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# On the identification of folium and orchil on illuminated manuscripts

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ABSTRACT

The identification of the two purple dyes *folium* and *orchil* has rarely been reported in the analysis of painted artworks, especially when analysing illuminated manuscripts. This is not consistent with the fact that ancient literary sources suggested their use as substitutes for the more expensive *Tyrian purple* dye. By employing non-invasive spectroscopic techniques, the present work demonstrates that these dyes were actually widely used in the production of ancient manuscripts. By employing UV–visible diffuse reflectance spectrophotometry with optic fibres (FORS) and spectrofluorimetry, the abundant identification of both dyes on medieval manuscripts was performed by comparing the spectra recorded on ancient codices with those obtained on accurate replicas of dyed or painted parchment. Moreover, examples are also reported whereby the considered purple dyes were used in mixtures with other colourants. The overall information obtained here allowed us to define new boundaries for the time range in which orchil and folium dyes were used which is wider than previously thought, and to focus on their particular uses in the decoration of books.



## 1. Introduction

The historical dyes known as *folium* and *orchil*, respectively obtained from *Chrozophora tinctoria* (L.) A. Juss. plant and from several genera of lichens, were in use in ancient times in painting art and in the dyeing of textiles. Many antique and medieval technical treatises [1–6] report recipes describing the procedures for obtaining these dyes from raw sources and for applying them to items to be coloured, either by painting or by dyeing. Their use was mostly as substitutes of the more expensive *Tyrian purple*, the famous dye obtained from *Murex* molluscs. Frequent citations support the hypothesis that these dyes must have been in use over a long time span, ranging from the Roman age (these dyes are in fact cited in Pliny's *Naturalis historia* [1]) to the Renaissance, even if, according to some sources [7] the use of lichen dyes ceased from Late Antiquity to 12–13th century, when the Rucellai family in Florence rediscovered orchil and transformed it into a highly valuable dye [8] for application on textiles.

Notwithstanding this, the identification and the number of these dyes on artworks is unquestionably too low if compared to the number of citations on literary sources. Regarding folium, one can speculate on the fact that, on texts, the name *folium* could be attributed to any organic colour made into a clothlet, i.e. a vegetal or animal aqueous extract saved onto a cloth by soaking and stored in a dry place such as inside a book like a *folium*, i.e. a leaflet used as a reservoir of dye until the artist needed it; according to this interpretation, *folium* could be a technical description rather than the dye specifically obtained from *Chrozophora tinctoria*. It is a fact, though, that descriptions do exist speaking unambiguously of a blue-violet colourant, a feature that should address to the true folium dye. Another major issue could be the fact that in the past there has been ambiguity in the scientific description of folium and lichen dyes, which frequently were exchanged one for the other; this ambiguity has been solved only recently [9,10]. In addition, the knowledge of their chemical nature has received relatively little attention if compared to other dyes (e.g. anthraquinonic dyes): in the case of folium, the comprehension of the structure itself is still missing, while in the case of lichen dyes it is not known whether different compositions can emerge from different lichen species (in the remainder of the text the word “orchil” will be used for simplicity to account for lichen dyes, even if this term has historically been used for dyes obtained from only some species. Finally, the general difficulty in identifying dyes must be taken into account, with main concern given to non-invasive analysis.

At present, indeed, the only clear identification of folium was by Guineau [11] on some 9th–11th century manuscripts by means of UV–

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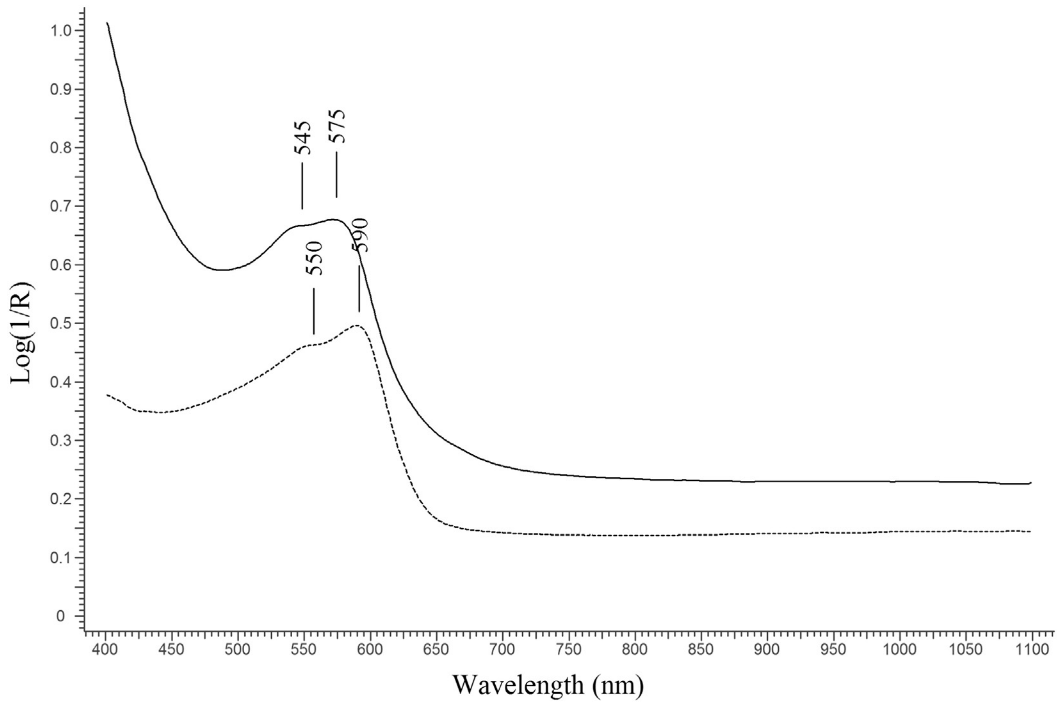


**Fig. 1.** FORS spectra of folium (solid line) and orchil (dashed line) in Log(1/R) coordinates.

visible diffuse reflectance spectrophotometry. Roger [12,13] reported similar results on two 9th–11th century manuscripts without showing analytical evidences, while tentative identification (indeed lacking in reliable diagnostic information) was proposed by Thomas and Flieder in the analysis of the parchment of the 6th century purple manuscript *Sinope Gospels* by means of GC–MS [14] and by Edwards and Benoy in the analysis by means of FT-Raman spectroscopy of a blue sample taken from the de Brécy *Madonna and Child* tondo [15].

As for orchil, some identification by means of UV–visible diffuse reflectance spectrophotometry is reported in the analysis of parchment of early Middle Ages purple codices [[16–18] and references therein], by means of fluorescence spectroscopy in the miniatures of the 8th century *Book of Kells* manuscript [19], and using fluorescence spectroscopy and Subtracted Shifted Raman Spectroscopy [20], later confirmed by means of HPLC [21], in the analysis of the parchment of the 9th century *Bible de Théodulfe*. Also, Beeby et al. [22] tentatively suggested the presence of orchil dyes in Early Middle Ages manuscripts from Northumbria. Contrarily to folium, the use of orchil and other lichen dyes has been documented for ages in textile dyeing; according to the literature, the oldest use could refer to 9th century BC textile fragments from Hallstatt [23,24].

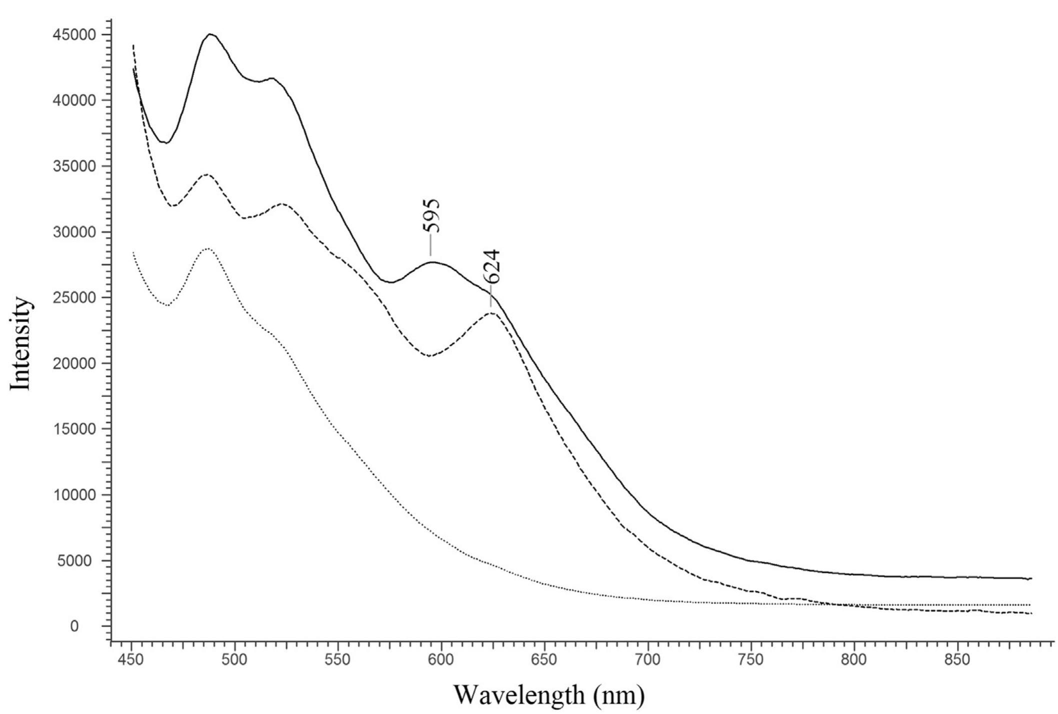


**Fig. 2.** Fluorimetry spectra of folium (solid line) and orchil (dashed line); the spectrum of parchment (dotted line) is also reported.

**Table 1**
List of manuscripts in which folium was detected. BCVC: Biblioteca Capitolare in Vercelli (Italy); BDS: Biblioteca Diocesana in Susa (Italy); BNB: Biblioteca Nazionale Braidense in Milan (Italy); BNF: Bibliothèque nationale de France in Paris (France); BNU: Biblioteca Nazionale Universitaria in Torino (Italy); MCAA: Museo Civico di Arte Antica in Torino (Italy).

| Subject | Manuscript | Provenance | Source | Period | Use of folium |
|---|---|---|---|---|---|
| *Commentarius in Apocalypsim* | J.II.1 | Catalunya (Spain) | BNU | 11-12th century | Figurative details |
| *Evangiles dits de Saint-Denis* | Latin 9387 | Saint-Denis (France) | BNF | 13th century | Parchment |
| *Liber psalmorum David* | XVI | ? | BCVC | 14th century | Filigrees |
| *Tractatus duo antiqui* | CCXVIII | ? | BCVC | 14th century | Filigrees |
| *Missale Romanum* or *Messale Rosselli* | D.I.21 | Avignon (France) | BNU | 14th century | Filigrees |
| *Corpus juris civilis* | E.I.5 | ? | BNU | 14th century | Filigrees |
| *Missale Romanum* | E.II.4 | Aosta (Italy) | BNU | 14th century | Figurative details |
| *Biblia sacra* | E.IV.44 | ? | BNU | 14th century | Filigrees |
| *Antiphonarium* | F·I.4 | Bobbio (Italy) | BNU | 14th century | Filigrees |
| *Breviario di San Michele della Chiusa* | RARI II.4 | Sacra di San Michele (Italy) | BDS | 14th century | Filigrees, initials |
| *Bibbia dei Santi Apostoli* | F.I.9 | Firenze | BNU | 14th–15th century | Filigrees |
| *Cordiale seu de quatuor novissimis* | CCXVII | ? | BCVC | 15th century | Filigrees |
| *Graduale* | CCXXXIV | Italy (Piedmont) | BCVC | 15th century | Filigrees |
| *Breviarum Romanum* | E.III.7 | Italy (Lombardy?) | BNU | 15th century | Filigrees |
| *Antiphonarium et graduale Ecclesiasticum* | J.II.9 | Italy? | BNU | 15th century | Filigrees |
| *Geografia* | AC.XIV.44 | Firenze | BNB | 15th century | Figurative details |
| *Messale Della Rovere* | 466/M | Parma (Italy) | MCAA | 15th century | Filigrees, figurative details |

A recent work by Aceto et al. [25] on this topic gave a significant contribution to the possibility of detecting the two dyes on manuscripts, by detailing the analytical features of the two dyes obtained with different micro-invasive and non-invasive analytical approaches. All the information reported was based on accurate historical reconstructions of the dyes, obtained following medieval recipes. On that basis, it was possible to consider a large number of manuscripts, in which folium or orchil were detected, with the aim of checking the actual distribution of the dyes and to identify the boundaries of the time span in which they were used. UV–visible diffuse reflectance spectrophotometry and molecular fluorimetry were employed.

## 2. Materials and methods

### 2.1. UV–visible diffuse reflectance Spectrophotometry with optic fibres (FORS)

FORS analysis was performed with an Avantes (Apeldoorn, The Netherlands) AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light source; detector and light source were connected with fibre optic cables to an FCR-7UV200-2-1,5 × 100 probe. In this configuration, light is sent and retrieved with a single fibre bundle positioned at 45° with respect to the surface normal, in order to exclude specular reflectance. The spectral range of the detector was 200–1160 nm; according to the features of the monochromator (slit width 50 μm, grating of UA type with 300 lines/mm) and of the detector (2048 px), the best spectral resolution was 2.4 nm calculated as FWHM (Full Width at Half Maximum). Diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile provided by Avantes and guaranteed to be reflective at least at 98% within the investigated spectral range. Blank correction was not efficient on both the extremes of the spectral range, therefore the regions 200–350 and 1100–1160 were not considered in the discussion. The diameter of the investigated area on the sample was 1 mm. In all of the measurements, the distance between the probe and the sample was kept constant at 2 mm, corresponding to the focal length of the probe. To visualise the samples, the probe was equipped with a USB endoscope. The instrumental parameters were as follows: 10 ms integration time, 100 scans for a total acquisition time of 1.0 s for each spectrum. The system was managed by means of AvaSoft v. 8™ dedicated software, running under Windows 7™.

### 2.2. Fluorimetry

An Ocean Optics (Dunedin, Florida, USA) Jaz model spectrophotometer was employed to record molecular fluorescence spectra. The instrument is equipped with a 365 nm Jaz-LED internal light source; a QF600-8-VIS/NIR fibre fluorescence probe is used to drive excitation light on the sample and to recover the emitted light. The spectrophotometer works in the range 191–886 nm; according to the features of the monochromator (200 μm slit width) and detector (2048 elements), the spectral resolution available is 7.6 nm calculated as FWHM. The investigated area on the sample is 1 mm in diameter. In all of the measurements, the sample-to-probe distance was kept constant to 12 mm, corresponding to the focal length of the probe. To visualise the samples, the probe was equipped with a USB endoscope. The instrumental parameters were as follows: 4 s integration time, 3 scans for a total acquisition time of 12 s for every spectrum. The system is managed by SpectraSuite™ software running under Windows 7™.

### 2.3. Preparation of painted and dyed standard samples

Paints and dyes of folium and orchil were obtained according to the procedures described in [25]. Upon extraction of dyes from respectively *Chrozophora tinctoria* purple fruits and *Roccella tinctoria* scraps, paints were prepared by mixing powdered dyes (ca. 0.25 g/ml) in a painting medium made of gum Arabic (1 g/ml) and sucrose (2 g/ml); in order to increase the hiding power, lead white (ca. 0.25 g/ml) was added to the medium. The painting medium was prepared at pH 7. Dyed samples were prepared according to the procedures employed for dyeing textiles with mordant dyes: parchment was soaked for 1 h in a neutral solution containing the dye and alum (both 30% with respect to the weight of parchment) and allowed to dry. Painted and dyed samples were used for obtaining FORS and fluorimetry reference spectra; note that no spectral differences were found between painted vs. dyed samples, both in FORS and fluorimetry measurements.

## 3. Results and discussion

### 3.1. Identifications of folium

The spectral features of folium, useful for its identification on artworks, were obtained upon analysis of standard paints and dyes on parchment. The FORS spectrum, when seen in Log(1/R) or *apparent absorbance* coordinates (Fig. 1), is characterised by an absorption band structured into two sub-bands occurring at ca. 545 and 575 nm [25]. These features are constant at varying pH conditions, as the behaviour of folium is relatively independent from pH, contrarily to what was previously known [26]; we verified that the absorption spectrum in solution is unchanged in the pH range 3–10. It is not possible to assign the electronic transitions, given the fact that the chemical structure of folium is at present unknown; the two chromophore systems could be

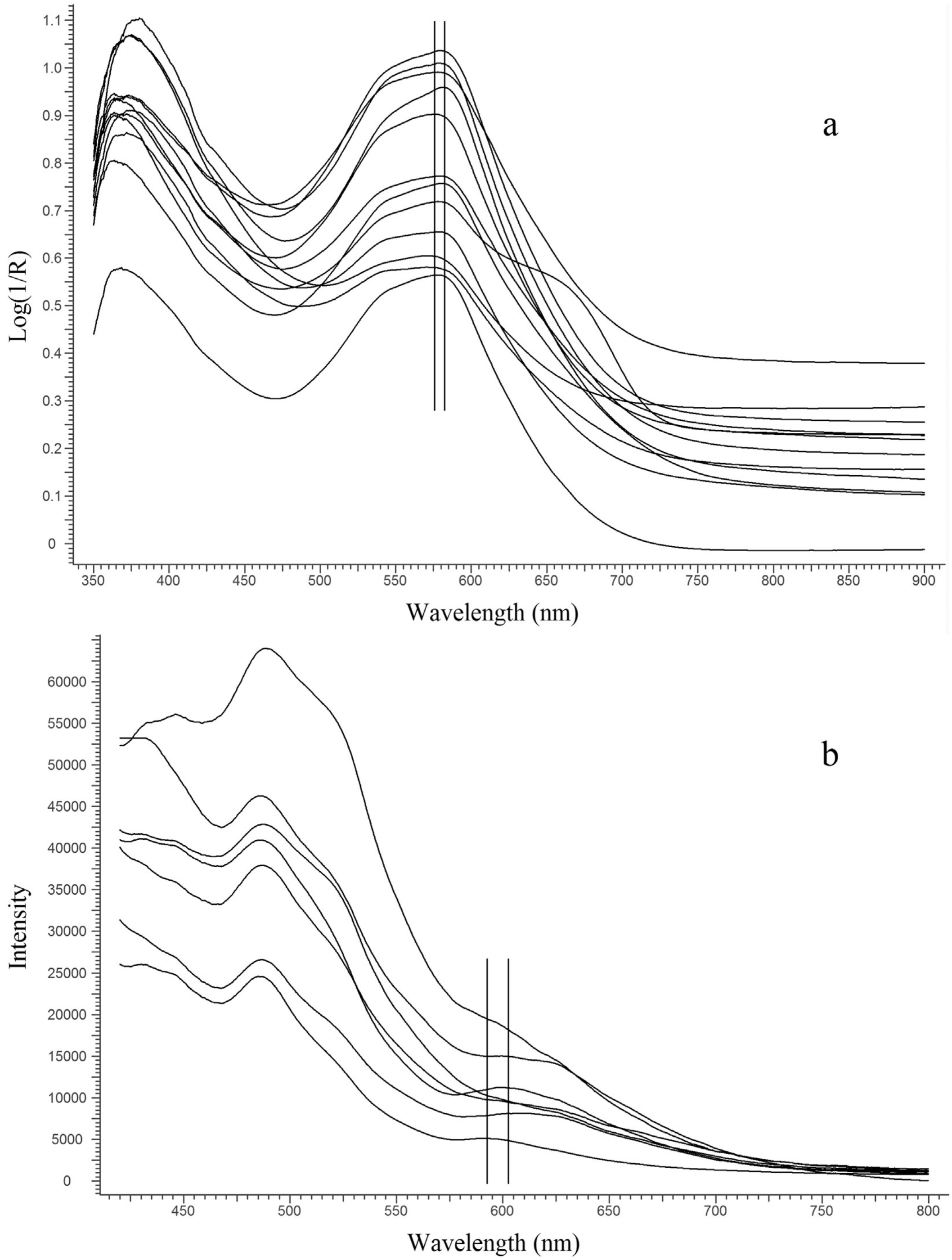


**Fig. 3.** (a) FORS in Log(1/R) coordinates and (b) fluorimetry spectra from purple and blue painted areas containing folium in a selection of the manuscripts analysed in this study; vertical bars define the range of variability of (a) the second absorption maximum and (b) the main emission peak.

due to two different molecules present in the dye. These positions are close to the absorption maxima of orchil, nevertheless the general shape of the band is different, even considering that folium is more bluish, therefore showing in reflectance coordinates a higher maximum peak in the blue region. Orchil, on the other hand, is more reddish, with its reflectance spectrum more dominated by the shoulder in the red region rather than a peak in the blue region (Fig. S1). Furthermore, the maxima allow distinguishing folium from anthraquinone dyes (madder, coccid dyes), from alkanet and of course from Tyrian purple. Fluorimetry analysis, when used alone, is not as useful as FORS in allowing discrimination of folium from other purple dyes; nevertheless the emission spectrum (Fig. 2) contains a feature at ca. 595 nm which is common to anthraquinone dyes but is absent in the spectrum of orchil. Additionally, a shoulder at ca. 625 nm can be present, but it is usually lower than the emission band occurring in the spectrum of orchil. Note that the spectral features were the same when using 365, 450 or 590 nm LED excitation sources.

The identification of folium by Guineau [11] and by Roger [12,13] refers to Early Middle Ages artworks; in these manuscripts the dye was used for some figurative details in the miniatures (e.g. backgrounds) or for parchment colouring. Using FORS and fluorimetry analysis, we identified folium on manuscripts dating from 11th to 15th century;

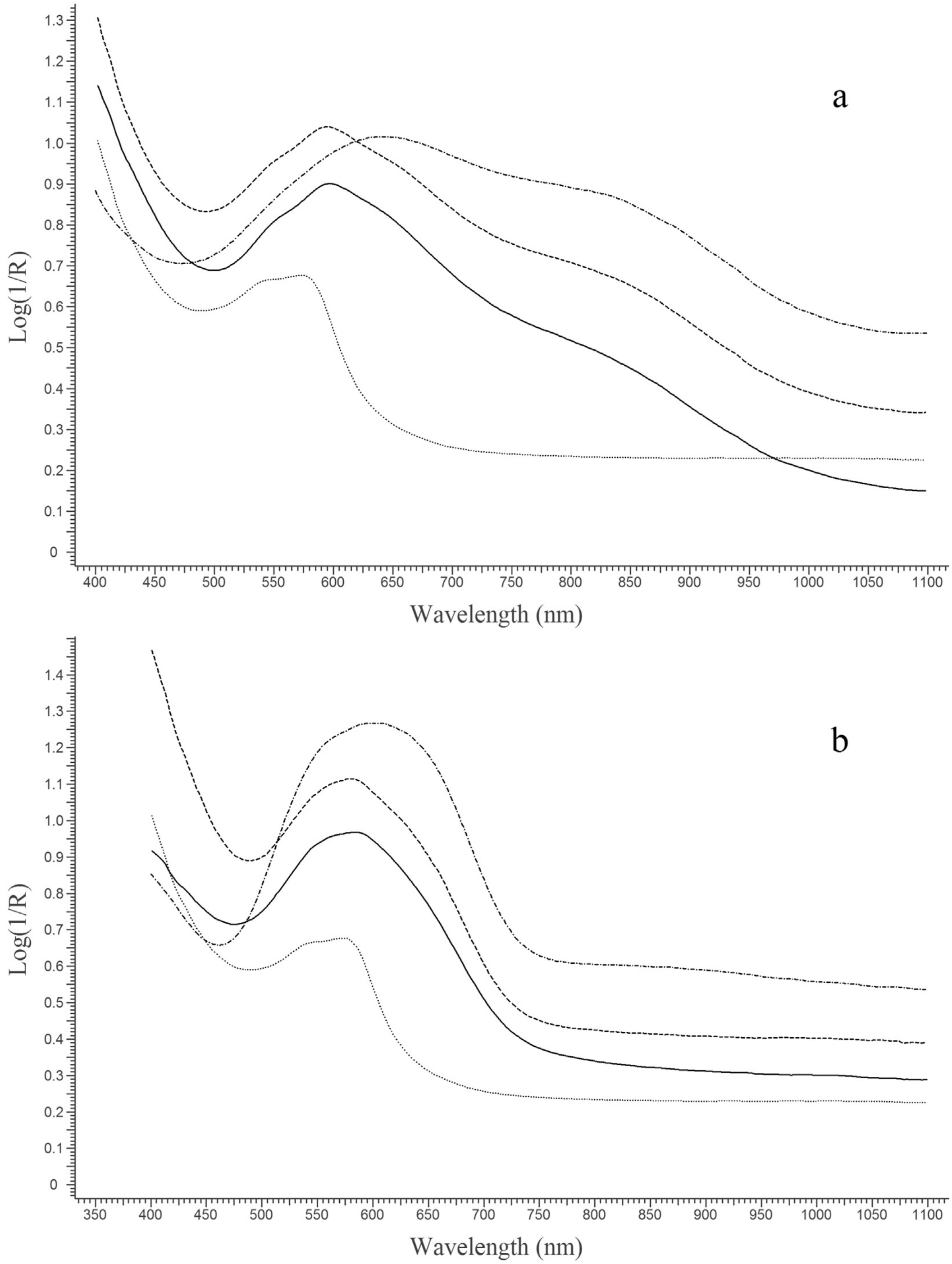


**Fig. 4.** FORS spectra from areas containing folium in mixture with blue pigments: (a) ms. BNU E.I.5 (solid line), folium (dotted line), folium/azurite 1:6 mixture (dashed line) and azurite (dashed-dotted line); (b) ms. BNU J.II.9 (solid line), folium (dotted line), folium/ultramarine blue 1:6 mixture (dashed line) and ultramarine blue (dashed-dotted line).

the list of manuscripts is reported in Table 1. The spectral features arising from both FORS and fluorimetry analysis are nearly identical in all instances (respectively Fig. 3a and b): the variation in the positions of the sub-bands in FORS spectra is $\pm 3$ nm, while for the main emission band in fluorimetry spectra is $\pm 5$ nm (it must be taken into account the fact that the emission peak can shift depending on the concentration of the fluorophore [27]). The emission bands occurring at 488 and 520 nm are actually due to the parchment support.

According to the information arising from this and previous studies [11–13,25], it is apparent that folium was used mainly as paint on earlier manuscripts, whereas it was used mainly as ink for delicate filigrees on later manuscripts, perhaps due to the fact that other purple-violet dyes (e.g. coccid dyes, brazilwood) had in the meantime become available for painting; it was still used as paint in the Renaissance, as it was identified in the *Messale Della Rovere* (Museo Civico di Arte Antica, Torino), a manuscript on paper datable to 1490–1492. In only one instance, i.e. on the manuscript Latin 9387 (Bibliothèque nationale de France, Paris), clear evidence was found of the use of folium for parchment dyeing (contrarily to orchil for which several evidences for this particular use were found, as it will be later discussed). Indeed, experiments of dyeing on

**Table 2**
List of manuscripts in which orchil was detected. BCVC: Biblioteca Capitolare in Vercelli (Italy); BDT: Biblioteca Diocesana in Tortona (Italy); BNF: Bibliothèque nationale de France in Paris (France); BNU: Biblioteca Nazionale Universitaria in Torino (Italy); BQB: Biblioteca Queriniana in Brescia (Italy); BUB: Biblioteca Universitaria in Bologna (Italy); BPLP: Biblioteca Passerini-Landi in Piacenza (Italy); KHM: Kunsthistorisches Museum in Vienna (Austria); MCAA: Museo Civico di Arte Antica in Torino (Italy); ÖNB: Österreichische Nationalbibliothek in Vienna (Austria); UUB: Uppsala Universitetsbibliotek in Uppsala (Sweden).

| Subject | Manuscript | Provenance | Source | Period | Use of orchil |
|---|---|---|---|---|---|
| *Codex Argenteus* | DG. 1 | Ravenna (Italy) | UUB | 5-6th century | Parchment colouring |
| *Codex Brixianus* [17] | – | Ravenna (Italy) | BQB | 6th century | Parchment colouring |
| *Codex Petropolitanus* | – | Near East | ÖNB | 6th century | Parchment colouring |
| *Codex Sarzanensis* | – | Italy | BDT | 6th century | Parchment colouring |
| *Codex Sinopensis* | Suppl. grec. 1286 | Near East | BNF | 6th century | Parchment colouring |
| *Psautier de S. Germain* | Latin 11947 | Saint-Germain-des-prés (France) | BNF | 6th century | Parchment colouring |
| *Vienna Genesis* [16] | cod. Theol. gr. 31 | Near East | ÖNB | 6th century | Parchment colouring |
| Fragment | 2804 | ? | ÖNB | ? | Parchment colouring |
| *Coronation Gospels* | Inv. XIII 18 | Aquisgrana (Germany) | KHM | 8th century | Parchment colouring |
| *Evangiles de Saint-Denis* | Latin 9387 | Northern France | BNF | 8th century | Parchment colouring |
| *Lectionnaire pourpre de Vérone* | Latin 9451 | Northern Italy | BNF | 8th century | Parchment colouring |
| *Hieronymus, in Isaiam* | Latin 11627 | Corbie (France) | BNF | 8th century | Figurative details |
| *Evangelia Matthei et Marc* | Latin 11955 | France? | BNF | 8th century | Parchment colouring |
| *Salterio di Angilberga* | Com. s.n. | Northern France? | BPLP | 9th century | Parchment colouring |
| *Libri S. Augustini de Trinitate* | CIV | Northern Italy | BCVC | 9th century | Figurative details |
| *Liber quattuor Evangeliorum* | CXXXIV | Bavaria (Germany) | BCVC | 9th century | Figurative details |
| *Homiliae S. Gregorii* | CXLVIII | Southern Italy (Italy) | BCVC | 9th century | Figurative details |
| *Apollo medicus* | CCII | Nonantola (Italy) | BCVC | 9th century | Figurative details |
| *Evangiles de Metz* | Latin 9383 | Metz (France) | BNF | 9th century | Parchment colouring |
| *Evangeliarium* | Latin 1126 | France? | BNF | 9-10th century | Parchment colouring |
| *Moralia sive expositio in job* | F.I.6 | Bobbio (Italy) | BNU | 9-10th century | Figurative details |
| *Benedictus* | G.V.4 | Bobbio (Italy) | BNU | 9-10th century | Figurative details |
| *Sacramentarium seu Missale* | CLXXXI | Fulda (Germany) | BCVC | 10th century | Figurative details |
| *Vita sancti Columbani discipulorum* | F.IV.12 | Bobbio (Italy) | BNU | 10th century | Figurative details |
| *Psalterium* | G.V.2 | Bobbio (Italy) | BNU | 10-11th century | Figurative details |
| *Orationes* | C.I.6 | Costantinopoli? | BNU | 11th century | Figurative details |
| *Liber decretalium* | V | Bologna (Italy) | BCVC | 14th century | Figurative details |
| *Messale Della Rovere* | 466/M | Parma (Italy) | MCAA | 15th century | Parchment colouring |
| *Statuta theologorum* | E.V.31 | Italy | BNU | 15th–16th century | Filigrees |
| *Lectionarium* | I.I.2 | Northern Italy | BNU | 15th–16th century | Figurative details |
| *Antiphonarium* | F.I.1 | Bobbio (Italy) | BNU | 16th century | Figurative details |
| *Tabula Colorum Physiologica* | | London (UK) | BUB | 1686 | Figurative details |

parchment with folium carried out in our laboratory revealed that this dye is less efficient than orchil, both as a direct dye and after mordanting with alum.

Examples of decorative features containing folium are reported in Fig. S2. In ms. J.II.1 (Fig. S2a, 11th–12th century, Biblioteca Nazionale Universitaria in Torino, Italy), folium was used for painting garments, animals and other features. In ms. RARI II.4 (Fig. S2b, 14th century, Biblioteca Diocesana in Susa, Italy) and ms. XVI (Fig. S2c, 14th century, Biblioteca Capitolare in Vercelli, Italy), which are illustrative of many other manuscripts, folium was used for filigrees. According to art historians, it is possible that these filigrees were in some cases 15th century additions to 13th or 14th century manuscripts.

### 3.1.1. Mixtures of folium with other colourants

Apart from the mixture of folium with white lead, which does not modify its spectral features except for the level of reflectance, in some cases it was found that folium was used in a mixture with inorganic blue pigments: in the examples reported the dye was mixed with azurite (Fig. 4a) and with ultramarine blue (Fig. 4b). The identification of folium was verified by preparing mixtures with known ratios of folium/blue pigment. In both cases, the spectral features of the dye are broadened and slightly red-shifted, since the main absorption band has additional contributions; in the case of folium/azurite mixtures the main absorption maximum is shifted to ca. 595 nm, whereas in the case of ultramarine blue it is shifted to ca. 585 nm. The presence of folium in such mixtures can be checked by means of spectrofluorimetry, as the typical emission bands at ca. 595 and 625 nm are still apparent, without additional contributions from any of the blue pigments. Moreover, the mixture can be appreciated by visual inspection under proper magnification: in Fig. S3 the 250x image taken from a blue paint in ms. E.I.5 (Biblioteca Nazionale Universitaria in Torino, Italy) highlights the apparent grains of azurite, as well as the presence of purple areas with much lower hiding power that can be attributed to folium.

### 3.2. Identification of orchil

The spectral features of orchil, already shown in [25], enable its discrimination from folium and other purple dyes. According to the studies by Musso et al. [28], the chromophore system of orchil has been shown to be the basic phenoxazonic skeleton. The FORS spectrum is dominated by an absorption band structured into two sub-bands, the first one occurring at ca. 545–550 and the second one occurring in the range 585–595 nm (Fig. 1a). The variability of the latter peak could be explained considering that orchil is obtained by extraction with ammonia from lichens [29], a process which turns the chemical precursors into orceins; different species of lichens could contain different chemical precursors and therefore generate orchil with slightly different orceins distributions. Contrarily to folium, orchil can change its absorption behaviour with pH. In agreement with Clementi et al. [[30] and references therein], we verified that the colour of orchil in solution turns from purple to orange-red at pH 3 and the absorption spectrum has a single band at ca. 495 nm; however, a far smaller change occurs when the pH turns from neutral to alkaline: the same two absorption bands occur at ca. 540 and 575 nm and the colour slightly changes from purple (pH 7) to violet (pH 11). We assume that the same behaviour holds in solid state, when the absorption measurement is carried out by means of reflectance. As stated before, apart from the absolute position of the two sub-bands, the whole profile of the absorption band of orchil can be safely distinguished from that of folium. As to fluorimetry, orchil shows an emission band at ca. 624 nm (Fig. 2) similarly to other purple dyes, e.g. coccid dyes; with concern to folium, orchil misses the additional feature at 595 nm. Similarly to folium, there were no differences in the emission spectrum when using 365, 450 or 590 nm LED excitation sources.

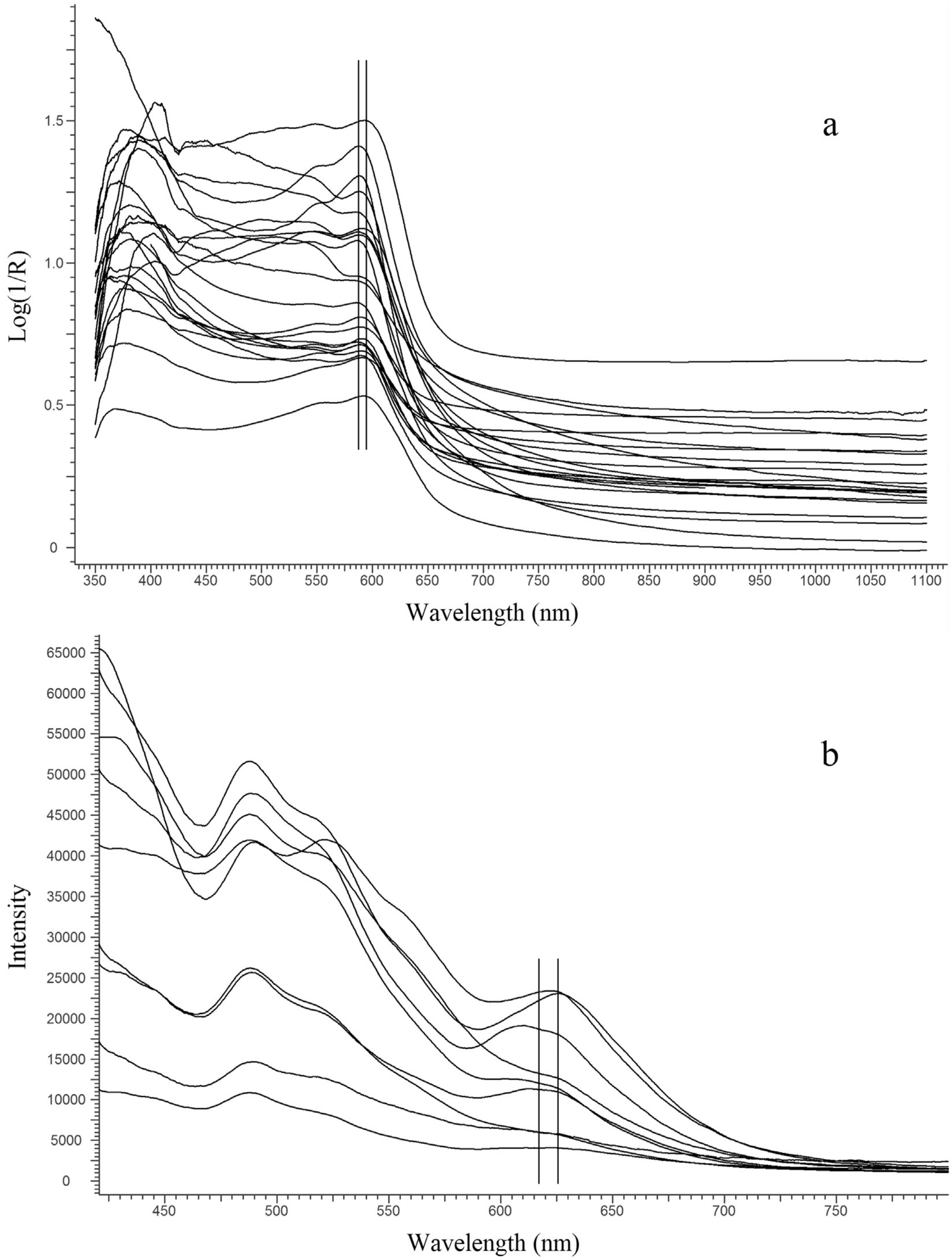


**Fig. 5.** (a) FORS in Log(1/R) coordinates and (b) fluorimetry spectra from purple areas containing orchil in a selection of the manuscripts analysed in this study; vertical bars define the range of variability of (a) the second absorption maximum and (b) the main emission peak.

The identification of orchil in the manuscripts analysed in this study (list in Table 2) relies on the overall shape of FORS spectrum, even if the position of the second sub-band has a large variability (Fig. 5a); in no case, though, it occurs outside the range 580–595 nm. The position of the emission band in fluorimetry spectra is as well variable in the range 615–630 nm (Fig. 5b; additional bands occurring at 488 and 520 nm are due to parchment), even considering the shift due to the fluorophore concentration; moreover, according to the information reported by Clementi et al. [30], photodegradation could induce an hypsochromic shift. Despite this variability, the band at 615–630 nm is usually high so that discrimination with respect to folium, in which a shoulder can occur at ca. 625 nm, can be achieved.

It has already been evidenced the fact that lichen dyes were already in use for textile dyeing several centuries before folium [23,24]. According to the information yielded by this study, the use of orchil in miniature painting can be dated at least between 6th and 16th century, therefore its use was older and more widespread and variegated than that of folium. A particular and highly relevant use of orchil was in the colouring of parchment of *purple codices*, the biblical texts written with gold and silver inks on purple parchment. The tradition of using purple dyes for colouring the writing supports started in the Roman age [31] and was still in use during the Renaissance [32] or even later on in 18th century [7]: the results of our investigations, together with other studies [[16–18] and references therein], confirm the almost exclusive use of orchil at the purpose, at least since the Renaissance as the latest evidence was found in the already cited *Messale Della Rovere* (late 15th century) which contains two paper folios entirely coloured in purple with a lichen dye. This is consistent with the indications for the production of purple pages contained in a 15th century treatise, the *Alphabetum Romanum* by Felice Feliciano [7,33], in which a recipe entitled "A tingier carte in colore pavonazo" (*To dye in purple colour*) explicitly cites orchil as the dye to be used for paper colouring.

Apart from this, orchil was frequently noted in paints, in particular on manuscripts of the Insular school [19,22] and in a single case, ms. E.V.31 at BNU, in filigrees. It is also important underlining the fact that lichen dyes were constantly used in a longer time range than previously reported. Wallert [7] highlighted the lack of references to lichen dyes in medieval treatises and suggested that their use was discontinued after the Late Antique age, to be restarted in 12–13th century upon the rediscovery by the Rucellai family, but it is apparent from our results that artists never ceased its use. At any rate, it is to be expected that the use of lichen dyes in painting decreased in the Late Middle Ages, as a consequence of the availability of other violet-purple dyes such as brazilwood or coccid dyes. For instance, a significant curiousity in which a lichen dye was revealed is the one cited by Baraldi et al. [34] in the *Tabula Colorum Physiologica*, a catalogue of colours published in 1686 in London by the Philosophical Transactions.

#### 3.2.1. Mixtures of orchil with other colourants

As in the case of folium, in some instances it was found evidence of the use of orchil in mixture or in double application with another colourant, mostly indigo (Fig. 6). Contrarily to the case of folium, the contextual presence of indigo does not modifies the spectral features of the dye, possibly because the apparent absorption band of indigo occurs at ca. 660 nm, that is at least 70 nm from the main one of orchil. Therefore, it was possible to identify the presence of both orchil and indigo on the parchment of some folios in the following purple manuscripts: *Codex Brixianus* (Brescia, Biblioteca Queriniana), *Codex Argenteus* (Uppsala, Universitetsbiblioteket), *Coronation Gospels* (Vienna, Kunsthistorisches Museum), *Evangiles dits de Saint-Denis* (BnF, ms. Latin 9387) and *Evangiles dits de Metz* (BnF, ms. Latin 9383).

## 4. Conclusions

By means of the combined contribution of two non-invasive spectroscopic techniques, i.e. FORS and fluorimetry, it was possible to identify folium and orchil in a large number of manuscripts, ranging respectively from 9th to 15th century and from 6th to 16th century. These time ranges are far wider than previously known regarding the use of the cited purple dyes. Despite the significant contribution given here, the accurate definition of the time span in which orchil and folium were in use, as well as the identification of production circumstances is still in progress and further analytical investigations on codices shall be encouraged.

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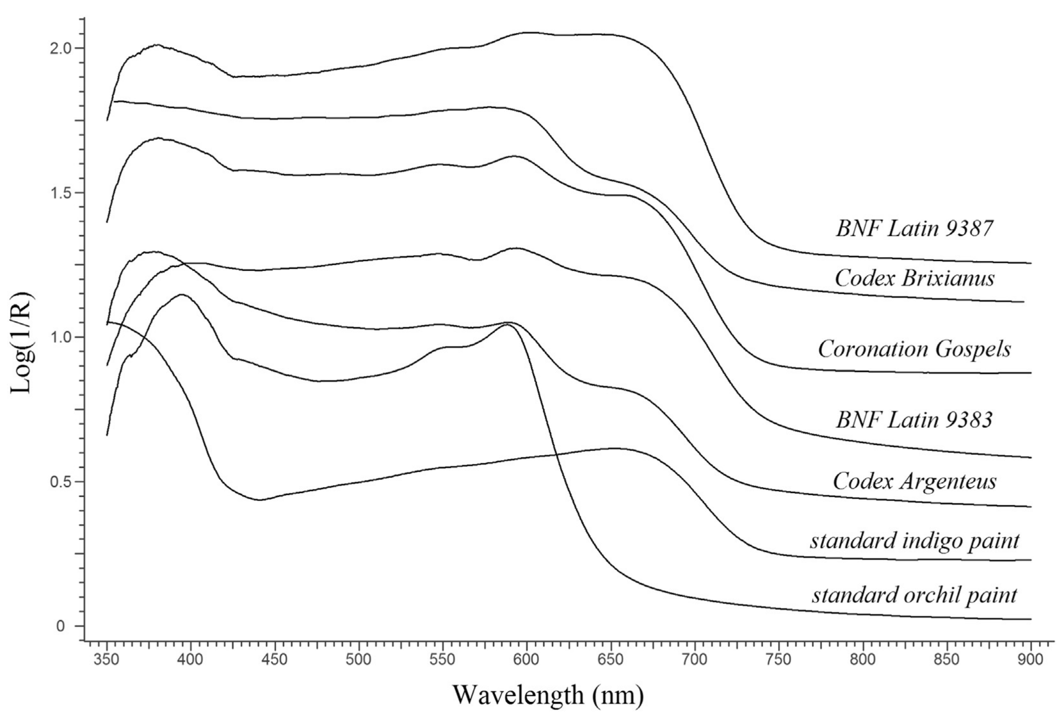


**Fig. 6.** FORS spectra from areas containing orchil in double application with indigo (spectra are offset for clarity).

## References


[1] Pliny the Elder, Natural History, Book 9, the Loeb Classical Library, Harvard University Press, Cambridge, Massachussets, 1952.
[2] C.R. Dodwell, Theophilus: The Various Arts, Nelson, London, 1961.
[3] F. Brunello, De arte illuminandi, Vicenza, Neri Pozza, 1971.
[4] E.R. Caley, The Stockholm Papyrus: an English translation with brief notes, J. Chem. Educ. 4 (1927) 979–1002.
[5] C.S. Smith, J.G. Hawthorne, Mappae Clavicula. A Little Key to the World of Medieval Techniques, American Philosophical Society, Philadelphia, 1974.
[6] D.V. Thompson, Materials of Mediaeval Painting, George Allen and Unwin, London, 1936 138–139.
[7] A. Wallert, Medieval recipes for the coloring of parchment, ICOM Committee for Conservation International Leather and Parchment Symposium, Offenbach am Main, Deutsches Ledermuseum 1989, pp. 447–456.
[8] K. Diadick Casselman, Lichen Dyes. The New Source Book, Dover Publication, Mineola (NY - USA), 2001.
[9] T. Brachert, Lexicon historischer Maltechniken. Quellen, Handwerk, Technologie, Alchemie, Callwey, München, 2001.
[10] K. Diadick Casselman, The etymology and botany of some European lichen dyes, in: J. Kirby (Ed.), Dyes in History and Archaeology, Archetype Publications, London 2002, pp. 31–36.
[11] B. Guineau, Le folium des enlumineurs, une couleur aujourd'hui disparue, Revue d'archéologie médiévale, Vol. 26, 1996, pp. 23–44.
[12] P. Roger, Étude des couleurs et de la pratique picturale, Art de l'enluminure, Vol. 20, 2007, pp. 46–65.
[13] P. Roger-Puyo, Les pigments et la technique picturale des Évangiles de Saint-Riquier, Art de l'enluminure, Vol. 46, 2013, pp. 34–39.
[14] M. Thomas, F. Flieder, La composition des parchemins pourprés démystifiée par la chromatographie en phase gazeuse, in: M. Hours (Ed.), La vie mystérieuse des chefs-d'oeuvres: la science au service de l'art, Editions de la Réunion des Musées Nationaux, Paris 1980, pp. 232–233.
[15] H.G.M. Edwards, T.J. Benoy, The de Brécy Madonna and Child tondo painting: a Raman spectroscopic analysis, Anal. Bioanal. Chem. 387 (2007) 837–846.
[16] M. Aceto, A. Agostino, G. Fenoglio, P. Zannini, P. Baraldi, C. Hofmann, E. Gamillscheg, First analytical evidences of precious colourants on Mediterranean illuminated manuscripts, Spectrochim. Acta A 95 (2012) 235–245.
[17] M. Aceto, A. Idone, A. Agostino, G. Fenoglio, M. Gulmini, P. Baraldi, F. Crivello, Non-invasive investigation on a VI century purple codex from Brescia, Italy, Spectrochim. Acta A 117 (2014) 34–41.
[18] M. Bicchieri, The purple codex Rossanensis: spectroscopic characterisation and first evidence of the use of the elderberry lake in a sixth century manuscript, Environ. Sci. Pollut. Res. 21 (2014) 14146–14157.
[19] A. Romani, C. Clementi, C. Miliani, B.G. Brunetti, A. Sgamelotti, G. Favaro, Portable equipment for luminescence lifetime measurements on surfaces, Appl. Spectrosc. 62 (2008) 1395–1399.
[20] F. Rosi, C. Clementi, M. Paolantoni, A. Romani, R. Pellegrino, B.G. Brunetti, W. Nowik, C. Miliani, Study of Raman scattering and luminescence properties of orchil dye for its nondestructive identification on artworks, J. Raman Spectrosc. 44 (2013) 1451–1456.
[21] M. Eveno, J. Delit, W. Nowik, La bible de Théodulfe (IXe siècle) de la cathédrale du Puy-en-Velay. Identification du colorant des feuillets pourprés et restauration du volume, Support/Tracé, Vol. 3, 2003, pp. 16–24.
[22] A. Beeby, A.R. Duchkworth, R.G. Gameson, C.E. Nicholson, R.J.H. Clark, B. Meegan, A.W. Parker, Pigments of the earliest Norhumbrian manuscripts, Scriptorium 69 (2015) 33–59.
[23] R. Hofmann-de Keijzer, M.R. van Bommel, I. Joosten, A. Hartl, A.N. Proaño Gaibor, A.G. Heiss, R. Kralofsky, R. Erlach, S. de Groot, The colours and dyeing techniques of prehistoric textiles from salt mines of Hallstatt, in: K. Grömer, A. Kern, H. Reschreiter, H. Rösel-Mautendorfer (Eds.), Textiles from Hallstatt, Weaving Culture in Bronze Age and Iron Age Salt Mines, Archaeolingua, Budapest 2013, pp. 135–162.
[24] K. Vajanto, Dyes and Dyeing Methods in Late Iron Age Finland, University of Helsinki, PhD dissertation, 2016.
[25] M. Aceto, A. Arrais, F. Marsano, A. Agostino, G. Fenoglio, A. Idone, M. Gulmini, A diagnostic study on folium and orchil dyes with non-invasive and micro-destructive methods, Spectrochim. Acta A 142 (2015) 159–168.
[26] M. Aceto, A. Arrais, E. Calà, C. Cassino, M. Clericuzio, F. Marsano, A. Agostino, G. Fenoglio, M. Gulmini, A. Idone, L. Menghini, L. Leporini, N. Di Matteo, C. Porter, The Quest for Folium. Proceedings of DHA34 - Dyes in History & Archaeology 34 Conference, Thessaloniki, 2015 36.
[27] C. Clementi, C. Miliani, G. Verri, S. Sotiropoulou, A. Romani, B.G. Brunetti, A. Sgamellotti, Application of the Kubelka-Munk correction for self-absorption of fluorescence emission in carmine lake paint layers, Appl. Spectrosc. 63 (2009) 1323–1330.
[28] H. Musso, H.G. Matthies, V. Über Orceinfarbstoffe, IR- und UV-Spektren Hydroxy- und Amino-Substituierter Phenoxazone, Chem. Ber. 90 (1957) 1814–1827.
[29] A. Kok, A short history of the orchil dyes, Lichenologist 3 (1966) 248–272.
[30] C. Clementi, C. Miliani, A. Romani, G. Favaro, In situ fluorimetry: a powerful non-invasive diagnostic technique for natural dyes used in artefacts. Part I. Spectral characterization of orcein in solution, on silk and wool laboratory-standards and a fragment of Renaissance tapestry, Spectrochim. Acta A 64 (2006) 906–912.
[31] S. Baroni, Pergamene purpuree e scritture metalliche nella tradizione tecnico artistica. Un quadro introduttivo, in: S. Baroni (Ed.), Oro, argento e porpora, Tangram Edizioni Scientifiche, Trento 2012, pp. 11–37.
[32] G. Mariani Canova, La porpora nei manoscritti rinascimentali e l'attività di Bartolomeo Sanvito, in: O. Longo (Ed.), La porpora. Realtà e immaginario di un colore simbolico, Istituto Veneto di Scienze, Lettere ed Arti, Venezia 1998, pp. 339–371.
[33] M.M. Marconcini, Procedimenti nell'Alphabetum Romanum di Felice Feliciano, in: S. Baroni (Ed.), Oro, argento e porpora, Tangram Edizioni Scientifiche, Trento 2012, pp. 107–111.
[34] P. Baraldi, C. Fagnano, P. Bensi, Raman study of a 'Tabula Colorum Physiologica' in a 1686 printed journal, J. Raman Spectrosc. 37 (2006) 1104–1110.