A state-of-the-art report on the analytical characterisation of purple codices

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THE PURPLE CODICES

The purple codices are a small group of religious manuscripts, produced in Late Antiquity and the Early Middle Ages, in which purple parchment was used as a support for writing with inks made of noble metals (silver and gold, dx) and, in few cases, for miniature paintings (below)

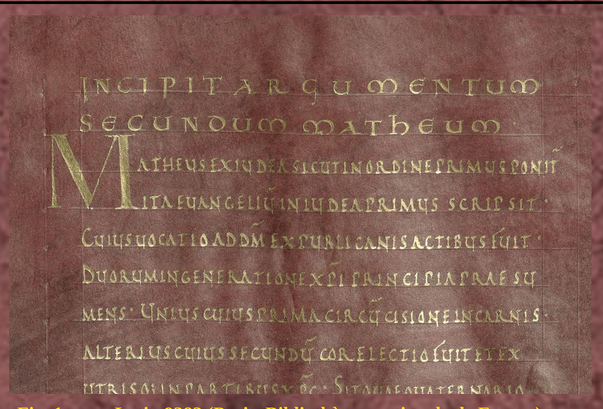

Fig. 1 – ms. Latin 9383 (Paris, Bibliothèque nationale de France)

Fig. 2 – *Vienna Genesis* (Vienna, Österreichische Nationalbibliothek))

Apart from the historical and artistic aspects, the analytical characterisation of these precious codices is relevant from the conservation point of view because of concerns about possible treatment procedures to be applied to the manuscripts and about the light sensitivity of the dyes. While the dye obtained from *Murex* is highly resistant to light,

It has long been assumed that the purple colour was obtained with Tyrian purple, the famous and highly prized dye produced from *Murex* molluscs. However, in the surviving medieval recipes, there is no explicit mention of the use of *Murex* for dyeing parchment. Furthermore, in earlier research on purple parchments, no direct evidence of Tyrian purple was found

Fig. 3 – A *Murex trunculus*

the purple colour imparted with lichens dyes or with folium (the dye obtained from the *Chrozophora tinctoria* plant) is highly fugitive

HISTORICAL RECONSTRUCTIONS

A strategic part in the research on purple codices (as in many other instances) is the making of *historical reconstructions*, i.e. the preparation of colourants according to ancient recipes and their application in paints or dyeings in order to build reference standards for spectroscopic analysis. The following dyes have been taken in consideration as possible candidates for parchment colouring:

- **orchil and other lichen dyes**
- **folium, the extract from *Chrozophora tinctoria***
- **Tyrian purple**
- **alkanet, the extract from *Alkanna tinctoria***
- **anthraquinonic dyes (e.g. madder, cochineal)**

Fig. 5 – *Chrozophora tinctoria* fruits of various hues

Fig. 7 – Palette with dyes laid on parchment

Fig. 4 – Different lichen species from which dyes were obtained upon extraction in ammonia (lichens provided by Isabella Whitworth)

Fig. 6 – Paints and dyeings with Tyrian purple prepared by Inge Boesken Kanold (thanks to Rolf Haubrichs)

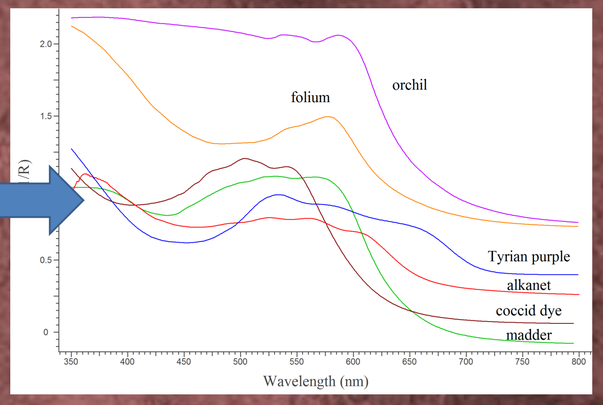

Fig. 8 – UV-visible diffuse reflectance spectrophotometry with optical fibres (FORS) analysis of standard purple dyes

CASE STUDIES

Scientific research on the purple codices has recently gained interest among conservators and curators, allowing analytical studies to be carried out in some cases. A list of analytical studies is shown below

Manuscripts	Library of museum	Period	Analysis	Dyes
Codex Veronensis	Verona, Biblioteca Capitolare, cod. VI	V	A. Wallert	alkanet
Codex Sarzanensis	Tortona, Biblioteca Diocesana	V-VI	M. Aceto *et al.*	orchil
Codex Palatinus	London, British Library, Add. ms. 40107	VI	C. Porter	?
Codex Brixianus	Brescia, Biblioteca Queriniana	VI	M. Aceto *et al.*	orchil, indigo, folium?
Codex Argenteus	Uppsala, Universitetsbiblioteket	VI	M. Aceto *et al.*	orchil, indigo
Psautier de S. Germain	Paris, Bibliothèque nationale de France, Latin 11947	VI	M. Aceto *et al.*	orchil, indigo
Vienna Genesis	Vienna, Österreichische Nationalbibliothek, cod. theol. gr. 31	VI	M. Aceto *et al.*	orchil
Codex Petropolitanus	Vienna, Österreichische Nationalbibliothek	VI	M. Aceto *et al.*	orchil
fragment of purple parchment	Vienna, Österreichische Nationalbibliothek, C2804	?	M. Aceto *et al.*	orchil
Codex Rossanensis	Rossano Calabro, Biblioteca Arcivescovile	VI	M. Bicchieri	orchil
Codex Sinopensis	Paris, Bibliothèque nationale de France, Suppl. grec 1284	VI	[1] M. Thomas, F. Flieder [2] M. Aceto	[1] folium [2] orchil
Zürcher Purpurpsalters	Zürich, Zentralbibliothek, RP 1	VI	R. Fuchs, D. Oltrogge	orchil
Coronation Gospels	Vienna, Kunsthistorisches Museum	VII-VIII	M. Aceto *et al.*	orchil, indigo
Evangiles dits de Saint-Denis	Paris, Bibliothèque nationale de France, Latin 9387	VIII	M. Aceto *et al.*	orchil, indigo
Evangiles de Saint-Germain-des-Prés	Paris, Bibliothèque nationale de France, Latin 11955	VIII	M. Aceto *et al.*	orchil
Lectionnaire de Vérone	Paris, Bibliothèque nationale de France, Latin 9451	VIII	M. Aceto *et al.*	orchil
Evangiles de Saint Riquier	Abbeville, Bibliothèque municipale, ms. 4	VIII	P. Roger	folium
Évangéliaire de Godescalc	Paris, Bibliothèque nationale de France, NAL 1203	VIII	P. Roger	folium
Bible dite de Théodulfe	Paris, Bibliothèque nationale de France, Latin 9380	IX	M. Eveno *et al.*	orchil
Salterio di Angilberga	Piacenza, Biblioteca Passerini-Landi	IX	M. Aceto *et al.*	orchil
Evangiles dits de Metz	Paris, Bibliothèque nationale de France, Latin 9383	IX	M. Aceto *et al.*	orchil, indigo
Evangeliarium	Paris, Bibliothèque nationale de France, Latin 1126	IX-X	M. Aceto *et al.*	orchil
Codex aureus Epternacensis	Nürnberg, Germanisches Nationalmuseum	XI	D. Oltrogge, R. Fuchs	orchil

Tab. 1 – List of the purple codices analysed up to now

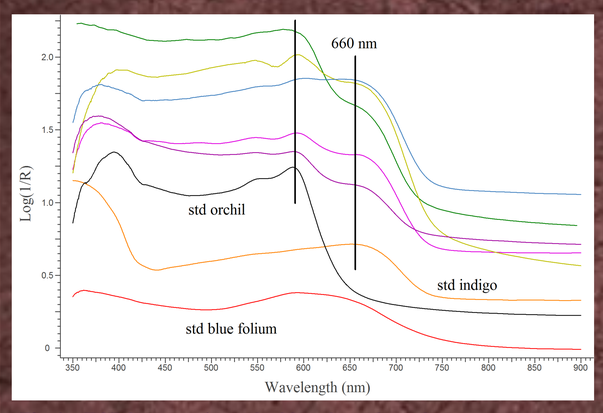

Fig. 9 – FORS spectra from double-coloured parchments

In a few instances it has been found analytical evidence that two dyes were used for colouring parchment. The first dye is orchil, while the second dye could be indigo according to the additional spectral features at 660 nm in the FORS spectra (*blue* folium, i.e. the extract from blue fruits of *Chrozophora tinctoria*, is another possible candidate). Most probably the final hue results from a two-steps procedure, with indigo applied first and orchil second, considering the respective hiding powers (indigo is indeed a pigment when used in painting artworks); additional analysis is needed in order to elucidate this features

ANALYTICAL DEVELOPMENTS

Besides non-invasive techniques (dx), powerful analytical techniques such as Surface Enhanced Raman Spectroscopy, MALDI-ToF-MS and HPLC-MS can be applied in a micro-invasive way (the table below shows the size of the samples needed by each technique) allowing to obtain a larger amount of information. This include:

- **a more reliable identification of the dye/dyes**
- **knowledge of their state of deterioration**
- **deeper insight into methods used to apply the dye/dyes**
- **identification of the species of origin of lichen dyes present (work in progress!)**

Technique	Information	Sample size
microscopic analysis	cross-section view	1 mm^2
MALDI-ToF-MS	dye/dyes identification	1 mm^2
SERS-Raman	dye identification	< 1 mm^2
HPLC-MS	dye/dyes identification	4 mm^2
C14	dating	20 mg

Tab.. 2 – List of sample sizes needed by micro-invasive techniques

Fig. 10 – Non-invasive measurements on the *Coronation Gospels*

The potential of micro-invasive techniques can be appreciated in the current study at Università degli Studi del Piemonte Orientale and Università degli Studi di Torino of a detached fragment of purple parchment from the *Codex Brixianus* (Brescia, Biblioteca Queriniana), on which it has been possible to perform micro-invasive measurements with SERS-Raman, MALDI-ToF-MS and HPLC-MS. Work is in progress in order to exploit the results obtained

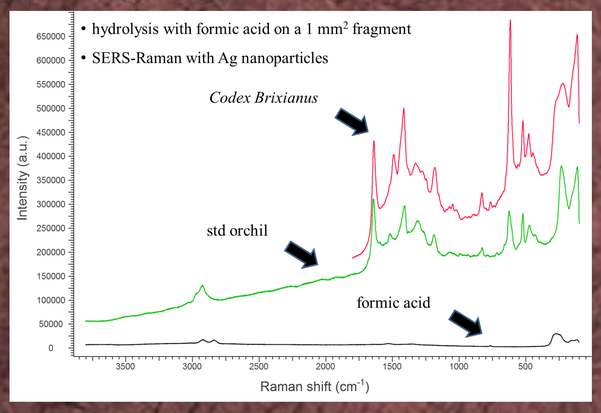

Fig. 11 – SERS-Raman analysis on a sample from *Codex Brixianus*

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