X-Ray Vision: Seeing Art in a New Light

Laura Smith Literature Seminar November 16, 2022

People have been curating collections of artworks and other objects of historical significance for centuries. While most past studies on these items approach them from an artistic or historical perspective, there has been a recent interest in applying scientific experimental methods to the study of historic artifacts. Chemical studies can give valuable new insights on the composition of the objects of interest, providing information on the provenance of the object, or studying damage that has occurred. X-ray diffraction and spectroscopy are excellent tools for this analysis since they can easily differentiate between different types of atoms and molecules and are non-destructive. In recent years, the use of synchrotron radiation x-ray spectroscopy has become more common for art analysis.

Synchrotrons accelerate electrons to relativistic speeds and then inject them into a large storage ring. The storage ring keeps the electrons moving in a circle with large bending magnets. As the bending magnets accelerate the electrons, they release electromagnetic radiation, since they are charged particles.[1] This light has energy in the x-ray region. Between bending magnets, insertion devices such as undulators can be added to produce more x-rays. The undulators are a series of opposite facing magnets to make the electrons accelerate back and forth very quickly, which creates a very intense, coherent photon beam.

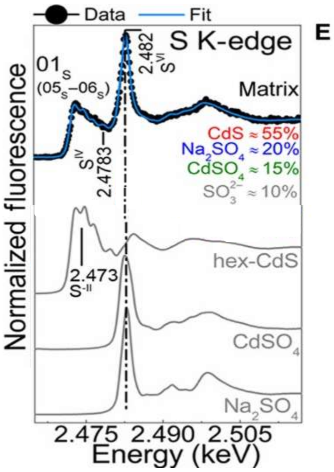

Figure 1. Linear combination fitting of the sulfur K-edge of a paint sample.

When x-ray photons collide with atoms, they can eject electrons from the core orbitals. X-rays with enough energy to eject electrons from the 1s orbital are at the K-edge, while those that eject 2s and 2p electrons are at the L-edges. Spectra around the edge of interest, called XANES (x-ray absorption near edge structure) spectra, contain information about the oxidation state and environment of the atom being studied. To determine the principal components in a mixture being studied, the XANES spectrum can be fit with a linear combination of reference spectra. In Figure 1, this is used to determine what sulfur compounds are present in a sample of paint.[3]

Another experimental method available at synchrotrons is x-ray diffraction mapping (μ-XRD). The high energy, and thus short wavelength, of the synchrotron beam allows for excellent spatial resolution. The x-ray beam can be focused to sub-micrometer diameters and scanned across the surface of a painting or paint fragment to map the distribution of different compounds.[4]

Edvard Munch's *The Scream* ca. 1910 has had a tumultuous history. The pigments were already beginning to degrade when the painting was stolen from a museum in 1994, and then again in 2004. It had suffered more damage to the backing when it was finally recovered in 2006. After that, it was kept stored in a cold, dry, and dark environment to prevent further damage or pigment degradation. Many regions that were painted with a cadmium yellow (CdS) pigment have faded to white.[3] However, XANES and μ -XRD experiments have recently been performed on faded flakes of paint from the painting, in order to determine the mechanism of the pigment degradation. Sulfur K-edge experiments showed the presence of $CdSO_4$ species along with the original CdS in the paint fragments, suggesting that the degradation could be caused by oxidation of the sulfur. Further studies of early 20th century paint samples that were artificially aged with high light, humidity, and both light and humidity, showed that the sulfates formed when the paint samples were exposed to high humidity or both high humidity and light, but not when they were only aged with light. This knowledge can help the museum decide how to display the painting while minimized further damage.

Another painting that was studied with μ -XRD and XANES is the *Maestà of Santa Maria dei Servi*, by the 13th century Italian painter Cimabue.[5] The painting featured "fake gilding", a combination of the arsenic pigment orpiment (As_2S_3) and metallic silver. This layer of paint quickly darkened, and was eventually painted in an attempt to hide the degradation. This degradation has also been noticed in paintings by other Italian painters from the same period. However, it was unclear whether the darkening is caused by the orpiment, the silver, or the combination of the two. Principal component analysis of the arsenic and sulfur K-edges showed the presence of Ag_2S, Ag_3AsO_4, and several arsenate species, indicating that the darkening of the paint is caused when the orpiment and silver react with each other. The μ -XRD mapping showed the degradation products Ag_2S_3 and As_2O_3 were mostly present at the surface of the paint, which suggests that the degradation is caused by exposure to the environment.

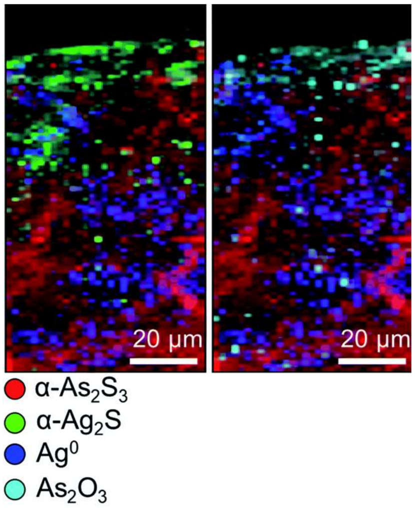

Figure 2. μ -XRD map of "fake gilding" sample

These methods can be applied to forms other than paintings. One pink zinc and chromium pigment has been used in the manufacture of porcelains since the 19th century, but in some porcelain mixtures, it turns from pink to brown.[6] XANES and μ -XRD were used to determine what caused this color change. In another study, historical glass fragments with degraded enamel were studied with μ -XRD to determine what was causing the deterioration.[7] These experimental methods are very valuable for elucidating the causes of degradation of artworks, which can lead to better care and conservation of them.

References

1. Wille, K., Synchrotron Radiation Sources, *Rep. Prog. Phys*. **1991,** *54*, 1005.
2. de Groot, F.; High Resolution X-ray Emission and X-ray Absorption Spectroscopy, *Chem. Rev.,* **2001**, *101*, 1779-1808.
3. Monico, L.; et. al. Probing the Chemistry of CdS Paints in *The Scream* by In Situ Noninvasive Spectroscopies and Synchrotron Radiation Techniques. *Science Advances*, **2022**, *6*, 20.

4. De Noulf, W.; Vanmeert, F.; Janssens, K. XRDUA: Crystalline Phase Distribution Maps by Two-Dimensional Scanning and Tomographic (Micro) X-Ray Powder Diffraction. *Journal of Applied Crystallography*, **2014,** *47*, 1107-1117.
5. Monico, L.; et. al. Development of a Multi-Method Analytical Approach Based on the Combination of Synchrotron Radiation X-Ray Micro-Analytical Techniques and Vibrational Micro-Spectroscopy Methods to Unveil the Causes and Mechanism of Darkening of "Fake-Gilded" Decorations in a Cimabue Painting. *J. Anal. At. Spectrum*. 2022, 37, 114-129.
6. Verger, L.; Dargaud, O.; Rousse, G.; Cotte, M.; Cormier, L.; The Stability of Gahnite Doped with Chromium Pigments in Glazes from the French Manufacture of Sevres. *Journal of the American Ceramic Society*, **2017**, *100*, 86-95.
7. Beltrán, M.; Schibille, N.; Brock, F.; Gratuze, B.; Vallcorba, O.; Pradell, T. Modernist Enamels: Composition, Microstructure and Stability, *Journal of the European Ceramic Society*, **2020**, *40*, 1753-1766.