***In-situ* spectroscopic analysis of the traditional dyeing pigment Turkey red inside textile matrix**

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ABSTRACT: Turkey red is a traditional pigment for textile dyeing and its use has been proven for various cultures within the last three millennia. The pigment is a dye-mordant complex consisting of Al and an extract from *R. tinctorum* that contains mainly the anthraquinone derivative alizarin. The chemical structure of the complex has been analyzed by various spectroscopic and crystallographic techniques for extractions from textiles or directly in solution. We present an *in-situ* study of Turkey red by means of μ -XRF mapping and NEXAFS spectroscopy on textile fibres dyed according to a traditional process to gain insight into the coordination chemistry of the pigment in realistic matrix. We find an octahedral coordination of Al that corresponds well to the commonly accepted structure of the Al alizarin complex derived from *ex-situ* studies.

KEYWORDS: μ -XRF; NEXAFS; alizarin; natural pigment; Turkey red.

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1. Introduction

Turkey red has been one of the most widespread natural pigments in textile coloration for many centuries [1, 2]. In its natural form it is gained from an extraction of the roots of *Rubia tinctorum* (also known as “common madder”) and forms a stable red lake with potassium aluminum sulphate ($KAl(SO_4)_2$). The dominant colourant in *R. tinctorum* is 1,2-dihydroxyanthraquinone or alizarin (Fig. 1a). Smaller portions of other anthraquinone derivatives – mainly purpurin (1,2,4-trihydroxy anthraquinone) – have minor influence on the exact resulting pigment shade [1, 2]. The use of alizarin as natural pigment has been detected in various ancient textiles since ~ 500 B.C. [1 – 3]. In 1869 a route for the production of synthetic alizarin was developed [4] and it became one of the most common industrial dyes [5].

Figure 1. a) Chemical structure of alizarin (1,2-dihydroxyanthraquinone). b) Sheep wool fibres dyed with alizarin and Al mordant.

The stable incorporation and binding of alizarin to the keratin matrix of wool requires the application of a mordant [2, 6]. Depending on the electronegativity of the mordant, the hue of the resulting pigment can vary from light red to dark violet [7, 8]. In combination with $KAl(SO_4)_2$, alizarin forms a dye-mordant-complex with high colour brilliance and persistence (figure 1b)). The absorption maximum in the visible range is at 514 nm for the pure complex [7]. The chemical structure of the Al lake of alizarin has been disputed over decades [7, 9, 10]. Meanwhile the structure of a bridging chelate complex proposed by Wunderlich and Bergerhoff

is commonly accepted [7]. They determined a crystal structure consisting of two Al^{3+} - and two Ca^{2+} -centres bridged by four alizarin anions. Alizarin binds to Al^{3+} by the 1- and 2-phenolate groups and to Ca^{2+} (from natural water) by the carbonyl and the neighbouring 1-phenolate function. In addition, the Al^{3+} centres are linked by HO^- bridges resulting in an octahedral coordination. The exact binding to the keratin matrix inside wool and its influence on the coordination of the mordant is not clear [2].

So far studies on the exact chemical structure of the alizarin Al complex have been limited to aqueous solution, dried lake or analysis of pigments extracted from previously dyed textiles [2, 7, 10 – 14]. Hence, it is not clear whether the proposed chelate complex is also present within wool and how stable binding to keratin fibres is achieved. Within the present study we have investigated red textile fibres dyed with *R. tinctorum* and $\text{KAl}(\text{SO}_4)_2$ by micro X-ray fluorescence (μ -XRF) mapping and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at the Al *K*-edge to gain insight into the coordination chemistry of Al in Turkey red within wool as its common matrix in practical use.

2. Experimental

The wool fibres used within the present study have been dyed with *R. tinctorum* and $\text{KAl}(\text{SO}_4)_2$ according to a traditional Anatolian process described elsewhere [15, 16]. The sheep wool has been fermented with *Geotrichum candidum* yeast prior to dyeing for improved fibre permeability and pigment uptake. Furthermore, the yeast acts as biochemical buffer resulting in a stable pH of 4.4. After fermentation madder roots and $\text{KAl}(\text{SO}_4)_2$ (yielding a 20 vol.-% solution) are added to the suspension at ambient conditions.

Specimens were embedded in an epoxy resin derived from a 1:1 mixture of 4,4'-methylenebis(2-methylcyclohexylamine) and trimethylolpropane triglycidyl ether. After drying the resin at 60°C for 10 h, the sample blocks were partially microtomed to obtain a flat cross-section surface along the diameter of several isolated wool fibres.

μ -XRF and NEXAFS studies were performed at the PHOENIX beamline at the Swiss Light Source in Villigen, Switzerland. The X-ray beam was focused to $3 \times 5 \mu\text{m}^2$ and the excitation energy for Al *K*-edge fluorescence mapping was 3.0 keV. The samples were mounted under 45° degree relative to the incoming beam to allow penetration of X-rays into the sample and an exit of the elemental fluorescence signals from the specimen (penetration depth: $\sim 45 \mu\text{m}$ at 3.0 keV). Images were recorded by scanning the sample relative to the fixed position of the microbeam. The energy dispersive X-ray fluorescence spectra were recorded for each position using a single-element solid-state detector (Ketec) with 160 eV energy resolution. NEXAFS spectra have been recorded close to the centre of the respective wool fibre cortex (to avoid contribution from contaminations of the fibre surface) by tuning of the incident photon energy and detection of the resulting fluorescence signal. We have recorded reproducible spectra for several individual fibres from two independent preparation batches. Fluorescence maps have been quantitatively fitted and analysed with PyMca [17], while NEXAFS spectra have been analysed with ATHENA [18].

Note that the natural metal content in sheep wool strongly depends on region and race [19]. Therefore, we also investigated undyed fibres from a comparable specimen and found no significant contribution of Al from natural sources to the fluorescence signal from inside the wool fibre cortex (surface contaminations excluded).

3. Results and Discussion

3.1 μ -XRF mapping

Figure 2a) shows an exemplary μ -XRF map over the cross section of a single wool fibre dyed with alizarin and $\text{KAl}(\text{SO}_4)_2$ (Al K -edge fluorescence peak). While the wool is exposed to the dyeing solution, the dye-mordant complex will diffuse from outside the fibres towards the cortex and, therefore, the Al concentration shows a clear gradient. However, according to the mordant distribution we detect a deep penetration of the dye complex into the wool fibre cortex that is typical for previously fermented wool [16]. Contaminations on the outer part of the fibres like the very intense spot in the upper part of the depicted specimen cannot be fully avoided, since the wool is not prepared and stored under clean room conditions. Therefore, we employed the high-resolution maps and the small beam size of the PHOENIX end station to determine proper positions in the inner part of the fibres for further NEXAFS analysis.

Figure 2. a) Exemplary μ -XRF map (Al K -edge; pixel size: $1 \times 1 \mu\text{m}^2$; dwell time: 2 s) of sheep wool fibre showing distribution of the alizarin Al complex (intensity in counts normalized to background from the embedding material). b) Exemplary Al K -edge NEXAFS spectrum (fluorescence detection) recorded close to the centre of the wool fibre cortex (energy steps: 1550 – 1581 eV: 0.3 eV, 1582 – 1611 eV: 1 eV, > 1611 eV: 2 eV; dwell time: 6s). Since there is no prominent peak in the energy regime corresponding to tetrahedral coordination and the strong peak in the octahedral region gives clear evidence on octahedral coordination of Al in Turkish red inside wool. The inset shows synthetic reference spectra for tetrahedral and octahedral Al complexes according to peak positions and relative intensities in Ref. [20].

3.2 NEXAFS spectroscopy

Al K -edge NEXAFS is ideally suited for the determination of the coordination chemistry of Al complexes [20, 21]. According to Ref. [20] the first two peaks in the pre-edge regime are attributed to mixed-states and interactions with the surrounding ligands. Comparing the two investigated ligand fields, tetrahedral complexes exhibit an earlier absorption edge (~ 3 eV) and a more intense first peak, while in octahedral complexes the second peak is dominating. Therefore, the photon energy of the dominant peak gives clear evidence on the coordination. Figure 2b) depicts the Al K -edge from the inner cortex of an investigated red wool fibre. We see

a dominating peak at 1571 eV and a minor shoulder at 1568 eV. The resulting finger print shape of the spectrum fits well to the literature reference for octahedral coordination (see also inset in figure 2b)).

We conclude that the Turkish red pigment is indeed an octahedral Al complex inside wool fibre matrix. This corroborates the consideration that the chemical structure proposed by Wunderlich and Bergerhoff does not significantly change upon binding to the keratin structure. We can, however, not clearly decide whether the binding happens via the Al centre upon loss of the HO⁻ bridges or via interactions of the alizarin ligands with the amino acid network of keratin. The first case appears more likely, since mordants increase the binding of Al to the fibre significantly [2, 6]. A more detailed spectroscopic analysis corroborated by spectra modelling might help to address this specific issue.

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