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A spectrometric and chromatographic approach to the study of ageing of madder (*Rubia tinctorum* L.) dyestuff on wool

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Abstract

In this work, the lightfastness of wool textile samples, dyed with madder and its principal components alizarin and purpurin, was investigated using two complementary experimental techniques: absorption and emission UV-vis spectroscopy and chromatography (HPLC-PDA). Spectroscopic techniques were used to follow the time course of ageing, whereas chromatography was applied to determine relative compositional changes that occurred after exposure of wool dyed samples to natural and artificial ageing. The results from the two techniques integrate well each other and provide complementary and useful indications about the sensitivity of the dyed textiles to ageing, showing that purpurin is the principal component responsible for the spectral and chromatic properties of madder as well as for its degradation. The fading of both the fibre and dye is reduced in the presence of alum and in the absence of oxygen. The multi-analytical approach used highlights the potential of the UV-vis spectroscopy for the investigation of dyes on textiles. The great sensitivity of the spectrofluorimetry makes this technique particularly promising for a non-destructive study of dyes on works of art.

Keywords: Madder (*Rubia tinctorum*); Alizarin; Purpurin; Ageing; UV-vis spectroscopy; Liquid chromatography (HPLC-PDA)

1. Introduction

Dyer's madder is one of the oldest and most popular red dyestuff found in nature on the Eurasian super-continent. Extracted from dried roots of *Rubia tinctorum* L., madder has been used since antiquity for dyeing textiles (in particular in Europe, the Middle East and India [1] where the plant was indigenous). Belonging to the group of mordant dyes, madder requires a pre-treatment of textile fibres with a solution of mordant. The metal salt most frequently used as mordant was alum, often together with cream of tartar. By using different metal ions and varying the dyeing recipes, a wide scale of shades can be obtained: pink, red, purple and black [2].

The colouring matter of *R. tinctorum* L. roots is funded on antraquinone dyes. The principal ones are alizarin (1,2-dihydroxy-anthraquinone) and purpurin (1,2,4-trihydroxy-anthraquinone), but other anthraquinones such as pseudopurpurin, xanthopurpurin, rubiadin and munjistin are also present, mostly in glycoside forms [3–5].

Several artistic objects, especially textiles, undergo colour changes which modify their appearance from the original chromatic conception. This not only has significant consequences on the aesthetic and iconographic interpretation of the works of art, but also makes the identification of natural dyes primary sources difficult. Dye ageing processes noticeably depend on environmental and conservation conditions. Photochemical degradation, due to light exposure, is one of the most important factors of ageing. The lightfastness properties (that is the degree to which a dye resists fading due to light exposure, today assessable using standardised methods [6]) of different classes of dyes in solution and in different substrates have been extensively investigated since the 1950s [7–11]. The results have shown that lightfastness of coloured textiles is highly influenced by intrinsic factors, such as the chemical structure [12,13] and the physical state of the dyes [14], and external conditions, such as the dye concentration [15], the nature of the fibres and the

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mordant used [16]. Fading processes also depend on environmental factors, namely the spectral distribution and intensity of illumination [17], temperature, humidity and atmospheric pollutants [18]. Photo-ageing may chemically alter the dye molecules, thus influencing their spectral and chromatographic behaviour. Therefore, for the purpose of restoration and conservation and for the knowledge of the technology of artistic artefacts, it is important to study how the physical properties and the chemical nature of dyes can be affected by light.

Recent studies have shown that madder has fair light fastness and wash resistance and is more stable on wool than on silk and cotton [19]. As found for many other natural dyes, UV radiation strongly affects the fading of madder on wool, while visible light contributes to a lesser extent [20]. Fading experiments with dyes on wool have traditionally been reported in terms of colorimetric measurements, whereas the literature dealing with the effects of light exposure on the spectral properties of natural dyes is scarce.

In this study a set of wool samples dyed with madder and its main components, alizarin and purpurin, in both the presence and absence of mordant, were analysed before and after 1 year of natural ageing. For purpurin dyed samples, accelerated ageing was also carried out under illumination and environmental (air or nitrogen) controlled conditions.

Two different experimental approaches were combined and compared: a non-destructive one, namely spectroscopy (absorption, fluorescence and colorimetry) and a micro-destructive one, that is, high-performance liquid chromatography (HPLC). The aim of this multi-analytical approach is to propose qualitative and semi-quantitative methods to evaluate the influence of mordant on dye lightfastness, investigate on the role of alizarin and purpurin in determining the chromatic properties and durability of madder dyestuff on textiles, and study the effect of oxygen on degradation. Since HPLC is the main analytical technique currently used for the detection and identification of dyes in artistic objects, the comparison of chromatographic with spectroscopic results should highlight the potentials and limits of non-destructive spectroscopic techniques in the analytical identification of dyes on textiles and detection of their degradation.

2. Experimental

2.1. Materials

The untreated wool (*Lana Gatto 5667800 2/28*, lotto P.ta FREE/TC, treatment Nm 09999, "*greggio*" *1201* quality) was obtained from Lana Gatto (Tollegno, Italy). Dried madder (*R. tinctorum* L.) roots (fragments) were purchased from Zecchi (Firenze, Italy). Purpurin (99%) was purchased from Aldrich (Milwaukee, WI, USA) and alizarin (97%) from Acros Organics (Geel, Belgium). The potassium–aluminium sulfate (alum), $Al_2(SO_4)_3{\cdot}K_2SO_4{\cdot}12H_2O$, (99,5%), potassium hydrogen tartrate (tartar), $KO_2CCH(OH)CH(OH)CO_2H$ (95,5%) and the Tween 20 scouring agent were purchased from Merck (Darmstadt, Germany).

For the extraction of the dyes from the fibres and HPLC analysis the following chemicals were used: hydrochloric acid, HCl (37%) and dimethylsulfoxide, DMSO (for gas chromatography) from Merck (Darmstadt, Germany), and acetonitrile, MeCN (HPLC Supra-gradient) from Biosolve B.V. (Valkenswaard, Netherlands). Methanol (G. Chromasolv) was obtained from Riedel-de Haën (Seelze, Germany), and formic acid from Acros Organics (Geel, Belgium). The ultra-pure water was provided from Milli-Q Plus system (Millipore, Molsheim, France).

2.2. Model samples

In the dyeing procedure, the aqueous extract of the coloured compounds from *R. tinctorum* L. roots was used. Scoured and mordanted wool was then immersed in the dye bath. Samples of undyed wool were treated as the dyed samples.

2.2.1. Scouring method

The wool was immersed in the scouring solution (500 mL deionised water containing 2.5 g of Tween 20), gently heated on a hot plate from ambient temperature to 40 °C for 25 min and maintained at this temperature for 10 min. Then it was rinsed several times in deionised water.

2.2.2. Mordanting procedures

The samples were mordanted according to three different methods by using 25% of alum (first method), 20% of alum together with 5% of tartar (second method) and 20% of alum (third method), following a general procedure. The mordants were dissolved in deionised water and heated to boiling point on a hot plate for 1 h, then the scoured wool skeins were added, maintained at this temperature for 50 min and allowed to cool in the dark overnight (20 h); then they were rinsed with deionised water and allowed to dry.

2.2.3. Dye bath

For 12 g of wool, 12 g of dried roots were soaked in 300 mL of deionised water for 20 h at room temperature. The dye bath was filtered, diluted to 600 mL with deionised water and then divided into four equal parts in order to separately dye the unmordanted and differently mordanted wool samples. The wetted, scoured, alum-mordanted and unmordanted wool (3 g for each mordanting procedure) was immersed in the dye bath at 40 °C, then heated to boiling point for 2 h. After cooling of the dye bath, the wool skeins were rinsed in deionised water and dried in the dark.

For the samples dyed with alizarin and purpurin, the same dyeing and mordanting procedures used for *R. tinctorum* L. were followed. For 12 g of wool, 30 mg of the compound were dissolved in 600 mL of deionised water. The dye bath was used to separately dye the unmordanted and differently mordanted wool.

Based on the colorant, method of dying and ageing conditions, a code (composed of 3–4 signs) was used for each sample:

- The first letter indicates the dyestuff (A: alizarin, P: purpurin and M: madder).
- The second sign refers to the mordanting method (U: unmordanted, 1, 2 and 3: mordanted with first or second or third method, respectively).