A Compositional Analysis Of Historic & Pre-historic Pigments

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Introduction

• X-ray Fluorescence spectroscopy (XRF) was developed as a technique for studying composition of historic and pre-historic pigments in ceramics and paintings.

• XRF techniques were applied to Native American pottery fragments from the southeastern and southwestern United States were analyzed, as well as two modern paintings.

• While the modern paintings analyzed were not artifacts in a strict sense, they served well as a stand-in for actual artifacts. However, some of the modern pigments used are not identifiable by their composition alone.

• XRF techniques were applied using an “Atlas X” X-ray florescence energy dispersive spectrometer by iXRF Systems.
In XRF/EDS, atoms in a material are bombarded by a high-energy X-ray beam. This beam takes electrons belonging to those atoms up to an excited state. Eventually, the electrons return to their ground state, releasing a characteristic X-ray that can be used to identify the atom that released it based on its energy.

Similar working principle to the energy dispersive spectroscopy (EDS) used in electron microscopy, except that an X-ray beam is used, rather than an electrons beam.

Pros (compared to electron microscope EDS) are higher compositional accuracy, faster measurements, no need for vacuum-pumping, and, most importantly, the ability to create large area maps.

Cons are lower spatial resolution and an inability to detect some lighter elements.
Background on Paintings and Pottery

Left to Right: Southeastern Pottery, Southwestern Pottery, Acrylic Painting, Oil Painting

• Southeastern Fragment (Left): The fragment features a slip, temper, and pigmentation
• Southwestern Fragment (Center-Left): The fragment features a slip, temper, and two different types of pigmentation
• Acrylic Painting (Center-Right): This painting features mixed pigments and undercoating
• Oil Painting (Right): This painting features mixed pigments, undercoating, and scraping
Southeastern Ceramic Results

Clockwise from top-center: Optical, Iron, Manganese, Potassium, Calcium.

- The darker blue image indicates that the red pigment contains high levels of iron.
- The light blue image indicates that the white temper seen on the surface contains high levels of calcium.
- The red image indicates that there is calcium present on the clay and pigment surface that is not present in the white temper.
- The green image indicates that there is manganese present in unidentified dark flecks on the surface.
Southwestern Ceramic Results

Bare Ceramic

Ca
Fe

Black Pigment

Red Pigment
Acrylic Painting Results

• Identified Pigments:
  • Lithopone ($BaSO_4$ and $ZnS$)
  • Titanium White ($TiO_2$)
  • Umber/Sienna ($Fe$ & $Mn$ Oxides)

• Undercoating can be viewed in the image below:

Clockwise from top-left: Optical, Manganese vs. Iron (Red and Blue respectively), Titanium, Zinc, Sulfur, Barium.
Oil Painting Results

- Pigments Identified:
  - Gypsum (CaSO$_4$·H$_2$O)
  - Orpiment (As$_2$S$_3$) or Realgar (As$_4$S$_4$)
  - Red (Anhydrite) or Yellow (Hydrated) Ochre
  - Titanium White (TiO$_2$)
- Undercoating and scraping can be viewed to the right:
Work Cited

“Pigments Checker V.5.” Cultural Heritage Science Open Source, chsopensource.org/pigments-checker/.


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