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

A. Mounier[a,*], G. Le Bourdon[b], C. Aupetit[b], S. Lazare[b], C. Biron[a], J. Pérez-Arantegui[c], D. Almazán[d], J. Aramendia[e], N. Prieto-Taboada[e], S. Fdez-Ortiz de Vallejuelo[e], F. Daniel[a]

[a] *IRAMAT-CRPAA. Institut de Recherche sur les Archéomatériaux (IRAMAT), UMR CNRS 5060, Centre de Recherche en Physique Appliquée à l'Archéologie (CRPAA) University Bordeaux Montaigne, Maison de l'archéologie, Esplanade des Antilles, 33607 Pessac, France*
[b] *ISM. Institut des Sciences Moléculaires, CNRS/University of Bordeaux - UMR 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. Pedro Cerbuna, 12. 50009 Zaragoza, Spain*
[d] *Departamento de Historia del Arte. Grupo "Japón", Universidad de Zaragoza, Pedro Cerbuna, 12. 50009 Zaragoza, Spain*
[e] *Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), 48940 Leioa, Spain*

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ABSTRACT

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),

* Corresponding author.
*E-mail address:* mounieraurelie33@yahoo.fr (A. Mounier).

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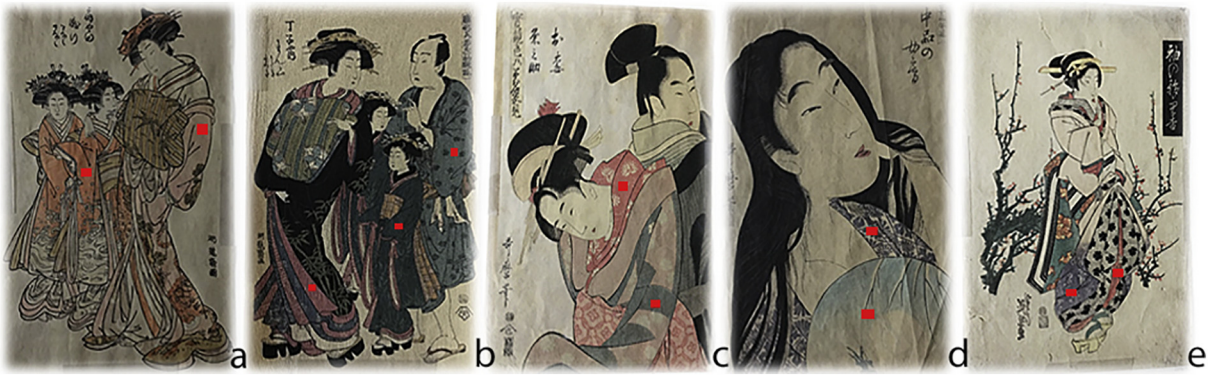


**Fig. 1.** Japanese printings in the Federico Torralba collection (Museum of Zaragoza, Spain), with the point fluorimetric measurements. a) 49572, Koryūsai: The courtesan Takigawa of the *Ogi-ya* house with two kamuro. b) 49148, Koryūsai: The Mazan courtesan of the *Choji-ya* house with the kamuro Utagi 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