X-Ray Mapping and Scatter Diagram Analysis of the Discoloring Products Resulting from the Interaction of Artist’s Pigments

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Abstract: The discoloring interaction between the artist’s pigments cadmium yellow and the copper-containing malachite, an interaction that is conjectured to cause black spotting in oil paintings of the 19th and early 20th centuries, was examined using X-ray mapping and scatter diagram analysis. The application of these coupled techniques confirmed that copper sulfide phases were produced during discoloration reaction. Scatter diagram analysis indicated that two copper sulfide stoichiometries \( \text{CuS} \) and \( \text{Cu}_3\text{S}_2 \) were present as reaction products where previously only crystalline \( \text{CuS} \) (covellite) had been identified by X-ray diffraction. The results demonstrate the potential of X-ray mapping coupled with scatter diagram analysis for the identification of both crystalline and X-ray amorphous phases produced by such complex heterogeneous interactions and their applicability to the investigation of interactions of artists’ pigments.

Key words: X-ray mapping, scatter diagram analysis, artist’s pigments, cadmium yellow, malachite, discoloration

INTRODUCTION

Pigment discoloration is a significant problem encountered in the conservation of 19th and early 20th century oil paintings. Due to scientific advances during the Industrial Revolution, artists were able to obtain a range of new synthetically produced bright pigments that have since been removed from circulation due to their propensity to degrade as well as due to their toxicity (Gettens & Sterner, 1941; Doerner, 1984; Carlyle, 2001).

Pigment discoloration may be attributed to environmental causes (Carlyle, 2001), impurities (Gettens & Sterner, 1941; Spring & Grout, 2002), or through the chemical interaction between pigments (Gettens & Sterner, 1941). The most contentious of these sources of discoloration is the discoloration due to the chemical interaction of pigments. Historically, there has been much conjecture over the pigments involved (Gettens & Sterner, 1941; Townsend et al., 1995; Carlyle, 2001). An interaction where some consensus has been reported is the interaction between cadmium sulfide pigments and any copper-containing pigment (Gettens & Sterner, 1941; White et al., 2006) or, for that matter, any source of copper ions (Salvadó et al., 2003). This particular interaction proceeds by ion exchange between mobile copper ions and the cadmium ions in the cadmium sulfide resulting in a heterogeneous reaction of the form:

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\text{Cu}^{2+} + \text{CdS} \rightarrow \text{CuS} + \text{Cd}^{2+}.
\]

The products of this reaction are dark colored (almost black) copper sulfides of varying stoichiometry that affect the visual appearance of the painting (Fielder & Bayard, 1986; Salvadó et al., 2003; White et al., 2006). It is this interaction that is the subject of the current article and, in particular, the interaction between a cadmium yellow pigment (cadmium sulfide with zinc sulfide in solid solution, \( \text{Cd}_{0.85}\text{Zn}_{0.15}\text{S} \)) and a malachite pigment [basic copper carbonate, \( \text{CuCO}_3\text{Cu(OH)}_2 \)]. Previous studies of this interaction have identified the phases resulting from the reaction as covellite (\( \text{CuS} \), the dark discoloring product), cadmium carbonate, and hydrated cadmium sulfate (White et al., 2006). The interaction has also been investigated using thermal analysis indicating that a number of phases are produced by this complex heterogeneous reaction (White et al., 2007). The current study furthers the characterization of the reaction products using the microanalytical techniques of X-ray mapping with the subsequent generation of scatter diagrams to aid phase identification.
X-ray mapping, also known as compositional imaging, is an X-ray microanalysis technique (Goldstein et al., 1992), where the X-ray signals (the K and L emission lines produced by the bombardment of the sample with the electron beam, which are characteristic of each element present at each pixel in the image) are analyzed using energy dispersive X-ray spectroscopy (EDS) and collected for selected elements over the area that is being imaged. (A recent review of the development of EDS can be found in Schamber, 2009 and references therein.) As the X-ray intensity is measured and is proportional to the concentration, maps of the concentration profile of each element across the image can be produced. The maps are usually produced using a two-tone or grayscale color scheme, where white is the maximum concentration and black represents zero concentration. As the intensity of the detected X-rays is proportional to the concentration of each element, cross-correlation can be carried out by plotting, for each pixel, the normalized intensity (0 to 100) of one element against a second element (Bright & Newbury, 1991; Moran & Wuhrer, 2006). This cross-correlation results in a scatter diagram that is essentially a concentration or frequency histogram. Clusters of points, or nodes, are formed in the scatter diagram that can be used to identify the relative association between elements. As a result, scatter diagrams may aid the identification of the stoichiometries of the phases represented by each node. Additionally, as the identity of each pixel in the scatter diagram is retained, the pixels in a node in the scatter plot can be replotted on the original micrograph to identify the phase associations in the imaged area (Bright, 1995; Moran & Wuhrer, 2006).

**EXPERIMENTAL METHOD**

Cadmium yellow (CdS containing approximately 15 mol% ZnS as an isomorphous solid solution) and malachite [a basic copper carbonate (Cu(OH)$_2$·CuCO$_3$)] were sourced as artists supplies manufactured by Kremer Pigments Inc. (New York, USA). The malachite and cadmium yellow pigments were blended together in a 1:1 ratio by mass and mixed with an excess of water and reacted for a period of two months at laboratory temperature, 22 ± 2°C. The samples were recovered by filtration and allowed to dry at room temperature. A sample of the unreacted mix was also retained for analysis.

Sample specimens were prepared for X-ray mapping analysis by pressing pellets of the blended powder mixtures (both of reacted and unreacted mixtures) in an infrared pelleting die (10 mm in diameter) at 14 MPa. Pellets of approximately 0.5 mm thickness were removed from the die and immediately placed onto conductive carbon stubs and carbon coated for analysis.

All X-ray mapping was performed using a JEOL 35CF scanning electron microscope with an Oxford Pentafet Si(Li) EDS. X-ray maps and scatter diagrams were produced using Moran Scientific microanalysis software. The background and overlap corrected region of interest X-ray maps were produced by mapping for K or L X-ray peaks for the elements sulfur, cadmium, and copper using ZAF matrix corrected standardless analysis (Goldstein et al., 1992). X-ray maps were produced at 15 kV and the images at 512 by 512 pixels. The software was then used to plot the scatter diagrams of copper or cadmium versus sulfur for the mapped regions. To carry out this procedure, first the total X-ray intensity for each element was determined and normalized to a value of 100. The X-ray intensity at each pixel was then determined for each element producing a grayscale intensity for each element. From these normalized data, the two-dimensional scatter diagrams were produced by plotting the normalized X-ray intensity of cadmium or copper against the normalized X-ray intensity of sulfur for each pixel in the cadmium, copper, and sulfur X-ray maps.

**RESULTS AND DISCUSSION**

The X-ray maps for the pressed discs of the unreacted pigment mixture are shown in Figure 1 for cadmium, copper, and sulfur. The bright regions of cadmium and sulfur X-ray maps show association as expected for the unreacted case, correlating with the presence of the cadmium yellow pigment. The dark regions of the cadmium and sulfur maps are observed to correlate with the presence of...
of copper, indicating regions where the unreacted malachite occurs.

The association of cadmium with sulfur and the lack of an association between the copper and the sulfur are exemplified by the scatter diagrams shown in Figure 2. The scatter diagram is a graphical representation of relative intensity of each signal at each pixel in the image. Association between two elements is seen as a node in the scatter diagram away from the axes. The ratio (or stoichiometry) of the two elements present can be calculated from the angle of the line drawn through the node to the origin, provided that the ratio of intensity to composition is known. Figure 2b indicates that there is a clear association between the cadmium and the sulfur, while Figure 2a shows little association evident between copper and sulfur other than adjoining phase (regions). The angle of the node-origin diagonal to the sulfur axis in the cadmium-sulfur diagram is 39°, which corresponds to an estimated stoichiometry for the cadmium yellow of Cd<sub>0.8</sub>Zn<sub>0.2</sub>S, a slightly lower proportion of cadmium than the 0.85 to 1 (Cd to S) ratio expected, but is in reasonable agreement indicating the potential for this technique to identify phase stoichiometries. This estimation, of course, has been carried out without compositional calibration and by simply using the normalized intensities. The phase correlation and the determined stoichiometry (i.e., the chemical formula) can therefore only be indicative of the stoichiometry of the phases present, particularly as the phases present can have variable composition.

From the scatter diagrams it is possible to select pixels and retrace them on the original micrograph. Figure 3 retraces the pixels encircled in Figure 2. The pixels encircled A are plotted in Figure 3a and correspond well with the copper X-ray map (Fig. 1c). Similarly, the pixels encircled B in Figure 2 are plotted in Figure 3b. These pixels correspond to an association between the cadmium and the sulfur and reflect the regions where cadmium and sulfur are observed in the X-ray maps, demonstrating the effectiveness of the scatter diagram technique to associate the elements to the phases present.

The X-ray maps for the pressed discs of the reacted blend are shown in Figure 4. The association of cadmium with sulfur is less evident in these maps. Indeed, the brightly colored regions of the cadmium map correspond to dark colored regions of the sulfur map indicating the absence of sulfur where cadmium is in its highest concentrations. The sulfur map corresponds more closely with the copper map indicating an association. This association is expected based on the phase analysis results of previous work where covellite (CuS), cadmium carbonate, and hydrated cadmium...
sulfate have been identified as the reaction products (White et al., 2006).

The scatter diagrams shown in Figure 5 for the reacted mixture confirm the new association of copper with sulfur. As this is a complex heterogeneous reaction (White et al., 2007), the broadened range of the nodes observed is unsurprising. The new phases produced are not necessarily completely stoichiometric in nature, and unreacted reactant phases are also likely to be present broadening the phase associations, but the overall the shape of the scatter diagrams is the reverse of Figure 2.

The association of copper with sulfur is apparently based on two compositions on node-origin diagonals at 47° and 56° to the sulfur axis that correspond, approximately, to 1:1 CuS and 3:2 Cu₃S₂ stoichiometries, the latter likely to be a mixed Cu(I)/Cu(II) sulfide. It should be noted that, as the stoichiometries have been determined from the uncalibrated normalized data and copper sulfides can have non-stoichiometric compositions, these stoichiometries are only indicative of the stoichiometries of the phases present.

X-ray diffraction (XRD) analysis of the products of this reaction did not show evidence of a Cu(I) phase present (White et al., 2006) suggesting that, if this phase is present, it has an amorphous morphology that is not readily detectable by XRD.

Plots of the pixels in the regions encircled in Figure 5 are shown superimposed on the secondary electron image in Figure 6. The nodes encircled show the association of copper with sulfur while cadmium appears to have little association with sulfur, indicating that cadmium has been substituted by copper to produce the black copper sulfide products that are responsible for the discoloration of 19th and 20th century paintings that contain cadmium sulfide pigments.

**CONCLUSIONS**

X-ray mapping and the subsequent generation of scatter diagrams has successfully identified the association between elements in unreacted and reacted mixtures of cadmium yellow and malachite. Although X-ray mapping and scatter diagram analysis cannot directly yield structural information about the compounds present, the ability to identify associations between elements present in particular phases aids compound identification. In this study of the interaction between cadmium yellow and malachite, scatter diagram analysis has not only indicated the presence of the expected CuS stoichiometry previously detected by XRD, but has also aided in the identification of another copper and sulfur phase with a possible Cu₃S₂ stoichiometry, demonstrating the strength of this microanalytical technique as an aid to phase determination. The ability of this technique to identify both the elements present and their spatial distribution, in the next stage of this work, will aid the application of this technique to the identification of these phases in discolored paint fragments of paintings where a limited amount of material is available for analysis.

![Figure 5](image5.png)

**Figure 5.** Scatter diagrams for (a) copper versus sulfur and (b) cadmium versus sulfur derived from the normalized X-ray intensities of the X-ray maps for the reacted pigments shown in Figure 4. Regions encircled correspond to the pixilation reproduced in Figure 6. The letters C, D, and E correspond to three different chemical phases (two different Cu and S phases and a Cd phase). The pixels outside the encircled areas are due to phases in contact with each other and/or interaction zones between phases.

![Figure 6](image6.png)

**Figure 6.** Pixels that are encircled as (a) C, (b) D, and (c) E in Figure 5 are superimposed on the original secondary electron image. Regions C, D, and E are those corresponding to regions C, D, and E on the scatter diagrams of Figure 5.
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REFERENCES


