CHARISMA

Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration

Review of extraction methods for the characterisation by HPLC of organic colorants in textiles and pigments in cultural heritage objects

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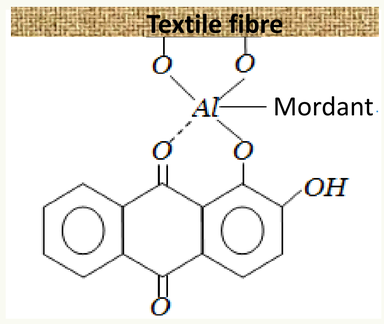
Introduction

Within the European project CHARISMA, five laboratories undertaking colorant research have reviewed the literature relating to the extraction of organic colorants in cultural heritage objects for HPLC analysis. A database is being created, to be made available to the scientific and heritage community, containing a standardised description of the extraction protocols. The project partners are undertaking comparative studies of the different extraction methods for a range of textile, pigment and paint standards in order to establish the advantages, limitations and applicability of the methods and propose an optimised approach for the study of colorant in the cultural heritage sector.

The unique nature and typically small size of samples, the effects of time and past treatment and the diverse range of potential biological sources make identification of the natural organic colorant source for dyes and pigments in cultural heritage contexts highly challenging. Selection of the most appropriate extraction method to solubilise the constituents of the colorant for HPLC analysis is a further problem. For samples from cultural heritage objects, extraction must not only dissolve the molecular constituents, but typically must free the colorant components from the fibre or dye–mordant complex (for textiles and other dyed materials), or from the pigment substrate and frequently also from an additional matrix (such as the paint binding medium) as illustrated.



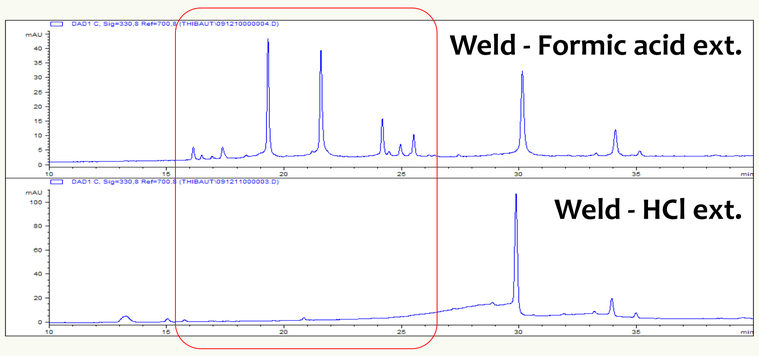
Workshop of Albrecht DÜRER, NG 5592: cross section with paint layers containing red lake pigments in oil

Results of the review

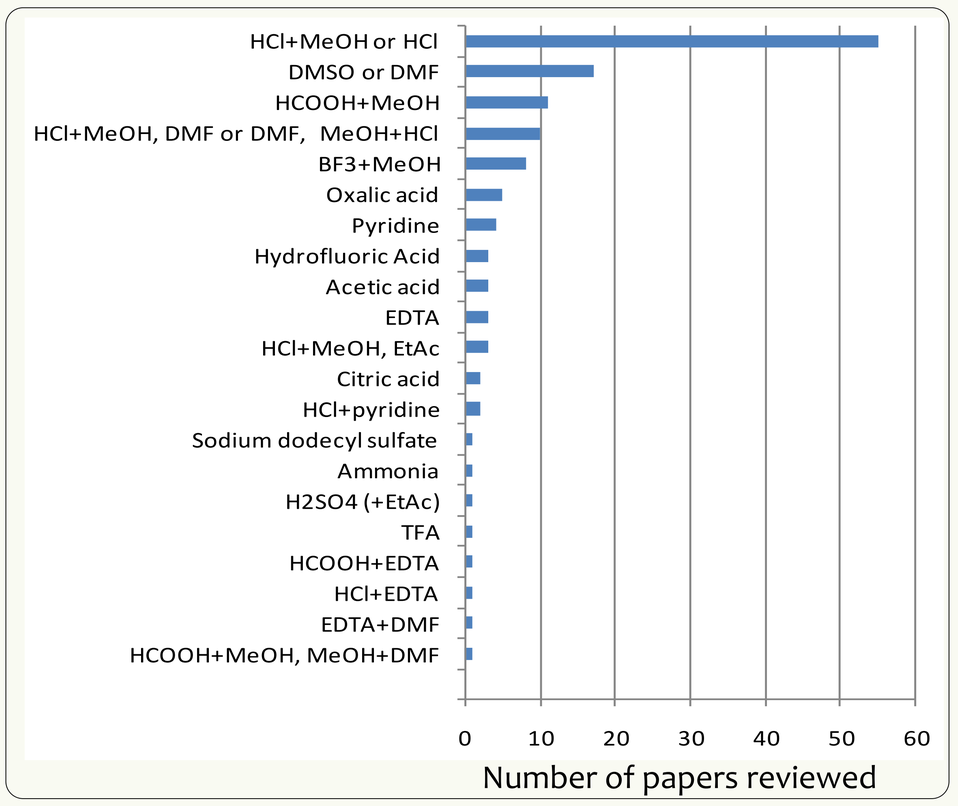
A number of different extraction methods have been developed and applied to characterise organic colorants used as dyes or pigments in a large range of objects from the cultural heritage. Some of these techniques have been optimised for particular colorant classes, or to allow highly quantitative extraction from tiny samples, or are designed for particular sample types (e.g. dyed textiles but not paint), etc. The template below was created to allow systematic review. This template includes a detailed description of the extraction procedure, the nature of the materials analysed, the chemical compounds identified, the instrumentation used and all bibliographic details.

Description of the extraction procedure	Cultural Heritage materials		Reference materials	Results				Instrument	Authors	Reference	Related publications
	Dyes (textiles)	Pigments (painting samples, ceramic, etc.)	Reference colorants	General statements	Anthra quinones	Indigoids	Flavonoids				

Over 100 papers were **reviewed** and **21 extraction methods for organic dyes and pigments** were **identified.** Most of the papers are dedicated to the study of dyed textiles. Only few papers present the study of pigments or painting samples. More than 50% of the papers refer to the method developed by Wouters using **HCl extraction** to free the dye from the fibre (particularly for mordanted fibres) [1]. 17 papers using **DMSO and DMF extraction** were also reviewed. These papers mainly focus on indigoids dyes. Surowiec developed a combined method allowing simultaneous extraction of anthraquinones and indigoids [2]. A number of other variants of the HCl method were also reported. The limitation of the HCl-based methods remains the hydrolysis of the glycosides (as illustrated on the chromatogram with analyses of weld) and loss of chemically labile components such as brasilein and carotenoids.



Therefore there is growing interest in so-called **'soft' extraction** methods that preserve the glycoside content or other chemically labile components which can be highly informative of the biological source and/or dyeing or pigment-making technologies [3], and multi-step or combined extraction procedures. Such approaches allow a wider range of colorant classes or mixtures of colorants to be explored.



Methods	Advantages	Limitations
HCl+MeOH or HCl	Good extraction and sensitivity particularly for mordant dyes on textiles	Loss of information: hydrolysis of glycosides/loss of labile components
DMSO or DMF	Good extraction for indigoids	Low extraction of other dye classes
HCl+MeOH, DMF or DMF, HCl+MeOH	Good extraction of indigoids and anthraquinones	Loss of information: hydrolysis of glycosides/loss of labile components
BF_3+MeOH	Good extraction of colorant from substrate contained in binding media	Methylation Not optimised for all sample types
Hydrofluoric acid	Good extraction of colorant from substrate contained in binding media	Health and Safety issues Not optimised for all sample types
Formic acid or oxalic acid or EDTA	Soft extraction	Not optimised for all dye classes

[1] J. Wouters, *Studies in Conservation*, 1985. 30, 119–128
[2] I. Surowiec, A. Quye and M. Trojanowicz, *Journal of Chromatography A*, 2006, 1112(1-2): 209-217
[3] X. Zhang and R. Laursen, *Analytical Chemistry*, 2005, 77(7) 2022-2025

Based on current knowledge, the advantages and limitations of some of the extraction procedures are noted in the table. The methods variously include steps to break the dye-metal or dye-substrate interaction, to chelate metals from the mordent/ substrate, to solubilise the dye components and to disrupt the matrix. Partners have selected a number of the extraction methods from the review to compare (DMF, DMSO and ethyl acetate, oxalic and formic acids, EDTA/DMF, BF3 and HF, TFA and citric acid) with a view to establishing their advantages, limitations and wider applicability. The most promising method(s) will also be optimised for a wide range of colorant classes and sample types and novel combined or multi-step approaches explored.

Conclusions

This review identified 21 extraction methods used for HPLC analysis of organic dyes and pigments in the cultural heritage sector, including many so-called 'soft' methods, and highlighted their advantages and limitations. This review will continue to be updated as new methods are published and will be made available via an online searchable database available to the scientific community, and extended to include relevant "non-cultural heritage literature". On the basis of this review, project partners are now testing and optimising selected extraction procedures using a standard set of reference materials (including the most common European dyes). The final aim is to develop a flow chart allowing analysts to choose the most appropriate extraction procedure for any kind of cultural heritage sample.

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