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High performance liquid chromatography as a micro-destructive technique for the identification of anthraquinone red dyestuffs in cultural heritage objects

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Abstract: This article describes two of the most common natural sources of red anthraquinones that have been used since antiquity for textile dyeing and as lake pigments, namely cochineal insect and the roots of *Rubia* and *Relbunium* plants. Carminic acid is the main component of carmine, the red colorant obtained from cochineal. Alizarin and purpurin are found in the extracts of *Rubia* roots, but *Relbunium* roots contain only purpurin. These red anthraquinones have been identified in a variety of cultural heritage objects. High performance liquid chromatography with diode array detection (HPLC-DAD) is described as the most suitable analytical technique for the identification of these dyestuffs, particularly in micro-samples from textiles or pigment layers in paintings and polychrome sculptures. Finally, application of HPLC-DAD analysis to the identification of lake pigments in micro-samples of mural paintings of two eighteenth century Andean churches in Peru is described.

Keywords: alizarin; carminic acid; cultural heritage; high performance liquid chromatography; purpurin.

Introduction

Organic colorants obtained from plants and insects have been the principal dyestuffs for textile dyeing until the discovery of synthetic dyes in the nineteenth century. They belong to various chemical types, such as flavonoids (yellow), anthraquinones (red) and indigoids (blue and violet) (Cardon, 2007; Hofenk de Graaff, 2004). The majority of natural dyes require a mordant to promote their fixing on the fibers and to prevent fading of the colors. Mordants work by forming chemical bonds between the dye molecules and the fiber. They are commonly salts of iron, aluminum, chromium, tin, and copper. It is well known that the color of a dye depends on the type of mordant used due to the formation of metal complexes that cause a change in the molecular orbitals energy and hence a shift in UV/visible absorption bands (Cardon, 2007). Natural organic colorants are also used as pigments mostly in the form of lakes. These are obtained by precipitation of the colorant on an inorganic support, such as potash alum (potassium aluminum sulphate) (Kirby et al., 2005). Anthraquinones are among the most used red

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colorants that are obtained from plant and animal sources. One of the oldest and most popular dyestuff used as pigment and dye is carmine, a red colorant obtained from cochineal, the dried bodies of the female scale insect *Coccus cacti (Dactylopius coccus* Costa), which are found on different varieties of cactus, including *Opuntia cochenillifera* Mill (Schweppe et al., 1986). Cochineal was the main red dye used in Central and South America before the Spanish conquest. During the sixteenth century it was imported into Europe and began to replace the domestic kermes as a source of colorant for dyeing and for the preparation of lakes for painting. Other cochineal species such as Polish cochineal (*Porphyrophora polonica* Linnaeus) and Armenian cochineal (*Porphyrophora hameli* Brandt) were known since Antiquity (Cardon, 2007). Carminic acid, an hydroxyanthraquinone linked to a glucose unit in the pyranoside form (Figure 1), is the main coloring principle of cochineal extract and accounts for *ca.* 95% of the colorants produced by *D. coccus* insects. This anthraquinone glucoside is also used in cosmetics and in the food industry to replace synthetic colorants (González et al., 2010; Schweppe et al., 1986).

Two shades of red are mainly obtained in the dyeing of textiles with cochineal. Crimson, a deep red color, is produced using alum as mordant while a brilliant scarlet is obtained with tin salts. Copper and iron have been less frequently used as mordants for cochineal (Hofenk de Graaff, 2004; Mikropoulou et al., 2009).

Among plants, the Rubiaceae family comprises the most used source of red anthraquinones in all civilizations, as for example madder (*Rubia tinctorum*). The fresh roots of this plant contain principally two coloring substances: alizarin (1,2-dihydroxyanthraquinone) (1) and pseudopurpurin (1,2,4-trihydroxyanthraquinonecarboxylic acid) (2). On storage and manufacturing of madder roots pseudopurpurin renders purpurin (1,2,4-trihydroxyanthraquinone) (3) (Figure 2) by decarboxylation (Schweppe & Winter, 1997). In this way, alizarin and purpurin are the main anthraquinones in madder extracts.

Purpurin is found in the roots of other Rubiaceae plants, such as *Relbunium hypocarpium* L. Hemsley, which are indigenous to South America (Schweppe & Winter, 1997). The absence of alizarin in *Relbunium* roots allows to distinguish it from *R. tinctorum*. These differences are helpful when trying to assess the plant source of these



Figure 2: Anthraquinones in madder: alizarin (1), pseudopurpurin (2) and purpurin (3).

anthraquinone compounds. As for cochineal, the mordants used for textile dyeing are mainly alum, iron and tin (Hofenk de Graaff, 2004). Madder was also prepared as a lake on inorganic supports such as gypsum, calcium carbonate, clays and lead (Schweppe & Winter, 1997).

The great interest in the identification of natural dyes in heritage objects has promoted the development of analytical procedures with high sensitivity. High performance liquid chromatography (HPLC) coupled with UV-visible or mass spectrometry detectors are today the main chromatographic techniques used to characterize colorant compounds in very small samples (Petroviciu et al., 2010; Rosenberg, 2008; Serrano et al., 2011). Carminic acid has been identified by HPLC with diode array detection (DAD) in historical textiles (Petroviciu et al., 2010; Serrano et al., 2011; Serrano et al., 2015), polychrome sculptures (Tomasini et al., 2016) and garments (Karapanagiotis et al., 2008). In South America, cochineal was detected in pre-Columbian Peruvian textiles associated with mummies from the Chancay, Chimu and Inca cultures (1000-fifteenth century A.D.). (Degano & Colombini, 2009). Carmine was frequently used as a lake pigment in seventeenth and eighteenth Colonial Andean paintings on canvas (Siracusano et al., 2015; Siracusano, 2011). Owing to its translucent nature, it was generally applied as a glaze or mixed with other pigments, such as basic lead carbonate (lead white) for flesh tones or indigo to obtain a dark purplish colour. In 2018, we reported for the first time the identification of carmine lake in a mural painting of an eighteenth century church of the town of Pachama in the north of Chile (Tomasini et al., 2018). This finding added new information on the Andean Colonial mural painting palette.

Madder lakes were identified by HPLC-DAD in wall paintings in Greece and Italy since Ancient times (Aceto, 2021). In South America, *Relbunium* species were used as source of red dyes by pre-Columbian civilizations. Father Bernabé Cobos registered the use of the so-called Chapi-chapi (*Relbunium hipocarpium*) by indigineous people in the Andes for wool dyeing (Cobo, 1890). Analysis by HPLC-DAD of textile fragments from the archaeological site Doncellas in Jujuy province (Argentina) identified purpurin as the red colorant and hence *Relbunium* roots as the dyeing source (Gómez, 2014). A mixture of alizarin and purpurin was identified in red wool fragments on a skeleton recovered from the wrecksite of the eighteenth century sloop of war HMS *Swift* in Patagonia. This last finding is in accordance with the use of madder as dyestuff in the manufacture of red coats born by British soldiers and marines from the seventeenth to the nineteenth centuries (Maier et al., 2010). Madder lake has been identified in an eighteenth century polychrome sculpture produced in the Jesuit Mission of Trinidad (Paraguay) (Gómez et al., 2010) and in a painting from the series of the Sybils housed at the church of San Pedro Telmo in Buenos Aires (Marte et al., 2014).

High performance liquid chromatography with diode array detection (HPLC-DAD)

This is an analytical technique that originates in column chromatography where compounds in a mixture are separated according to their interactions with a solid stationary phase and a liquid mobile phase. In traditional column chromatography, stationary phases with particles of 63–200 μ m diameter are generally used and atmospheric pressure is enough to elute the mobile phase through the column. In analytical HPLC, stationary phases with spherical particles generally of 3 or 5 μ m are utilized. Therefore, pumps are needed to apply the mobile phase with high pressures, ranging from 20.3 to 40.5 kPa (equivalent to 200–400 atmospheres), to deliver a constant and stable flow of the solvent, even if its composition changes during the analysis. In reverse-phase (RP) HPLC, the most commonly used stationary phase consists of modified silica with octadecyl (C₁₈) groups chemically bonded to silica, rendering a non-polar stationary phase. In this way polar compounds elute at lower retention times than non-polar compounds. Typical solvents used in RP-HPLC are mixtures of methanol or acetonitrile with water, with the addition of low percentages (1% (v/v)) of aqueous orthophosphoric or trifluoroacetic acids. Diode array detectors allow detection of the separated compounds in the column at a wavelength range of 200–700 nm together with the acquisition of UV-visible spectra of the compounds, which can help in their identification (Bidlingmeyer, 1992).

Analysis of cochineal and madder by HPLC-DAD

Commercial samples of carminic acid and madder lake were purchased from Merck and Kremer Pigmente, respectively. As components in the madder lake are fixed on an inorganic support by forming a chelate complex, a hydrolysis step is required to release the dyestuffs for HPLC analysis. This was achieved by acid hydrolysis with a mixture of H₂O:MeOH:37% HCl (1:1:2, v/v) at 100 °C for 15 min. After evaporation of the liquid phase under nitrogen, the dry residue was dissolved in MeOH, filtered and submitted to HPLC (Tomasini et al., 2016). HPLC–DAD analysis of carminic acid and madder components was carried out with a Gilson 506C HPLC system using a Phenomenex Gemini 5 μ column (25 cm \times 4.6 mm internal diameter). Gradient elution was performed with mixtures of MeOH and 1% (v/v) aqueous orthophosphoric acid as solvents, as described previously (Tomasini et al., 2016).

Analysis by HPLC-DAD of commercial carminic acid revealed the presence of carminic acid as the main component together with small amounts of other red colorants, such as two isomers of carminic acid that differ in the stereochemistry of the anomeric carbon of the glucofuranose moiety (2-C-glucofuranosides of kermesic acid (DCIV and DCVII)) and 3,4-dideoxycarminic acid (DDCA) (Figure 3) (Stathopoulou et al., 2013).

Carminic acid and its isomers DCIV and DCVII showed identical UV-visible spectra with a strong UV peak at 275 nm and a broad peak at 495 nm. Similarly, DDCA displayed a peak at 276 nm and a broad peak at 488 nm (Figure 4).

Analysis of hydrolysed madder lake by HPLC-DAD rendered two peaks at 18.4 and 19.9 min corresponding to alizarin and purpurin, respectively. The UV-visible spectrum of alizarin is characterized by a strong peak at 248 nm with a shoulder at 281 nm and a broad peak at 431 nm. Purpurin exhibits a strong peak at 255 nm and two broad peaks at 293 and 480 nm (Figure 5).

The difference in retention times and UV-visible spectra for alizarin, purpurin and carminic acid enables their identification in the same HPLC analysis. For example, in Figure 6 the chromatogram of a yarn of a textile from the archaeological site Doncellas housed at the Ethnographic Museum of the University of Buenos Aires showed the presence of carminic acid and purpurin, revealing the use of a mixture of cochineal and *Relbunium* roots extracts as the dyeing sources (Gómez, 2014). Interestingly, the use of a DAD detector allowed the analysis of the chromatogram at two different wavenumbers: 255 nm is adequate for the detection of purpurin while 274 nm is more appropriate for the identification of carminic acid.

Case study: characterization of a red lake in two Colonial Andean mural paintings

Traditional methodologies for the characterization of pigments in works of art involve the application of multianalytical techniques to characterize inorganic and organic components in painting layers. Generally, microsamples are collected with a scalpel from different areas of a painting and are embedded into an acrylic



Figure 3: Red anthraquinones DCIV, DCVII and DDCA.



Figure 4: HPLC chromatogram of commercial carminic acid and UV-visible spectra of carminic acid and DDCA.

transparent resin. After polishing up to the exposure of the different ground and painting layers, cross-sections of the samples are obtained. These can be analyzed by microscopic and spectroscopic techniques to obtain information on pigments and the painting technique. Scanning electron microscopy with an energy dispersive X-ray detector (SEM-EDS) and micro-Raman spectroscopy are the most applied techniques for the analysis of inorganic pigments in cross-sections (Casadio et al., 2016). Indigo, an organic colorant that does not require the preparation of a lake for its use as pigment is easily detected by micro-Raman spectroscopy (Tomasini et al., 2018). On the contrary, lake pigments such as carmine show Raman spectra with high fluorescence together with peaks from the inorganic support in the lake. This fact and the low concentration of the dyestuff in the lake can hinder its identification by micro-Raman spectroscopy in an artwork sample (Tomasini et al., 2016). Surfance-enhanced Raman spectroscopy (SERS) has made a great contribution to the analysis of organic dyes in cultural heritage, but in comparison to HPLC it is not the best choice for the identification of mixtures of dyestuffs (Casadio et al., 2010). Therefore, HPLC analysis of a micro-sample where the presence of a lake pigment is suspected provides a reliable and sensitive methodology for the identification of organic pigments in works of art.

In South America, several Colonial churches in the Andean region preserve seventeenth and eighteenth century mural paintings. These artworks show the iconography of the life of Christ, the Virgin Mary and the saints, together with punishment scenes like the Hell and the figure of Leviathan, all enclosed with decorations of flowers, birds and trees. These paintings were vital for the Catholic evangelization of the native population during the Spanish domain in the Andean region (Guzmán et al., 2017).



Figure 5: HPLC chromatogram of hydrolysed madder lake and UV-visible spectra of alizarin and purpurin (Gómez, 2014).



Figure 6: HPLC chromatogram of an archaeological textile at two different wavelength, CA: carminic acid. (Gómez, 2014).

During a campaign carried out in 2015, in the framework of an interdisciplinary project between art historians, chemists and restorers from Argentina, Chile and Bolivia, we have surveyed the mural paintings of two Andean Colonial churches located in the south of Peru, namely the Holy Cross of Our Lady of the Rosary of Orurillo and Saint Francis of Assisi of Marcapata. The aim of our investigation was to characterize the pigment palette and the paining technique. Therefore, several micro-samples were collected from the mural paintings of both churches. Analysis by infrared spectroscopy of the preparation layer of the samples indicated a mixture of gypsum (CaSO₄.2H₂O) and anhydrite (CaSO₄) as the ground applied onto the adobe walls (Careaga et al., 2021). Optical microscopy examination of the cross-sections of two red samples, Oru 10 and Marca 02, collected from the mural paintings of the Orurillo and Marcapata churches, respectively, revealed a very simple painting technique with a thin red pigment layer on the calcium sulfate ground (Figure 7).

Due to the absence of a red inorganic pigment in Oru 10 and Marca 02 samples, as determined by infrared spectroscopy of the pigment layers, the presence of a lake pigment was inferred. Particles of both red samples were selected under the stereomicroscope and submitted to acid hydrolysis for HPLC-DAD analysis. Chromatograms of both samples (Figure 8) revealed a peak at 13.7 min whose UV-visible spectrum showed bands at 275 and 495 nm, in accordance with the reference of carminic acid. In this way, we confirmed the use of a carmine lake in the mural paintings of both churches. These results, together with our previous identification of carmine lake in a mural painting in the church of Pachama in the north of Chile (Tomasini et al., 2018), are indicative of the importance of this red organic pigment in the palette of eighteenth century Andean mural paintings. Further research on red pigments in mural paintings from other Colonial churches of the Andean region will contribute to determine how widespread the use of carmine lake was in these unique artworks.



Figure 7: Mural paintings of two Andean Colonial churches in Peru. (A) Detail of mural painting of the church of Saint Francis of Assisi of Marcapata and indication of sample Marca 02 location and its cross-section; (B) detail of mural painting of the church of the Holy Cross of Our Lady of the Rosary of Orurillo and location of sample Oru 10 and its cross-section.





Conclusions

HPLC-DAD is a fast and sensitive analytical technique for the reliable and specific detection of organic dyestuffs in micro-samples from cultural heritage objects. Characterization of the composition of colorants in ancient textiles gives information on the availability of natural resources and dyeing practices of different cultures around the world. On the other hand, identification of lake pigments in paintings contributes to the knowledge about original organic pigments and the way they were used in the creation of artworks. This can be contrasted with past manuscripts, manuals and treatises refering to painting techniques, and lists of materials in inventories, testaments, or churches' fabric books that frequently include lakes without specifying their composition. All this information is relevant for the selection of suitable restoration and conservation methods of cultural heritage objects.

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