AN INFRARED MICROSCOPIC AND X-RAY ANALYSIS OF ARTISTS’
PIGMENTS ADORNING A FIFTEENTH-CENTURY STATUE OF ST. WOLFGANG

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The Ball State University Museum of Art is home to many different works of art from a multitude of countries and cultures. One of these treasures is St. Wolfgang, a fifteenth-century statue originally from Austria. The statue depicts the likeness of one of the most popular saints in Germanic-speaking countries. The patron saint of carpenters, Wolfgang is best known for single-handedly building a church in the Alps.\footnote{According to legend, standing in the middle of a dense forest, Wolfgang threw his hatchet up into the air. The spot where the hatchet landed marked the location that God wished him to build the church. St. Wolfgang's likeness can be found in many churches throughout Austria and Germany. Sculpted by artist Anton Pilgram, the statue in the Ball State Museum of Art is believed to have come from one of these chapels.}

Little is known about the history of the five hundred-year-old sculpture, which has sustained some damage over time. The right shoe is broken, as is the object St. Wolfgang carries in his right hand. This may have been a crosier in reference to St. Wolfgang's religion. The statue also retains a substantial amount of original paint. Learning the colors and identities of the pigments remaining will provide insight into the history and authenticity of the statue. Two different methods of identification will help accomplish
First, FT-IR spectroscopy reveals information concerning the chemical structure of each pigment sample. Second, X-ray microscopy uncovers the elements present in each sample. Matching the results from both techniques allows for the identification of the pigments adorning St. Wolfgang. Once these pigments have been identified, their origins will provide valuable information about the history of the statue as well as the artistic styles of the fifteenth century.

Analysis procedures:
In order to analyze each location on the statue, a small sample of each pigment must be removed. Using FT-IR spectroscopy and X-ray microscopy has significant advantages over other identification methods. First, sampling does not require removing St. Wolfgang from the museum, and calls for little handling of the statue itself. Also, the instruments need only microscopic samples, and alteration of the sculpture is minimal. In fact, the samples were so small; the removal was virtually invisible to the naked eye. The pigments were removed by carefully scraping away samples using a clean, sharp knife. Each was carefully transferred to a slide, cleaned with 95% ethanol. The slide was sealed and labeled according to the location of the statue it was removed from. Pigments were sampled from eleven different locations on St. Wolfgang.

Each of the samples removed from the statue was analyzed using the same basic microscopy technique. Examination under a stereomicroscope revealed the colors, homogeneity, and general appearance of the samples. One by one, the samples were separated by color using a probe. A small amount of each color from each slide was transferred from the slide to a salt plate, using the metal probe. Rolling the sample onto the salt plate creates a thin, almost transparent layer ready for analysis. The spectrum was obtained with a Perkin-Elmer 1760-X Infrared Fourier Transform Spectrometer using a microscope accessory, in the transmission mode.
When gathering infrared spectra, the prepared sample is placed on the stage, which can be moved to find an appropriate area of the sample. Apertures placed above and below the sample narrow the area to be sampled and shield the detector from saturation. The Cassegrain objectives focus the infrared radiation onto the sample. Finally, a mirror is flipped, allowing infrared radiation to pass through the sample on the stage and into the detector.\(^7\)

The spectra were taken using a mercury-cadmium telluride (MCT) detector. Each spectrum consisted of ten scans taken at a 4 cm\(^{-1}\) resolution.\(^7\) The picture above illustrates the FT-IR setup. FT-IR analysis provided initial spectra of each sample, which was referenced with those in Artists and Artisans Materials Infrared Spectral Library (July 1993). Each location was sampled multiple times to establish consistency and then compared with the reference spectra. When a parallel spectrum was located, the sample traveled to the Scanning Electron Microscope and x-ray analysis confirmed the findings of the infrared spectra.
The picture above shows the setup for the Scanning Electron Microscope. The SEM begins with an electron gun powered by a source of high voltage. The gun sends an electron beam down a vacuum column. The beam is sent through the condensing lenses, which are similar to the cassegrainian lenses found in the infrared microscope. The condensing lenses consolidate the beam as it progresses to the scanning coils. The two coils, labeled x and y, bend the beam and raster it across the sample. An objective lens focuses the angled beam and sends it on to the sample. Secondary electrons rebound from the sample, move to the detector and amplifier, which analyze the data, and produce the image on the monitor.
An image is generated by three different methods, involving three different types of electrons. As the beam is sent to the sample, the illustration is created when electrons bounce back from the sample at one of three different levels. Auger electrons produce an image of the surface of the sample. Secondary electrons generated the images that we viewed by creating the image from below the sample's surface. Delving even deeper into the sample are the backscattered electrons. Those electrons that are not bounced back head into the heart of the sample. They interact with the atoms and induce inner electronic transitions. For example, if an electron excited to the L shell falls to the ground state, or K shell, a x-ray photon known as $K_{\alpha}$ is emitted. The K shell is synonymous with the principle quantum number of n=1. The L shell corresponds to n=2, M shell is n=3, and so on. If an electron is excited to the M shell and falls to the K shell, the result is the release of a $K_{\beta}$ x-ray photon. The energy released in photons is uniquely characteristic to each element, from Boron to Uranium. These photons are then sent to the detector, which measures them, creating and labeling peaks based on energy in keV and the quantity of each element present.

After all the locations had been samples and analyzed by both the infrared and x-ray methods, the pigments were identified. The identifications were made based on the results from the visual tests, infrared and x-ray spectra.
The table below illustrates the essential elements found in each x-ray spectrum for the different pigments sampled from St. Wolfgang.

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Color</th>
<th>Chemical Composition</th>
<th>Key elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lac Dye</td>
<td>Red</td>
<td>C_{26}H_{19}NO_{12}</td>
<td>C, O</td>
</tr>
<tr>
<td>Ultramarine Blue</td>
<td>Blue</td>
<td>Na_{8-10}Al_{6}Si_{6}O_{24}S_{2-4}</td>
<td>Na, Al, K, Si, O, S</td>
</tr>
<tr>
<td>Zinc Chromate</td>
<td>Yellow</td>
<td>ZnCrO_{4}</td>
<td>Zn, Cr</td>
</tr>
<tr>
<td>Orpiment</td>
<td>Yellow</td>
<td>As_{2}S_{3}</td>
<td>As, S</td>
</tr>
<tr>
<td>Prussian Blue</td>
<td>Blue</td>
<td>FeNH_{4}Fe(CN)_{6}</td>
<td>Fe</td>
</tr>
<tr>
<td>Ultramarine Red</td>
<td>Orange</td>
<td>Na_{8-10}Al_{6}Si_{6}O_{24}S_{2-4}</td>
<td>Na, Al, K, Si, O, S</td>
</tr>
<tr>
<td>Satin Ochre</td>
<td>Brown</td>
<td>Fe_{2}O_{3}</td>
<td>Fe, O</td>
</tr>
<tr>
<td>Calcium carbonate &amp;</td>
<td>White</td>
<td>CaCO_{3} &amp; TiO_{2}</td>
<td>Ca, C, O, Ti</td>
</tr>
<tr>
<td>Titanium Dioxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barium sulfate</td>
<td>White</td>
<td>BaSO_{4}</td>
<td>Ba, S, O</td>
</tr>
</tbody>
</table>

**Red pigments:**

One prominent red pigment covers the entire outer robe of St. Wolfgang. The organic red pigment, lac dye, is produced by the insect, *Coccus laccaei*, which lives on certain trees in India.\(^2\) The use of lac dye dates back to medieval times. The essential elements, carbon and oxygen, in the x-ray spectrum strongly support the organic lac dye, instead of a more common iron or mercury-based inorganic red pigment. Lac dye contains a natural varnish, known as shellac, which darkens with age. This may be an indication as to why such a large amount of red paint has survived the centuries in comparison with other pigments. The figure below is an infrared spectrum of the red pigment.
Yellow pigments:
The yellow pigment adorning various locations of St. Wolfgang was not introduced as an artist's material until 1750. Orpiment, an arsenic trisulfide, replaced the popular iron and lead-containing yellow pigments.\(^3\) The pigment, also known as King's Yellow, was artificially made by powdering the native mineral orpiment. Orpiment is not infrared active, and therefore, the infrared spectrum did not reveal any clues into the identity of the pigment. However, the key elements, As and S, in the x-ray spectrum distinctly identify the yellow pigment found on St. Wolfgang’s waistband, church windows and staff, as orpiment. This popular pigment has since become extinct with the introduction of cadmium yellows.

Blue pigments:
A very popular, distinct blue pigment can be found on the statue of St. Wolfgang. Ultramarine Blue occurs naturally in the form of lapis lazuli. In medieval times, the ultramarine blue pigment was as expensive as gold, and was used only for important details in a work of art.\(^6\) On St. Wolfgang, the ultramarine blue can be seen on the waistband, church windows and staff. All three are symbols of St. Wolfgang's religion and rank within the church, and therefore considered of the utmost importance. Six
essential elements identified ultramarine blue in the x-ray spectrum. Na, Al, Si, S, O, K are all distinct components of the lapis lazuli mineral. The figure below is an infrared spectrum of the blue paint removed from St. Wolfgang’s waistband.

Also discovered in the infrared spectrum and confirmed by the presence of Ba, S, and O in the x-ray spectrum is barium sulfate. This is a white pigment commonly used as a primer or filler in medieval times. Ultramarine blue is a notoriously poor pigment when used alone. For this reason, barium sulfate was often mixed with ultramarine blue to achieve a better consistency to the paint.3

Green pigments:
Two different pigments combine to form the green hue covering the church at St. Wolfgang’s feet and the platform upon which he stands. The first is the yellow Orpiment discussed in the earlier section. Again, the key elements As and S appearing in the x-ray spectrum identified Orpiment. The other component is a modern blue pigment identified as Prussian blue. Prussian blue is a ferriferrocyanide, or iron blue.3 The key element, Fe, found in the x-ray spectrum helped to confirm the identification of Prussian blue.
However, the most distinct evidence comes from the infrared spectrum. Prussian blue contains a cyanide group, with a carbon-nitrogen triple bond (C≡N), whose stretch is infrared active in the triple bond region at approximately 2085 cm\(^{-1}\). This region of the infrared spectrum is not overly popular, and an absorption in this area, especially for a blue pigment, is strongly indicative of Prussian blue. The figure below depicts the peaks found for Prussian blue. Peaks appearing that correspond to China Clay indicate the presence of a filler in order to achieve a more consistent painting medium, much the way barium sulfate is mixed with ultramarine blue.

![Infrared Spectrum of Prussian Blue and China Clay](image)

A different shade of green can be found on St. Wolfgang's waistband, the church windows and on the staff. The green paint was removed sparingly from these locations because very little of the original paint remains. Again, the green comes from a mixture of two pigments, one blue and one yellow. Ultramarine blue and zinc chromate were identified from their characteristic peaks appearing in the infrared spectrum. Unfortunately, not enough paint was available for x-ray analysis. The spectrum below was removed from the green layer of St. Wolfgang's waistband. The peaks for ultramarine blue, barium sulfate and zinc chromate are labeled.
Orange pigments:
St. Wolfgang's face and hands are shaded with a peach-colored pigment. Under the stereomicroscope, the sample is revealed an orange color. The infrared spectrum suggested the presence of another ultramarine pigment, ultramarine red. The key elements of Na, Al, S, Si, O and K all appeared in the x-ray spectrum, confirming the ultramarine red. Again, barium sulfate is combined with the ultramarine in order to achieve a smooth texture to the paint.³ Ultramarine red can take on a number of different hues, ranging from deep, blood red to pink to a bright orange.
Brown pigments:
A deep, brown pigment was removed from the rim of St. Wolfgang’s hat. This brown is a naturally occurring earth pigment known as Satin Ochre. Satin Ochre is an iron oxide, and the strong presence of both O and Fe in the x-ray spectrum help to confirm this identification. The infrared spectrum also reveals many peaks corresponding with the reference spectrum for the Satin Ochre pigment. Below is a spectrum of the Satin Ochre pigment removed from St. Wolfgang’s hat. A mixture of both the pigment and the primer layer of calcium carbonate was obtained in the sample.

White pigments, zinc tungate and China Clay:
The brilliant mix of colors adorning St. Wolfgang has survived miraculously well throughout the past five centuries. However, several constituents have worked “behind the scenes” to conserve this work of art. The statue itself is composed of limestone, which absorbs paint easily. Therefore, a primer layer of calcium carbonate was applied first. This allows the intended colors to show more vividly, and increases the quality of the work of art. Calcium carbonate is a very popular white pigment, which was most
commonly used as a filler and primer. The infrared bands for calcium carbonate are very distinct and easy to identify. This primer layer can be found in nearly every location sampled from St. Wolfgang. In some locations, such as the waistband, church windows, staff, platform and hat, the element titanium appears in the x-ray spectrum. This is indicative of titanium dioxide, the most common white pigment currently in use. Titanium dioxide is also mined as rutile, sometimes found in conjunction with limestone. Therefore, the titanium dioxide found in these samples could have originated from a mixture with the calcium carbonate or as an accessory to the limestone itself.

Another white pigment that is found among the paint adorning St. Wolfgang is barium sulfate. Barium sulfate is another common primer and filler pigment. As previously mentioned, barium sulfate is used in conjunction with both ultramarine blue and ultramarine red in order to improve upon the quality of the paint. In the x-ray spectra, BaSO₄ is confirmed by the appearance of Ba, S and O peaks. Significant peaks can be labeled corresponding to BaSO₄ in the infrared spectra as well.

Barium sulfate is an important additive for the ultramarine pigments. However, other pigments need fillers as well. In this case, China Clay was used as an additive for pigments such as Prussian blue and lac dye. China Clay is an aluminum silicate, and its
presence is supported by Al and Si peaks in the x-ray spectra. The infrared spectra also display peaks that correspond to China Clay.

The calcium carbonate allows the paint to show more vividly. Barium sulfate and China Clay ensure a better quality pigment. Finally, the statue must be protected from the elements. A mixture of zinc oxide and Tung Oil, zinc tungate was probably used as a varnish because it formed a protective coating over St. Wolfgang. Zinc tungate can be found in every location except the red pigment covering St. Wolfgang's gown. One explanation for this is that lac dye contains a natural varnish, known as shellac, as described previously. Tung Oil is an organic substance that displays many distinct peaks in the infrared spectra. The zinc is easily identified in the x-ray spectra by the appearance of large Zn peaks. Another use for zinc tungate is as a medium for the pigments. The Tung oil may have been used to in a similar way to the barium sulfate, as a way to create a better consistency to the paints as they were applied to the statue.

While the pigments are definitely the main attraction of St. Wolfgang, the primers, fillers and varnishes help to maintain the original look of the statue. These players did an excellent job, as St. Wolfgang retains a significant amount of original paint, and has sustained little damage over the past five centuries.

**Layering:**
Some of the locations on the statue have had more than one layer of paint applied. These all display the same layering pattern. The waistband, church windows and staff all have five different layers of paint still adhering to the statue. The bottommost layer is the primer layer of calcium carbonate and titanium dioxide pigments. Next is a yellow layer of orpiment, the arsenic trisulfide pigment. Following that, the mixture of ultramarine blue and barium sulfate. After that comes a green layer composed of the ultramarine blue and zinc chromate. Finally, the outermost layer was identified as brass.
Layering is an indication that the statue was painted multiple times throughout its five hundred-year history. The timeline for the applications of the paints upon the statue can be categorized as follows:

The first pigment layer is the yellow orpiment. This arsenic trisulfide was in use at the time of the creation of the statue. It has since become obsolete, however, with the introduction of cadmium yellows. Some pigments in the non-layered areas are also ancient pigments, in use at the same time as orpiment. Such locations include the red lac dye covering the outer gown and the brown satin ochre adorning the hat. The first painting of St. Wolfgang hypothetically included only the waistband, church windows, staff, the outer gown and the hat.

Next is the layer of ultramarine blue and barium sulfate. This mixture is also seen on St. Wolfgang's shoe. On the cheeks and hands, another ultramarine pigment, ultramarine red is found. Theoretically, the second painting included the addition of the orange pigment to the hands and cheeks, followed by the covering of the waistband, church windows and staff with the blue layer.

Above the blue is a thin layer of green paint. This layer is a mixture of ultramarine blue and zinc chromate. Although ultramarine blue is an ancient pigment, it is still popular among artists today. On the other hand, zinc chromate was not introduced as an artist's pigment until the mid-nineteenth century. Therefore, zinc chromate is classified as a modern pigment. Another modern pigment is located on the church and platform in the other green layer adorning St. Wolfgang. Prussian blue was not used as a pigment until the middle of the eighteenth century. Since these are all modern pigments, the idea is plausible that these locations were painted at the same time, making this the third painting of the statue.

Finally, the top layer found on the waistband, church windows and staff can also be seen on the inner sleeve, collar and hatchet. This was identified as brass gilding. However,
the other locations were not altered, and therefore the final painting of St. Wolfgang included only the application of the brass gilding.
References:


