DYES IN A 15-TH CENTURY LITURGICAL MANTLE FROM THE MNIR COLLECTION

IDENTIFICAREA COLORANȚILOR DINTR-O MANTIE LITURGICĂ DE SECOL XV, DIN COLECȚIA MUZEULUI NATIONAL DE ISTORIE A ROMANIEI

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Abstract

Dyes identification is a powerful tool in the study of textiles in museum collections. This is explained by several facts (i) natural dyes were the only source of colouring textile fibres from Antiquity and until the last decades of the 19-th century (when synthetic dyes became available); (ii) each dye source was originally used in its place of origin before being traded and (iii) commercial routes may be documented as being connected with geographical discoveries and historical events. Since 1997, a large number of textiles from Romanian collections have been studied in terms of dye analysis, first within a joint research between Romanian institutions and the Royal Institute for Cultural Heritage (KIK/IRPA) in Brussels and more recently due to an analytical protocol built for the first time in Romania, by using liquid chromatography with UV-Vis (diode array) and mass spectrometric detection.

The present study discusses the results obtained by applying this new analytical procedure in the identification of dyes in a 15-th century liturgical mantle, made of brocaded velvet - assumed as "Venetian workshop" - with an embroided cross applied on the reverse. Dyes investigation are part of a larger project on the occasion of the liturgical mantle restoration, in 2015. Lac dye (*Kerria lacca*) and madder (*Rubia tinctorum* L.) were identified in the velvet, madder and tannins in the lining (understudy) and dyer's broom (*Genista tinctoria* L.), young fustic (*Cotinus coggygria*), madder and redwood type (*Caesalpinia* sp.) in the embroidery.

Except for lac dye, whose detection in "Venetian" brocaded velvet is surprising, all the other sources are in perfect agreement with literature and previous analysis and therefore confirm the object authenticity and date.

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Introduction

Natural dyes represented the only source of colour for textile fibres until de discovery of synthetic dyes, in the last decades of the 19-th century. Natural sources of colour were used only in their place of origin before becoming universal available, and their trade routes may be connected with geographical discoveries and historical events. Consequently, identification of natural dyes in historical textiles would reveal useful information about the context an object was created. Moreover, the status of those who ordered and/or owned the object may be deduced based on the fact that some dye sources were more expensive than others. Dyes identification could also unveil the manufacturing technique, based on the fact that light fugitive dyes were used in the hidden parts of the fabrics, and could also contribute to the objects conservation, as selection of the most appropriate microclimate conditions for preservation and exhibition is based on the properties of the dyes detected.

Identification of natural dyes in textiles from Romanian collections has been performed for more than 20 years, first by liquid chromatography with UV-Vis detection (LC-DAD), within a joint research between Romanian institutions and the Royal Institute for Cultural Heritage (KIK/IRPA) www.kikirpa.be in Brussels [1], and later on by liquid chromatography with UV-Vis and mass spectrometric detection (LC-DAD-MS), based on an analytical protocol developed for the first time in Romania [2, 3]. The latter combines the use of the UV-Vis and mass spectrometric detectors to associate the information and distinguish between major and minor dyes, and facilitates a clear attribution of the dyes and biological source/sources used. Analysis performed on the most representative categories of textiles from Romanian collections, mainly from Moldavia and Wallachia - (Orthodox) liturgical embroideries (15-th to 18-th century), documents with hanging seals (15-th to 17-th c.), Oriental textiles (15-th to 19-th c.) and traditional (ethnographical) textiles (19-th to 20-th c.) - evidenced the use of a large variety of dye sources: lac dye (*Kerria lacca*), kermes (*Kermes vermilio*), Polish and Armenian carmine scale insects (*Porphyrophora polonica* and *Porphyrophora hamelii*), Mexican Cochineal (*Dactylopius coccus*), weld (*Reseda luteola* L.), dyer's broom (*Genista tinctoria* L.), young fustic (*Cotinus coggygria* Scop.), *Rhamnus* berries, redwood type *Caesalpinia* species, and indigoid dyes (*Indigofera* sp. or *Isatis tinctoria* L.) [1, 2, 4-9]. Based on the detection of lac dye which, according to literature, was used in textiles of Oriental origin but not in Western Europe, it was stated that in the 15-th century, materials in (Orthodox) liturgical embroideries would rather have an Oriental origin and brocaded velvet were weaved in Western European workshops [7].

The present article describes the results obtained by the application of the LC-DAD-MS analytical protocol to the identification of natural dyes in a 15-th century liturgical mantle from the collection of the National Museum of Romanian History (MNIR). According to the museum archives, the object, with the inventory number MNIR 47443, is part of the liturgical costume and belonged to the Evangelical Church in Sibiu, Transylvania (Romania). It is dated in the second half of the 15-th century and is made of brocaded velvet, assumed as "Venice workshop" [10], with an embroided cross applied on the reverse. Only about half of the front part of the object was preserved (Figure 1). The liturgical mantle presents earlier interventions and was selected for restoration in 2015 [11].

Experimental

Materials and methods

Samples and sample preparation

Samples about 0.5 cm long (~3mg) were taken during the restoration procedures, from the brocaded velvet and the embroidery. Two sets of samples were provided by Cristina Moșoiu (MNIR): a first one (encoded as set_1) was taken in October 2015, under the coordination of dr. Ileana Crețu, expert in textile restoration, National Museum of Art of Romania (MNAR) and a second one (encoded as set_2) in October 2016, under the coordination of dr. Iolanda Turcu, expert in textile restoration (MNAR) (Figure 2).

Fibre investigation

Fibres were first observed under the microscope, at 10-80x and then non-destructively analysed by attenuated total reflectance infrared spectroscopy (FTIR-ATR). A Nikon SMZ 1000 stereomicroscope was used for fibres observation. For documentation and images collection, the microscope was coupled with a Nikon DSLR camera, model D3100 Kit AF-s 18-55mm VR DX. For FTIR-ATR, a Bruker Optics Alpha spectrometer was used equipped with a Platinum ATR single reflection diamond ATR module. Spectra were acquired in the 4000-400 cm^{-1} domain, with a resolution of 4 cm^{-1}. Spectra collection and data processing were made with a dedicated software, Opus 7.0.

Dyes extraction and analysis

Dyes extraction was made by acid hydrolysis, according to the method developed by Wouters [12]. 200µl mixture 37%HCl/ CH_3OH/ H_2O 2:1:1 (v/v/v) were added to each fibre and the mixtures were kept at 100^oC for 10 minutes. The solutions were evaporated to dryness in a vacuum desiccator. Each sample was re-dissolved in 100µl solution CH_3OH/ H_2O 1:1 (v/v) and centrifuged at 12000 rpm for 10 minutes. The supernatants were transferred in chromatographical vials and injected into the chromatographical system. More details on sample preparation and the instrumentation used were described in an earlier publication [3].

Database

Dyes were identified according to retention, UV-Vis and mass spectrometric data, as compared to information collected on standards. Analysis of standard dyed fibres (fibres dyed in the laboratory with known biological sources, by following traditional dyeing methods) and information available in literature [13, 14] are the basis of biological sources attribution. The biological sources of dyes, as well as retention, UV-Vis and mass spectrometric data, are given in Table 1.

Instrumentation

Samples were analysed by liquid chromatography with diode array and (triple quadrupole) mass spectrometric detection (LC-DAD-MS). An Agilent 1260 LC system was used, composed of the following modules: quaternary pump (Model G1311C), automatic injector (G1367E) and column thermostat (G1316C). The diode array detector (G4212A) and the triple quadrupole mass spectrometer (G6410B) were serially connected. The latter was using an ESI ionization source (ESI, Model G1948B), operated under negative ion monitoring mode.

Chromatographic separation

A Zorbax C18 column, 150mm L x 4.6 i.d. x 5 μm d.p. was used, thermostated at 40^{o}C. The mobile phase consisted in a mixture of aqueous 0.2% (v/v) CH_2O_2 (formic acid, solvent A) and CH_3OH / CH_3CN (1:1, v/v, solvent B). Gradient elution was applied according to the following profile: at 0 min, 15% solvent B; from 0 to 5 min, linear increase to 25% solvent B; from 5 to 10 min, linear increase to 55% solvent B; from 10 to 16, linear increase to 100% solvent B; from min 16 to 18, constant at 100% solvent B; and step jump at 15% solvent B, with a 4 min re-equilibration step (period between runs). The flow rate was set at 0.8 mL/min. 5 μL were injected for each sample, from the 100 μL volume resulting from sample preparation.

Detection

UV-Vis spectra were acquired with a DAD detector which was placed between the column and the MS ion source. Spectra were collected over the 190-640 nm range, with a resolution of 2 nm. A triple quadrupole MS detector was used, which was operated in negative ion monitoring mode, with the following ESI operation parameters: drying gas temperature 350^{o}C; drying gas flow 8 L/min; pressure of the nebulising gas 40 psi; Vcap 2500 (-). The triple quadrupole used MS2 type Scan when used as a single MS instrument; the data storage was set on profile and the peak width at 0.07; fragmentor 135 V; ΔEMV 400 V. The scanning interval for the mass to charge ratio (m/z) was between 100 – 600 a.m.u., acceleration voltage on the collision cell: 7 V; Dwell Time 500 ms.

Data processing

Agilent MassHunter Quantitative Analysis B.06.00 software was used to control the chromatographic system, for data acquisition and processing. The analytical procedure was described in detail in an earlier publication, where an ion trap mass spectrometer was used instead of the triple quadrupole [3]. Each sample was first analysed with single MS detection exploited in the Full Scan mode and the resulted data was processed by extracting chromatograms, according to the molecular ions of the dyes in the database. If necessary, a second injection from the sample was made, by using MS/MS detection. In such a case, the first mass analyzer filters the m/z of the molecular (or major) ion of compounds according to database, while the second mass analyzer is exploited in the Full Scan mode. In most cases, retention, UV-Vis and mass spectrometric data were used for the major compounds identification. The minor ones, associated in the biological source with the major dyes detected, were only recognized based on retention and mass spectrometric data.

Results

Brocaded velvet

Analysis performed on samples from the plush and warp in the brocaded velvet (samples 2_set 2, 3/26_set 1, 3/27_set 1, 5_set 2 and 8_set 2, see Table 2) evidenced the presence of several dye components: laccaic acid A, laccaic acid B, flavokermesic acid, erythrolaccin, alizarin, purpurin and rubiadin (Figure 3). Laccaic acid A, alizarin and purpurin were evidenced by retention, UV-Vis and mass spectrometric (MS) data, which assign them as major components. For the MS data, information was collected with the MS working in full scan mode (FS) followed by data procession through ion extracted chromatograms (IEC) according to the molecular ions of dyes in the database. The presence of laccaic acid A (m/z=536 a.m.u., $[M-H]^-$) suggests the use of lac dye (*Kerria lacca*), while alizarin (m/z=239 a.m.u. $[M-H]^-$) and purpurin (m/z=255 a.m.u. $[M-H]^-$) point to the use of madder (*Rubia tinctorum* L.). The other compounds detected, laccaic acid B (m/z=495 a.m.u., $[M-H]^-$), flavokermesic acid (m/z=313 a.m.u., $[M-H]^-$) and erythrolaccin (m/z=285 a.m.u., $[M-H]^-$) in lac dye, and rubiadin (m/z=253 a.m.u., $[M-H]^-$) in madder should be considered as minor dye components in the respective sources, as they were only identified by the MS detector, which is more sensitive, as compared to the UV-Vis. In sample 3_set 2, also from the warp, no dye was present in the UV-Vis chromatogram and laccaic acid A was the only dye evidenced, in the chromatogram collected in FS mode followed by IEC of m/z=536 a.m.u. A possible explanation would be the sample size, considerable smaller as compared to the others, which made all the other dyes fall under the detection limits of the two detectors.

Analysis performed on samples from the weft in the brocaded velvet (samples 1_set 1, 2_set 1, 3/25_set 1, 1_set 2 and 9_set 2) revealed the presence of alizarin and purpurin, as major dyes and rubiadin as minor dye (Figure 4). Alizarin and purpurin were present in both the UV-Vis and MS chromatograms, while rubiadin only in the latter. In three of these samples, ellagic acid was also detected as minor compound, as suggests the presence of its molecular ion, m/z=301 a.m.u., in the MS chromatogram collected in FS mode followed by IEC. Detection of ellagic acid suggests the use of tannins, substances of vegetable origin, mainly used to process animal hides and skins to leather [13]. In textile dyeing they may be used as mordants in wool, silk and cotton dyeing, for silk weighting and as source of black, when used with iron salts. In the above mentioned samples, the use of tannins in the presence of a dye source (madder), suggests they were rather used for silk weighting, a treatment to recover silk properties after degumming (the process of removing sericin).

The difference in colour between the red-orange hue warp samples only dyed with madder, a dye of vegetal origin, as compared to the red-violet weft samples, where a mixture of vegetal and insect dyes were used, should be noted (Figure 2).

For a yellow sample taken from the brocaded velvet edge decoration line, no dyes were detected, as the available sample was too small and the dyes were situated under the detection limit of the method.

Embroidery

Samples from two embroidery threads and a sewing thread were available for analyis. Luteolin, genistein and apigenin were identified by both UV-Vis and mass spectrometric detection in a yellow embroidery thread from the back side (Figure 5). Their identification was based on retention, UV-Vis spectra and molecular ions ($[M-H]^-$) observed in the IECs according to the molecular ions of the three compounds: m/z=285 a.m.u. for luteolin and m/z=269 a.m.u. for genistein and apigenin. The combination of the three dyes suggest the use of dyer's broom (*Genista tinctoria* L.). Recent studies demonstrated that the two minor compounds, chrysoeriol and diosmetin, should be also expected in dyer's broom dyed samples [15]. Their presence was also observed in the sample under discussion, where the chromatograms extracted according to m/z=299 a.m.u., the molecular ion of both compounds, was evidenced by data processing of the chromatogram obtained with the MS in FS mode.

For another embroidery thread, with a yellow-orange hue, luteolin and genistein, as well as another compound, sulphuretin, were present in the UV-Vis chromatogram (Figure 6). Their detection was confirmed by the MS data, observed in the chromatogram recorded with the mass spectrometer in the FS mode followed by data procession according to the molecular ions, m/z=285 a.m.u. for luteolin and m/z=269 a.m.u. for genistein and sulphuretin. Identification of sulphuretin suggests

the use of young fustic (*Cotinus coggygria*) wood; consequently, another dye, fisetin should be also present. It is confirmed by m/z=285 a.m.u. in the IEC and finally suggests that a mixture of young fustic and dyer's broom (*Genista tinctoria* L.) was responsable for dyeing. Ellagic acid was also detected as a minor compund which is not surprising as it is known that tannins should be expected in young fustic wood [14].

Alizarin and purpurin were detected, as major compounds, in a red-orange silk sewing thread which suggests the use of madder. A minor compound encoded in literature as "srw" (soluble redwood) or "type C" was also detected in the chromatogram recorded with the mass spectrometer in the FS mode followed by data procession according to the ion, m/z=243 a.m.u. "srw" is a marker compound to suggest the use of redwood type (*Caesalpinia sp.*), as it remains present in the chromatograms of the acid extracted samples when brasilein, the main dye component in redwood type is too degraded to be observed. After more than 20 years of being used as marker, the structure of "srw" was recently revealed [16]. Consequently, a mixture of madder and redwood type is responsible for dyeing the red silk sewing thread.

Lining (understudy)

Alizarin and purpurin, as major dyes and rubiadin and ellagic acid as minor, were detected in the cotton linen which suggest that madder, was used for dyeing. In this case, the presence of tannins could be a result of their use as mordant and to give the final colour a darker hue.

Discussion about the biological sources detected

Lac dye (*Kerria lacca*), has been cultivated in India, Indochina and the south of China for thousands of years. It had also been used in the Mediterranean since Antiquity, as being exported from India via Egypt. It became available to dyers in the Muslim world after the Arab conquest the Mediterranean [14]. The use of lac dye in these regions was proved by its identification in 3-rd century textiles in Palmyra and in Coptic textiles from the mid 7-th century onwards [14]. According to literature [14], lac dye was not so popular in Western Europe, where other insect dyes were preferred. Its rare use in textiles from the period 1450-1600 was suggested by dye analysis of textiles from various museum collections in Western Europe, where mostly kermes (*Kermes vermilio*), and Polish carmine scale insects (*Porphyrophora polonica*) were identified [17].

In textiles from Romanian collections, analysis performed on (Orthodox) liturgical embroideries from Moldavia and Wallachia evidenced lac dye, in combination with madder, as the main source of red in the silk satin support of pieces dated from the 15-th to the last decades of the 16-th century [8, 9]. Lac dye was also identified in many silk threads from documents with hanging seals emitted by the Chancellery of Moldavia in the last decades of the 15-th century [5].

Previous analysis on red plush and warp samples in brocaded velvets from Moldavia and Wallachia revealed the use of kermes and Polish and Armenian carmine scale insects, no lac dye being present [8, 9].

Identification of lac dye in the liturgical mantle brocaded velvet, attributed as "Venetian" is surprising, if we take into account that lac dye was rarely used in Western European workshops. For example, in the study cited above [17], which involved about 250 samples, from which about a third belonged to textiles of Italian origin, lac dye was detected in only one case (position 61), in a silk velvet from the Abegg Stiftung collection (Bern, Switzervald), dated from the 2-nd half of the 15-th century. Therefore, the present detection, very similar otherwise to the one mentioned above, could be interpreted as one of the rare uses of lac dye in Western European workshops. On the other hand, the existence of other (maybe Oriental?) workshops, where Italian style brocaded velvets could have been woven with fibres coloured with dyes more frequently used in Orient, such as lac dye, should not be excluded. In depth investigation of dyes in other brocaded velvet liturgical mantles from Romanian collections (and more precisely from Transylvania), would be worthwhile to clarify this aspect.

Madder (*Rubia tinctorum* L.) played an important role in textile dyeing since Antiquity. This may be explained by its large scale cultivation - which made it much cheaper as compared to insect dyes - and to its ability to dye in a large variety of hues, from orange to violet and brown [14]. Madder was used in ancient Egypt, in Mesopotamia, in Greek and Roman times, in India and the surrounding countries as well as in the Mediterranean area and Western Europe [14]. It was detected in archaeological textiles in China (estimated 3000 years old) and Iran (around 2000 years old) [18], Roman Egypt [19], Coptic textiles [20, 21, 22], European [16], post Byzantine and Ottoman textiles (16-th to 18-th c.) [23], Arraiolos carpets [24] and many others. It was also identified in all the categories of textiles from Romanian collections studied [1-9].

Identification of madder in the liturgical mantle brocaded velvet (weft and warp) and lining is in perfect correspondence with literature and previous analytical data, which mention and evidence its use in both silk and cotton dyeing, in Europe and Minor Asia.

Dyer's broom (*Genista tinctoria* L.) was mentioned in recipes dating from the Middle Ages [25]. It has been known and used in England, as attested by the large quantities of stems found during archaeological discoveries [14, 25]. In the 19-th c., it was also known and used in Eastern Europe as also confirmed by its frequent mentioning in a collection of dyeing recipes edited by the Romanian Academy, in 1914 [26].

Young fustic (*Cotinus coggygria*) was mentioned as "yellow wood" by an 11-th c. Persian manuscript [14, 25] and in European medieval documents as "young fustic" or "Venice sumac". It was very appreciated for its orange hue and

the large quantity of colorant that may be obtained from each tree [14, 25]. It played an important economic role in European dyeing until the 19-th c., both as dye and source of tannin. Identification of dyer's broom and young fustic in the liturgical mantle embroidery threads come to support literature references on these sources.

Redwood type (*Caesalpinia sp.*) are species of soluble woods from Asia and America. Native of Asia where it was used since the 2-nd century BC, *Caesalpinia sappan* was imported in Europe in the early Middle Ages, under the commercial name "brazil" [14, 25]. Its use in various European textiles from the 14-th century onwards was confirmed by analytical investigation [17, 24, 27]. The importance of redwood in the 15-th century was evidenced by its name given to the country on the South American coast, Brazil, where this dye source was found in abundance. Redwood type was also identified in (Orthodox) liturgical embroideries and in brocaded velvets from the 15-th and 16-th centuries and in silk threads in documents with hanging seals from the late 15-th century [4-9], either as single dye source or in mixtures. Its identification in an embroidery sewing thread, in a dyeing combination with madder is in perfect agreement with literature data and previous analysis.

Conclusion

Lac dye (*Kerria lacca*), in a dyeing combination with madder (*Rubia tinctorum L.*), was identified in the brocaded velvet silk plush and warp, and madder was detected in the weft. For the embroided cross, dyer's broom (*Genista tinctoria* L.) and young fustic (*Cotinus coggygria*) were detected in silk embroidery threads and the combination of madder and redwood type (*Caesalpinia* sp.) in a silk sewing thread. Madder (with tannins as mordant) was responsible for the colour in the cotton lining (understudy). All the biological sources mentioned above were used in Europe and Minor Asia in the 15-th century and should be considered an argument for the object date. It is also worth to underline the use of the more expansive insect dyes in the visible parts of the velvet (plush and warp) and cheaper vegetal sources for the hidden threads. However, the presence of lac dye in the brocaded velvet is surprising as, according to previous analysis and literature data, it was not used as dye source in Western European textiles, and looks inappropriate for a "Venetian" velvet. Investigation of dyes in similar textiles would be helpful to establish if lac dye was occasionally used in Western European workshops, or "Venetian style" velvets were made in Eastern workshops, which would be revealed by dye analysis.

Once more, development of analytical strategies for investigation of materials in museum objects - as for example liquid chromatography with UV-Vis and mass spectrometric detection for the identification of dyes in historical textiles – contribute to better understand, preserve and valorise our cultural heritage.

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Table 1. Biological sources (Latin and common names) and analytical data (retention, UV-Vis [(1)] and MS data) for the dyes discussed in the present study. For each source, dyes are listed in alphabetical order.

Note: (*) – UV-Vis data is given only for the major dyes (dyes identified by DAD in the present study);

Biological source	**Dyes**	**Abv.**	**Retention (min)**	**UV-Vis [(*)] (min)**	**[M-H]**
Rubia tinctorum L. (madder)	alizarin	al	15.1	202;248;280;430	239
	purpurin	pu	16.2	204;256;294;480	255
	rubiadin	ru	17.4	-	253
Kerria lacca (lac dye)	laccaic acid A	laA	10.3	200;226;288;492	536
	laccaic acid B	laB	10.3	-	495
	flavokermesic acid	fk	13.5	-	313
	erythrolaccin	eryth	15.8	-	285
Caesalpinia sp. (redwood type)	"Soluble redwood"	srw	10.5	258;306;336	243
Genista tinctoria L. (dyer's broom)	apigenin	ap	13.7	210;268;336	269
	genistein	ge	13.4	208;260	269
	luteolin	lu	12.7	208;254;266;348	285
	chrysoeriol	chry	13.9	-	299
	diosmetin	dios	14.0	-	299
Cotinus coggygria (young fustic)	fisetin	fi	11.3	206;248;320;360	285
	sulphuretin	sul	12.2	256;398	269
Tannins	ellagic acid	ea	9.8	254;366	301

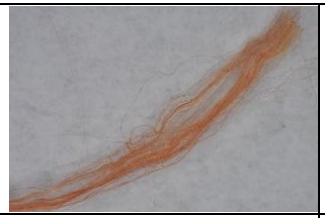
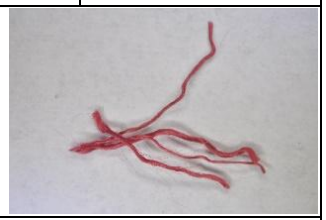
Table 2. Sample code, sample description and results (dyes and biological sources). For dyes abbreviation and analytical data, see Table 1.

Sample code (colour, fibre)	Sample description	Results	
		Dyes	Biological source(s)
BROCADED VELVET			
sample_1_set 1 red-orange, silk	weft, front side, bottom edge, beside the strip	al, pu, ru, ea(-)	madder (*Rubia tinctorum*) and traces of tannins
sample _2_set 1 red-orange, silk	weft, front side, bottom edge, beside the strip	al, pu, ru, ea(-)	madder (*Rubia tinctorum*) and traces of tannins
sample _3/25_set 1 orange, silk	weft, front side, brocaded velvet fragment	al, pu, ru, ea(-)	madder (*Rubia tinctorum*) and traces of tannins
sample _3/26_set 1 red silk	warp, front side, brocaded velvet fragment	laA, laB, fk, eryth, al, pu, ru	lac dye (*Kerria lacca*) and madder (*Rubia tinctorum*)
sample _3/27_set 1 red silk	warp, front side, brocaded velvet fragment	laA, laB, fk, eryth, al, pu, ru	lac dye (*Kerria lacca*) and madder (*Rubia tinctorum*)
sample _1_set 2 red-orange, silk	warp, front side, top right	al, pu	madder (*Rubia tinctorum*)
sample _2 _set 2 red, silk	warp and plush, front side	laA, laB, fk, eryth, al, pu, ru	lac dye (*Kerria lacca*) and madder (*Rubia tinctorum*)
sample _3 _set 2	warp, front side,	laA	lac dye (*Kerria lacca*)

red, silk	strip reverse		
sample _5 _set 2 red, silk	warp, back side, under the embroided cross	laA, laB, fk, eryth, al, pu, ru	lac dye (*Kerria lacca*) and madder (*Rubia tinctorum*)
sample _8 _set 2 red, silk	plush, front side (front side reverse, top strip)	laA, laB, fk, eryth, al, pu, ru	lac dye (*Kerria lacca*) and madder (*Rubia tinctorum*)
sample _9 _set 2 red-orange, silk	weft, front side reverse, broken edge	al, pu, ru	madder (*Rubia tinctorum*)
sample _10 _set 2 yellow silk	yellow line, front side reverse, under the cross	*no dyes detected* *(small sample, dyes under detection limit)*	
EMBROIDERY			
sample _16 _set 2 yellow, silk	embroidery thread, back side	lu, ge, ap, chry, dios	dyer's broom (*Genista tinctoria L.*)
sample _17 _set 2 yellow-orange, silk	embroidery thread, back side	fi, sul, lu, ge, ap, ea	young fustic (*Cotinus coggygria*) and dyer's broom (*Genista tinctoria L.*)
sample _20 _set 2 red-orange, silk	sewing thread (possible intervention)	al, pu, srw	madder (*Rubia tinctorum*) and redwood type (*Caesalpinia* sp.)
LINING (UNDERSTUDY)			
sample _12 _set 1 red, cotton	weaving, front side	al, pu, ea	madder (*Rubia tinctorum*) and tannins

Figure 1. Liturgical mantle, front side (left) and back side (right) (images from the MNIR archive)

Figure 2. Images of the samples received for dye analysis, 10x if not otherwise stated. Smaller samples, of about 5mm each, were cut and used.

<table>
<tr><td>  </td><td>  </td><td colspan="3">  </td></tr>
<tr><td>sample_1_set 1 (20x)
red-orange, silk</td><td>sample _2_set 1 (20x)
red-orange, silk</td><td>s _3/25_set 1
orange, silk</td><td>s_3/26_set 1
red silk</td><td>s_3/27_set 1
red silk</td></tr>
<tr><td>  </td><td>  </td><td>  </td><td colspan="2">  </td></tr>
<tr><td>sample _1_set 2
red-orange, silk</td><td>sample _2 _set 2
red, silk</td><td colspan="2">sample _3 _set 2
red, silk</td><td>sample _5 _set 2
red, silk</td></tr>
</table>

		
sample _8 _set 2 red, silk	sample _9 _set 2 red-orange, silk	sample _10 _set 2 yellow silk

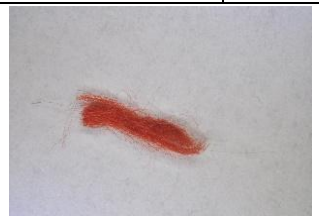
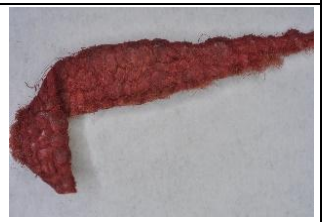
			
sample _16 _set 2 yellow, silk	sample _17 _set 2 yellow-orange, silk	sample _20 _set 2 red-orange, silk	sample _12 _set 1 red, cotton

Figure 3. UV-Vis spectrum, UV chromatogram (255 nm), Total Ion Current (TIC) chromatogram (resulting after single stage Full Scan MS detection) and Ion Extracted Chromatograms (m/z = 536, 495, 313, 285, 239, 255, 253 a.m.u.) indicating a combination of lac dye (*Kerria lacca*) and madder (*Rubia tinctorum* L.) being responsible for the colour in samples from plush and warp in brocaded velvet (sample _2 _set 2, sample _5 _set 2,sample _8 _set 2, sample 3/26_set 1, sample 3/27_set 1).

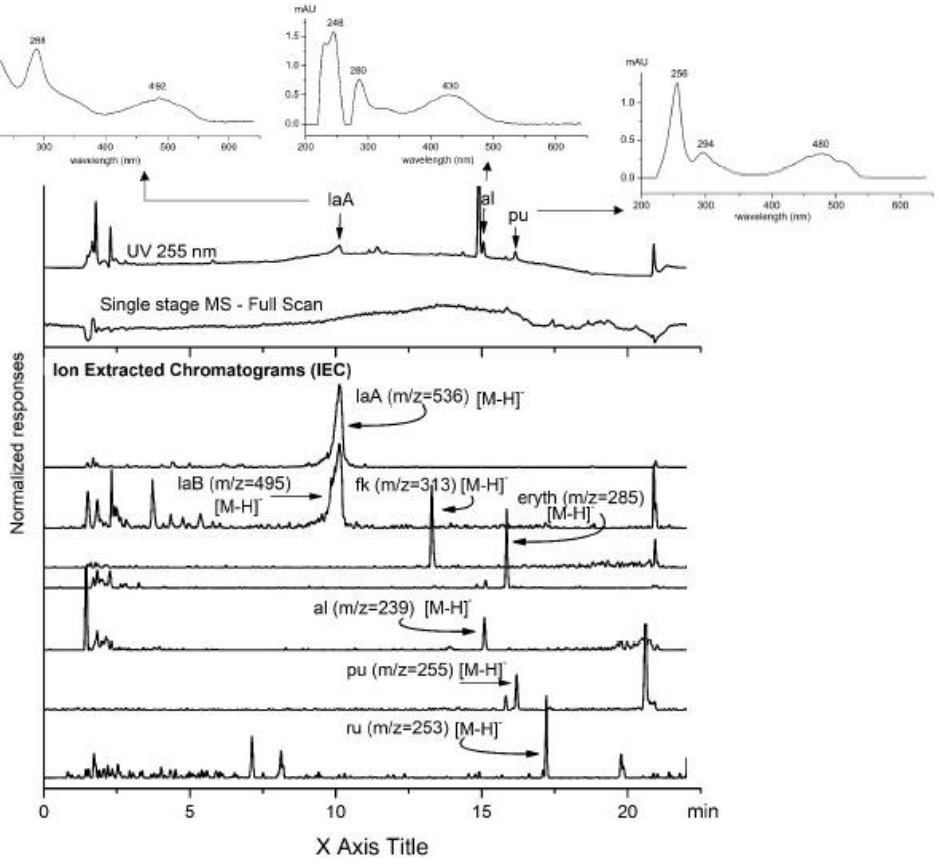


Figure 4. UV-Vis spectrum, UV chromatogram (255 nm), Total Ion Current (TIC) chromatogram (resulting after single stage Full Scan MS detection) and Ion Extracted Chromatograms (m/z = 239 and 255 a.m.u.) indicating madder (*Rubia tinctorum* L.) being responsible for the colour in samples from weft in brocaded velvet (sample _1 _set 1, sample _2 _set 1, sample _3/25 _set 2 and sample _9 _set 2).

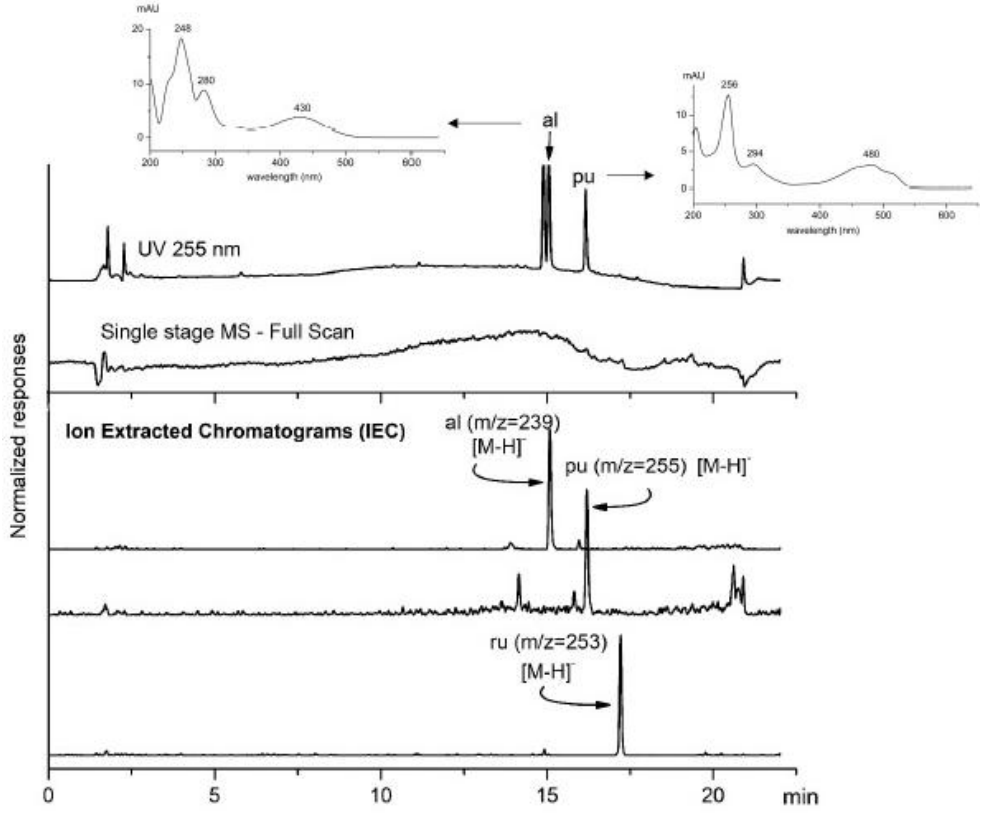


Figure 5. UV-Vis spectrum, UV chromatogram (255 nm), Total Ion Current (TIC) chromatogram (resulting after single stage Full Scan MS detection) and Ion Extracted Chromatograms (m/z = 285, 269 and 299 a.m.u.) indicating dyer's broom (*Genista tinctoria* L.), being responsible for the colour in sample coded sample _16 _set 2 from an embroidery thread.

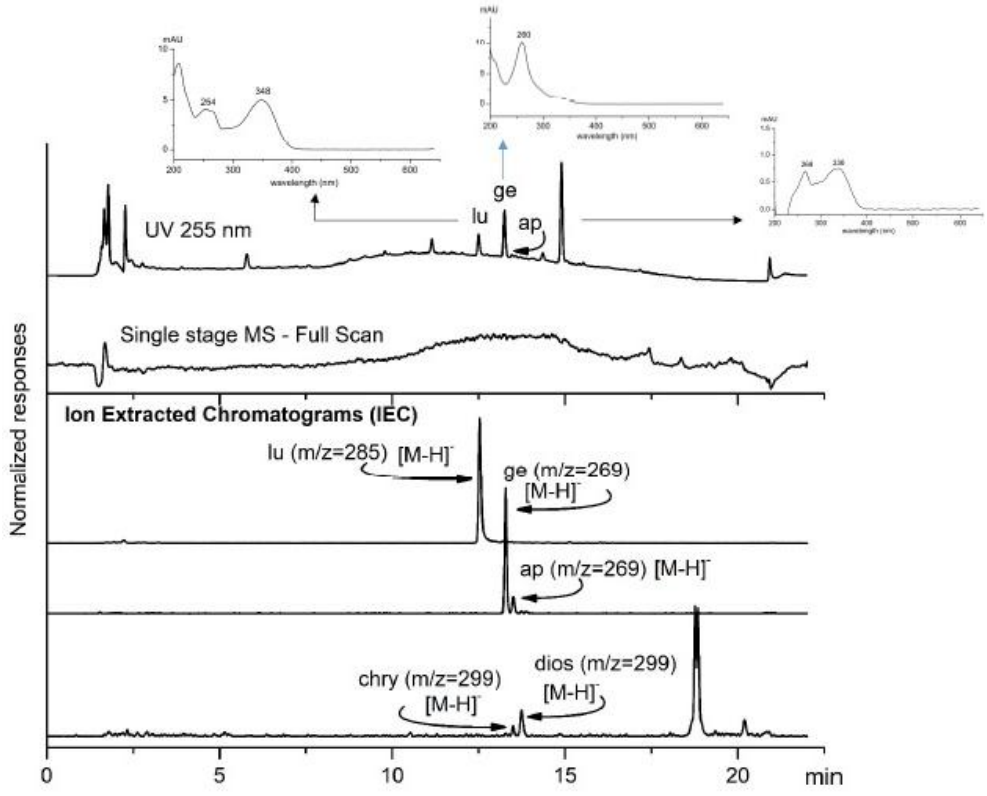


Figure 6. UV-Vis spectrum, UV chromatogram (255 nm), Total Ion Current (TIC) chromatogram (resulting after single stage Full Scan MS detection) and Ion Extracted Chromatograms (m/z = 285, 269 and 301 a.m.u.) indicating a combination of young fustic (*Cotinus coggygria*) and dyer's broom (*Genista tinctoria* L.) being responsible for the colour in sample coded sample _17 _set 2 from an embroidery thread.