Characterization of traditional Japanese colorants in woodblock printing using multispectral imaging

Gwenanne Edwards, Paper Conservation Fellow; Cyntia Karnes, Senior Paper Conservator; Dr. Lynn Brostoff, Conservation Scientist

Library of Congress

INTRODUCTION.

Colorants in traditional Japanese woodblock printing inks may be dramatically altered by exposure to light, pollutants, high humidity, pH extremes, water and other solvents. Characterization of colorants in Japanese prints can help conservators make better decisions regarding their treatment, housing, storage environment, and exhibition. In addition, characterization of colorants may also aid in the identification of the artist or time period in which the print was created.

This poster presents a woodblock pillar print as a case study for the possibility of using spectral imaging to characterize traditional Japanese colorants. Imaging was conducted using two methods: a multispectral digital camera system; and, as a less expensive alternative, a modified digital camera with external filtration. Colorants were also characterized through examination with a stereomicroscope and elemental analysis with X-ray fluorescence. Micro-Raman spectroscopy was used to assess the accuracy of colorant characterizations.

The conservation treatment to remove the print from a damaging mount and to reduce the blackening of red lead in select areas is also summarized.

BEFORE TREATMENT
Torii Kiyonaga (1752-1815), *Two Beauties Under a Cherry Tree*, 1782-3, woodblock print, 69x11.6 cm, Library of Congress, FP2-JPD no. 530

METHODOLOGY.

Thirty two different colorant samples from two sources were used as references for visual examination and imaging analysis. Linda Stiber Morenus provided samples made from traditional Japanese dyes or pigments bound with rice starch paste and brushed onto unsized kozo-fiber Japanese paper (*usu-mino*). The samples had been artificially aged in an oven at 80ºC and 65% RH in increments of 0, 3, 7, 14, 21, & 28 days. Additional known samples were obtained from a set of naturally-aged colorants tipped into a 1931 academic journal (see references).

Prior to imaging, colorants were examined using a Zeiss steREO Discovery V8 stereomicroscope with a Zeiss AxioCam MRc5 digital camera. Physical characteristics such as relative particle size, edge definition, surface reflectance, and transparency or opacity were compared with known samples. Imaging was conducted with both a multispectral imaging system and a digital camera, modified by removing internal infrared (IR) and ultraviolet (UV) filters, used with external lights and filtration.

Colorants were characterized by their spectral responses using an Art Innovation Artist® multispectral imaging system with a spectral range of 300-1100 nm. The system utilizes a digital camera to capture spectral responses in seven imaging modes: visible, near-UV induced visible fluorescence, near-UV reflectance, reflected IR in two bands (700-950 nm & 1000-1100 nm), and false-color reflected IR derived from the two IR images. A halogen light source was used for visible and IR modes, and a high-pressure mercury near-UV floodlight was used for UV modes. To expand on the imaging capability of the multispectral system, false-color UV images were created from two multispectral images, as described in the next paragraph.

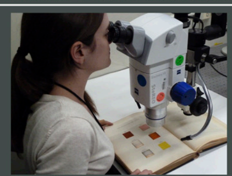
Imaging with a multispectral system is similar to imaging with a modified digital camera with lens filtration. However, wavelength bands are more clearly defined in the multispectral camera system. To demonstrate the practical utility of a less expensive option for imaging, the print was photographed with a UV-VIS-IR modified Nikon D300 digital camera with filters to approximate the modes in the multispectral system. Imaging modes with filters included visible (Peca 918), near-UV induced visible fluorescence (Peca 918 and Kodak Wratten 2E), near-UV reflectance (Peca 900 and MaxMax X-Nite BP1), and reflected near-IR (Peca 914). The spectral sensitivity of the Nikon D300 (approximately 350-1000 nm) prevented imaging of the 1000-1100 nm IR band of the multispectral camera system. However, a longwave near-IR image was obtained with a Peca 906 filter (950-1000 nm). False-color UV images were created by combining visible and reflected near-UV images, while false-color IR images were created by combining visible and reflected near-IR images. Images were adjusted using channel substitutions in Adobe Photoshop, as described in the second edition of the *AIC Guide to Digital Photography and Conservation Documentation* (see references). Visible and IR images were captured using high intensity discharge (HID) copy light sources, while UV images were captured using low-pressure (fluorescent) near-UV light sources.

In addition to visual examination with a stereomicroscope and imaging analysis, print colorants were analyzed for elemental composition with X-ray fluorescence spectroscopy (XRF) using a handheld Bruker Tracer III-SD spectrometer with a rhodium anode, silicone drift detector (SDD), and vacuum pumping. The unit was set at 40 kV and 20 μA, and utilized a titanium filter. Exposures lasted 180 seconds with an approximate spot size of 3 x 4 mm.

Identification of three of the four separate printing inks, excluding the black, was achieved through in-situ μRaman spectroscopy using a Renishaw InVia Raman spectrometer outfitted with a Leica microscope and a macrosampling arm. Spectra were collected with a 514 nm Ar^+ laser and 2400 l/mm grating or a 785 nm Diode laser and 1200 l/mm grating. Laser power at the sample was 0.25 – 1.15 mW, exposure integration time was 10 – 200 seconds, and the spot size was approximately 20 microns.

RESULTS AND OBSERVATIONS

Visual Examination



Visual comparison with knowns

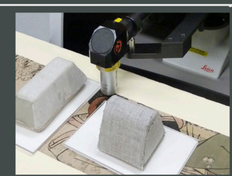
Spectral Imaging

visible	UV-induced visible fluorescence (UVF)	ultraviolet reflectance	false-color ultraviolet (FCUV)
infrared 1 (IR1)	infrared 2 (IR2)	false-color infrared 1 (FCIR1)	false-color infrared 2 (FCIR2)

Woodblock Print

Known Samples

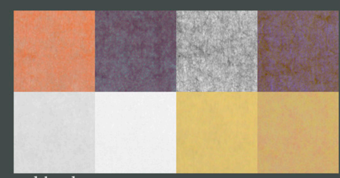
Instrumental Analysis



In-situ μRaman analysis

orange-red printing ink

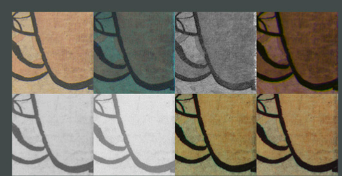
UVF: absorbs; appears dark red
FCUV: appears dark red
IR1: transmits; appears similar to paper
IR2: transmits; appears similar to paper
FCIR1: appears cool yellow
FCIR2: appears warm yellow
● **spectral match to red lead**



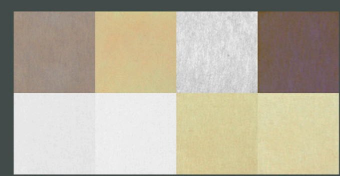
red lead

XRF detected Pb in the orange-red printing ink; red lead (Pb_3O_4) was confirmed through μRaman spectroscopy. No new phases were detected in areas of red lead treated with H_2O_2. Further study is planned.
● **conclusion: red lead** (lead tetroxide; *tan*)

pink printing ink

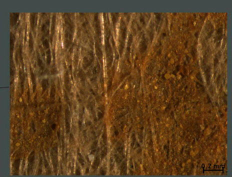


UVF: fluoresces bright orange
FCUV: appears red-gray
IR1: transmits; appears similar to paper
IR2: transmits; appears similar to paper
FCIR1: appears bright yellow
FCIR2: appears yellow
● **spectral match to safflower**

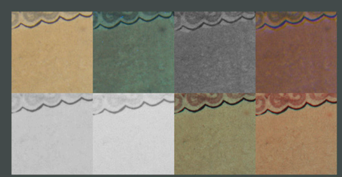


safflower

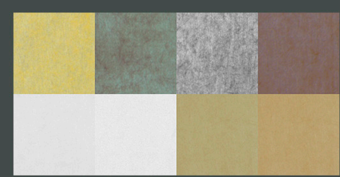
Analysis of the pink printing ink suggests an organic colorant since no elements were detected with XRF other than trace Ca. μRaman yielded high fluorescence and no clear peaks. Visual examination and spectral imaging suggests safflower (*carthamus tinctorius*; *benibana*).
● **conclusion: organic colorant, possibly safflower**



yellow printing ink

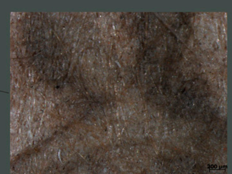


UVF: absorbs; appears dark yellow-orange
FCUV: appears light red
IR1: transmits; appears similar to paper
IR2: transmits; appears similar to paper
FCIR1: appears pale lemon yellow
FCIR2: appears pale orange-yellow
● **spectrally similar to orpiment & gamboge**

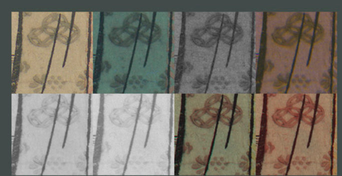


orpiment

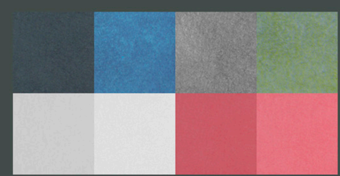
XRF of the yellow printing ink detected strong peaks for As and S, trace Fe and possibly Ca. μRaman confirmed identification of **orpiment** (As_2S_3); no other phases or alteration products were detected.
● **conclusion: orpiment** (arsenic trisulfide; *kio*, *shio*)



blue-gray printing ink

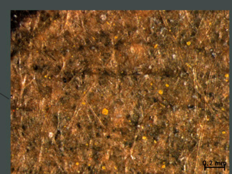


UVF: absorbs; appears dark blue-gray
FCUV: appears gray-green
IR1: absorbs; appears darker than paper
IR2: slightly absorbs; appears darker than paper
FCIR1: appears dark pink
FCIR2: appears bright pink
● **spectral match to indigo**

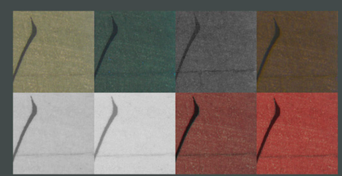


indigo

No elements were detected with XRF in the blue-gray printed design. μRaman analysis confirmed the presence of **indigo**. A white particle was positively identified as phosgenite ($Pb_2(CO_3)Cl_2$), most likely in combination with cerussite ($PbCO_3$).
● **conclusion: indigo** (*polygonum tinctorium*; *ai*, *bero-ai*)



green printing ink



UVF: absorbs; appears dark blue-green
FCUV: appears gray-green
IR1: absorbs; appears darker than paper
IR2: slightly absorbs; appears darker than paper
FCIR1: appears dark pink
FCIR2: appears bright pink
● **spectral match to indigo** (overrides orpiment)

Mixed green samples unavailable for comparison

XRF analysis of the green areas detected As and S, along with trace Fe and Pb. μRaman confirmed the presence of **orpiment** and **indigo**. Scattered white particles could not be identified by μRaman, but may be presumed to be related to the detection of Pb and phosgenite / cerussite in the blue-gray area.
● **conclusion: orpiment and indigo**

CONCLUSION.

The spectral imaging techniques used in this study offer a non-destructive method for identifying certain, but not all, colorants used in traditional Japanese woodblock printing inks. In addition, spectral imaging for successful characterization of those colorants can be performed with a modified digital camera with external filtration and does not necessarily require the use of a specialized multispectral imaging system.

Specifically, spectral imaging is a useful tool for successfully characterizing red lead, indigo, and safflower, but does not adequately distinguish between the yellow colorants orpiment and gamboge. Treated blackened red lead is indistinguishable from untreated red lead with the spectral and μRaman techniques used in this study, suggesting that H_2O_2 reverted what is likely lead sulphide to lead tetroxide. Spectral responses of all other colorants were similar before and after treatment.

Spectral imaging with a modified digital camera with external filtration to identify certain colorants is an effective, lower-cost option to a specialized multispectral imaging system. With either method, image processing must be standardized to accurately compare responses of unknown colorants to known samples and to assess the effects of treatment.

AFTER TREATMENT
Torii Kiyonaga (1752-1815), *Two Beauties Under a Cherry Tree*, 1782-3

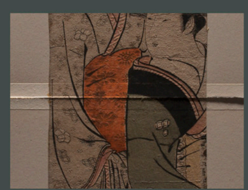
TREATMENT SUMMARY.

The print had been adhered overall across two brittle, acidic boards hinged together with paper tape, causing a tear to form through the center of the print. The adhesive used to mount the print contributed to the yellow discoloration of the paper. The colorants appeared significantly diminished, possibly caused by wetting of the print during mounting and prolonged exposure to light. Furthermore, a black degradation product of red lead obscured the printed pattern in the *obi*.

Before treatment, the printing inks were extensively tested and found to be insoluble in both deionized water and in ethanol. Nevertheless, exposure to water was minimized throughout treatment due to the known water sensitivity of safflower. After thinning the boards, a blotter saturated with 50:50 ethanol:water was applied to the verso to soften the adhesive. The facing paper of the mount and a Western paper lining were lifted off. The print was blotter washed with calcium-adjusted water to reduce the adhesive. The pH was not raised above neutral, given the known sensitivity of safflower and indigo to alkalinity.

The print exhibited several areas of blackened red lead in the *obi* and hair combs. As lead tetroxide may be intentionally altered by the printer to produce a silver effect in the pigment (which then degrades to black lead sulphide), reversion treatment was limited to areas where degradation had obscured printed patterns in the *obi*. A solution of 0.5-1.0% hydrogen peroxide was brush applied to the degraded black pigment to revert it to red, thereby revealing the textile pattern. During treatment, reference to false-color images of the area helped to distinguish between blackened red lead and the dark indigo pattern.

The print was rinsed on the suction table to remove residual hydrogen peroxide. After treatment, the print was hinged to a mat made from unbuffered, 100% cotton rag board. Unbuffered board was chosen due to the known pH sensitivity of indigo and safflower dyes. Low light levels during exhibition will help protect particularly light-sensitive colorants, such as safflower and indigo, from fading.

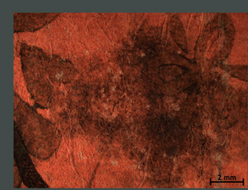


Raking light detail, before treatment

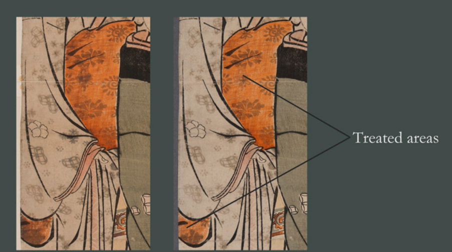
Mechanically thinning mount

Removing mount facing paper

Reducing Western paper lining



Blackened area of red lead in *obi*



Before treatment
After treatment

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