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Colours of the « images of the floating world ».

Non-invasive analyses of Japanese ukiyo-e woodblock prints (18th and 19th centuries) and new contributions to the insight of oriental materials

Carole Biron^{a,b}, Aurélie Mounier^a, Josefina Pérez Arantegui^c, Gwénaëlle Le Bourdon^b, Laurent Servant^b, Rémy Chapoulie^a, Clodoaldo Roldán^d, David Almazán^e, Nerea Díez-de-Pinos^f and Floréal Daniel^a

^a Université Bordeaux Montaigne, IRAMAT-CRPAA. Institut de Recherche sur les Archéomatériaux (IRAMAT), UMR CNRS 5060, Centre de Recherche en Physique Appliquée à l'Archéologie (CRP2A), Maison de l'archéologie, Esplanade des Antilles 33607 Pessac, France

Corresponding author: carole.biron@u-bordeaux-montaigne.fr

^b Université de Bordeaux, ISM, Institut des Sciences Moléculaires, UMR CNRS 5255 - Bâtiment A12, 351 Cours de la Libération, 33405 Talence, Cedex, France

^c Instituto Universitario de investigación en Ciencias Ambientales de Aragón (IUCA), Universidad de Zaragoza, 50009 Zaragoza, Spain

^d Instituto de Ciencia de Materiales (ICMUV), Universidad de Valencia, Catedrático José Beltrán, 2. 46980-Paterna, Spain

^e Instituto de Patrimonio y Humanidades (IPH). Dep. Historia del Arte, Universidad de Zaragoza, 50009 Zaragoza, Spain

^f Museo de Zaragoza, 50001 Zaragoza, Spain

Abstract

In the Edo (1615-1868) and Meiji (1868-1912) periods, Japanese woodblock prints were a commercial form of art that reproduced the everyday life of ordinary people (the *ukiyo-e* style). Since different dyes and pigments were used to produce these prints, changing over time, the knowledge of these materials can be very important for the history and the conservation of ukiyo-e prints.

This study will present the results of the investigation of several woodblock prints, produced between the 18th and 19th centuries. The artworks belong to the Asian art collection at the Museum of Zaragoza (Spain). The aim of the study is the identification of organic colorants and inorganic pigments employed by Japanese printers, specially emphasising the introduction of new synthetic compounds in the 19th and 20th centuries. Because prints are fragile artworks, several non-invasive methods in a multi-analytical approach were employed, as hyperspectral imaging in the visible and NIR range (HSI), in-situ point-by point Diffuse Reflectance Spectroscopy (DRS), LED μ -spectrofluorimetry, and Fiber Optic Reflectance Spectroscopy in the near-infrared range (FORS NIR) and mid-infrared spectroscopy (MIR), combined with X-ray Fluorescence to confirm the presence of some elements. [The identification of the diverse materials was made upon a dedicated database involving Japanese pigments, dyes, mixtures \(blue, green, orange, purple colours\) and papers.](#) By combining all these methods, all the inorganic compounds were identified, and also some organic colourants, especially for the blue and red areas. Finally, a chronology of the use of the colourants in the ukiyo-e woodblock prints between 1700 and 1900 is proposed.

Keywords : Pigments, dyes, non-invasive methods, characterisation, Japanese woodblock prints

1. Introduction

The first Japanese woodblock prints date back to the 7th-8th century thanks to the importation from China of the woodblock engraved technique. From the beginning of the Edo era (1615 – 1868), a new style of woodblock prints, the *ukiyo-e*, appears following the social and economic changes of this period of peace and prosperity, which sees the growth of an urban culture.

Ukiyo-e literally means the « picture of the floating world ». The term *ukiyo*, referring to the ephemeral side of life, was described by the 17th century Japanese writer Asai Ryoi. The *ukiyo-e* prints adopt a new iconography depicting scenes of everyday life and of the pleasures of life, such as beautiful women and courtesans, *kabuki*¹ actors or landscapes.

Following these new trends and evolutions, the techniques and materials used by artists were also changing. The first coloured prints appeared in the early 18th century, first with few colours (red, green, yellow). In the second half of the 18th century, the *nishiki-e* technique allows the use of a large palette of colours and the production of brocade picture [1]. This technique involved several woodblocks used for printing, one for each colour, thanks to the presence of the *kentō*, guides engraved in the woodblock to maintain the paper sheets [2]. The traditional colour palette was mainly composed of natural organic dyes (safflower, madder, indigo, gamboge, etc.) and some inorganic pigments (orpiment, red lead, ochres, etc.). From the 19th century, with Japanese economic opening, various chemical pigments imported from the West enriched the available palette, such as Prussian blue [3].

Few studies have been conducted on the material aspect of these objects. Information on the kind of materials, either paper or colouring material, are, however, of interest for different reasons. Analyses conducted on these artworks mainly aimed to improve our knowledge on the history of art and techniques of the *ukiyo-e* by identifying the matters used to produce them. Thus, information such as technical, aesthetic or economic choices (for example natural or synthetic pigments, local or imported pigments) can be gathered and it may shed light on the artistic trends at that time and on politic and social history of Japan. Previous studies were focused on the identification of the pigments used in the *ukiyo-e* prints and paintings. However, they mainly considered some specific aspects or materials, such as colour (blue [4–8], yellow [9,10], for example), particular types of materials using specific analytical methods (organic colourants with spectrofluorimetry [11,12]; synthetic organic dyes with Raman spectroscopy [13–15]), and sometimes considering limited time (early prints 1650 – 1800 [12] or from the second half of the 19th century [14]).

The main part of this work consisted in the global identification of the colouring matters employed to create the Japanese woodblock prints in order to follow the evolution of the use of pigments and dyes throughout the late 18th century to the second half of the 19th century. Non-invasive techniques, such as X-Ray fluorescence spectroscopy, visible reflectance spectroscopy, infrared spectroscopy or spectrofluorimetry have proven to be suitable for the identification of the colourants used on prints on paper and specifically *ukiyo-e* [16–19]. Thus, analyses have been conducted on a corpus of ten *ukiyo-e* prints belonging to the Museum of Zaragoza, Spain.

2. Material and methods

2.1. Prints of the Asian art collection (Museum of Zaragoza, Spain)

The “Federico Torralba” collection, kept in the Museum of Zaragoza (Spain), is a collection of Asian arts gathering more than a thousand of Asian artworks, such as bronze sculptures, Chinese paintings, pieces of lacquerware and a hundred of Japanese woodblock prints. Among them, there are prints from

¹ *Kabuki* is a Japanese traditional and popular theatre

the 18th and the 19th centuries signed by some of the greatest Japanese artists such as Harunobu, Utamaro or Koryûsai (figure 1). Among the selected woodblock prints to be studied (see supplementary material), as well as some artworks already described in previous works [23, 24], one of the most ancient woodblock prints in the collection by Suzuki Harunobu 鈴木春信 (1725-1770), dedicated to poetess Ise and dated 1767-1768 (n.°49571), was included (figure 1.left) [20]. In order to span the period from the second half of the 18th century to the end of the 19th c., also three other woodblocks prints were studied: one by Teisai Senchō 貞斎 泉晁 (1812-?), *Sugatano Sugata Ebi-ya*, dated in the 1830s (n.°49909); another by Utagawa Kuniyoshi 歌川国芳 (1797-1861), *Shimazoroi onna Benkei*, in c.1844 (n.°49872); and the third one by Tsukioka Yoshitoshi 月岡芳年 (1839-1892), *Tsuki no haykushi*, published in 1885-1891 (n.°49861) [21]. To complete the corpus, a triptych print, designed by Kunisada/Toyokuni III during the year 1855 (collection of the IRAMAT-CRP2A laboratory), has been added to the study (figure 1. right).

2.2. Non-invasive analyses employed

2.2.1.X-Ray Fluorescence spectroscopy (XRF)

Non-destructive analysis of the paintings was made *in situ* at the building of the Museum of Zaragoza. The Energy Dispersive X-Ray Fluorescence (XRF) analyses were performed by means of a portable spectrometer equipped with a Peltier cooled semiconductor SDD (25 mm² detection area, 500 µm thickness, 12.5 µm Be window) with an energy resolution of 135 eV (FWHM at 5.9 keV). The spectrometer used included a low power X-ray transmission tube (silver anode) operating with an excitation potential of 30 kV and an acquisition time of 200 s. The X-ray beam impinges orthogonally on the sample surface and it is collimated by an aluminium pinhole, resulting an analysed area of about 15 mm² at the sample surface. The X-ray tube and detector were fitted on a mechanical device with excitation-detection geometry of 45° and a sample-detector distance of 1.5 cm. The focus of two laser beams controlled the sample position and the point of analysis. All XRF measurements were performed in ambient air and only qualitative identification of the elemental composition of the samples was accomplished. The fluorescence X-ray spectrum of every given measurement point was normalized to the total counts of the spectrum in order to facilitate the qualitative comparison with other spectra minimizing geometrical effects and fluctuations of the tube intensity. The XRF spectra process was performed by the PyMCA software [22].

Because the X-rays applied to the area of interest can penetrate through the layered structure of the analysed artworks (paint layers and paper backing), the discrimination between the characteristic elements of the pigment and those of the paper backing was made by spectra comparison. XRF spectra of paper backings showed a similar elemental composition constituted by Ca, Fe, S and K. The relative intensity of these elements varied for each print. The XRF spectra of a painted surface were directly compared to those derived from the paper backing, and the detected elements were also correlated with the named 'key elements' in a list of plausible pigments [23–25]. Argon and silver were identified in all XRF spectra, but these elements were artefacts linked to the air (Ar) and the X-ray tube (Ag) and not to the sample composition. Several works make reference to the XRF pigment identification and are available by consulting scientific and academic publications (see bibliographic sections of the references [23–25] or online databases [26]).

For the analyses of the print of Kunisada (BDX), we used an energy dispersive X-ray fluorescence spectrometer Seiko 6000vx equipped with a rhodium source (50 kV/mA) and a SDD Vortex detector. A helium flush is used in order to detect light elements ($> \text{Na}$). The SDD type detector (50 mm²; resolution 155 eV) is cooled by Peltier effect. The specimen holder is motorized and the repositioning accuracy is about 5 μm . This allows qualitative and quantitative analyses (with standards) and qualitative mapping. Only qualitative analyses at 15 kV without filter for light elements ($\geq \text{Na}$) and 50 kV with a lead filter for the heavy elements ($\leq \text{U}$) have been done on the woodblock print. Two collimators were used (3x3 mm and 1.2x1.2 mm) depending on the size of the analysed area. As for the *in-situ* data, the spectra recorded on the coloured areas were compared with the spectra of the underlying paper and a list of ‘key elements’ was established.

2.2.2. Hyperspectral imaging (HSI)

Hyperspectral remote sensors collect image data simultaneously in hundreds of narrow, adjacent spectral bands giving a continuous spectrum for each image cell. In this research, the hyperspectral CCD camera (HS-XX-V10E), developed by SPECIM, has a 1600 \times 840 pixels resolution, a 2.8 nm spectral resolution and a wavelength range from 400 to 1000 nm. The painting was illuminated by two halogen lamps oriented at 45° from the sample. Spectral IDAQ software provided data acquisition, storage and wavelength calibration. The treatment of the data cube was performed with ENVI 5.2+IDL software. This technique generates data (reflectance spectra) which can be treated to obtain images (RGB, IRFC, grey colours...) [27]. By a procedure named “classification,” the software compares the reference spectra of our database with those obtained from the painting [28–30]². Several algorithms allow to get the spatial distribution (supervised, unsupervised, endmembers collection. . .) of the pigments. One of the most common spectral mapping methods is the Spectral Angle Mapper (SAM). This method considers each spectrum as a vector in an n-dimensional scatter plot (or n-D space). The mathematical treatment computes an angle between the reference and the observed spectrum. Smaller angles represent closer matches to the reference spectrum, and endmember spectra used by SAM can come from our spectral library. SAM is a similarity measure, not an identifier. A supervised classification of the HSI data spectra was done using the SAM algorithm (with an angle of 0.4, a good compromise for the mapping of most of the pigments) in order to obtain the spatial distribution of the pigments. An example is given in complementary material. The database must be comprehensive to provide good mapping. Studies have shown that reflectance spectra vary with mixtures or mixing proportions [31], which sometimes makes mapping difficult. Thus, other complementary methods (EDXRF, FORS-NIR, ...) are necessary to refine the results.

2.2.3. Diffuse Reflectance Spectroscopy (point-by-point)

Reflectance spectra and colour were measured in several points of the prints. Reflectance UV-Vis spectra were recorded using a Minolta CM-2600d model portable spectrophotometer, equipped with a 52-mm barium sulphate integrating sphere, dual-beam geometry, di:8°, de:8°, a 360-740 nm wavelength range with 10 nm measurement intervals, and irradiating a 3-mm diameter area. The standard illuminant was D65, using a CIE 1964 10° standard observer. A plate of barium sulphate was

² The quality of the hyperspectral data interpretation (images and spectra) is based on that of the reference database. That of the CRP2A considers 200 organic and inorganic pigments used from medieval to contemporary times and prepared on parchment, Japanese paper... according to the ancient recipes. These “palettes” of reference pigments also allowed us to define the optimum analytical parameters (exposition time, working distance, power of beams, *etc.*) for the study of these types of fragile objects.

used as white reference to calibrate reflectance spectra. From the dispersion of the reflectance measurements, colour coordinates (L^* , a^* , b^*) of the CIELab 1976 colour space were calculated.

2.2.4. 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 and using an external reflection module. The spectra were obtained by averaging 200 scans, at a resolution of 4 cm^{-1} in the $7500\text{--}400\text{ cm}^{-1}$ range and expressed as function of pseudo-absorbance ($\log(1/R)$, R being the reflectance measured by calculating the ratio of the intensity of the beam reflected by the sample to the intensity of the beam reflected by a reference gold mirror). The colour charts were positioned vertically on an easel in front of the reflection module of the spectrometer.

2.2.5. Fibre Optic Reflectance Spectroscopy in Near Infrared (FT-NIR FORS)

A portable FT-NIR Rocket spectrometer (ARCOptix), equipped with an InGaAs photodiode detector and an HL2000 halogen lamp (Ocean Optic, 20 Watts) was used. Measurements were collected through an optical fibre bundle constituted of seven optical fibres ($400\text{ }\mu\text{m}$ diameter - 6 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 $11000\text{--}4000\text{ cm}^{-1}$ range ($900\text{--}2500\text{ nm}$) by averaging 200 scans 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.

2.2.6. Spectrofluorimetry

The fluorescence emission spectra were acquired using the LED μ SF. It is composed of a Thorlabs spectrometer (CCS200/M) with a spectral range from 200 to 1000 nm and an optical fibre ($\varnothing 400\text{ }\mu\text{m}$) [32]. The UV excitation sources are composed of two low power LEDs at 285 nm ($300\text{ }\mu\text{W}$) and 375 nm (5 mW). They are used with associated filters to remove the signal due to the reflection of the LED and the second order effects (320 nm for the first LED and 455 nm for the second one, respectively). The investigated area on the sample was about 1–2 mm in diameter for a working distance of 4 cm. The analysis time was set between 10 μs to 50 s. For each measure, a background was recorded and subtracted to the sample spectrum. This background constituted the environmental noise during measurement. The subtraction allowed to increase the signal-to-noise ratio. Then a spectral smoothing was performed. The LED μ SF is powered and controlled by USB connection to a portable computer and by means of a graphic interface. The instrument stands on a tripod equipped with a micrometric device and two red lasers in order to adjust the working distance and the positioning without any contact.

3. Results

The analytical results for each print are summarised in table 1 (the localisation of the analysed zones is proposed in supplementary material). Three colours are predominant in Japanese woodblock prints: red, blue and yellow. One or more colourants can be used to get the primary colours or different hues (green, violet, etc.).

Table 1. Summary of the analytical results by HSI, point-by-point diffuse reflectance spectroscopy, FT-NIR FORS, FTIR, spectrofluorimetry and XRF spectroscopy in the coloured areas of the studied prints.

Museum no.	Artist	Estimated date	Analysed Colour	L*; a*; b*		HSI VNIR (nm)	VIS DRS (nm)	FT-NIR FORS (cm ⁻¹)	FTIR (cm ⁻¹)	LEDuSF (nm)	XRF	Analyses interpretation		
49571	Harunobu	1767-1768	Bluish kimono	-		520, 560, 640 ^a 660 ^a						indigo		
			Greenish-blue <i>obi</i>	54.4; -1.27; 14.67		660 ^a	600 ^r , 650 ^a					-	Indigo + orpiment	
			Greenish mountains	67.17; 0.55; 17.51	67.17; 0.55; 17.51	660 ^a	630 ^r , 650 ^a					As, S	Indigo + orpiment	
			Grey mountains	55.7; 1.15; 13.03		660 ^a	650(?) ^a , 690 ⁱ							Indigo + black ink (?)
			Greyish-green floor	57.29; 1.30; 15.81			650(?) ^a , 690 ⁱ						-	Indigo + black ink (?)
			Brown kimono	41.1; 10.13; 15.84		~580 ⁱ	575 ⁱ	11000-8000 / 6950				570	As, S, Fe	Orpiment + Ochre
			Pinkish-red balcony	66.5; 11.76; 17.33		560 ⁱ	560 ⁱ	4330	2960, 2920, 2850, 1740 ^{sh}	570, 690	Pb	Red lead + red safflower		
49572	Koryûsai	1776-1781	Yellow courtesan's <i>obi</i>	54.42; 9.37; 29.61			No Max., no Min.		1600 ^{sh} , 1150, 1105, 1075 & 1025 ^{inv}				Turmeric	
			Orange left <i>kamuro</i> 's kimono	54.8; 26.3; 33.06 [*]		565 ^{i*}	565 ^{i*}				595 [*]	Pb [*]	Red lead [*]	
			Light-red courtesan's kimono sleeve	52.2; 13.84; 20.2 [*]		530 ^a & 570 ^{i*}	515 ^a , 575 & 440 [*]				595 [*]		Safflower [*]	
49868	Eisen	c. 1825	Violet kimono (bottom)	48.06; 1.29; 4.31 [*]		530, 594 / 645 ^{ab*}	540 & 590 & 640 ^{ab*}						Dayflower* + red safflower	
			Green <i>obi</i> background	49.1; -9.15; 9.88 [*]		480 ⁱ , 660 ^a	480 ⁱ , 660 ^{ab*}					As, S [*]	Indigo + As sulphide [*]	
			Red fold kimono	53.97; 25.5; 23.4 [*]		530 ^a , 580 ^{ab*}	520 ^a , 455 & 585 ^{i*}				590 [*]		Red safflower [*]	
			Orange <i>obi</i> flowers	52.6; 23.05; 25.8 [*]		530 ^a / 580 ^{ab*}	520 ^a , 450 & 585 ^{i*}					As, S [*]	Red safflower + As sulphide [*]	
49909	Senchô	1830s	Light-blue kimono	44.83; -8.79; -0.43		490 ^r	500 ^r	11000-7500	~2090			Fe	Prussian blue	
			Dark blue kimono	24.75; -3.50; -13.5		455 ^r	450 ^r	11000-7500, 4220	~2090			Fe	Prussian blue	
			Light red kimono	43.45; 23.17; 19.6		530 ^a	520 ^a , 440 & 580 ⁱ				590	-	Red safflower	
			Dark red kimono	44.89; 26.47; 20.8		530 ^a	520 ^a , 440 & 580 ⁱ					-	Red safflower	
			Yellow headdress	65.95; 4.78; 27.98			500 ⁱ					535	-	Organic yellow
49872	Kuniyoshi	c.1844	Yellow hand-mirror	65.66; 6.84; 35.91		520 ⁱ	510 ⁱ					550	(As) Organic yellow / gamboge (?) / traces of arsenic sulphide	
			Light-blue kimono	46.71; -4.61; 3.06		525 ^r , 690 ^a	525 ^r , 690 ^a			2095		Fe, Ca	Prussian blue + calcite (?)	
			Blue cartouche	39.72; -9.19; -13.0		465 ^r , 690 ^a	460 ^r , 690 ^a	4220 ^{sh}	2100			Fe	Prussian blue	

			Greyish blue kimono	36.51; - 2.66; 1.94		525 ^r , 690 ^a	525 ^r , 690 ^a				Fe, Ca	Prussian blue + black ink (?)
			Light green background	49.81; - 9.99; 16.29			530 ^r , 680 ^a	2095				Prussian blue + As sulphide (?)
			Dark green stem	32.42; - 9.47; -2.23			450 ⁱ , 490 ^a	2095			Fe, As, S	Prussian blue + As sulphide
			Red lips	-		440, 530 ^a , 580 ⁱ	-					Red safflower
			Orange-red flower	38.83; 21.95; 18.1			520 ^a , 440 & 580 ⁱ		590		-	Red safflower
BDX	Kunisada	1855	Light blue Sakura's headdress	-		525 ^r , 690 ^a		11000-8000	2100			Prussian blue
			Dark blue valet's kimono	-		460 ^r , 630 ^a		11000-8000	2100		Fe (Pb)	Prussian blue + lead white (?)
			Green floor	-		520 ^r , 690 ^a		11000-8000	2100	515	S, As, Fe	Prussian blue + As sulphide
			Khaki Seigen's kimono	-		550 ^a , 680 ^a		11000-8000	2100		S, As, Fe (Pb)	Prussian blue + As sulphide + lead white (?)
			Purple Seigen's kimono	-		530, 590, 640 ^a				570, 610, 680 591	As	Dayflower + red safflower (+ few particles of As sulphides, observed under the microscope)
			Light red cherry blossom	-		530 ^a						Red safflower
			Dark red Sakura's kimono	-		530 ^a				595	Fe	Red safflower + red ochre ?
			Yellow cherry blossom	-		505 ⁱ /440 ^a				540		Organic yellow (?)
49225	Utamaro	Meiji reprint, 2 nd half 19 th c. (1 st edition 1798-1799)	Light-blue man's sleeve	47.90; 2.71; 14.91			No Max., no Min. 660 ^a , 590 ⁱ *		2100			Prussian blue
			Bluish-pink woman's sleeve	39.94; 2.18; 11.5*		560 & 660 ^a , 590 ⁱ *			2100	725*	Hg, S*	Vermilion + indigo* + Prussian blue
			Light-pink woman's sleeve	61.1; 12.98; 25.3*		590 ⁱ *	595 ⁱ *					Vermilion*
			Red woman's kimono	53.9; 10.55; 22.2*		590 ⁱ *	595 ⁱ *			607*		Vermilion*
49445	Utamaro	Meiji reprint, 2 nd half of 19 th c. (1 st edition 1801-1802)	Light blue fan	62.9; -4.61; 16.45*		550 ^r *	560 ^r , 670 ^a	11000-8000	2100			Prussian blue*
			Blue fan	48.52; - 4.04; 9.79*		550 ^r *	560 ^r , 670 ^a	11000-8000	2100			Prussian blue*
			Purplish blue kimono	40.19; 2.32; 4.15*		525 & 660 ^a *	520 & 670 ^a *	11000-8000	2100		Hg*	Vermilion + Prussian blue*
			Red lips	48.45; 19.5; 20.5*		590 ⁱ *	595 ⁱ *			610*		Vermilion*
49148	Koryūsai	Meiji reprint (~1880-1890)	Blue courtesan's kimono	34.58; - 2.87; 1.54*		635 ^a , 540 ^a *	670 ^a , 510 ^a *	11000-8000	2100			Prussian blue + red (?)*
			Blue <i>kamuro</i> 's kimono	30.18; - 4.59; 4.46*		570 ^r *	670 ^a , 560 ^a *	11000-8000	2100*		Fe, As*	Prussian blue + orpiment*
			Blue man's kimono	44.08; - 5.04; 8.26*		635 ^a , 570 ^a *	670 ^a , 560 ^a *	11000-8000	2100* / 1480-1460		Fe*	Prussian blue + indigo + yellow (?)*
			Green courtesan's <i>obi</i>	48.2; -4.68; 10.85*			670 ^a , 560 ^r		2100 / 3600-3700, 475, 540			Prussian blue / Yellow ochre
			Yellow <i>kamuro</i> 's <i>obi</i>	49.15; 12.6; 29.72			515 & 590 ⁱ		3600-3700, 475, 540			Yellow Ochre
			Pink courtesan's kimono	46.8; 20.6; 18.24*		530 & 565 ^a *	600 ⁱ , 530 & 570 ^a *				Hg*	Vermillion + Cochineal*

49861	Yoshitoshi	1886	Light-blue man's kimono	54.31; -14.8; -4.11	700	490 ^r , 690 ^a	11000-8000	2100	Fe	Prussian blue
			Purplish-blue man's kimono	40.33; -1.64; -1.12		585 ^a	11000-8000	-	Methyl or crystal violet (?)	
			Grey sky	40.32; 0.66; 6.16		No Max., no Min.		2100	Prussian blue (diluted) + black ink (?)	
			Dark-green upper fabric	44.61; -19.8; 19.91		490 ⁱ , 525 ^r , 690 ^a	11000-8000	2100	As, S	Prussian blue + As sulphide
			Light-green floor	69.57; -2.33; 18.47		580 ^r				Prussian blue (?) + ?
			Brown monster's foot	45.85; 3.95; 10.84		570 ⁱ			Fe, (As)	Black ink (?) + Fe oxides (?) + traces of As sulphide
			Yellow moon	73.67; 3.25; 33.61		No Max., no Min.		1740, 1598		Gamboge
			Yellow man kimono	66.26; 10.0; 31.51		490 & 560 ⁱ			As, S	Synthetic (?) As sulphide
			Light-pink man's face	65.02; 11.38; 24.58		565 ⁱ			(Fe)	White pigment + Fe oxides (?)
			Red stamp	37.03; 35.81; 19.71		585 ⁱ			590	Pb, (Ba)
Dark-red man kimono	31.00; 39.90; 17.54	615 ⁱ			630	Ba, S	Naphtol red (+BaSO ₄)			
49770 - January	Shuntei*	1898-1899	Dark-blue fan	59.23; -13.7; -5.32	455 ^r	460 ^{r*}	11000-8000, 4220	-		Prussian blue
			Blue child's kimono	37.85; -8.73; -24.63	460 ^r , 550 ^a , 590 ⁱ	460 ^{r*}	11000-8000, 4220	-		Prussian blue + ?
			Flower green kimono	60.9; -10.73; 17.24		480 ⁱ , 540 ^r , 690 ^{a*}		520		Prussian blue + yellow pigment (?)
			Bright green kimono	59.9; -18.55; 37.23	540 ^r , 700 ^a	490 ⁱ , 540 ^r , 690 ^{a*}		520		Prussian blue + yellow pigment (?)
			Yellow shoes	65.16; 7.60; 55.35	500 ⁱ	500 & 550 ^{i*}		550		Synthetic (?) As sulphide
			Dark-purple kimono	30.67; 15.95; -2.50	570 ^a	450 ^r , 550 ^a , 590 ^{i*}		600		Prussian blue + vermilion (?)
			Pink kimono	65.32; 36.03; 10.59	500 ^a , 540 ^a	440 ^r , 500(sh.) & 530 ^{a*}		570		Eosin
			Light-violet kimono	59.91; 4.01; -0.83	470 & 570 ^r , 535 & 600 ^a	470 & 570 ^r , 530 & 590 ^{a*}		550		Synthetic violets
			Red kimono	47.60; 48.93; 33.89	590 ⁱ	595 ^{i*}		593		Vermilion
			Red cartouche	51.39; 43.91; 35.61	590 ⁱ	590 ^{i*}		600		Vermilion

r = reflectance maximum, a = absorbance maximum, i = inflexion point, sh = shoulder, inv = inverted; * Results already published in [18,19]

3.1. Blue colours

Three different blues have been identified in the studied prints. Indigo, whose Japanese name is *ai*, was used in Japan since, at least, the ninth-century [3,33]. It was obtained from the indigenous indigo plant *Polygonum tinctorium*, from dyed fabrics as described by Hokusai [34] or as already-made sticks, imported from China [35].

Indigo was identified thanks to its specific visible feature, a maximum of absorbance at around 660 nm, and infrared bands, a doublet at about 1480 and 1460 cm^{-1} (figure 2.b and 2.d). On each print where indigo was identified, it involved also at least another colourant (table 1) as Prussian blue for blue areas (n°49148, figure 2. b), orpiment to obtain green hues (n°49571 and 49868, figure 2.d)) or with vermilion (n°49225). Fluorimetry allowed also the identification of indigo (emission band at about 730 nm) sometimes mixed with Prussian blue, while the latter is not detected by UV fluorescence because of the iron presence [18,31]. Unfortunately, portable XRF is not a suitable technique to identify organic pigments, because working in air it does not detect light elements with Z lower than 13 (Al).

Prussian blue, or *bero-ai* ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$), was easily identified using mid-infrared spectroscopy thanks to the strong cyano stretching vibration $\nu(\text{C}\equiv\text{N})$ at around 2080 - 2100 cm^{-1} , combined with characteristic narrow near infrared bands, including the most intense about 4220 cm^{-1} (figure 2.a and 2.b) [16]. It was mainly used alone for blue areas thanks to its ability to provide very different hues of blue, from lighter sky blue to a dark, almost black, blue [31]. Prussian blue was also employed in mixture to get mainly green shades, combined with orpiment (table 1, n°49872, 49861, 49148 and BDX), identified thanks to visible reflectance spectra (figure 2.d, inflection point at about 490 nm) and confirmed by the presence in the XRF spectra of the K-lines of iron at 6.40 and 7.06 keV. Due to the high tinting strength of the Prussian blue, often present in low concentrations, the X-ray fluorescence lines of Fe may be weak. We have compared the intensity of the XRF lines of Fe from the blue zones with the XRF lines of Fe in the paper backing areas. In the case of the blue zones identified as Prussian blue, the intensity of the XRF lines of Fe in the pigment is always higher than in the paper backing. Dayflower, also known as Japanese *tsuyukusa* (wild species) or *aobana* (hybridised species), gives a blue colourant, extracted with water from paper sheets soaking with the blue liquid (*aigami*), only used in Japan. Dayflower showed a characteristic visible spectrum with two apparent maxima of absorption at 590 and 640 nm (Figure 2.c). In the studied prints, dayflower was not identified alone but always in mixtures with a red colourant to get a purple hue.

3.2. Red colours

Several red colourants have been found in the prints. Red safflower is an organic red obtained from the petals of the specie *carthamus tinctorius* and it showed an apparent absorption band at 530 nm in the visible range [36] as several bands in the mid-infrared range, principally at 1736 and 1603 cm^{-1} [16]. Red safflower was also identified by fluorimetry with a characteristic emission band at 580-590 nm on several prints (spectra not shown, n°49571, 49572, 49868, 49861, 49872, 49909, BDX). These spectral features have allowed the identification of red safflower on six of the woodblock prints studied. The mid infrared bands ascribed to red safflower (2920, 2850, 1730 and 1630 cm^{-1}) have also been highlighted using spectral subtraction of the paper signal, for example for the most ancient analysed print of the collection (print n°49571, figure 3.a). It was used alone to get pinkish red to red colours or in mixture with dayflower for the purple colours, as found in the prints n°49868 or BDX (figure 2.c). Three kinds of inorganic pigments were also identified thanks to visible reflectance spectroscopy and XRF analyses. Red lead (*tan* in Japanese, Pb_3O_4), vermilion (*shu*, HgS) and red ochre (*bengara*) were recognised using their specific visible reflectance features, which are inflection

points at respectively 560 nm, 590-600 nm and 580 nm (figure 3.b) [36], and confirmed by the main XRF spectra L-lines of Pb in red lead at 10.54 and 12.63 keV, by the main XRF spectra L-lines of Hg in vermilion at 9.98 and 11.86 keV, and the K-lines of Fe at 6.40 and 7.06 keV in red ochre.

Finally, cochineal and synthetic red were identified in the recent prints.

Cochineal was revealed in a Meiji reprint, following a design by Koryûsai (n°49148). The organic pigment was mixed with vermilion [18]. The reflectance spectrum presented two absorption bands at 530 and 565 nm (Table 1), characteristic of this insect-based pigment. The ultraviolet (UV) excited fluorescence emission spectra were disturbed by the fluorescence emitted by the paper at about 500 nm and therefore the maximum of fluorescence emission of cochineal was shifted towards the short wavelengths (from 640 nm down to 610 nm), which limits the identification of the cochineal based only on the UV fluorescence emission spectra [18].

Among the most recent woodblock prints, new synthetic red pigments were also identified. Naphthol red was detected in the dark red of the Yoshitoshi design (n° 49861, dated in 1886) by its visible reflectance spectrum, with its characteristic inflection point at 615 nm. However, the use of this red pigment was mainly confirmed because of its association to the presence of barium sulphate (probably barium white) [18-20], a common ingredient of lithographic inks used as an extender or as a substrate of the lake pigment, detected by the presence of the characteristics XRF L-lines of Ba, at 4.46, 4.84 and 5.16 keV, and the K-line of S, at 2.31 keV (figure 4).

3.3. Yellow colours

As mentioned above, yellow pigments and colourants were employed in the *ukiyo-e* woodblock prints. Orpiment (or arsenic sulphide) was mainly detected in mixtures with indigo and Prussian blue, using XRF, by the presence of the K-lines of As at 10.53 and 11.72 keV, and its inflection point around 490 nm on visible reflectance spectra (Figure 2.d). Arsenic sulphide was found alone only in the most recent woodblock prints (Yoshitoshi n° 49861, figure 5.a, and Shuntei n° 49770). In both cases visible reflectance spectra exhibited two inflection points at 490-500 nm and 550-560 nm, suspecting a mixture of As pigments and then the use of synthetic As sulphides [9,19].

Infrared analyses have revealed the presence of yellow ochre in one print (n°49148) with the identification of the specific bands of kaolin, known as an accessory mineral of ochre (bands observed at 475 cm⁻¹, 540 cm⁻¹ and between 3600 and 3700 cm⁻¹) (figure 5.b) [37,38].

Organic colourants were also part of the palette of the woodblock printer and yellow dyes are challenging to discriminate. Indeed, all of them present almost the same spectral features in the visible range, as absorptions occur mainly between 200 and 400 nm [36]. However, this is a first step to characterise the nature of the yellow colourant as it is recognised as an organic one. In some cases, infrared can define the nature of the colourant used, when sufficient pigment was used to be detected and when the signal of the paper does not overlap entirely with the signal of the colourant [16].

Thus, organic yellow colourants were detected in five woodblock prints of the studied corpus. Among them, infrared analyses allowed the particular identification of turmeric, bands at 1600 and 1520 cm⁻¹ (n°49572, figure 5.c) and gamboge, bands at 1735 and 1598 cm⁻¹ (n°49861, figure 5.d) [16]. The UV fluorescence spectra on yellow zones also suggested the presence of gamboge on the print n° 49872 with a maximum at about 550 nm (table 1). Besides, visible reflectance spectra in yellow areas of this print (n° 49872) showed an inflection point at 510 nm, similar to that of gamboge, but undistinguishable from As sulphide spectrum; in fact, XRF analyses detected traces of As and S, proving that a mixture of organic and inorganic pigments has been employed. Another organic product

such yellow safflower could have been used (maximum of fluorescence at 525-535 nm, and visible reflectance spectrum with the inflection point around 500 nm), but it was not possible to confirm this attribution for the moment (n°49909, for instance).

4. Discussion

The prints studied exhibit vivid and varied hues of colours covering almost all the rainbow colours, from deep violet to bright red. The colour-skilled craftsmen obtained these shades using pure colourants or mixtures of pigments. The non-invasive analyses demonstrated the use of a restricted palette, limited to around fifteen pigments and dyes. Only primary colours were used, except for the most recent woodblock prints and the possibility of getting pink and purple colours directly with synthetic dyes, like eosin, methyl violet or crystal violet (Shuntei, n°49770, see also [19]). No one of the green pigments as malachite or copper-based green pigments were employed. However, all the colours of the rainbow were obtained with these materials from purple to dark blue. Thus, the identification of the materials was less simple than it seemed, because of the presence of several mixtures and the possible combinations of various pigments. For instance, purple corresponded mainly to a mixture of dayflower and red safflower, whereas greens were obtained either with a mixture of orpiment with blue (indigo or Prussian blue) (n°49571, 49868, 49872, BDX, 49861, 49148) or by printing a layer of Prussian blue over a yellow ochre one (n°49148). Even for primary colours, mixtures were evidenced by the combined use of Prussian blue and indigo (n°49225 or 49148) or cochineal and vermilion (n°49148). Colourants were therefore used for their proper colours, and prepared and mixed in the printers' workshops for this purpose, following the artist or publisher directives.

Regarding the results obtained on the analysed woodblock prints, an evolution of the amount of hues chosen and the palette of colourants used is noticeable. Indeed, latest prints showed more complex colour associations and a larger palette of colourants, composed of five or more colourants identified, without taking into account black inks and white pigments. On the contrary, woodblock prints dated between 1780s and 1840s were achieved using no more than four pigments. This long period encompassed notably eras of austerity, Kansei era (1789 – 1801) and Tempō era (1830 – 1843), which hit also artistic production, so of course occurred in *ukiyo-e* production. Moral and artistic edicts were issued in order to forbid the production of *ukiyo-e*, considered luxurious products, by mainly limiting the authorised colours and colourants [39,40]. To a certain extent, this might explain the limited palette encountered in the woodblock prints dated from this period.

The evolution of the palette of the printer can be summarised in figure 6, involving results of this study [18,19] as well as summarised results from the literature [3,9,10,12,14,41–43]. To complete the previous comments, only primary colours, except modern synthetic pink and violet dyes, were used by the *ukiyo-e* printmakers. The colourants considered as 'traditional' and part of the palette from the beginning of the *ukiyo-e* printing, namely red lead, ochre, red safflower, orpiment, organic yellow, dayflower and indigo [39,44], were almost used until the end of the 19th century. The new imported pigments, as Prussian blue, organic red (cochineal and synthetic reds), did not replace the old ones, but enlarged the colour chart available. Even woodblock printers seemed to have conserved old practices for usual hues of colours, such as mixture of indigo and orpiment for green colours, until the second half of the 19th century and the arrival of new synthetic pigments [14], easy-to-use because of their high tinting power and their very-high water solubility, completely suitable for printing process. Changes occurred during this period, and especially from the 1870s. Some colourants turned out not to be used anymore, such as dayflower or red safflower. New synthetic red and violet dyes prevailed in the palette, but used in the same way as the old colourants. These facts revealed the changes in the

Japanese society between traditions (red and purple were important colours, generally associated with high-society clothes since the Heian period) and the westernisation process (new materials were considered as new technology and, by extent, progress) [45].

5. Conclusion

A holistic non-invasive analytical approach was proposed to study Japanese *ukiyo-e* woodblock print. Results obtained with this different method turned out to be complementary. Most of the identifications of the colourants remained based on the visible reflectance spectroscopy, whose results were extended and confirmed by XRF, near- and mid-infrared and fluorescence analyses. By combining all these methods, all the inorganic compounds were identified, even in the case of mixtures. Regarding the organic colourants, which were largely used in Japanese *ukiyo-e*, the results were also conclusive especially for the blue and red areas. Yellow organic pigments were also detected, but determining their nature remains challenging. Infrared investigations allowed to improve the assignments for the yellow colourants.

Finally, a general chronology of the use of the colourants in the *ukiyo-e* woodblock prints between 1700 and 1900 is proposed. Traditional Japanese organic pigments (red safflower and yellow dyes, such as gamboge, and to some extent dayflower), as well as inorganic pigments (red lead, orpiment) were used almost until the end of the 19th century, in other words, until the end of the production time of *ukiyo-e* woodblock prints. New colourants, such as Prussian blue, cochineal or synthetic red and violet dyes, enriched the palette. However, they did not entirely replace the old colourants and printmakers could use the available colours following their needs and the taste of the time.

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