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Non-invasive investigation on a VI century purple codex from Brescia, Italy



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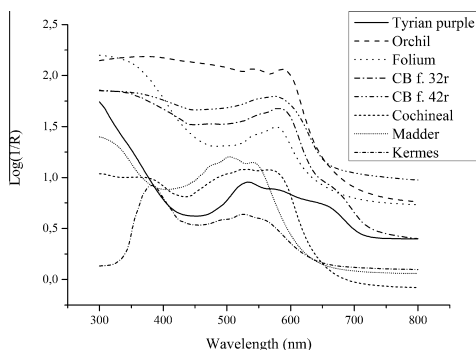
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HIGHLIGHTS

- Purple codices are among the most prestigious artworks of Medieval age.
- Parchment was dyed with Tyrian purple mixed with other lesser value dyes such as folium or orchil.
- Only non-invasive techniques were used.

GRAPHICAL ABSTRACT



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ABSTRACT

Purple codices are among the most relevant and prestigious book productions of Late Antique and Medieval age. They usually contained texts from Holy Writings written with golden or silver inks on parchment dyed in a purple hue. According to the tradition, the colour of parchment was obtained by the well renowned Tyrian purple dye. From the material point of view, however, very little is known about the compounds actually used in the manufacture of these manuscripts. Presently, the information available is limited to the ancient art treatises, with very few diagnostic evidences supporting them and, moreover, none confirming the presence of Tyrian purple. It is more than apparent, then, the need to have at disposal larger and more complete information at the concern, in order to verify what came to us from the literary tradition only. In this study, preliminary results are presented from non-invasive investigation on a VI century purple codex, the so-called *Codex Brixianus*, held in the Biblioteca Civica Queriniana at Brescia (Italy). Analyses were carried out with XRF spectrometry, UV–visible diffuse reflectance spectrophotometry, molecular spectrofluorimetry and optical microscopy. The results suggest the hypothesis that Tyrian purple had been used as a minor component mixed with other less precious dyes such as folium or orchil.

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Introduction

Purple codices are among the most important and prestigious book productions of Late Antique and Medieval ages. They usually

contained texts from Holy Writings, written with golden or silver inks on parchment dyed in purple. The colour of parchment, according to the tradition, was obtained with a procedure similar to that used on textiles, employing the well-known Tyrian purple dye. The association between inks made of precious metals [1] and the purple colour of parchment charged these manuscripts with a highly symbolic value, so that they were usually produced to be owned by kings and emperors.

The practice of creating purple codices is witnessed by several citations from Roman sources already [2,3]. From the material point of view, though, very few information is known about the compounds actually employed in the manufacture of these artworks, in particular for what concerns the colour of parchment. How was this process done? Was parchment dyed or painted? What colourants were used? The starting point in order to find this information is, of course, to consult ancient technical treatises. In bibliographic sources, though, there is sometimes ambiguity among the term “purple” and the actual compounds used to dye in purple which can be different from Tyrian purple itself. Another issue is the fact that ancient treatises can be compilations of more ancient sources; in the process of transferring knowledge, the text can be intentionally or unintentionally polluted and therefore it can accumulate misunderstandings in the successive versions.

Several technical treatises from Roman or Medieval ages such as the *Leyden Papyrus X* [4], the *Stockholm Papyrus* [5] and Pliny the Elder's *Naturalis Historia* [6] are plenty with information regarding dyeing of textiles with Tyrian purple or other purple dyes; the use of a Tyrian purple lake in painting is cited as well (Pliny the Elder called it *purpurissimum*) but information concerning the process of imparting colour to parchment is relatively rare. Medieval treatises report generically about the use of Tyrian purple or of its cheaper substitutes; the most important treatise on miniature painting, the XIV century manuscript *De arte illuminandi* [7], did not even mention the use of Tyrian purple. In VII century, Isidore of Sevilla in his *Etymologies* [8] tells that “. . . purple parchment is stained with purple dye. . .” with no further indication. In the VIII century manuscript known as *Manoscritto di Lucca* or *Compositiones ad tingenda musiva* [9] three recipes are reported suggesting the use of different dyes to impart the purple colour to writing supports: n.24 “*De pelles alithinae tingere*” (On the dyeing of leather in purple red) using kermes, n.34 “*Tertius pandius*” (The third pandius) using madder and n.107 “*De tinctione porfire*” (On the dyeing in purple), the only one explicitly citing a purple dye from molluscs. Recently, Brun [10] cited a small treatise on the production of purple codices called *Conchylum*, datable to IV–V century A.D., in which a recipe describes a dyeing procedure typical of vat dyes such as indigoid dyes; this recipe does not explicitly mention the application to parchment, but one can reasonably think about parchment dyeing since the following recipes in the treatise describe preparation of gold and silver inks, which are typically used in writing on purple codices. Finally, Travaglio [11] cited another Early Medieval treatise, *Ut auro scribatur*, in which it is described the use of orchil, not of Tyrian purple, to colour parchment in purple; moreover, this treatise suggests that parchment has to be painted, not dyed. A similar procedure for colouring parchment is described in ms. Palatino 941, a XV century manuscript held at the Biblioteca Nazionale Centrale in Florence [12], in which the use of cloth shearings, the so-called *pezzuole* or *cimature*, is described. *Pezzuole* were soaked into extracts obtained from natural dyestuffs and rubbed on the parchment.

According to the above described bibliographic information, we can hypothesise that artists had the following materials at their disposal in order to impart the purple colour to parchment:

- Folium, the extract from *Chrozophora tinctoria*, a plant also known as turnsole.

- Orchil, the alkaline extract from lichens such as *Rocella tinctoria*.
- The application of a red anthraquinonic dye (e.g. madder, the extract from roots of *Rubia tinctoria*; kermes, the extract from *Kermes vermilio* scale insects; cochineal, the extract from *Porphyrophora polonica* or *Porphyrophora hamelii* scale insects – cochineal from *Dactylopius coccus* was not considered in this context for historical reasons) on a surface previously dyed with blue indigo, a technique already known to Romans and cited by Pliny the Elder [6].
- Tyrian purple, obtained from different species of molluscs (*Hexaplex trunculus*, *Bolinus brandaris* and *Stramonita haemastoma*).

The information coming from chemical analysis of purple codices is poor as well. In no case has Tyrian purple been identified on codices, but it must be noted that the direct identification of this substance is troublesome from the diagnostic point of view. HPLC has been frequently used in the analysis of textiles or of archaeological remains [13–15] but it must be considered that every chromatographic technique is intrinsically invasive and destructive, therefore its application is unfavourable for purple codices. In few cases non-invasive techniques such as Raman spectroscopy were used to identify Tyrian purple [16,17] but never on manuscripts.

The alternative to direct identification can be the detection of bromine, which is a key element in the molecule of 6,6'-dibromoindigotine (Fig. 1), acting therefore as indirect marker of Tyrian purple.

On the basis of this assumption, the presence of Tyrian purple has been hypothesised on some fresco paintings of Minoan age after X-ray fluorescence analysis [18]. Bromine could occur in historical and archaeological samples due to contamination, for example as a consequence of diagenesis processes in samples kept buried, of exposure to seawater aerosols or of the use of chemicals for conservation purposes; all these instances, though, are highly improbable if we consider an item kept inside museums or libraries such as a manuscript. We can therefore safely assume that, for what concerns purple colour in codices or miniatures, bromine could reasonably be paired to 6,6'-dibromoindigotine only. Bromine would have been identified by Porter [19,20] in a miniature painting of the *Barberini Gospels* codex (Vatican City, Biblioteca Apostolica Vaticana, ms. Barb. lat. 570); in that case, a single occurrence of bromine was found overall the codex and the presence of Tyrian purple was never confirmed with other direct techniques such as Raman spectroscopy or FT-IR. It must be noted that in other early Medieval codices analysed by Porter, bromine was not found at all. Aceto et al. [21] identified bromine in the VI century A.D. purple codex known as *Vienna Genesis* (Vienna, Österreichische Nationalbibliothek, Cod. Theol. Gr 31) but analysis with UV-visible diffuse reflectance spectrophotometry did not confirmed the presence of Tyrian purple in the same context.

Apart from these studies, very few other analytical works were performed on purple codices. In the pioneering work by Thomas and Flieder on the *Sinope Gospels* purple codex (Paris, Bibliothèque Nationale de France, ms. Suppl. gr. 1286) [22], GC-MS analysis

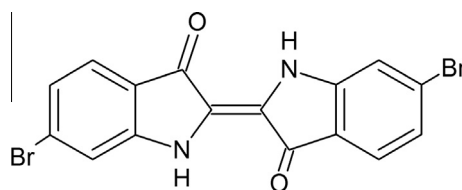


Fig. 1. Structure of 6,6'-dibromoindigotine.

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