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Analysis of Western African Textiles Through Analytical Methods

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ANALYSIS OF WESTERN AFRICAN TEXTILES THROUGH ANALYTICAL METHODS

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Abstract

A technical art analysis of select objects (88.04, 73.02, 70.07, and 86.01) from the Western African collection at the Frank Museum of Art at Otterbein University (Westerville, Ohio) was executed. Since little is known about the materials used in the Western African collection, the characterization of the surface may help better understand the historical aspects and origins of the objects. In order to identify pigments, binding materials, and dyes on the object's surface a multi-pronged approach was implemented, including x-ray fluorescence (XRF), X-ray diffraction (XRD), widefield fluorescence microscopy (WFM), liquid chromatography-mass spectrometry (LC-MS) and gas chromatography-mass spectrometry (GC-MS). Object 88.04 was identified to have kaolinite and hematite pigments while mask 70.07 was found to have a calcite mixture as well as ultramarine pigments within the samples taken. Artifact 86.01 was suggested to be a calcite mixture while the fabric analysis provided an unconvincing identification of brazilwood and camwood dyes. The waxy surface appearing on artifact 73.02 was suggested to be palm oil due to identification of methyl palmitate in palm oil and artifact samples. With this new information further research can be conducted in order to fully characterize the objects within the collection and uncover historical aspects of these objects.

Introduction to Western African Artifacts

Dyes have been known to be used by humanity since ancient times in clothing, art, and other fabric based projects.[1] Dyes until 1856 were exclusively from natural sources, plants, or animals.[1-6] Natural dyes are known to stain best on natural fibers such as linen, cotton silk, and wool; however, natural dyes tend to fade in light or after repeating washes.[1] The discovery of the first synthetic organic dye in 1856 was by an eighteen-year-old English college chemistry student, William Perkins. From the first discovery of synthetics, from 1880 and 1900 over 950

patents for new synthetic dyes were registered.[1] Today, there are over 100,000 synthetic dyes and 2,000 of these are produced in commercial quantities.[1] In the present day, all dyes are classified as organic aromatic compounds which contains a conjugated system of double bonds where functional groups attach. With these aromatic compounds, the applications of dyes are numerous. Some dyes require a mordant to enhance the binding of the dye on the fiber otherwise known as a linkage molecule for the dye and fiber. Dyes are not the only colorants used, for pigments are generally insoluble substances which impart color onto another material.[1]

Pigments are derived from minerals which are naturally occurring and then once collected are finely ground. These pigments do not dissolve in either water or organic solvents due to being mineral based. Pigments require a binder to clench onto a substrate. With few exceptions, pigments are known to be inorganic compounds while dyes are considered organic compounds. These pigments are known to be colored, colorless, black, white, or even metallic in exterior manifestation as they are naturally stone-based derivatives. Most synthetic pigments were not manufactured until the 19th century.[1] Today, most inorganic pigments are created from synthetic methods.[1] Since pigments and dyes have been noted for usage since ancient times, Africa is no different, for coloring occurred in textiles, ritualistic masks, and clothing.

Significant art and historical objects from Africa have been colored using dyes and pigments isolated from regional resources. Previous studies have determined the natural material used in the creation of objects, such as fabric and masks, from various regions of Africa, but the individual materials used on a majority of Western African pieces remains relatively unknown.[7] The diverse materials, dyes, and pigments used on historical objects have been previously identified in regions such as Ethiopia[8], Egypt[9], and Uzbekistan[10]; however, for regions such as Nigeria, Liberia, and the Ivory Coast, the details of these African objects remain relatively

unknown. These recent scientific studies on African art have shown to be significant in the understanding of the origin, cultures, and beliefs in which the objects originated and can be helpful in future studies.

In some cases, information has been collected about how an artist makes their piece and the pigments or dyes used; however, the plants were identified only by the local name.[1] From a chemical analysis perspective, this makes the identification of the dyes and pigments more difficult since common analysis methods compare an unknown material to standards representing a slate of possible compounds. A collection from the Cross-River region of Nigeria and Cameroon from the National Museum of African Art embodies this issue. The masks were decorated with dyes and pigments of plant origins known only in the local language. For future analysis of this mask collection, additional research must be done to identify the plants involved in the practice of creating and applying dyes and pigments for this region.[2] Other possible African pigment binders have been identified as palm kernel, iron oxides (red and yellow ochre), kaolinite white, smalt, ultramarine, carbon black, and possibly Tulka paste (powdered wood from Pterocarpus genus trees) within the Congo area.[3] Natural materials of all sorts have been identified for African mask and textile creation. An exceptional example in the Bamana society is the use of blood for ritual application to Komo masks, which results in protein accumulation in the colored areas of the mask.[5] Other white pigments previously identified in Africa include the excrement of lizards or snakes as well as ground schoolroom chalk.[4, 6] The prospect of identifying the natural materials used both to create the object and applied during rituals in scientific terms and through comparison of known natural materials and plants used for dyes will broaden the understanding of the historic and scientific significance of these artifacts.

The potential of expanding upon information of Western African artifacts is possible within the Frank Museum of Art at Otterbein University. Four distinct artifacts were chosen from the Western African collection in consultation with Dr. Janice Glowski, the Museum and Galleries Director at Otterbein University. Limited information about these four objects (88.04, 86.01, 73.02, 70.07) (Fig. 1) is known, except that they were collected between 1890 and 1970.

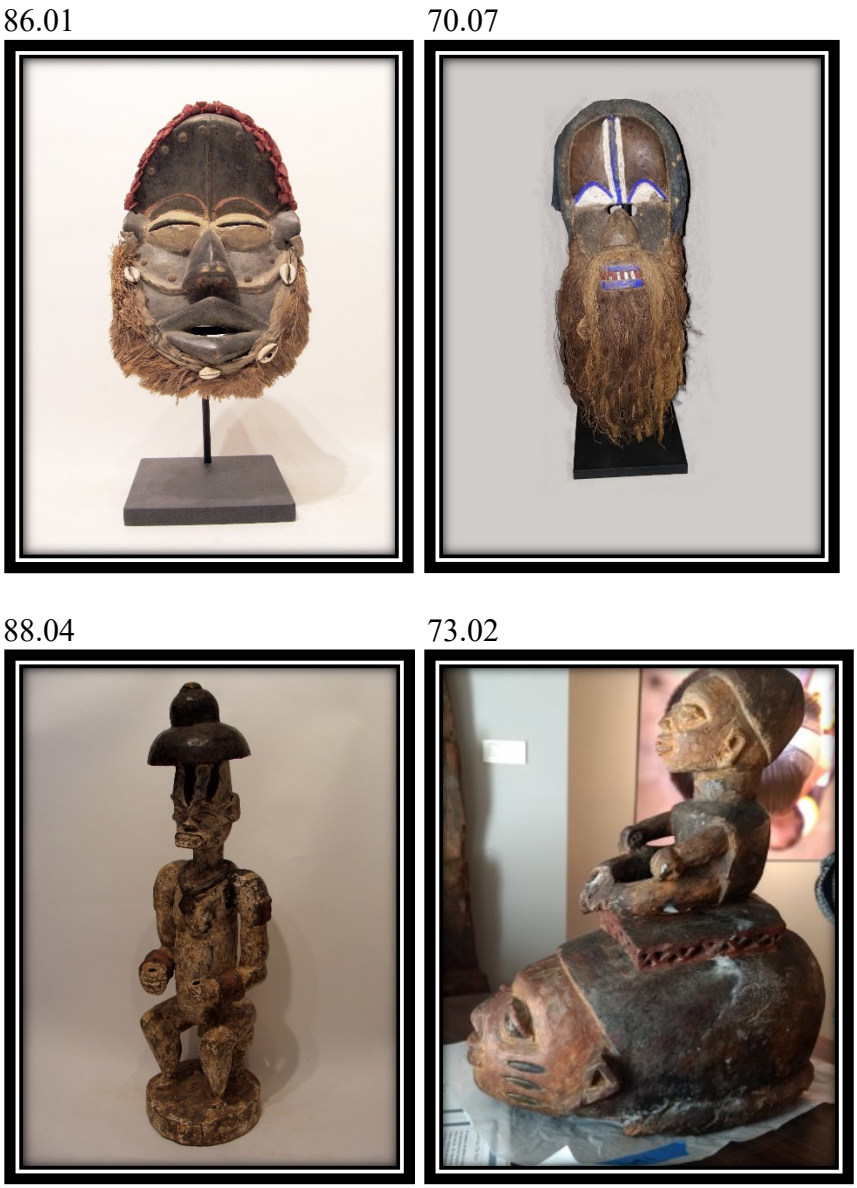


Figure 1. Western African Artifacts from Otterbein's Frank Museum

For figure 88.04 the museum database describes the statue as a "*Seated Figure in symmetrical pose. Hands in front of body - Wide smiling face teeth showing. Hat on top of high head. Tie around neck. Bracelets. Feet merging with base*, *a seated figure, handcrafted from wood possibly from the Urhobo or Igbo people within Nigeria*". This seated figure had no set origin of history due to the lack of information when donated.

Artifact 73.02 is a wood carved mask, otherwise known as a Glede mask, from Nigeria of the Yoruba tribe. The background of this object within the database is "*Gelede mask-carved wood. Face mask with Seated small figure as headdress attached to top of head.*"

The wood carven mask, 70.07, is attributed to the Kran tribe found within Liberia. The Frank Museum database states "*Painted wood mask with raffia & cloth. White & blue paint around eyes & mouth. Raffia attached to lower half of face (beard). Cloth band outside edge. Eyehole above bridge of nose.*"

Object 86.01 is a handcrafted wooden mask from either the Ivory Coast or Liberia from the Dan (Wobe) people. The database for this mask is very unsure of the materials used for the mask. The entry includes "*Carved wood mask of human face with eyes painted and closed and mouth slightly opened forming a diamond shape. all around the face attached textile (?) or leather(?) with shells and fur around the bottom half*," leaving more questions than answers of the composition of the materials used to decorate the wood.

The Analytical methods applied, for a series of procedures, transpired to suggest multiple pigments and dyes for the objects. Analytical approaches such as X-Ray Fluorescence (XRF), Widefield Fluorescence Microscopy (WFM), X-Ray Diffraction (XRD), Gas Chromatography/Mass Spectrometry (GC/MS), and Liquid Chromatography/Mass Spectrometry were applied for these artifacts. Specific instruments have been used for certain artifacts due to the

questions desired to be answered about the objects. The types of techniques for analysis can be destructive and non-destructive, and so it's important to understand if the methods will damage the objects permanently or not.

X-Ray Fluorescence (XRF) is a non-destructive technique due to causing no harm to the object as the data are collected via a scan on the surface. This technique uses an XRF gun to bombard the surface with x-ray radiation that causes ejection of an inner core electron in an atom and movement of a higher energy electron to the lower energy vacancy. A photon is released during this process that is different in energy from the initial x-ray radiation. The energy is indicative of the strength of attraction of the inner core electron to the atomic nucleus. Thus, XRF is used to assess the elemental composition of the sample. XRF is used to determine trace elements and characterize rocks, ores, and salts which can lead to the identification of mineral based pigments. Therefore, this method is used to characterize the elements on objects 88.04, 70.07, and 86.01.

Widefield Fluorescence Microscopy (WFM) is a destructive technique as a result of requiring samples to be taken for analysis and although a sample must be taken from the object, the sample size is no larger than the head of a pin. This technique identifies materials on the surface such as oils, carbohydrates, or proteins which can be the material which binds mineral pigments and dyes to a surface or applied to the object during its use. Similar to XRF, WFM is a spectroscopic method in which the excitation and emission energies of the radiation are different from one another. However, in WFM ultraviolet and visible light are used to study molecules instead of x-ray radiation. In WFM, molecular dyes, such as Nile Red, Alexa Flour 488 and triphenyl tetrazolium chloride are added to the samples collected from the artifact that interact with oils, proteins, and carbohydrates, respectively. If one of these binders is present, the molecular dye will fluoresce.

WFM is used in this study to analyze oily and proteinaceous materials on the surface of objects 88.04, 70.07, and 86.01.

X-Ray Diffraction (XRD) is a destructive technique since samples must be taken from the object for analysis. Single crystal diffraction is the specific technique applied for the testing of the artifacts due to only needing a sample of around 10 micrometers. The instrument emits X-rays onto the sample and when the sample and x-rays interact, scattering of these x-rays occurs. The angle, otherwise known as 2^{θ}, at which the rays enter the detector are measured. This technique is applied to analyze a unit cell or the smallest repeating group of atoms and allows for the identification of minerals. XRD is used to study artifacts 70.07, 86.01, and 88.04.

Gas Chromatography/Mass Spectrometry (GC /MS) is a method that is capable of identifying volatile molecules based on their polarity, boiling point, and mass. Since the molecule will be analyzed in the gas phase, this method is considered to be destructive. In this study, GC/MS is used to identify the composition of a waxy area on object 73.02. A sample was collected by passing a cotton swab over the surface and dissolving any collected material in hexane. A small volume (10 µL) of the sample liquid is then injected onto the column through a heated injection port that causes the compounds to vaporize. Once the compounds enter the column, they are separated based on boiling point and polarity and then enter the mass spectrometer. The mass spectrometer collects data based on the mass of a sample. The MS for the GC is an electron impact instrument which bombards the compounds with higher energy electrons causing the molecule to fragment. The mass-to-charge ratio or m/z of the fragments in then recorded as it passes through the mass analyzer and reaches the detector. By analyzing the sample in comparison to standards, the identity of the compounds in the sample can be found.

Liquid Chromatography/Mass Spectrometry (LC/MS) is another destructive method that is commonly used to analyze non-volatile compounds, such as dyes present in textiles. LC/MS is used in this study to examine the red material on mask 86.01. A small sample of fabric (less than half an inch) is placed in semi-polar solvent to remove the dyes and the solvent is then injected onto the LC column. The compounds are separated based on polarity and detected using UV and MS. The mass spectrometer attached to the LC is an electrospray MS. The electrospray ionization is considered to be a softer ion source than the electron impact used in GC/MS. Because it ionizes by proton transfer, no fragmentation occurs meaning that the observed m/z value is directly indicative of the molecular mass after accounting for the proton transfer.

By using a multi-pronged analytical approach incorporating XRF, WFM, XRD, GC/MS and LC/MS, the composition of materials on the surface of select objects in the Frank Museum of Art can be determined. This information may aid in the authentication of the origin of the objects as being from a particular region and dating in the age of the artifacts. Overall the objective of this research is to investigate the objects from the Western African collection at Otterbein's Frank Museum. Under this long-term goal, several other objectives were composed. Exploring available art and historical research for Western Africa, due to objects' unknown origin and material compositions. Completing a technical art analysis to identify the materials, origin or age of the artifacts. As well as developing a Liquid Chromatography/Mass Spectrometry method for dye extraction and analysis. The findings of this research are steps towards a deeper understanding of these historical artifacts.

Materials and Methods

Materials

Brazilin (≥98%) was purchased from Sigma-Aldrich (Saint Louise, MO). HPLC Water, HPLC Methanol, and Oxalic Acid were supplied by Fisher Scientific (Fair Lawn, NJ). Brazilwood (Paubrasilia echinata) Chips were acquired from The Woolery (Frankfort, KY). Camwood (Baphia nitida) powder (100% unrefined) was bought from Lola Lounge Botanicals (Huston, TX). PTFE membrane syringe filters and syringes (0.45 µm pore size) were obtained from Sigma-Aldrich (Saint Louise, MO). Hexanes (≥95%), NaOH pellets, and HPLC Methanol were purchased from Fisher Scientific (Fair Lawn, NJ). Red Palm Oil (100% unrefined) was obtained from Amazon through the Spicy World company (Huston, TX). The Food Industry FAME mixture/35077 was purchased from RESTEK Corporation (Bellefonte, PA).

Sample Collection

A sample from 86.01 of the fabric on the lower side of the mask was obtained from a surgical scalpel in a non-noticeable side (1 cm in length). Samples were collected from three masks in the most damaged areas in order to limit the amount of disturbance on the artifacts. From 88.04, samples were taken from the left side of the base, and the right arm band. Samples for 70.07 were collected at the left eye and bottom lip. 86.01 had a sample collected from the right eye.

Widefield Fluorescence Microscopy (WFM)

Images of embedded cross samples were collected using a Widefield MS Olympus BX40 system under visible, ultraviolet, blue and green light before and after exposure to Alexa Fluor 488, Nile Red, and triphenyl tetrazolium chloride (TTC) to identify protein-, lipid-, and carbohydrate-based binding materials, respectively. Nile Red was chosen as the addition to the

sample as a result of it historically being used to localize lipids within cells. It fluoresces in nonpolar environments but is almost nonfluorescent in water. The following fluorochrome stains were mixed in appropriate solvents for fluorescent filter cubes in widefield fluorescence microscopy.[11] Alexa Fluor 488, was made by dissolving 0.02% in a borate buffer, Nile red was made by dissolving 0.02% in ethanol, triphenyl tetrazolium chloride was made by dissolving 4% in methanol.

X-Ray Fluorescence (XRF)

X-Ray Fluorescence is a technique in which the elemental composition of materials is determined. A portable Olympus InnovXSystem XRF from Columbus State Community College (CSCC) (Figure 2) was used to collect spectra from an average of five regions on each object, and each K and L band from the spectra identified and correlated to a specific element.

Figure 2. Portable XRF Instrument from CSCC

X-Ray Diffraction (XRD)

X-Ray Diffraction is a method for which a sample around 10 micrometers in size is analyzed to determine a unit cell. The samples were inspected on a Bruker AXS SMART Apex II instrument. A single sample was then placed onto the tip of a sample holder to be situated in the proper location

and analyzed with APEX3 and OLEX2 software. The unit cell was then converted into a powder X-ray spectrum of 2θ and counts for analysis in comparison to mineral powder data from the American Mineralogist Crystal Structure Database. The comparison between angles of 2θ for the mineral and pigment was achieved through Excel.

Gas Chromatography/Mass Spectrometry (GC/MS)

A FISIONS Instruments GC 8000 Top MD 800 instrument was used for data analysis. Also, a RESTEK-5MS 30 m x 0.25 mmID x 0.25 µm column (Cat#: 12623, Serial# 1066228) was used with Xcalibur software for chromatographic separation. Multiple methods were employed throughout the project in order to identify if palm oil was upon the object. To analyze the standard mixture of fatty acid methyl esters (a FAME mixture), a sample volume of 8 µL and 2 µL of air injected onto the column. A multi-gradient setup was selected from the FAME mixture certificate of analysis with a full scan, electron impact (EI) ionization mode.[12] An initial temperature of 35°C was first ramped at 30°C/min until 100°C and remained at 100°C for five minutes. A second ramp of 3°C/min occurred until 240°C where it remained for ten minutes. The total run time for one sample lasted 65 min. with this method.

The method of analysis for palm oil varied from that of the FAME analysis. Although the injection process is similar, a different temperature program was used based on a previous publication.[13] The Palm Oil method had a sample volume of 8 µL and 2 µL of air injected onto the column. A starting temperature of 35°C was used and ramped at 10°C/min to 270°C. The oven then remained at 270°C for one minute. The total run time for a sample was 25.50 minutes with this method.

The wood samples and artifact samples were swabbed in a back and forth motion 10 times when collecting samples for analysis. In creation of the tongue depressor samples, the liquified

palm oil was spread on top of the depressors until super saturated and left to soak into the wood for a week in order to mimic the wooden masks. In order to retrieve the sample from the Q-tip, the head was submerged in hexanes and kneaded until the cotton was clear of sample. The sample solution was then filtered with a 0.45 µm filter and placed into a GC vial for analysis (Figure 3).

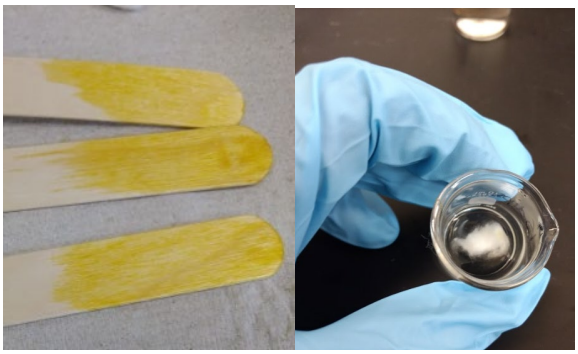


Figure 3. Tongue Depressor Samples and Sample Extraction

Left: Tongue depressors saturated with palm oil
Right: Technique for removing sample from Q-tip

LC/MS

A Thermo Scientific UHPLC focused Dionex Ultimate 3000 containing a BDS hypersil C18 (50 x 2.1 mm) column with 5-micron particles was used along with a Variable Wavelength Detector at a wavelength of 290 nm and an LCQ FLEET MS in positive mode. This instrument was used in order to analyze possible dyes of artifact 86.01 such as brazilwood and camwood.

Brazilwood dye was abundant in quantity at the start of the project and used in Western Africa due to the slave trade of Brazil since the early 16th century, which continued until around World War II.[14] It wasn't until the 1930's when relations began to mend and so trade between the two countries expanded into a welcoming agreement.[14] Since brazilwood is an import into Africa, it was decided upon as the test dye and a standard in order to begin the development of a method for dye identification.[7, 14] The brazilwood dye used for analysis was created through a beaker of distilled water and brazilwood chips. The chips were left to boil for 20 minutes or until a dark color

is achieved. The dye was then strained to remove any left-over brazilwood chips from the created dye. Camwood was another potential source of a natural dye due to the camwood trees residing in Western Africa and previous literature sources.[7] The creation of camwood dye was similar although it was a powder added to the distilled water instead of wood chips. The camwood dyed fabric sample was conducted through soaking in the created dye for a week. In order to use these for LC/MS analysis, it was filtered through a 0.45 μm filter. To analyze this dye, a series of methods had been developed to investigate an efficient gradient producing the most advantageous chromatogram. From Brazilwood1 to Brazilwood14, the run time was shortened, became a multi-step gradient, and was able to conceive a bell-shaped curve identifying the dye (Table 1). The Brazilwood14 method was also applied for the camwood dye producing a bell-shaped curve as well.

Table 1. Description of LC/MS Methods for Dye Analysis

<table>
<tr><th>Method</th><th>Gradient Type</th><th>Mode (+/-)</th><th>Scan Events</th><th>Total Run Time (min)</th></tr>
<tr><td>Brazilwood1</td><td>Ramp
3%D to 93%D*</td><td>+</td><td>1</td><td>15.00</td></tr>
<tr><td>Brazilwood2</td><td>Ramp
3%D to 93%D</td><td>+</td><td>1</td><td>30.00</td></tr>
<tr><td>Brazilwood3</td><td>Multi-Step
<table><tr><th>Retention (min)</th><th>Flow (mL/min)</th><th>%D</th></tr><tr><td>0.000</td><td>0.100</td><td>3.0</td></tr><tr><td>0.000</td><td>0.100</td><td>3.0</td></tr><tr><td>3.000</td><td>0.100</td><td>3.0</td></tr><tr><td>36.000</td><td>0.100</td><td>53.0</td></tr><tr><td>40.000</td><td>0.100</td><td>93.0</td></tr></table></td><td>+</td><td>1</td><td>30.00</td></tr>
<tr><td>Brazilwood4</td><td>Multi-Step
<table><tr><th>Retention (min)</th><th>Flow (mL/min)</th><th>%D</th></tr><tr><td>0.000</td><td>0.100</td><td>3.0</td></tr><tr><td>0.000</td><td>0.100</td><td>3.0</td></tr><tr><td>3.000</td><td>0.100</td><td>3.0</td></tr><tr><td>26.000</td><td>0.100</td><td>53.0</td></tr><tr><td>36.000</td><td>0.100</td><td>93.0</td></tr></table></td><td>+</td><td>1</td><td>36.00</td></tr>
</table>

<table>
<tr><td>Brazilwood5</td><td>Multi-Step<table><tr><th>Retention (min)</th><th>Flow (mL/min)</th><th>%D</th></tr><tr><td>0.000</td><td>0.100</td><td>3.0</td></tr><tr><td>0.000</td><td>0.100</td><td>3.0</td></tr><tr><td>7.000</td><td>0.100</td><td>3.0</td></tr><tr><td>27.000</td><td>0.100</td><td>43.0</td></tr><tr><td>37.000</td><td>0.100</td><td>93.0</td></tr></table></td><td>+</td><td>1</td><td>37.00</td></tr>
<tr><td>Brazilwood6</td><td>Multi-Step<table><tr><th>Retention (min)</th><th>Flow (mL/min)</th><th>%D</th></tr><tr><td>0.000</td><td>0.100</td><td>3.0</td></tr><tr><td>0.000</td><td>0.100</td><td>3.0</td></tr><tr><td>10.000</td><td>0.100</td><td>3.0</td></tr><tr><td>26.000</td><td>0.100</td><td>43.0</td></tr><tr><td>40.000</td><td>0.100</td><td>93.0</td></tr></table></td><td>+</td><td>1</td><td>40.00</td></tr>
<tr><td>Brazilwood7</td><td>Multi-Step<table><tr><th>Retention (min)</th><th>Flow (mL/min)</th><th>%D</th></tr><tr><td>0.000</td><td>0.100</td><td>3.0</td></tr><tr><td>0.000</td><td>0.100</td><td>3.0</td></tr><tr><td>15.000</td><td>0.100</td><td>3.0</td></tr><tr><td>30.000</td><td>0.100</td><td>43.0</td></tr><tr><td>45.000</td><td>0.100</td><td>93.0</td></tr></table></td><td>+</td><td>1</td><td>45.00</td></tr>
<tr><td>Brazilwood8</td><td>Multi-Step<table><tr><th>Retention (min)</th><th>Flow (mL/min)</th><th>%D</th></tr><tr><td>0.000</td><td>0.100</td><td>0.0</td></tr><tr><td>0.000</td><td>0.100</td><td>0.0</td></tr><tr><td>3.000</td><td>0.100</td><td>3.0</td></tr><tr><td>23.000</td><td>0.100</td><td>90.0</td></tr><tr><td>33.000</td><td>0.100</td><td>90.0</td></tr></table></td><td>-</td><td>1</td><td>33.00</td></tr>
<tr><td>Brazilwood9</td><td>Multi-Step<table><tr><th>Retention (min)</th><th>Flow (mL/min)</th><th>%D</th></tr><tr><td>0.000</td><td>0.050</td><td>0.0</td></tr><tr><td>0.000</td><td>0.050</td><td>0.0</td></tr><tr><td>3.000</td><td>0.050</td><td>3.0</td></tr><tr><td>30.000</td><td>0.050</td><td>90.0</td></tr><tr><td>40.000</td><td>0.050</td><td>90.0</td></tr></table></td><td>-</td><td>1</td><td>40.00</td></tr>
<tr><td>1Brazilwood10</td><td>Multi-Step<table><tr><th>Retention (min)</th><th>Flow (mL/min)</th><th>%B</th></tr><tr><td>0.000</td><td>0.050</td><td>0.0</td></tr><tr><td>0.000</td><td>0.050</td><td>0.0</td></tr><tr><td>3.000</td><td>0.050</td><td>3.0</td></tr><tr><td>30.000</td><td>0.050</td><td>90.0</td></tr><tr><td>40.000</td><td>0.050</td><td>90.0</td></tr></table></td><td>-</td><td>1</td><td>40.00</td></tr>
<tr><td>Brazilwood11</td><td>Multi-Step<table><tr><th>Retention (min)</th><th>Flow (mL/min)</th><th>%D</th></tr><tr><td>0.000</td><td>0.050</td><td>0.0</td></tr><tr><td>0.000</td><td>0.050</td><td>0.0</td></tr></table></td><td>-</td><td>1</td><td>40.00</td></tr>
</table>

	3.000	0.050	3.0	
	9.000	0.050	12.0	
	40.000	0.050	90.0	
Brazilwood12	Multi-Step		-	1	18.00
	Retention (min)	Flow (mL/min)	%D	
	0.000	0.050	0.0	
	0.000	0.050	0.0	
	3.000	0.050	3.0	
	9.000	0.050	6.0	
	18.000	0.050	90.0	
Brazilwood13	Multi-Step		-	1	18.00
	Retention (min)	Flow (mL/min)	%D	
	0.000	0.050	0.0	
	0.000	0.050	0.0	
	3.000	0.050	3.0	
	9.000	0.050	4.5	
	20.000	0.050	90.0	
Brazilwood14	Multi-Step		+	1	18.00
	Retention (min)	Flow (mL/min)	%D	
	0.000	0.050	0.0	
	0.000	0.050	0.0	
	3.000	0.050	3.0	
	9.000	0.050	4.0	
	20.000	0.050	90.0	
Data Dependent	Multi-Step		+	1,2,3	18.00
	Retention (min)	Flow (mL/min)	%D	
	0.000	0.050	0.0	
	0.000	0.050	0.0	
	3.000	0.050	3.0	
	9.000	0.050	4.0	
	20.000	0.050	90.0	

*D is a representation of HPLC Methanol, HPLC Water was the other solvent used in the mobile phase. Constants: Column Temperature (30°C), UV Lamp (290 nm), Inject Volume 100 µL, Flow Rate (mL/min), and Scan Range 50.00-2000.00 m/z

In addition to completing mass spectral (MS) analysis, Ms^n studies were also completed using a data dependent mass spectrometry method. In this case, Brazilwood method 14 was modified by adding two additional segments to the mass spectrometry program. In the first segment, the method was programmed to isolate the most intense mass-to-charge (m/z) peak and fragment it through collision with helium atoms. In the second segment, the second most abundant peak is isolated and fragmented. These fragments are then detected and provided additional structural characteristics about the molecules eluting from the LC column.

In addition to LC/MS analysis of standard liquor dyes (camwood and brazilwood) and standard compounds (brazilin), extracts from textiles were also studied. The extraction method was taken from a previous study.[4] A 25 mL solution of 4 mM of oxalic acid in HPLC water was prepared. HPLC methanol (6 mL) and 4 mL of the oxalic acid solution were mixed thoroughly. 150 µL of the solution was added to a LC/MS vial with 1 cm of the dyed fabric. The vial was then screwed shut and placed in the analytical oven at 60℃. The sample vial was left in the oven for an hour. The solution and the sample had changed color (Fig. 4) indicating a successful extraction. The now colored extract was pipetted into a syringe with a 0.45 µm filter and then within a new LC/MS vial. The vial was then placed into the LC/MS and ran with the data dependent method.

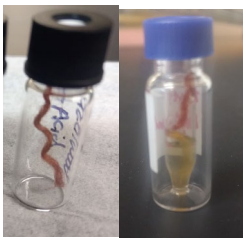


Figure 4. Pictures of Extraction Vials Containing a Thread Dyed with Brazilwood Before (Left) and After (Right) Extracted into a Water, Oxalic Acid, Methanol Mixture.

Results and Discussion of Artifacts

Object No. 88.04 – Surface analysis of object no. 88.04

This object may be Ikenga or shrine figure and likely was used for ceremonial purposes. Unlike most Ikenga though that feature animal attributes, such as horns on the heat, object 88.04 includes a European style hat. This together with the seated position suggests a position of honor. Object 88.04 likely used to hold a sword in the right hand and a staff or other item in the left. Object 88.04 appears to have a white material over the majority of its body, as well as red pigment over arm

bands and bracelets, and black on its hat, necklace, and facial design. Two samples were taken – a white one from the rear bottom of the object and a red one taken from its right bracelet (Fig. 7).

X-Ray Fluorescence (XRF)

As shown in Fig. 6, the white sample was found to have a significant amount of silica followed by aluminum and smaller amounts of additional elements. The high amounts of silicon and aluminum, the white color and the fact that this material flakes suggested it is likely kaolin ($Al_2Si_2O_5(OH)_4$), a type of white clay. Kaolin is used widely throughout Africa and is applied on the human body and artifacts to signify spirituality.[7,18] The silicon and aluminum relationship for this sample resulted in a 2.4 ratio. For Nigerian kaolin the ratio of aluminum and silicon varies between 1:2, 1:4, and 3:2.[15, 16] The ratio of this object matches the ratio of site N2.2 on the map of Nigeria (Fig. 5), which is near the city Abeokuta. Thus, these data support the attribution of object 88.04 as originating from Nigeria. The red sample displayed high amounts of silicon and sulfur with an almost equal amount of iron and aluminum (Fig. 6). From this elemental composition, iron ochre is suggested to be present (Fig. 6). Iron ochre is composed of hematite and iron (III) oxide, which is also known in Greek as hema (blood).[16]

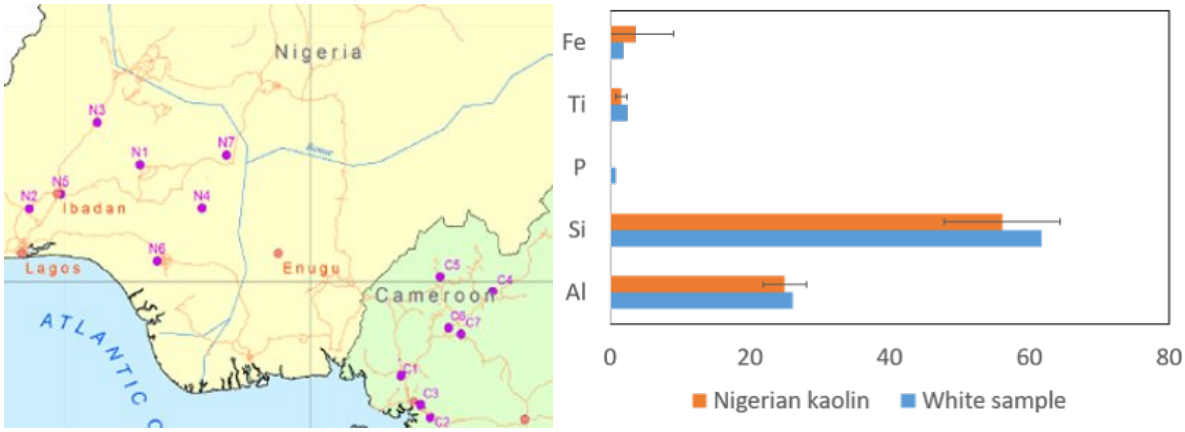


Figure 5. Object 88.04 XRF Results

Shown is the map of Nigerian kaolin deposits, and at right is the graphical comparison of the white sample's element percentages compared to Nigerian kaolin which falls within the appropriate range.

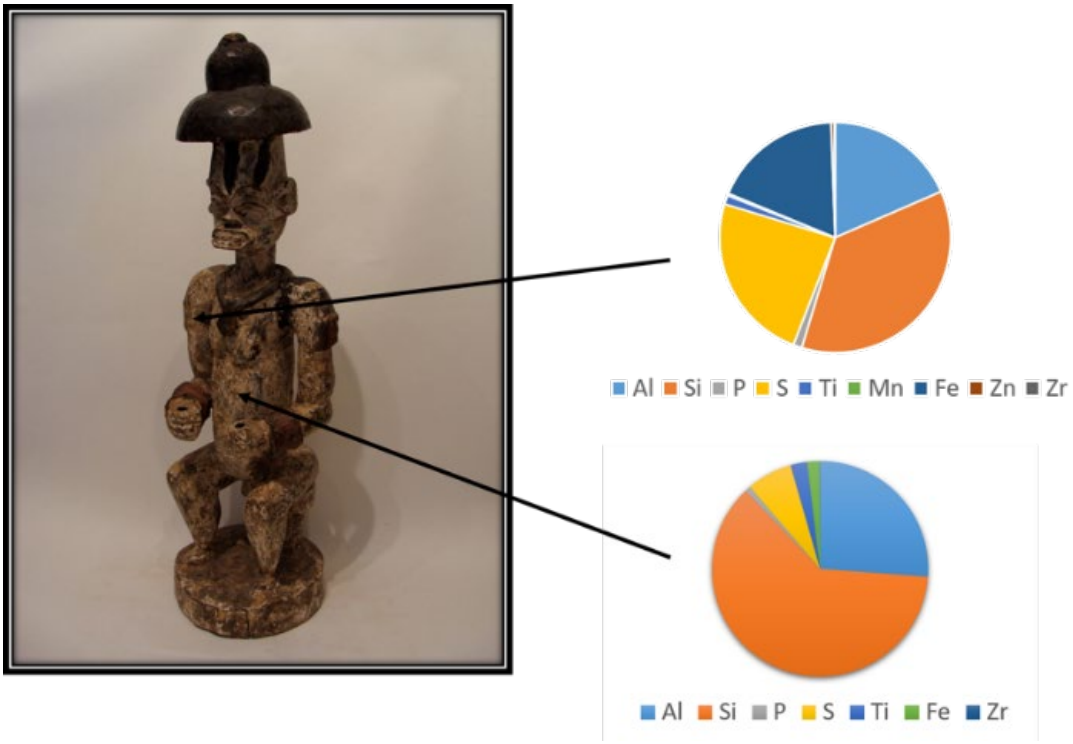


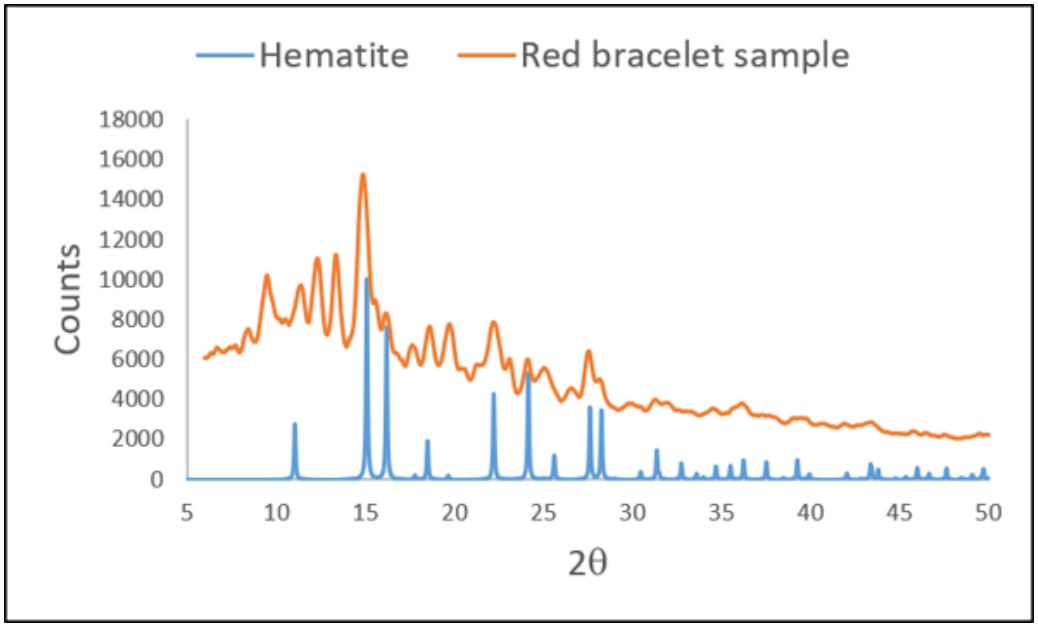
Figure 6. Object 88.04 XRF Results

Graphical analysis of the elemental compositions of the red and white samples.

X-Ray Diffraction (XRD)

To further confirm the results obtained with XRF, X-Ray Diffraction (XRD) was also performed on the white and red samples taken from object 88.04. From the American Mineralogist Crystal Structure Database, hematite and two forms of kaolin were graphed in comparison to the red and white samples, respectively. The angles at which the sample and hematite scattered the x-rays matched in multiple areas suggesting the red sample is made of hematite. When both types of kaolin and the white sample were graphed together there were multiple peaks which matched, supporting the idea of the white sample being composed of kaolin (Fig. 7). Multiple peaks may not match the literature data due to completing a single crystal diffraction instead of a powder x-ray diffraction from which the literature data is provided. Peaks missing from the literature which

appear in the samples may be due to the pigment being predominately composed of these matching materials but overall is in an unknown mixture of the mineral pigment.



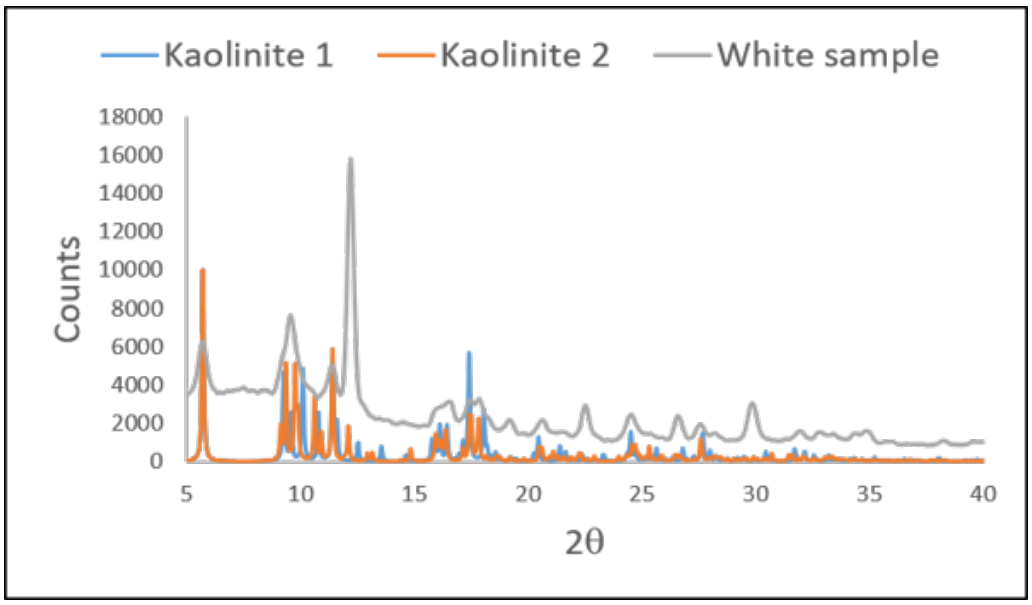


Figure 7. XRD Results for Object 88.04[24,25, 26]

(Top) Red sample in comparison with hematite
(Bottom) White sample in comparison to kaolin from two different regions

Widefield Florescence Microscopy (WFM)

With this method, Nile red was added to the sample for microscopic analysis. Nile red has historically been used to localize lipids within cells and the structure is shown (Fig. 8). It is almost nonfluorescent in water but fluoresces in nonpolar environments. From the luminescence of the sample after Nile red addition, the presence of oil on both samples is confirmed (Fig. 8). What is significant about this confirmation is that sculptures of Western African artifacts are known to use coloring agents mixed with animal fat, palm oil, and shea butter.[7]

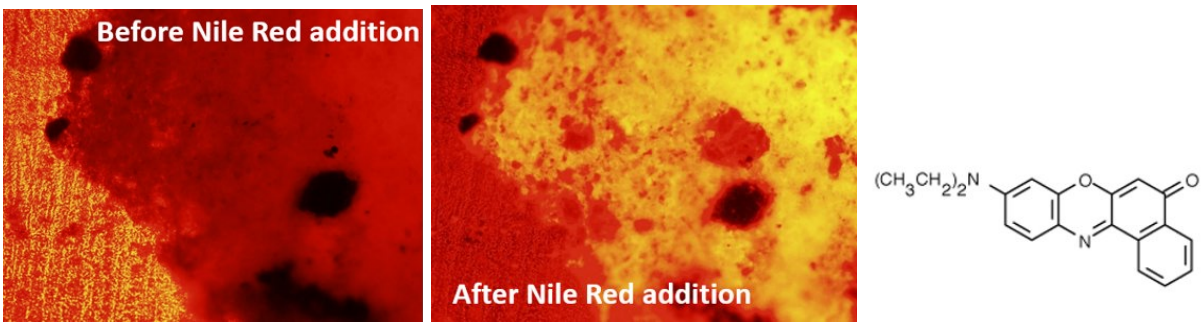


Figure 8. Artifact 88.04 WFM Results

Shown are the before and after pictures of the samples to display how adding Nile red suggests the presence of fat and oil. The structure of Nile Red is also shown (left).

Through the use of XRF, XRD, and WFM, the materials used on the object 88.04 were found to be kaolin, red ochre, and a fatty material, which are consistent with materials known to be used in Western Africa. Further, the attribution of creation of object 88.04 to a tribe in Nigeria is supported through the relative ratio of aluminum and silicon in the kaolin found using XRF.

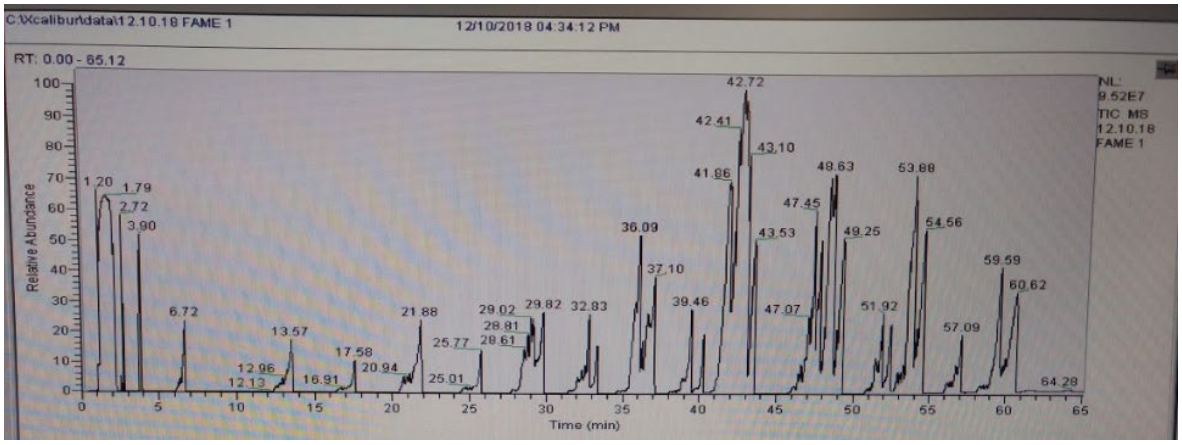
Object No. 73.02 – Surface analysis of object no. 73.02

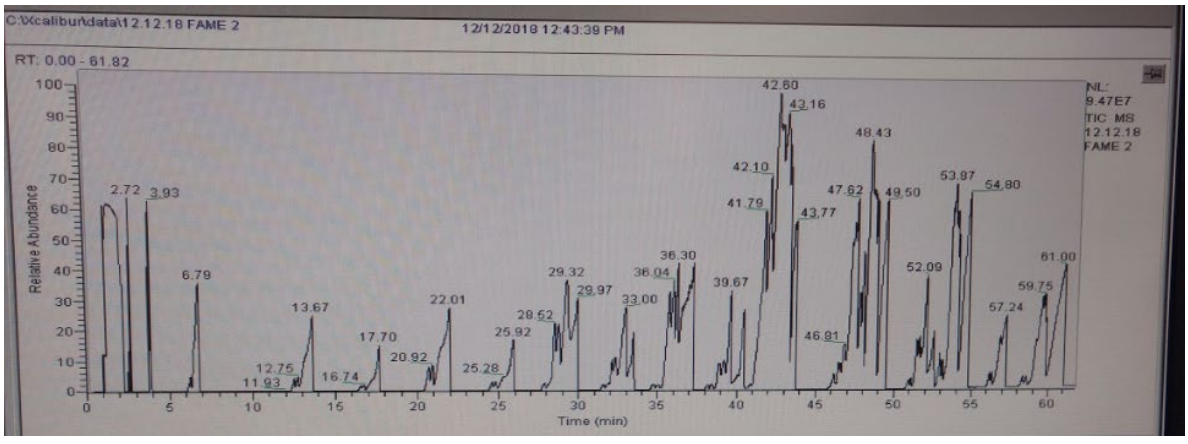
Gas Chromatography/Mass Spectrometry (GC/MS)

Since object 73.02 is not currently being exhibited, it is kept in storage at the Frank Museum of Art and is removed to showcase during various classes and discussions. Dr. Janice Glowski, the Museum and Galleries Director at Otterbein University, noted that a white, waxy substance appeared to build up on its surface and then disappear as it is moved in and out of storage. Gas chromatography-mass spectrometry (GC/MS) was employed in an effort to identify the material. In order to analyze the possible source, research was conducted for possible pigment binders. Applications of vegetable oils and fats are commonly used as pigment binders within Western Africa.[17] A foremost option for a binder is palm oil, due to the plant being a cash crop for a majority of Western Africa.[18] In support of identifying the compound, multiple methods and steps were completed to undertake identifying the unknown cause of a waxy surface. The GC/MS of fatty

acid methyl ester (FAME) standard mixture, tongue depressor (artifact mock-up made using palm oil on the wood) samples, derivatized palm oil, and the samples collected from object 73.02 was conducted. GC/MS has proven to be an instrument which presents superior and elegant detection of vegetable oils and so it is the instrument of choice when identifying oil binders.[13]

The results of the analysis of the FAME mixture are shown in Figure 9 and are consistent with its certificate of analysis. However, the severe peak fronting suggests that the column was overloaded during the analysis. The chromatogram of derivatized palm oil is shown in Fig. 10 and reveals the presence of X components. Of the compounds present, one is also found in the FAME mixture, methyl palmitate (Fig. 9).





Methyl Palmitate	270, 239, 227, 185, 171, 143, 129, 87, 74

Methyl Palmitoleate	268, 236, 194, 192, 165, 152, 141, 138, 123, 110, 96, 87, 83, 74, 69, 55, 41, 29

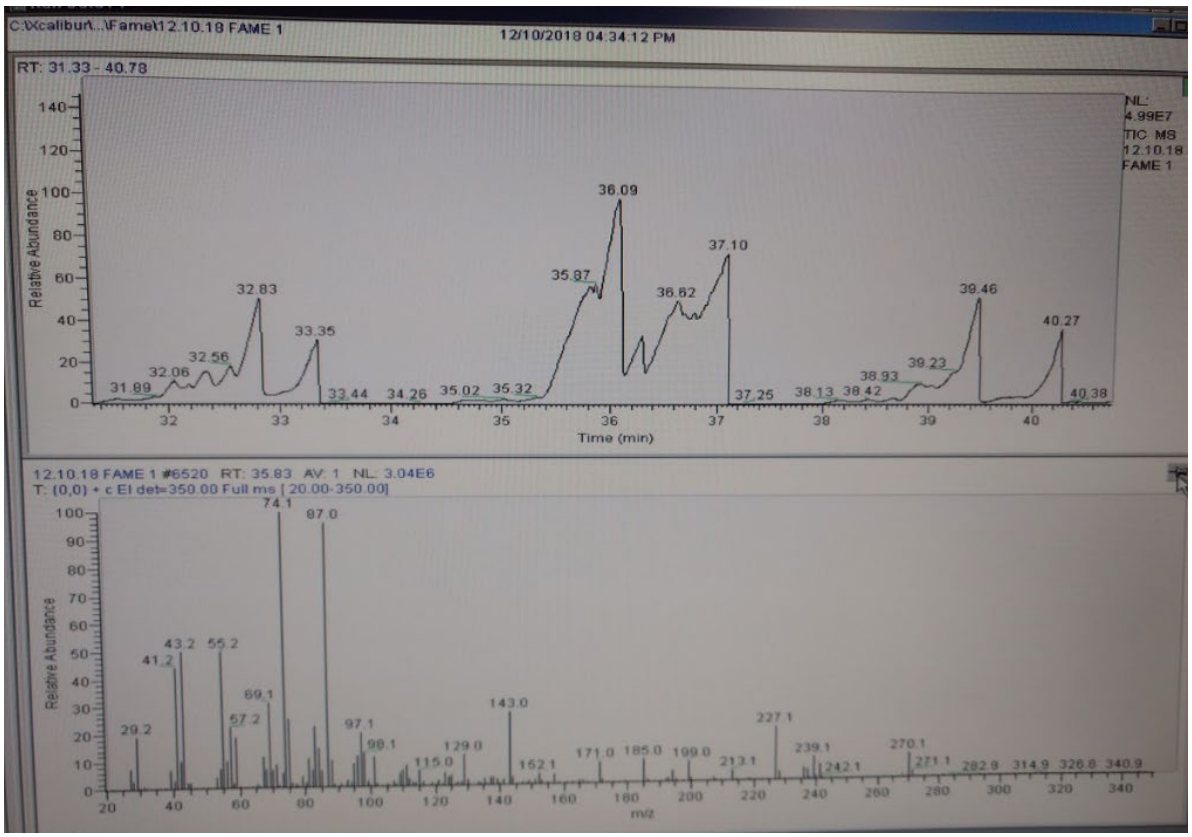


Figure 9. Gas Chromatography of a Standard FAME Mixture.

Shown is the FAME1 method for identification of methyl palmitate and methyl Palmitoleate (the compounds of interest) as well as the table of m/z ratios of the compounds of interest.

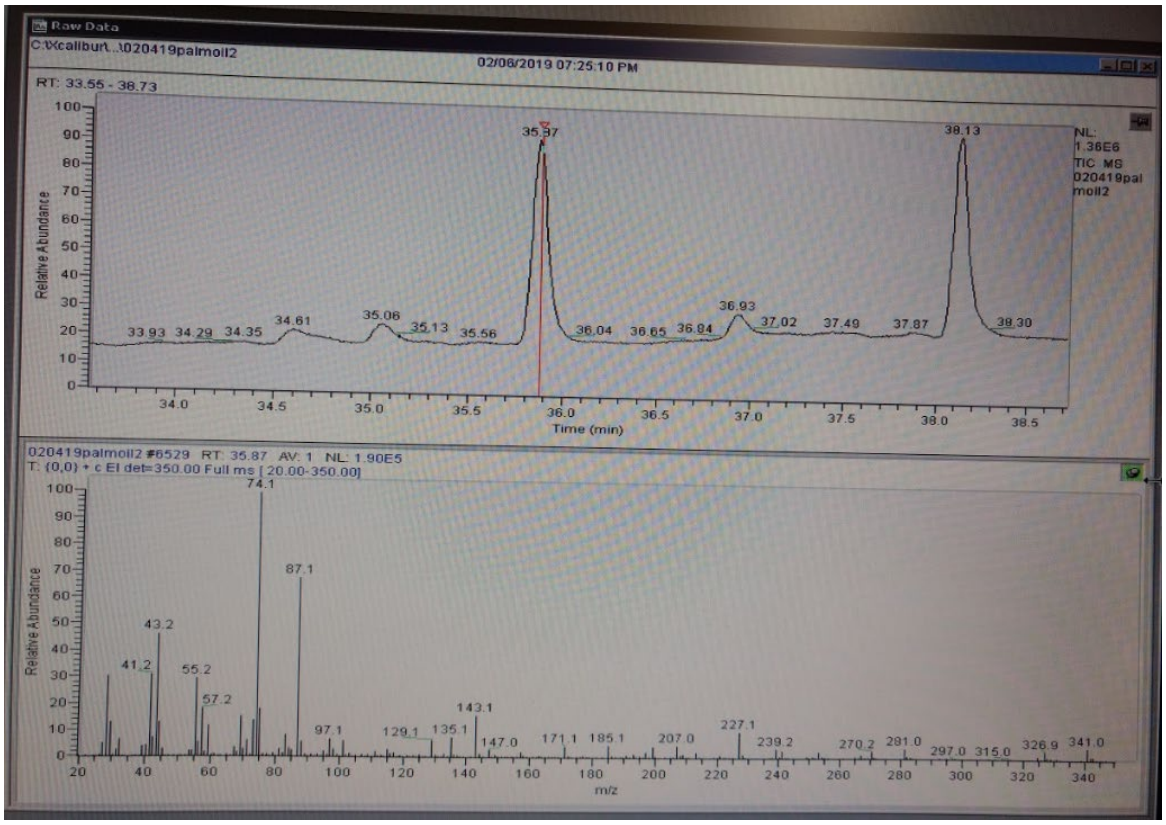


Figure 10: Gas Chromatography of Derivatized Palm Oil

1:1 Ratio of Palm Oil and Hexanes

Before analyzing a sample from object 73.02, a simulated artifact was created using palm oil painted onto wood (a tongue depressor) and a swab from it analyzed by GC/MS. As shown in Fig. 10, there is little discernible signal above the noise is the resulting chromatogram. However, to determine if palm oil could be identified, the mass spectrum at the expected retention time for methyl palmitate was examined and found to agrees with that seen in the palm oil standard.

The artifact samples were collected in November of 2018 within the Frank Museum of Art. The artifact samples were not analyzed until March of 2019. For analysis, only a few samples were processed to determine if palm oil could be detected from this smaller set of samples, from the six total samples, only three were analyzed (sample # 3,4,5). The other three samples appeared to

contain less and so were not analyzed; for if palm oil was appearing in the samples after this long wait, the most concentrated would appear in the GC/MS. As shown in Fig. 11, only peaks due to the solvent were observed, indicating sample degradation had occurred or simply the amount of material is below the detection limit of the instrument.

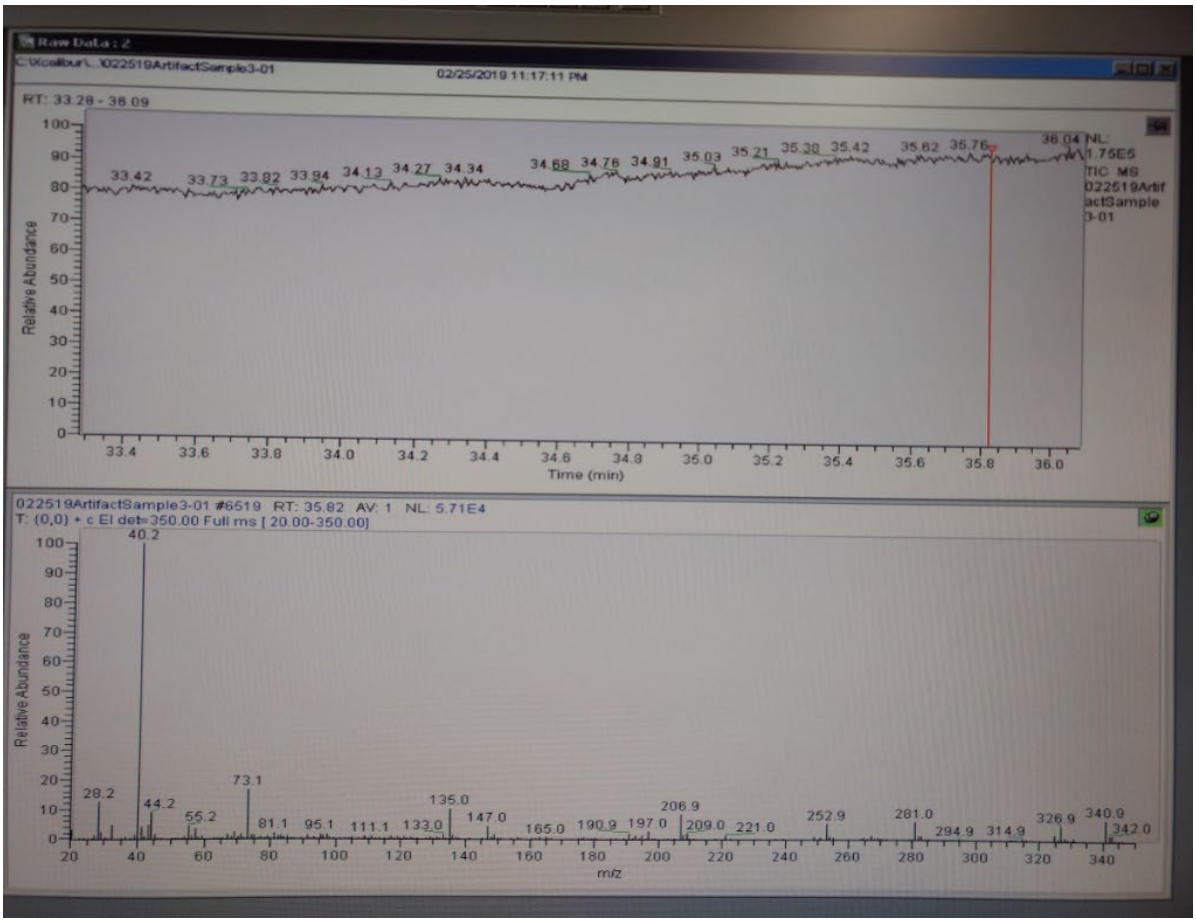


Figure 11. Gas Chromatogram (Top) of Samples from Artifact 73.02 and mass spectrum at 35. 82 a Retention Time of min Showing Lack of Methyl Palmitate

New samples of object 72.02 were collected and analyzed in the same day in March of 2019. These new samples provided peaks which indicate the presence of methyl palmitate and therefore, suggests the object's surface to be enclosed in palm oil. Through the use of GC/MS, the material on the object 73.02 was suggested to be palm oil, which is consistent with materials known to be used in Western Africa.

Object No. 70.07 – Surface analysis of object no. 70.07

Widefield Florescence Microscopy (WFM)

Similar to figure 88.04, WFM results suggest the presence of some type of oil on mask 70.07 due to increased fluorescence upon the addition of Nile Red (data not shown).

X-Ray Fluorescence (XRF)

As shown in Fig. 12, XRF data of the white area about the eye of the mask indicated a high percentage of silicon and aluminum. The presence of both silicon and aluminum suggests kaolin ($Al_2Si_2O_5(OH)_4$). The XRF data for the blue sample from the lip indicated a sizable percentage of silicon, sulfur, and just under a forth of aluminum. With this elemental composition, the data suggest ultramarine ($Al_6Na_8O_{24}S_3Si_6$) as the pigment (Fig. 12). The first reported use of ultramarine by Western visitors to Africa occurred in the 1960's.[7] However, it is unknown when African peoples may have started to use this material. If the actual first date of use in Africa coincides with this first report, object 70.07 may not have been made or at least painted until the 1960's.

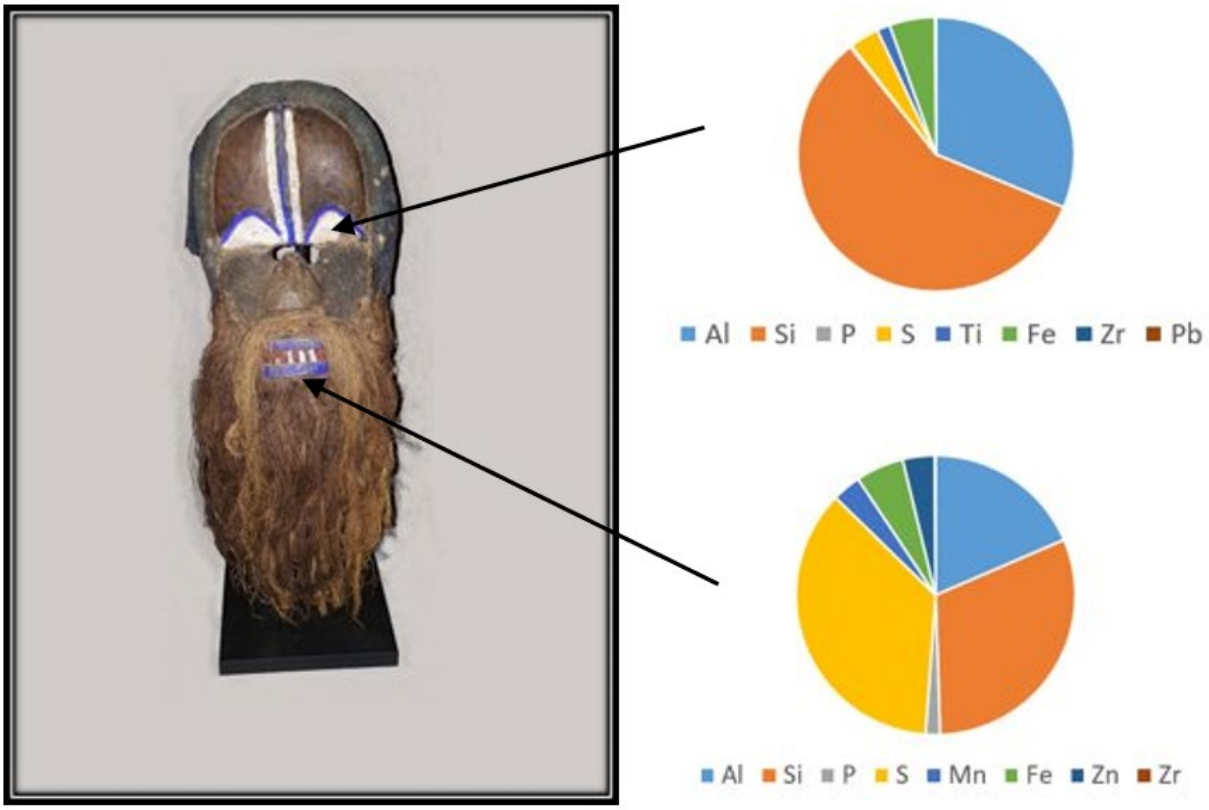


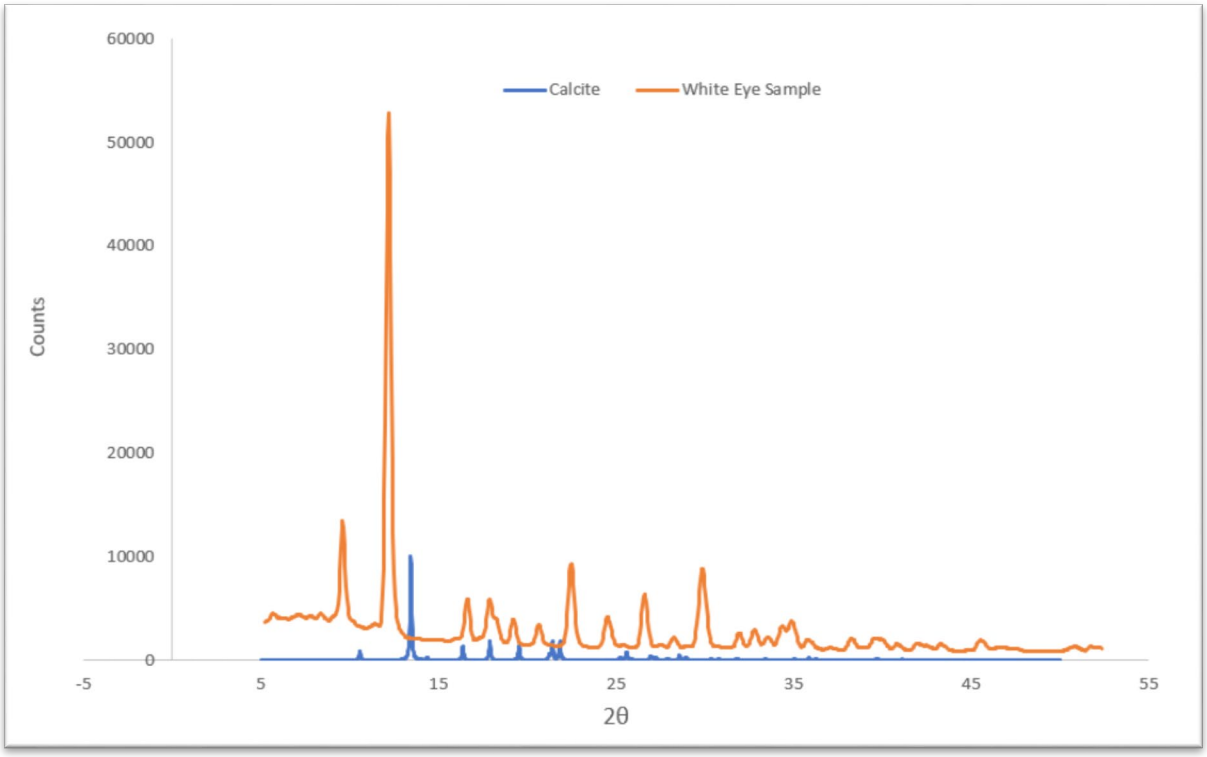
Figure 12. Object 70.07 XRF Results

X-Ray Diffraction (XRD)

To further confirm the XRF implications of the presence of kaolin and ultramarine on object 70.07, a white sample from the left eye and a blue sample from the lip were taken and analyzed with XRD. The white sample data from XRD was then compared to kaolin due to the XRF findings. From Fig. 13, it can be seen that the white eye sample form object 70.07 is not a strong match due to the multiple missing peaks. The signal was also compared with calcite due to its use in Africa.[4,6] From the unit cell determination and multiple trials from the crystal database, the white sample related the closest to calcite (chalk) (Fig. 13). Since the XRD results do not match exactly, a calcite mix is suggested as the pigment used for the eyes of this object. A mix is suggested due

to chalk paint easily weathering.[28] Further research is needed to conclusively identify what other minerals the sample incorporates.

The blue sample of the object when graphed against ultramarine from the mineral database strongly supports the lip sample as ultramarine with majority of the peaks matching the mineral (lazurite).[7] More research must be conducted in order to determine if the blue is a synthetic or natural ultramarine color (Fig. 14). By determining if the sample is synthetic or natural, the time period for which this object may have been created or repainted can be further narrowed.



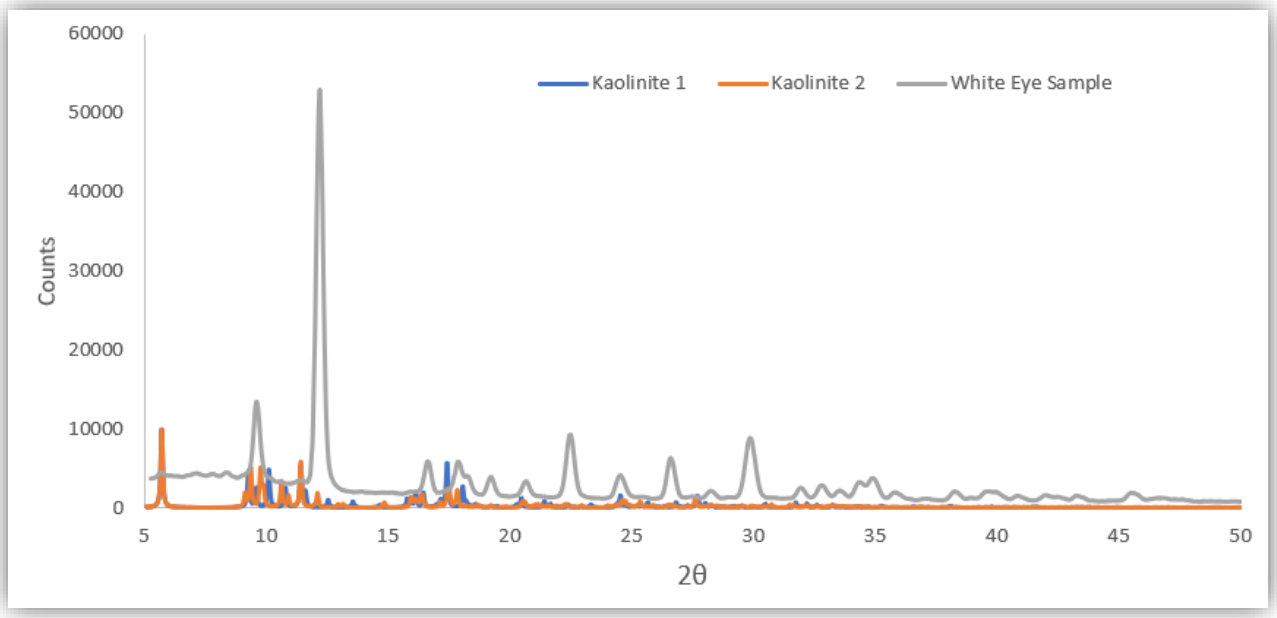


Figure 13. Mask 70.07 White Eye Sample XRD Results[25, 26, 28]

Shown (top) is the calcite comparison and shown (bottom) is the comparison of kaolinite and the white eye sample.

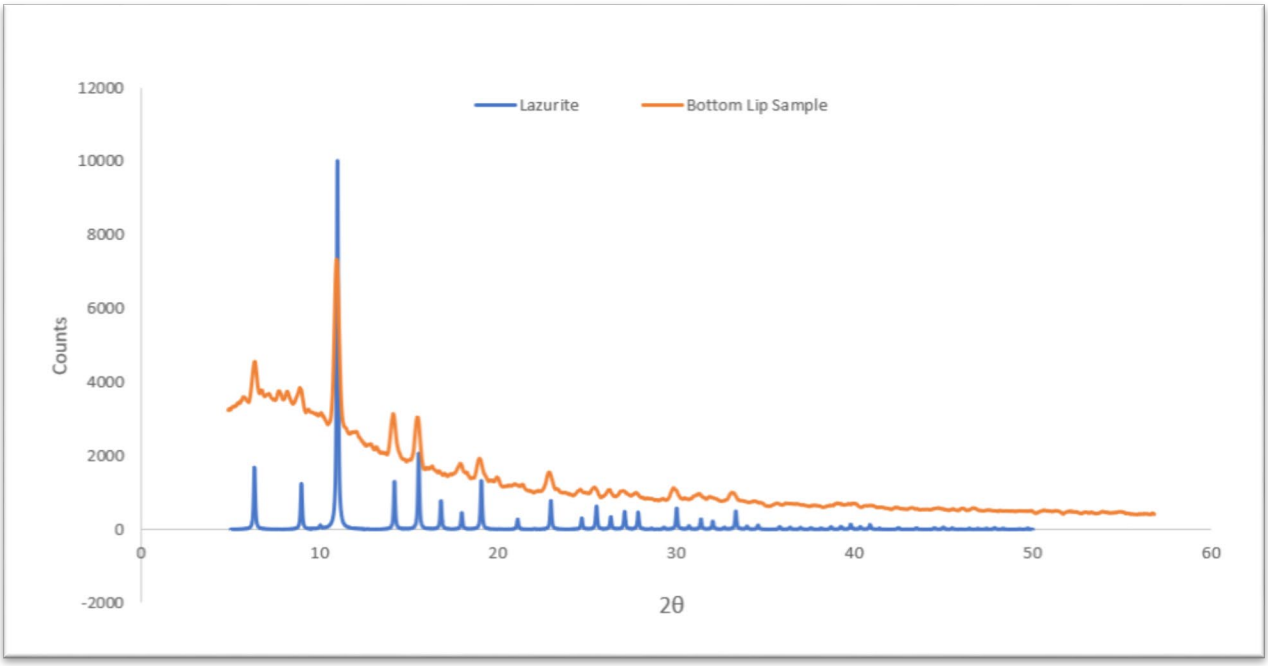


Figure 14. Mask 70.07 Blue Lip Sample XRD Results[27]

Object No. 86.01– Surface analysis of object no. 86.01

Widefield Fluorescence Microscopy (WFM)

Similar to findings on other objects in the Western African collection, results from object 86.01 suggest the presence of some type of oil due to increased fluorescence upon the addition of Nile Red.

X-Ray Fluorescence (XRF)

The white area around the eye of the mask 86.01 was analyzed using a portable XRF. The mask's surface in the eye region resulted in almost 50% of the elemental composition as titanium (Fig. 15). The remainder was divided almost evenly among sulfur, zinc, silicon, and aluminum. With such high levels of titanium, the data suggest titanium white (TiO_2) which was not manufactured until 1916.[19] It was not until 1921 when it was produced for painting.[19] The minerals anatase and rutile were commonly broken down for preparation of the pigment.[19] These XRF finding suggest that the earliest the mask could have been made, or at least painted, was in the early 1920's.

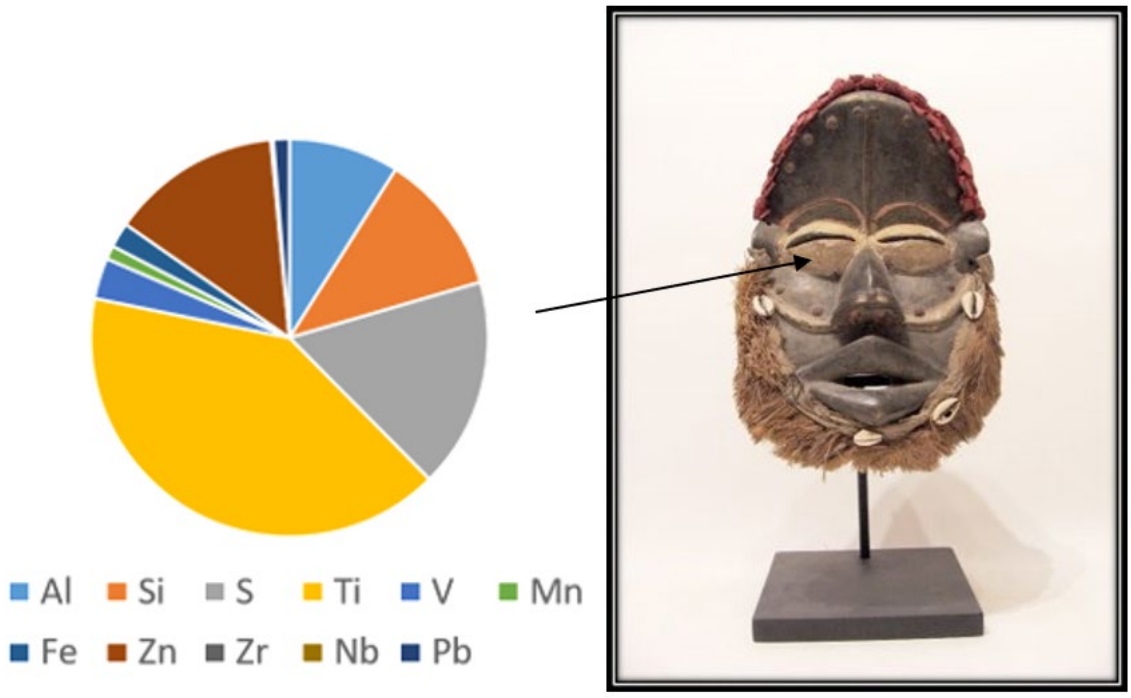


Figure 15. Object 86.01 XRF Results Suggesting Titanium Oxide as a Possible Pigment

X-Ray Diffraction (XRD)

To confirm the XRF data, XRD was completed on a sample taken from the right eye of mask 86.01. The single cell determination of the sample was compared to the possible minerals in titanium white (rutile and anatase). With various peaks matching and several nonmatching for both rutile and anatase, a mixture of the two minerals is suggested. When compared to other possibilities such as kaolin and calcite, there were nonmatching peaks declining the possibility that these minerals are part of the mixture. Further research is needed to conclusively identify the mixture for the sample (Fig. 16).

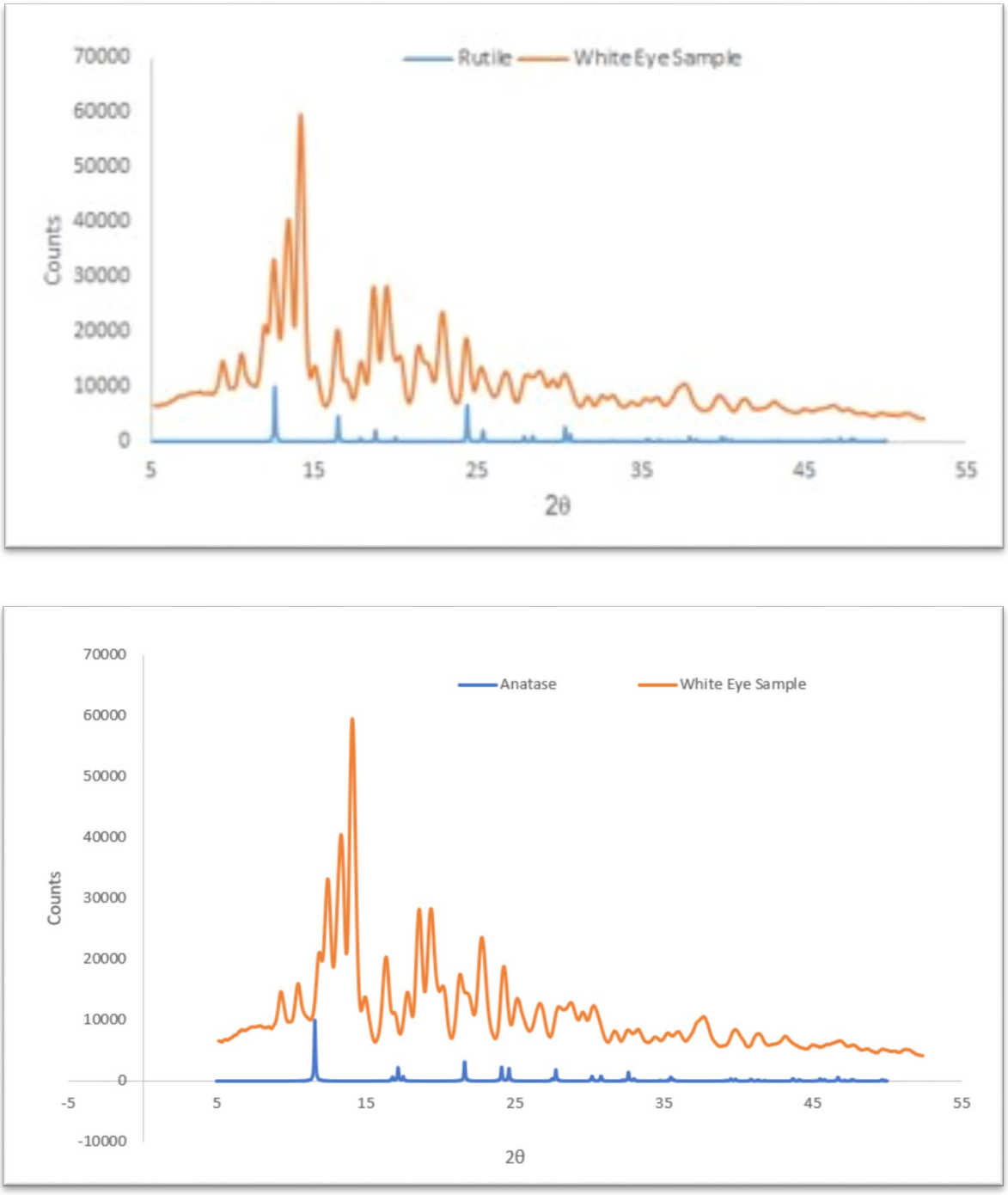


Figure 16: Object 86.01 XRD Results[29, 30]

Displayed below is the minerals for which titanium oxide is created from (rutile and anatase) compared to the white eye sample. Due to matching peaks within the sample a rutile and anatase mixture is suggested[29, 30].

Liquid Chromatography / Mass Spectrometry (LC/MS)

Mask 86.01 is covered on the top by a red fabric. In order to identify the dye, liquid chromatography-mass spectrometry was used to analyze an extract of this material. Prior to analysis of the extract, an LC/MS method was developed that utilized brazilwood and camwood as models. Brazilwood (*Paubrasilia echinata*) was used due to the available quantity as well as the possibility of being a dye for the red fabric on the object.[7] Camwood (*Baphia nitida*) was also chosen for analysis due to also being a probable dye for the fabric on the mask as well as possible to obtain in the United States for analysis.[7]

Brazilwood is a dark almost brown colored dye; however, when it interacts with fabric, it can range from an orange to vibrant red color. When combined with a metallic mordant such as aluminum or tin, a red color is produced on fabrics. The compound within the bark of a brazilwood tree is known as brazilin, while the dye form or oxidized form of brazilin (from air interaction) is known as brazilein (Fig. 17). The brazilein attaches to the fabric through hydrogen bonding or in conjunction with metallic mordants through coordinative bonding.[20] The brazilein compound is the target compound from the brazilwood dye for analysis with LC/MS.

Initial experiments involved direct injection of an aqueous solution of brazilwood into the electrospray ionization (ESI) – mass spectrometer. The MS is shown in Figure 18 and is consistent with published information about brazilein that documents a $[M+H]^+$ peak at 285 m/z (Table 2).[20] Collision induced dissociation (CID) through MS^2 analysis of the component at 285 m/z resulted in fragments at 255, 183, and 167 m/z (Fig. 18). Once the positive ion signals were characterized by ESI-MS, brazilwood was studied using LC-MS. Initially, method brazilwood1 was used. However, this suffered from issues such as unresolved peaks and long retention times. Therefore, a series of modifications was made to optimize the LC separation, such as changing mobile phase

from methanol to acetonitrile or changing the multi-step gradient to create smaller peaks. Method brazilwood 14, which uses methanol, was used for the remaining studies. The separation of aqueous brazilwood using method brazilwood 14 is shown in Figure 18. The mass spectrum of the component that elutes at 2.21 min is indicative of brazilein having a $[M+H]^+$ signal at 285 m/z. Additional experiments should be conducted to further improve the separation since the peak at 2.21 min has a long tail and may be two unresolved peaks.

Table 2. Direct Injection Charts for Brazilwood Dye

Name	Chemical Formula	Mol. Weight	Positive or Negative mode ~(+1/-1) m/z	MS_n Peaks	Direct Inject - In Camwood Dye? Through MS_n
Brazilin	$C_{16}H_{14}O_5$	286.28	+ and -	255, 256, 167, 287, 283	Yes
Brazilein (oxidized form of brazilin)	$C_{16}H_{14}O_5$	284.28	+ and -	255, 167, 183	Yes

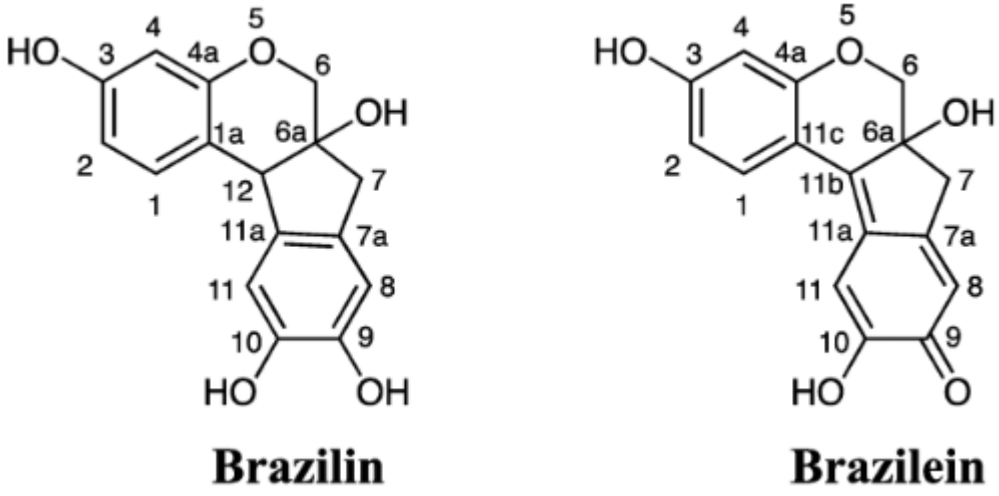


Figure 17. Structures Found in Brazilwood

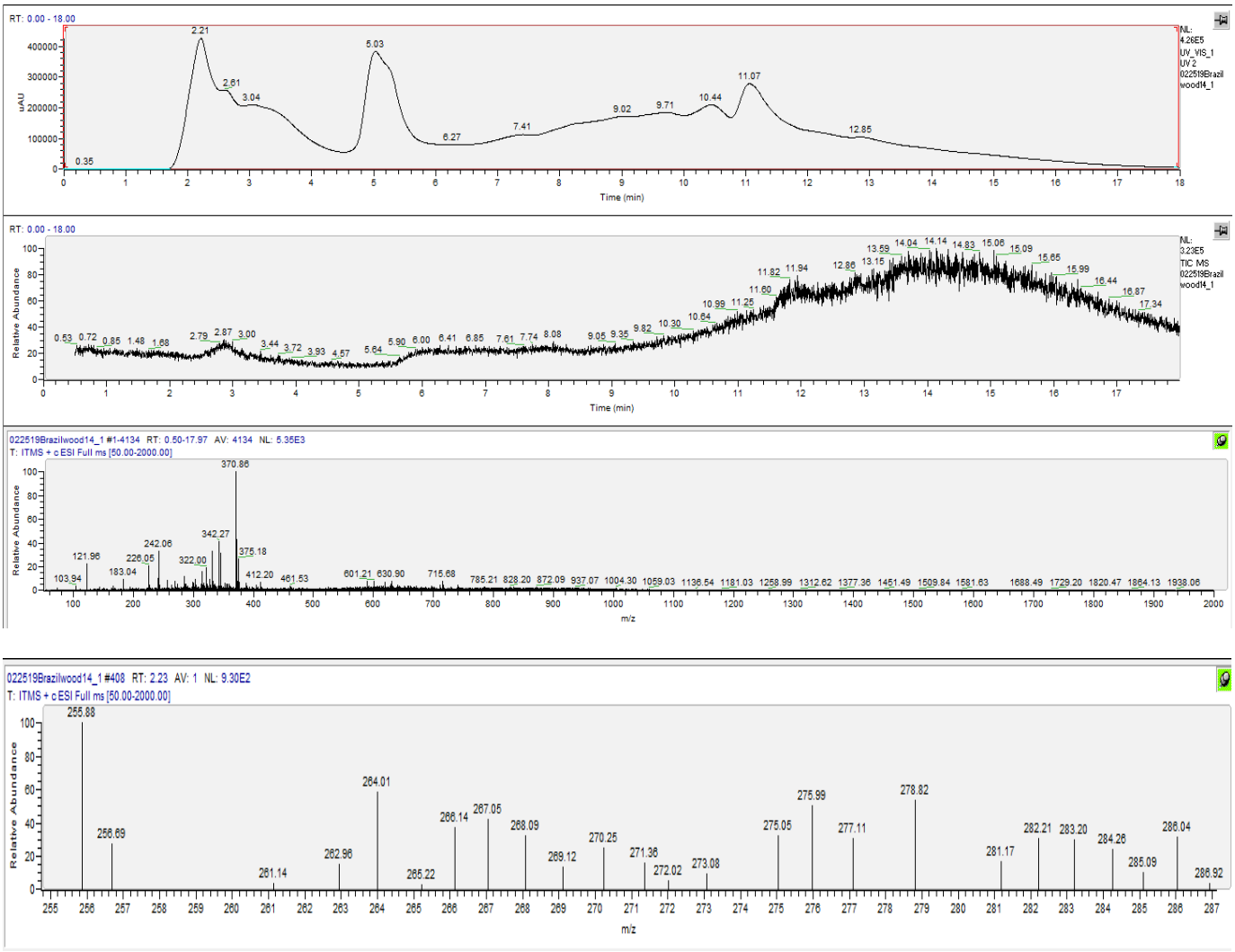


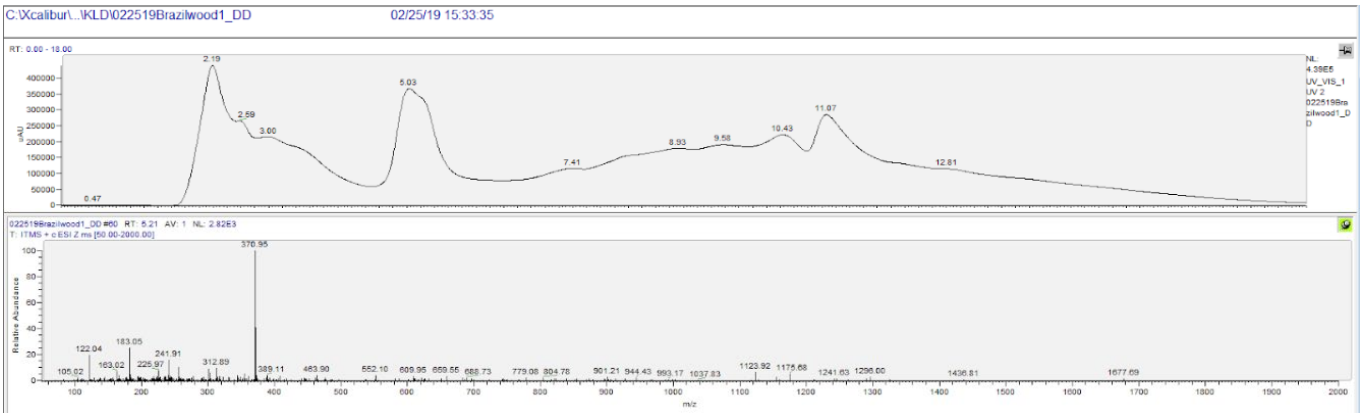
Figure 18. Analysis of Aqueous Solution of Brazilwood Using Method Brazilwood14.

Chromatogram with detection in nm (top), with total ion count (middle), MS of peak at 2.25 min and MS^2 of peak 2.25 min using CID of the 285 m/z peak (bottom).

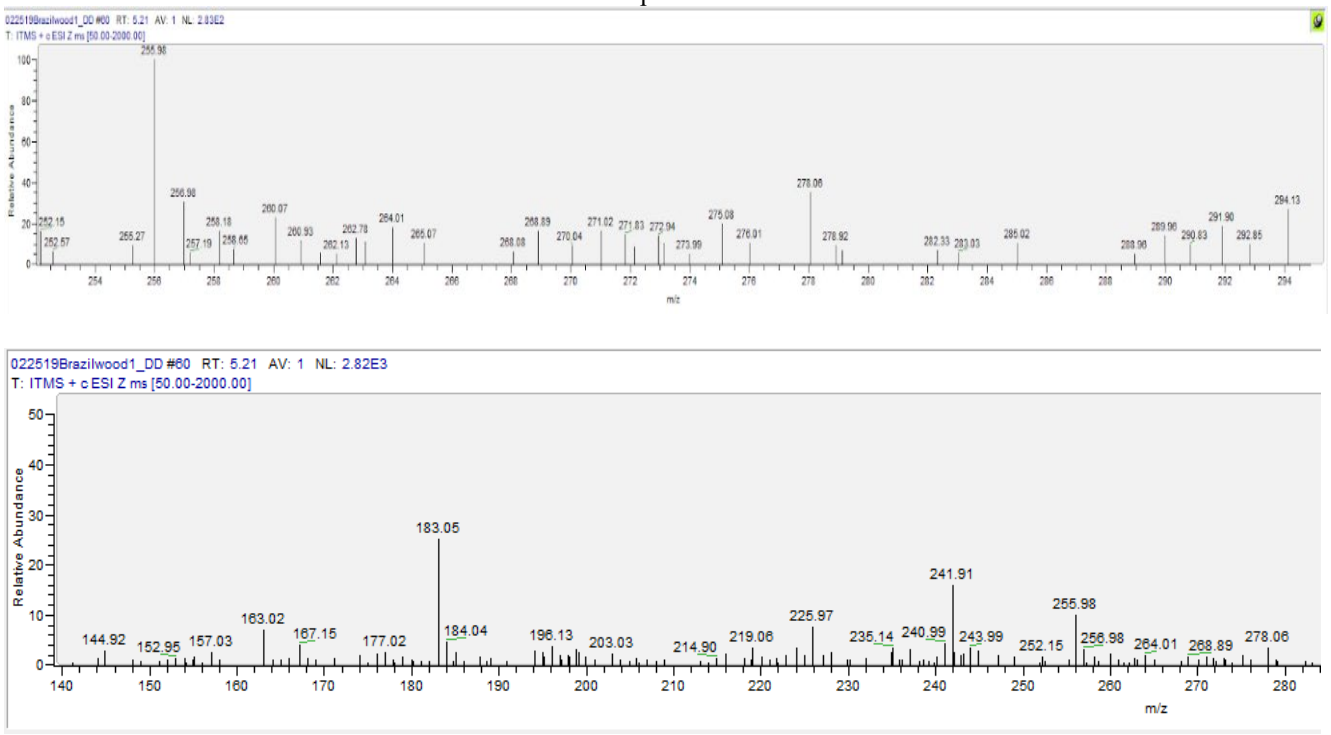
Once brazilein could be identified in brazilwood dye, an extraction was completed to conclude if the compounds could be identified from a fabric sample (Fig. 19). Surprisingly, a peak at a retention time of 2.2 min was observed but did not have a $[M+H]^+$ signal at 285 m/z. This suggests that brazilein is not present in the dyed fabric or was not removed in the extraction process that was used. However, the peak at 5.2 min did exhibit a $[M+H]^+$ signal at 285 m/z with CID fragments that matched brazilein. The reason for such a large difference in the retention time between the

aqueous dye and fabric extract is not understood at this time. Regardless, brazilein could be observed in both materials.

Chromatogram collected using UV detection at 290 nm (top) and mass spectrum at 5.2 min (bottom).



RT of 5.21 presented peaks of 285, 284, 283, 255, 183, and 167 m/z ratios indicating brazilein is present within the extract sample.



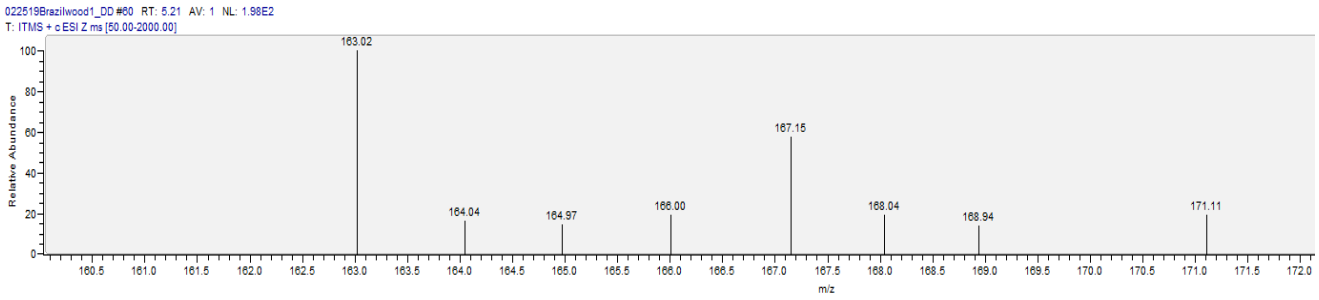


Figure 19. LC/MS Data of the Extract from Fabric Dyed with Brazilwood.

Camwood is otherwise known as the Western African red wood or sandalwood.[21,22] As described in Table 3, there are several dye components present in camwood.[23] An aqueous extract of camwood was analyzed using direct injection in both positive and negative modes. Baphiin, maackiain, homopterocarpis, and santarubin A were all detected in negative mode, while santalin, santalin A, santal, and deoxysantalin were detected in positive ion mode. Santarubin, santalin B, santarubin C, and pterocarpan were not detected in either mode indicating these compounds are not present in camwood sample.

Table 3. List of Compounds Present in Camwood Along with Their Formula, Molecular Weight, and Mass Spectral Data.

Name	**Formula**	**MW**	**Positive or Negative mode $[M+H]^-$ or $[M+H]^+$**	**MS_n Peaks**
Santarubin	$C_{34}H_{28}O_{10}$	596.588	Not Detected	Not Detected
Baphiin	$C_{24}H_2O_8$	436.417	-	436, 417, 413, 285
Santalin	$C_{15}H_{14}O_5$	274.272	+	274, 257, 233, 174, 177
Santalin A	$C_{33}H_{26}O_{10}$	582.561	+	582, 463

Santalin B	$C_{34}H_{28}O_{10}$	596.588	Not Detected	Not Detected
Santal	$C_{16}H_{12}O_6$	300.266	+	300, 284, 260
Deoxysantalin	$C_{10}H_{10}N_2O_4$	222.2	+	222, 204, 194, 166, 99
Maackiain	$C_{16}H_{12}O_5$	284.267	-	284, 283, 275, 262, 148
Pterocarpin	$C_{17}H_{14}O_5$	298.294	Not Detected	Not Detected
Homopterocarpin	$C_{17}H_{16}O_4$	284.311	-	284, 267, 265,147
Santarubin A	$C_{35}H_{30}O_{10}$	610.615	-	610, 587, 570, 451, 220
Santarubin C	$C_{33}H_{26}O_{11}$	598.56	Not Detected	Not Detected

After the mass spectral information was identified for the dye components in camwood using direct injection ESI-MS, the camwood dye was analyzed using LC/MS with method brazilwood14 in positive mode. The peak that eluted at 13.11 min was identified as santalin and the 14.68 min as santarubin A based on their MS and MS^n data (Fig. 20). The latter is a questionable identification due to this compound not being present within the pure camwood dye extract. The deoxysantalin and santal were missing from the spectrum even though the trial was run in positive mode. They may be able to be found within the camwood dye through an LC/MS method once optimization

has occurred to produce sharp, distinct peaks. Other compounds within the camwood dye did not appear due to the trials running in positive mode instead of negative mode.

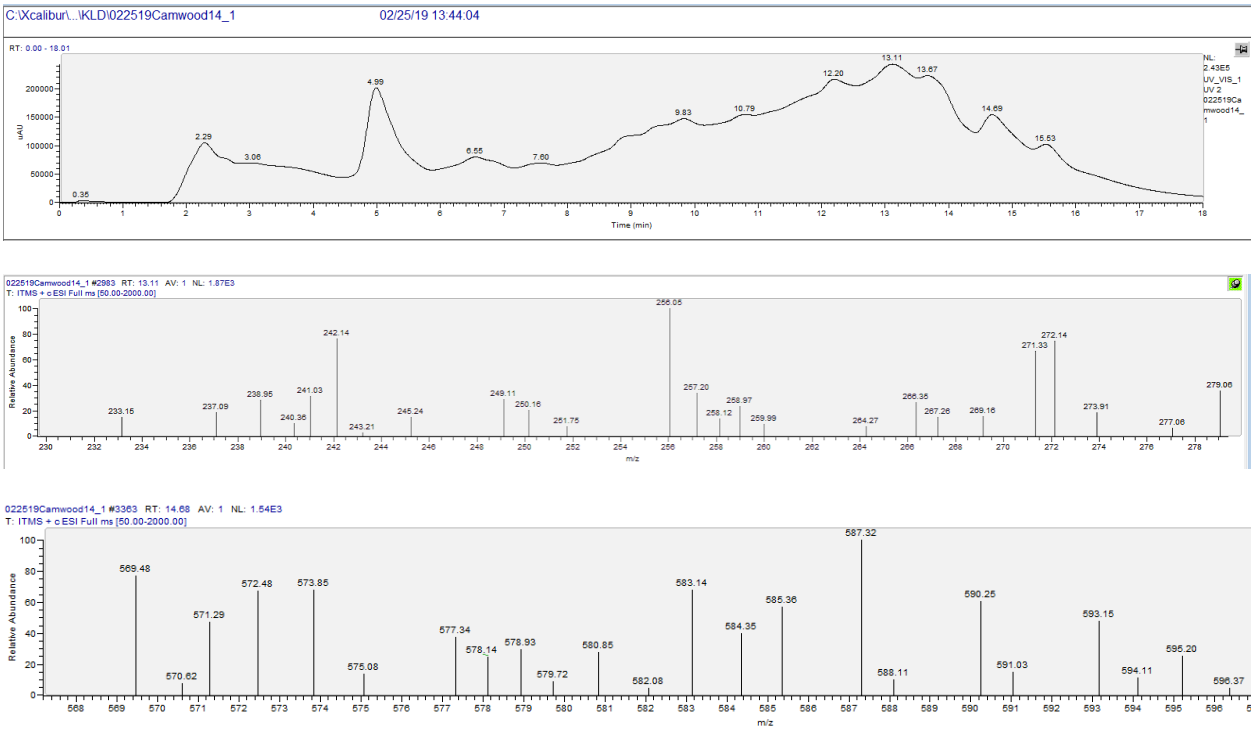


Figure 20. LC/MS Analysis of Camwood Dye.

Chromatogram measured at 290 nm (top), MS of the 13.11 peak (middle), and MS of the 14.69 min peak (bottom).

To ensure that camwood could be identified on dyed materials, fabric that was dyed with camwood was extracted and then analyzed by LC/MS using a data dependent method (Fig. 21). At retention time 4.0 min, two compounds from camwood were identified. Deoxysantalin and santalin were the only compounds which appeared through the extraction, which were identified based on the alignment of their mass spectra with that collected during direct injection (Fig. 21). However, the retention time of santalin in the fabric extract (4.0 min) does not match that of santalin in the dye (13.1 min), similar to how the retention time of the brazilein in the dye did not agree with that in the fabric extract. The MS peaks observed around 13 min in the fabric extract are shown in Fig. 23. The reasons for the differences in retention time are not understood. Regardless, since santalin

was found during direct injection, analysis of camwood dye, and analysis of dyed fabric extracts, santalin is considered the primary indicator for camwood dye. However, optimization of the method may also lead into recovering more compounds within the LC/MS trials.

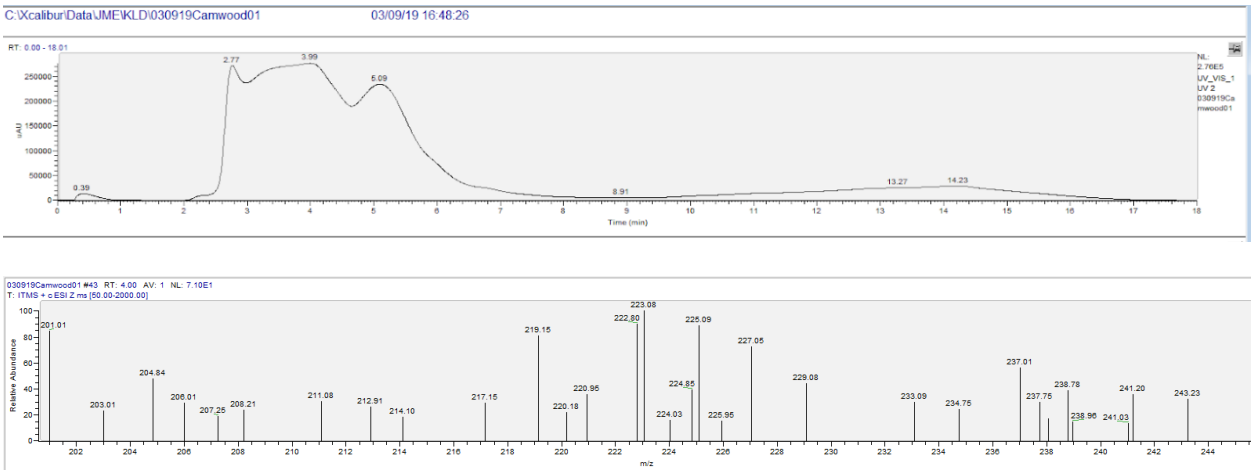


Figure 21. LC/MS Analysis of an Extract from Fibers Dyed with Camwood.

Chromatogram taken at 290 nm (top), deoxysantalin MS at retention time of 4.00 min (middle), and santalin MS at retention time of 4.00 min (bottom).

Once an LC/MS method has been tested for brazilwood and camwood, a fabric sample from artifact 86.01 was extracted and analyzed using the same LC/MS. As seen in Fig. 22, the extract was found to contain santalin and brazilein. Since thread form artifact 86.01 is a vibrant red that has a much brighter color than that of brazilwood, it was surprising to see brazilein in the sample. Further, although camwood creates a bright red fabric, the coloring when compared to the thread sample is dull. To be sure that there was not carry over from previous samples, blanks were run until no over from brazilein and santalin were observed (Fig. 22). Even after this, LC/MS analysis of the artifact indicated the presence of both brazilein and santalin. This suggests that the sample may have been dyed with both brazilwood and camwood. Since brazilwood was not traded in Western Africa until the 1930's[14], this suggests that artifact 86.01

was not created or at least the fabric not added until at least 1930. Further exploration of possible red dyes must be completed in order to possibly identify the sample.

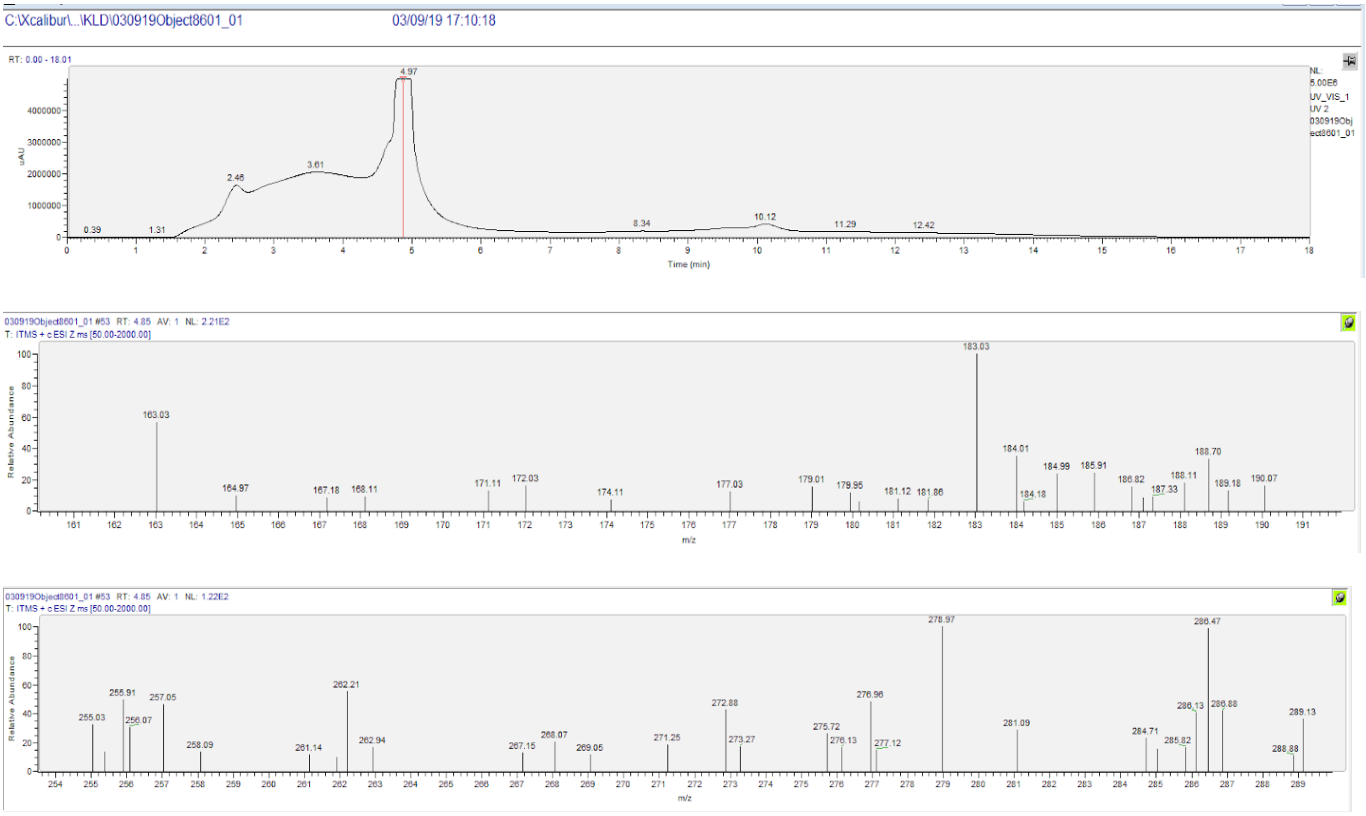


Figure 22: LC/MS Extraction of Artifact 86.01 Thread Sample

Chromatogram measured at 290 nm (top), MS of the 4.85 peak (middle), and MS of the 2.46 min peak (bottom).

Conclusion

Throughout this project multiple discoveries were made about these Western African artifacts using XRD, GC/MS and LC/MS. Materials, including kaolin, calcite, ultramarine as well as a calcite, anatase, and rutile mixture were identified using XRD. This also helped data object 86.01 to at least 1910 since titanium dioxide, made from anatase and rutile was not commercially distributed until the early 20th century. Through LC/MS, the construction of methods (brazilwood14, data dependent, extraction, and direct injection) for dye identification were made

a reality with brazilwood and camwood as reference samples and object 86.01 was identified as being made from both camwood and brazilwood. Methyl palmitate was identified using GC/MS on artifact 73.02 indicating the white material that sometimes appears during storage is likely palm oil, a material used by African sculptors.

Although the materials used on the surfaces of select objects in the Western African collection at the Frank Museum of Art have been identified, additional work is needed. The liquid chromatography suffered from poor resolution, and, thus, additional studies to optimize the separation are needed such as altering the gradient, the solvent composition, and the column stationary phase.

Future Exhibit for Science Center

In collaboration with the art department, the artifacts chosen for this ongoing project were researched deeper to create an exhibit for the third floor of the science center. The four artifacts were planned to sit on pedestals within the empty space of the science center with a brief excerpt underneath each piece. A TV borrowed from the art department was set to be used to display the collaborated presentation of history and science. Once the exhibit was complete, a brief event was to take place in order to explain any lingering questions on the pieces or the presentation itself.

This presentation includes historical slides over the possible tribes the artifacts are believed to have originated from. Historical information on the slides included location, population, religious practices, farmed produce, and art pieces similar to the artifacts chosen from the collection. The information on these tribes is fairly easy to gather due to surviving in present day. From a historical side of the presentation, the science side was also added as a portion.

For the scientific portion of the presentation, multiple parts were completed. For each piece, a description of the tests completed along with a diagram for visual representation were implemented. After a description of the test completed, the results of each instrumentation method were included to display what is suggested to be the pigment of the artifacts. Overall, the presentation is meant to be a merger of historic and scientific analysis in order to explore possibilities of the mostly unknown artifacts. Once the glass to cover the artifacts has arrived, the exhibit can be complete and put on display for the Otterbein community. With this presentation, the goals of informing students and community members of what the scientific community can be present within can be accomplished.

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References

1. Hill, Patricia. (2002). *The Molecular Basis of Color and Form: Chemistry in Art.* Millersville, Materials Research Forum LLC.
2. Owczarek, N. Skin covered masks from the Cross-River region of Nigeria and Cameroon at the National Museum of African Art: A technical study. *Journal of the American Institute for Conservation*, 53(3), 182-197. (2014).
3. Dolph, B.; Fuentes, A.; Griswold, G.; Mallinckrodt, C.; Mahony, C.; Neiman, M.; North, A.; Tzadik, C. The significance of surface in central African masks: Pigment Identification of polychrome wood masks from the Congo. *UCLA/Getty Program in the Conservation of Ethnographic and Archaeological Materials*. (2012).
4. Mazel, V.; Richardin, P.; Touboul, D.; Brunelle, A.; Richard, C.; Laval, E.; Walter, P.; Laprevote, O. Animal urine as painting materials in African rock art revealed by cluster ToF-SIMS mass spectrometry imaging. *Journal of Mass Spectrometry*. 45(8), 944-950. (2010).
5. Fraser, D.; DeRoo, C. S.; Cody, R. B.; Armitage, R. A. Characterization of blood in an encrustation on an African mask: spectroscopic and direct analysis in real time mass spectrometric identification of haem. *Analyst*. 138, 4470-4474. (2013).
6. Roy, C. D. The Art of Burkina Faso. *Art & Life in Africa – The University of Iowa Museum of Art*. https://africa.uima.uiowa.edu/topic-essays/show/37?start=3.
7. Page, D.; Kahan, L.; Imperato, P. J. *Surfaces: color, substances, and ritual applications on African sculpture.* Indiana University Press: Bloomington, 2009.

8. James, E. Technical study of Ethiopian icons, National Museum of African Art, Smithsonian Institution. *Journal of the American Institute for Conservation*, 44(1), 39-50. (2005).
9. Abdallah,M.; Kamal, H.; Abdrabou, A. Investigation, preservation and restoration processes of an ancient Egyptian wooden offering table. *International Journal of Conservation Science*, 7(4), 1047-1064. (2016).
10. Chen, V.J.; Smith, G.D.; Holden, A.; Paydar, N.; Kiefer, K. Chemical analysis of dyes on an Uzbek ceremonial coat: Objective evidence for artifact dating and the chemistry of early synthetic dyes. *Dyes and Pigments*, 131, 320-332. (2016).
11. Norbutus, A. J. *St. Jerome* paint analysis. *Winterthur/University of Delaware Program in Art Conservation*. 9-10. (2008).
12. 35077 / Food Industry FAME Mix. *RESTEK: Safety Data Sheet.* www.restek.com.
13. Kamatou, G. P. P.; Viljown, A. M. Comparison of Fatty Acid Methyl Esters of Palm and Palmist Oils Determined by GCxGC-ToF-MS and GC-MS/FID. *South African Journal of Botany*, 112(2017), 483-488. (2017).
14. Dumbuya, P. (2014). Africa and Brazil: Race, Culture, and Diplomacy during the Presidency of Luiz Inácio Lula Da Silva. *Journal of Third World Studies*, *31*(2), 37–56. http://ezproxy.otterbein.edu/login?url=https://search.ebscohost.com/login.aspx?direct=true&db=slh&AN=102179583&site=eds-live&scope=site
15. Bukalo, N. N.; Ekosse, G. E.; Odiyo, J. O.; Ogola, J. S. Geochemistry of Selected Kaolins from Cameroon and Nigeria. *Open Geoscience*. 9, 600-612. (2017).
16. Ekosse, G. E. Kaolin Deposits and Occurrences in Africa: Geology, Mineralogy and Utilization. *Applied Clay Science*. 50, 212-236. (2010).

17. Pearlstein, E. Fatty bloom on wood sculpture from Mali. *Studies in Conservation*, 31(2), 83-91. (1986).

18. Igbo Peoples. *Art & Life in Africa – The University of Iowa Museum of Art.* https://africa.uima.uiowa.edu/peoples/show/Igbo. (Accessed: 16nd August 2018).

19. Douma, M.; Lipscher, J. Titanium White. *Pigments Through the Ages.* http://www.webexhibits.org/pigments/indiv/recipe/titaniumwhite.html. (Accessed: 12th November 2018).

20. Dapson, R. W.; Bain, C. L. Brazilwood, Sappanwood, Brazilin and the Red Dye Brazilein: From Textile Dyeing and Folk Medicine to Biological Staining and Musical Instruments. *Journal of Biotechnic & Histochemistry*. 90(6), 401-423. (2015).

21. . Arnone, A.; Camarda, L.; Merlini, L; Nasini, G.; Taylor, D. A. H. Isolfavonaoid Constitutes of the West African Red Wood *Baphia Nitida*. *Phytochemistry*. 20(4), 799-801. (1981).

22. Chaabi, M.; Chabert, P.; Vonthron-Senecheau, C.; Weniger, B.; Ouattara, M.; Corstjens, H.; Sente, I.; Declercq, L.; Lobstein, A. Acylated Flavonol Pentaglycosides from Baphia nitida Leaves. *Photochemistry Letters.* 3, 70-74. (2010).

23. Surowiec, I.' Nowik, W.; Trojanowicz, M. Identification of "Insoluble" Red Dyewoods by High Performance Liquid Chromatography–Photodiode Array Detection (HPLC-PDA) Fingerprinting. *J. Sep. Sci*. 27, 209-216. (2004).

24. Blake R.; E, Hessevick R.; T, Zoltai; W, Finger L. Refinement of the Hematite Structure. *American Mineralogist Crystal Structure Database*. 51, 123-129. (1966).

25. Bish D. Rietveld Refinement of the Kaolinite Structure at 1.5 K. *American Mineralogist Crystal Structure Database.*41, 738-744. (1993).

26. W, Gruner. The Crystal Structure of Kaolinite. *American Mineralogist Crystal Structure Database.*83, 75-88. (1932).

27. I, Hassan; C, Peterson R.; D, Grundy, H. The Structure of Lazurite, Ideally $Na_6Ca_2(Al_6Si_6O_{24})S_2$, a Member Sodalite Group. *American Mineralogist Crystal Structure Database.*C41, 827-832. (1985).

28. L, Graf D. Crystallographic tables for the Rhombohedral Carbonates. *American Mineralogist Crystal Structure Database.*46, 1283-1316. (1961).

29. J, Swope R.; R, Smyth J.; C, Larson A. H in Rutile-Type Compounds: I. Single-Crystal Neutron and X-Ray Diffraction Study of H in Rutile. *American Mineralogist Crystal Structure Database.* 60, 448-453. (1995).

30. J, Howard C.; M, Sabine T.; F, Dickson. Structural and Thermal Parameters for Rutile and Anatase Locality: Synthetic. *American Mineralogist Crystal Structure Database*. B47, 462-468. (1991).