2024

Red Dyes from West to East in Medieval Europe: From Portuguese Manuscript Illuminations to Romanian Textiles

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Keywords: natural dyes, illuminated manuscripts, Byzantine liturgical embroideries, brocaded velvets, liquid chromatography, microFTIR, microspectrofluorimetry

1. Introduction

1.1 *Natural dyes*

Red is the color *par excellence*,[1] its symbolism being linked with protection and magic through its primary attributes, fire and blood.[2] It was the predominant color from the earliest times, certainly during the Greek and Roman periods and into Medieval Europe, until blue became a competitor around the 13th century.[3] Mineral pigments, like iron oxides, were the first red sources, used to draw lines, dots, or spots on cave walls or stones.[4] Later, other mineral red pigments were also exploited: Cinnabar, natural mercury sulfide, since the Neolithic, and realgar, arsenic trisulfide, in Ancient Egypt.[5] Scientific investigation revealed that, although inorganic pigments were mainly used in painting, iron oxides and cinnabar were also the first available sources for coloring textiles.[6] Plant dyes have been known since the Neolithic, exploited by people living in climatically mild areas rich in vegetation. Their use is strongly connected with two other fundamental textile processes: Spinning and weaving.[7] Scholarly literature indicates Egyptian privet (henna, *Lawsonia inermis*) as the oldest red vegetal source used.[8] Although widely known as a source of brown, the dried leaves, when powdered and treated with lime water, yield an intense orange red, which is efficient for dyeing the body — skin and hair — and textiles of animal origin. Madder (*Rubia tinctorum* or relatives) was the first dye to be reported from archaeological European Bronze and Iron Ages textiles preserved in the Hallstatt salt mines, Scandinavian bog sites, and other European burials.[9] Apart from madder, the most widely appreciated red dye sources in the European Classical period were kermes (*Kermes vermilio* and *K. ilicis*), purple (species of sea snails from the *Muricidae* family), and extracts of red tree resins, as dragon's blood (*e.g. Dracaena draco*, *Dracaena cinnabari*, and *Daemonorops draco*). These sources were used for textile dyeing and as organic pigments in paintings.

[1] https://theamericanscholar.org/red/ ; https://www.thesmartset.com/seeing-red/ ; https://iris-janvier.com/en/red/, accessed 14 November 2023.
[2] Pastoureau 2022, 23–31; Brunello 1973, 23–26.
[3] Pastoureau 2022, 105.
[4] Pastoureau 2022, 15–16.
[5] Siddall 2018, 201–236.
[6] Gleba *et al.* 2021, 21918; Tamburini *et al.* 2019, 3761–3779.
[7] Brunello 1973, 9.
[8] Brunello 1973, 23.
[9] Hofmann-de Keijzer *et al.* 2013, 135–162; LaBerge 2018.

In *Textile Crossroads: Exploring European Clothing, Identity, and Culture across Millennia. Anthology of COST Action "CA 19131 – EuroWeb".* Kerstin Droß-Krüpe, Louise Quillien, & Kalliope Sarri, Editors. Zea Books, Lincoln, Nebraska, 2024.
 DOI: 10.32873/unl.dc.zea.1807

Medieval Europe merged the benefits of Eastern influences, regarding the development of new materials and techniques, with the experience of the Classical period.[10] An important achievement was gaining knowledge about silk production. The increase in the number of items in silk resulted in an improvement in dyeing, with a beneficial effect not only for silk, but also for wool and other textiles.[11] New dyes became available, such as redwood (*Caesalpinia sappan*), imported from the East, or folium (*Chrozophora tinctoria*), whose first mention dates from this period.[12] In the Middle Ages, prestigious dyes were probably traded along the Silk Road, a network of terrestrial and sea routes that connected various regions of Asia with East Africa and southern Europe. The Silk Road facilitated economic, cultural, political, and religious interactions between these regions from the 2nd century BC to the 15th century AD.[13] Study of historical sources have shown that, during the Renaissance, an artisan had six pigments at their disposal for dyeing silk thread in red: Madder, orchil (*Rocella tinctoria*), brazilwood/redwood, lac dye (*Kerria lacca* and *Kerria chinensis*), grain, and kermes.[14] The last two, which derive from the words *granum* and *krmi* (worm) respectively, refer to the valuable insect dyes *Porphyrohora hameli*, *P. polonica*, *Kermes vermilio*, and *K. ilicis* (Fig. 1). Documents from the Renaissance should be very carefully interpreted, as similarities between grain and kermes, and the scientific names of these insects, can make it difficult to distinguish between them.[15]

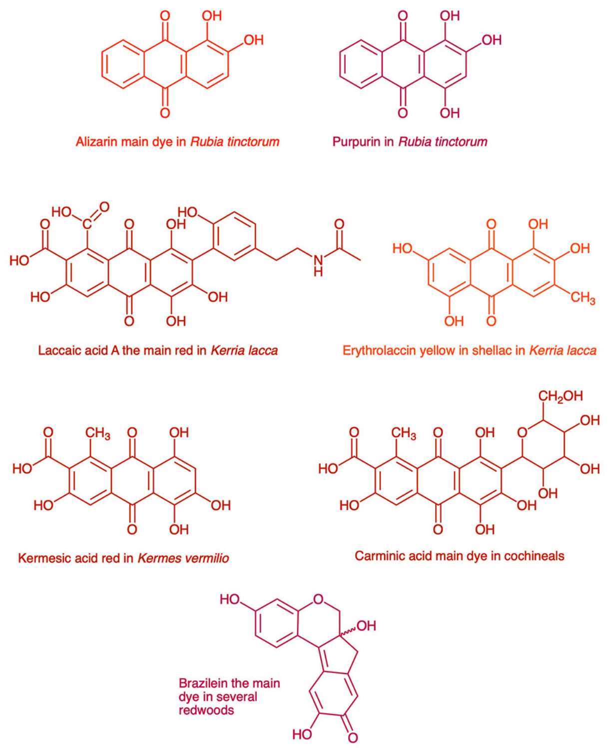

Fig. 1: Molecular structures for the relevant dyes discussed, the colors of which vary from translucent pink to purple, passing through various shades of red and carmine.

1.2 *Advanced analytical methods*

Several advanced analytical methods are now available to investigate dyes and pigments applied to objects from Medieval Europe.[16] In paint or textile reproductions, every analytical technique necessary for in-depth characterization can be used, which includes a study of dyes through High-Resolution Mass Spectrometry (HRMS/MS) coupled with High Performance Liquid Chromatography (HPLC-HRMS/MS) or Ultra Performance Liquid Chromatography systems (UHPLC-HRMS/MS).[17] This cannot be conducted on original Medieval paints, because we cannot obtain a micro-sample from an illumination with enough material to be extracted for HPLC analysis.

For dye identification in medieval paints, a multi-analytical approach is used, combining high spatial resolution (microRaman) and the highest sensitivity (microspectrofluorimetry). UV-VIS spectra in absorbance or reflectance are also very useful for preliminary dye investigation, while Fourier Transform Infrared microspectroscopy (microFTIR) is needed to discover more details regarding lake pigment formulations. Consequently, the main components of Medieval paint (the paint formulation), including colorants, binders, varnishes, and other additives, can be

[10] Brunello 1973, 119.
[11] Brunello 1973, 117–174.
[12] Brunello 1973, 132–133.
[13] https://en.wikipedia.org/wiki/Silk_Road, accessed 21 March 2023.
[14] Mola 2000, 107–137.
[15] Mola 2000, 107–137.
[16] Brunetti *et al.* 2016, 1–35; Melo *et al.* 2010, 857–866; 2019, 20180017; Picollo 2018, 1–14; Vitorino *et al.* 2015, 891–901; Nabais *et al.* 2020, 1–8; Veneno *et al.* 2021, 422–436; Petroviciu *et al.* 2010, 247–254.
[17] Petroviciu *et al.* 2010, 247–254; Petroviciu *et al.* 2017d, 164–171; Sharif *et al.* 2020, 908–924.

identified.[18] All these constituents are essential for the applicability and durability of Medieval paint. Therefore, heritage materials are typically highly complex systems of intrinsically heterogeneous compositions that can be very resilient. The systematic investigation of historical reproductions has proved crucial for the advancement of dye analysis research.[19]

1.3 *A Medieval color*

A Medieval color based on lac dye can be revealed by combining its infrared spectra with its molecular fluorescence spectra.[20] The former quantifies the binders and additives, and their conservation condition.[21] Microspectrofluorimetry allows the acquisition of emission and excitation spectra in the same micro spot (in situ, without any contact with the sample or work of art being analysed).[22] These molecular data provide essential information on the specificities of the recipe, which can be determined by using a database of historically accurate reproductions,[23] preferably in combination with statistical approaches, such as chemometrics.[24]

In the present article, the use of red dye sources in Medieval Europe is documented based on an analytical investigation of materials in Portuguese illuminated manuscripts and Romanian textiles.

2. Lac dye reds in Portuguese illuminated manuscripts (12th–13th centuries)

2.1 *Lac dye reds in the Medieval Period*

In Medieval times, the raw materials for preparing lac dye colors mainly originated from India and China. They were produced by a scale insect, namely by the female insect that secretes a red resin, stick lac, from which both lac dye and shellac resin are obtained.[25] *Kerria lacca* and *Kerria chinensis* are examples of species that have been widely exploited. Based on a multi-analytical investigation, it has been observed that the main dye in these colors is laccaic acid A (Fig. 1).[26] It is based on an anthraquinone core, shared with three other essential reds from the past: Cochineal, kermes, and madder. More details regarding the chemical composition of the resin and other dyes can be found in earlier publications.[27]

2.2 *The importance of lac dye colors in Portuguese monastic scriptoria (12th–13th centuries)*

During the Romanesque period in Portugal, the three most important monasteries had active scriptoria that produced unique illuminated manuscripts.[28] The manuscripts studied here were produced in the Portuguese monasteries of São Mamede of Lorvão, Santa Maria of Alcobaça, and Santa Cruz of Coimbra. These collections have been kept in Lisbon, National Library (Biblioteca Nacional de Portugal, BNP), the National Archives (Arquivo Nacional da Torre do Tombo, ANTT) and the Municipal Library of Porto (Biblioteca Pública Municipal do Porto, BPMP).

Interdisciplinary research into color in Portuguese monastic collections during the 12th and first quarter of the 13th centuries has included a detailed molecular identification of paints, which has made possible a discussion of the cultural significance of the colors in the context of monastic production.[29] This has been achieved through ‘color mapping’, which systematically quantifies the main colors in a codex.[30] Using color mapping, specificities in the palette of each scriptorium were identified based on their three dominant colors: Red (vermilion; lac dye), green (proteinaceous copper green, named *bottle green*), and blue (mainly lapis lazuli; indigo was used to produce darker blues) (Fig. 2). These pigments were mixed with a proteinaceous matrix, hereafter defined as tempera. Analytical investigation evidenced that

[18] Melo *et al.* 2019, 20180017.
[19] Melo *et al.* 2018a, 1–8; 2022, 110815.
[20] Valeur 2012; Rosi *et al.* 2019, 20180006.
[21] Melo *et al.* 2019, 20180017; Salvadó *et al.* 2009, 419–428; Miguel *et al.* 2009, 1966–1973.
[22] Valeur 2012
[23] Melo *et al.* 2018a; 2022.
[24] Nabais *et al.* 2021, 1–18; Castro *et al.* 2014a, 1172–1179.
[25] Cardon 2007, 656–666.; Melo 2023, 6; Oliveira 2016.
[26] Castro *et al.* 2014; Petroviciu *et al.* 2017d.
[27] Nabais *et al.* 2021, 1–18; Tamburini *et al.* 2017, 14784; Santos *et al.* 2015, 129–136.
[28] Melo *et al.* 2014, 170–192; Miranda *et al.* 2014, 1–29.
[29] Melo *et al.* 2014, 170–192; Miranda *et al.* 2014, 1–29.
[30] Melo *et al.* 2014, 170–192; Melo *et al.* 2018, 132–143.

Fig. 2: Color mapping applied to the colors of the manuscripts produced in the Portuguese monasteries of Lorvão, Alcobaça, and Santa Cruz during the 12th and first quarter of the 13th centuries (quantifying the main colors in a codex). The color palette of each scriptorium is based on three dominant colors: Red (vermilion; lac dye), green (proteinaceous synthetic copper green named *bottle green*), and blue (mainly lapis lazuli; indigo was used to produce darker blues).

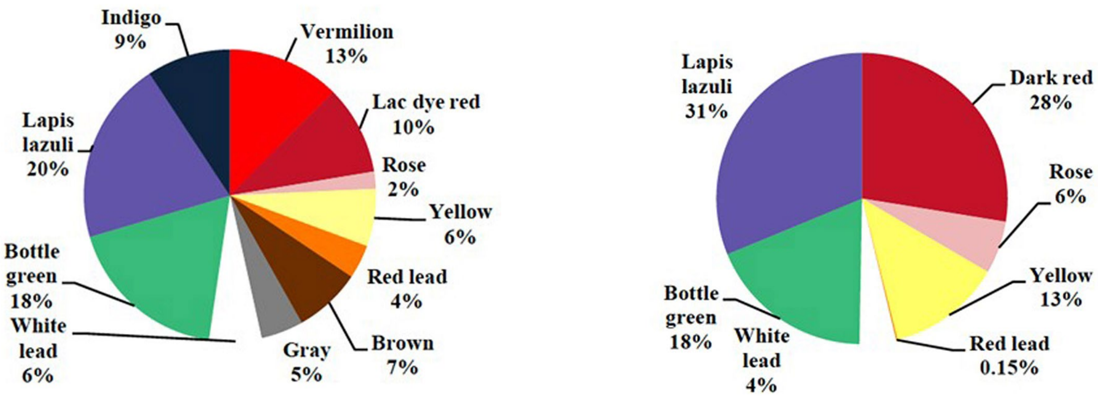

Fig. 3: Relative area distribution of the colors used in two emblematic manuscripts, the Bibles Alc. 427 and Ms. Sta Cruz 2 produced in, respectively, Alcobaça and Santa Cruz in the 12th century, adapted from Oliveira 2016.

tempera could be based on a single protein source, such as parchment glue, egg white, yolk, or a mixture.[31] Fillers, such as calcium carbonate, were also detected; these compounds are essential to the paint's mechanical performance. Color mapping for all the manuscripts studied can be accessed in the doctoral thesis of Rita de Castro (Appendix VIII. Mapping colors data, pp 314–319, lac dye colors are described as dark red).[32]

Analyzing the distribution of colors has allowed us to highlight distinctive tendencies, such as a preference for green at Alcobaça and red/purple at Santa Cruz (Fig. 2). Detailed observation of the manuscripts has also revealed that a rich chromatic diversity is associated with important manuscripts, such as the Bible produced in the Alcobaça scriptorium (ALC 427), in which gray and pink are hallmarks of the illuminators (Fig. 3).

Also fascinating is the use of pink, in a very expressive proportion, occupying 6% of the relative area (total color coverage). In the collections of the three monasteries, these reds and pinks are based on lac dye, with the exception of one color, for which lac dye was admixed with a brazilwood pigment lake; this is found in two manuscripts from the Alcobaça scriptorium, *De avibus* and *Sermones de verbis Domini*, Alc. 238 and Alc. 347.[33] Its identification was made possible by combining microspectrofluorimetry and SERS

[31] Melo *et al.* 2022; *et al.* 2014.
[32] Oliveira 2016.
[33] Nabais *et. al.* 2021, 1–18.

Fig. 4: The *Dove diagram* in the Lorvão Book of Birds f. 6, in which the book's project is summarized. A detail of the brilliant red produced with lac dye, together with the raw resin material, as well as the acquisition of molecular fluorescence spectra on the red color applied in the D initial in f. 4, in situ. ANTT collection, Lisbon. Detail acquired with a Leica microscope (KL 1500 LCD microscope, equipped with a 12x objective lens).

(Surface-Enhanced Raman Spectroscopy). This new methodology for studying and characterizing dyes in illuminated manuscripts was developed in partnership with Marco Leona and Federica Pozzi within the PhD research project of Rita Castro, and further expanded within the PhD research of Paula Nabais.[34] The colors based on lac dye in these three collections include pinks, carmines, dark reds, and brownish reds as illustrated in Figs. 4–6.

From the Lorvão monastery, the exquisite application of lac dye paints in the *Dove diagram* of the Book of Birds (Lorvão 5) should be highlighted (Fig. 4). It was a Medieval 'bestseller' created by Hugh of Fouilloy in France. The Book of Birds, also known by its most common Latin name, *De Avibus*, appeared in a specific cultural context as a teaching text, where *lectio*, *memoria*, and *meditatio* were the main evocative aspirations.[35] From the Santa Cruz monastery, the lavish application of the reds and pinks in the two monumental Bibles, Sta Cruz 1 and 2, stands out (Fig. 5). The Bible Santa Cruz 1 was probably the most emblematic codex produced by the monastery; it reunited the Old Testament books and was possibly exhibited in the choir. The monumental Bible of the Santa Cruz Monastery (Sta Cruz 2) included the books of the major prophets. This exceptional codex is the only manuscript in which vermilion was not found, and the red color was based solely on lac dye (Fig. 3).

From the Alcobaça monastery, the main highlight is to mention the stunning ornate initial on f. 115v opening the book of Deuteronomy in the precious Bible Alc. 427 (Fig. 6).

2.3 *Disclosing the recipes used in the bright reds and pinks*

Several technical written sources, such as treatises and recipe books, have been explored in order to determine the paint formulations for lac dye colors. The

[34] Nabais *et. al.* 2021, 1–18; Castro *et. al.* 2014a, 1172–1179.
[35] Oliveira 2016; Castro 2014b, 31–55; Cordonnier 2007.

Fig. 5: Five initials illustrating the diversity of lac dye applications in Santa Cruz 2, 12th century. In the monumental Bible Sta Cruz 1, detail of a pink on f. 14v, and of carmine red and a brownish red produced with lac dye on f. 37, BPMP collection, Porto. The details were acquired with a Leica microscope (KL 1500 LCD microscope, equipped with a 12x objective lens).

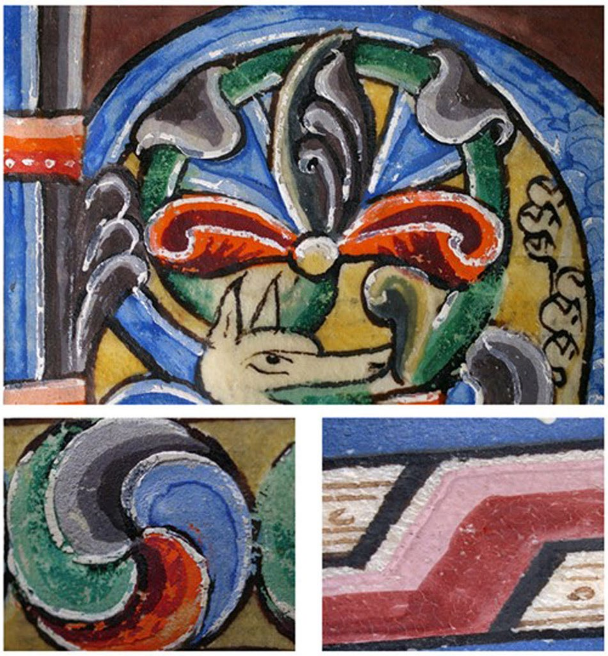

Fig. 6: Details of the use of dark reds based on lac dye in the Alcobaça Bible (Alc 427), 12th century. Top, the ornamented initial opens the book of Deuteronomy, f. 115v. Bottom right, detail of a pink color from Alc 421. BNP collection, Lisbon.

information included there, together with an analysis of the original colors from Medieval manuscripts, has facilitated the preparation of color reproductions. This methodology enabled the production of reference materials with as much historical accuracy as possible, validated by their "closeness to the true value" of the historic material or artwork under study.

For lac dye colors, a diversity of recipes is found among Medieval treatises, and it is possible to distinguish different methods for their preparation. The Ibn Bādīs manuscript (c. 1025), chapter 6, describes a recipe for preparing a 'red ruby' color from *lukk* (lac dye). It describes the dissolution of lac in water, with the possible addition of *ushnān* (sodium carbonate) and *bauraq* (borax, sodium tetraborate). The lac is placed under the fire "*until all of the redness of the lukk is brought out*." After filtering and boiling again, the red *lukk* is ready to be used for writing. In a different treatise, the manuscript *Mappae Clavicula* (12th century), in recipe 253, there is a description of an entirely different method of preparation for lac dye colors. Here the lac is finely ground and boiled in urine. To this solution, alum is added, and the color is immediately ready to be used. By closely analyzing these two recipes, it can be understood that they describe two different preparation methods for lac dye colors: One where lac dye is not complexed with a metal ion, *i.e.*, free lac (Ibn Bādīs) and the other with the addition of a complexing agent (alum) to create a lake pigment (*Mappae Clavicula*). These different formulations lead to different molecular compositions of the final paint, which, in turn, lead to different colors. Hence, lac dye can provide a wide range of shades and hues, from red to purple, making it challenging to identify the colorant visually.

2.4 *Lac dye reds as "the brightest color of all"*

In Medieval times, lac dye colors may have been associated with purple, one of the most prestigious colors of Antiquity. True purple dye, *Tyrian purple*, was obtained from Mediterranean shellfish of the genus *Purpura* and could have a blue, red, or purple color. Therefore, this *brightest color of all* in Medieval times could vary from red to purple.

The purple color was associated with something saturated and bright,[36] as with lac dye colors. As described by Mark Bradley, "Pliny interrupts his account of purpura, the eastern sea-snail, with an account of purpura the Roman colour (...). It illuminates (*inluminat*) every garment and on the triumphal robe it is blended with gold."[37] These precious colors, based on lac dye and masterfully applied in Medieval manuscripts, will continue to fascinate and enchant us forever.

3. Red dyes in Romanian Medieval textiles (15th–16th centuries)

3.1 *Byzantine liturgical embroideries*

The metal thread embroidery also known as "Byzantine embroidery", was part of a cultural phenomenon influenced by the East Christian Church for about 1000 years.[38] In the Romanian provinces — Moldavia, Wallachia and Transylvania (to a less extent) — its evolution flourished after the fall of Constantinople, in 1453.[39] It preserved the original Byzantine tradition, technique, drawing, and symbolism, and is therefore referred to as "Byzantine," although this association is not based on provenience and date, but on the original manufacturing technique and materials.[40] Situated at the border between the Catholic West and the Orthodox East, the territory north to the Danube joins the artistic refinement of two textile civilizations in a specific cultural synthesis: Traditional embroidery with metal threads.[41] It is characterized by a complex technique to embroider metal threads on layers of textile materials, to create relief and light reflection.[42] Byzantine embroidery remained a sacred art, the technique being reserved for religious objects only, with no reproduction in the laic world. It was an extremely expensive technique, the value of an object being equal to its weight in gold.[43]

Byzantine metal thread embroidery had two backings: A cellulosic one to give support and one of colored silk, with an aesthetic role. The two were held together with a starch- or protein-based glue, and this join was strengthened with cotton threads. Embroidery was carried out using colored silk and precious metal threads, wires, and bands. Systematic research on Byzantine embroidery technique and materials has been carried out by Ileana Crețu, National Museum of Art of Romania (MNAR). The book, entitled "*The History of the Liturgical Embroidery Restoration (15th–19th century)*",[44] is based on her observations on objects conserved in Romanian museums and monasteries. As part of her research, dye analysis was also performed, first within a joint research project between Romanian institutions and The Royal Institute for Cultural Heritage (KIK/IRPA) in Brussels,[45] and later based on an analytical protocol built especially for this purpose under the coordination of the University of Bucharest, Faculty of Chemistry.[46] The objects studied are part of the two largest collections of Byzantine embroideries in Romania: The MNAR collection, with objects representative of Wallachia, and the collection in Putna Monastery, illustrative of Moldavia. Putna Monastery was built around the mid-15th century by Prince Stephan the Great, as the necropolis for his family and himself. During his long reign (1457–1504), he gifted his most important foundation with valuable liturgical treasures, including embroideries, most of them executed in the monastery's workshop.

[36] Gage 1999, 64.
[37] Bradley 2011.
[38] Crețu 2019, 35.
[39] Crețu 2019, 22.
[40] Crețu 2019, 35–72.
[41] Crețu 2019, 158.
[42] Crețu 2019, 132.
[43] Crețu 2019, 132.
[44] Crețu 2019.
[45] Petroviciu *et al.* 2017a, 18–29; 2017b, 200–207; 2017c, 208–224; 2012, 89–97.
[46] Petroviciu *et al.* 2017d, 164–171; 2011, 155–162; 2021, 103–125; 2020, 331–352; Petroviciu 2021.

Fig. 7: Examples of Byzantine liturgical embroideries preserved in Putna Monastery: Epitrachelion 37 (15th century) and detail; Bedernita 'Maria of Mangop' (15th century) and detail. (Images from CD-Rom Putna Monastery, Multiart SRL Suceava, Ed. Cygnus Suceava, ISBN 973-85304-6-6)

3.2 Red dyes in Byzantine liturgical embroideries

Due to its religious symbolism, red is the most common color in the Byzantine liturgical embroideries silk supports. This color is given by the visible warp, which preserves the original hue, due to the excellent light fastness of the dyes used. On the contrary, for the weft, which is less visible to the viewer and is now discolored to yellow-reddish or beige hues, cheaper alternatives were applied. Analytical investigation performed by Liquid Chromatography with Diode Array (UV-VIS) (LC-DAD) and Diode Array and Mass Spectrometric detection (LC-DAD-MS) on warp and weft samples support these observations. Expensive insect dyes were identified for the warps, and dyes with poor light fastness, such as redwood, for the wefts[47] (Table 1).

Lac dye (in combination with madder) was the most frequently used dye source for the warps of the silk support in embroideries from Wallachia and Moldavia, while other insect dyes, such as cochineal species and kermes, were also identified in a few warp samples. Lac dye was detected based on the evidence of the main compounds, laccaic acid A, laccaic acid B, flavokermesic acid, and erythrolaccin.[48] As already mentioned in Section 2, during the discussion of red dyes in Portuguese illuminated manuscripts (12th–13th centuries), it is documented that lac dye was imported into Europe from the East. Analytical investigation revealed that, although lac dye was used as an organic pigment in mural paintings and illuminated manuscripts,[49] it has been rarely identified in Western European textiles,[50] probably due to competition from other available insect reds, like kermes and Polish cochineal. Considering the geographical position of the Romanian provinces, between East and West, and that lac dye was a common source of red in Oriental textiles, often in combination with madder,[51] its identification in the liturgical embroidery supports would suggest an Oriental origin for the materials.

[47] Petroviciu *et al.* 2017a, 18–29; 2017b, 200–207; 2017c, 208–224; 2012, 89–97; 2017d, 164–171; 2011, 155–162; 2021, 103–125; 2020, 331–352; Petroviciu 2021.

[48] Petroviciu & Crețu 2020, 163–177.

[49] Nabais *et al.* 2021, 1–18; Cardon 2007, 664; Kirby 2008, 69–108.

[50] Hofenk de Graaff & Roelfs 1972, 1–34.

[51] Enez & Böhmer 1995, 39–44.

Table 1: Red dyes identified by Liquid Chromatography (LC-DAD or LC-DAD-MS) in samples from Byzantine liturgical embroideries (15th–16th centuries) from Romanian collections, studied between 2003 and 2021.† More information regarding the analytical procedures are given in the publications cited above and in the one describing the protocol.‡ Explanation about the liturgical embroideries can be found in the publication cited here.#

† Petroviciu *et al.* 2017a, 18–29; 2017b, 200–207; 2017c, 208–224; 2012, 89–97; 2017d, 164–171; 2011, 155–162; 2021, 103–125; 2020, 331–352; Petroviciu 2021.
‡ Petroviciu *et al.* 2017d, 164–171.
# Petroviciu *et al.* 2017c, 208–224

	Color	Sample location	Dye sources*	Reference
Epitaph, Moldavia, 15th century *Sucevița Monastery*	red	silk support	kermes	Petroviciu *et al.* 2011, 155–162
Epitrachelion (inv. B 255/15900), Govora Monastery, Wallachia, 16th century *MNAR** Collection*	red	silk support	lac dye + madder	Petroviciu *et al.* 2017a, 18–29
	red	reverse, additional warp	cochineal + tannins	Petroviciu *et al.* 2017a, 18–29
Epitrachelion (inv. B 258/15903) Tismana Monastery, Wallachia, 16th century *MNAR Collection*	red	decoration	lac dye + madder	Petroviciu *et al.* 2017a, 18–29
	red	support texture	tannin + madder	Petroviciu *et al.* 2017a, 18–29
	pale red	tassel	redwood	Petroviciu *et al.* 2017a, 18–29
Little sleeves (inv. B121/15766) Vintila Voda Mon., Wallachia, 16th century *MNAR Collection*	red	silk support	lac dye + madder	Petroviciu *et al.* 2017a, 18–29
Curtain veil (inv. 15802) Wallachia, 1602–1608 *MNAR Collection*	red	thread	madder + cochineal + tannin	Petroviciu *et al.* 2017a, 18–29
	violet	tassel	madder + cochineal + tannin	Petroviciu *et al.* 2017a, 18–29
Tomb veil of Princess Maria of Mangop, 15th century *Putna Monastery*	red	silk support — warp	kermes	Petroviciu *et al.* 2017b, 200–207
	yellow	silk support — weft	redwood	Petroviciu *et al.* 2017b, 200–207
Epitrachelion (inv. 34), 1504 *Putna Monastery*	red	silk support — warp	lac and madder	Petroviciu *et al.* 2017c, 208–224
Epitrachelion (inv. 35), 15th century *Putna Monastery*	red	silk support — warp	lac and madder	Petroviciu *et al.* 2017c, 208–224
	red	tassel	lac and madder	Petroviciu *et al.* 2017c, 208–224
Epitrachelion (inv. 36), 15 June 1469 *Putna Monastery*	yellow-orange	thread	young fustic, redwood and tannin	Petroviciu *et al.* 2017c, 208–224

Table 1 (continued)

Epitrachelion (inv. 37), 15th century *Putna Monastery*	red	silk support — warp	lac and madder	Petroviciu *et al.* 2017c, 208–224
	red	tassel	lac and madder	Petroviciu *et al.* 2017c, 208–224
Epitrachelion (inv. 38), 15th century *Putna Monastery*	red	silk support — warp	lac, madder and some kermes (-)	Petroviciu *et al.* 2017c, 208–224
	yellow-reddish	silk support — weft	redwood, tannin and weld or eq.	Petroviciu *et al.* 2017c, 208–224
	red	tassel	lac, madder and tannin	Petroviciu *et al.* 2017c, 208–224
Epitrachelion (inv. 39), before 1496 *Putna Monastery*	red	silk support — warp	lac and madder	Petroviciu *et al.* 2017c, 208–224
	red	tassel	lac and madder	Petroviciu *et al.* 2017c, 208–224
Epitrachelion (inv. 50), 15th century *Putna Monastery*	black	support	madder	Petroviciu *et al.* 2017c, 208–224
	red	tassel	lac and madder	Petroviciu *et al.* 2017c, 208–224
	red	tassel	Mexican cochineal and tannin	Petroviciu *et al.* 2017c, 208–224
	red	thread	cochineal (Polish?), madder and tannin	Crețu *et al.* 2017, 75–94.
	red	thread	kermes	Crețu *et al.* 2017, 75–94.
	yellow-reddish	thread (to fix the metal)	redwood and tannins	Crețu *et al.* 2017, 75–94.
Epitrachelion (Inv. 51), 15th century *Putna Monastery*	yellow-pinkish	tassel	safflower and weld or eq.	Petroviciu *et al.* 2017c, 208–224
Epitrachelion (inv. 70), 15th century *Putna Monastery*	red	tassel	lac and madder	Petroviciu *et al.* 2017c, 208–224
	red	understudy (original)	lac and madder	Crețu *et al.* 2017, 75–94
	red	thread (sewing and embroidery)	redwood, madder and tannin	Crețu *et al.* 2017, 75–94
	red	thread (embroidery)	lac and madder	Crețu *et al.* 2017, 75–94
Epitrachelion (inv. 134), 17th century *Putna Monastery*	red	tassel	madder and redwood	Petroviciu *et al.* 2017c, 208–224
Epitrachelion (inv. 560), 16th century *Putna Monastery*	red	silk support — warp	Mexican cochineal and tannin	Petroviciu *et al.* 2017c, 208–224
	yellow-reddish	silk support — weft	redwood and tannin	Petroviciu *et al.* 2017c, 208–224

Table 1 (continued)

Epitrachelion (inv. 602), 15th–16th century, *Putna Monastery*	red	support	madder	Petroviciu *et al.* 2017c, 208–224
Epitrachelion (inv. 242), 15th–16th century *Putna Monastery*	red	silk support — warp	cochineal, tannin and madder	Petroviciu *et al.* 2017c, 208–224
	yellow-reddish	silk support — weft	redwood	Petroviciu *et al.* 2017c, 208–224
Epitrachelion (inv. 241), 15th–16th century *Putna Monastery*	red	silk support — warp	Mexican cochineal and tannin	Petroviciu *et al.* 2017c, 208–224
	yellow-reddish	silk support — weft	redwood, tannin and madder	Petroviciu *et al.* 2017c, 208–224
	red	thread	madder and tannin	Petroviciu *et al.* 2017c, 208–224
	reddish	silk support — weft	redwood, dyer's broom and tannin	Petroviciu *et al.* 2017, 208–224
Bedernita 'Maria of Mangop' (inv. 151), 15th century *Putna Monastery*	red	silk support — warp	Polish cochineal and tannin	Petroviciu *et al.* 2017c, 208–224
	yellow-reddish	silk support — weft	redwood	Petroviciu *et al.* 2017c, 208–224
	ochre-pinkish	thread	redwood, young fustic and tannin	Petroviciu *et al.* 2017c, 208–224
	ochre	tassel	redwood and dyer's broom	Petroviciu *et al.* 2017c, 208–224
Embroidery with eagles 16th century *Putna Monastery*	beige-reddish	support	redwood	Petroviciu *et al.* 2017c, 208–224
Curtain veil 'Resurrection' 1500 *Putna Monastery*	red	support	lac and madder	Petroviciu *et al.* 2017c, 208–224
Bedernita Inv. 10652, 16th century *Putna Monastery*	ochre	sewing thread (cotton)	redwood	Petroviciu 2021
	red	thread (embroidery)	madder and redwood	Petroviciu 2021
	red	thread (sewing)	madder and redwood	Petroviciu 2021
Curtain veil 'Mother of God Dormition', 15th–16th century *Putna Monastery*	yellow-orange	thread	redwood and dyer's broom	Petroviciu 2021

Table 1 (continued)

Donor inscription (embroidery on velvet) (inv. 15618), 15th–16th century *MNAR Collection*	red	tassel	lac dye + madder	Petroviciu *et al.* 2017a, 18–29
	red	velvet — pile	lac dye + madder	Petroviciu *et al.* 2017a, 18–29
	orange	velvet — weft	madder + tannin	Petroviciu *et al.* 2017a, 18–29
	brown	velvet — warp	redwood	Petroviciu *et al.* 2017a, 18–29
Lectern cover (inv. 61) (embroidery added to brocaded velvet), 1502 *Putna Monastery*	red	support — warp inscription	kermes, tannin and cochineal	Petroviciu *et al.* 2017c, 208–224
	yellow-orange	support — weft	redwood and young fustic	Petroviciu *et al.* 2017c, 208–224
	red	support weft border	kermes, redwood, tannin and cochineal	Petroviciu *et al.* 2017c, 208–224
	yellow-orange	thread	redwood, young fustic and tannin	Petroviciu *et al.* 2017c, 208–224

Notes:

* The following correspondence between the common and scientific names should be considered (alphabetical order): Cochineal (term used in early studies for all carminic-acid-based dyes) — *Dacylopius coccus* (Mexican cochineal), *Porphyrophora polonica* (Polish cochineal, also called Polish carmine scale insect), *Porphyrophora hameli* (Armenian cochineal, also called Armenian carmine scale insect); dyer's broom — *Genista tinctoria* (yellow dye); kermes — *Kermes vermilio* or equivalent; lac dye — *Kerria lacca*; madder — *Rubia tinctorum* or equivalent; redwood — *Caesalpinia* species; safflower — *Carthamus tinctorius*; young fustic — *Cotinus coggygria* (yellow dye); weld — *Reseda luteola* (yellow dye). Yellow dyes will not be discussed in the present study.

** MNAR — National Museum of Art of Romania.

The use of madder in combination with lac dye could be explained by an interest in lowering the cost, by adding a cheaper dye of vegetal origin to supplement the more expensive insect dye, with no visible consequence to the color hue. In the analytical protocol used for dye investigation, madder was identified by the presence of alizarin and purpurin. Minor compounds such as pseudopurpurin, xanthopurpurin, munjistin, or anthragallol were also present in some cases. The dyeing combination of lac dye and madder was also identified in other silk yarns, used as embroidery threads or in tassels, and it was similarly common in the silk threads on documents with hanging seals that emanated from the Chancellery of Moldavia during the time of Prince Stephan the Great.[52]

Kermes, which became the most expensive dye after the fall of Constantinople and the associated change in trade routes, was identified in the red support of the tomb veil of Princess Maria of Mangop, wife of the Moldavian Prince Stephan the Great (Fig. 8). Based on the presence of kermesic and flavokermesic acids, the detection of kermes strongly supports the hypothesis that the object was designed to be of high monetary value. Moreover, detection of kermes confirms the financial power of the Prince, who could afford the most expensive dye sources available at that time. Kermes was also identified as an individual dye source in an epitaph from another monastery (Sucevita), as well as in combination with cochineal and redwood in a few other objects, despite the fact that the

[52] Petroviciu *et al.* 2017d, 164–171.

use of kermes mixed with cheaper dye sources was forbidden by guild regulations.[53,54,55]

Cochineal was the term used in early studies for all the carminic-acid-based dyes, although more recent publications suggest its use should be reserved exclusively for the Mexican insect, with the *Porphyrophora* representatives of the Old World referred to instead as Polish and Armenian carmine scale insects. Apart from carminic acid, minor dye components such as kermesic and flavokermesic acids, and flavokermesic acid-C-glycoside are expected in all these species, in various relative proportions.[56] Although several methods to differentiate the species from each other have been proposed, this is not always possible, due to the small quantity of sample available, which restricts calculation.[57] However, Polish cochineal (carmine scale insect) has been identified in two objects, both from Putna monastery: Epitrachelion inv. 50 — explicitly mentioned as "Byzantine" and 'bedernita Maria of Mangop' (Fig. 7), also referred to as "Byzantine", due to the symbols embroidered around its border. It should be underlined in this context that Princess Maria of Mangop, the last descendant of the imperial Byzantine dynasty, arrived in Moldavia in 1472 when she married Stephan the Great, and it may be supposed that the two objects were part of her dowry. These objects could have been an inspiration for the embroidery workshop at Putna, which had been established soon after the monastery was founded, between 1466 and 1469.[58] In-depth research of epitrachelion inv. 50, and its comparison with another apparently identical one, epitrachelion inv. 70, proved that while the latter is similar to all the other objects donated to the monastery in the last decades of the 15th century (donor inscriptions embroidered on the objects), epitrachelion inv. 50, on which kermes and Polish cochineal were detected, was made earlier, and therefore provided a model for the later example.[59]

Mexican cochineal was identified in the silk support of embroideries dated to the 16th century,[60] confirming its adoption in Europe very soon after the discovery of the New World.[61] Hence, the unattributed objects in which Mexican cochineal has been detected should be dated to not earlier than the mid-16th century.[62]

Redwood was identified in the wefts of the silk supports, and in embroidery or sewing threads, as an individual source or in various combinations with madder, yellow dyes (weld, young fustic or dyer's broom), and/or tannins. Redwood attributions are based on the presence of a marker compound, recently revealed as urolithin C.[63] This compound is still visible in the chromatogram when brazilein, the main dye component (which is formed from the oxidation of brazilin, the dye in redwood) is too degraded to be observed.[64] Imported from the East as *Caesalpinia sappan*, redwood was a common dye source in Medieval Europe.[65] However, due to its poor light fastness, the red-violet original hue becomes pink or dull ochre, and consequently its use was restricted by guild regulations.[66] Its adoption as a cheaper alternative has also been confirmed by the detection of redwood in two documents with hanging seals preserved in the Romanian Academy Library. The documents were assumed to have been issued by the Chancellery of Moldavia in the time of prince Stephan the Great, but the text and the quality of materials used (parchment, inks) revealed them as forgeries, although still dated to the same period.[67]

Safflower, a plant originating from the Orient and Asia, was revealed in a yellow-pinkish silk tassel sample. It has been well known since Antiquity that safflower petals contain both red and yellow dyes. Several washings of the petals in cold water are needed in order to completely remove the soluble yellows. The remaining material is then treated with

53 Petroviciu *et al.* 2011, 155–162.
54 Petroviciu *et al.* 2017c, 208–224.
55 Mola 2000, 107–137.
56 Serrano *et al.* 2015, 116–127.
57 Wouters & Verhecken 1989, 393–410; Vanden Berghe 2016, 303–310; Serrano *et al.* 2015, 116–127.
58 Crețu 2019, 173–178.
59 Crețu *et al.* 2017, 75–94.
60 Petroviciu *et al.* 2020, 163–177.
61 Cardon 2007, 630.
62 Phipps 2010, 1–50.
63 Peggie *et al.* 2018, 617–623.
64 Wouters 1995, 48–58.
65 Wouters 1995, 48–58.
66 Mola 2000, 107–137.
67 Petroviciu *et al.* 2017d, 164–171.

Fig. 8: Full image and detail, tomb veil of Princess Maria of Mangop, preserved at Putna Monastery (photos: Ileana Crețu*). For the red silk support, kermes was identified for the weft and redwood for the warp.

* Crețu 2019, annexes.

an alkaline solution to extract the red dyestuff, and the filtrate is neutralized with a weak acid in order to promote precipitation of the red-orange dye, which may then be used as a direct dye or as a red organic pigment.[68] The use of safflower in European textiles is quite rare, and literature mentions that it was not imported to Europe before the 17th–18th centuries, although it was recently detected in a 16th-century Italian tapestry.[69] Though carthamin, the main dye, is rarely detected in historical textiles, identification of safflower is based on the presence of four uncolored marker compounds,[70] whose structures were recently elucidated.[71] The Oriental origin of safflower, its confirmed use in a 13th-century fabric from West Turkey,[72] together with its rare use in Europe are all indicators that the safflower-dyed threads in the liturgical embroidery from Putna Monastery arrived via an Eastern commercial route.

3.3 Brocaded velvets

Mural paintings which decorate 14th–17th-century churches in Wallachia and Moldavia often illustrate the founders (and their families) wearing brocaded velvet ceremonial costumes, so-called "caftans". These costumes, which are documented as being of Oriental

[68] Cardon 2007; Clementi *et al.* 2014, 127–137.
[69] Degano et al. 2011, 295–299.
[70] Wouters *et al.* 2010, 186–203.
[71] Clementi *et al.* 2014, 127–137.
[72] Hofenk de Graaff 2004, 159–163.

Table 2: Red dyes identified by Liquid Chromatography (LC-DAD or LC-DAD-MS) in samples from brocaded velvets (15th–16th centuries) from Romanian collections.† See Table 1 for the correspondence between the common and scientific names.

† Petroviciu *et al.* 2017a, 18–29; 2017b, 200–207; 2017c, 208–224.

	Color	Sample location	Dye sources	Reference
Brocaded velvets				
Tomb veil of Stephan the Great, 1504 *Putna Monastery*	red	velvet — plush (pile)	Polish cochineal and tannins	Petroviciu *et al.* 2017b, 200–207
	red	threads	lac dye, madder, Polish cochineal and tannins	Petroviciu *et al.* 2017b, 200–207
Ceremonial costume: Caftan, Inv. 15620, 15th–16th centuryies *MNAR Collection*	red	velvet — pile	kermes + cochineal + tannin	Petroviciu *et al.* 2017a, 18–29
	beige	velvet — weft	redwood	Petroviciu *et al.* 2017a, 18–29
	pink	velvet — weft	redwood + tannin	Petroviciu *et al.* 2017a, 18–29
	yellow	velvet — weft	redwood + tannin	Petroviciu *et al.* 2017a, 18–29
	red	satin lining	lac dye + madder	Petroviciu *et al.* 2017a, 18–29
Ceremonial costume, Caftan Inv. 15618, 15th–16th centuries *Putna Monastery*	brown-violet	weft	indigoid dye, kermes and weld or eq.	Crețu *et al.* 2017, 75–94.
Embroideries added to brocaded velvets				
Lectern cover Inv. 61 (embroidery added to brocaded velvet), 1502 *Putna Monastery*	red	sup/warp inscription	kermes, tannin and cochineal	Petroviciu *et al.* 2017c, 208–224
	yellow-orange	sup/weft	redwood and young fustic	Petroviciu *et al.* 2017c, 208–224
	red	sup/weft border	kermes, redwood, tannin and cochineal	Petroviciu *et al.* 2017c, 208–224
	yellow-orange	thread	redwood, young fustic and tannin	Petroviciu *et al.* 2017c, 208–224
Liturgical mantle, 15th century *MNIR Collection*	red-orange	weft, brocaded velvet	madder and tannin	Petroviciu 2020
	red	warp, brocaded velvet	lac dye and madder	Petroviciu 2020
	red-orange	warp, brocaded velvet	madder	Petroviciu 2020
	red	warp and plush, brocaded velvet	lac dye and madder	Petroviciu 2020
	red	warp	lac dye	Petroviciu 2020

origin, were worn by the high-status Byzantines in the 14th and 15th centuries, and were later adopted in the Romanian provinces, in the ceremonies at the princes' courts. "Caftans" are extremely elegant, brocaded velvet clothes, with an ample cut at the bottom, given by the triangle gussets on both sides of the chest and back, and tight long sleeves.[73] When they became too degraded to be worn, princes used to donate their "caftans" to the monasteries, where they were dismantled and transformed into tomb veils. Three examples of "caftans" entered the National Museum of Art in Romania as rectangular tomb veils, in the 1950s. During their restoration, performed about ten years later, it was observed that their cut followed the "caftan" configuration, and the museum specialists decided to reconstitute, preserve, and exhibit the objects in their original "caftan" form.[74] Small pieces of materials kept in the conservation documentation were sampled years later for dye analysis[75] (Table 2).

Results provided by scientific investigation revealed the use of kermes in all the red samples,[76] as well as in combination with cochineal (not possible to identify the species) and tannins. Indigoid dyes were also present when darker shades were intended.[77] Kermes, in the same dyeing combinations, was also identified in a lectern cover, dated 1502, from Putna Monastery.[78] Kermes is mentioned as an important red dye source in the silk industry during the Venetian Renaissance,[79] and its identification supports the Italian origin of the brocade, as well as the exceptional value of the objects in which it was used. Although it was not proved analytically, it is more probable that *Porphyrophora* insects from the Old World were used together with kermes, rather than Mexican cochineal. There are no records in literature to document the use of kermes together with the American insect.

Polish cochineal, also an expensive dye source, was revealed in the brocaded velvet tomb veil of Prince Stephan the Great, dated 1504 in accordance with the prince's death.[80] The use of the Polish insect in 15th and 16th-century Venetian brocaded velvets is in perfect correlation with historical sources.[81]

Fig. 9: Ceremonial costume ("caftan"), inv. 15620, preserved at the National Museum of Art of Romania (image from https://www.mnar.arts.ro/descopera/galerii-permanente/75-galeria-de-arta-veche-romaneasca/descopera-lucrarile-din-galeria-de-arta-romaneasca-veche/68-caftan-tara-romaneasca-secolul-xv, accessed 28 March 2023). Kermes, in combination with cochineal and tannin, was identified in the velvet pile (see text).

In contradiction to the hypothesis stated earlier, which proposed the use of lac dye in the Oriental world and its absence from western European textiles, including brocaded velvets, lac dye has been

73 *** Arta Ţării Româneşti în secolele XIV–XVI (Art in Wallachia in the 14th–16th Centuries) 2001, 120.
74 Petroviciu *et al.* 2017b, 200–207; *** Arta Ţării Româneşti în secolele XIV–XVI (Art in Wallachia in the 14th–16th Centuries) 2001, 120–122.
75 Petroviciu *et al.* 2017b, 200–207.
76 Petroviciu *et al.* 2017a, 18–29; 2017c, 208–224; 2017, 75–94.
77 Crețu *et al.* 2017, 75–94.
78 Petroviciu *et al.* 2017c, 208–224.
79 Mola 2000, 107–137.
80 Petroviciu *et al.* 2017b, 200–207.
81 Mola 2000, 107–137.

Fig. 10: Brocaded velvet liturgical mantle from the Evangelical Church of Transylvania, preserved in the National Museum of Romanian History. Lac dye in combination with madder was identified in the velvet warp and plush (see text).

identified, in combination with madder, in a brocaded velvet liturgical mantle from the Evangelical Church of Transylvania, preserved in the National Museum of Romanian History (Fig. 10).[82] In the museum archive, the mantle is attributed to a "Venice workshop".

However, although lac dye is mentioned as one of the six red dye sources available in Renaissance Venice, it has been rarely identified by analytical investigation in Western European textiles.[83] As this liturgical mantle is the only textile from the Evangelical Church of Transylvania studied so far, and these objects have a different history in comparison to those from Moldavia and Wallachia, it remains unclear if lac dye was occasionally used in Italian workshops, or if "Venetian style" velvets were, in fact, made in Oriental workshops.[84]

4. **Conclusion**

Research on Portuguese manuscript illuminations and Romanian textiles has revealed similar dye sources in these masterpieces, dating from the 12th–13th and 15th–16th centuries respectively.

In the Romanian textiles, lac dye, redwood, kermes, and carminic-acid-based insect dyes were evidenced by high-resolution analytical instrumentation, such as liquid chromatography, in diverse configurations. For the monastic manuscripts, a multianalytical approach, supported by an extensive database of historically accurate reproductions, has revealed different methods and techniques of color preparation to produce a wide variety of hues, ranging from translucent reds, to carmines, and opaque pinks.

Regarding Byzantine liturgical embroideries and brocaded velvets in Romanian collections, dye research enriches our existing information about the objects under study with details of the materials used. Identification of the same color sources, already known to have been used in other parts of Europe, reinforces new arguments for integrating Romanian textile heritage into a European and worldwide context.

Special mention must be made for lac dye, extracted from insects coming from the East, which proved to be the main source of red, both in Western Europe in the 12th–13th centuries, and in Eastern Europe in the 15th–6th centuries; present in both Portuguese manuscript illuminations, produced in monastic scriptoria of the Catholic Church, and Byzantine liturgical embroideries, made in workshops belonging to Orthodox monasteries.

Advanced analytical methods have made it possible to better value these masterpieces of cultural heritage representing two European countries located in Western and Eastern Europe, and to celebrate these dyes as true ambassadors of a united and culturally diverse Europe.

Acknowledgements

I. P. express her gratitude to Putna Monastery and the National Museum of Art of Romania for their kind help, and their agreement to use images from their collections in scientific articles. She is also grateful to the institutions who provided access to the analytical instrumentation: The Royal Institute for Cultural Heritage, Bruxelles, Belgium; Agilrom Scientific SRL Romania; University of Bucharest, Faculty of Chemistry, Romania; National Research Institute for Physics and Nuclear Engineering "Horia Hulubei", IRASM Department, Romania.

M. J. M and P. N. would like to thank the staff and directory board of the Arquivo Nacional da Torre do Tombo (ANTT), Biblioteca Nacional de Portugal (BNP), and Biblioteca Pública Municipal do Porto (BPMP) for their generous support and collaboration.

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