



Probing some organic *ukiyo-e* Japanese pigments and mixtures using non-invasive and mobile infrared spectroscopies

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Abstract

Non-invasive identification of organic colourants in paintings still remains a challenging issue, especially in the case of extremely thin layers of paint on printed paper such as Japanese *ukiyo-e* prints. Because prints are fragile artworks, various non-invasive analytical methods need to be employed. The present work focuses on results obtained by combining fibre optic reflectance spectroscopy in the near-infrared range (FORS NIR) with mid-infrared (MIR) spectroscopy. The first step consists of identifying spectroscopic marker bands typical of some organic pigments (indigo, gamboge, cochineal, turmeric, safflower, dragon's blood). Some reference printouts involving paper substrate, binder and pigments (seldom used or as mixtures) were then investigated in order to establish a straightforward way to extract the marker bands of the pigments. Some data post-treatments were applied to the spectra, such as spectral subtraction, in order to abstract the signal from overlapping bands originating from both substrate and binder, and second derivative calculation to emphasise the pigment marker bands' frequency positions. These data treatments turned out to be relevant to extract information on the organic pigments of interest, even within complex mixtures.

Keywords Infrared spectroscopy · Organic pigments · Japanese woodblock prints · Non-invasive method · Data post-treatment · FORS NIR

Introduction

The study of paintings on paper, such as miniatures, watercolours or Japanese *ukiyo-e* prints, is a challenging task due to the thinness and the fragility of the artefacts. Their investigations are generally limited by the impossibility to move the artworks out of the museum and to collect samples

in order to perform measurements. Thus, non-invasive, contactless and portable analytical techniques are requested. Moreover, the possible degree of complexity of the pigment mixtures used to obtain the desired colours requires the use of methods that are selective enough to discriminate all the compounds probed, including ideally inorganic and organic materials.

Recent studies on such objects have proposed adapted analytical strategies or methods in order to identify the pigments used in watercolours, manuscripts or prints on paper. They are mainly based on the combination of three non-invasive techniques: X-ray fluorescence spectroscopy, Raman spectroscopy and visible reflectance spectroscopy [1–8]. Presently, studies have demonstrated the capability to identify many inorganic pigments but the identification of organic compounds using these well-established techniques remains challenging. Indeed, XRF is an elemental method that is not suited for the identification of organic compounds. In some circumstances, Raman signal can be hidden by the fluorescence emission of the sample. SERS (surface-enhanced Raman spectroscopy) analyses have been conducted on synthetic red organic dyes with success [9, 10] but the analytical

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protocol remains micro-invasive. UV-VIS reflectance spectroscopy is not selective enough to discriminate all pigments, especially in the case of mixtures of pigments. Indeed, when the painting layer comprises several colouring species, the spectroscopic characterisation of its constituents becomes difficult due to the overlapping of their few broad absorption bands. It can lead to significant band shifts and attribution uncertainties. Furthermore, other parameters, as particle size, pigment concentration and nature of the binder or substrate, can also affect the band positions, thereby making the identification of the pigments more complex [7, 11–13].

Among the available non-sampling techniques, Fourier transform infrared spectroscopy (FTIR) is of great interest as it provides highly specific molecular vibrational signatures characteristic of the matter that are well suited to characterise both inorganic and organic materials and also to discriminate between various organic compounds.

Mid-infrared spectra provide information on the molecular state of the sample thanks to several fundamental bands, especially in the fingerprint region between 1800 and 1000 cm^{-1} providing the identification of compounds via band assignments. From an experimental point of view, non-invasive analyses are made possible thanks to reflectance devices, and portable spectrometers are available for in situ measurement campaigns. Since the 2000s, non-invasive infrared reflectance spectroscopy has been applied to pigments, dyes and binders identification on paintings, using various sampling techniques such as reflection specular reflectance [14–20] and diffuse reflectance (DRIFTS) [21] in the mid-infrared (MIR) range. However, spectra acquired in the reflection mode may turn out to be difficult to interpret as fundamental band profiles can be distorted [14, 17].

The near-infrared (NIR) range has also been explored on artworks for two decades thanks to the use of fibre optic reflectance spectroscopy (FORS) [22, 23] and more recently through multispectral or hyperspectral imaging [24, 25]. Near-infrared spectra are known to be less selective than the mid-infrared features due to the wide absorption of combinations and overtones of the MIR fundamental bands, notably of the NH, CH and OH groups. However, NIR spectroscopy presents some advantages such as its ease of use and its fast acquisition without any sample preparation. NIR studies of polychrome artworks have mainly focused on the identification and discrimination of inorganic pigments, organic binders and substrates. Indeed, some papers mainly reported the identification of mineral compounds such as azurite, calcite or gypsum [7, 11, 22, 26–28]. Regarding the organic compounds found in the paintings, the possible spectroscopic discrimination between organic binders (lipids, proteins, polysaccharides, resins) has been discussed [26, 27, 29, 30]. NIR spectroscopy has also proven to be effective in the study of the degradation of historical papers, as for example in ancient Japanese *washi* [31, 32], or in the distinction between different

natural fibres in dyed textiles [13, 33]. Much less discussed is the application of NIR spectroscopy to the identification of organic pigments and dyes. To our knowledge, two occurrences can be found in Delaney et al. [24], where indigo was included in their infrared reflectography study of blue pigments, and in Carlesi et al. [34], who identified twentieth synthetic yellow organic dyes in modern paintings.

Therefore, the goal of this study is to evaluate the benefit of using near-infrared (NIR, 11000–4000 cm^{-1} /900–2500 nm) spectroscopy combined with portable mid-infrared (MIR, 4000–400 cm^{-1} /2500–25,000 nm) to probe some organic pigments that could be found in the eighteenth and nineteenth centuries' Japanese woodblock prints, also called *ukiyo-e*. The present work reports the results obtained by FTIR measurements on a selection of organic pigments and reference prints. For this purpose, model samples (colour chart) were first prepared according to well-documented printing methods [35–37] and considering single pigments and the mixing of two pigments. We investigate the spectra obtained on the model samples and suggest data treatment in order to discriminate the contributions of the pigments, the organic binders and the underlying paper substrate.

Materials and methods

Japanese woodblock prints are thin and complex artworks, made up of one or several inorganic and/or organic pigments bound with rice starch and printed on a substrate. The substrate is formed by Japanese paper, sized with rice starch and prepared from different plant fibres, such as *kozo* or *gampi*. Mineral fillers (calcium carbonate, kaolinite) can be added to whiten the paper or increase its opacity [35, 36]. The application of IR spectroscopy to the identification of the colouring matters will follow three steps:

1. Studies of neat standards (pigment powders, binder, paper) in the MIR and NIR ranges to identify their characteristic features and build a database. ATR-FTIR (attenuated total reflectance–Fourier transform infrared spectroscopy) in MIR range has been used to evidence the fundamental bands of chemical groups of these reference compounds. In addition, the spectral range was expanded to the near-infrared range by using FT-NIR FORS (Fourier transform–near-infrared fibre optic reflectance spectroscopy) in order to probe possible combinations and overtones of the MIR fundamental bands.
2. Investigations of colourant(s) mixtures bound with rice starch printed on paper (colour chart) thanks to the use of remote analysis, in reflection mode, using a mobile FT-MIR spectrometer and a FT-NIR FORS instrument.
3. Application of post-treatments on the spectra: spectral subtraction and derivative manipulation are suggested.

Reference pigments and colour chart

Three colours are predominant in Japanese woodblock prints: red, blue and yellow [37]. The colourants have been seldom used, mixed before printing or superimposed in order to get different hues (green, violet etc.). The objective of the present work is not a comprehensive overview of the colourants used in Japanese prints but the development of an adapted spectroscopic methodology for the characterisation and discrimination of the organic colourants by infrared spectroscopy. We focused on six organic colouring agents that have been selected (Table 1). This list is not exhaustive and other organic colourants that have been used in prints such as the blue dayflower [38, 39] or other yellow dyes (various flavonoids, berberine or gardenia) [40]. Their studies are ongoing.

Except for safflower, all the pigments were purchased as powders (supplied by Kremer Pigmente).

Safflower (*Carthamus tinctorius*) is composed of quite a few white and coloured (yellow and red) glycosidic compounds, belonging to the quinochalcone family [41, 42]. The main red chromophore of safflower is carthamin, a C-glucoside quinochalcone [43]. Red safflower was prepared from raw petals (*Carthamus tinctorius* L.) following the indications given by Riffault et al. [44]. After removing the soluble yellow safflower colourant by immersing the petals in distilled water, the petals were plunged in a sodium carbonate solution and pressed in order to extract the red dye. Acetic acid was then added to promote the precipitation of the red pigment. The pigment was filtered, washed with distilled water, dried and ground in an agate mortar. Cochineal is known as carmine in Japan but its composition seems to be unknown until the nineteenth century [36, 37]. Contrary to indigo or safflower, the red soluble dye of cochineal, carminic acid, needs to be fixed onto an inorganic substrate to form an organo-metallic complex in order to produce the solid pigment [45]. In the case of the pigment supplied by Kremer Pigmente, the lake is composed of 60% of carminic acid (red chromophore of the cochineal *coccus cacti*) fixed on aluminium or calcium salts.

Dragon's blood and gamboge are materials obtained from the exudate of East-Asian trees. Once dried, the exudates are crushed to get a coloured powder.

The deep red resin of dragon's blood is obtained from the fruits or of the bark of the trees of several plant genera. In East Asia, the plant used is *Daemonorops draco* (Palmae). The resin is a complex mixture whose composition depends on the plant source and localisation [46]. The main chromophores present in dragon's blood obtained from *Daemonorops draco* are dracorubin and dracorhodin [47].

Gamboge is a yellow pigment produced from the exudate of the trees of the genus *Garcinia*. It is a gum resin composed of 15–25% of water-soluble gum and 70–80% of resin. Among the several constituents of gamboge, the main chromophore is gambogic acid [48].

Turmeric, extracted from the roots of the plant *Curcuma longa* L., provides a bright and strong yellow dye. The colour is due to the presence of curcuminoids (curcumin, demethoxycurcumin, bis-demethoxycurcumin) present in amounts of only 3–5% [42, 49]. The roots of turmeric are dried and crushed into powder.

Finally, indigo is obtained from the leaves of the plant *Persicaria tinctoria* or *Indigofera tinctoria* and is mainly constituted of indigotin. The leaves of indigo are humidified and fermented in order to lead to the formation of indigotin from indican (indoxyl glucoside) [50].

Rice starch glue was also prepared in laboratory using powder of rice starch from Kremer Pigmente according to the following proportions: 5 g of rice starch for 100 mL of distilled water. The mixture was then heated (around 200 °C) to obtain a creamy mixture.

A reference colour chart (11 depositions) was prepared using seven pigments and dyes. They were mixed with a drop of rice starch glue. The mixtures were applied on wooden blocks and printed on paper, previously slightly moistened with distilled water. The chosen paper is made of 100% cellulose (Whatman no. 1 without coating or sizing) in order to avoid the contribution from other compounds like lignin or

Table 1 Reference materials selected to realise the reference colour chart

	Colour	Japanese name	English name	Main chromophores [37–39]	Molecular class [38, 40]	Species source
Substrate		<i>Washi</i>	Paper	Cellulose	Carbohydrates	
Binder		<i>Himenori</i>	Rice starch	Starch	Carbohydrates	
Pigments	Blue	<i>Ai</i>	Indigo	Indigotin	Indigoid	<i>Indigofera tinctoria</i> (leaves)
	Red	<i>Beni</i>	Red safflower	Carthamin	Flavonoid (Chalcone)	<i>Carthamus tinctorius</i> (flower petal)
		<i>Shoyenji</i>	Cochineal	Carminic acid	Anthraquinone	<i>Coccus cacti</i> (insect)
		<i>Kirin-Kakketsu</i>	Dragon's blood	Dracorubin; dracorhodin	Flavonoid (Neoflavone)	<i>Daemonorops draco</i> (exudate from the berries)
Yellow	<i>Tō-ō/gambōji</i>	Gamboge	Gambogic acid	Flavonoid (Xanthone)	<i>Garcinia</i> (exudate from the trunk)	
	<i>Ukon</i>	Turmeric	Curcumin	Curcuminoid	<i>Curcuma longa</i> (roots)	

inorganic fillers to the infrared spectra. Pigments could be used alone or mixed in Japanese *ukiyo-e* until the desired hue was obtained. Three different cases were considered in this work and are summarised in Table 2. The mixtures involving two pigments (mixture volume ratio of 1:1) were chosen on the basis of the literature and the results of analyses previously conducted on several *ukiyo-e* [3–5, 48, 51].

Instrumentation

Attenuated total reflectance FTIR spectroscopy

Infrared analyses in ATR mode were performed using a Nicolet iS50 FTIR spectrometer (Thermo-Scientific) equipped with a deuterated L-alanine-doped triglycine sulfate (DLaTGS) detector and a diamond iS50 ATR module. Each spectrum was collected in the 4000–400 cm^{-1} range at a resolution of 4 cm^{-1} and by averaging 200 scans.

Portable reflectance FTIR

In situ mid-FTIR reflectance analyses were carried out using a portable instrument ALPHA FTIR Spectrometer (Bruker) equipped with a DTGS detector, using an external reflection module. Spectra were obtained over 128 scans, at a resolution of 4 cm^{-1} in the 7500–400 cm^{-1} range and expressed as function of pseudo-absorbance ($\log(1/R)$, R being the reflectance measured by calculating the ration of the intensity of the beam reflected by the sample to the intensity of the beam reflected by a reference gold mirror). The beam diameter is about 5 mm. The colour chart was positioned vertically on an easel in front of the reflection module of the spectrometer.

Table 2 Composition of the reference paint printouts studied

Pigments	Binder	Colour
Single organic pigment		
Indigo	Rice starch	Blue
Dragon's blood	Rice starch	Red
Cochineal	Rice starch	Red
Red safflower	Rice starch	Red
Gamboge	Rice starch	Yellow
Turmeric	Rice starch	Yellow
Two organic pigments		
Indigo + gamboge	Rice starch	Green
Indigo + red safflower	Rice starch	Violet
Indigo + cochineal	Rice starch	Violet
1 organic pigment + an inorganic one		
Prussian blue + indigo	Rice starch	Blue
Prussian blue + gamboge	Rice starch	Green

Fibre optic reflectance spectroscopy in near infrared

A portable FT-NIR Rocket spectrometer (ARCOptix), equipped with an InGaAs photodiode detector and an HL2000 halogen lamp (Ocean Optic, 20 W), was used. Measurements were collected through an optical fibre bundle constituted of seven optical fibres (400- μm diameter—six illumination fibres around one collecting fibre) resulting in a beam diameter of approximately 3 mm. The probe was positioned perpendicularly upon the surface at a distance between 3 and 5 mm. Spectra were measured in the 11,000–4000 cm^{-1} range (900–2500 nm) by averaging 30 scans (acquisition time of 20 s) and at a resolution of 8 cm^{-1} .

NIR reflectance (R) spectra were obtained using a white Spectralon® standard as reference. They were expressed as pseudo-absorbance via $\log(1/R)$ conversion.

Spatial and spectral parameters are summarised in Table 3.

Data post-treatments

The overlapping of absorption bands is a well-known limitation of infrared spectroscopy. Several data treatments can be performed on raw data to overcome this difficulty such as spectral subtraction, spectral derivative calculation or more complex multivariate analyses [30, 52].

In this first approach, spectral subtraction was applied on the NIR spectra recorded on the reference colour chart in order to remove the overlapping bands of the paper substrate and to highlight the absorption bands due to the pigment. The subtraction technique is used to process spectra of mixtures involving various compounds, as this is the case for paintings. The spectrum of a reference component, in our case the paper, is multiplied by an adapted scaling factor in order to cancel its contribution by subtraction [52]. The resulting spectrum is then examined for any residual bands that can be related to the presence of additives or to the colouring agents.

Moreover, second derivative calculation was applied on spectra where subtraction of the paper was not effective to evidence the marker bands of the colourants. The second derivative order is commonly used to determine the frequency positions of the absorption bands, especially when these appear as shoulders. Indeed, the second derivative spectra preserve the original band positions. Additionally, the second derivative spectrum exhibits sharper bands than those of the original spectrum, enabling to minimise the band overlap, and it can enhance the weak and narrow absorption bands. However, each derivative operation leads to an increase of the noise level of the spectrum. Therefore, the algorithm developed by Savitzky-Golay, which includes a smoothing step prior to the derivative calculation, was applied to maintain a suitable signal-to-noise ratio. The choice of the parameters (degree of the fitted polynomial and number of data points used to calculate the polynomial) is of critical importance as

Table 3 Technical parameters for each IR technique

Infrared technique	Working distance	Spatial resolution or spot size (mm)	Scan average	Spectral resolution (cm ⁻¹)	Spectral range
ATR-FTIR	Contact	2 mm	200	4	4000–400 cm ⁻¹ 2500–25,000 nm
Mobile reflection FTIR	~1.5 cm	5 mm	128	4	4000–400 cm ⁻¹ 2500–25,000 nm
FT-NIR FORS	~5 mm	5 mm	30	8	11,000–4000 cm ⁻¹ 900–2500 nm

smoothing can lead to a loss of information. In this work, a polynomial order of 2 and window sizes of 11 points (for the neat reference materials) and 17 points (for the printouts) were selected for the smoothing.

Results and discussion

Characterisation of the reference materials

The spectra of the reference materials (Table 1) are presented in Fig. 1, in the MIR and NIR ranges.

Paper and starch show similar spectra in MIR and NIR ranges and reveal features specific to the carbohydrates (Fig.

1). In the MIR range, the main intense bands are ascribed to the absorptions of the glycosidic bonds ($\nu(\text{C}-\text{O}-\text{C})$, 1200–1100 cm⁻¹), to OH groups ($\nu(\text{OH})$, 3600–3200 cm⁻¹) and to CH groups ($\nu(\text{CH})$, around 2900 cm⁻¹; $\delta(\text{CH})$, 1450–1200 cm⁻¹) [53, 54]. In the NIR range, the spectra of rice starch and paper also show bands related to OH, CH and CO groups: between 7000 and 6200 cm⁻¹ ($2\nu(\text{OH})$) and around 5180 cm⁻¹ ($\nu(\text{OH}) + \delta(\text{OH})$) which are mainly assigned to adsorbed water, and between 5000 and 4400 cm⁻¹ ($\nu(\text{OH}) + \delta(\text{CO})$ combination). The most distinguishing bands between the substrate and the binder can be noted in the regions ascribed to CH group vibrations. The spectrum of paper displays bands at 4275 cm⁻¹ ($\nu(\text{CH}) + \delta(\text{CH})$), around 5600 cm⁻¹ ($2\nu(\text{CH})$), and other combination

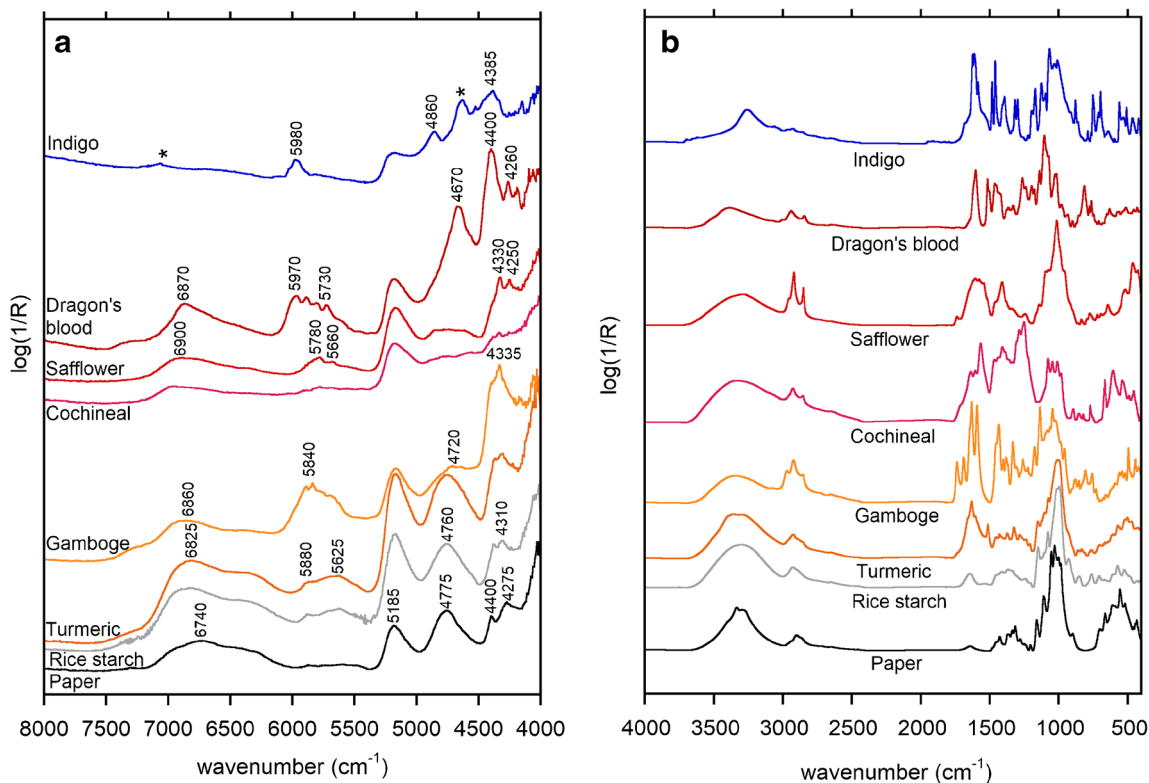


Fig. 1 a FT-NIR FORS and b ATR-FT-MIR spectra of the pigments, binder and paper substrate studied. Bands identified by a star are ascribed to the presence of kaolinite in the pigment of indigo

bands situated between 4270 and 4000 cm^{-1} . The spectrum of rice starch reveals peaks at 4775 cm^{-1} , between 6000 and 5600 cm^{-1} ($2\nu(\text{CH})$) and centred at 4310 cm^{-1} (CH combination bands) [55].

Fourier transform infrared spectra of the organic pigments under study indicate typical bands in the range between 1800 and 900 cm^{-1} assigned to the vibrations of their molecule functional groups (Fig. 1, II). The bands in the NIR range appear, as expected, broader than those in the MIR range. However, some marker bands can be highlighted on the raw spectra (Fig. 1a) or using a second derivative order treatment (Fig. 2).

The NIR spectrum of indigo (Fig. 1, I, spectrum h) exhibits several bands between 6000 and 4500 cm^{-1} . In particular, the well-defined multiplet observed around 5980 cm^{-1} is assigned to the first overtone of CH group stretching vibrations. Some combinations of CH group vibrations are certainly involved in numerous narrow bands between 4700 and 4000 cm^{-1} . The band located at about 4860 cm^{-1} is ascribed to the combination of NH stretching and bending vibrations [56]. The bands at 7065 and 4630 cm^{-1} are not ascribed to indigo but to kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) [57] which may be used as an extender in order to increase the quantity or the bulk of the pigment or to modify its colour. Moreover, indigo spectrum presents

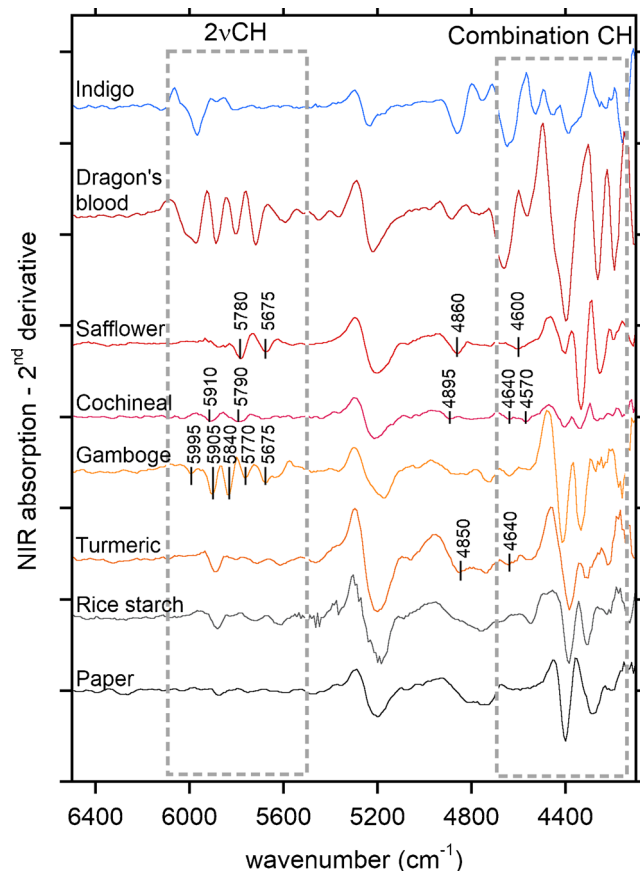


Fig. 2 Second derivative order (Savitsky-Golay algorithm, polynomial order 2, 11 points) of NIR spectra of reference pigments, paper and binder

bands in the MIR range around 3300 cm^{-1} and between 3000 and 2800 cm^{-1} ascribed to N–H and C–H stretching vibrations, respectively. Several sharp bands between 1800 and 400 cm^{-1} (Fig. 1, II, spectrum h) are also observed: 1630 cm^{-1} (C=O stretching mode), 1585 cm^{-1} (CC stretching vibrations in a six-membered ring of the indigo molecule), doublet at 1480 and 1460 cm^{-1} (C–H bending and C–C stretching combination modes). A thorough spectral attribution can be found in Baran et al. [50].

Infrared spectra of the three red pigments under consideration (Fig. 1, I and II, spectra e, f, g) exhibit several bands relevant for their discrimination.

Dragon's blood NIR spectrum (Fig. 1, I, spectrum g) exhibits very specific bands assigned to CH groups, including a pattern with four well-defined peaks at 5970, 5890, 5805 and 5730 cm^{-1} ($2\nu(\text{CH})$), bands between 9000 and 8000 cm^{-1} ($3\nu(\text{CH})$), at about 7300 cm^{-1} and between 4350 and 4000 cm^{-1} (CH combination bands). An intense distinctive band can also be noted at 4670 cm^{-1} that can be assigned to the CO stretching and CH_2 stretching combination [26, 55]. The MIR spectrum (Fig. 1, II, spectrum g) also presents numerous narrow bands in the fingerprint region (at 1600, 1516, 1500, 1463 cm^{-1} , 1364 and 1263 cm^{-1}) that might be used as marker bands for dragon's blood pigment. However, the assignment of these different bands is made difficult as this natural resin is a complex mixture of organic molecules including chromophores (dracorhodin or dracoflavilium) but also many other components [46, 47].

In the case of cochineal, the chemical dye carminic acid is the major component. The NIR spectrum (Fig. 1, I, spectrum e) exhibits weak bands located at 6955 cm^{-1} ($2\nu(\text{OH})$), between 5900 and 5600 cm^{-1} ($2\nu(\text{CH})$) and at 4330 and 4260 cm^{-1} ($\nu(\text{CH}_2) + \delta(\text{CH}_2)$). Carminic acid is present in its salt form due to interactions with the metal cations used for the cochineal lake preparation (Al^{3+} or Ca^{2+}). This is confirmed by the MIR spectrum (Fig. 1, II, spectrum e) showing bands ascribed to COO asymmetric and symmetric stretching vibrations of the ionic form COO^- , located at 1570 and 1390 cm^{-1} respectively. Bands around 1600 cm^{-1} can be ascribed to the C=C stretching vibrations (1636 and 1565 cm^{-1}), notably present in benzene cycles of the carminic acid molecule, associated with bands between 1000 and 600 cm^{-1} (CC ring deformation modes). Finally, bands related to the glucose substituent of carminic acid are visible around 1350 cm^{-1} and between 1100 and 1000 cm^{-1} (1077, 1046 and 1008 cm^{-1}) [58].

Red safflower spectra acquired in the NIR and MIR ranges (Fig. 1, I and II, spectrum e) are defined by the features related to carbohydrate signatures, due to the presence of glucose groups in the molecule of the carthamin colourant. They are mainly located at about 1000 cm^{-1} (glycosides bonds), at 6900 cm^{-1} ($2\nu(\text{OH})$), around 5180 cm^{-1} ($\nu(\text{OH}) + \delta(\text{OH})$) and between 5000 and 4400 cm^{-1} ($\nu(\text{OH}) + \delta(\text{CO})$). Bands

of interest can also be noted in the MIR range at 1736 cm^{-1} that can be ascribed to the C=O stretching vibration of acetic acid added for the precipitation of the pigment, and at 1603 , 1576 and 1543 cm^{-1} . In the NIR domain, the discrimination between red safflower and cochineal is made difficult due to the fact that their main bands are related to the presence of the glucose function in both chromophore molecules and are located at similar positions at 5780 , 4330 and 4250 cm^{-1} . The second-order derivative treatment was very helpful to highlight the differences between the spectra of these two red organic pigments. The absorption features located in the regions ascribed to CH group vibrations (dotted squares in Fig. 2) appear to be centred at different wavenumber positions for the two pigments (at 5780 , 5675 and 4600 cm^{-1} for safflower; at 5910 , 5790 , 4640 and 4570 cm^{-1} for cochineal). This result is consistent with the respective positions of the CH stretching ($3200\text{--}2900\text{ cm}^{-1}$) and bending vibrations (around 1400 cm^{-1}) of safflower and cochineal in MIR spectra which also show slight differences.

Two yellow pigments (gamboge and turmeric) were studied in this work and the results are reported in Figs. 1 and 2.

In the NIR range, the spectrum of gamboge (Fig. 1, I, spectrum d) is mainly characterised by absorption bands due to CH groups. The first and second overtones of CH stretching vibrations are observed respectively between 6100 and 5500 cm^{-1} and around 8445 cm^{-1} and well-defined absorptions could be revealed thanks to the second derivative treatment (Fig. 2). Combination bands involving CH groups are located at about 7300 cm^{-1} and between 4350 and 4000 cm^{-1} . Finally, the broad absorption observed between 7000 and 6200 cm^{-1} is ascribed to the first overtone of OH stretching vibrations. The gamboge MIR spectrum (Fig. 1, II, spectrum d) shows bands at 1736 , 1688 , 1631 and 1592 cm^{-1} ascribed to C=O stretching vibrations of the chromophore molecule gambogic acid, present among the other constituents of the pigment [59]. These four intense and narrow bands in the MIR spectrum may be relevant spectral markers for the identification of this yellow colourant.

Regarding turmeric pigment, IR spectra evidence features mainly related to carbohydrate signature (Fig. 1, I and II, spectrum c) certainly due to the starch contained in turmeric roots. The OH stretching vibration (nearly 3300 cm^{-1}), CH vibrations (stretching around 2900 cm^{-1} ; bending between 1500 and 1200 cm^{-1}) and a main intense broad band at about 1000 cm^{-1} specific of glycosides (CO stretching vibration) are observed. However, supplementary bands are noted in the MIR range at 1631 , 1604 , 1513 , 1451 , 1430 , 1371 , 1284 and 1236 cm^{-1} which are presumably due to the curcuminoid chromophores: this view is supported by the comparison with the spectrum of curcumin from the Infrared & Raman Users Group (IRUG) Database [60]. These bands are of main interest because they are specific to the colouring molecules and provide a direct identification of turmeric, as well as its

discrimination from the rice starch binder. In the NIR range, the use of the second-order derivative is requested to reveal some distinguishing features at 4850 and 4640 cm^{-1} on the turmeric spectrum in regard to the rice starch spectrum (Fig. 2).

Investigation of the colour chart

The results in MIR reflection mode presented in this paper were obtained with the portable spectrometer. Disturbances on the spectra have been observed between 1200 and 850 cm^{-1} with distorted bands, phenomena generally noticed in reflectance MIR spectroscopy [14, 17]. However, between 1800 and 1200 cm^{-1} , spectra are not affected by distorted bands. The presentation of the results will be focused on this range to find the specific bands of each deposit of the colour chart in the MIR range.

One organic pigment mixed with rice starch and printed on paper

As shown above (section “[Characterisation of the reference materials](#)”), the spectra of the selected organic pigments present some characteristic absorptions in both NIR and MIR ranges. Spectra were recorded on the colour chart (Table 2) to mimic analyses on historic prints and to evaluate the capability of the techniques to discriminate between the substrate (paper), the binder (rice starch) and the pigment(s).

The six organic pigments deposited on the colour chart were investigated in the two IR ranges (Fig. 3). The MIR fundamental marker bands of indigo (1630 , 1587 , doublet at 1482 and 1463 cm^{-1}), dragon's blood (shoulder at about 1600 cm^{-1} , bands at 1517 and 1642 cm^{-1}) and gamboge (1736 , 1687 , 1643 and 1598 cm^{-1}) are identified despite the spectra of rice starch and the underlying paper substrate (Fig. 3d). However, for turmeric, cochineal and red safflower, only weak bands and shoulders are visible on their MIR spectra: at 1660 and 1630 cm^{-1} (shoulders) and at 1520 and 1460 cm^{-1} (bands) for turmeric, at 1573 cm^{-1} (band) for cochineal and at 1735 cm^{-1} (shoulder) and 1530 cm^{-1} (weak band) for red safflower.

On the NIR spectra acquired on the colour chart, some shoulders can be observed for dragon's blood, turmeric, gamboge and indigo. However, broad bands attributed to paper are predominant (Fig. 3a) and overlap with the pigments peaks. Scaled absorbance subtraction of the paper signal was performed in order to highlight the signal of the pigments as reported in Fig. 3b. The subtraction allows extracting the signatures of indigo, gamboge and dragon's blood and enables their unambiguous identifications, supporting the results observed by using MIR spectroscopy.

On the contrary, spectra of safflower and cochineal deposits show few specific bands in the MIR range. Adding the information obtained in the NIR domain demonstrated to be very

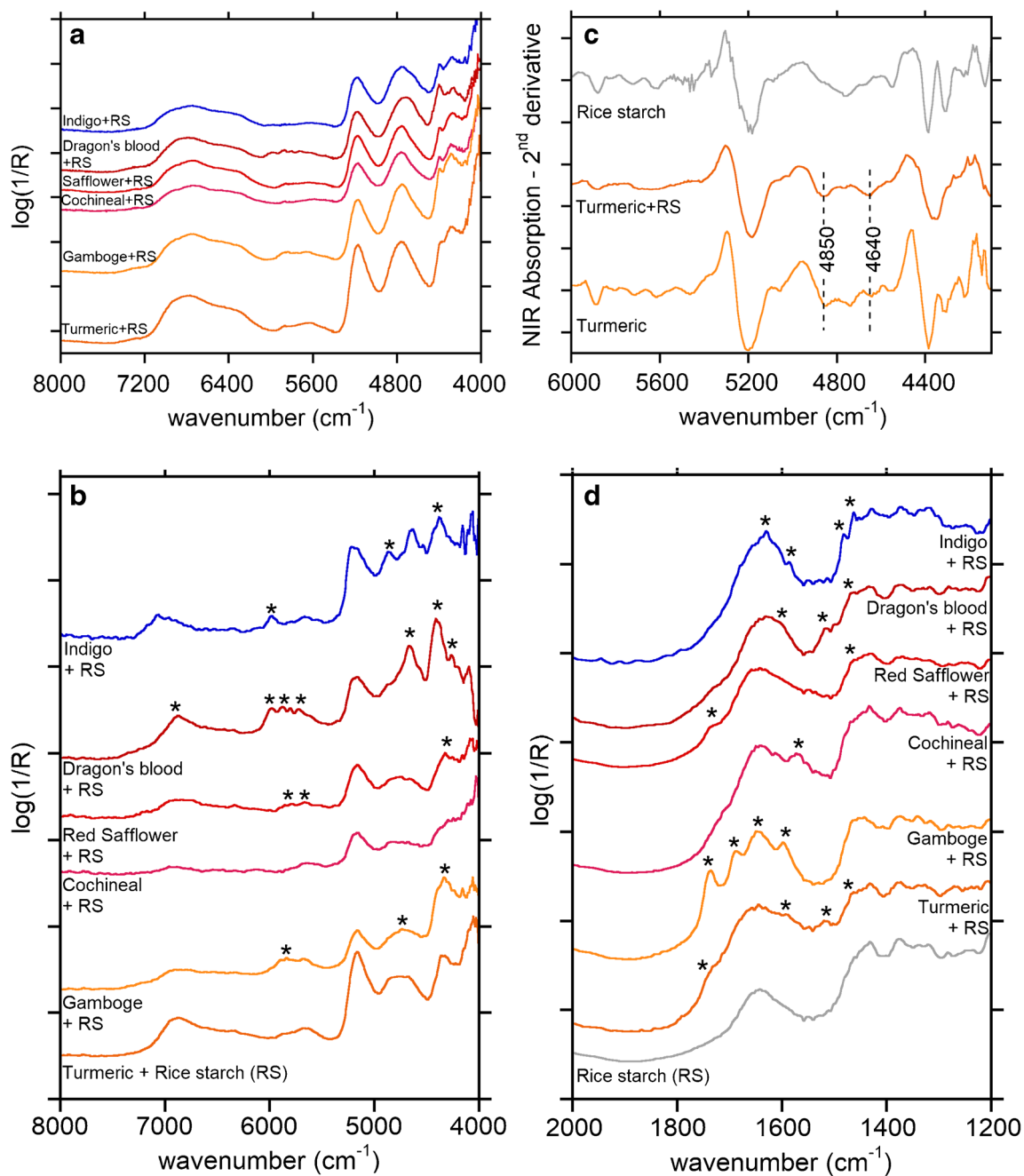


Fig. 3 **a** Raw FT-NIR FORS spectra on deposits of the colour chart, **b** FT-NIR FORS after subtraction of the paper signal (8000–4000 cm^{-1}) and smoothing (window size: 7 points) (RS, rice starch), **c** second derivative of FT-NIR FORS spectra of neat turmeric and rice starch and of deposit of

turmeric + rice starch on paper and **d** portable reflection mid-infrared spectra (2000–1200 cm^{-1}) of paint deposits on paper. Stars indicate the presence of bands attributed to pigments

useful for the identification of safflower. Indeed, the NIR spectrum of red safflower obtained after subtraction of the spectral contributions of the paper highlights its characteristic marker bands at 5780, 5660 and 4330 cm^{-1} whereas only weak and broad bands are observable on the cochineal spectrum. In this case, the use of combined NIR and MIR spectroscopies allows the identification of safflower, and to a certain extent, the discrimination between the two red organic colourants: red safflower and cochineal.

Finally, the spectrum of turmeric after paper spectrum subtraction mainly shows some remaining spectral features ascribed to carbohydrates, which are not specific to the pigment as they are also present on the rice starch signature. The application of the second-order derivative procedure on the spectrum after paper spectrum subtraction highlights the presence of small feature characteristic of turmeric at about 4850 and 4640 cm^{-1} (Fig. 3c). The combination of the absorption patterns in the NIR and

MIR ranges allows identifying the presence of turmeric in the deposits.

Mixture of two pigments bound with rice starch and printed on paper

Five mixtures involving two pigments that are likely to have been used in Japanese *ukiyo-e* prints were studied: indigo and gamboge, indigo and red safflower, indigo and cochineal, Prussian blue and indigo, Prussian blue and gamboge.

The second derivative function procedure (Savitsky-Golay algorithm, using a smoothing with 17 data points window and a second-order polynomial) was applied to the NIR FORS spectra of the mixture deposits after the subtraction of the paper signal (Fig. 4, D).

In the case of samples involving Prussian blue (Fig. 4, spectra d and e), the inorganic blue pigment was identified whatever the mixture, mainly thanks to its well-known strong cyano stretching vibration $\nu(\text{C}\equiv\text{N})$ [61] at about 2080 cm^{-1} , combined with its three characteristic narrow NIR bands, including the most intense feature at 4224 cm^{-1} attributed to a combination band involving the $2\nu(\text{C}\equiv\text{N})$ [62].

In all the mixtures including indigo, the blue organic pigment was identified thanks to its bands at about 1630 , 1585 ,

1480 and 1460 cm^{-1} in the MIR range and absorption features in the near-infrared range around 5980 , 4870 , 4780 , 4550 and 4430 cm^{-1} (Fig. 4).

In the case of the mixtures of indigo with organic red colourants, the use of the red colouring component can be evidenced thanks to the shoulder observed around 1735 cm^{-1} for safflower and to a weak band around 1565 cm^{-1} for cochineal in the MIR (section “One organic pigment mixed with rice starch and printed on paper”) and thanks to bands at about 5800 and 5680 cm^{-1} and around 4340 and 4250 cm^{-1} on the NIR spectra. However, marker bands that were identified for both pigments and highlighted above (section “Characterisation of the reference materials”) are hidden by the absorption of indigotin between 5000 and 4500 cm^{-1} and of rice starch between 6100 and 5500 cm^{-1} making the discrimination between red safflower and cochineal harder in the mixtures.

Gamboge was easily identified in both mixtures thanks to its intense MIR bands around 1735 , 1680 , 1640 and 1600 cm^{-1} . In the NIR range, the identification of its specific absorption features is quite challenging, due in part to the increasing of the noise when applying the derivative function. A strong absorption band at about 4335 cm^{-1} is visible but the different bands related to the second overtone of CH groups ($6000\text{--}5500\text{ cm}^{-1}$) are broad and not specific enough to ensure the discrimination of the yellow pigment without the use of the MIR range.

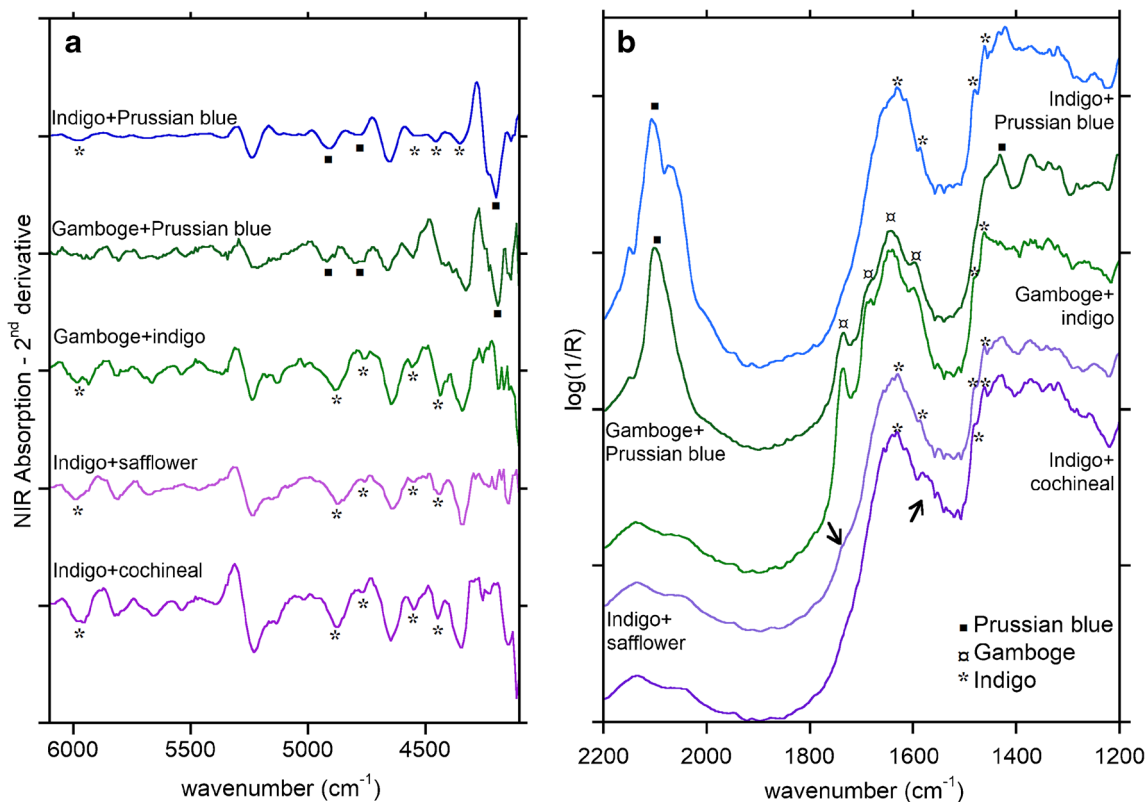


Fig. 4 a Normalised second derivative order after spectral subtraction of paper signal of FT-NIR FORS spectra (polynomial 2, window size 17 pts) and b portable FT-MIR spectra of mixtures of pigments of the colour chart. The arrows indicate the presence of shoulders due to the pigments

Conclusion

Near- and mid-infrared reflection spectroscopies were applied on a selection of six organic pigments that are expected to have been used on Japanese *ukiyo-e* prints. This study is to our knowledge the first to report NIR spectroscopic results combined with MIR data on organic pigments such as dragon's blood, red safflower and turmeric. Both IR domains turned out to be relevant for the identification of organic pigments alone and within mixtures printed on paper, even when an inorganic compound with a high IR absorption coefficient, such as Prussian blue, was used. Indigo and gamboge were better discriminated using FT-MIR reflection spectroscopy whereas dragon's blood appeared to have more specific absorption features in the NIR domain. Red safflower, cochineal and turmeric also showed some few distinguishing bands in both ranges; however, the NIR domain appears to be more effective for safflower and turmeric identification.

More generally, MIR and NIR ranges provided complementary molecular information. The MIR spectra showed specific features corresponding to fundamental vibrations for all the investigated pigments, mainly in the fingerprint region and despite the disturbance occurring in reflection mode. All the pigment spectra also revealed specific absorptions in the NIR range, especially in the spectral region involving CH overtones and combination. The limitation due to the overlapping effect of the paper substrate spectral signature in the NIR range could be overcome using simple spectral manipulations (subtraction and second-order derivative procedures) and specific marker features of each pigment could be extracted. This work allowed identifying spectral region of interest for the characterisation of the selected pigments in both NIR and MIR ranges. In addition, the application of well-suited post-treatments demonstrated to improve the discrimination between the pigments in paintings, especially in more complex mixtures involving more than one pigment. Based on this preliminary investigation, spatially resolved techniques, such as hyperspectral imaging in the short-wave infrared (SWIR) range, would therefore be of high interest for in situ study of specific artworks such as Japanese *ukiyo-e* prints.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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