Effect of Metal Cations on Absorption and Emission Properties of Colorants of Cultural Heritage Importance

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Background

- Over the course of art history, some paints have been made by mixing together a colorant and mordant
- A mordant is a compound that chemically bonds a colorant to its substrate. [3] Mordants contain metal cations which form a complex with the dye (Figure 1). These complexes can alter the color of the paint from the original hue of the colorant.
- Some colorants used include the anthraquinones: alizarin, purpurin, and quinizarin
- By identifying the chemical makeup of a paint, one can identify the colorant and metal ratios which correspond to a known historical paint recipe
- One example is the "Mummy Portrait of a Bearded Man" (Figure 2). [2] Experts at the Walters Art Museum accurately identified aluminum and multiple lead-aluminum nanoparticles in different concentrations. By matching the concentrations with other portraits around the world, it may be possible to identify which other portraits were created in that same time period.
- By identifying the metals used in mordants, one may be able to trace the time period and geographical location of the specific mordant used in an art piece

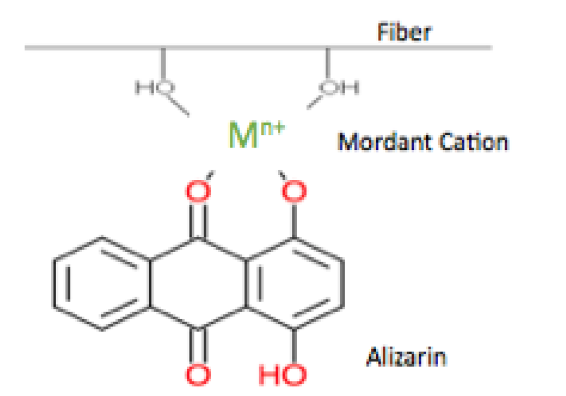


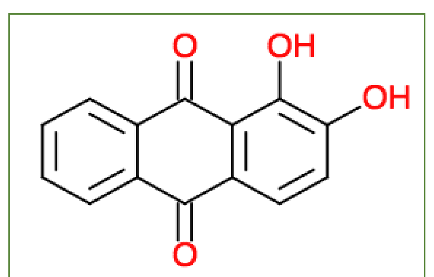
Figure 1: Chemical complex between textile, mordant, and pigment (alizarin). Possible coordination complex between metal salt in mordant and dye is shown.

Figure 2: "Mummy Portrait of a Bearded Man" from The Walters Art Museum

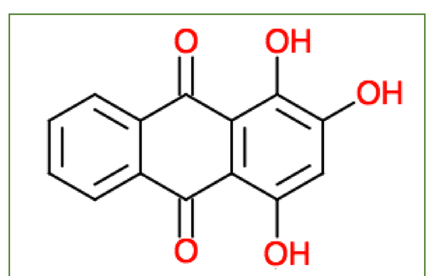
Goals of Research

- To determine if absorbance and emission spectra can be used to identify the cation(s) present in mordants
- To determine if mordant concentration in antiquity was intentional in order to achieve a specific color

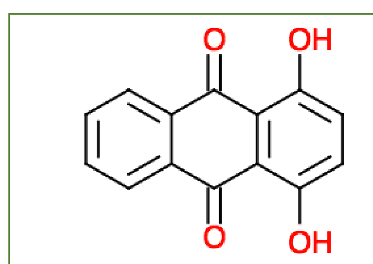
Results



Alizarin (Al)



Purpurin (Pu)



Quinizarin (Qu)

Metal Cations Tested

- Ca(II)
- Cd(II)
- Co(III)
- Cr(III)
- Cu(II)
- Fe(II)
- Fe(III)
- Mg(II)
- Mn(II)
- Ni(II)
- Pb(II)
- Sn(II)
- Sn(IV)
- Zn(II)

Absorption of Alizarin and Quinizarin at Low Metal Concentrations

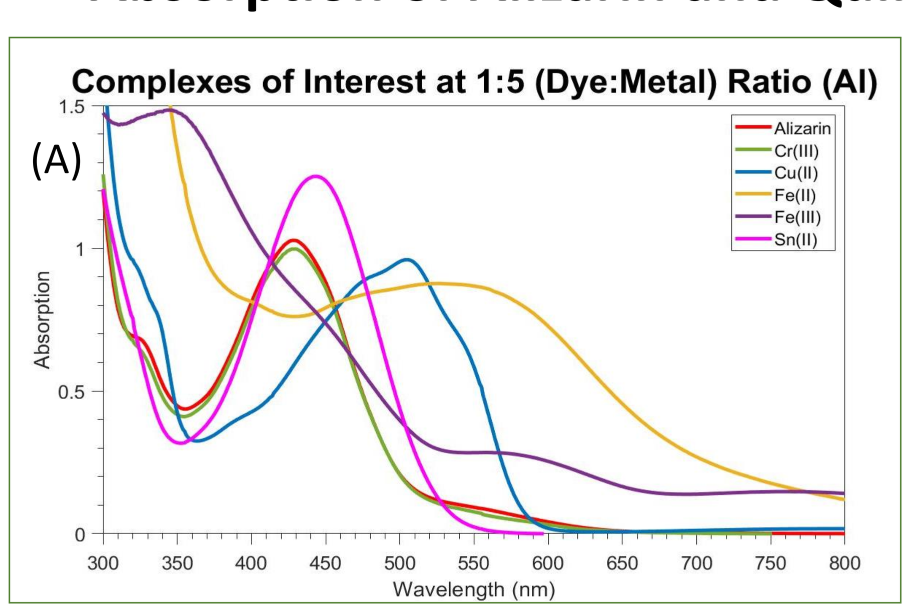


Figure 3 (A) The absorption spectra of Alizarin and metals which created the most change when the ratio of metal to dye was approximately 1:5 (Alizarin:Metal)

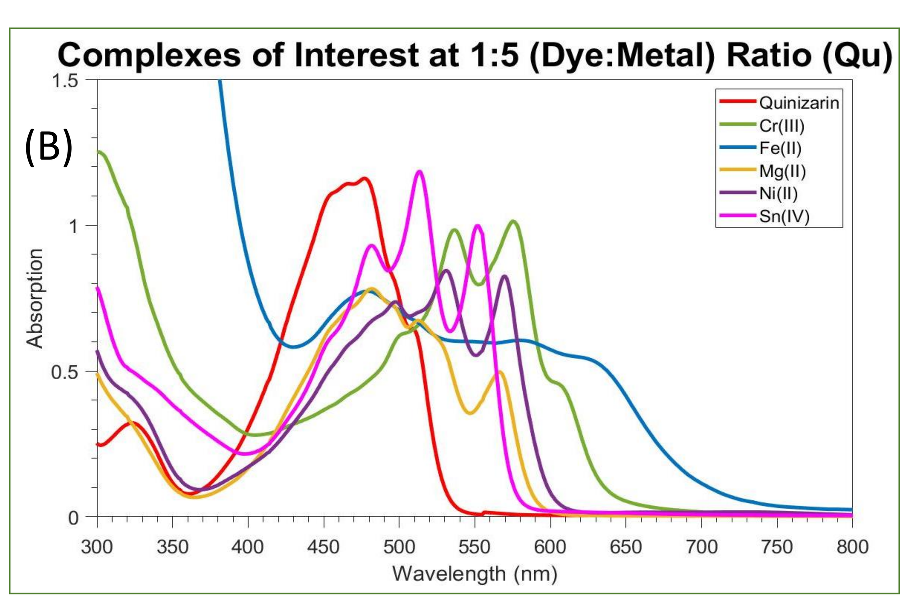


Figure 3 (B) The absorption spectra of Quinizarin and metals which created the most change when the ratio of metal to dye was approximately 1:5 (Quinizarin:Metal)

Absorption of Alizarin and Quinizarin at High Metal Concentrations

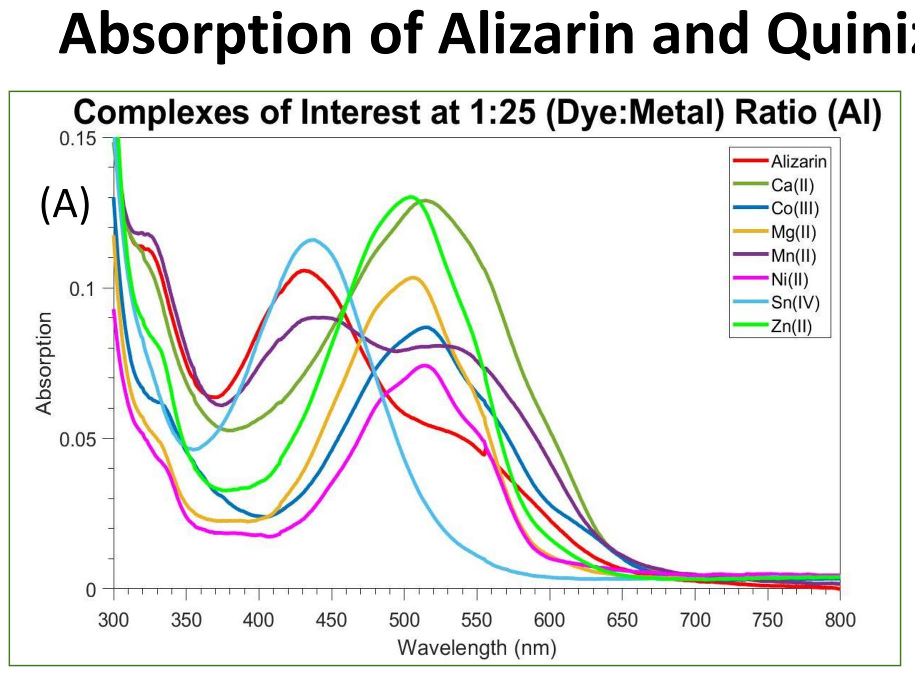


Figure 4 (A) The absorption spectra of Alizarin and cations which created the most change when the ratio of metal to dye was approximately 1:25 (Alizarin:Metal)

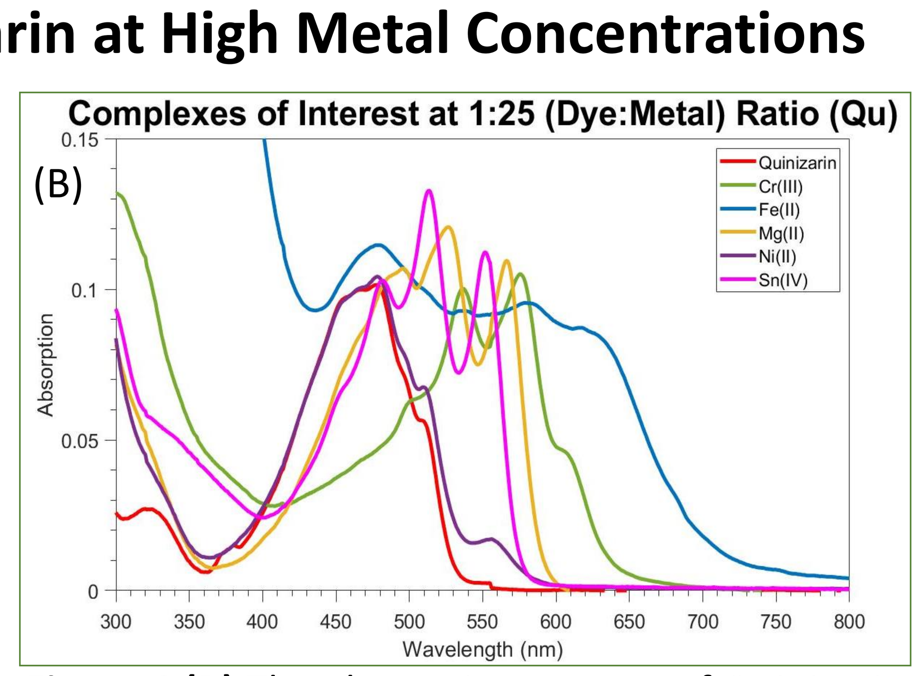


Figure 4 (B) The absorption spectra of Quinizarin and cations which created the most change when the ratio of metal to dye was approximately 1:25 (Quinizarin:Metal)

Emission of Alizarin at High Metal Concentrations

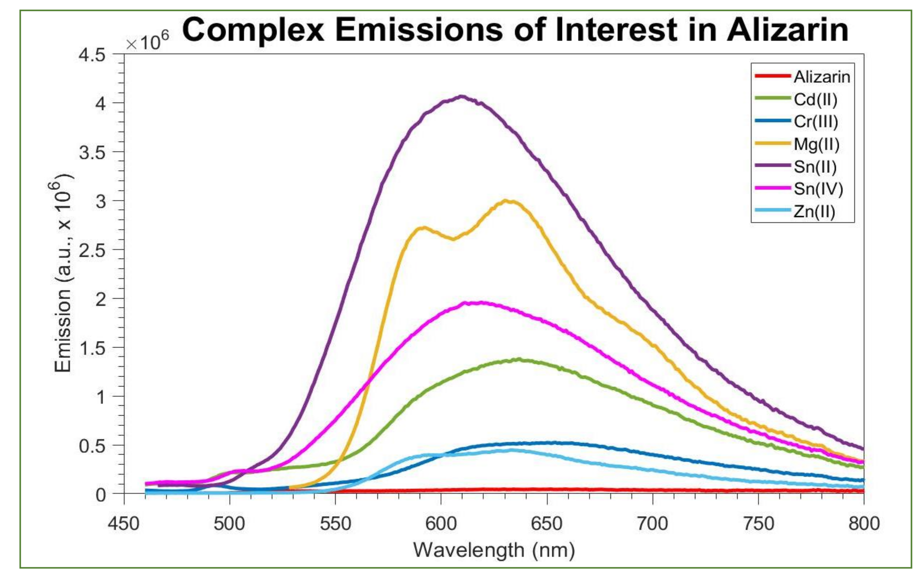
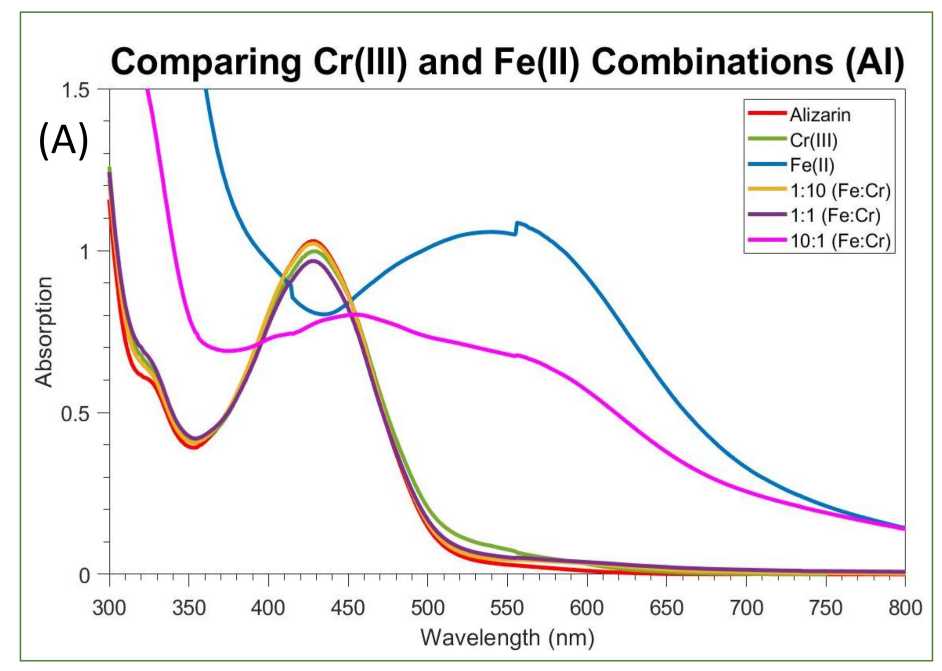


Figure 5 The emission spectra of Alizarin at high dye to metal concentrations (1:25). The excitation wavelength was 350, and slit widths were all 5nm.

Cr(III) and Fe(II) Combination Spectra at High Metal Concentrations



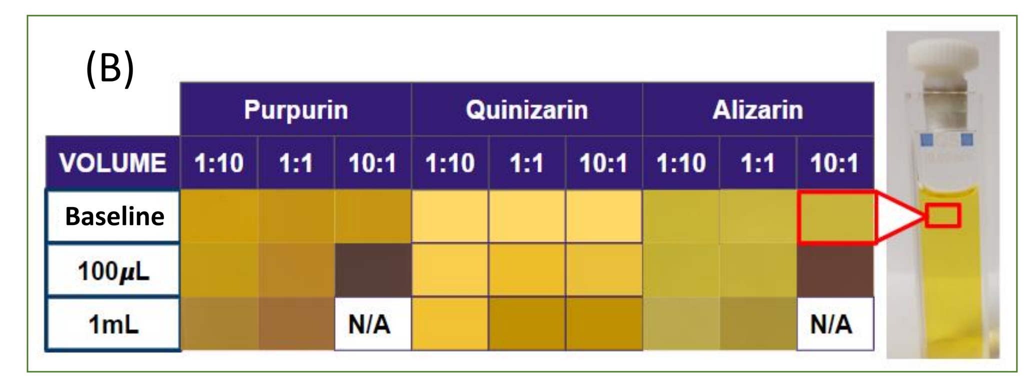


Figure 6 (A) The absorption spectra of three different combinations of Cr(III) and Fe(II) in Alizarin.
(B) Pictures were taken of the cuvette with the base solution of each dye and 100μL and 1mL additions of 25mM solution for each iron-chromium combination

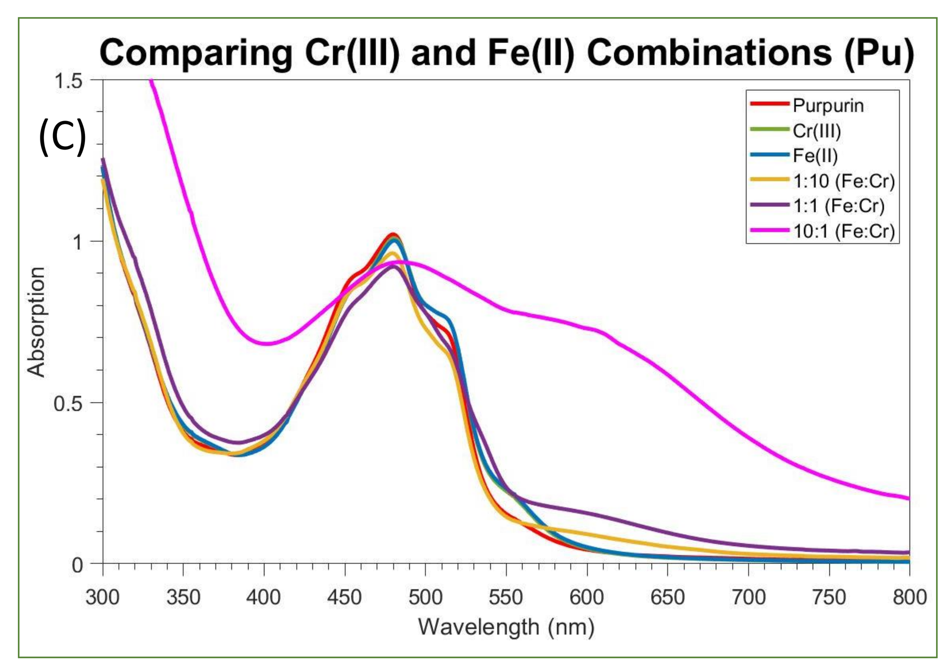


Figure 6 (C) The absorption spectra of three different combinations of Cr(III) and Fe(II) in Purpurin.

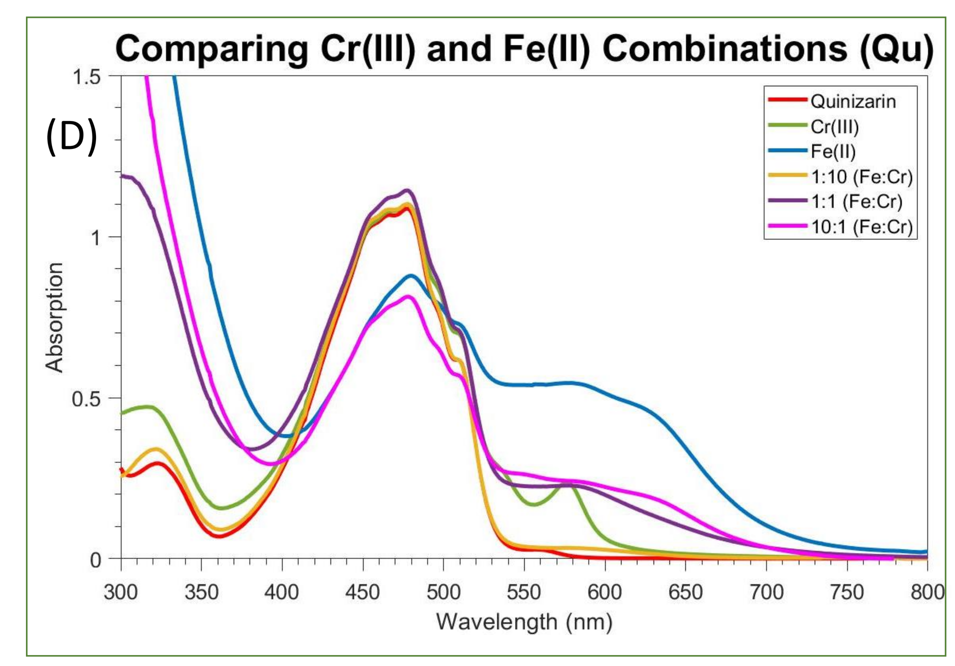


Figure 6 (D) The absorption spectra of three different combinations of Cr(III) and Fe(II) in Quinizarin.

Conclusions

- Determined that the addition of metal cations have a distinctive impact on the absorption and emission spectra of the dyes of interest
- Observed no significant effects of the combination of Cr(III) and Fe(II)

Future Directions

- Will reproduce paint according to ancient recipes provided by Glenn Gates at The Walters Art Museum and measure those spectra
- Will redesign experiments to apply to solid media

References

[1]Fröse, A., Schmidtke, K., Sukmann, T., Juhász Junger, I., & Ehrmann, A. (2019). Application of natural dyes on diverse textile materials. Optik, 181, 215–219.

[2]Gates, G., Butt, D., Burns, J., Wu, Y., Alanko, G., & Watkins, J. K. (2018). The Internal Morphology and Composition of a Purple Pigment Particle Extracted from an Ancient Faiyum Mummy Portrait. Microscopy and Microanalysis, 24(S1), 2128–2129.

[3]Kakuee, O., Fathollahi, V., Oliaiy, P., & Mesbahi, S. (2019). Investigation of mordants for dyeing of yarns in ancient Persian carpets (15th–17th century) by IBA methods. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 450, 294–298.

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