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Multi-technique characterisation of commercial alizarin-based lakes

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ABSTRACT

The characterization of ancient and modern alizarin-based lakes is a largely studied topic in the literature. Analytical data on contemporary alizarin-based lakes, however, are still poor, though of primary importance, since these lakes might be indeed present in contemporary and fake paintings as well as in retouchings.

In this work we systematically investigate the chemical composition and the optical features of fifteen alizarin-based lakes, by a multi-analytical technique approach combining spectroscopic methods (i.e. Energy Dispersive X-ray Fluorescence Spectroscopy, EDXRF; Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy, ATR-FTIR; X-ray Powder Diffraction, XRD; UV induced fluorescence and reflectance spectroscopies) and chromatography (i.e. High-performance Liquid Chromatography coupled with a Photodiode Array Detector, HPLC-PDA). Most of the samples contain typical compounds from the natural roots of madder, as occurring in ancient and modern lakes, but in two samples (23600-Kremer-Pigmente and alizarin crimson-Zecchi) any anthraquinonic structures were identified, thus leading to hypothesize the presence of synthetic dyes.

The detection of lucidin primeveroside and ruberythric acid in some lakes suggest the use of *Rubia tinctorum*. One sample (23610-Kremer-Pigmente) presents alizarin as the sole compound, thereby revealing to be a synthetic dye. Moreover, gibbsite, alunite and kaolinite were found to be used as substrates and/or mordants.

Visible absorption spectra of the anthraquinonic lakes show two main absorption bands at about 494–511 nm and 537–564 nm, along with a shoulder at about 473–479 nm in presence of high amounts of purpurin. Finally, from the results obtained by UV induced fluorescence spectroscopy it is possible to figure out that, although it is commonly assumed that the madder lake presents an orange-pink fluorescence, the inorganic compounds, added to the recipe, could induce a quenching phenomenon or an inhibition of the fluorescence, as occurring in some commercial alizarin-based lakes.

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1. Introduction

Red dyes are organic substances that were commonly used as artists' materials since ancient times. Some of them are based on the anthraquinonic structure and can be obtained from insects, such as cochineal (carminic acid), kermes (kermesic acid) or can be extracted from plants, such as dyers' madder (containing alizarin). To use them in paintings, a mordant must be added to the dyes (the most common compound was potash alum [Al₂(SO₄)₃K₂SO₄·12H₂O]). The metal ions (for example Al³⁺) links to specific functional groups of the dyes forming an insoluble metal–dye complex; the excess of the mordant

precipitates into a solid compounds, which becomes the lake substrate [1].

Madder lake is a pigment commonly used in art since ancient times, indeed its employment has been found in Egyptian, Roman and Asian context. It was used for dyeing textiles like cotton, silk, wool, and as pigment for paintings [2]. It was rarely used in Europe in Middle Ages paintings [3], but its application became common from the fifteenth to the eighteenth century [4].

This type of lake is obtained from a vegetable dye, mainly extracted from the roots of *Rubia tinctorum* L. The main organic compounds contained in the madder lake are the hydroxyanthraquinones, such as alizarin (1,2-dihydroxy-anthraquinone), purpurin (1,2,4-trihydroxy anthraquinone), pseudopurpurin (1,2,4 trihydroxy-3-carboxyanthraquinone), lucidin (1,3-dihydroxy-2-hydroxymethylanthraquinone), xanthopurpurin (1,3-

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dihydroxyanthraquinone) and rubiadin (1,3-dihydroxy-2-methylanthraquinone) [2].

However, the composition of the organic fraction of the lake is mainly related to extractive methods of the dye from the roots.

For example, by treatment of the root with acids, the constituting glycosides (e.g. garancine or similar products) hydrolyze and, ultimately, the lake contains low quantity of ruberythric acid (alizarin-2- β -*O*-primeveroside) while the pseudopurpurin, which converts into purpurin, is completely absent [4]. On the other hand, by soaking the madder roots in sulphurous acid a mixture of pseudopurpurin, purpurin and traces of other anthraquinones is obtained. This type of lake was called “Kopp's purpurin” and was widely used in France until the nineteenth century [5]. In the eighteenth and nineteenth centuries, the use of natural dyes has been largely widespread due to the technological advancement of the textile industry and chemical science applied to dyes. In this period the development of more efficient methods for the extraction of the colorants from natural dyes increased, leading to the introduction of lake recipes different from those previously used [4]. While several practical procedures for the manufacture of madder lakes are available until the XIX century [2,4,6,7], there are only limited information on contemporary formulations yet. In particular, the technical datasheets of the commercial products report the chemical reduction of the *Rubia* species used for the production of madder lakes; additionally, there is also indication of the use of roots coming from the same geographic area (i.e. Turkey) to realize different target products. Moreover, contemporary madder lakes could contain synthetic (i.e. alizarin) rather than natural dyes, the former being available on the market by the end of the XVII century [4].

Besides the extraction methods, the final composition of the lakes depends on the nature of the substrates and mordants used. The mordants determine a specific hue and are typically aluminium, tin, iron, copper and barium salts that could have been intentionally added to fix the dyes to a substrate [2]. Traditionally, aluminium-based compounds and alkali metals, obtained from wood ashes, as well as calcium compounds such as chalk, marble powder and egg shells have been added during the manufacture process of lakes.

The identification of the inorganic fraction of the lakes can be performed either in situ by means of portable X-ray fluorescence spectroscopy (XRF) and Infrared and Raman Spectroscopies or through the analysis of samples by means of Scanning Electron Microscopy with Energy-Dispersive Spectroscopy (SEM-EDS), X-ray Diffraction (XRD) and fixed spectroscopies. For the analysis of the dyes, chromatographic techniques are commonly preferred, but to employ this protocol it is necessary to withdraw a sample and perform a proper chemical-physical treatment. In the early 1980s the identification of natural dyes was performed using Thin Layer Chromatography (TLC): later on, this technique was replaced by High-performance Liquid Chromatography (HPLC) [8–10] and barely by Gas Chromatography coupled to Mass Spectrometry (GC–MS) [11].

In recent years, some authors have applied the reflectance spectroscopy [12] and the visible fluorescence emission induced by UV sources [13–15] to the identification of madder lake on painted surfaces, since the optical properties of madder lakes are dependent on the transitions between the electronic states of the hydroxy-anthraquinones [16] and of the organo-metallic complexes [1].

Moreover, the addition of metal salts into the dyeing matter induces different hues of the madder lake pigments [4,17,18], which means that the absorption bands may occur at different wavelengths. Some research groups focused on the complexation of alizarin or purpurin or quinizarin [18–20].

The identification of madder lakes on paintings by UV induced fluorescence spectroscopy, is still an issue, considering that, in some cases, they might do not show any fluorescence [21], although it is commonly reported that they emit a pink-orange fluorescence under UV radiation [2,7]. Schweppe et al. [2] argue that the madder lake, illuminated by an UV source, emits an orange fluorescent colour,

enabling a distinction from animal lakes, such as kermes and cochineal, which conversely show a bright pink; lake of alizarin does not display fluorescence. Daniels et al. [7] report that Purpurin- Al^{3+} and Alizarin- Al^{3+} complexes show emission maxima at about 551–595 nm and 640 nm. Kirby et al. [4] argues that in many paintings of the second half of the nineteenth century the lakes that have low concentration of alizarin and very high amounts of pseudopurpurin show an intense orange fluorescence. Clementi et al. [1] investigate madder lakes obtained from different sources (wool fibers and plants), demonstrating that the plant-derived lake only presents a maximum of fluorescence emission around 600 nm, while those obtained from textile fibers shows an additional shoulder at about 570 nm. Larson [22] reports that alizarin precipitated with potassium, zinc and aluminium salts, shows a luminescence, while in the complexations with cobalt, nickel and copper any luminescence is detected. This implies that also the type of metal ion can induce a fluorescence phenomenon. Indeed, Claro et al. [13] argues that the addition of metal ions may induce a significant contribution in the global fluorescence emission.

From this brief review it is clear that a multi-analytical approach that enables the identification of both the organic and inorganic fractions of madder lakes, could be useful to gain insights into the correlation between the spectral behaviour and the chemical composition. Moreover, although the identification of ancient and modern madder lakes or lakes produced following historical recipes is a subject of great topical interest, analytical data on commercial madder lakes are still poorly available. These latter may be used for retouchings and/or forgeries of paintings and their characterization is required to distinguish them from ancient ones, where possible.

The aim of this work is to assess if commercially available alizarin-based lakes show the same chemical composition and optical properties of ancient or modern madder lakes. Fifteen commercial alizarin-based lakes have been characterised performing a multi-technique analytical study by integrating complementary spectroscopic methods (X-ray Fluorescence Spectroscopy, XRF; X-ray Diffraction, XRD; Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy, ATR-FTIR; UV induced Fluorescence and Reflectance Spectroscopies) and chromatography (High-performance Liquid Chromatography coupled with a Photodiode Array Detector, HPLC-PDA). The collected results have been compared with those reported in literature for the ancient and modern lakes or recipes in terms of organic fraction, dyestuff substrates and mordants. By using modern products as reference, the indirect identification of the matter constituting a painting may be possible, being the original materials generally not available. However, modern products could be different from the original ones, thus this work provides not only scientific data to perform an appropriate choice of the commercial madder lake reference that could be present in fake and retouched paintings, but also lays the foundations for the future pictorial material identification of the contemporary paintings, that should be a topic for the future generation, such as the investigation of ancient paintings is for us. This analytical report, performed on sample powders, is the first step for a more extensive study that will involve the analysis of pigment/binder mixtures like those found in real paintings.

2. Materials and Methods

2.1. The Samples

The fifteen alizarin-based lakes analysed in this study were purchased as powders from two Sales Companies: Zecchi (Florence) and Kremer-Pigmente (Germany). We analysed also a sample of *Rubia tinctorum* in pieces purchased from Zecchi (Florence). The identification code, the product name, the description and the colours of the samples used in this study as provided by the Sale Company are reported in Table 1. The appearance of the fifteen lakes is shown in Fig. 1.

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