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REGIONAL STYLISTIC AND TECHNICAL VARIATIONS IN SOME ROMANIAN MANUSCRIPTS

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Abstract

The paper focuses on characterizing the writing and decorating materials of some 19th century Romanian documents. The results of a technical investigation on inks, pigments and binders by means of *in-situ* XRF and ATR-FTIR methods pointed out to the use of an organic dye in addition to red lead and cinnabar, orpiment -or realgar- for yellow also used in a mixture with a blue organic pigment for the green colour, along with calcite, gum Arabic as inks' binder and a protein-based binder in yellow and green pigments.
Along with the identification of materials, the data provided by qualitative and quantitative analysis emphasize a vast range of raw materials available, diversity in fabrication methods and stylistic variations in painting technique along Romanian regions.

Keywords: 19th century manuscripts, gall inks, ATR-FTIR spectroscopy, XRF analysis

1. Introduction

The tradition of old Romanian miniatures, marked by centuries of changes in the art language announcing the converting into modern aquarelle, has slowly evolved and in the 19th centuries it has been in a permanent competition with the print. As a decorative art, the book painting illustrates the need for polychromy, reflected in the abundance of decorations representing trees, birds, animals, but especially stylized ornamental motifs.

Comparing to the investigation of painting materials on different supports, the research on pigments and inks used in writing and adorning the documents is still at its beginning. There are only few instrumental analytical methods for non-destructive or, at least, micro-destructive investigation on the materials used by miniaturists and calligraphists, the limitations being due to restrictions in sampling and also to the extreme thinness of colour layers [1-3].

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The progressive introduction of scientific investigations onto cultural heritage domain is mainly focused towards the evaluation of the objects' state of conservation, identifying the specific causes and parameters of degradation processes, with the aim of reducing the impact on collections permanence through restoration-conservation means.

At the same time, more general information gained in the research about the materials, like: establishing the chronology and identification of provenance, interferences between different cultures, reconstruction of industrial traditions, identifying of trade routes, authentication, permit to outline the historical and cultural context of the documents manufacturing. The present paper is oriented in this direction, the investigations carried out in order to characterize the writing and decoration materials of some documents from the 19^{th} century offering useful information about the materials, techniques and means, specific to the society of that time.

2. Experimental

The studied documents comes from different Romanian geographical areas, as it follows: **D1** - 'Molitvenic', manuscript realized at Curtea de Arges; **D2** and **D3** – two 'Psaltichie' (Psaltiki, religious music book) copied in Bucharest monasteries scriptoriums and **D4** – official document edited at Vaslui. All the objects belong to private collections. The analytical methodology used for the evaluation of the technique used in the manuscripts realization implied a progressive transition from in-situ characterization of materials to the investigation of micro-samples, were available.

In this paper we present the preliminary results of a technical investigation on inks and pigments from texts and decorations, obtained by two complementary methods: XRF (X rays fluorescence analysis) for inorganic compound identification, and ATR-FTIR, for organic compound determination. Some investigations presented difficulties due to pigments mixing, superposing of a varnish layer or to interferences between adjacent zones, as a consequence of the minute dimension of the analyzed areas comparing with the relatively large spot of the analytical instrument (2 cm in diameter).

2.1. Materials

The four manuscripts are written on cellulose supports and the black ink has been used for text writing. Among them, only D1 uses a richer chromatic palette, the title ornamentation being realized by applying large touches of yellow and green pigment layers into a shape sketched in black ink (Figure 1). The decoration of Psaltichies is limited to red inks used for headings, decorative frames and in the decoration of initials. A red ink has been used also for the authentication seal (Figure 2). On the document D3 there are shades of cherry red, realized in semi-transparent layers, revealing the use of diluted inks (Figure 2).

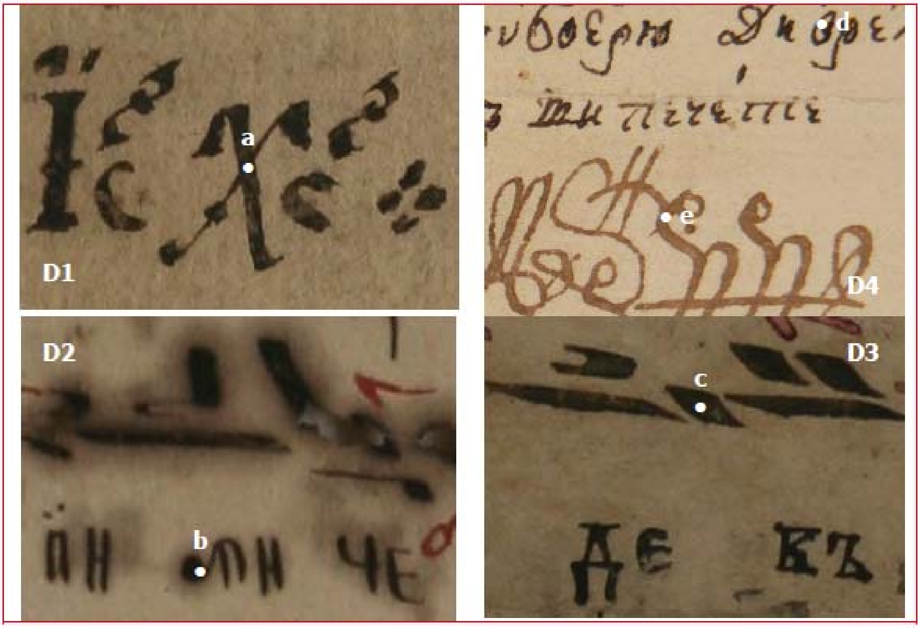

Figure 1. The black inks from the manuscripts written at: Curtea de Arges – D1, Bucharest - D2 and D3, Vaslui – D4.

Figure 2. The visual aspect of coloured inks in the four manuscripts.

2.2. Methods

2.2.1. X Rays fluorescence spectrometry

The application of XRF method in analyzing cultural heritage items became a current practice, being one of the most used multi-elemental, non-destructive analytical technique, of a great sensitivity and applicability in getting qualitative and semi-quantitative information about a large range of materials [4-6].

Aiming at establishing the chemical composition of pigments and inks an *in-situ* investigation has been carried out on written surfaces and on decorations, using a portable XRF apparatus, *Alpha 4000*, Innov-X Systems, with a dedicated soft for non-metallic matrix.

2.2.2. ATR-FTIR analyses

The spectrophotometric techniques FTIR have an extended range of applications in the domain of cultural heritage. These methods are especially relevant for painting pigments characterization, offering the possibility of identifying organic as well as inorganic compounds: pigments, binders, varnish [7-9].

The ATR-FTIR spectra for black and colour inks were collected by a *Digilab FTS 2000* spectrophotometer, with an ATR (ZnSe) attachment, in 650-4000 cm^{-1} spectral domain, with 24 scanning of the spectrum, at a 4 cm^{-1} resolution. In order to facilitate pigments and binders identification the reflection FTIR spectra have been compared with conventional data bases and were corroborated with the results of elemental analysis.

3. Results and discussion

Regarding the analyzed manuscripts, even if some stylistic variations are obvious, the common features of the whole circulation period of the manuscript documents are prevailingly the use of black inks for texts, decorative frames and signatures, of red inks for headings and ornamentation of initials or frames. Direct observations, subsequently confirmed by XRF spectrophotometry, suggest the diversity of preparation methods of pigments and inks.

3.1. Black inks

The visual aspect of the black inks in the manuscripts points out to the use of different types of writing materials (Figure 1).

The spectra collected on the texts of the four documents clearly indicate the presence of metal gall inks, by the detection of higher concentrations of iron than in the document paper (Table 1).

Table 1. Identification of metal gall inks based on characteristic elements.

Document/ Analyzed area		D1/a	D2/b	D3/c	D4/d	D4/e
Charact. elem. (ppm)	Fe	12062	7428	3417	2584	1529
	Other elem.	Ca = 6756 K = 17283 Zn = 3378 Mn = 535 Cu = 503	Ca = 2453 K = 39261 Cu = 361 Mn = 199 Ni = 529	Ca = 18594 K = 889 Zn = 282 Mn = 121 Pb = 302 Cr = 147	Ca =5164 K = 1602 Cu = 137 Mn = 251 Ni = 618 Ba = 181	Ca=4675 K = 1913 Cu = 361 Mn =278 Ni = 529 Ba = 207

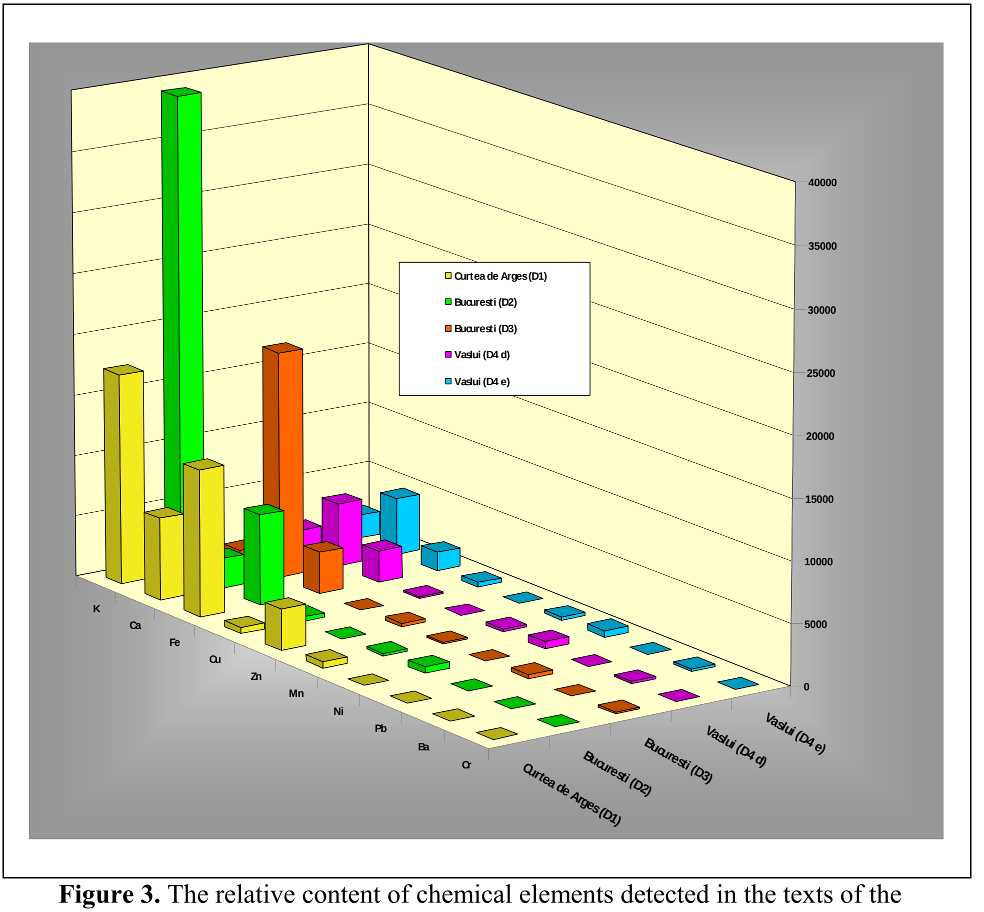

Figure 3. The relative content of chemical elements detected in the texts of the manuscripts D1-D4.

At the same time the elemental analysis permitted the evaluation of compositional differences among inks regarding the metallic impurities (Figure 3). Figure 3 illustrates not only regional variations of the receipts of metal gall inks, but also local ones: the manuscripts D2 and D3 have been written in

Bucharest monastery scriptoriums, but the preparation receipt is obviously different.

Even if the visual aspect suggests using different inks for the text – title and signature - in manuscript D4, the minor variations of the relative content of chemical elements confirm the use of a single type of ink at different dilutions.

3.2. Red pigments

The study of the red inks from the four manuscripts (Figure 2) reflects the variety of materials available in the epoch, used to obtain chromatic effects with the intended shade, as well as their application method (writing, brushing or printing).

The characteristic peaks of lead and mercury detected in the XRF spectra for the red colour layers permitted the identification of certain red pigments frequently used in the book miniature: cinnabar and lead minimum (Table 2).

Table 2. Identification of red pigments by XRF spectrometry based on characteristic elements.

<table>
<tr><th>Document</th><th>Colour</th><th colspan="2">Characteristic elements (ppm)</th><th>Comp.</th><th>Pigment</th><th>Obs.</th></tr>
<tr><td>D1</td><td rowspan="6">red</td><td colspan="2">Pb ≥ 10%</td><td>Pb_3O_4</td><td>red lead</td><td></td></tr>
<tr><td rowspan="2">D2</td><td>S ≥ 10%</td><td>Hg ≥ 10%</td><td>HgS</td><td rowspan="2">cinnabar
red lead</td><td rowspan="2">- mixture</td></tr>
<tr><td colspan="2">Pb = 13563</td><td>Pb_3O_4</td></tr>
<tr><td rowspan="2">D3</td><td>S ≥ 10%</td><td>Hg = 9095</td><td rowspan="2">Pb_3O_4
HgS</td><td rowspan="2">red lead
cinnabar</td><td rowspan="2">- mixture
- mixed with a red organic dye</td></tr>
<tr><td colspan="2">Pb = 20349</td></tr>
<tr><td>D4</td><td>S ≥ 10%</td><td>Hg = 25968</td><td>HgS</td><td>vermillion</td><td></td></tr>
</table>

For manuscript D3, the information derived from FTIR investigations point to a possible use of an organic dye of anthraquinone class, in addition to the red lead – cinnabar mixture [10] (Table 3). The characteristic bands of the organic dye partly overlap with the organic binder bands.

The red pigment used for the seal on the manuscript D4 consists of cinnabar mineral or vermillion pigment, synthesized from Hg and S (Figure 2 and Table 2). While red lead has been applied as such in the pictorial layer of the manuscript D1, the documents D2 and D3 contain a mixture of two pigments, employed in order to obtain a particular colour or to diminish the costs related to the cinnabar utilization.

Table 3. Absorption bands (cm^{-1}) in ATR-FTIR spectra of red letters from the document D3 and the absorption bands in the reference spectrum [11] of carminic acid.

Absorption bands in the spectrum of red ink from D3 (cm^{-1})	3408	2905	1674	1556 1455 1376	1258	
Absorption bands in carminic acid spectrum (cm^{-1})	3416	2933		1573 1448 1379	1240 1234 1227	
Absorption bands in the spectrum of red ink from D3 (cm^{-1})	1202 1130	1091	1045	1001	898	719
Absorption bands in carminic acid spectrum (cm^{-1})		1082	1062 1052	1000	891 821 816	

3.3. Yellow pigment

The analysis of yellow pigment of the ornamentation of manuscript D1 led to the identification of orpiment (and/or realgar), characterized by the picks of As and S (Table 4 and Figure 4)

It is worth noting the big amount (more then 10%) of some chemical elements like Ca in the composition of the orpiment based colour from the manuscript D1 (Table 4 and Figure 4). In this context one could formulate the hypothesis of the addition of calcium carbonate as filling material in the preparation of orpiment [11].

Table 4. The identification of pigments by XRF based on the characteristic elements.

Document	Colour	Characteristic elements (ppm)	Compound	Pigment	Observations
D1	yellow	S ≥ 10%	As_2S_3 or As_4S_4	orpiment or realgar	- other elements: Ca > 10%, K, Fe, Zn, Pb
		As ≥ 10%			
	green	S ≥ 10%	As_2S_3 or As_4S_4	orpiment or realgar	- mixed with a blue organic pigment

At the same time the supposition that calcite comes from using of realgar (As_4S_4) as orange-yellow pigment cannot be excluded. Realgar mines on Romanian territory, known from the medieval period and appreciated throughout Europe, has been documented at Baia Sprie and Cavnic, and the minerals most frequently associated in mining were orpiment As_2S_3, calcite $CaCO_3$, stibine

Sb_2S_3 and other sulphides. The product resulted from the photo-induced transition of the realgar (pararealgar) has also a yellow coloration [12].

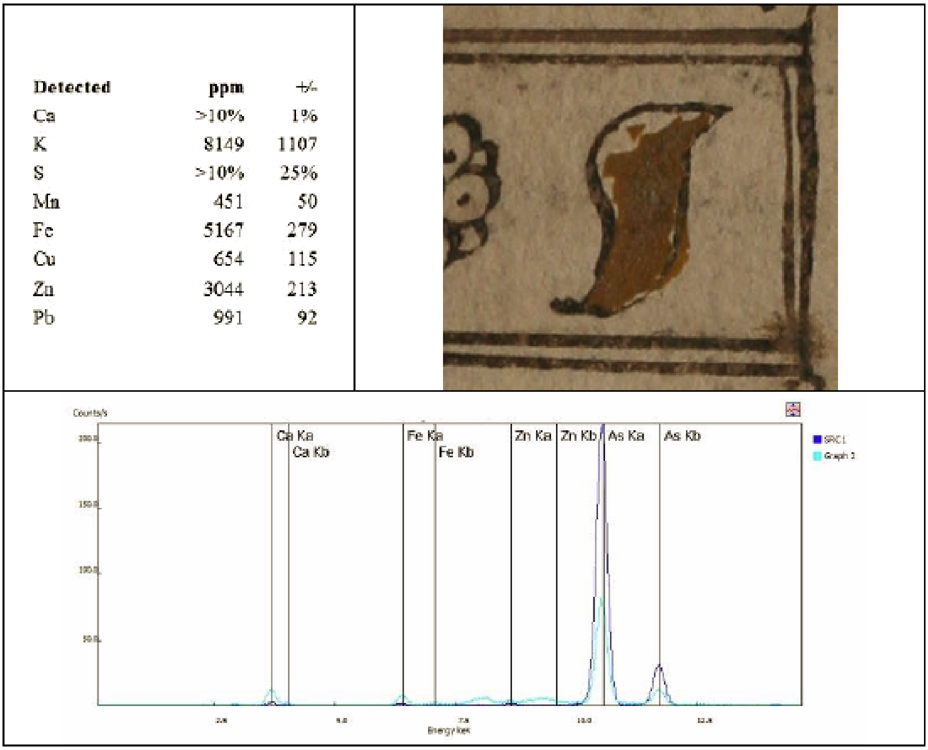

Figure 4. XRF spectrum of yellow pigment from the manuscript D1.

Table 5. Characteristic bands of yellow and green pigments on the document D1 in ATR-FTIR (cm^{-1}) spectrum.

Absorption bands yellow pigment (cm^{-1})	3408 3360	2928	1680 1558 1477	1424	1398 1334 1249	1161	1049	982	877 727
Absorption bands- green pigment (cm^{-1})	3402 3362	2974	1678 1567 1462	1430	1396 1323 1246	1176	1053	988	886 716

The FTIR spectra of the yellow and green pigment layers show absorption bands at 1424, 877 and 703 cm^{-1} and, respectively, at ~1430, 881 and 716 cm^{-1}, suggesting the presence of calcium carbonate, the characteristic bands of this mineral showing up at 1430, 875 and 712 cm^{-1} in the reference spectrum (Table 5) [13, 14].

The characteristic peaks of Pb in the XRF spectrum may be assigned to lead white. The popular name of 'ceruza', denominating the $PbCO_3$ in the miniature tradition, has been subsequently extended to a mixture with calcite.

3.4. Green pigment

The presence of As and S characteristic peaks in the green pigment XRF spectrum (Table 4) allows the affirmation that the colour layer is obtained from the already mentioned yellow mineral pigment (orpiment or realgar) mixed with a blue organic dye. The documentary sources [15, 16] suggest the possible use of indigo, unidentifiable by XFR and difficult to detect in FTIR spectrum because of the overlapping of the bands of the organic binder, organic pigment, orpiment and calcite in the fingerprint zone. The supposition needs additional researches.

3.5. Binders

Some absorption bands characteristic for protein structures appear in ATR-FTIR spectra of pigments and red ink on the document D1 (Table 5). In 2800–3400 cm^{-1} region strong absorption bands has been detected, corresponding to stretching vibrations of C-H and N-H bonds. The dominant maximum of the amide I (assigned to the stretching oscillations of C=O bond) appears at ~1680 cm^{-1}, and at ~1560 cm^{-1} a combination of bands is found, corresponding to stretching vibrations of C-N bond and to deformation vibration of N-H bond, characteristic of the amide II. In the region 1200 – 1300 cm^{-1} there are some weak absorption bands, due to stretching vibrations of C-N bond and deformation vibration of N-H bond, associated with the amide III [17].

Table 6. Absorption bands (cm^{-1}) in ATR-FTIR spectra of red inks from D2 and D4.

Absorption bands - red ink D2 (cm^{-1})	3408	2941	1740 1682 1652	1541 1458 1422	1392
Absorption bands - red ink D4 (cm^{-1})	3406	2918	1684 1651	1541 1460 1421	1371
Absorption bands - red ink D2 (cm^{-1})	1319 1246	1161	1049	843	773
Absorption bands - red ink D4 (cm^{-1})	1244	1138	1042	841	739

The spectral characteristic bands of red inks from the documents D2, D3 and D4, presented in the Tables 3 and 6, may indicate the presence of a polysaccharide. The band in the 3200-3600 cm^{-1} region is composed of the stretching vibrations of O-H bond and the stretching vibrations of N-H bond, characteristic of the amine present in the Arabic gum. The stretching oscillations of the C-H bond in 2900–2940 cm^{-1} domain are characteristic for the groups CH and CH_2. In the range 1200-1500 cm^{-1} some partly overlapped bands are present, mainly due to the O-H alcohol group. The absorption band situated near 1380 cm^{-1} may be assigned to the methyl group of rhamnose from the naturally aged polysaccharide [18].

The domain 900-1200 cm^{-1} includes: valence vibrations of C-O and C-C bonds, corresponding to the pyranose and furanoze cycles of a monosaccharide and to deformation oscillations of alcohol and carboxyl O-H bond [17-19]. Another indication of Arabic gum use as binder for inks is the detection of potassium and calcium in XRF spectra of inks, because of the calcium and potassium salts of carboxylic groups in the polysaccharide [19].

3.6. Fabrication techniques

The data provided by qualitative and quantitative investigations on the black inks emphasize the variety of preparation receipts and the vast range of raw materials available in the epoch, resulting from trade or from local sources, based on impurities introduced by the natural raw materials into the composition of historical metallo-gallic inks.

The red inks show variable compositions, reflecting the large number of ink receipts used on Romanian territories. The preparation techniques of the red inks, different for the four manuscripts, suggest regional influences. At the same time, even if mixing with a low cost pigment alters the purity of the pigment, the association of cinnabar and minimum minerals is frequently found in documents and manuscripts ornamentation. The fine granulation of vermillion, used for the authentication seal, suggests an improved synthesis method.

The employment of red organic dye (cochineal) in decorating the common use manuscripts in monasteries ateliers confirms the high level of European imports of raw materials – insects of *Dactylopius* genre from Central and South America, in the 19^{th} century.

The identification of orpiment, used as such or mixed, in the manuscript miniature from the 19^{th} century leads to the hypothesis of the availability of raw materials provided by local mining exploitation (Maramures), including the associated minerals (realgar, calcite).

The identification of the arsenical based pigment in a 19^{th} century manuscript outlines the observation that, despite its toxicity, the pigment has remained in use in Romanian miniature due to its vibrant colour.

The preparation methods of mineral pigments directly affect the granulation finesse and the homogeneity of physical mixture in the pictorial layers of manuscripts is emphasized. The manual preparation of colours inevitably implies the presence of some impurities and contaminants.

3.7. Artistic techniques

The techniques used in manuscripts achievement are established in conformity with the social significance of the manuscripts: orthodox rite book (D1), utilitarian books (Psalter manuals D2 and D3) or official documents (D4).

Analyzing the 'Molitvenic', written in 1865 at Curtea de Arges, one may allege that book ornamentation in monastic media perpetuates the tradition of Orthodox iconography until the 19th century, alongside the conception about the page, considered not only a writing but also a painting support, so becoming a real work of art.

The painting technique on a cellulose support in the 19th century implied the preparation of pigments mixtures – organic, inorganic or any derived combination, a protein binder addition – animal glues, egg albumin, followed by the colours application on paper.

The layers of pigment were applied in large touches, inside frames previously sketched with ink.

The semitransparent shades were modelled using organic dyes solutions. The range of shades reflects the variety of available materials used in epoch for chromatic effects realisation, as well as their application methods (writing, brushing).

4. Conclusions

The information gained following the technical investigation on inks and pigments employed during the 19th century emphasizes the long use of ornamentation and writing materials.

Beside the much used metal gall inks some other materials were identified: the red pigment based on cinnabar, often mixed with red lead, sometimes with an addition of a red anthraquinone colorant, orpiment for yellow or a mixture of orpiment with an organic blue dye for obtaining the green colour. In the pictorial layer the pigments were applied in a protein binder, while the universal binder for inks was the Arabic gum.

All these pigments and dyes have the roots in the miniature tradition, vastly spread in medieval Europe, with which the Romanian manufacturing ateliers were acquainted.

While the materials preparation methods have an evident regional character (Walachia, Moldavia), sometimes even a local one (exemplified by Bucharest monastery scriptoriums), the stylistic considerations confirm the framing of all analyzed manuscripts within the Romanian school of miniature.

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