

RESEARCH ARTICLE

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Creation and reference characterization of Edo period Japanese woodblock printing ink colorant samples using multimodal imaging and reflectance spectroscopy

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Abstract

The Library of Congress Prints and Photographs Division holds a large collection of Edo period (1615–1868) *nishiki-e*, Japanese multicolored woodblock prints. The sensitivities of some of the traditional colorants to environmental and conservation treatment factors results in numerous preservation concerns. Characterization of colorants in these prints can help guide preservation policies, however, identification of colorants can be difficult and re-creation methodologies for reference samples have been elusive. This paper details reproducible colorant preparation methods and characterizes these samples using accessible non-invasive techniques, multimodal imaging and reflectance spectroscopy. A majority of the colorants can be identified using the two techniques as complementary methods.

Keywords: Japanese woodblock prints, Nishiki-e, Ukiyo-e, Colorants, Sample-making, FORS, Multimodal imaging

Introduction

Until recently, identification of colorants used in Edo period *nishiki-e*, Japanese multicolored woodblock prints, was speculative, based on suggestions in the literature [1–4] and analytical studies of Japanese painting [5–8] and textile [9] colorants. New analytical research has started to shed light onto the colorants used in Edo period *nishiki-e*, resulting in identification instead of conjecture [10–22]. Overall literature is scarce regarding methods of colorant preparation for the woodblock printing process, making it difficult to replicate samples for use as references during characterization.

This study aims to explain the creation of reproducible reference samples of Edo-period Japanese woodblock printing ink colorants (Fig. 1) and to determine markers for their characterization using nondestructive analytical methods. The intended focus is on organic colorants, as they are more difficult to analyze and therefore have

been less definitively identified in the literature, although common inorganics are included for reference. Easily accessible nondestructive analytical techniques, multimodal imaging and fiber optic reflectance spectroscopy (FORS), are used complementarily for characterization. FORS and multimodal imaging are not new to the field of cultural heritage research, however there has yet to be an exhaustive study of Japanese woodblock ink colorants using these techniques as a means of characterization geared towards reproducibility and accessibility.

Ultimately, the identification of these colorants is vital to their preservation. Traditional Japanese woodblock printing ink colorants have numerous preservation concerns, including sensitivity to environmental conditions such as light, pollutants, and high humidity, as well as sensitivity to some conservation treatment conditions, such as pH, water, and other solvents [21–25]. Identification of organic colorants in Japanese prints can help guide preservation policies regarding their conservation treatment, housing materials, storage environment, and exhibition.

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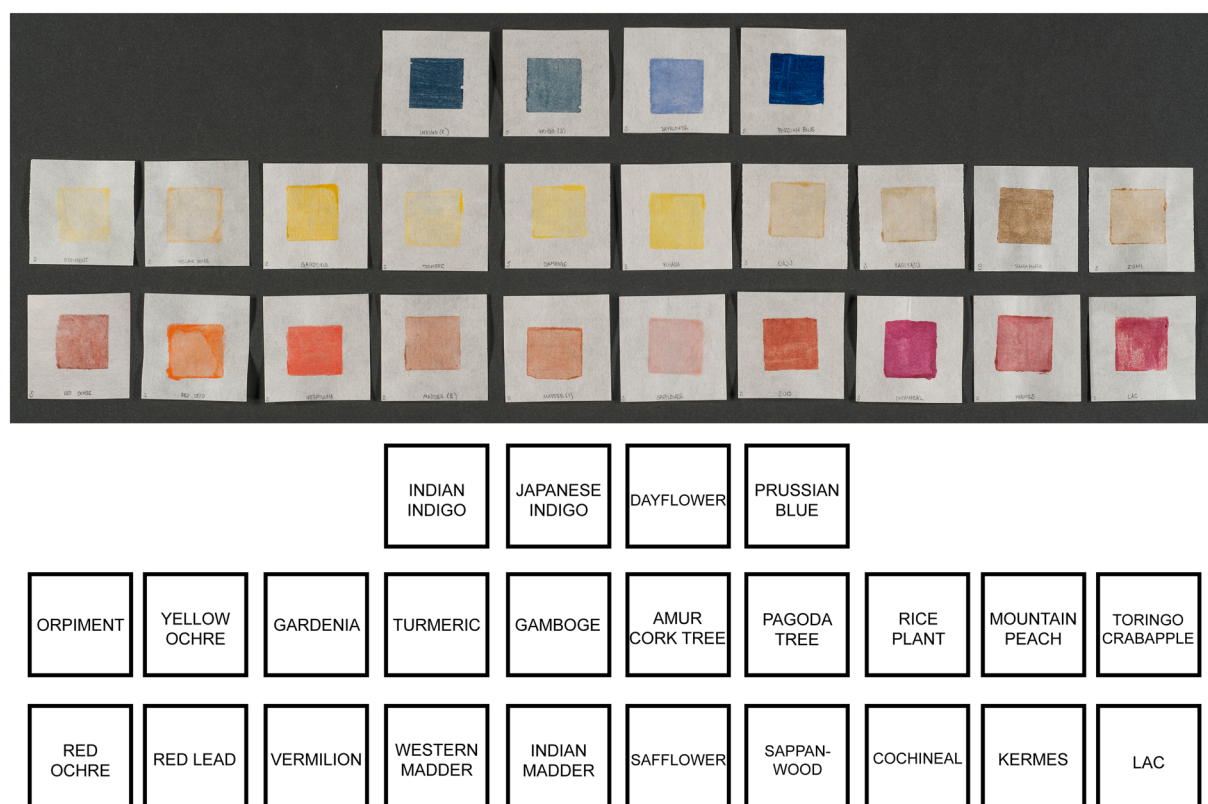


Fig. 1 Woodblock printed colorant samples on sized paper in normal illumination (above) and a diagram identifying the colorants (below)

Methods

Sample-making

Colorants included in the study are listed in Table 1. Colorants were selected from literature on Edo period Japanese woodblock ink colorants, both historic sources [1–3] and analytical studies [10–23], as well as analytical studies on Japanese painting [5–8] and textile [9] colorants from the Edo period. Therefore, inclusion of a colorant in the study does not indicate that it was definitively used in Edo *nishiki-e*, or that the list is comprehensive. Only pure colorants are included, although using mixtures and overprinting of colorants were common in Japanese woodblock printmaking. Mixtures were made for this study, but are beyond the scope of this paper.

Inorganic colorants commonly found in Edo-period *nishiki-e* were included in the study for reference. Prepared powders were used for inorganic Prussian blue, red ochre, vermilion, red lead, yellow ochre, orpiment, as well as organic indigo, gamboge, turmeric, and lac. Dayflower was extracted from the traditional dye-infused paper [25].

Safflower was extracted from the plant source, following the process outlined in literature [11, 26–28] and shown in Fig. 2. First, the flowers were wrapped in

rinsed and dried cotton cheesecloth, secured in a beaker, and placed under running tap water for about 10 h, until the water went from yellow to clear, to remove the soluble yellow colorant. When dry, the rinsed flowers were soaked in a closed jar of deionized water adjusted to pH 11 with ammonium hydroxide for 5 h, then vacuum filtered to extract the red colorant. The pH of the filtered extract (10) was then adjusted to 3.5 with 5% rice vinegar (acetic acid). Newly rinse and dried cotton cheesecloth was then used to absorb and concentrate the acidic dye extract. The safflower dye was stored in the cloth until printing, when it was then extracted with deionized water adjusted to pH 12 with ammonium hydroxide.

All other organic colorants were extracted from their raw plant or insect source. Traditional extraction methods [29–32] were adopted when possible, although the majority of literature on dye extraction is in relation to fabric dyeing, not lake pigment creation. This may be partially due to the fact that some dyes were extracted from dyed cloth, not the raw source itself [33]. Literature is even more scant in relation to dye extraction for use in Japanese woodblock inks. Therefore, the following methods describe only a few of numerous extraction methods possible (Fig. 3).

Table 1 Colorants included in the study

Colorant source	Japanese name	English name	Material type	Supplier and number
Blue				
<i>Commelina communis</i> L.	<i>Tsuyukusa</i>	Dayflower	Dye-infused paper	Tanaka Nao 21900100
<i>Indigofera tinctoria</i> / <i>Polygonum tinctorium</i>	<i>Ai</i>	Indigo (Indian/Japanese)	Prepared powder	Kremer 36000/36004
Ferrocyanide salt	<i>Bero-ai</i>	Prussian blue	Prepared powder	Kremer 45202
Red				
<i>Carthamus tinctorius</i> L.	<i>Beni</i>	Safflower	Flowers	Tanaka Nao 13520620
<i>Caesalpinia sappan</i> L.	<i>Suo</i>	Sappanwood	Heartwood	Tanaka Nao 13521120
<i>Rubia tinctorum</i> L./ <i>Rubia cordifolia</i> L.	<i>Akane</i>	Madder (Western/Indian)	Roots	Kremer 37201/Tanaka Nao 13520320
<i>Dactylopius coccus</i> Costa/	コチニール	Cochineal	Dried lice	Kremer 36040
<i>Kermes vermilio</i> Planch.	ケルメス	Kermes	Dried lice	Kremer 36045
<i>Laccifer lacca</i> Kerr	ラック	Lac	Prepared powder	Kremer 36020
Hematite	<i>Bengara</i>	Red ochre	Prepared powder	Sinopia PCP400
Mercuric sulfide	<i>Shu</i>	Vermilion	Prepared powder	Kremer 42000
Lead tetroxide	<i>Tan</i>	Red lead	Prepared powder	Kremer 42500
Yellow				
<i>Miscanthus tinctorius/senensis</i>	<i>Kariyasu</i>	Rice plant	Grass	Tanaka Nao 13500320
<i>Sophora japonica</i> / <i>Styphnolobium japonicum</i>	<i>Enju</i>	Pagoda tree	Flower buds	Tanaka Nao 13500220
<i>Myrica rubia</i>	<i>Yamamomo</i>	Mountain peach	Bark	Tanaka Nao 13502020
<i>Malus sieboldii</i>	<i>Zumi</i>	Toringo crabapple	Bark	Arnold Arboretum
<i>Phellodendron amurense</i>	<i>Kihada</i>	Amur cork tree	Inner bark	Tanaka Nao 13500420
<i>Gardenia augusta/jasminoides</i>	<i>Kuchinashi</i>	Gardenia	Dried fruit	Tanaka Nao 13500520
<i>Garcinia morella</i>	<i>Tō-ō</i>	Gamboge	Prepared powder	Kremer 37050
<i>Curcuma xanthorrhiza</i>	<i>Ukon</i>	Turmeric	Prepared powder	Kremer 37220
Goethite	<i>Ōdo</i>	Yellow ochre	Prepared powder	Kremer 40301
Arsenic sulfide	<i>Sekiō</i>	Orpiment	Prepared powder	Kremer 10700

Sappanwood, cochineal, kermes, gardenia, amur cork tree, rice plant, pagoda tree, mountain peach, and Toringo crabapple were soaked in deionized water adjusted to pH 11 with ammonium hydroxide for 1 week. All soaking occurred in closed jars. Madder was soaked for 1 week in unadjusted pH 6.5 deionized water, then the soaking liquid was discarded and the roots were soaked in deionized water adjusted to pH 11 with ammonium hydroxide for an additional week. Other madder extraction methods were attempted to attain a more vivid red, instead of a dull red-brown. Variations included boiling the roots in unadjusted pH 6.5 deionized water and soaking the roots in ethanol, rice vinegar, and sake. These modifications achieved similar color results, so the original madder extraction was used for printing.

Each solution was then vacuum filtered and left to dry for a week in a crystallization dish in order to concentrate the extract by allowing the water to evaporate from the aqueous solution in ambient room temperature conditions. The dyes in this study were not laked, as there is no consensus about whether the dyes, or which dyes, used in Japanese woodblock printing were used pure or

precipitated onto a mordant (metal salt ion). Analysis of this is complicated by the *dosa* paper sizing containing alum, a popular mordant for laking dyes.

The binder for the printing ink, rice starch paste, was prepared immediately before printing in the following manner for all colorants except safflower. First, 57 g rice starch was soaked in 400 mL deionized water overnight, allowing the starch to swell. The mixture was then cooked in a pot over high heat for 20 min while continually stirring, first slowly then more vigorously as the paste became thick and translucent. The resulting 300 g of cooked rice starch paste was then strained and diluted with 750 mL of deionized water to create a consistency appropriate for printing. For safflower, the rice starch paste was prepared using rice vinegar (5% acidity) instead of deionized water to intensify the red color by eliminating any remaining safflower yellow [28]. A similar procedure was used: 10 g of rice starch was soaked in 50 mL of rice vinegar for 1 h, then cooked. The resulting 20 g of cooked paste was then diluted with 50 mL of rice vinegar.

Samples were printed on 100% *kozo*-fiber paper. Two samples sets were created; one on unsized paper and

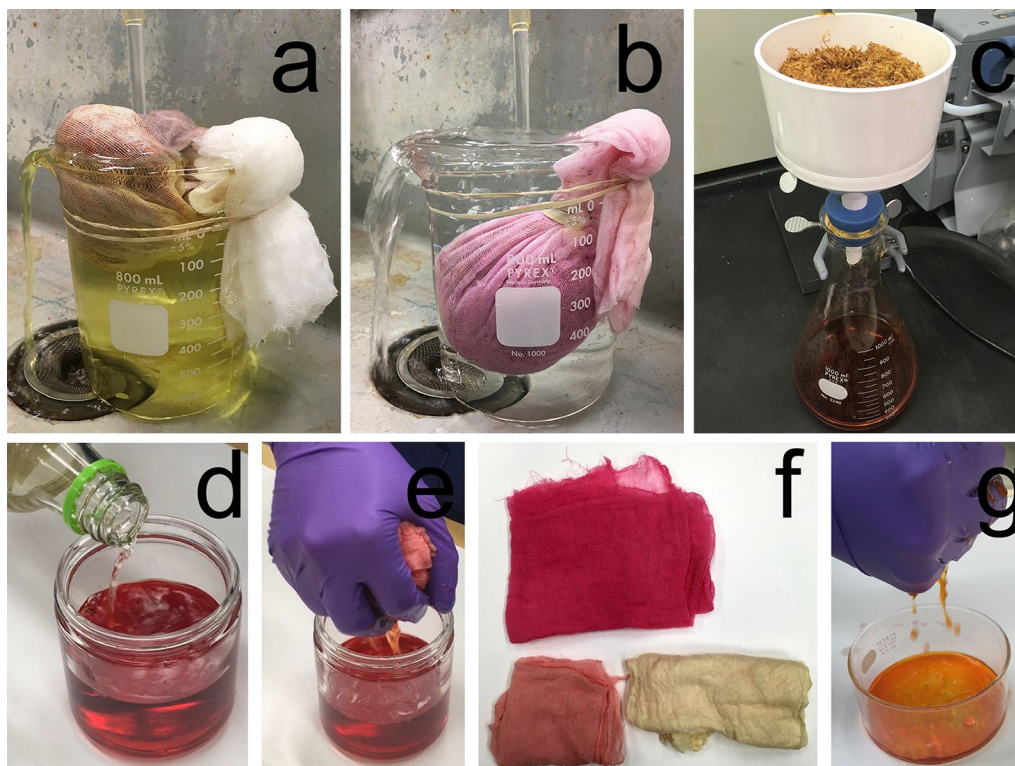


Fig. 2 Safflower extraction process. Clockwise from top left: **a** rinsing safflower to remove yellow colorant **b** until clear; **c** vacuum filtration of safflower soaked in deionized water adjusted to pH 11 with ammonium hydroxide; **d** adjusting the pH of the filtered extract with acetic acid; **e** absorbing the concentrated acidic dye extract in cheesecloth; **f** concentrated dye extract in cheesecloth when dry—the intensity of the color decreases with successive dips; **g** extracting the dye with deionized water adjusted to pH 12 with ammonium hydroxide before mixing with the binder for printing

the other on paper sized with *dosa*, a mixture of alum (*myoban*) and cow skin glue (*nikawa*). Paper used for Japanese woodblock printing required sizing to prevent the ink from bleeding into the paper fibers outside of the printed area; to promote uniformity of ink application; to prevent abrasion of the paper created from pressure applied by the baren; and to ensure paper fibers did not stick to the printing blocks. Samples for this study were printed on both unsized and sized papers to observe the effect of the sizing on the printing process and for the unsized samples to approximate prints that have been altered by moisture damage or aqueous conservation treatments, which would reduce or remove the sizing.

Several historic *dosa* recipes for the sizing of woodblock printing paper were consulted [34–36]. As with many historic recipes, each contained varying ratios of the ingredients. Besides variation by user, the ratios were historically modified based on the region and season, the type and sides of the paper being sized, and “the frequency of application of the baren required for the print” [35]. Therefore, approximate average measurements of each component from the historic recipes

were then calculated, resulting in the following mixture: 50 g of cow skin glue, 25 g alum, and 1 L water.

To make the sizing, 50 g of cow skin glue was soaked in 100 mL deionized water overnight. The swelled glue was then heated in a glue pot and 600 mL of warm deionized water (60 °C) was added. Then, 25 g alum and 400 mL of warm deionized water were added. The sizing was heated in the glue pot to 60 °C and mixed while heating. The *kozo* paper was then prepared by lightly spraying both sides of the paper with deionized water to relax and open the fibers. The warm sizing was applied to the humidified paper by brushing the sizing through a nonwoven polyester sheet onto both sides of the paper. Traditionally sizing was applied directly to the paper; the sizing for these samples was brushed through a nonwoven polyester sheet to prevent pilling and abrasion of the paper and promote even application. The paper was then dried between nonwoven polyester sheets and felts under an acrylic sheet and weight, although traditionally the paper was hung on a line to dry. The papers were then cut into two-inch squares.

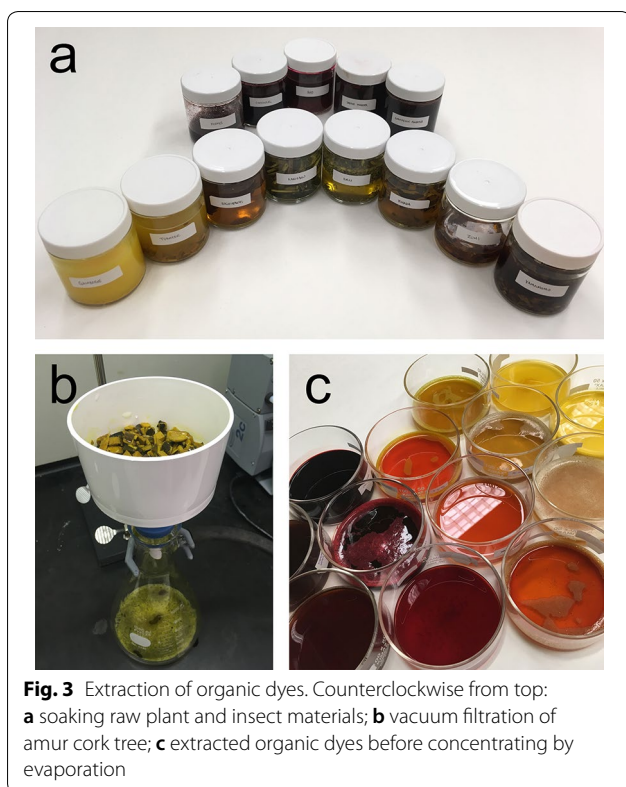


Fig. 3 Extraction of organic dyes. Counterclockwise from top: **a** soaking raw plant and insect materials; **b** vacuum filtration of amur cork tree; **c** extracted organic dyes before concentrating by evaporation

When ready to print, the colorants were mixed with the prepared rice starch binder at 5 wt% colorant in binder. For these calculations, the weight of the dried dye extract, prepared pigment, or dye-infused paper was used. In practice, the amount of colorant added to the binder depended on the tinting strength of the colorant and the desired intensity, however the same percentage was used for all colorants in this study to maintain consistency and repeatability. The rice starch paste binder was mixed directly with the colorants, in the crystallization dish with the dried dye extracts and onto the day-flower-infused paper. Prepared pigment powders were slowly added to a mortar containing rice starch paste and incorporated with a pestle. To intensify the colors of some dyes, approximately 1 mL of ammoniated water (pH 12) was added to sappanwood, madder, cochineal, lac, and kermes inks immediately before printing.

One-inch cherry wood blocks were used as printing matrices. Prior to printing, the blocks were moistened and the paper was humidified with deionized water. Ink was brushed onto a block, the humidified paper placed on the inked block, and the back of the paper was burnished with a Teflon folder instead of a traditional baren to lift the ink. The printed samples were then air dried. For reference, controls were retained of sized and unsized paper samples containing no ink, as well as sized and

unsized paper samples printed with just the rice starch paste binder and no colorant.

Readily available chemicals, such as ammonium hydroxide instead of a historic alkalizing agent, and standardized chemicals, such as deionized water instead of fresh or tap water, were used throughout whenever possible so that samples could be easily reproduced and to limit the variables caused by impurities.

Multimodal imaging

The completed samples were characterized using various imaging modes, including photographic and processing techniques, in broad bands across the UV–visible–IR spectrum. The responses of the samples were photographed and processed using methods detailed in an internal manual describing the adaptation of these techniques for the specific setup in the Conservation Division at the Library of Congress [37]. The manual is based on guides used by conservation professionals for the photographic documentation of cultural heritage [38, 39]. The imaging modes used in the study are: visible-reflected, infrared-reflected, visible-induced infrared luminescence, near ultraviolet (UVA)-induced luminescence, near ultraviolet (UVA)-reflected, infrared-reflected false color and ultraviolet-reflected false color. Photography was conducted with a Nikon D700 camera modified to remove its internal IR-blocking filter and a CoastalOpt UV–Vis–IR 60 mm lens. The specific filters and their transmission ranges, as well as the light sources used for photography, are noted in Table 2. The selection of a filter is not only based on its transmission range, but also its percent transmission over that range. Post-processing was done in Adobe Photoshop. False color modes are specific processing techniques that combine two images using RGB and grayscale channel substitution, which are also noted in Table 2.

Fiber optic reflectance spectroscopy

The samples were also characterized using fiber optic reflectance spectroscopy (FORS), a technique that uses a white light source and a spectrometer to irradiate an object and then measure the amount and the color of light that is reflected. Light that is not reflected from the object has been absorbed (appearing as dips in the reflectance spectra) and many materials have unique absorption patterns. The fiber optic spectroradiometer (FieldSpec4, PANalytical) operates in a range from 350 to 2500 nm with a collection area of ~3 mm. Spectral resolution is 3 nm at 700 nm and 8 nm at 1400 and 2100 nm. Ten spectra were averaged with a total acquisition time of <5 s. Spectra were normalized to a Spectralon white reference standard.

Table 2 Imaging modalities included in the study

Mode	Filter(s)	Transmittance (approximate) (nm)	Radiation/light source
Visible-reflected	PECA 916	400–750	North light high-intensity discharge (HID) copy light (2)
	PECA 918	380–700	
Infrared-reflected	PECA 910	850–1000	North light high-intensity discharge (HID) copy light (2)
Visible-induced infrared luminescence	PECA 904	795–1000	PowerSmith LED work light with 2 BG38 filters attached
UVA-induced luminescence	PECA 916	400–750	UV systems triple bright II LW370 (2)
	PECA 918	380–700	
UVA-reflected	PECA 900	250–400	UV systems triple bright II LW370 (2)
	X-Nite BP1	300–650	
Photographs used			Channel substitutions
IR-reflected false color		Visible + infrared-reflected	G to B; R to G; RIR to R
UVA-reflected false color		Visible + UVA-reflected	G to R; B to G; RUVA to B

Results and discussion

There are no discernable distinctions in the data acquired from multimodal imaging and FORS between the different species of madder (*Rubia tinctorum* L. and *Rubia cordifolia* L.) and indigo (*Indigofera tinctoria* and *Polygonum tinctorium*) included in the study. Therefore the species

will not be discussed separately. Mixing and overprinting colorants can cause a shift in the response of a printing ink to imaging and the inflection point in FORS, which is beyond the scope of this paper. A summary of the identifying markers of the colorants using imaging and FORS is presented in Table 3.

Table 3 Summary of most useful imaging and FORS markers for identification of ink colorants on sized paper

Colorant	Imaging markers	FORS markers		
Blue				
Dayflower	VIL: luminesces	IRR: reflects	IRRFC: pink	590 ^a , 645 ^a
Indigo	VIL: no luminescence	IRR: reflects	IRRFC: pink	660 ^a
Prussian blue	VIL: absorbs	IRR: absorbs	IRRFC: dark blue/purple	600–1000 ^a , 2365 ^a
Red				
Safflower	VIL/UVL: luminesces	IRRFC: yellow	UVRFC: red-brown	530 ^a
Sappanwood	VIL: luminesces UVL: absorbs	IRRFC: orange-red	UVRFC: brown	530 ^a
Madder	VIL/UVL: luminesces	IRRFC: orange-red	UVRFC: red-brown	510 ^a , 525 ^a
Cochineal	VIL/UVL: luminesces	IRRFC: orange-red	UVRFC: green	520 ^a , 555 ^a
Kermes	VIL/UVL: luminesces	IRRFC: orange-red	UVRFC: gray	520 ^a , 555 ^a
Lac	VIL/UVL: luminesces	IRRFC: orange-red	UVRFC: blue	520 ^a , 555 ^a
Red ochre	VIL/UVL: absorbs	IRRFC: orange-red	UVRFC: purple-brown	500 ^a , 650 ^a , 900 ^a
Vermilion	VIL/UVL: absorbs	IRRFC: yellow	UVRFC: purple-brown	590–600 ⁱ
Red lead	VIL/UVL: absorbs	IRRFC: yellow	UVRFC: red	565 ⁱ
Yellow				
Flavonoids*	VIL: no luminescence	UVL: absorbs	UVRFC: brown	~460 ⁱ
Amur cork tree	VIL: luminesces	UVL: luminesces	UVRFC: orange	440–450 ^a , ~495 ⁱ
Gardenia	VIL: luminesces	UVL: luminesces	UVRFC: pink	450 ^a , 485 ^a , 460 ^j , 510 ^j
Gamboge	VIL: no luminescence	UVL: absorbs	UVRFC: orange	440–450 ^a , ~495 ⁱ
Turmeric	VIL: luminesces	UVL: luminesces	UVRFC: pink	440–450 ^a , ~495 ⁱ
Yellow ochre	VIL: no luminescence	UVL: absorbs	UVRFC: pink	500 ^a , 650 ^a , 900 ^a
Orpiment	VIL: no luminescence	UVL: absorbs	UVRFC: pink	485 ⁱ

Flavonoid yellows include rice plant, pagoda tree, mountain peach, and Toringo crabapple which do not luminesce with the exception of pagoda tree

^a Absorption

ⁱ Inflection point

Effect of sizing

Reflectance spectra were taken on control samples of sized and unsized papers containing no ink, as well as sized and unsized paper samples printed with just the rice starch paste ink binder (Fig. 4). Rice starch paste is indistinguishable from the paper. The presence of protein in the *dosa* paper sizing [40] is indicated by a small shoulder around 2170 nm. Besides this protein peak, all spectra contain indistinguishable peaks attributed to the cellulose and polysaccharide content of the paper [41] in the infrared range of FORS. Therefore, only the visible region is presented in the spectra obtained from printed colorant samples to highlight the marker peaks for colorant identification.

The visual appearance and spectral response of some organic red dyes are different on sized paper compared to on unsized paper (Fig. 5). Sappanwood, cochineal, kermes, and lac printed on unsized paper appear less saturated and tonally different to varying degrees when compared to the same colorants printed on sized paper. Cochineal completely decolorizes on unsized paper, but retains its vibrant red color on sized paper. These color changes also result in spectroscopic changes. The inflection points shift, as is expected with a color change [42], however absorption features that are due to the dye molecule also change.

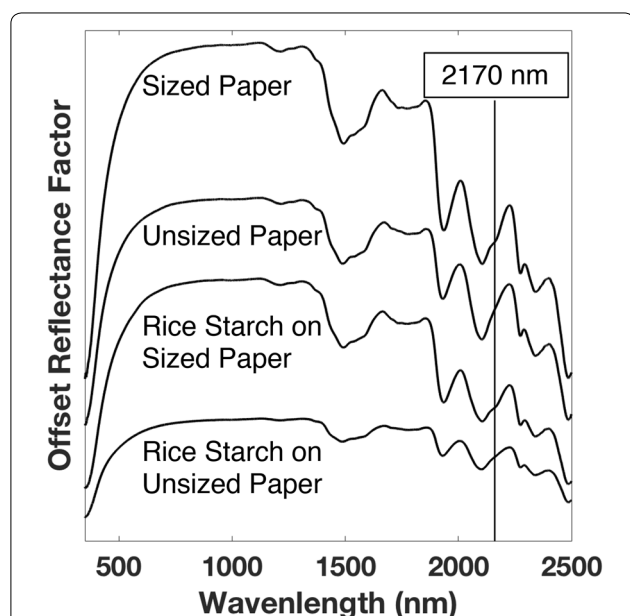


Fig. 4 FORS spectra of sized paper, unsized paper, rice starch paste on sized paper, and rice starch paste on unsized paper. Each spectrum has the hallmark peaks for cellulose-based paper with the exception of the sized papers, which contain a shoulder peak around 2170 nm due to the protein content of animal glue in the paper sizing

This is not entirely surprising as the optical properties of red dyes in particular are dependent on dye concentration, surrounding environment (media, other pigments or chromophores), pH, the original extraction technique, and metal mordant and precipitation procedure for the dye if laked [33, 43]. These effects have been extensively studied particularly for cochineal, kermes, lac, madder, and brazilwood [44–48]. It is possible that the alum in the paper sizing coupled with the alkalinity of the dye extract allowed the dyes to form lakes in situ as previously speculated [11]. In order to test the theory that these dyes are forming lakes with the alum in the paper sizing, we compared the cochineal and madder dye extracts to prepared cochineal (Kremer 42100) and madder (Kremer 37202) alum-laked pigments printed on both sized and unsized paper (Fig. 6).

The prepared alum-laked pigments are unaffected by the present or absence of sizing on the paper because fixing the dye on a mordant creates a stable pigment. The alum-laked pigments printed on both sized and unsized papers and the dye extracts printed on sized paper feature identifying peaks, which are cited in literature for red lakes [33, 43, 45], and are nearly spectroscopically identical. The dye extracts on unsized paper have no identifiable features. Given the sensitivity of the red dyes and the spectroscopic similarity between the alum-laked pigments and the dyes on sized paper, we believe that certain dyes, particularly organic reds, had to have been laked prior to use.

Multimodal imaging

Multimodal images of the colorant samples on sized paper are shown in Fig. 7. Reflected modes on their own do not provide much information to distinguish the colorants in this study. With infrared-reflected, Prussian blue is the only colorant that strongly absorbs infrared radiation (appearing darker than the paper). Most other colorants transmit infrared (appearing similar to the paper). With near ultraviolet-reflected, all colorants absorb UVA radiation (appearing darker than the paper).

Other imaging modes are more useful in distinguishing the colorants in this study. With visible-induced infrared luminescence, dayflower is the only blue colorant that luminesces. Of the yellow colorants, gardenia, turmeric, amur cork tree, and pagoda tree luminesce. This may be a good method of differentiating pagoda tree from the other flavonoid yellows that do not luminesce (mountain peach, rice plant, and Toringo crabapple), which have been indistinguishable using nondestructive methods until this point. All of the organic red colorants luminesce, while the inorganic colorants do not.

With near ultraviolet-induced luminescence, both the paper sizing and the ink binder fluoresce, which

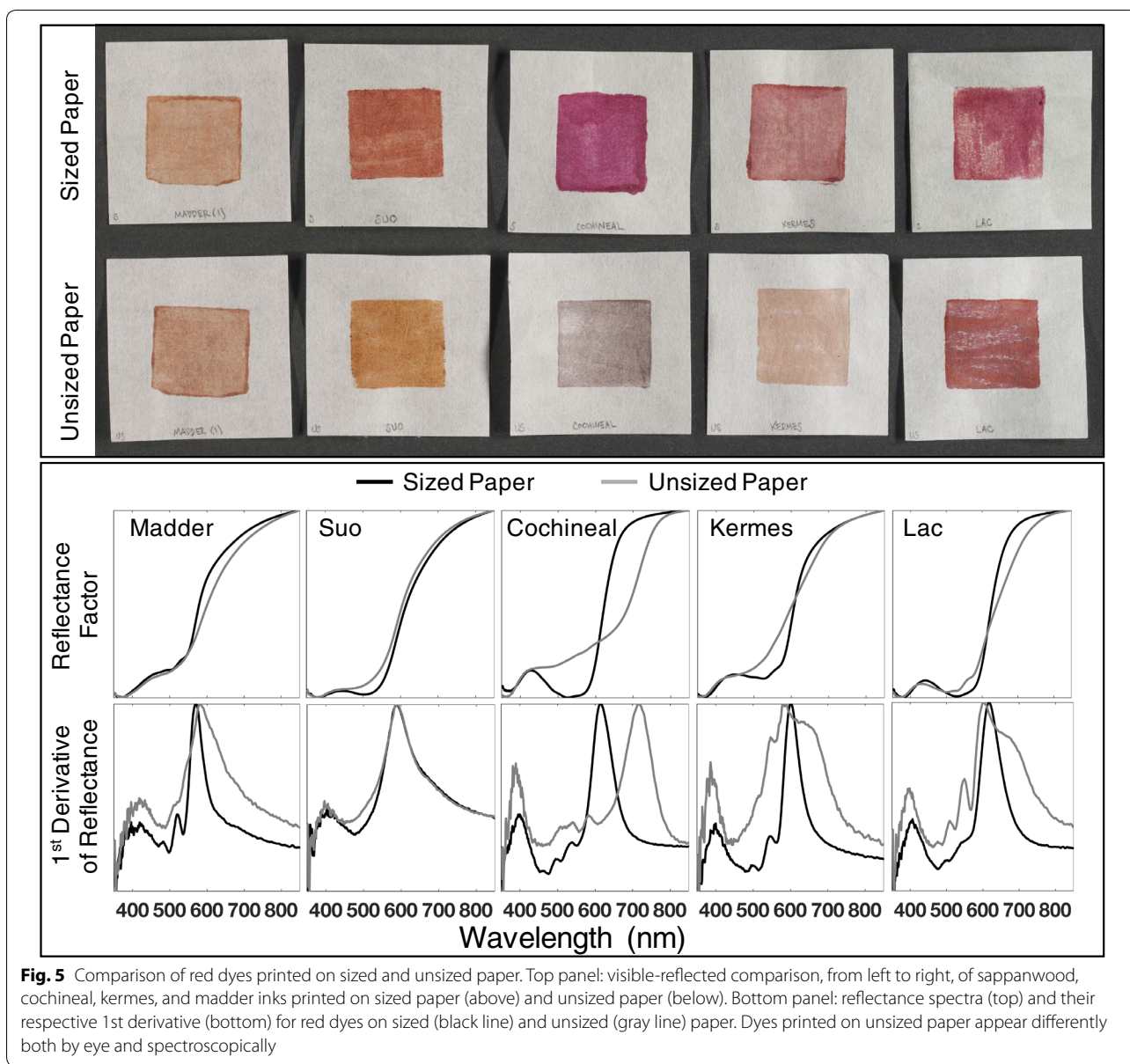


Fig. 5 Comparison of red dyes printed on sized and unsized paper. Top panel: visible-reflected comparison, from left to right, of sappanwood, cochineal, kermes, and madder inks printed on sized paper (above) and unsized paper (below). Bottom panel: reflectance spectra (top) and their respective 1st derivative (bottom) for red dyes on sized (black line) and unsized (gray line) paper. Dyes printed on unsized paper appear differently both by eye and spectroscopically

must be taken into consideration during interpretation. Indigo and Prussian blue samples do not fluoresce, while dayflower fluoresces on sized paper and does not fluoresce on unsized paper. The immediate solubility of dayflower in water could explain this difference, as the dayflower colorant may have solubilized in the fluorescent sizing of the humidified paper during printing and therefore may appear fluorescent in areas of application. Of the yellows, gardenia, turmeric and amur cork tree fluoresce, while the flavonoid yellows (pagoda tree, rice plant, mountain peach, and Toringo crabapple), gamboge, yellow ochre, and orpiment do not fluoresce. The fluorescence of the paper sizing may interfere

with the response of some of the organic yellow colorants (such as pagoda tree and rice plant), however the absorption of these colorants is clear on unsized paper. Of the reds on both sized and unsized samples, sappanwood and the inorganic reds do not fluoresce, while madder and safflower fluoresce. The insect dyes (cochineal, kermes, and lac) fluoresce on sized papers and do not fluoresce on unsized papers.

After infrared-reflected false color processing, dayflower and indigo appear pink, while Prussian blue appears dark blue-purple. The flavonoid yellows appear in the orange-red-brown range, while all other yellow colorants appear pale yellow. Red lead, vermilion, and

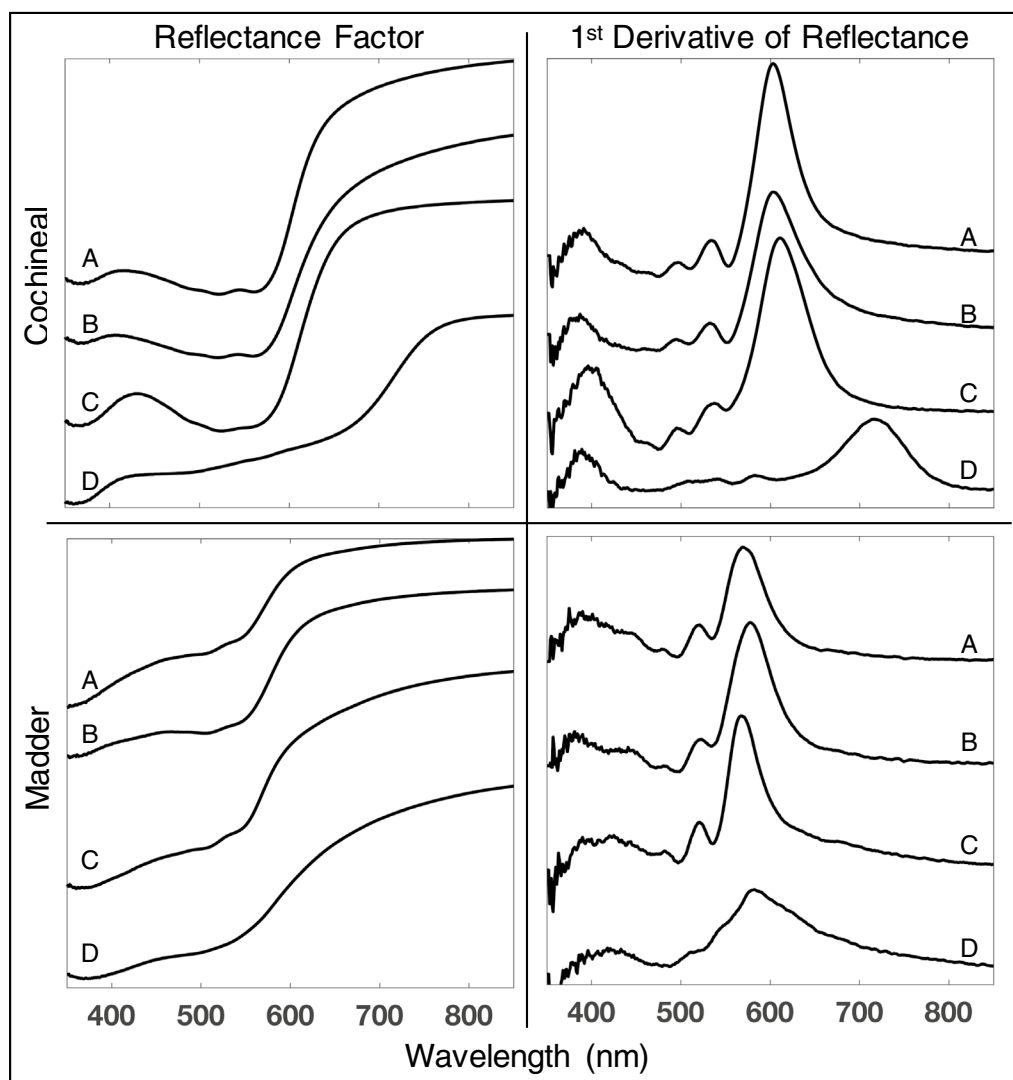


Fig. 6 Offset FORS comparison of laked and dye extracts printed on sized and unsized paper. For each figure, spectra are organized as A laked pigment on sized paper, B laked pigment on unsized paper, C dye extract on sized paper, and D dye extract on unsized paper. In both cochineal (top) and madder (bottom) the dye extract on sized paper behaves similarly to the alum-laked pigment. The alum-laked pigment is not effected by the sizing or lack of sizing on the paper

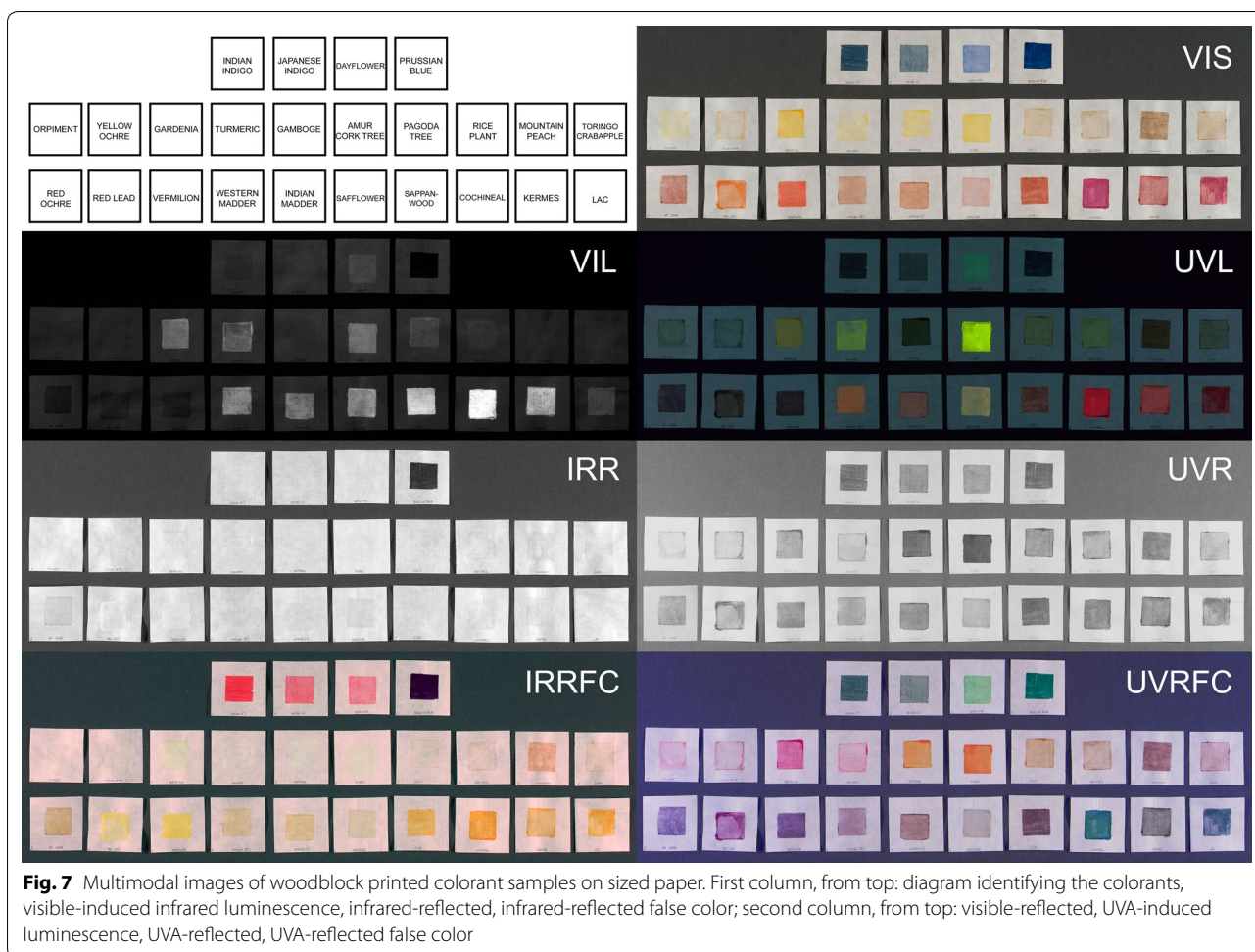
safflower appear yellow; red ochre, madder, sappanwood, and the insect dyes appear orange.

With near ultraviolet-reflected false color processing, all blue colorants appear a variation of blue-green. Orpiment, yellow ochre, gardenia, and turmeric appear pink; gamboge and amur cork tree appear orange; and the flavonoid yellows appear brown. Red lead appears red; red ochre and vermilion appear purple-brown; madder and safflower appear red-brown. The remaining organic red colorants appear differently on sized and unsized papers, which again may be due to colorant interaction with the paper sizing. On sized paper, sappanwood appears

brown, cochineal appears green, kermes appears gray, and lac appears blue. On unsized paper, sappanwood appears red, cochineal appears gray, kermes appears brown, and lac appears purple. Comparative color tone and intensity observations can be subjective, however this information has been paired with reflectance spectroscopy for objectivity.

Fiber optic reflectance spectroscopy

Reference spectra are presented and discussed in the visible range for red, blue, and yellow colorants on sized paper. Reflectance spectra and their respective 1st



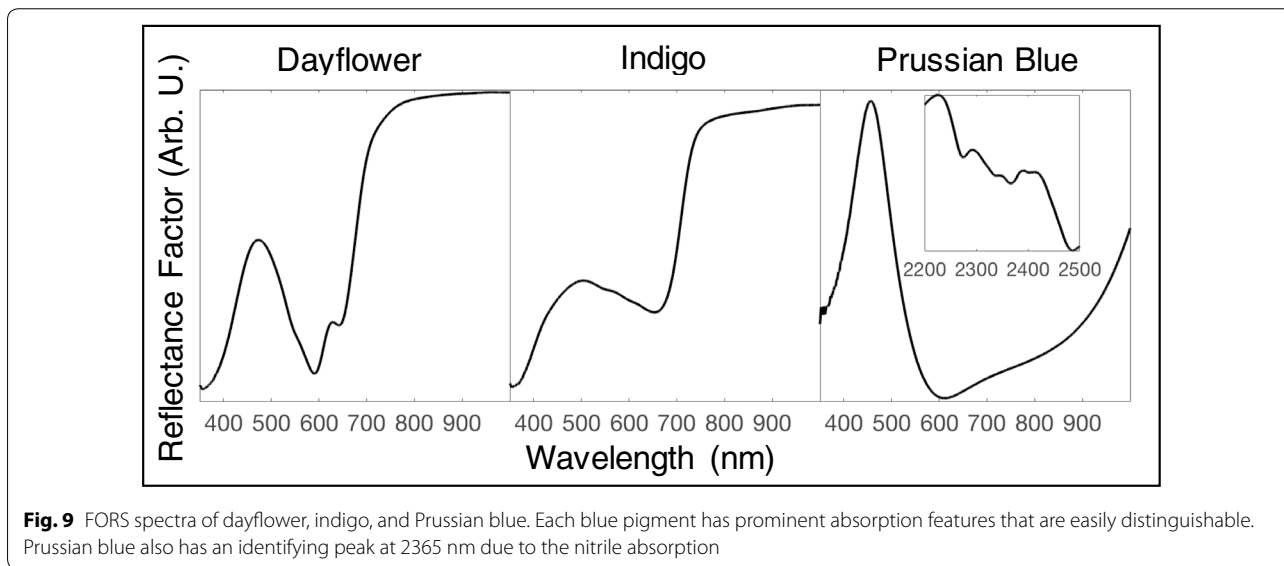
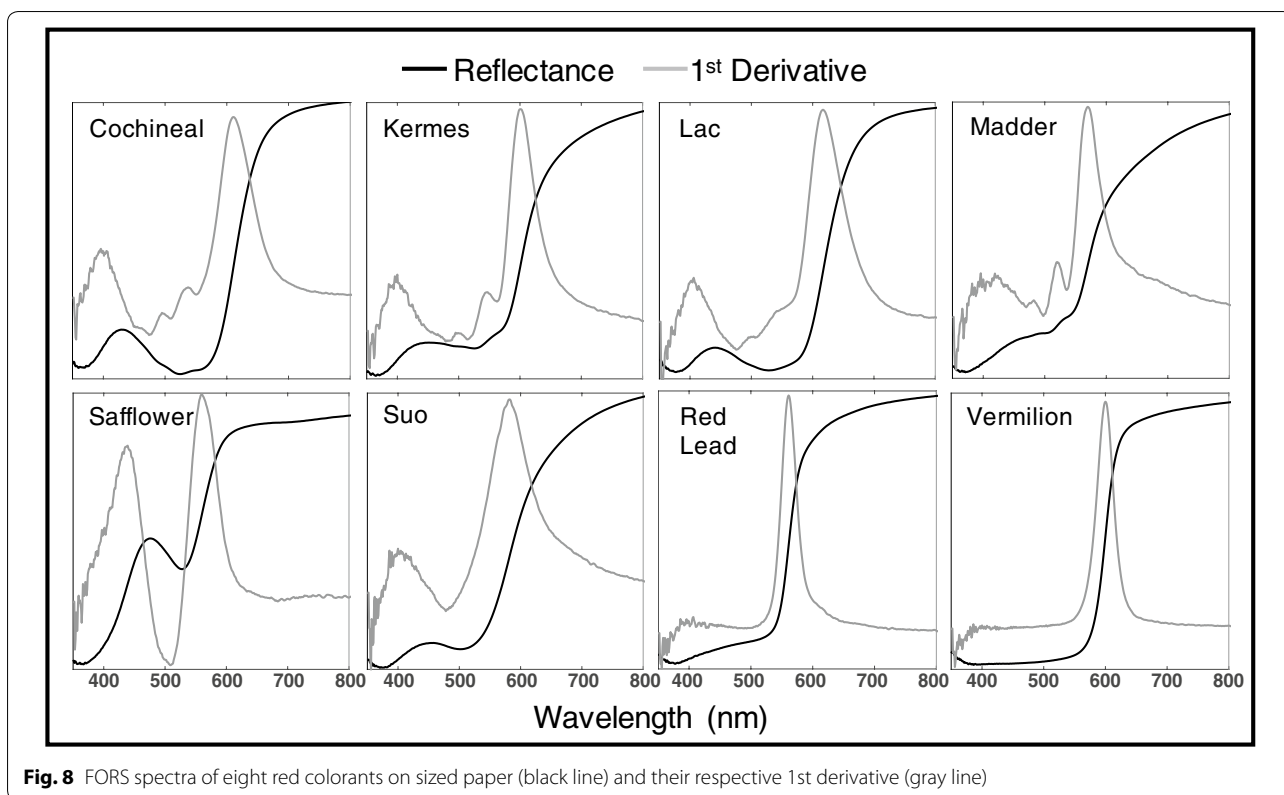
derivatives are shown for all the red and yellow reference materials, as these colorants tend to have small features that can be difficult to see. Blue pigments have easily recognizable features that can be seen in the raw reflectance spectra and as such are shown without derivative analysis.

Figure 8 shows identifying markers for both organic and inorganic reds. Cochineal, kermes, and lac (all scale insects) have similar absorption peaks (~520 and 555 nm) and typically cannot be distinguished from one another with reflectance or fluorescence emission spectroscopy [43, 49]. However, these insect-based dyes can be distinguished from plant-based dyes; madder has two peaks closer to ~510 and 525 nm [49], while sappanwood and safflower tend to have only one absorption peak close to 530 nm. Safflower has a prominent reflection peak near 450 nm. Red ochre is characterized by three peaks near 500, 650, and a broad 900 nm absorption, similar to most iron based earth pigments. Red lead and vermilion have characteristic FORS spectra featuring a sharp S-shaped curve with narrow inflection points

near 565 nm for red lead and 590 to 600 nm for vermilion [49].

The three blue colorants are straightforward to identify with FORS (Fig. 9). Dayflower has two absorptions at 590 and 645 nm; indigo has a single absorption near 660 nm; Prussian blue is characterized by a broad absorption from 600 to 1000 nm, as well as a nitrile absorption at 2365 nm [50], differing from the surrounding cellulose absorptions of paper.

FORS spectra for the yellow colorants are shown in Fig. 10. Organic yellow colorants are notoriously difficult to identify [11, 42, 49]; the main spectral feature for organic yellows tends to be the inflection point (found by calculating the first derivative of the reflectance spectrum). Unfortunately the inflection point can change depending on the color of the underlying support and the overall color of the yellow; for example, fading or mixing with a white pigment can change the inflection point. While this is true for most colorants, it causes the most complications for yellows which do not have an absorption peak in the visible range of the



FORS to aid identification [42]. The spectral contribution of the paper substrate further complicates 1st derivative analysis; our sample papers all have a broad 1st derivative feature between 380 and 400 nm rendering spectral features in this area inappropriate for pigment markers. In this study, FORS was only able to

distinctly identify yellow ochre. Earth pigments have a characteristic absorption pattern, noted by three absorption bands around 500, 650, and 900 nm, with a first inflection point close to 540 nm. As a semiconductor pigment, orpiment only contains an inflection point around 485 nm as a marker with FORS, however

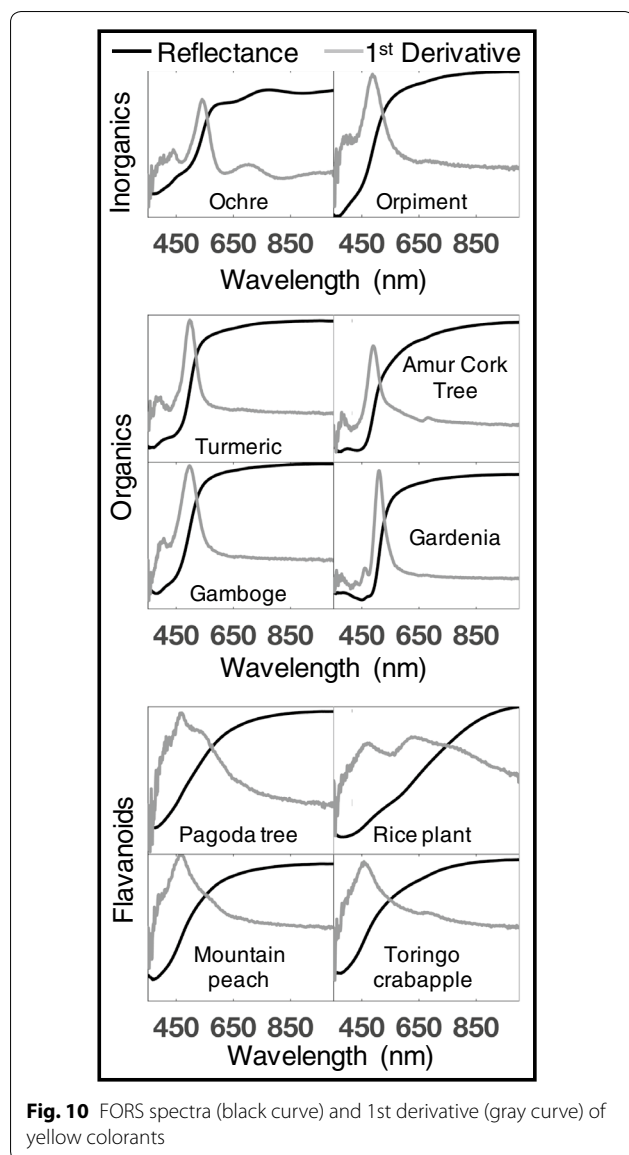


Fig. 10 FORS spectra (black curve) and 1st derivative (gray curve) of yellow colorants

this pigment is more easily identified using XRF (finding arsenic) or Raman spectroscopy (distinct spectra matching R. Clark's database [51]).

The non-flavonoid organic yellow dyes turmeric, gamboge, and amur cork tree each have very similar FORS features: UV absorptions around 370 nm, visible absorptions between 440 and 450 nm, and inflection points close to 495 nm. The only exception is gardenia, which features two small absorption features at 450 and 485 nm, as well as two inflection points, a weak intensity feature at 460 nm and a strong maximum at 510 nm. Flavonoid yellows all have slow rising reflectance curves that give rise to broad first derivative peaks distinguishing them from non-flavonoid dyes.

Pagoda tree, mountain peach, and Toringo crabapple have a broad 1st derivative feature around 460 nm, while rice plant has two broad inflection features near 470 and 625 nm.

Conclusion

This work outlines a straightforward method for creating samples to replicate Edo period woodblock printing inks and presents complementary methods for characterization, in the hopes that other institutions may be able to better identify colorants in their *nishiki-e* collections or create their own reference materials. Detailed instruction for dye extractions and printing, using easily accessible chemicals, are included for reproducibility. Although some of these materials, such as ammonium hydroxide, may not replicate historic recipes, the reflectance spectroscopy results of these samples matched known absorption values for many of the dyes that have been characterized in literature. This work was performed in conjunction with an analytical case study of two Edo period Japanese woodblock prints from the Library of Congress. We were able to identify most of the colorants in the prints by comparison with the reference materials and data described in this paper. Results of the case study will be published in a forthcoming publication.

The biggest challenge during the course of preparing the samples was extracting the organic red dyes and maintaining vivid red colors. With the exception of safflower, the organic red dye extractions were sensitive to pH and decolorized as the extract sat in open air. Further, the red dyes reacted differently to the paper dependent upon whether or not there was sizing. The color and reflectance properties of the red dyes changed in the presence of alum in the paper sizing indicates that the red dyes are forming a lake in situ, leading to the conclusion that printers used laked organic dyes. The only way to control and maintain the color of a large quantity of ink for multiple prints would be to use a red dye fixed to a mordant. Future work includes investigating different laking of common Japanese red dyes and how the optical properties could be affected.

Multimodal imaging and fiber optic reflectance spectroscopy were found to be complementary methods that identify most of the materials. While the reflectance system used in this study may not be readily available due to its cost, identifying markers for most colorants are found in the range of 350 to 1000 nm, meaning more affordable equipment could be used for these purposes while keeping in mind the loss of information in the IR region (binder, varnishes, coating, substrate). Similarly, multimodal imaging can be accomplished with a copystand setup that is relatively inexpensive when compared to other multispectral and hyperspectral imaging systems.

Capture and post-processing techniques follow the publicly available instructional manual, as noted in the text. Overall, reproducible preparation and characterization methods for Japanese woodblock inks have been presented.

Abbreviations

FORS: fiber optic reflectance spectroscopy; IRR: infrared-reflected; IRRFC: infrared-reflected false color; UVL: ultraviolet-induced luminescence; UVR: ultraviolet-reflected; UVRFC: ultraviolet-reflected false color; VIL: visible-induced infrared luminescence; VIS: visible-reflected; XRF: X-ray fluorescence spectroscopy.

Acknowledgements

The authors would like to thank Joan Wright, Michiko Adachi, and Michele Derrick (Museum of Fine Arts, Boston) for their openness, support, and guidance. Joan Wright graciously provided the Torongo crabapple bark sample obtained from Arnold Arboretum. Masumi Takeuchi helped the authors obtain the Tanaka Nao colorant samples. Juan–Juan Chen provided imaging instruction and introduced the term “multimodal imaging” to the Library of Congress during workshops presented to the Conservation Division in 2016 and 2017. The authors would also like to thank Elmer Eusman, Fenella France, Yasmeen Khan, and Holly Krueger (Library of Congress) for their support.

Authors' contributions

Samples were prepared by TV and GE. FORS data was collected by TV. Multimodal imaging was conducted by GE. TV and GE prepared, revised, the manuscript. Both authors read and approved the final manuscript.

Funding

The study was performed at the Library of Congress with no additional funding provided.

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

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Received: 3 July 2019 Accepted: 18 October 2019

Published online: 14 November 2019

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