tannins	Ellagic acid	8.82	258, 369

Saffron	Crocin	5.71	519

*Sh: peak shoulder

5.1.4.2. *Types of fibers and mordants*

SEM-EDX spectroscopy has effectively investigated the feasibility of identifying the forms of fibers and mordants taken from the costumes (Tables 5.4- 5.5), each form of fiber has a specific morphology that can be easily detected under some magnification, (Figs. 5.17- 5.20).

Table 5.4. Types of fibers detected by SEM spectroscopy

Samples number	Name of sample	Color	Type(s) of fiber
1a	Man's cloak	Black	Cotton
1b	Black cloak lining	Red	Silk
2a	Man's cloak	Brown	Wool
2b	Man's cloak	Yellowish Brown	Synthetic fibers
3a	Woman dress	Blue	Cotton and silk
3b	Blue dress lining	Light Green	Cotton
4a	woman dress	Green	Cotton and silk
4b	Green dress lining	Red	Cotton and silk

Table 5.5. Elements detected in the represented samples

Sample wt% element	Sample number	Color	Al	Fe	Cu	Cr	S
Mans cloak	1	Black	0.51	**1.37**	---	---	.61
Mans cloak	1a	Red	0.32	0.22	0.00	0.08	0.58
Mans cloak	2	Brown	0.09	**0.29**	0.64	----	1.74
Mans cloak	2a	Yellowish Brown	0.78	**4.06**	1.04	---	2.29
Woman's dress	4	Blue	0.74	4.21	0.08	----	0.34
Dress lining	5	Light Green	**4.69**	2.74	0.95	0.1	1.71
Woman's dress	3	Green	0.29	0.12	**2.82**	**0.44**	0.34
Dress lining	3a	Red	**0.28**	----	----	.03	0.27

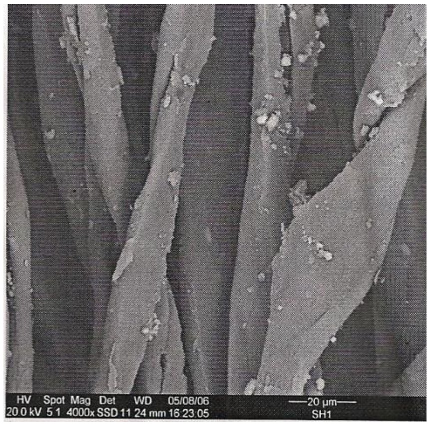

Fig. 5.17. SEM image **-**Cotton fibers of black cloak

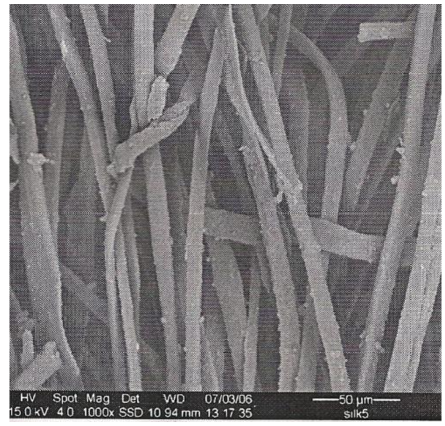

Fig. 5.18. SEM image **-**Silk fibers of the red lining

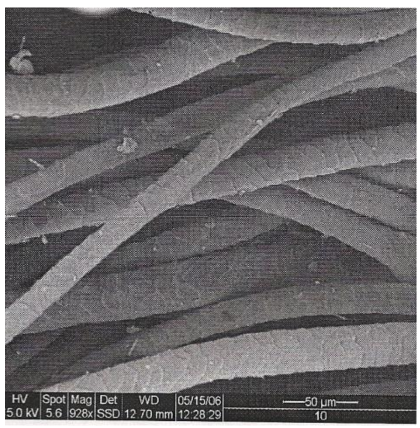

Fig. 5.19. SEM image **-**Wool fibers of brown cloak

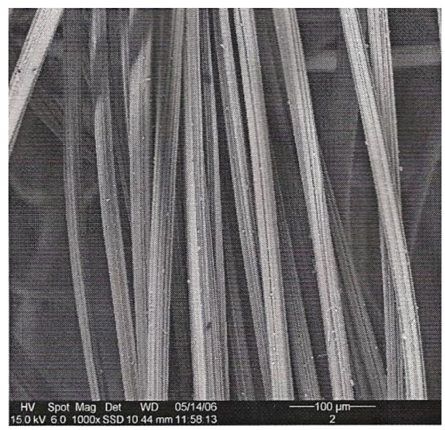

Fig. 5.20. SEM image **-**Synthetic fibers

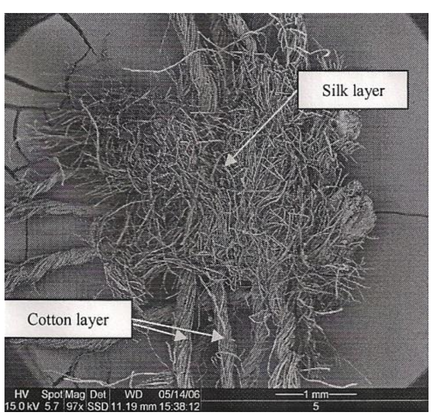

Fig. 5.21. SEM image **-**Layers of the blue dress

Fig. 5.22. SEM image **-**Dye/pigment matter

5.2. Romanian Textiles

5.2.1. Optical microscopic (OM) analysis

All the historic samples are brownish hues according to the average normal human eyes, in contrast to the optical microscopic images. The initial invistigation with OM method also showed that all of the fragments are made of silk fibers and suffering from several forms and levels of deterioration like stifness, fibers breakages and lots of impurities (dust, stains and perhabs microbals) – (Fig. 5.23).

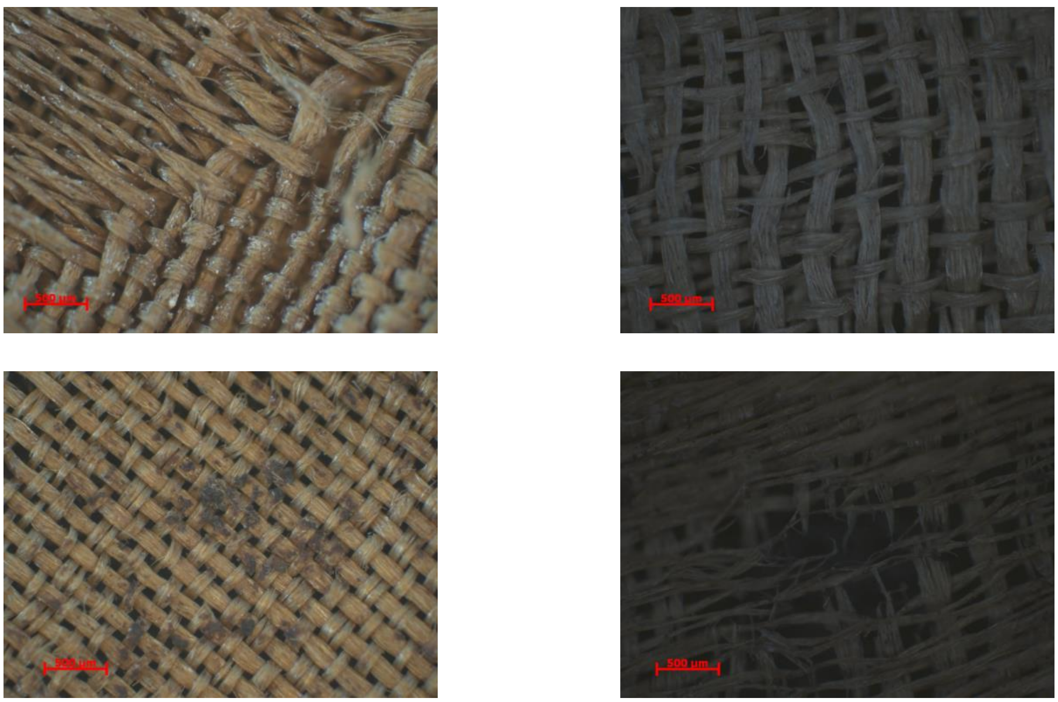

Fig. 5.23. frorms of deterioration of Romanian historical textiles samples

Furthermore, samples no. 4 and no.6 appear to contain metal threads inside of the weaved silk textiles. The initial inspection of the threads shows sampleno.4 metallic threads consisting of silver-gilded threads weaving the weft pattern of silk fibers crossed side. The threads suffer of possible type of oxidation causing the lose of almost all of the gilt layer, while sample no.6 metallic threads appear to consist of silver threads twisted in Z-shape spun within the warp fibers weaving(Fig. 5.24).

Fig. 5.24. metal threads wift with samples OT4 and OT6

5.2.2. SEM-EDX investigation analysis

The SEM-EDX analysis of the historic Romanian samples understudy confirms the preliminary data results obtained earlier by OM; that is all of the historic fragments are made of silk as well as samples no.4 and no.6 contains metal threads. Results in (table 5.6) show the considerable percentage amount by weight of Al as well as sulfur for all of the eight historic samples.

Table 5.6. EDX results of Romanian historical samples*

Sample no. / Element	1	2	3	4	5	6	7	8
C	27.45	32.9	33.6	32.3	34.9	29.3	33.1	34.02
O	50.24	51.7	53.3	43.8	45.01	48.8	51.8	48.9
Al	1.05	0.54	0.62	0.25	0.07	0.93	0.9	0.15
S	0.048	0.35	0.15	0.53	0.2	0.34	0.6	0.25
Ca	1.09	0.62	1.48	-	0.77	1.05	1.5	0.95
Si	1.12	0.2	0.04	0.3	0.13	1.6	0.53	0.17
P	1.24	0.14	0.03	-	-	0.3	0.77	0.01
K	0.65	0.48	0.82	-	-	-	-	-
Mg	-	0.04	0.03	-	-	-	-	-
N	16.67	15.8	22.1	22.9	18.96	15.8	10.8	15.4

*Composition of elements (in atomic % a) based on EDS analysis. Uncertainty of oxygen and carbon is _3%, for other elements _0.1%; elements detected below 0.1% have been labelled as "traces".

a. Historical Romanian metal threads

The EDX analysis for sample no.4 shows the metallic wire consist silver as a major compound and gold as a minor compound as shown in spectra (Fig. 5.30) with an average amount of silver (Ag) about 54.1%wt, and for the gold (Au) about 23.9%wt. while the metal threads of sample no.6 composed entirely from silver with an average of about 84.7% wt.

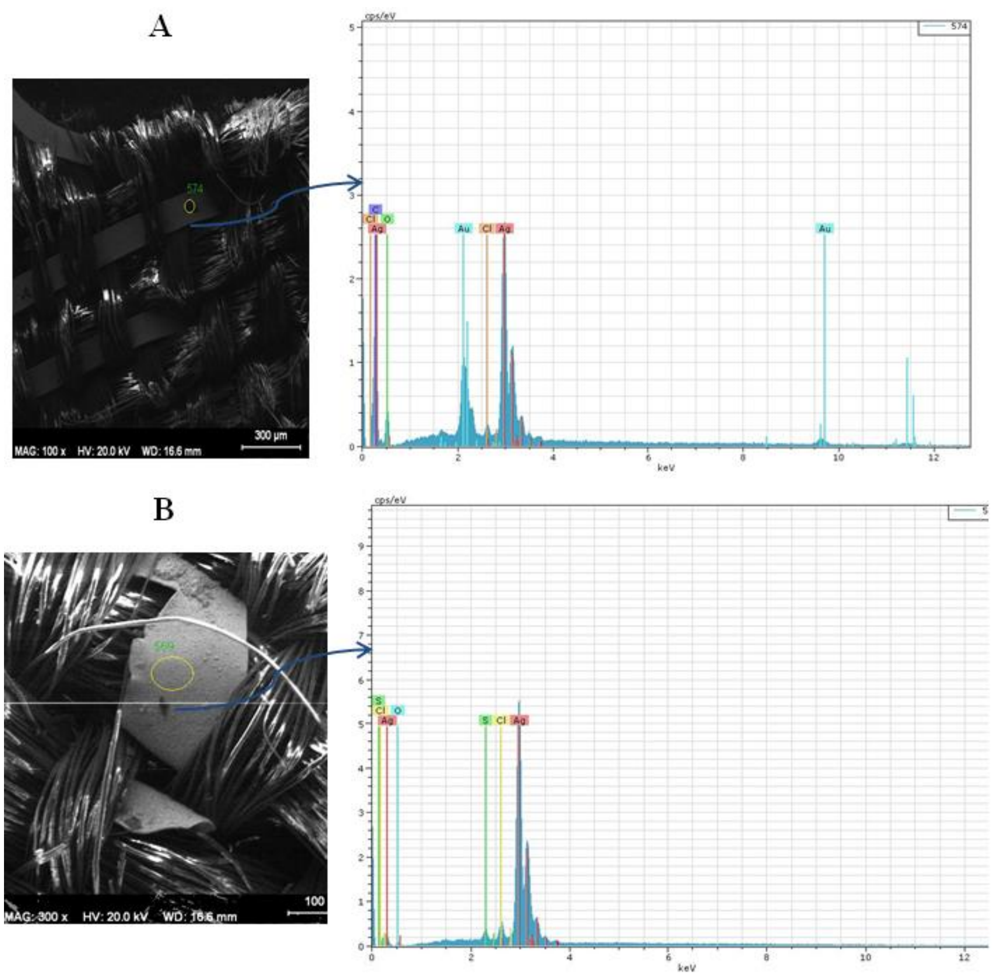

Fig. 5.30. EDX spectra for metal threads samples; **A-** OT4 and **B-** OT.6

b. Corrosion of metal threads

Cracking, staining, and delamination of corrosion were found on samples No.4 and No.6. Delamination and variations in the cracking system were historically due either to the causes of pressure-corrosion or to the production process. Some structural or chemical damage might be caused by silver sulphide on the silk (Fig. 5.31), [Jaro and Toth, 1993].

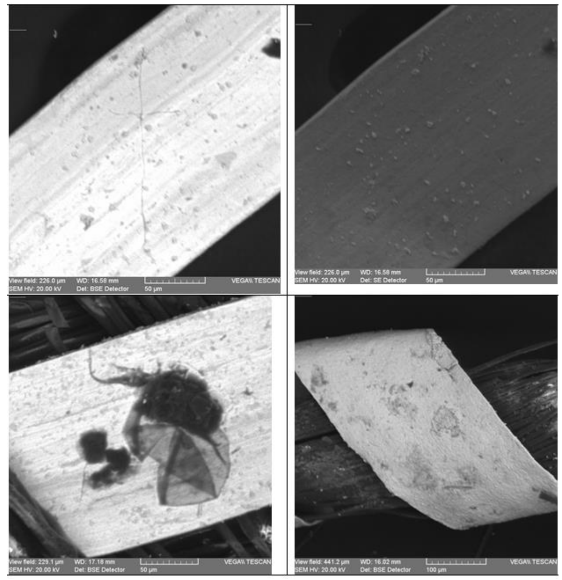

Fig.5.31. Forms of corrosions of historical metal threads

5.2.3. FT IR interpretation for Romanian historical textiles samples

Silk is not environmentally friendly and is readily targeted by several factors including wind, microorganism, light and heat. As a result, most of the traditional silk textiles diminished their mechanical strength and became more or less brittle after long degrading. Figure 5.35 depicts FTIR-ATR spectra gathered for the eight historical samples [Koperska *et al.*, 2015; Ying Li *et al.*, 2013].

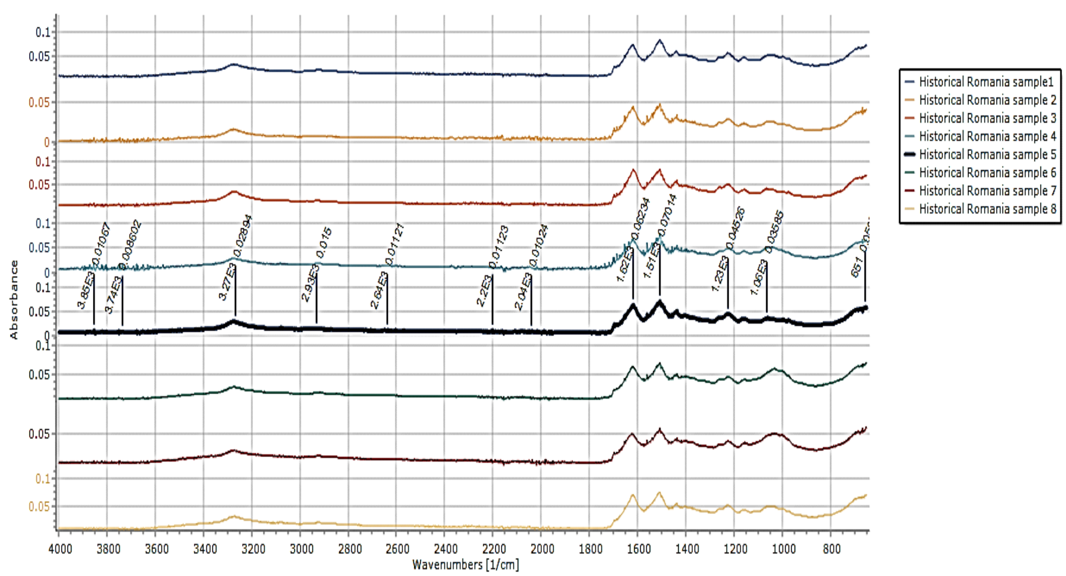

Fig.5.36. ATR-FTIR absorbance spectrum for all of the Romanian historical samples

For comparing and spectral matching purposes, a spectral library data, in addition to the existed build in libraries, was constructed from about 40 newly silk dyed samples to provide references for the interpretation of the spectra obtained from the dyed fibers. Comparison results has been done either by twinning the spectral patterns, or after subtracting two spectrums of un-dyed silk to obtain new residual spectrum.

As far as concerns historical samples, a new weld-dyed sample shows comprehensive matching with historic sample no. 1 (Fig. 5.37a). On the basis of a database for individual compounds in the band from 1700 to 1100 cm^{-1}, significant similarities between absorption bands and characteristic values for the weld dye (*Reseda luteola* L.) can be seen.

Moreover, a similar spectra pattern was clear between sample dyed with Persian berries (Buckthorn) and historic sample no. 2 (Fig. 5.37b).

In addition, new dyed sample with walnut gives a close matching with historic sample no. 3 (Fig. 5.37c).

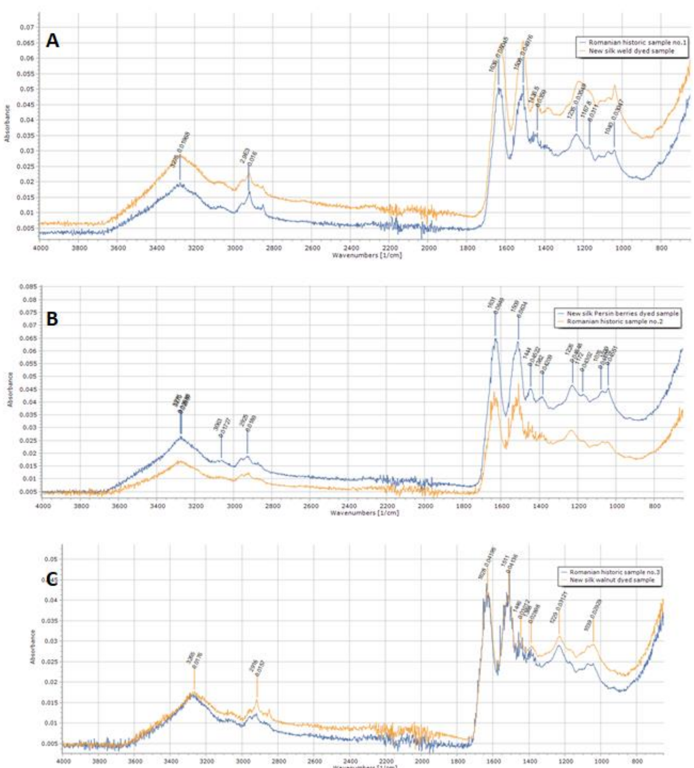

Fig.5.37. FTIR- ATR spectra for: **A** -weld, **B** - Persian berries and **C**- walnut silk dyed fibers compared to samples no OT1, OT2 and OT3 respectively

For historic samples no. 4-8 the spectral appears to have anthraquinone based group. This has been indicated after obtaining quality IR spectra of dyes from the fiber, by conducting spectrum subtraction. Reference spectra of un-dyed silk fiber were subtracted from the spectrum, the result is a spectrum that can be interpreted as an IR spectrum that corresponds to each of dyes on the fibers [Jemo and Parac-Osterman, 2017].

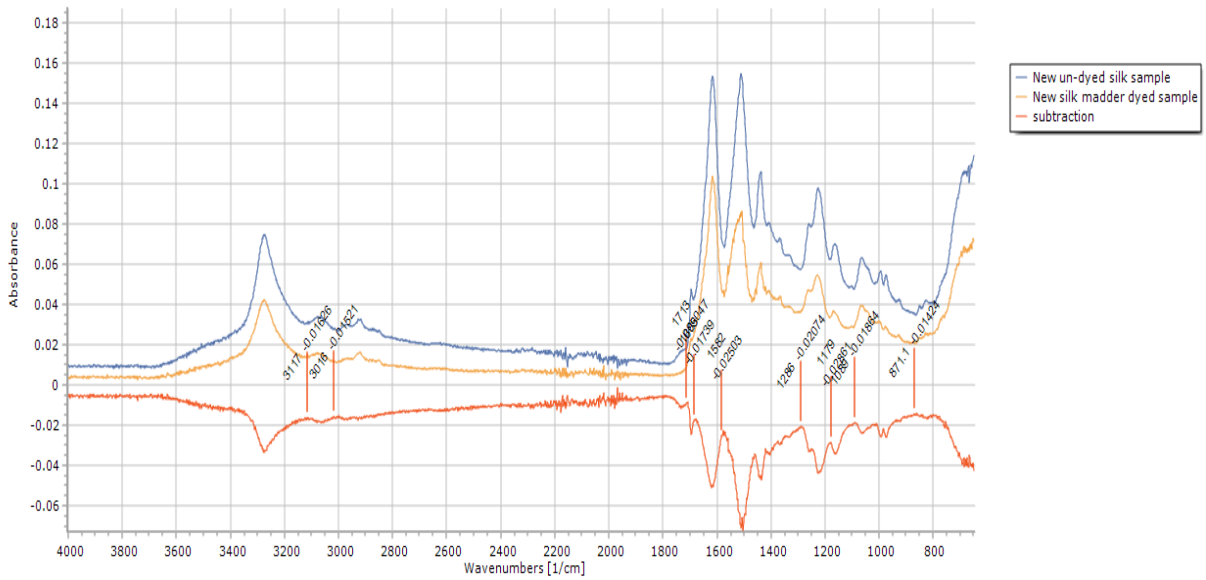

Fig. 5.38. ATR-FTIR spectrum for subtraction, madder dyed and new un-dyed silk fiber

Samples no. 4 and 6 matched with sample dyed with kermes, sample no. 5 with cochineal dyed sample, sample no. 7 with silk madder dyed and sample no. 8 matched with lac dye silk sample (Figs. 5.39 and 5.40). However, the anthraquinone derivative structures behave almost with the same vibrational spectral pattern when dyed with silk, making the differences observed between the spectra of anthraquinones compounds types inconclusive [Vilaplana *et al.*, 2015; Kourkoumelis *et al.,* 2013; Sanyova, 2002].

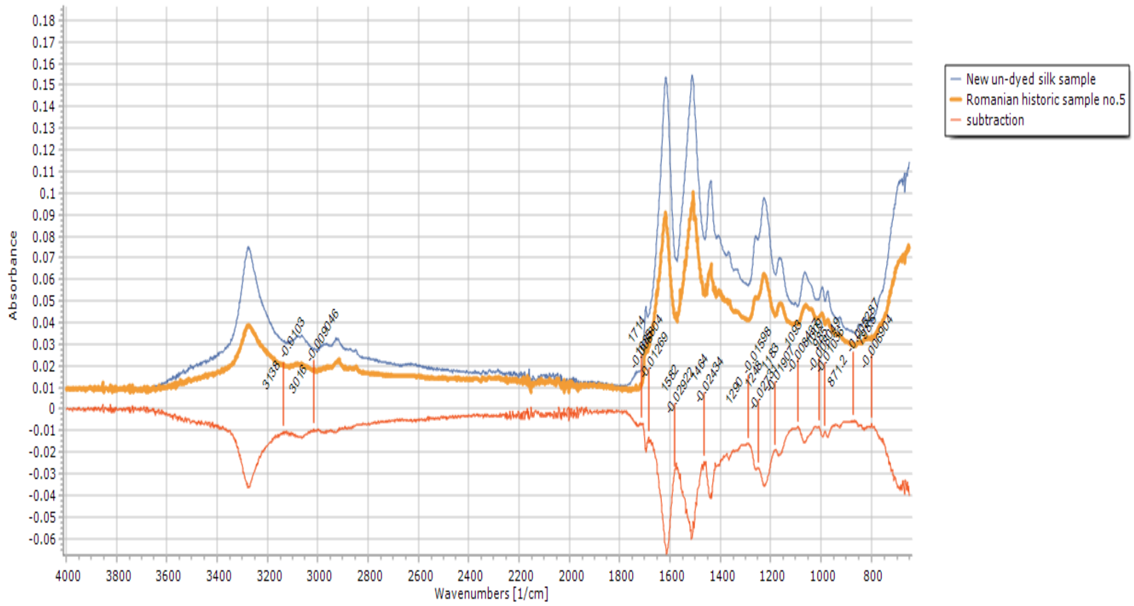

Fig. 5.39.. ATR-FTIR spectrum for subtraction, historic sample OT.5 and new un-dyed silk fiber

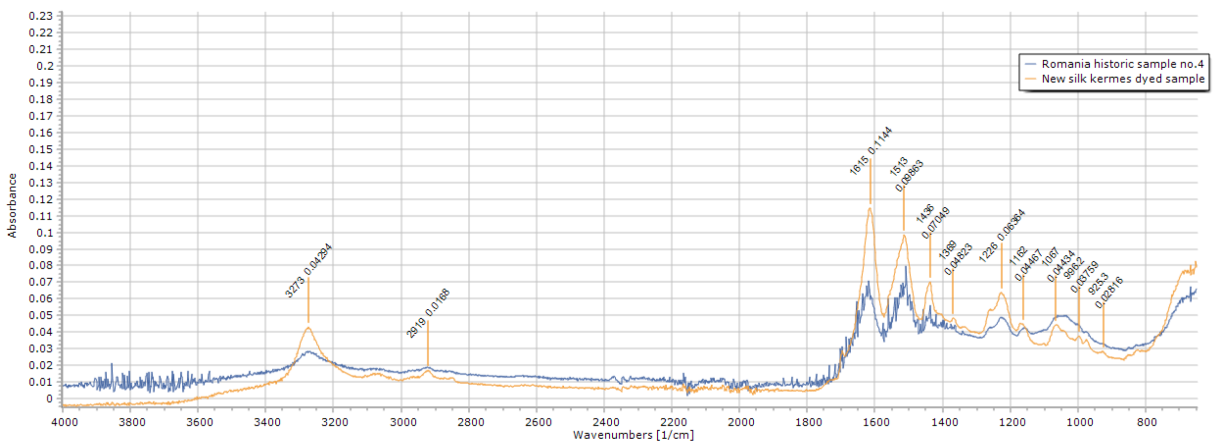

Fig. 5.40. ATR-FTIR spectrum for historic sample OT.4 and new silk kermes dyed fiber

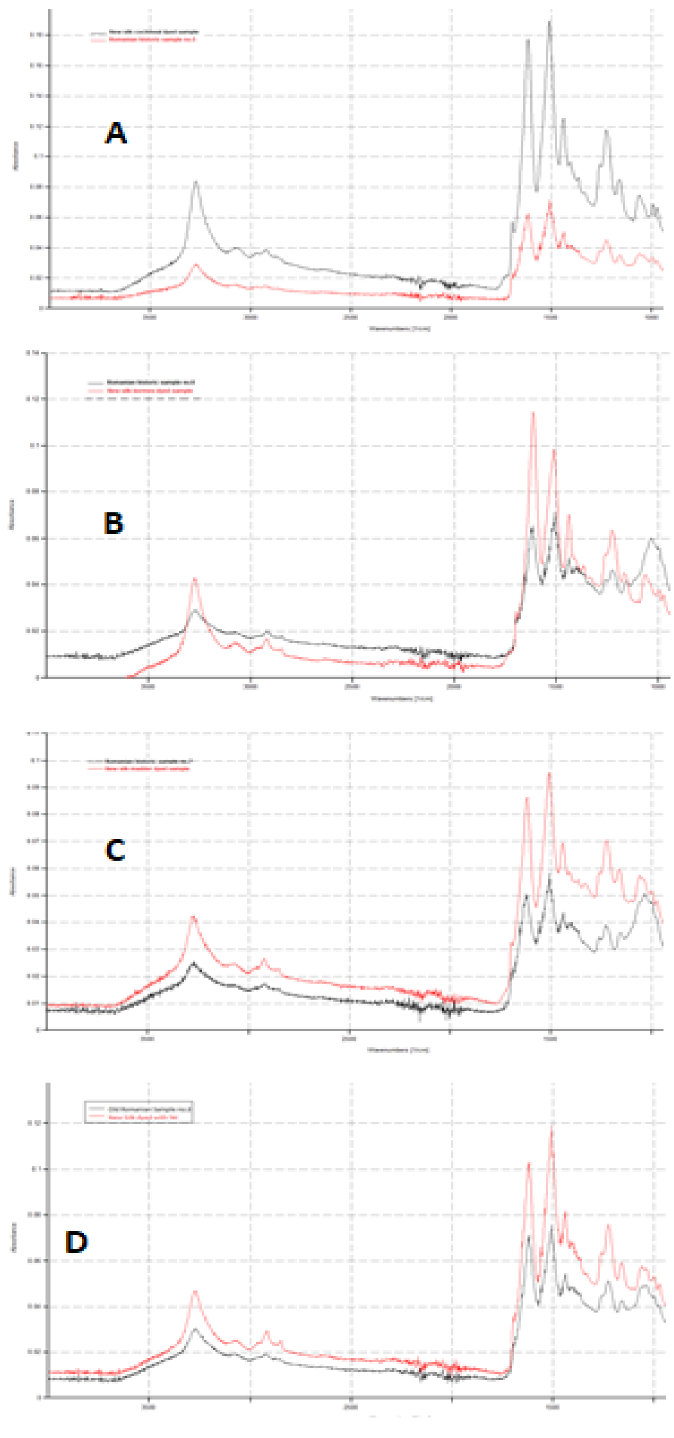

Fig. 5.41. ATR-FTIR spectrum of new silk dyed fibers **A -** cochinedal, **B -** kermes, **C -** madder and **D -** lac with historical samples OT.5; 6; 7 and 8 respectively

5.2.4. High Performance Liquid Chromatography (HPLC) results

High performance liquid chromatography identification of coloring compounds is performed by comparing their retention times and UV-Vis spectra peaks.

5.2.4.1. Results

The chromatographic profile of sample no.1 is quite similar and comparable to the chromatogram of the weld extract (Fig. 5.42).

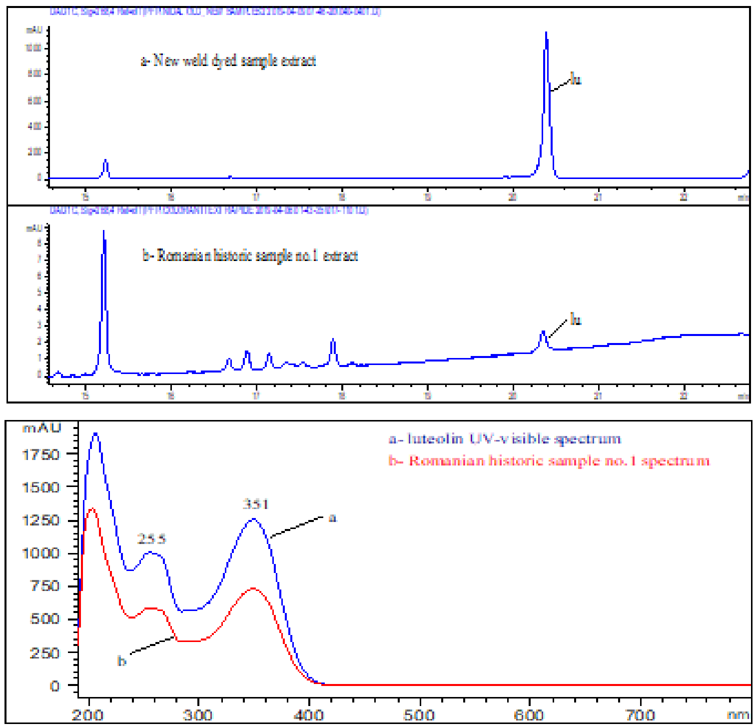

Fig. 5.42. Chromatogram of new weld dyed sample extract with UV-visible spectrum of luteolin Vs. sample OT1 extract;

Persian berries (Buckthorn) plant was, most probably, used to dye the fabric of sample no.2 (Fig. 5.43). Three compounds in the chromatogram are identified, namely quercetin-3-arabinosid, rhamnetin and emodin [Deveoglu *et al.*, 2012].

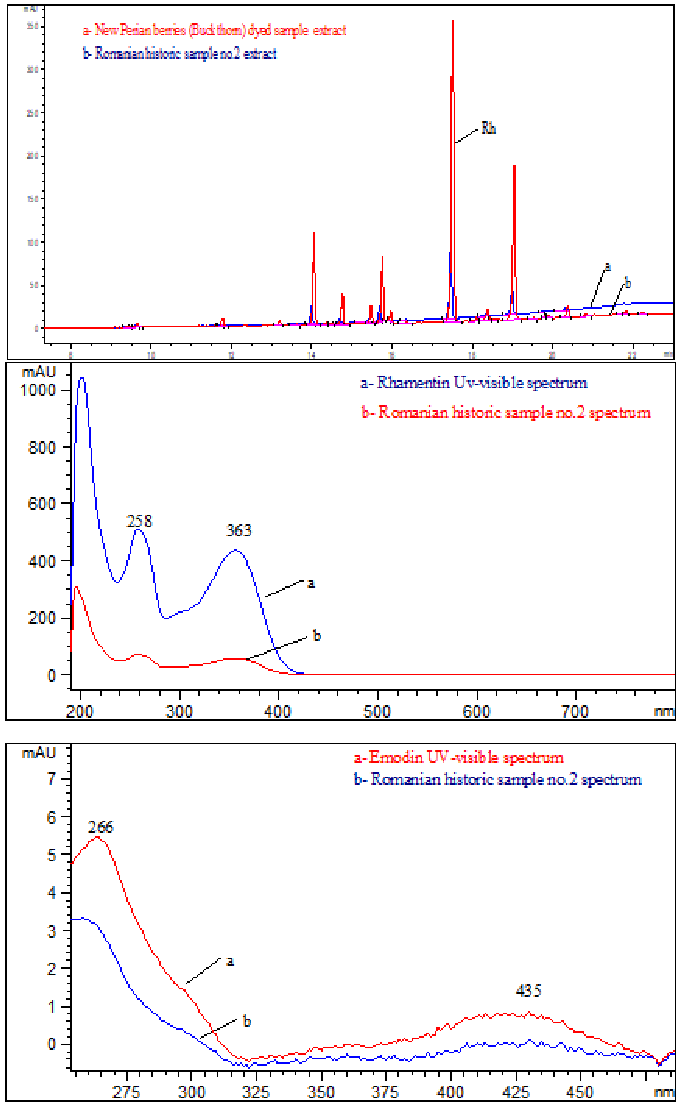

Fig. 5.43. Chromatogram of new Persian berries dyed sample extract with UV-visible spectrum of rhamnetin and emodin-like compound vs. sample OT2

For historic sample OT3 the chromatographic peak at retention time around 12.4 min. is similar to that of walnut dyed sample extract (Fig. 5.44). [Bukhari *et al.*, 2017].

The UV-visible spectrum at r.t. 12.4 is typical to naphthoquinone-based structure; juglone compound [Viana and Bauman, 2006; Medeleanu *et al.*, 1998].

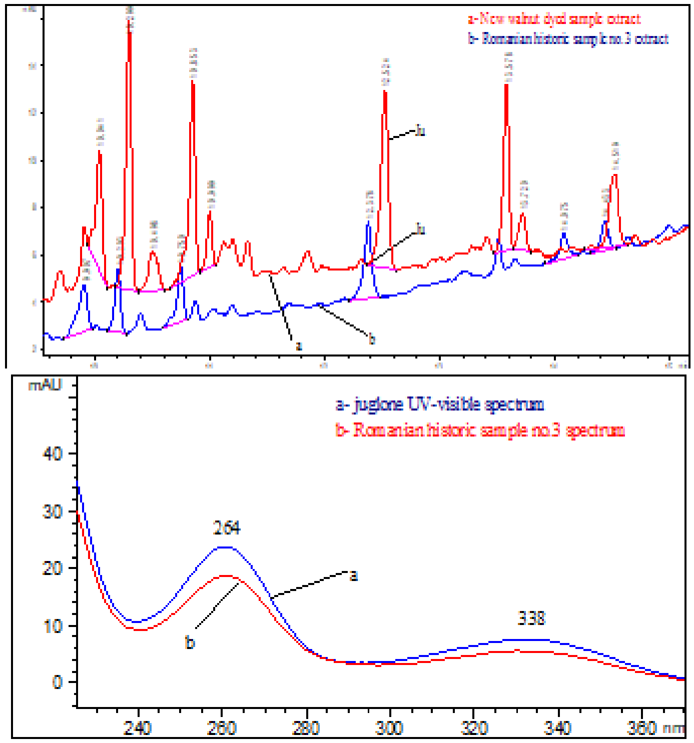

Fig. 5.44. Chromatogram of new walnut dyed sample extract with UV-visible spectrum of juglone compound vs. sample OT3 extract

For samples no.4-8 the chromatographic and UV-Visible spectra peaks suggest they were dyed with red dyestuffs from plants and insects sources. These red dyes, commonly, have anthraquinones-based structure [Rosenberg, 2008].

Samples no.4 and no.6 are found to be dyed with kermes dye. The chromatographic peaks correspond to kermesic and flavokermesic acid (Figs. 5.45 and 5.46).

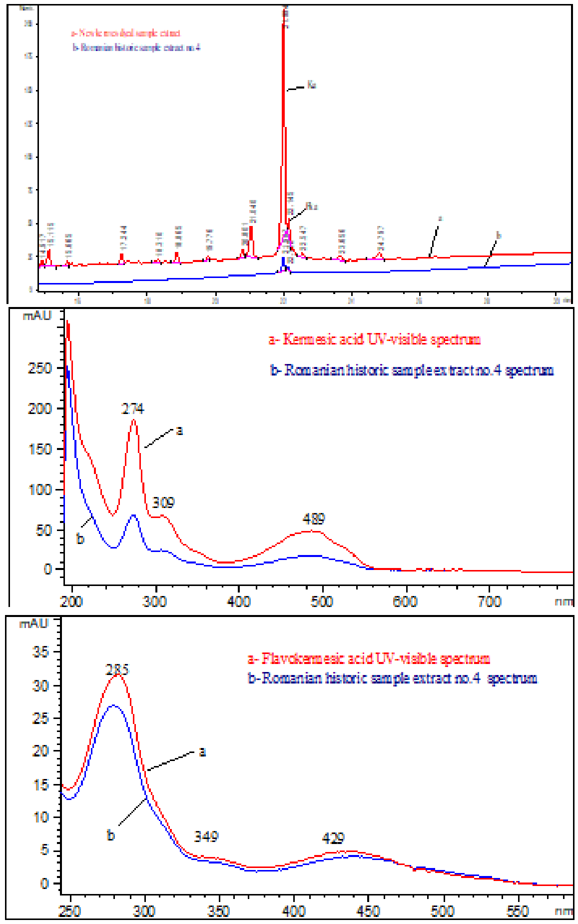

Fig. 5.45. Chromatogram of new kermes dyed sample extract with UV-visible spectrum of kermesic acid compound; UV-visible spectrum of flavokermesic acid compound.vs. sample OT4 extract;

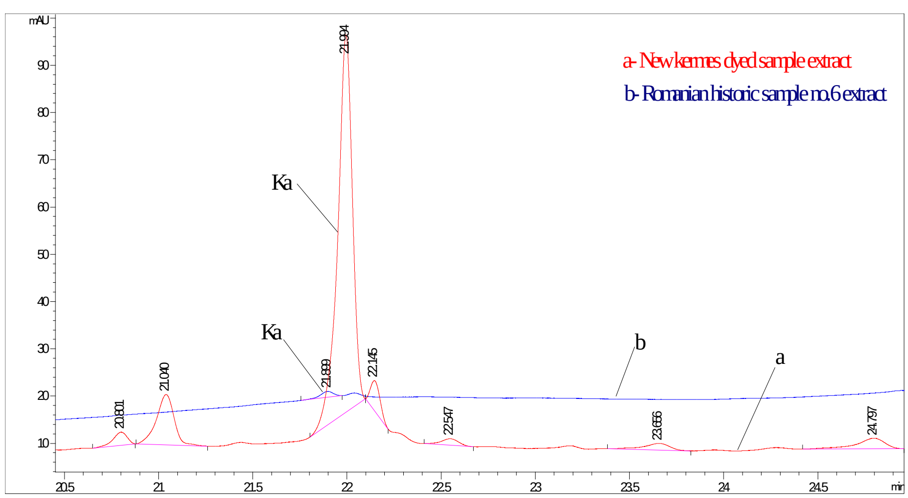

Fig. 5.46. Chromatogram of new kermes dyed sample extract vs. sample OT6 extract

Cochineal insect dye separated components are with significant matching with those in historic sample no. 5 that correspond to carminic acid according to UV-visible spectra pattern (fig. 5.47).

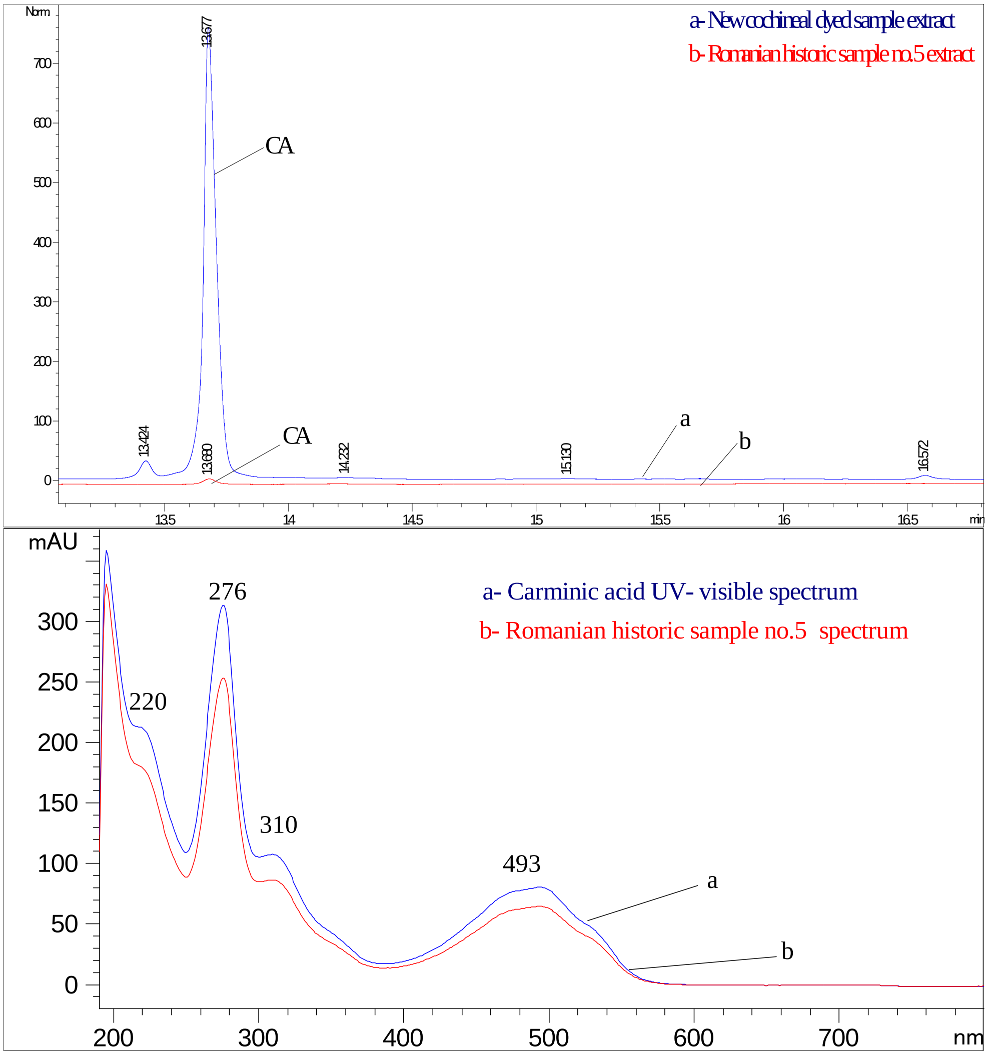

Fig. 5.47. Chromatogram of new cochineal dyed sample extract with UV-visible spectrum of carminic acid compound vs. sample OT5 extract

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Alizarin was detected in sample no. 7 which is an indication of using madder plant dye. Similar chromatographic peaks and spectra are detected and compared between sample extract no.7 and new madder dyed sample extract (Fig. 5.48).

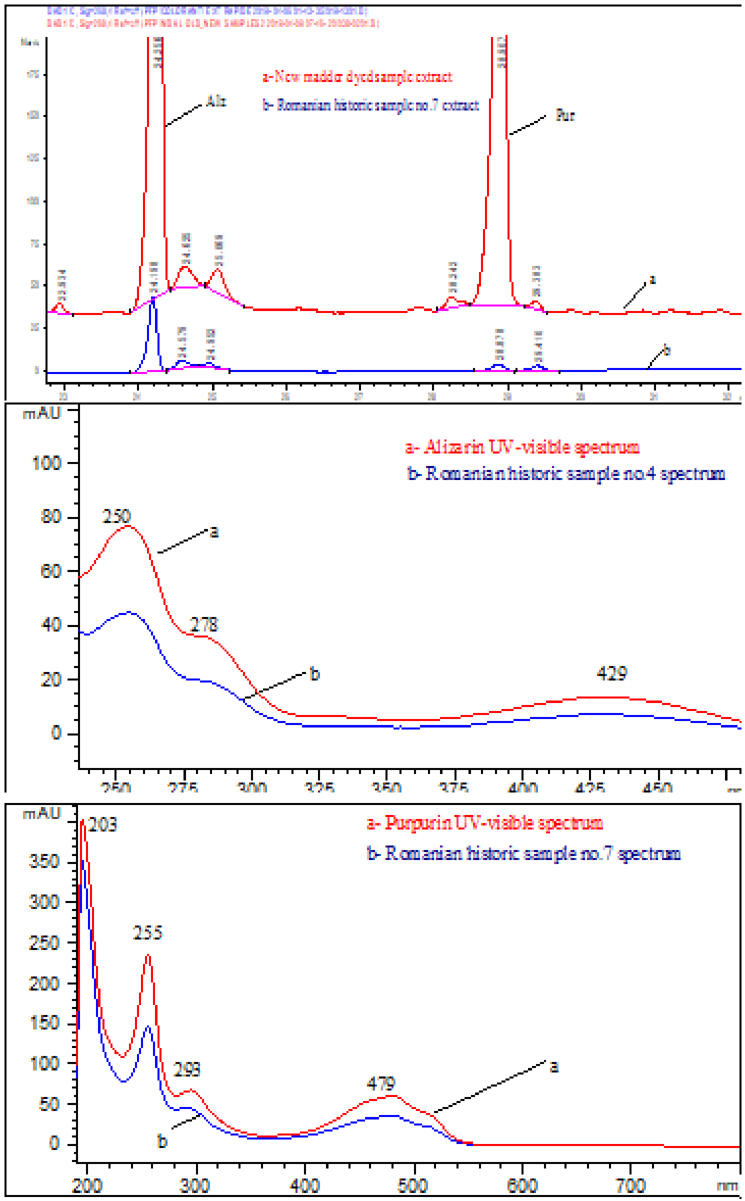

Fig. 5.48. Chromatogram of new madder dyed sample extract with UV-visible spectrum of alizarin compound; UV-visible spectrum of purpurin compound vs. sample OT7 extract

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As to historic sample no.8, the chromatographic peaks for the compounds separated correspond to the chromatographic extracts of lac dye solution at retention time 16.5 min. a (fig. 5.48). Lac differs in its composition from the cochineals in that its main constituents are the two laccaic acids A and B [Rosenberg, 2008].

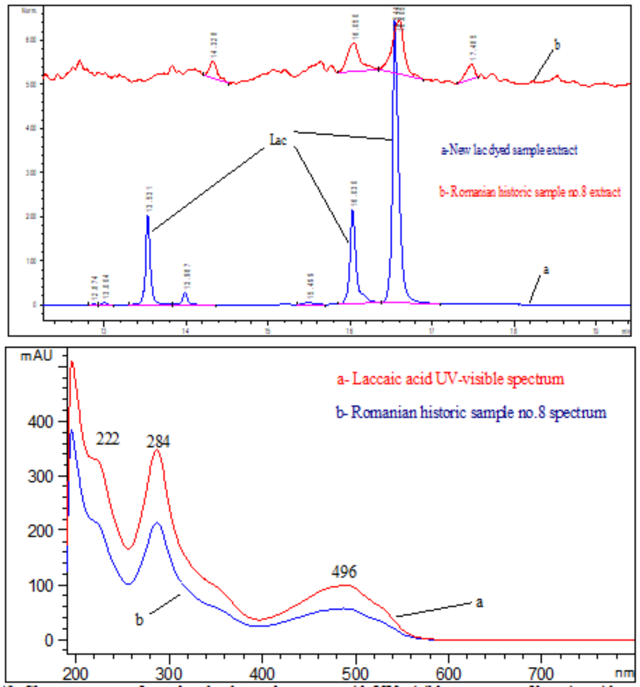

Fig. 5.49. Chromatogram of new lac dyed sample extract with UV-visible spectrum of laccaic acid compound vs. sample OT8 extract;

Table 5.8 include detailed list of red dyes from different origins, modified from [Recep *et al.*, 2014; Rosenberg, 2008; Wouters and Verheken, 1989; Ferreira, 2004; Hofenk-de-graaff, 2004].

It has been noticed for all of the historic samples different chromatographic peaks at Retention times between 4-14 min with differentiation in positions and intensities for each sample within. These peaks values might be attributed to gallic or ellagic acids from tannins source as an additive during the dyeing process. The second possibility is the existence of tannins materials, none deliberately, due to the burial conditions of the fragments for centuries. The third possibility of the presence of ellagic acid is indicates the use of a tannin-containing plant material either for textile dyeing or for weighting the silk [Otlowska *et al.*, 2018; Nowik *et al.*, 2005].

Chapter six

General Conclusions

In this study, data were presented, analyzed and interpreted as results, and then discussed through integration of all optical, elemental, spectral and chromatographic information gathered. The analysis and discussion of the two historical (Ottoman and Romanian) groups were elaborated respectively.

For Ottoman samples, dyes were successfully identified in all of samples; various natural and synthetic dyes have been detected. Indigo, madder, Prussian blue, Scheel's green, synthetic alizarin and tannin additives were used to impart colors on fabric. The dyes indigo, madder and synthetic alizarin, were common to the 19^{th} century. While Prussian blue and green Scheele's weren't mentioned in the historical context of the Ottoman sources. Wool, cotton, and silk fibers were detected for weaving the costumes. For making the luxurious velvet layers silk and cotton were the primary fibers used to make the costume's fabrics, while mix of silk, cotton and wool fibers were used to weave the lining parts.

These findings from dye analysis may help to recreate damaged textiles with threads dyed with the same natural dyes as those identified. This could mean that further textile aging would be standardized, and no variations would occur between supplements and historical material(s).

As to Romanian fragments, the preliminary investigation, analysis and results obtained using OM, SEM-EDX and ATR-FTIR were helpful in limiting the possibilities of dyes recognized using HPLC-DAD. Taking into the fact the brownish color all of the samples have according to the normal human eye. Multi-analysis approach proved to be very efficient in identification of the textiles components under scrutiny.

This approach succeeded to identify the type of natural silk, traditional colorants (weld, Persian berries, walnut, kermes, cochineal and lac), and metallic threads (silver and golden strips), often used in the manufacturing technology for the textiles used for producing fine clothing used by high-ranking individuals, as well as the period and area of use.

The identification of the luxurious silk as fabric, weaved with fine gilt or silver strips and dyed with costly precious dyestuffs such as cochineal and kermes, indicate that these samples were part of a garment with a highly-prized status symbol. It, hence, can be assumed that they were made as part of ceremonial or decorative purposes in religious practice, given that they were found in monasteries.

The data obtained in the experimental part generated a series of conclusions related to the unique contributions of the research, of which was pioneered, namely;

The results of the study provided sufficient explanation for the use of different types of fibers from the social and economic point of view.

For the ottoman costumes, knowing the kind of the dyes, helped in concluding the dyeing techniques that were used, and predicted an approximate date for the textiles; since there are some dyes appeared in a known time. The presence of the identified dyes that have a known discovery date enabled the study to date the Ottoman costumes:

- The presence of synthetic alizarin in the black cloak indicates that it was not made before 1868.
- Identifying Prussian blue on the woman dress refers that it was made after 1810.
- Detecting Scheele's green (Arsenic- copper based matter) in the green dress shows that the dress was not made before 1778.

The local production of Prussian blue, Scheele's green and synthetic alizarin weren't familiar; they were rather imported from Europe and dyed locally, since it was a usual way to avoid more expenses.

As regard to the Romania fragments, the identification of cochineal and lac dyes correlates with the suggested dating period of the samples (17^{th} – 18^{th} century), since these two dyes were introduced to Europe after the 16^{th} century, and begun to be used on commercial level and spread widely after that to replace other red dyes because of its supreme fastness properties.

Despite of identification successes, it was relatively difficult to obtain exact dyeing recipes similar to traditional ones, based on data obtained. This is due to the fact that the exact details during the dyeing process remain unrecorded. Since dyeing industry, historically, was considered a highly skilled craft that contain details which were handed down from father to son through generations as trade secrets. Causing the loss of many of these small "secrets", but yet crucial, over time.

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APPENDIX 1

The work of this thesis has been covered in the following publications and comunications:

Publications ISI:

- **Nidal Al-Sharairi**, Irina Crina Anca Sandu, Viorica Vasilache, Ion Sandu , (2020), *Recognition of natural silk fibers, dyes and metal threads of historical Romanian textile fragments using the multi-analytical techniques approach*, **Textile Research Journal**, **90, no.** 4, 2020, pp. 1-18, https://doi.org/10.1177/0040517519898827./Q1
- **Nidal Al Sharairi**, Irina Crina Anca Sandu, (2018), *Characterization of Dyeing Techniques of Late 19th Century Ottoman-Style Costumes*, **Revista de Chimie, 69**, no. 4, pp. 901-905./Q3
- **Nidal Al-Sharairi,** Ziad Al-Saad, Ion Sandu, (2017), *Identification of dyes applied to ottoman textiles*, **International Journal of Conservation Science**, **8**, no. 2, 2017, pp. 251-258. /Q4.

Publications non-ISI (BDI):

- **N. Al Sharairi**, I.C.A. Sandu, V. Vasilache, I. Sandu, (2020), *Deterioration and Corrosion Detection of Medieval Silk Fibers and Metal Threads from Romania,* **EUROINVENT - INTERNATIONAL WORKSHOP, Scientific, Technological and Innovative Research in Current European Context**, 12th edition, 21 May 2020, Iasi, **Topics: Scientific Inquiries through Elective Elaborations**, (Editors: I.G. Sandu, I. Sandu and A.S. Ciornei), Ed. PIM, 2020, pp. 9-31./BDI (Academic Google)

Communications at international workshops and conferences:

- **Nidal AL-SHARAIRI**, Ion SANDU, *Studiul analitic al textilelor şi al vopselurilor antice (Analytical Study of Ancient and Historical textiles and dyes)*, **Workshop Internaţional Creşterea relevanţei învãţãmântului universitar tehnic în relaţie cu dezvoltarea industrialã regionalã**, Ediţia a II –a, Universitatea Dunărea de Jos, Galați, 9-10 Mai 2018, Ed. GUP, Galati University Press, ISBN 978-606-696-111-0, 2018, pp. 19-20;
- **N. Al-SHARAIRI**, Viorica VASILACHE, Maria BOUTULICA, Kamel EARAR, Ion SANDU, *Deterioration And Degradation of Ancient Textiles Under the Influence of Environmental and Anthropogenic Factors*, **The Fourth International Conference New Trends in Environmental and Materials Engineering (TEME)** 25-27 October 2017, Galati, ROMANIA, Poster Session, 28.10.2017, P70, Book Abstracts, GUP Galati University Publishing Press, 2017, p. 92.