Red and blue colours on 18th–19th century Japanese woodblock prints: *In situ* analyses by spectrofluorimetry and complementary non-invasive spectroscopic methods

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A R T I C L E   I N F O

A B S T R A C T

The study of fragile artworks kept in museums requires mobile devices, short time of analysis and minimal disturbance to insure their good preservation. *In situ* reflectance spectroscopy and spectrofluorimetric studies are mostly developed for pigment characterization. A recently-designed μspectrofluorimeter (LED μSF) dedicated to *in situ* measurements, that uses UV-light emission diodes (LED) as excitation sources, was used to verify its potentiality for the identification of pigments and dyes. The colours of five Japanese woodblock prints from the Museum of Zaragoza (Spain) were studied by the combination of UV-VIS-IR spectroscopies and hand-held energy dispersive X-ray fluorescence spectrometer (HHED-XRF), together with Raman Spectroscopy. This study focused on the analysis of red and blue colours in prints by Koryūsai, Utamaro and Eisen (18th–19th centuries). The interpretation of the *in situ* fluorescence emission spectra could be rather difficult because of the variety of pigment mixtures, natural ageing of colorants and fluorescence of the support (paper), that could lead to spectral changes or band shifts. The combination with diffuse reflectance spectroscopy (DRS), hyperspectral imaging techniques (HSI), and HHED-XRF completed the interpretation of these results. A specific database was built analyzing reference samples made in accordance with Japanese printings techniques and materials. Inorganic and organic red (vermilion, red lead, cochineal, red safflower) and blue (Prussian blue, indigo, dayflower) pigments were used alone or as a mixture to modify the hues. The identification of Prussian blue could be a clue about the relations existing between East and West and, its presence sometimes questioned the dating of some early printings.

1. Introduction

The Oriental-Asia art collection at the Museum of Zaragoza (Spain) counts about 143 printings, dated from the end of the 18th century AD to the beginning of the 20th century. Among them there are many examples in *ukiyo-e* style. This fact offers a good opportunity to improve the knowledge on painting materials in some woodblock printings from this collection.

Ukiyo-e style illustrates various facts of the Edo city (Tokyo) and scenes of everyday life (famous courtesans, Kabuki theatre, nature *etc.*). An important part of the collection is the prints representing *bijin-ga* (beautiful women) from Edo period (1615–1868), a genre with noted artists as Isoda Koryūsai 礒田湖龍斎 (1735–1790), Kitagawa Utamaro 喜多川 歌麿 (1753–1806) and Keisai Eisen 渓斎英泉 (1790–1848) [1].

Five *ukiyo-e* woodblock prints (Fig. 1) were selected for the analytical study. The main characteristics of these prints are summarised in Table 1. In the selected *ukiyo-e* prints, there are many shades and colour tones. Among them, blue and red pigments are very common.

In *ukiyo-e* prints, there are red pigments and colorants with mineral or artificial origin (like vermilion and red lead), insect-based pigments (cochineal), or of vegetal origin [2]. In this last case, the pigments were prepared from petals (safflower), barks (Sappan wood), roots (madder),

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Fig. 1. Japanese printings in the Federico Torralba collection (Museum of Zaragoza, Spain), with the point fluorimetric measurements. a) 49572, Koryūsai: The courtesan Takigawa of the *Ogi-ya* house with two kamuro. b) 49148, Koryūsai: The Mazan courtesan of the *Choji-ya* house with the kamuro Utagi and Tasuta. c) 49225, Utamaro: O-ume and Kumenosuke. d) 49445, Utamaro: A wife of the middle rank. e) 49868, Eisen: Shuzaki on rakugan.

Table 1
Selected prints from the Oriental-Asia Art collection (Museum of Zaragoza, Spain).

Museum catalogue no.	Author	Print title	Chronology	Series title	Size (cm)
49572	Koryūsai	"The courtesan Takigawa of the *Ōgi-ya* house with two kamuro"	1776–1781	"Models for fashion: New designs as fresh as young leaves"	31 × 21.4
49148	Koryūsai	"The courtesan Mazan of the *Chōji-ya* house with the kamuro Utagi and Tasuta"	Meiji era (~1890)	"Models for fashion: New designs as fresh as young leaves"	25.1 × 17.2
49225	Utamaro	"O-ume and Kumenosuke"	Meiji era (1868–1912)	"True Feelings Compared: The Founts of Love"	38.2 × 26
49445	Utamaro	"A Wife of the Middle Rank"	Meiji era (1868–1912)	"A Guide to Women's Contemporary Styles"	37.4 × 25.4
49868	Eisen	A *bijin* (a beauty), with non-listed name	1825	"Lingering Fragrance of the Sleeve"	38.5 × 26.5

or from resin (dragon's blood).

Six blue pigments were used in Japanese woodblock engravings: inorganic (like azurite, Prussian blue, ultramarine or smalt) and organic (indigo and dayflower). Prussian blue was firstly introduced in the mid-18th century for the paintings and later for prints (at the beginning of the 19th c.). Since the introduction of Prussian blue (~1830), there are few references about mixtures with this pigment in the prints. Some researches revealed that it was mixed with yellow or red pigments, surely mixed with the same red colours as they used for indigo [3].

To obtain a purple colour, pure pigments or mixtures were used. Dayflower, the most characteristic Japanese pigment, is known to fade easily, becoming grey in contact with humidity. From about 1860, aniline, a synthetic dye, was used to obtain purple tones. Concerning the mixtures, the red pigments could be mixed with indigo and sometimes with dayflower or smalt. The combination of two or three pigments was usual and offered a large variety of hues and colours.

The study of easily-faded colorants, such as safflower or dayflower, is important for artwork conservation [4,5]. Recently, specific studies on the fluorescence of red and yellow organic colorants were done, allowing the better understanding of the main coloured species of safflower by laboratory studies [6]. Identification of madder, gardenia and berberine has been completed by *in situ* fluorimetric measurements [7].

Mobile devices are used when there is the impossibility to sample and to move artworks to the laboratories. We focused our research on the ability of three main techniques (fluorimetry, reflectance spectroscopy and X-ray fluorescence (XRF)) to draw, from ultraviolet to infrared range, the main features of the materials used in Japanese prints. Although Japanese artworks have always attracted high interest [8], materials on Japanese paintings and printings have been specially studied since 2000 by the works of Elizabeth West FitzHugh, Marco Leona and John Winter [2,9]. In their studies, the identification of pigments and dyes has been achieved by reflectance spectroscopy. Some examinations under UV light were also conducted by Fiske and Stider Morenus [10].

Although fibre optic reflectance spectroscopy (FORS) is currently used, spectrofluorimetric studies have also proved their potential for the identification of pigments and colorants on paintings, medieval manuscripts or codex [11–13]. For ten years, works have been done on mobile instrumentation, and instrumental systems for fluorimetric analysis have been especially adapted or developed [14,15]. The fluorescence study of materials used on Japanese paintings began thirty years ago by Miyoshi using a N_2 Laser for the study of some traditional pigments, recording reference spectra [16]. He analyzed an ancient painting where vermilion and gamboge were identified.

The present study focuses on the ability of combined methods as μ-spectrofluorimetry (LED μSF), patented in 2014, and reflectance spectroscopy in the visible and infrared range to identify red and blue pigments used on a selection of five Japanese woodblock printings kept in the Museum of Zaragoza (Spain). Complementary methods have also been implemented, such as hyperspectral imaging in the visible range (HSI), XRF and portable Raman Spectroscopy.

2. Materials and methods

2.1. Materials

One of the most important steps for this study was to build a database of reference spectra. Forty samples were prepared in accordance with the Japanese woodblock printings techniques and materials. First, a mixture of pigments with a binder (rice starch) were deposited on wooden blocks, and then printed on pure cellulose paper by hand pressure. Several mixtures of pigments and colorants were done. Rice starch powder needs to be mixed with hot water to obtain the good viscosity. Most of the pigments (vermilion, red lead, cochineal, dragon's blood, madder lake, orpiment, gamboge, smalt, azurite, and indigo) and the rice starch were supplied by Kremer Pigmente. Brazilwood, red and yellow safflower are "homemade" pigments. Mixtures of pigments, such as indigo with vermilion and cochineal or indigo with orpiment, in

equal volume concentration, have been made to reproduce the mixtures described in the literature [2]. For the study of the support fluorescence, the paper was supplied by Atlantis-France, specialist in the distribution of permanent papers and cartons, equipment and supplies for preventive conservation, restoration and binding. The paper used in this study was made by paper makers from the natural fibers of *mitsumata* according the traditional methods of cooking, refining in piles and drying.[1]

2.2. Instrumentation

2.2.1. LED μ-spectrofluorimeter (LED μSF)

A detailed description of the device and its components is included in a previous article [15]. The fluorescence emission spectra were acquired using a system composed of a Thorlabs spectrometer (CCS200/M) with a spectral range from 200 to 1000 nm and a fibre optic (Ø 400 μm). The UV excitation sources are composed of two low power LEDs: 285 nm (300 μW) and 375 nm (5 mW), used with associated filters: a 320-nm filter for the first LED and a 455-nm filter for the second one, respectively. Filters allow removing the band due to the reflection of the LED and to the second order effects. Depending on the artworks to be analyzed, it may be necessary to lower the intensity of the UV sources. For fragile objects or when the signal is saturated, the source can be adjusted by neutral density filters (0.1, 0.3 or 0.6). A black occultation system can be added to exclude contributions from external light. One of the main advantages of the LED system is that it does not release heat during the measurement unlike the benchtop devices, which usually use xenon lamps requiring a cooling system.

The investigation area on the sample was about 1–2 mm in diameter for a working distance of 4 cm. Typical analysis time was set between 10 μs to 50 s. Each spectrum was corrected taking into account the background during measurement to increase the signal-to-noise ratio. A spectral smoothing was performed.

The LED μSF is light (weight < 1.5 kg), portable (15 × 15 × 8 cm) and is powered and controlled by USB connection to a portable computer and by means of a graphic interface. The prototype stand is a tripod on which a motorized translation system is easily adapted to provide a horizontal or vertical motion for accurate positioning without contact on fragile objects.

For the reference samples, the results obtained by LED μSF were compared with those obtained using a benchtop device.

2.2.2. UV-illumination control on sensible materials

The question of the impact of UV light on the studied materials was essential. Considering the portable system, LEDs deliver low power and very short time of analysis is used (50 s maximum instead of 5 min for benchtop devices). Furthermore, density filters can be used to reduce the intensity of the incident beam on the sample. 375 nm is a commonly used excitation wavelength to observe repairs and damages on paintings that may be invisible in day light. Because LED at 285 nm is more harmful, the integration time is progressively increased, depending on the nature of the fluorescence. Iterations tests (between 5 and 10 iterations) on a same point of analysis showed that the maximum wavelength does not change.

2.2.3. Benchtop fluorescence system

Fluorimetric measurements were performed using a Horiba Jobin-Yvon Fluorolog-2 spectrofluorimeter, equipped with double monochromator on both excitation and emission beams. The excitation lamp is a 450-W high-pressure xenon lamp. A thermoelectrically cooled photomultiplier (Hamamatsu R928) is used for the signal detection, using the photon counting mode. The measurements were performed in the "front face" mode, so that, the emitted light was collected within an

angle of 22.5° in respect of the excitation beam. Fluorescence signals are expressed in "counts per second" (cps). Data acquisition and processing were computer controlled (SpectrAcq Datamax run by the Grams/32 software). Both excitation and emission spectra (recorded with 4-nm bandwidth) were corrected by instrumental factors.

2.2.4. Reflectance spectroscopy

2.2.4.1. 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 × 840 pixel 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 paint. For the study of the Japanese woodblock printings, the experimental conditions were: working distance 80.5 cm, and analysis time about 30 s. 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…) [13]. In this study, only the reflectance spectra were considered.

2.2.4.2. Point-by-point diffuse reflectance spectroscopy.
Colour and reflectance spectra were also measured in several points of the coloured areas 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 (Konica Minolta), 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 used as white reference to calibrate reflectance spectra. From the dispersion of both reflectance measurements (RSCI, specular component included; and RSCE, specular component excluded), colour coordinates (L*, a*, b*) of the CIELab 1976 colour space were calculated.

2.2.4.3. Reflectance infrared spectroscopy.
In situ infrared reflectance analyses were carried out using a portable instrument ALPHA Fourier Transform InfraRed (FTIR) Spectrometer (Bruker), equipped with a DTGS detector and 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)). Colour chart and *ukiyo-e* prints were positioned vertically on an easel in front of the reflection module of the spectrometer to perform every measurement.

2.2.5. Hand-held energy dispersive X-ray fluorescence spectrometer (HHED-XRF)

A Hand-held energy dispersive X-ray fluorescence spectrometer HHED-XRF XMET5100 (Oxford Instruments, UK) equipped with a Rh tube working at a maximum voltage and current of 45 kV and 50 mA respectively, and 9 mm spot collimation was used for the *in situ* elemental characterization of the red and blue pigments of the five Japanese woodblock printings. The instrument includes: *i)* a Peltier cooled silicon drift detector (SDD) of high resolution that is able to provide an energetic resolution of 150 eV (FWHM value of the Mn Kα line at −20 °C) and *ii)* a PDA to control the conditions of the measurement and the spectrometer and also to save the spectral and semi-quantitative information. First, before of each *in situ* measurement day, spectra of an instrumental blank (a PTFE block) were acquired in the same conditions of the *in situ* measurements. The analyses were performed directly on the Japanese woodblock printings. The spectra (three replicates in each point of analysis) were acquired during 50 s (real time) and the voltage and current of the X-ray tube was set at
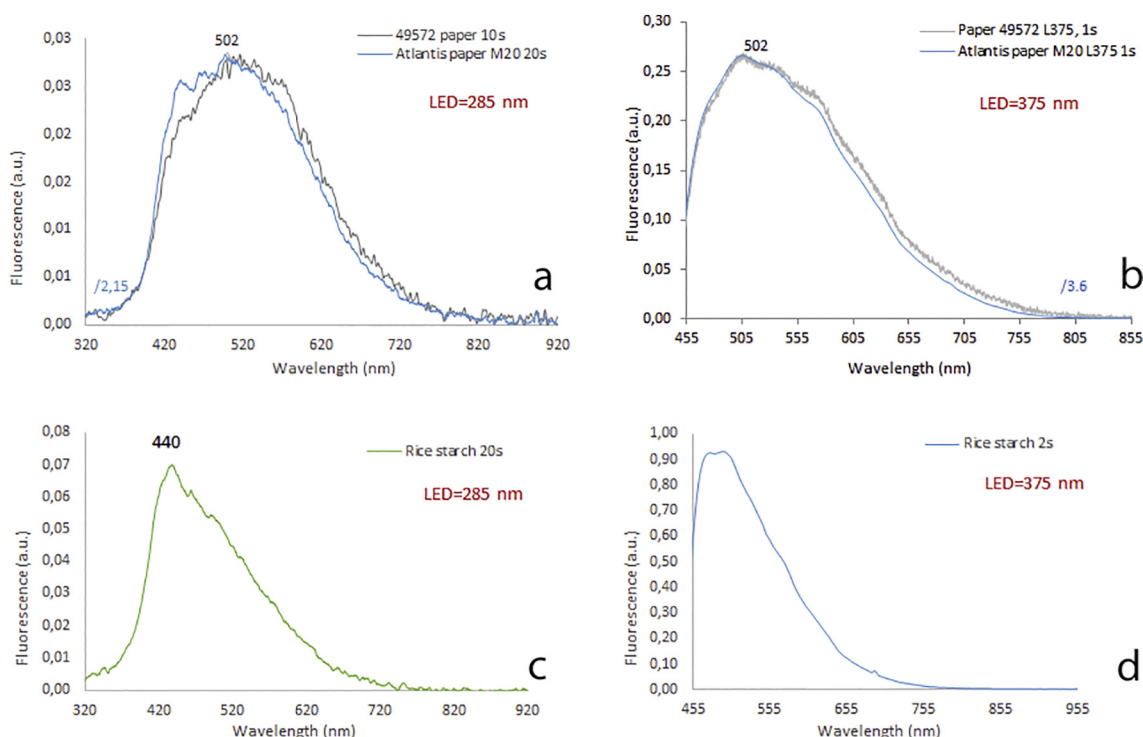
Fig. 2. Fluorescence emission spectra of the paper at λ_{em}285 nm (a) and at λ_{em}375 nm (b); fluorescence emission of the binder, rice starch at λ_{em}285 nm (c) and at λ_{em}375 nm (d), comparing the two LEDs. The paper emitted a large fluorescence band around 500 nm (a & b) and rice starch around 440 nm with the LED 285 nm (c), and the end of the diffusion with the LED at λ_{em}375 nm was visible until 655 nm (d).

40 kV and 15 μA respectively. The instrument implements different semi-quantification methods based on Fundamental Parameters. Considering the samples under study, two methods were used SoilFP method (for the determination of heavier elements, with atomic number higher than 18) and SoilLEFP method (for detection of lighter elements, with a lower atomic number, $Z \leq 17$). To compare the elemental results of the red and blue areas, instead of using the semi quantitative data given by the HHED-XRF, we used the normalized counts of the characteristics Kα, Kβ, Lα or Lβ lines of each element detected in the spectra.

2.2.6. Portable Raman spectroscopy

The *in situ* Raman analyses were carried out with a portable InnoRam spectrometer (B&WTEKINC., Newark, USA) equipped with a 785 nm diode laser. The spectrometer worked in a spectral range from 65 to 2500 cm^{-1}. The maximum laser power of the system is 300 mW at excitation source. For the analyzed samples, the laser power was adjusted to 1% of the total power. Spectra acquisition was done with the software BWSpec™ 3.26 (Newark, USA). The spectra were recorded with an integration time varying from 0.5 to 10 s, and with a number of accumulations varying between 10 and 50 (depending on the point of analysis in each Japanese woodblock printing, the presence of high fluorescence radiation due to the fluorescence of the Japanese paper and of the rice starch and the signal-to-noise ratio). The obtained Raman spectra were processed by the Nicolet Omnic 7.2 software (Madison, Wis., USA) and the identification was based on a comparison of the recorded spectra with standard Raman spectra from own databases as e-Visart and e-Visarch [17,18].

3. Results and discussion

3.1. Interferences in the fluorescence spectra

Before the identification of the pigments, the interferences in the spectra due to the fluorescence of the Japanese paper and of the rice starch were examined (Fig. 2). The spectra obtained with both LED sources presented the same features. The paper of the printing (49572) emitted large fluorescence around 500 nm and it corresponded to that of the reference Japanese paper (Atlantis-France). For the rice starch, there was a fluorescence emission at about 440 nm. The fluorescence emission spectra, measured on the papers and rice starch with the LED at λ_{em} 375 nm, showed large spectra, until 655 nm. For the binder, the maximum was at 440 nm (λ_{em} 285 nm), the LED at 285 nm is more adapted to reveal this fluorescence because on the spectrum at λ_{em} 375 nm, just the end of the curve is represented due to the filter at 455 nm (Fig. 2d). Cellulose and rice starch consist of macromolecules of polysaccharides. Starch is composed essentially of polymers of anhydro-D-glucose with two fractions of glucosic polymers: amylose and amylopectin. Starch contains also < 2% of impurities (lipids, proteins and minerals) [19]. The observed fluorescence emission can be attributed to these impurities but also to the oxidation of cellulose and/or starch leading to double bonds (ketones, aldehydes). This can also be due to the remains of lignin, optical brighteners in contemporary papers, *etc.*

3.2. Red and blue pigment references

A fluorescence emission spectrum was recorded on each red and blue pigments mixed with rice starch and printed on pure cellulose (Fig. 3). The analysis time was very short (5 s maximum, except for madder-lake printing spectrum which required 20 s). For the red pigments, LED at 375 nm was the most adapted to excite the fluorophores which re-emit fluorescence in the visible range [13]. The binder had an influence on the spectra and it showed a large band between 400 and 555 nm (Fig. 3a). Despite the fluorescence of the paper and the binder, the red pigments showed different characteristic bands (Fig. 3a).

Vermilion (HgS), *shu* or *shin-sha*, had a maximum of fluorescence emission at 610 nm (Fig. 3a). The fluorescence of vermilion is well known and it is due to the HgS semiconductor [20,21]. The intensity was very low, therefore the band was embedded in the fluorescence caused by the binder.
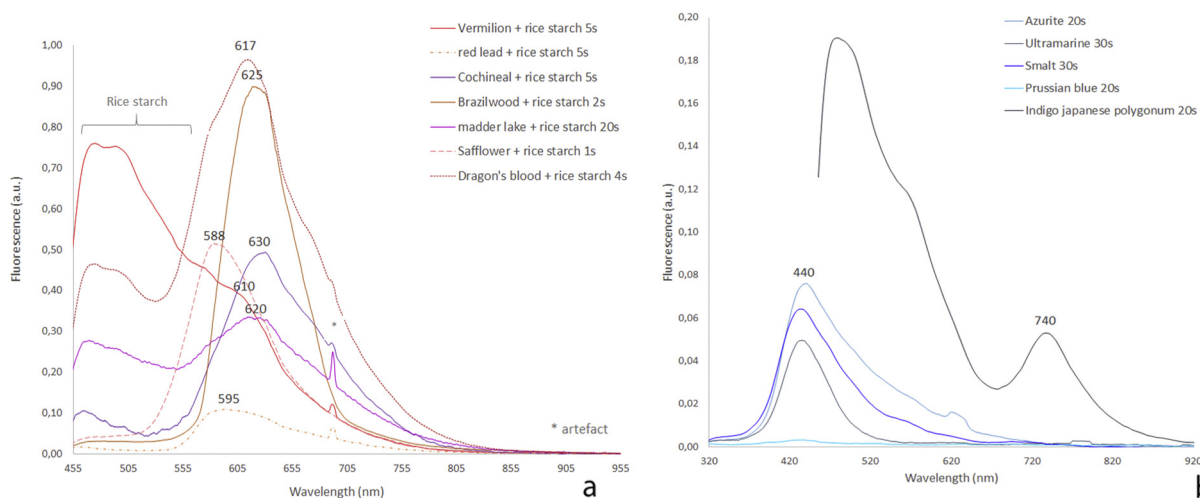
Fig. 3. a) Reference fluorescence emission spectra of the 7 reds (a) and 5 blues (b), currently used in Japanese woodblock printings, mixed with rice starch. For the red pigments (λ_{em}375 nm), the contribution of the binder was visible between 455 and 555 nm. The reds presented different spectra and features which allowed us to distinguish them. The inorganic blue pigments had the same maxima around 440 nm (λ_{em}285 nm), Prussian blue did not give any fluorescence while indigo had one specific band at 740 nm (λ_{em}375 nm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
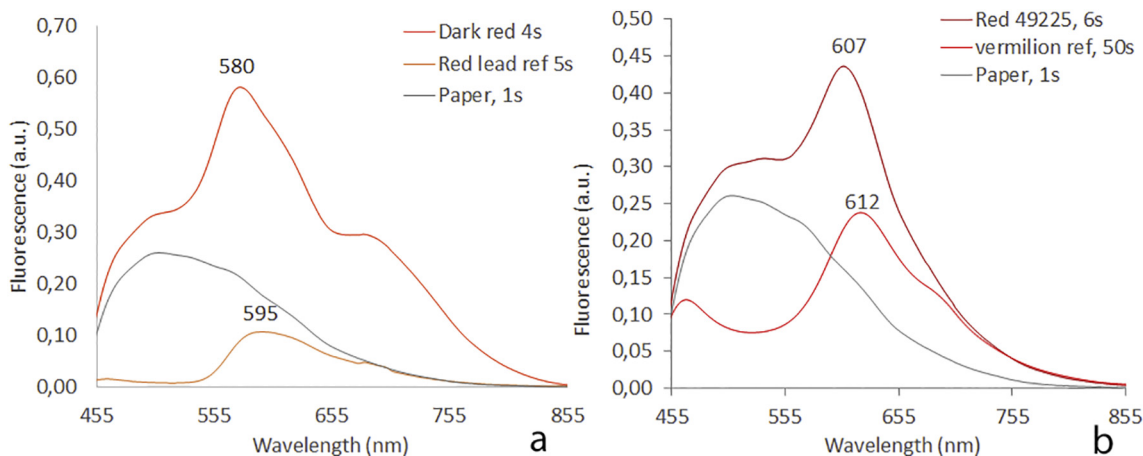

Fig. 4. Fluorescence emission of inorganic red pigments identified on the printings 49572 and 49225 (λ_{em}375 nm). Red lead (a) and vermilion (b) (in accordance with the reflectance spectra and the inflection points) seemed to have been used, even if the fluorescence of the paper shifted the characteristic band of the pigment towards shorter wavelengths. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Red lead (Pb_3O_4), *en*tan or *tan*, presented a large band around 595 nm (Fig. 3a), and its fluorescence is due to irregularities in the crystal structure or to the presence of impurities [22].

It is known that Brazilwood (*Caesalpinia echinata)* existed in the Japanese palette, but Sappanwood (*Caesalpinia sappan*), imported from India, was more usual. The term "sappan" came to Europe through Dutch that named Sappan the brazilwood imported from Japan [19]. From a chemical point of view, in both cases, the main chromophore is an organic acid: brazilein [12]. The maximum fluorescence emission depended on the substrate used for the fixation of the dye, alum in our case. This maximum centred at 625 nm (Fig. 3a) can shift if other additives such as chalk or lead are used to fix the colorant [12]. Even if the analysis time was very short (2 s), the fluorescence intensity was very strong.

The fluorescence emission of cochineal can be attributed to its fluorescent anthraquinone-based constituents which are predominantly carminic, kermesic, and flavokermesic acids, and also other recently-identified minor anthraquinones [23,24]. Cochineal was known in Japan by 1800 [2]. The fluorescence maximum emission was located at 630 nm (Fig. 3a), which is in accordance with previous results obtained in pigments on medieval miniatures [15]. Several previously-published fluorimetric studies of anthraquinoid colorants showed the same

maximum (630 nm) [25–27], such as purpurin and alizarin currently used as madder lake [11,28]. In Europe madder lake was extracted from the rhizome of the *Rubia tinctorum*. Because it presents a low fluorescence, it needed an integration time of 20 s for analysis. The maximum was at about 620 nm (Fig. 3a) and it seemed to be shifted towards short wavelengths because of the fluorescence of rice starch.

Safflower (*Carthamus tinctorius*), *beni*, original from Eastern, is a sort of big thistle up to 1.5 m tall, with stiff and thorny leaves. Its composition includes two colorant groups: a yellow dye (carthamol, iso-carthamol…), and a red one (the carthamone = carthamin, carthamin acid) [19]. The first presented a very intense fluorescence (Fig. 3a) and the spectrum acquisition needed an analysis time of 1 s. The wavelength of maximum fluorescence of the carthamin was about 588 nm, when it was mixed with rice starch on pure cellulose.

Dragon's blood is a resin of *Daemonorops sp.* (India, Sumatra or Malaisia). The resin is provided by the fruit, a small round berry with the size of a large cherry, covered with reversed scales. At maturity, it is covered with a layer of red resin that exudes between the scales. The dyes are flavonoids, the main of which is dracorubin, but dracorhodin, flavanes, chalcones, biflavonoids and a triflavonoid are also found as minor dyes [19]. The fluorescence intensity was very strong and the band presented its maximum at 617 nm with two small shoulders

Table 2

Spectrum features summary of reflectance spectra obtained by HSI and point-by-point diffuse reflectance spectroscopy in blue and red colours (abs.: absorption bands, infl.: inflection points, min.: minimum and max.: maximum of reflectance). The symbol * indicates doubtful assignment of a second pigment.

| Museum no.	Analyzed area	Colour	Colour parameters (L*; a*; b*) (RSCE)	HSI	Diffuse reflectance spectra	Pigment
49572	Kamuro kimono	Orange	54.77; 26.27; 33.06	565 nm (infl.)	565 nm (infl.)	Red lead
49572	Courtesan kimono sleeve	Light red	52.23; 13.84; 20.2	530 nm (abs.)/570 nm (infl.)	515 nm (min.)/575 & 440 nm (infl.)	Red safflower
49572	Courtesan kimono	Light red	57.81; 11.65; 21.38	530 nm (abs.)/570 nm (infl.)	515 nm (min.)/575 & 440 nm (infl.)	Red safflower
49148	Kamuro kimono	Dark greenish blue	30.18; −4.59; 4.46	570 nm (max.)	670 nm (min.)/560 nm (max.)	Prussian blue + yellow As sulphide
49148	Man dress	Light greenish blue	44.08; −5.04; 8.26	635 nm (min.)/570 nm (max.)	670 nm (min.)/560 nm (max.)	Prussian blue + yellow *
49148	Courtesan *obi* flowers	Lighter greenish blue	48.17; −4.68; 10.85		670 nm (min.)/560 nm (max.)	Prussian blue + *
49148	Courtesan kimono folds	Violet blue	34.58; −2.87; 1.54	635 nm (min.)/540 nm (max.)	490-520-570-670 nm (min.)/510 nm (max.)	Prussian blue + red *
49148	Courtesan kimono folds	Pink red	46.84; 20.61; 18.24	530 & 565 nm (abs.)	600 nm (infl.)/530 & 570 nm (min.)	Vermilion + cochineal
49225	Woman kimono collar	Light red	49.47; 26.48; 24.54	590 nm (infl.)	600 nm (infl.)	Vermilion
49225	Small bow (woman)	Red	50.22; 23.42; 20.69	596 nm (infl.)	600 nm (infl.)	Vermilion
49225	Big bow (woman)	Red	46.63; 29.17; 24.89	596 nm (infl.)	600 nm (infl.)	Vermilion
49225	Woman kimono	Orange red	53.91; 10.55; 22.23	590 nm (infl.)/560 & 660 nm (abs.)	590 nm (infl.)/660 nm (min.)	Vermilion + indigo
49225	Woman kimono (decor.)	Light pink	61.09; 12.98; 25.33	590 nm (infl.)	595 nm (infl.)	Vermilion (diluted)
49225	Woman kimono sleeve	Blue + pink	39.94; 2.18; 11.48	590 nm (infl.)/560 & 660 nm (abs.)	590 nm (infl.)/660 nm (min.)	Vermilion + indigo
49445	Fan	Light blue	62.92; −4.61; 16.45	550 nm (max.)	670 nm (min.)/560 nm (max.)	Prussian blue + *
49445	Fan design	Dark blue	48.52; −4.04; 9.79	550 nm (max.)	670 nm (min.)/560 nm (max.)	Prussian blue + *
49445	Kimono flowers	Violet	40.19; 2.32; 4.15	525 nm & 660 nm (min.)	520 nm & 670 nm (min.)	Prussian blue + vermilion
49445	Lips	Red	48.45; 19.5; 20.54	590 nm (infl.)	595 nm (infl.)	Vermilion
49868	Kimono (bottom)	Light red	53.97; 25.54; 23.44	530 nm (abs.)/580 nm (infl.)	520 nm (min.)/450–460 & 585 nm (infl.)	Red safflower
49868	Sleeve edge	Light red	53.15; 25.86; 20.89	530 nm (abs.)/580 nm (infl.)	520 nm (min.)/450–460 & 585 nm (infl.)	Red safflower
49868	*Obi* flowers	Orange	52.61; 23.05; 25.76	530 nm (abs.)/580 nm (infl.)	520 nm (min.)/450 & 585 nm (infl.)	Red safflower + yellow pigment (As sulphide)
49868	*Obi* background	Green	49.08; −9.15; 9.88		660 nm (min.)/520 nm (max.)	Indigo + yellow pigment (As sulphide)
49868	Kimono (bottom)	Violet	48.06; 1.29; 4.31	594 & 645 nm (abs.)	540 & 590 & 640 nm (min.)	Dayflower
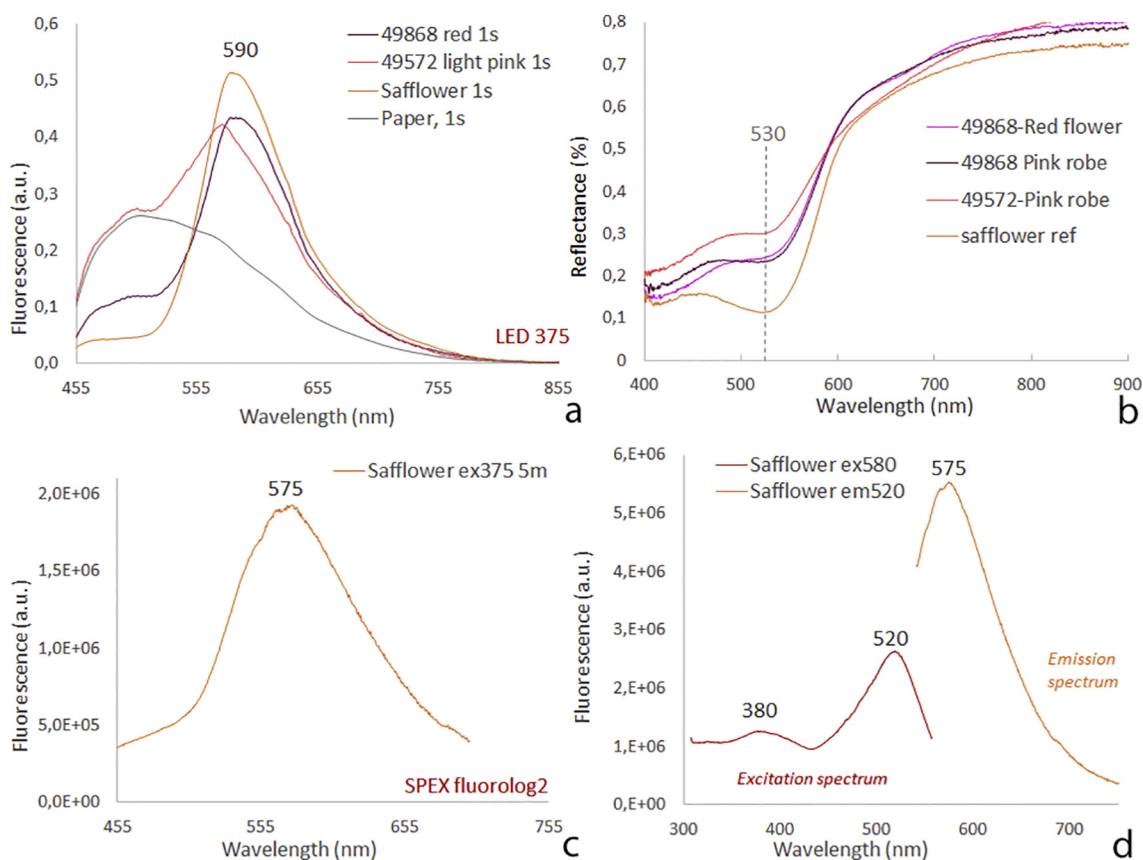
Fig. 5. Fluorescence spectra of organic red pigments of the printings 49868 and 49572 (λ_{em}375 nm) (a) and reflectance spectra (b) in the same measurement point, with the absorption band at 530 nm which confirmed the presence of red safflower. Fluorescence emission spectrum of red safflower obtained in the benchtop device at λ_{em}375 nm excitation wavelength (c). Excitation spectrum (observation wavelength λ_{obs}580 nm) and emission spectrum at λ_{em}520 nm measured in benchtop device (d), which allowed the identification of the fluorophore: the carthamin. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

around 580 and 675 nm, respectively (Fig. 3a). However, this maximum could be shifted towards short wavelengths because of the fluorescence of the binder.

Concerning blue colours, several products were used in Japanese printings. Azurite, *gunjo*, is a basic copper carbonate (2CuCO$_3$·Cu(OH)$_2$). Even mostly imported from Germany, it is also Japan native. Natural ultramarine was commonly used in Japan since the 17th c. AD [2]. Ultramarine, *ruri*, is a sulphur-containing sodium aluminium silicate and its natural form is lazurite. Its identification is rare; no source is known in Japan and it was probably imported by the Dutch [2]. Artificial ultramarine was first produced in France in 1828. Smalt, *hana-konjo*, used since the 16 or 17th c., is an artificially-made pigment rich in potassium glass and its blue colour is due to cobalt [2]. Smalt and azurite have particles sized too coarse to yield smooth colours in woodblock printings, so Prussian blue was a good alternative pigment to obtain blue hues [3]. Prussian blue, *bero*, *bero-ai* or *beroin*, is an artificial pigment, a ferric ferro-cyanide (Fe$_4$(Fe(CN)$_6$)$_3$·xH$_2$O), first made in Germany at the beginning of the 18th c. It is not mentioned in the list of traditional Japanese palettes, but it was imported by Dutch and Chinese in mid-18th c. for paintings [2,3]. At the end of the 18th c., an increasing demand for Prussian blue in Japan was observed and its use for printings was attested around 1820–30 [3]. Prussian blue was more expensive than indigo or dayflower, but it appeared to be more resistant in time and therefore it replaced them quickly [3].

Azurite, smalt and ultramarine spectra showed bands at 440 nm when they were excited at 285 nm (Fig. 3b), which can correspond to

rice starch fluoresce. The intensity was very low. Prussian blue did not show any fluorescence, as iron is known to be a fluorescence inhibitor [29].

Indigo, *ai*, is an organic colorant and the blue constituent is indigotin (C$_{16}$H$_{10}$O$_2$N$_2$), extracted from several species of plants: *Polygonum tinctorium* (from China), *Indigofera tinctoria* (from India and south of Asia) and *Isatis tinctoria* (from Europe), imported later. Indigo was used in Japan in paintings since the 8th c. AD. In the 19th c., the best indigo was imported from China to Japan [2]. Indigo is known to be a stable pigment.

Indigo was revealed by using the 375 nm LED and the fluorescence spectrum presented an emission at 740 nm due to indigotin (Fig. 3b). The maximum of fluorescence emission can vary from 720 to 740 nm depending on the binder, the mixture, *etc.* Romani et al. showed that indigo fluoresces at 730 nm on a medieval folio dated around 800 AD, and their published spectrum was in agreement with the fluorescence-emission reference spectrum of indigo mixed with gum Arabic [30].

Dayflower (*Commelina communis*), *tsuyukusa*, is a vegetable blue/purple dye. The colorant is extracted from the petals and stored in paper leaves known as *aigami* ("indigo paper"). It loses its colour and becomes grey in presence of moisture [5]. The flowering of dayflower, a hybridized dayflower (*Commelina communis* L. var. *hortensis*, Makino) occurs during summer [5]. Today the pigment is still produced using traditional techniques. The cultivation is rare in Europe and the picking season is only one month from middle July, because the flower needs relatively high temperature (30 °C) and, as blooming is in early
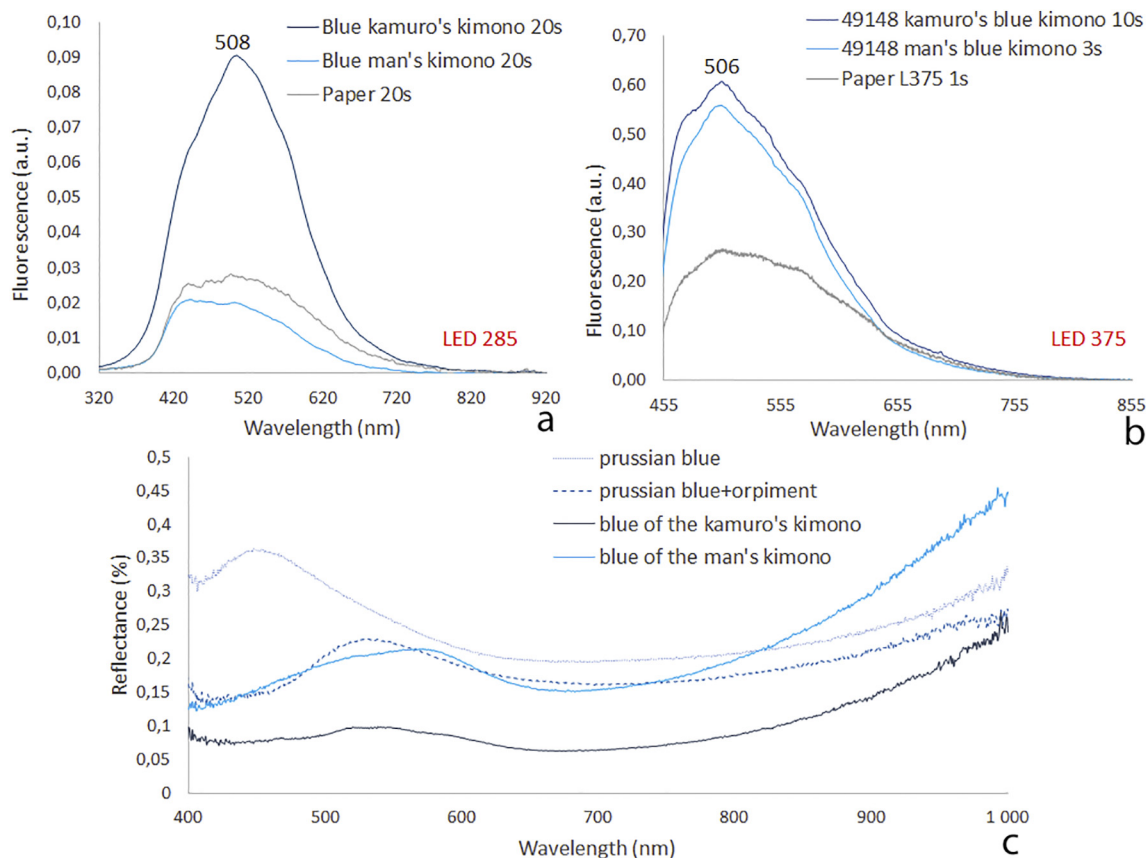
Fig. 6. Fluorescence emission obtained with both LEDs (a & b) and reflectance spectra (c) of the blue in the kimono of 49148 woodblock printing. No fluorescence due to a pigment was visible, only that of the paper appeared. Reflectance spectra indicated the presence of a mixture of Prussian blue, confirmed by infrared spectroscopy, and another red or yellow colour. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

morning, it is over before noon; the petals have to be picked from six o'clock in the morning [31]. For these limiting reasons, we have not been able to record its fluorescence spectrum yet. The pigment is a metalloanthocyanin (commelinin) composed of six molecules which have each an anthocyanin and a flavone and two atoms of magnesium [32]. In our knowledge, only reflectance spectra of dayflower have been published in an attempt to follow the fading of the dye in presence of light or moisture [4,5].

3.3. Red colours in the five woodblock printings selected for the study

Two red inorganic pigments were identified: vermilion and red lead. An orange-red pigment was used in the kamuro kimonos on a print by Koryūsai (49572). The artist is known for having used specially this colour [2]. The maximum of fluorescence emission band is at 580 nm, but it is located at 595 nm in the red lead reference (Fig. 4a). This shift towards shorter wavelengths can be explained by the important fluorescence due to the paper (455–555 nm). The use of this red pigment was confirmed by the reflectance spectra, obtained with both HSI and diffuse reflectance spectrometry, which showed an inflection point at 565 nm, attributed to red lead [33] (Table 2). The presence of Pb was also confirmed in the XRF spectra. Since, in the XRF spectra, the line at 10.5 keV could be considered as the Kα line of As and an interference with the Lα line of Pb, thus the Lβ line at 12.5 keV for Pb was considered and the PbLα/PbLβ intensity ratio was calculated in the red area and in the Japanese paper without red pigment. The ratio was

higher in the red pigment than in the Japanese paper, and then the presence of Pb was verified.

Another inorganic pigment concerned the printings by Utamaro, where bright red was used for a woman kimono (49225) and for the lips of the characters (49225 and 49445). Fluorescence spectra indicate a maximum at 607 nm, which can be attributed to vermilion (Fig. 4b). This was confirmed by the reflectance spectra which showed an inflection point near to 600 nm [33] (Table 2), and by the presence of Hg (Hg Lα line, shown at 9.98 keV and Hg Lb line at 11.82 keV) in only the XRF spectra of the red area measurement.

Two red organic pigments had been found. The same pigment was identified in the pink edges of the kimono of the printing by Eisen (49868) and in the light pink of the courtesan kimono in that by Koryūsai (49572). The fluorescence-maximum bands (580–590 nm) (Fig. 5a) matched with red safflower, even if the fluorescence contribution due to the paper was higher for the light-pink pigment of the kimono (49572), and the paper fluorescence shifted the emission maximum towards shorter wavelengths. These results were confirmed by the reflectance spectra which showed an absorption band at 530 nm, characteristic of red safflower (Fig. 5b) [33].

In reference samples, red safflower mixed with rice starch on quartz slide showed a fluorescence maximum at 575 nm, obtained with both the portable and the benchtop devices (Fig. 5a and c). However, it is worth noting that the analysis time was 5 s with the mobile device, and 5 min with the benchtop system. Carthamin was identified as the main chromophore of safflower. This chromophore absorbed at 520 nm [6]
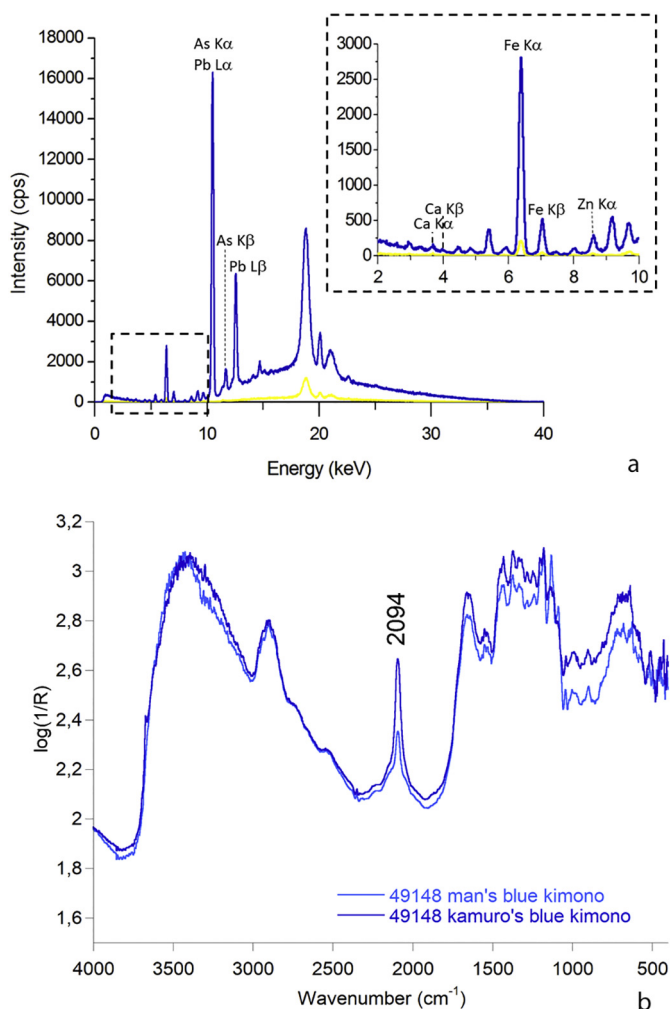
Fig. 7. a) ED-XRF spectra of the Japanese paper (yellow spectrum) and the blue of the woman kimono (blue spectrum) in the printing by Koryūsai 49148; b) infrared spectra in reflection mode of the blue in the kimono of 49148 woodblock printing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and, when it was excited at this wavelength, the maximum fluorescence in the emission spectrum was centred at 575 nm (Fig. 5c and d). This indicated that a LED at 520 nm would be more suitable to reveal the fluorescence of the safflower.

In the other printing by Koryūsai (49148), an insect-based colour seemed to have been used in the red-pink kimonos. The fluorescence of the paper shifted the characteristic band of the cochineal towards shorter wavelengths. The band maximum shifted from 640 nm in our reference to 610 nm. However, the reflectance spectra presented two absorption bands at 530 and 565 nm (Table 2), characteristic of this insect-based pigment, and thus they confirmed the use of cochineal [25,33].

3.4. Blue colours in the five woodblock printings selected for the study

On the second print by Koryūsai (49148), there were at least two different blue colours: a dark greenish blue in the kamuro kimono, and a light greenish blue in the man kimono. The fluorescence spectra obtained with both LEDs showed a maximum around 508 nm (Fig. 6a and b), which corresponded to the paper fluorescence. In the reference

samples, the maximum was pointed at 440 nm for azurite, smalt and ultramarine (Fig. 3b). Since no fluorescence band was observed at that position in the spectra acquired on these blue areas, Prussian blue or another blue pigment not yet registered in our database could have been used. Regarding the reflectance spectra, Prussian blue had a maximum of reflectance at 450 nm and no clear minimum band (Fig. 6c), that did not completely match with those spectra obtained on the printings. The spectra obtained in the blues of the kamuro kimono and in the man kimono presented a large absorption band, that started between 550 and 600 nm and finished slightly after 800 nm (Fig. 6c). However, the spectra matched better with the mixture of Prussian blue and a yellow pigment. The characteristic Kα line at 6.4 keV and Kβ line at 7.08 keV of Fe, the Lα line at 10.5 keV and Lβ line at 12.5 keV of Pb, the Kα line at 10.5 keV and the Kβ line at 11.8 keV of As, and finally the line Kα at 8.6 keV of Zn were found in the blue areas of the kamuro kimono measured by HHED-XRF. As it can be seen in Fig. 7a, As and Pb characteristic lines appeared only in the blue area (blue spectrum of Fig. 7a), not in the Japanese paper (yellow spectrum in Fig. 7a), and the Kα and Kβ lines of Fe had lower intensity (around 210 cps for Kα) on the Japanese paper than on the kamuro kimono of the print by Koryūsai (49148). The Kα line of Zn was not found in ED-XRF spectra of the man kimono. Likely, in the two blue colours, Prussian blue seemed to be mixed with a yellow pigment. The presence of both characteristic lines of As in the ED-XRF spectra could refer to orpiment (As_2S_3). The presence of Pb can come from details in the drawing of the kimonos. Finally, the identification of Prussian blue was also confirmed by Raman spectroscopy which was identified for its characteristic Raman band at 2151 cm^{-1}, which is caused by the ν(C≡N) stretch and mostly by infrared spectroscopic analyses. Indeed, Prussian blue ($Fe_4[Fe(CN)_6]_3 \cdot xH_2O$) exhibited a very specific signature in the infrared range. An intense band at about 2090 cm^{-1} was observed in the IR reflectance spectra, ascribed to the cyano stretching vibration ν(C≡N) (Fig. 7b) [34].

In conclusion, Prussian blue was identified by infrared reflectance and Raman spectroscopy; the ED-XRF spectra showed the presence of As and Fe, which confirmed the hypothesis based on reflectance spectra whose information was insufficient to verify the nature of the blue pigment. In this case, fluorimetry only made possible to propose an identification by exclusion.

Concerning the printing by Utamaro (49225), with both LEDs the fluorescence maximum around 500 nm could only be attributed to the paper (Fig. 8a and b). The absence of a band relative to a blue pigment could also suggest the presence of Prussian blue. However, a shoulder around 725 nm was observed with the 375 nm LED, which can be attributed to indigo (Fig. 8b). In this print, the reflectance spectra also suggested the use of several pigments, the blue colour being applied on a light-red pigment (Fig. 8c). The reflectance spectra could refer to the presence of indigo mixed with vermilion and another unidentified blue pigment (shoulder around 550 nm). The presence of the Kα line at 8.04 keV of Cu in the ED-XRF spectra could be explained by the presence of azurite ($Cu_3(CO_3)_2(OH)_2$), but also by impurities coming from the board on which was placed the paper of this printing.

For the second woodblock printing by Utamaro (49445), two blue hues were employed: a dark-purple blue in the woman kimono, and a light blue in the fan. Despite the difficulty for interpreting fluorescence or reflectance spectra, ED-XRF analyses indicated the presence of Fe in both blue hues, which can be attributed to Prussian blue, and Hg in the dark-purple blue in the woman kimono, which could be a mixture of the Prussian blue with a red pigment such as vermilion, the mixture visible on the images under the microscope of Raman (Fig. 9) (Table 2). Thanks to the reflectance spectra and the elemental HHED-XRF analysis, this red pigment was identified as vermilion.
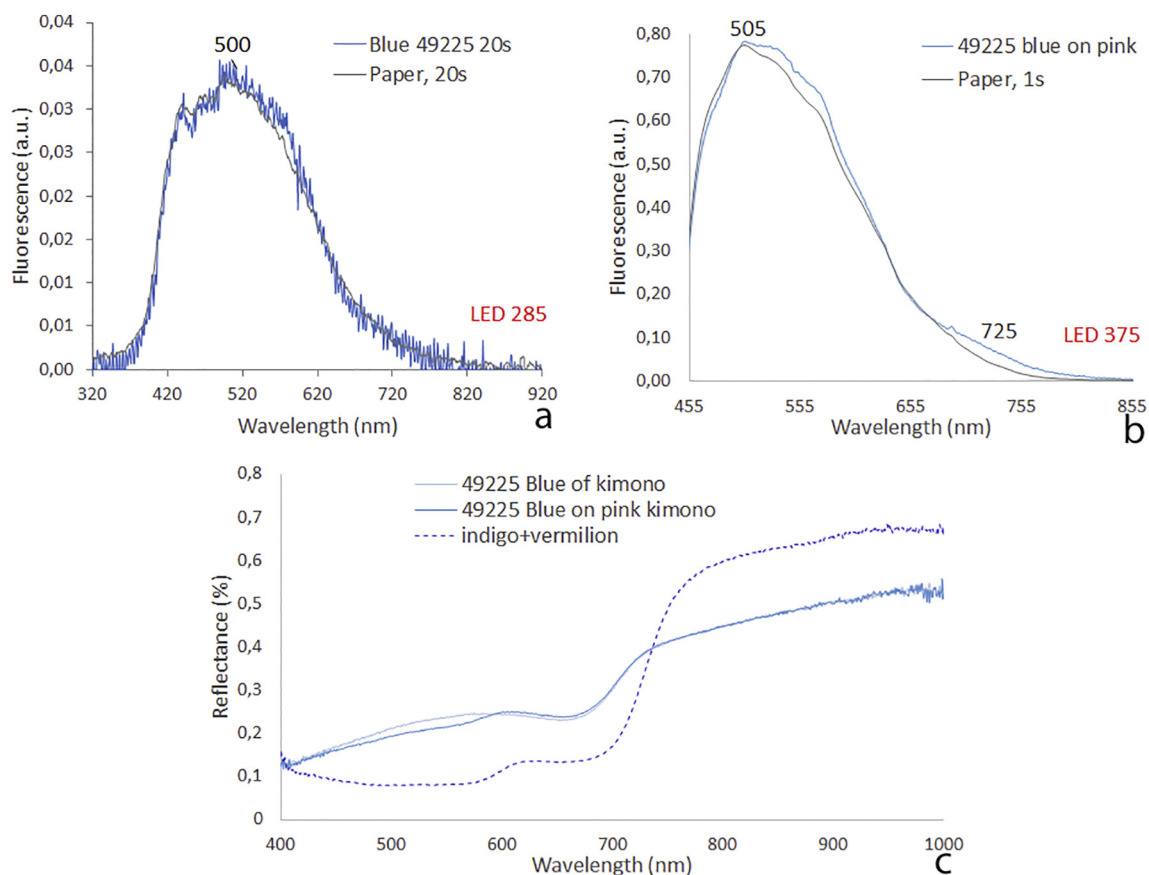
Fig. 8. Fluorescence emission obtained with both different LEDs (a & b) and reflectance spectra (c) of the blue in the kimono in the Utamaro printing 49225. A small fluorescence shoulder around 725 nm could refer to indigo. Reflectance spectra indicated a mixture of blue and red pigments, perhaps indigo, Prussian blue and vermilion. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
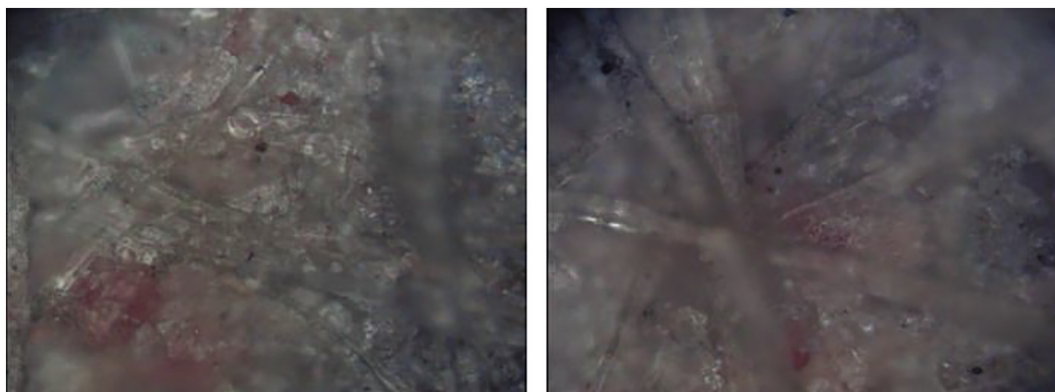
Fig. 9. Photomicrographs (×50) of the dark-purple blue surface of 49,148 woodblock printing (image length: 0.5 mm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.5. Purple colours in the five woodblock printings selected for the study

Among the five printings, only that by Eisen (49868) presented a purple colour. The fluorescence spectrum obtained on the purple in the kimono bottom showed several bands (Fig. 10a). The band centred at 502 nm was due to the paper and the binder, and bands at 560, 610 and 685 nm were attributed to the pigments, surely shifted towards shorter wavelengths due to the paper fluorescence (Fig. 10a). The band at 685 nm may be due to the fluorescence of chlorophyll residues coming from flavonoids of the leaves or flowers used during the making of the pigment [25,35]. As regards the reflectance spectrum, the two absorption bands at 594 and 645 nm indicated the presence of dayflower (Fig. 10b) [4,5,36]. At this moment, the reference fluorescence spectrum has not been recorded for this colorant, which does not allow to
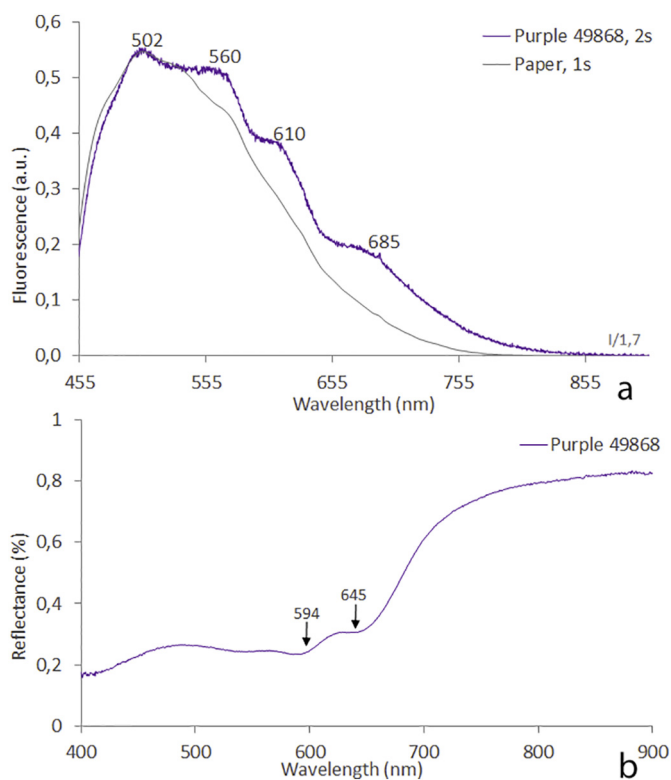
Fig. 10. Fluorescence emission λ_{em}375 nm (a) and reflectance spectra (b) of the purple colours of the Eisen printing 49868. Several bands appeared in the fluorescence spectrum and they could refer to the paper and the pigment. In the reflectance spectrum, the two absorption bands referred to dayflower [4,5]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

certify the use of dayflower. However, the reflectance spectrum confirmed the identification of this dye in comparison with published spectra of previous studies where two absorption bands at 590 and 650 nm appeared [4,5]. In the ED-XRF spectra of this colour, the same elements that in the Japanese used paper were found, which could be attributed to an organic origin of this pigment.

To obtain a purple colour, several red and blue pigments combinations were possible. From an analytical point of view, mixtures made difficult the interpretation of fluorescence bands. For example, in vermilion/indigo mixtures excited at 375 nm, the fluorescence bands of each pigment were shifted towards shorter wavelengths. Comparing the reference fluorescence emission spectra of a single pigment and mixtures of two of them, the band at 730 nm of the indigo shifted towards 725 nm, and the band of vermilion at 612 nm shifted to 590 nm (Fig. 11a). For indigo/red safflower mixtures, the fluorescence maximum of indigo did not change, but safflower maximum shifted from 587 to 580 nm (Fig. 11b). To differentiate between vermilion (590 nm) and red safflower (580 nm) can be difficult considering only the fluorescence maximum. In this case, one solution was to consider also the fluorescence intensity and to compare the analysis time. For indigo/safflower mixture, the analysis time was short (1 s) and the band was intense, while for the indigo/vermilion mixture the time of analysis was longer (about 30 s) and the spectrum presented less fluorescence (Fig. 11c).

Some post-treatments were tested (Principal Component Analysis (PCA), subtraction, deconvolution, or Kubelka-Munk (K-M)) in order to distinguish pigments and to remove the contribution of the support and the binder. The main treatment used for this type of analysis was the K-M theory, which consists in removing the contribution due to the absorption and auto-absorption of the pigments, it worked well when only one pigment was used and for an opaque layer. In the majority of the tests, a shift of about 10 nm towards shorter wavelengths was observed. This result was in accordance with observations in other researches [25,35,37] and it indicated a partial re-absorption by the pigment itself. This work was in progress to determine the best treatment to be applied on the case of the Japanese printings.

4. Conclusions

On this set of five Japanese woodblock printings, Prussian blue and indigo were used alone or in mixtures with red colours. The presence of Prussian blue was interesting because it can question the dating of the prints. Prussian blue was first introduced in Japan in the mid-18th c. for the paintings and in the beginning of the 19th c. for the prints. This information indicated that printings attributed at Koryūsai and Utamaro production could be reprints of the 19th or 20th c.

For the red colours, cochineal, red lead and red safflower were identified on Koryūsai printings. Vermilion was identified on Utamaro prints, on the lips and the kimono. Safflower was identified on kimonos on one by Koryūsai and on that by Eisen.

For purple colour, dayflower seemed to have been used on the Eisen print. Looking into details on the purple colour, it can be observed a grey colour which matched well with the hypothesis of the use of dayflower, known to become grey in presence of moisture.

Reflectance spectroscopy and spectrofluorimetry provided a good combination for the non-destructive analysis of fragile paintings. FORS and LED μSF presented the advantage of being mobile and rapid techniques. As concerns LED μSF, most of the measurements required 1 or 2 s for this application. It was a good complementary technique with reflectance spectroscopy and a good help for organic materials identification.

Finally, a special effort was done in this project to enlarge the database of fluorescence emission spectra of colorant mixtures and to improve data treatments. For a better identification of the materials, one solution would be to use a wider range of LEDs as excitation sources, to develop a post-treatment of the spectra to remove the fluorescence due to the paper and the binder, and then to correct the spectra in order to obtain the intrinsic fluorescence of the pigment.

There is no single non-invasive method for the identification of the materials in paintings. All analytical methods have advantages and limitations, *i.e.* fluorescence perturbs Raman spectra, XRF is a method for elementary analysis of inorganic compounds, IR spectroscopy does not always discriminate organic materials, and reflectance spectroscopy is difficult to interpret in the case of mixture of pigments, binders and varnishes. That is why the LED μSF is a new method for the identification of organic and inorganic products and it is a good help in combination with more conventional non-invasive methods for the application on paintings materials.

The advantages of the method are: 1) a large database of materials can be built in similar conditions by LED μSF, 2) in simple painting layers (one pigment type) the identification is rather good, as proved in some previous papers, 3) in complex paintings we get some information, which can be combined with other analytical techniques, and which can lead to accurate identification with data post-treatment, 4) a new device will be improved, *i.e.* having a wide choice of LED sources, in order to excite some specific fluorophores and then allowing a good discrimination between close materials.
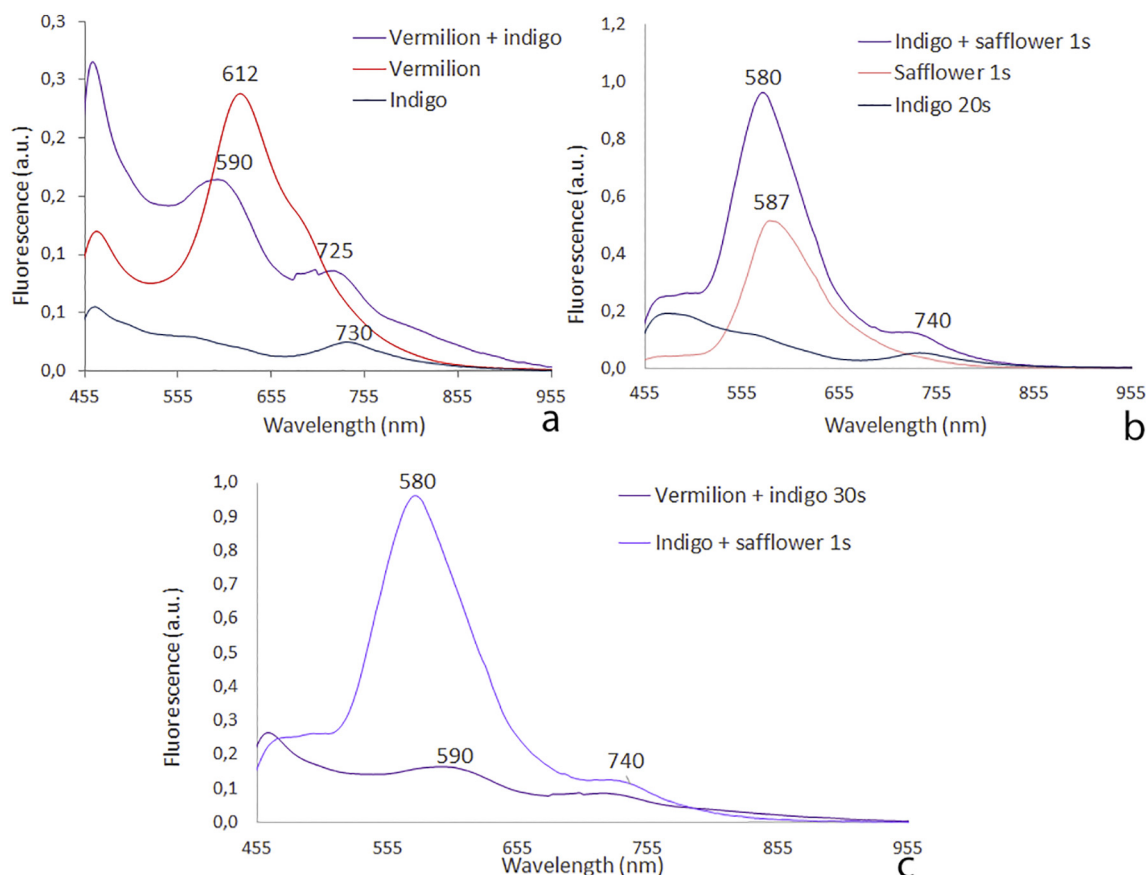
Fig. 11. Fluorescence emission spectra (λ_{em}375 nm) of purple colours from mixtures: vermilion + indigo (a), indigo + red safflower (b), and the comparison of the two mixtures (c). To explain the difficulty of identification of each pigment in the case of mixtures, the fluorescence spectra of each pigment were also included. The mixture shifted the characteristic bands and it made difficult the identification. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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