Accepted Manuscript

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PII:	S0026-265X(17)30899-8
DOI:	doi:10.1016/j.microc.2018.02.015
Reference:	MICROC 3054
To appear in:	*Microchemical Journal*
Received date:	31 August 2017
Revised date:	25 January 2018
Accepted date:	15 February 2018

Please cite this article as: Josefina Pérez-Arantegui, David Rupérez, David Almazán, Nerea Díez-de-Pinos , Colours and pigments in late ukiyo-e art works: A preliminary non-invasive study of Japanese woodblock prints to interpret hyperspectral images using in-situ point-by-point diffuse reflectance spectroscopy. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Microc(2017), doi:10.1016/j.microc.2018.02.015

Colours and pigments in late *ukiyo-e* art works: a preliminary non-invasive study of Japanese woodblock prints to interpret hyperspectral images using in-situ point-by-point Diffuse Reflectance Spectroscopy

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ABSTRACT

Dyes and pigments have been used in traditional Japanese woodblock printings in the *ukiyo-e* style for several centuries. However, the possible introduction of new European pigments and the extraordinary quality of the works of the later period led to take a keen interest in the analytical study of these *ukiyo-e* prints manufactured at the end of the 19th century. The present research discusses the analytical results of the series *Bijin jūni kagetsu* ("Beauties in the Twelve Months") by Shuntei, dated in 1898-1899. Due to the characteristics of this type of artworks, diffuse reflectance spectroscopy (DRS) has been chosen as a portable, non-invasive analytical technique to identify pigments and colorants used in the woodblock prints. The analytical possibilities offered by the in-situ point-by-point DRS as a preliminary tool to better interpret hyperspectral imaging (HSI) data were highlighted. Reflectance spectra of more than 190 points sampled throughout the artwork were recorded between 360 and 740 nm, and characterised. Throughout an statistical classification of the spectral data using unsupervised pattern recognition methods, twenty-two different colour composition was confirmed. These groups of reflectance spectra were then identified according the presence of characteristic maxima, minima and inflection points in every spectrum. Some micro-samples extracted from the pigments still remained in a woodblock (used for a 20th century print) were analysed by FESEM-EDS to better interpret some reflectance spectra. Traditional Japanese pigments (like vermilion, red lead, and indigo) and synthetic materials introduced in the 18th and 19th centuries (Prussian blue, synthetic arsenic sulphides, eosin, and methyl violet or crystal violet) were identified in the Shuntei's series colours, together with some mixtures of pigments to prepare blue, green, orange and purple. Based on these twenty-two reflectance patterns, the point-by-point spectra make easier the task of interpreting the very complex HSI data, and reduce the time of treatment and interpretation required by HSI.

KEYWORDS

Reflectance Spectroscopy; Hyperspectral imaging; non-invasive; in situ; Japanese woodblock prints; pigments

1. INTRODUCTION

Many colorants and pigments have been used in traditional Japanese woodblock prints (a commercial form of art) for centuries, from the late 16th century AD to the beginning of the 20th century, but here we want to emphasize those used in prints in the *ukiyo-e* style [1]. Since different dyes and pigments were used to produce these prints, changing over the centuries, the knowledge of these materials can be very important for the history of *ukiyo-e* prints. Identification of compounds used in woodblock prints can highlight new data to confirm the use of traditional materials and the introduction of new ones, especially those imported pigments proving commercial contacts [2]. Moreover, characterisation of the pigments and study of their spectral behaviour, together with colour pattern of these materials, can be an important tool to track pigment evolution and conservation treatments [3-5].

Paintings and prints in the *ukiyo-e* style reproduce the everyday life of ordinary people: the so-called "floating world" (Fig. 1). Their chronology includes the Momoyama period (1573-1615) since the late 16th century, the Edo period (1615-1868) between the 17th and 19th centuries, and the early years of the Meiji period (1868-1912) in the 19th century [2]. Works from the end of the 19th century (Meiji era) have been sometimes unjustly considered to correspond to a declining period; however, the introduction of new pigments and the extraordinary quality of the works could demonstrate a Silver Age of Japanese *ukiyo-e*. Several materials for colouring (dyes and pigments) were used throughout all the period, like vermilion, red lead or indigo, but other compounds were not used during the early years, and were introduced in the later periods, for instance, orpiment, Prussian blue or ultramarine [2].

We can find the expression of the *ukiyo-e* style in the production of both paintings and woodblock prints, but in this case our interest was only focused on the prints. Woodblock printing was the method for printing books and texts, and for producing art in Japan. Images could be monochrome (only using a black ink), or reproduced in few colours (two or three), but they became really polychrome at the later periods, sometimes with the use of more than ten colours [1]. In the production of a woodblock print, the image was first drawn on Japanese paper, and the woodblocks were chiseled based on these drawing outlines. Pigments were directly applied and spread on the woodblock, using a brush or brushes, and it was then pressed onto the new paper to create a very-thin coloured layer of the design. A specific woodblock was prepared for each colour. The use of two registration marks (*kentō*) carved into the woodblock helped to place the paper sheet and to produce multiple colours with precision [1].

Pigments on woodblock prints generally require different analytical methods from those used in painting studies, because the amount of coloured material available from a print is substantially smaller due to the very-thin pigmented layer and the sub-micron particle size of some pigments. Also the fragility of these objects must be considered. This is why non-invasive analytical techniques have been chosen to characterise dyes and pigments in Japanese prints. Diffuse Reflectance Spectroscopy (DRS) was chosen in several analytical studies [3-10]. Reflectance spectroscopy is a well-established technique for the characterization of pigments [7, 11-15]. DRS has three areas of application: the identification of materials, measuring colour changes, and colour-matching. It offers some advantages: *in-situ* non-invasive methodology, inexpensive portable instruments, very short acquisition times, none exposure to heat or high-energy beams, avoiding mechanical stress of the artwork support, and notably the high degree of selectivity for colorants. Despite these potentialities, poorer wavelength resolution and limited 'fingerprinting' ability in comparison with techniques such as Fourier transform infrared (FTIR) spectroscopy or Raman spectrometry are also some disadvantages.

FTIR spectroscopy offers spectra with best wavelength resolution, but inorganic pigment identification is limited, the contact with the sample is not permitted for the study of prints, and the FTIR signal of Japanese paper and binders is usually predominant in the spectrum, making hard the identification of the pigments [16].

Raman spectroscopy is with no doubt the analytical method with the best diagnostic power for pigment identification [17-19]. However, it has some drawbacks that limit its application in Japanese prints: it requests lengthy times of analysis and, then, local heating on the paper can be caused, induced by laser irradiation; also dyes and lakes are generally poor Raman scatterers and their identification is very difficult or even impossible, at least in a non-invasive approach; and particularly the interferences produced by fluorescence emission (because of pigments, paper and/or the binder in Japanese prints) increase background signal and it drastically decreases sensitivity, reducing the possibility of identification. Surface Enhanced Raman Scattering (SERS) seems to be successfully used for analysis of Japanese prints [20-21], since the enhancement of the amplitude of Raman scattering can be the solution to the problem of identifying very low concentrations of pigments in micro-samples, but not all museums or collections allow the necessary micro-sampling or the use of extracting gels.

Among other non-invasive analytical techniques with good diagnostic power, X-ray Fluorescence spectrometry (XRF) has been frequently applied to pigment analysis, also in Japanese artworks [22]. Nevertheless, some limitations for the identification are due to the fact that X-rays go right through the paper, not only the coloured layer, including emission lines in the X-ray spectrum from elements that belong to pigments, paper and even the support placed under the print. Moreover, XRF is an elemental technique which does not provide unique pigment identification, and it cannot be used to identify most organic compounds.

On the other hand, fluorescence molecular emission of some pigments, that was a drawback in Raman spectroscopy, has been also used for the characterisation of some compounds in Japanese prints, with good results for some red, blue and yellow pigments [9, 23].

Diffuse Reflectance Spectroscopy (DRS) was then chosen as a portable, non-invasive analytical technique to identify pigments and colorants used in these woodblock prints. Hyperspectral Imaging (HSI) can be considered as a combination of digital imaging and Reflectance Spectroscopy. This powerful tool for non-invasive material characterisation provides an in-situ complete examination of the work of art (even of large areas), but the application of HSI for the identification of dyes and pigments needs a complex treatment of the reflectance spectra measured in every image element, by comparison of reference pigments with the different observed spectra [24-26]. The quality of the hyperspectral data interpretation is based on the quality of the reference database. For the investigation of Shuntei's pigments, in a work with so many colours and hues, the preliminary use of point-by-point DRS can provide a previous knowledge of the possible materials to attain, then, the correct classification and identification of the pigments in these prints by HSI.

Therefore, the analytical possibilities offered by the in-situ point-by-point DRS as a preliminary tool to better interpret hyperspectral data were evaluated in the present paper. As part of a longer project for the study of the Japanese printing collection at the Museum of Zaragoza, the aims of the analytical research were to identify pigments and colorants used in woodblock prints from the late *ukiyo-e* period, and to verify the use of some historical materials and the introduction of new ones. Reflectance spectroscopic studies will also contribute to establish a colour pattern for future investigations of the pigment evolution and the conservation treatments.

2. MATERIALS & METHODS

2.1. The studied woodblock prints

This study presents the results of the series *Bijin jūni kagetsu* 美人十二ヶ月 ("Beauties in the Twelve Months") by Miyagawa Shuntei (Fig. 1), edited in Tokyo and dated at the end of the 19th century, in 1898-1899 [27]. The series was published by Matsuki Heikichi 松木平吉 (1871-1931), owner of Daikokuya 大黒屋.

Miyagawa Shuntei 宮川春汀 (1873-1914) was a neotraditional *ukiyo-e* illustrator specializing in the genre of *bijin-ga* (portraits of beautiful women) of the new bourgeois class of the Meiji era (1868-1912). Shuntei was born in Hatake (Aichi prefecture). When he was 18 years old went to Tokyo, studied with Tomioka Eisen (1864-1905) and worked as illustrator for several publishers [28]. Due to the quality of his woodblock prints he had some international recognition [29]. Other authors working in the same period, like Tsukioka Yoshitoshi, Yōshū Chikanobu, Mizuno Toshikata or Ogata Gekkō, were more famous than Miyagawa Shuntei, but his woodblock prints were edited in Tokyo by Matsuki Heikichi and Akiyama Buemon, the best publishers in the Meiji era.

In the series *Bijin jūni kagetsu* ("Beauties in the Twelve Months"), Shuntei reproduces twelve triptychs, one for each month, from January to December: no. 1 *Hago* 羽子, no. 2 *Kanbai* 観梅, no. 3 *Sakura gari* 桜が, no. 4 *Botan* 牡丹, no. 5 *Fujimi* 藤見, no. 6 *Shōbu* 菖蒲, no. 7 *Kaisuiyoku* 海水浴, no. 8 *Tsukimi* 月見, no. 9 *Akikusa* 秋くさ, no. 10 *Momiji* 紅葉, no. 11 *Yomeiri* 嫁入, and no. 12 *Yukimi* ゆき見. Women and children wear traditional Japanese kimono clothing at their leisure time in beautiful landscaped gardens. In Fig. 1 we can see one of these printings: no. 11 November, the preparation for a wedding. This masterpiece has a traditional theme and a great technical quality. Heikichi, the publisher, sought to raise the quality of the woodcut and used traditional and new colorants and pigments. Even there are pigments adorned with luxurious metal powders and sophisticated printing techniques like *bokashi* (creating a gradation) and *karazuri* (*gauffrage* or embossing).

Complete series of Japanese woodblock prints are very rare in Spanish collections. *Bijin jūni kagetsu* was property of Federico Torralba (1913-2012) [30] and since 2002 belongs to the Museum of Zaragoza (catalogue number 49939), to the Oriental Asia Collection. Triptychs are bound in *orihon* system (*nishiki-e ōban* triptychs: 35.6 cm. x 73.2 cm), like a concertina album. The series in Torralba collection contains the twelve triptychs plus the table of contents. This series has never been framed. For this reason, pigments and colorants are in very good condition and there have been no problems with ultraviolet light. These woodblock prints have only been displayed twice: in the exhibition *Cien años de gráfica japonesa* ("A Hundred Years of Japanese Graphic", Pablo Gargallo Museum, Zaragoza, 1982) and in *La fascinación por el País del Sol Naciente* ("Fascination for the Country of the Rising Sun", Museum of Zaragoza, 2013). Currently *Bijin jūni kagetsu* is not exhibited.

Because the possibility of micro-sampling the Shuntei's series was completely excluded, the opportunity to analyse some pigment microsamples taken from nine woodblocks used to print a Japanese design dated at the beginning of the 20th century (private collection) was also exploited to understand some reflectance spectra of blue and orange-yellow areas. The analytical results were obtained by Field-Emission Scanning Electron Microscopy (FESEM) with Energy-Dispersive Spectrometry (EDS); analyses were performed with a Merlin^{TM} FESEM microscope equipped with a Gemini column (both from Carl Zeiss Nano Technology

Systems, Germany), and coupled with an X-Max X-Ray microanalyzer (Oxford Instruments, UK). Microsamples (with diameter less than 1 mm) were collected with a scalpel from woodblock cavities, mounted in aluminium holders using carbon adhesive tape, coated with carbon and fixed to the FESEM holder.

2.2. Diffuse reflectance spectroscopy measurements

Point-by-point DRS has been chosen as a portable, non-invasive analytical technique to identify pigments and colorants used in these woodblock prints. We performed the in-situ study by direct measurement in the museum, in a controlled environment and protection. Canson® papers were used to put the contact spectrophotometer not directly on the print, and a Melinex® (PET) film was used to protect the coloured area in every measurement, avoiding any damage of the Japanese prints.

Colour and reflectance spectra were measured point-by-point in the coloured areas of the prints. Reflectance UV-Vis spectra were recorded using a Minolta CM-2600d model portable spectrophotometer (Konica Minolta, Germany), equipped with a 52-mm barium sulphate integrating sphere, dual-beam geometry, di:8°, de:8°, a 360-740 nm wavelength range (10-nm intervals), and irradiating a 3-mm diameter area. The standard illuminant was D65, using a CIE 1964 10° standard observer. A barium-sulphate plate was used as white reference to calibrate reflectance spectra. From the dispersion of both reflectance measurements (RSCI, reflectance specular component included; and RSCE, reflectance specular component excluded), colour coordinates (L^*, a^*, b^*) were calculated according to the International Commission on Illumination (usually known as the CIE, *Commission Internationale de l'Eclairage*), using the Spectramagic NX software (Konica Minolta). In the (L*, a*, b*) space, defined by CIE as uniform colour space, the L^* measure represents the perceived lightness from 0.01 for black to 100.00 for a diffuse white, and the a^* and b^* dimensions, which represent red–green and yellow–blue perceptions, respectively, include the information regarding chromaticity. The spectra (360-740 nm) were recorded in more than 190 points (areas of 3-mm diameter), and throughout the complete artwork.

In order to compare the results obtained on Shuntei's work, a reference database of some traditional and modern pigments used in Japanese woodblock printings was prepared in our laboratory (a chart with 108 colours printed on Japanese paper: 28 pigments, alone and mixed with two different whites, and 12 mixtures of pigments in two proportions) and analysed using the same protocol. The pigments used to prepare this database were purchased to Kremer Pigmente GmbH & Co. KG (Germany), and Sigma-Aldrich (now Merck, Germany). In our reference pigment database, the spectrometric measurements were taken protecting also the chart with the Melinex® film in order to work in comparable conditions. Because of the presence of the polymer surface in both measurements (in Japanese and reference pigments), most of the specular effects came from this protection and not from the pigment surface; then, we found more correct to compare only the RSCE measurements. As well as the comparison with our reference database, some spectra measured in Shuntei's woodblock prints were also contrasted with other published reflectance spectra [13-15].

Due to the high number of measured data, all the results were statistically treated to compare and to group them and to evaluate their similarities, performing multivariable classification treatments (IBM SPSS Statistics, v. 22): Principal Component Analysis (PCA) and Hierarchical cluster analysis were used as methods of unsupervised pattern recognition. Also first and second derivatives of the spectra were calculated to obtain the exact wavelength position for maxima, minima and inflection points of the reflectance spectra, considered as the main spectrometric features of every pigment and used to compare them with our reference database [11].

2.3. Hyperspectral imaging

The hyperspectral imaging VNIR system (SPECIM, Finland) is composed of the V10E imSpector spectrograph (CCD camera, 30 fps, 1600×1200 pixels, 400 to 1000 nm) and the mirror scanner (optimized from 380 to 1700 nm, field of view: 80×30°, and scan speed between 0.01 and 25°/s). The spectral camera has a slit of 30 µm (spectral resolution 2.8 nm, numerical aperture F/2.4), and it uses a Xenoplan 1.4/17 lens (Schneider, Kreuznach, Germany) with a focal length of 17.6 mm. The hyperspectral system uses “a mirror-scanning” technique adapted to studying reduced areas [26]. The scan speed of the mirror scanner was optimized in order to obtain good resolved images but avoiding long-time exposures to the halogen lamps. Scan angles of 40 and 50° were used. A calibrated diffuse reflectance target (Spectralon, by Labsphere, USA) was used to calibrate the resulting spectra. The treatment of the datacube was performed with ENVI 5.1+IDL software.

3. RESULTS AND DISCUSSION

The work of Shuntei was edited with a splendid variety of colours and hues. The Japanese editor used very different pigments and a rich palette to print the triptychs of Shuntei (from red to pink and violet, brown, orange or yellow, and green or blue). This richness of colours can be verified in Fig. 2, where the colours parameters (b^* *vs*. a^*) are represented for all the analysed points.

Hyperspectral imaging allowed us to obtain images of the triptychs in the visible and near infrared (NIR) ranges (400-1000 nm). The complexity of these images can be observed in Fig. 3, where a section of the March triptych is represented in a red-green-blue (RGB) image (R: 640 nm; G: 550 nm; B: 460 nm) from the HSI datacube, and in an infrared false-colour

(IRFC) image displayed by selecting an infrared band instead of the red band, and selecting two others in the visible range for the false green and blue bands (R: 900 nm; G: 650 nm; B: 550 nm). The mathematical treatment of this datacube to interpret and classify the different colours in March can give more than 30 endmembers, hence the preliminary study by point-to-point DRS will help to reveal some of the pigments and to complete the reference database.

The analytical results of the DRS study of Shuntei's triptychs are summarised in Table 1. For every colour, the pigments were first grouped, then studied and identified through the main features of their reflectance spectra (the position of maxima, minima and inflection points), comparing with the spectra of our reference data chart and with other published reflectance spectra [13-15]. For every colour or group of colours, the spectra were first treated by Principal Component Analysis in order to explore possible similarities. Then, the spectra were classified by Hierarchical cluster analysis according to Pearson correlation coefficient.

First of all, because one of the most characteristic colour in Suntei's work was blue, all DRS measurements related to blue, greenish blue and green colours were treated together by multivariable analysis (in Fig. 2 we can see that many green measurements are very close to the blue ones) (see Fig. 1S in the supplementary material). Most of the blue areas were grouped in one cluster (21 points) (cluster BC1), whose spectra have the reflectance maximum between 450 and 470 nm (Fig. 4). When the blue colour was lighter, a broader peak was observed, with a shifting of the maximum to higher wavelengths, from 450 to 470 nm (see sample 59NV in Fig. 4). In the spectra of this group, there were no minimum of reflectance, with a nearly horizontal profile at wavelengths higher than 600-610 nm. The absence of any characteristic minimum band of reflectance (none of those minima included in the main Japanese blue pigments: azurite-640 nm, indigo-660 nm, dayflower blue-590 & 644 nm, ultramarine blue-600 nm, or smalt-545, 600 & 640 nm [4, 10, 13-15]) led to identify the pigment through a process of elimination. Consequently, considering the main features of the reflectance spectra, the most important blue pigment was identified as Prussian blue in these woodblock prints, specially used to obtain dark and medium blues, and recognised in every page of the series. Prussian blue, *bero*, *bero-ai*, or *beroin*, is an artificial pigment (a ferric ferrocyanide, $Fe_4(Fe(CN)_6)_3.xH_2O$), firstly made in Germany at the early 18th century and already known in Japan by the last half of the 18th century, but it was increasingly available and used also in printings during the 19th century, from the late 1820s especially by Katsushika Hokusai (1760-1849) and his school [2, 3, 8, 9, 31].

Another blue pigment used in Japanese printing was indigo. Indigo, *ai*, an organic colorant whose blue constituent is indigotin ($C_{16}H_{10}O_2N_2$), is extracted from several species of plants. Although it is unknown which plant or plants were the source of this colorant in Japan, it was the responsible of a common blue in Japanese paintings, used as early as in the 8th century AD and identified in works until the 19th century [2, 8]. We have confirmed this colorant in one blue (74DC) of December triptych, because of the reflectance minimum (apparent-absorbance maximum) at 660 nm of its spectrum [14] (see Fig. 5). However we suspected the presence of indigo in mixtures with other pigments in several printed pages. The Hierarchical classification highlighted a second group (5 points) of very-light blues (see cluster BC2 in Fig. 1S), the reflectance spectra showed a minimum band at 660 nm, and the maximum of reflectance was between 510 and 530 nm (see sample 66NV in Fig. 5). The minimum band at 660 nm confirmed the presence of indigo, but the maximum band (510-530 nm) was shifted to higher wavelengths (maximum at 500 nm in the reference indigo spectrum).

The third cluster observed in the Hierarchical classification was also a group of six light-blue areas (cluster BC3 in Fig. 1S). The spectra had a maximum of reflectance at 500 nm and a minimum broad band at 670 nm (see sample 54NV in Fig. 6). In these areas, the reflectance behaviour seemed to correspond to mixtures of Prussian blue and indigo, with a band of minimum reflectance around 670 nm (see the spectrum of a mixture of Prussian blue and indigo in Fig. 6). Similar reflectance spectra had been also confirmed to be a mixture of indigo and Prussian blue in the study of two paintings by Hokusai in the Freer Gallery of Art by Fibre Optics Reflectance Spectroscopy (FORS) [7].

The fourth and fifth groups (4 and 8 points) (clusters BC4 and BC5, Fig. 1S) of the Hierarchical classification corresponded to areas of very-light blue and very-light greenish or greyish blue colours. The spectra had the reflectance maximum at 530-540 nm and 560-570 nm, respectively, and again a broad band with a minimum at 660-670 nm (see samples 15FB and 35MZ in Fig. 7). These features supported again the use of mixtures of Prussian blue with indigo, and the use of white and black pigments to prepare lighter and greyish colours.

In order to explore whether these spectra with a broad band of minimum reflectance around 670 nm could be mixtures of Prussian blue and a second blue pigment, the reflectance signals were also compared with those obtained in the 20th-century pigments sampled from the woodblock (see this spectrum compared with two light blue samples, 54NV and 66NV, in Fig. 8a). In this case, the reflectance-spectra response of blue was similar, repeating the maxima shifting to higher wavelengths (to 500 nm) when the colour became lighter and a minimum band around 670 nm. EDS analysis showed that the elements in the blue pigment were Fe, and especially Zn and O (Fig. 8b). Then, the use of blue copper pigments was excluded in these samples. The presence of Zn corresponded to the use of zinc oxide (zinc white, ZnO) to prepare white pigments or to lighten colours in these 20th-century samples (see bottom inset in Fig. 8b). Sulphur traces in the same EDS spectrum (see top inset in Fig. 8b) came to the presence of the white pigment. Zinc oxide dates from the end of the 18th century as white pigment, but it was introduced in Europe especially in the 19th century. Its presence caused also the reflectance suppression at wavelengths less than 400 nm (see 20th c.-sample spectrum in Fig. 8a), because of its strong ultra-violet absorbance. The presence of Prussian blue can be confirmed, but the use of another organic pigment cannot be verified.

Therefore, Prussian blue and indigo have demonstrated to be the most important blue pigments in Shuntei's prints. Among other blue pigments, ultramarine blue was identified by its reflectance spectrum with a minimum at 610 nm [13-15] only in the decoration of the table of contents, but not in the twelve-months pages. Ultramarine, *ruri*, is a complex sulphur-containing sodium aluminium silicate. In this case, the pigment was possibly the artificial version, firstly made in France in the 19th century, so probably imported, and also found in 19th-century Japanese paintings [2]. The fact that this pigment was only used in the table of contents and not in the main pages demonstrates that it was not considered an important pigment at that moment.

The last three clusters in the first Hierarchical classification corresponded to three groups of green areas. One of them with 5 points included dark green colours (cluster GC1 in Fig. 1S). The spectra had the reflectance maximum at 520 nm, and no minimum band can be confirmed (Fig. 9). Green colour could be related to the use of malachite, in the form of dark green. Malachite, *rokushō* (the green basic copper carbonate mineral, $CuCO_3.Cu(OH)_2$), is the common green pigment in Japan and it has been used there continuously from the 7th century to the present day. Then it was used by *ukiyo-e* artists throughout the period. However other green, copper-containing compounds have been also found in Japanese paintings, especially in those dating after the late 17th century [2]. The green spectra in Shuntei's work did not seem to have a reflectance minimum at 800 nm like in malachite mineral. Their behaviour is more similar to that of verdigris (an artificial copper acetate of varying composition) (see Fig. 9), whose preparation by application of vinegar to copper was known in the 19th and early

20th centuries in Japan [2]. However, other mineral copper pigments also show reflectance bands similar to verdigris and cannot be easily distinguished from it [14]. In addition other artificial copper pigments could be available in Japan during Shuntei's prints edition, like emerald green (a copper aceto-arsenite, $3Cu(AsO_2)_2.Cu(CH_3COO)_2$), a synthetic pigment firstly produced in Germany at the early 19th century and very popular in paintings at the end of that century in Europe. Therefore, a variety of artificial copper greens were accessible in Asia at the end of the 19th century, and few definite conclusions on Shuntei's green pigments can be drawn until further investigations are closed.

Among these last three groups, the most numerous cluster had 12 points of green and greyish-green areas (cluster GC2 in Fig. 1S). In this group, the maximum of reflectance appeared at 530-540 nm and the broad minimum band was at 670 nm (see samples 53NV and 5EN in Fig. 10). The spectrum features were very similar to that of some very-light blues (see sample 15FB in Fig. 10 and in Fig. 7); the only minor difference was that the first inflection point of the maximum was slightly clearer (at 470 nm). Then, the presence of a mixture of pigments is supposed, probably Prussian blue, indigo and a yellow pigment.

Finally, the last cluster (4 points) of light-green colour (cluster GC3 in Fig. 1S) had spectra with the maximum of reflectance at 540 nm (see sample 36EN in Fig. 11), but the slope of this peak at lower wavelengths was steeper, with the inflection point at 490 nm, causing a non-symmetric maximum. The spectrum features were very similar to those of a mixture between Prussian blue and a yellow pigment (see the spectrum of a mixture of Prussian blue and gamboge in Fig. 11), it maintained the position of the inflection point of the yellow spectrum and the features of the blue band.

The second chemometric classification using Hierarchical clustering was performed with red, orange-red and orange colours (see Fig. 2S in the supplementary material). Shuntei used the red as one of the principal colours, specially for cloths and details. Red was mainly obtained by using vermilion (its reflectance spectra is a sigmoid with the inflection point at 600 nm), a traditional red pigment in Japanese artworks (see sample 43MZ in Fig. 12). This pigment is present in every month; the main cluster included 23 red measured areas (cluster RC1 in Fig. 2S). Vermilion, *shu*, or cinnabar, *shin-sha*, is a red mercuric sulphide, α-HgS. The synthetic form of vermilion, prepared by two methods (the dry process and the wet process), appears in paintings as bright red. In Japan production of dry-process pigment is known to have begun at the early 17th century. Vermilion was used as a pigment in Japan from the 8th century on, and it was commonly used on paintings during the whole of the *ukiyo-e* period [2].

In some of the series months (a second group of six points, cluster ORC2 in Fig. 2S), orange-red colour spectra showed a shifted inflection point at 590-580 nm (see sample 46OC in Fig. 12), this fact led to suppose whether a mixture of vermilion with small quantities of red lead (characteristic inflexion point at 570 nm [13-15]) was used, another traditional inorganic red material. Red orange in several details in the triptychs was obtained using probably vermilion and red lead. Red lead, *entan* or *tan*, artificial lead tetroxide, Pb_3O_4, appears on the Japanese paintings as a bright orange-red, or sometimes as a dull orange. The earliest known use of red lead pigment in Japan is on late-7th-century wall paintings, and it was used throughout the *ukiyo-e* period [2].

The third group of this second classification is a cluster of nine light-orange and orange areas (cluster OC3 in Fig. 2S). The spectrum profile is shown in Fig. 13 (see sample 21FB). The reflectance increased with two different inflection points, at 470-480 and 570 nm. In this colour a mixture of orange and yellow pigments is proposed, similar at that explained later on about orange-yellow cluster.

Some ochre and brown hues were also present in these Japanese prints: from orange-brown to dark brown, whose features were related to the use of yellow, red, and brown earths, with colours due to different iron oxides (ten areas were analysed). Two examples of these spectra are shown in Fig. 14 (samples 8JL and 49 OC), they presented a profile related to the irregular increasing of reflectance in iron-oxides compounds (see two references in Fig. 14).

Other colours and hues included in Shuntei's series were orange-yellow and yellow. The term *shiō* is a Japanese general word for yellow colour. The traditional organic yellow on Japanese paintings was probably gamboge, *tō-ō* or *gambōji*; it is a yellow gum resin, obtained from trees of the genus *Garcinia* throughout South and Southeast Asia. Orpiment, *sekiō*, is the yellow arsenic sulphide, As_2S_3, a naturally occurring mineral, and realgar, *yūō*, is the red to orange arsenic sulphide, α-AsS, that occurs with orpiment. Also, the manufacture of artificial orpiment is documented, indicating that it was already made in Japan in the Edo period [2]. Following on from the Hierarchical classification of DRS measurements, these colours were divided into two clusters (see Fig. 3S in the supplementary material): one including 10 yellow areas (cluster YC1) and a second group with 5 orange-yellow points (cluster YC2) (see samples 63NV and 27AG, respectively, in Fig. 15). The spectral responses of yellow regions in the prints were similar to those of gamboge and arsenic sulphide (see the reference spectra in Fig. 15), a sigmoid with an inflection point at 500 nm. Some orange-yellow areas had spectra with two clear inflection points at 490-500 nm and 550-560 nm. Even spectra from yellow regions seemed to have also a second inflection point (see sample 63NV in Fig. 15). This spectral behaviour led to suspect a mixture of pigments, probably because of the presence of two, less expensive, synthetic arsenic sulphides (realgar spectrum is also a sigmoid with an inflection point at 560 nm, see reference in Fig. 15), although the use of an organic yellow mixed with an orange pigment was not totally excluded. A documented multi-analytical study of Japanese woodblock prints, dated between the very end of the Edo period and the middle of the Meiji period (1864-1887), showed a widespread use of arsenic sulphides for yellow and green coloured regions (the latter obtained by mixing Prussian blue to the yellow arsenic sulphides) [32].

The possible use of synthetic arsenic sulphides in Shuntei's prints was also supported by the results found in micro-samples of orange-yellow pigments taken from the 20th-century woodblocks. Orange-yellow pigments showed analogous reflectance spectra with two inflection points at 500 nm and at 580 nm (Fig. 16a). During the FESEM observation, the pigment appeared as irregular particles whose semi-quantitative composition has an average sulphur content of 54 ± 2 wt% and arsenic of 40 ± 3 wt%, consistent with that of arsenic sulphide pigments, but without the foliated structure of natural orpiment (see Fig. 16b).

Finally, the last group of colours treated by multivariable classification was that of pink, violet and purple areas in order to highlight significant differences (see Fig. 4S in the supplementary material). The samples were classified in five clusters, and two couples of areas remained as outliers. In several small details of the series designs, bright pink or fuchsia colour was applied; they corresponded to a cluster with 4 samples (cluster PiC1 in Fig. 4S). In their spectra (see sample 35EN in Fig. 17), the minimum at 530 nm, with a small shoulder at around 500 nm, led to detect the use of a synthetic pigment, eosin (see also its reference spectrum in Fig. 17), already arrived to Japan before the end of the 19th century [33]. Eosin was obtained in 1873 by full bromination of the hydroxyl-phthalein dye fluorescein and the pigment could be prepared as different eosin-derived lakes [34]. Pink and violet colorations were typical of Meiji period prints and they were made possible by inks based on synthetic dyes imported from Europe [20, 33]. Also a second cluster with 6 light-pink areas (cluster PiC2 in Fig. 4S) showed spectra with a minimum of reflectance at 530 nm (see sample 56NV in Fig. 17), but in this case the shoulder at 500 nm was not so clear. In this second group, the eosin was probably mixed with a white pigment to prepare light-pink colour.

In fact, the last studied colours in Shuntei's prints were purple and violet, distributed in three clusters. In this case, the use of several organic pigments was confirmed to obtain these colours. In some violet areas (one group with 9 samples, cluster VC3 in Fig. 4S), the minima in the reflectance spectra seemed to belong to a synthetic violet, with two apparent absorbance maxima (reflectance minimum) at 530-540 nm and 590 nm (see sample 1EN in Fig. 18). The pigment was not yet identified, it is probably a mixture of pink-red (eosin?) and blue.

Another cluster with four dark violet areas (cluster VC4 in Fig. 4S) was highlighted with reflectance spectra with a minimum at 560 nm, and a shoulder at 530 nm (see sample 27EN in Fig 18). This colour could be prepared with a mixture of red pigments (fuchsine-eosin) and probably a black pigment to become darker.

Moreover, in four cases (last cluster of dark-purple colour, cluster PuC5 in Fig. 4S) the use of a mixture of red and blue pigments to obtain the colour was not ruled out, because mixtures of indigo and red pigments have been also found in some Japanese prints [8]. The spectra of this group had a minimum band around 550 nm,, the reflectance maxima at 450 nm, and a inflection point at 585-595 nm (see sample 35SP in Fig. 19), very close to the inflection point of vermilion, at 600 nm. This is the case of a mixture of a blue pigment (Prussian blue) with a red one (vermilion).

Finally, the spectra measured in two purple areas (cluster PuC6 in Fig. 4S) showed a broad band (530-600 nm) of minimum reflectance centred around 570-580 nm (see sample 70JN in Fig. 20). According our reference database, the spectrum was similar to those of methyl violet and crystal violet (see reference spectra in Fig. 20). For instance, the SERS spectrum obtained in a purple region of a print by Kunichika, dated to 1892, matched that of crystal violet, N-hexamethylpararosaniline, or methyl violet (a mixture of crystal violet with the tetra- and penta-methyl homologues, not easily distinguished by SERS from crystal violet); both pigments were equally possible because methyl violet was patented in 1861 and crystal violet in 1883 [20]. Diffuse reflectance spectra acquired in the same location than SERS spectrum during the cited study [20] had also a minimum band around 580 nm and the same shape than Shuntei's purple pigment. Purple shades seem to have been the first access of synthetic dyes into prints ca. 1864-65; the dyes used were the arylmethane dyes magenta (mixed with Prussian blue) and methyl violet [33].

4. CONCLUSIONS

The reflectance spectra of more than 190 points sampled throughout the artwork were recorded between 360 and 740 nm, and these spectra contributed to the characterisation and in-depth study of the different existing pigments. The comparison of these spectra with the generated reference database allowed a preliminary knowledge of the pigment composition, which will contribute to the interpretation of the whole HSI datacube. Twenty-two different colour compositions were highlighted throughout the Hierarchical classification of the reflectance spectra. This classification will be the basis for the later treatment of the whole HSI datacube. New spectrum profiles have been defined to support colour references for pigments used to produce woodblock prints.

Although not all the pigments were surely identified, at least about ten pigments were recognised, by means of the chemometric protocol and the comparison of the main features of the spectra (maximum, minimum and inflection points). Some traditional pigments (indigo, vermilion, red lead), used since the late 16th century, were found in Shuntei's prints, but the introduction of new artificial pigments (not only Prussian blue and ultramarine blue, but also synthetic arsenic sulphides, eosin, and methyl violet or crystal violet) was highlighted, confirming the quality of the works edited in the Meiji period. In addition, the use of some mixtures were also confirmed: in the woodblock prints they were prepared mixtures between Prussian blue and indigo to modify the blue hue; also with Prussian blue and yellow pigments (probably gamboge) to give green; between yellow and red-orange compounds (two arsenic sulphides) to give orange-yellow; and Prussian blue and vermilion were used to give purple. Some limitations were observed to identify some of the components in these mixtures, because the database should be improved in some yellow, red and violet components (especially those introduced from the end of the 19th century).

The point-by-point DRS analysis seems to provide more specific data. In contrast, HSI gives more general information which facilitates the representativeness of the results regarding the whole artwork, but the point-by-point spectra make easier the task of interpreting the very complex HSI data, and the results will be improved. Also the preliminary examination by DRS will reduce the time of treatment and interpretation required by HSI data.

ACKNOWLEDGEMENTS

We want to thank the head of the Museum of Zaragoza, who made available the collection of woodblock prints and authorizes us to come regularly for our measurements. D. Almazán wants to thank the financial support of the Ministerio de Economía y Competitividad (Spain), research projects: HAR2014-55851-P and HAR2013-45058-P. Authors would like to acknowledge the use of the FESEM utilities in the Servicio General de Apoyo a la Investigación-SAI, Universidad de Zaragoza.

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LEGENDS (Tables and Figures)

Table 1. Summary of the analytical results obtained by point-by-point diffuse reflectance spectroscopy in the main colours of Shuntei's series (12 months and table of contents, TC) (sh.: shoulder).

Figure 1. November triptych: *Yomeiri* (嫁入), "Wedding" (by Miyagawa Shuntei, 1898-1899). Photo: J. Garrido. Museum of Zaragoza.

Figure 2. Colour parameters measured in Shuntei's prints (CIELab system: b^* vs. a^*) (the names of the different colours correspond to a preliminary classification, previously to the statistical treatment).

Figure 3. Hyperspectral imaging. a) Visible red-green-blue (RGB) image of a section of March triptych: *Sakura gari* (桜が), "Cherry flowers" (R: 640 nm; G: 550 nm; B: 460 nm); b) Infrared false-colour (IRFC) image of the same section (R: 900 nm; G: 650 nm; B: 550 nm).

Figure 4. Reflectance spectrum of reference Prussian blue and some spectra obtained in blue regions of Shuntei's series (samples 12FB and 59NV).

Figure 5. Reflectance spectrum of reference indigo and some spectra obtained in blue regions of Shuntei's series (samples 74DC and 66NV).

Figure 6. Comparison of the reference reflectance spectra of Prussian blue, indigo, a mixture of Prussian blue and indigo, and a blue region of Shuntei's series (sample 54NV).

Figure 7. Comparison of the reference reflectance spectra of a mixture of Prussian blue and indigo, with indigo and two light-blue regions of Shuntei's series (samples 15FB and 35MZ).

Figure 8. Characterisation of a blue 20th-century pigment. a) Comparison of the reference reflectance spectra of a mixture of Prussian blue and indigo, with two blue regions of Shuntei's series (samples 54NV and 66NV) and the spectrum of a 20th c. blue pigment. b) FESEM image of the 20th c. blue pigment, mixed with ZnO (top inset: EDS spectrum; bottom inset: ZnO crystals, x10 magnified).

Figure 9. Reflectance spectra of reference malachite and verdigris, and the spectrum obtained in a green region of Shuntei's triptychs (sample 61MY).

Figure 10. Comparison of the reference reflectance spectra of a mixture of Prussian blue and indigo, with three light-green regions of Shuntei's series (samples 53NV, 5EN and 35MZ).

Figure 11. Comparison of the reference reflectance spectra of a mixture of Prussian blue and indigo, with another one of gamboge and Prussian blue (60:40), gamboge, and a green region of Shuntei's months (sample 36EN).

Figure 12. Reflectance spectra of reference vermilion, red lead, and some spectra obtained in red regions of Shuntei's triptychs (samples 43MZ and 46OC).

Figure 13. Reflectance spectra of reference red lead, realgar, orpiment, and the spectrum obtained in an orange region of Shuntei's series (sample 21FB).

Figure 14. Reflectance spectra of two reference ochres, and some spectra obtained in orange-brown regions of Shuntei's triptychs (samples 8JL and 49OC).

Figure 15. Reflectance spectra of reference realgar, orpiment, gamboge, and the spectra obtained in two orange-yellow regions of Shuntei's series (samples 63NV and 27AG).

Figure 16. Comparison with an orange-yellow 20th-century pigment. a) Comparison of the reference reflectance spectra of realgar and orpiment, with an orange-yellow region of Shuntei's series (sample 27AG) and the spectrum of the 20th c. orange-yellow pigment. b) FESEM image of the orange-yellow pigment, showing the arsenic sulphide particles (inset: EDS spectrum).

Figure 17. Reflectance spectra of reference eosin, and the spectra obtained in two pink regions of Shuntei's triptychs (samples 35EN and 56NV).

Figure 18. Reflectance spectra of reference eosin and fuchsine, and the spectra obtained in two pink-violet regions of Shuntei's series (samples 1EN and 27EN).

Figure 19. Comparison of the reference reflectance spectra of Prussian blue, vermilion, and a mixture of vermilion and Prussian blue (60:40), with the spectrum of purple region of Shuntei's months (sample 35SP).

Figure 20. Reflectance spectra of reference methyl violet and crystal violet, and the spectrum obtained in a violet region of Shuntei's series (sample 70JN).

Table 1. Summary of the analytical results obtained by point-by-point diffuse reflectance spectroscopy in the main colours of Shuntei's series (12 months and table of contents, TC) (sh.: shoulder).

Colour	Pigment	Month triptychs	Diffuse reflectance spectra			Observations
			Maximum (nm)	Minimum (nm)	Inflection point (nm)	
Blue (very dark, dark, light)	Prussian blue	1, 2, 3, 5, 6, 7, 9, 10, 11, 12	450-470	No		In light blue, Prussian blue was probably mixed with a white pigment or prepared as very-fine particles
Light blue	Prussian blue + indigo	2, 4, 6, 11, 12	500	670 (band)		
Very light blue	Indigo	12	490	660 (band)		
Very light blue	Indigo + Prussian blue	7, 10, 11	510-530	660 (band)		
Very light blue	Prussian blue + indigo + white	2, 4, 7	530-540	670 (band)		
Very light greenish and greyish blue	Prussian blue + indigo + ?	TC, 3, 4, 7, 9, 12	560-570	670 (band)		The maxima shifting to longer wavelengths would be related to the presence of a white pigment and a yellow one. The greyish blue could be produced by the addition of indigo or a black pigment
Very light blue	Ultramarine blue	TC	490	610		Probably it is considered a secondary pigment in these prints, then it only appeared in the table of contents
Dark green	Malachite / Copper-containing compounds	3, 5, 6, 7	520	No		Also possible verdigris, or another artificial green pigment
Green and greyish green	Prussian blue + indigo + yellow pigment	1, 2, 6, 8, 9, 10, 11, TC	530-540	670 (band)		The broad minimum at 670 suggests the presence of a mixture with Prussian blue and indigo, but the identity of the yellow contribution cannot be verified with the spectrum feature
Light green	Prussian blue + yellow pigment	1, 3, 5	540	670-690 (band)	490	It would be possible that the yellow pigment was gamboge
Red	Vermillion	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, TC	Sigmoid	--	600	In some cases, probably mixed with a little red lead
Orange-red	Vermilion + red lead	1, 2, 6, 7, 8, 10	Sigmoid	--	580-590	

Orange	Mixture of orange and yellow pigments	2, 4, 5, 12, TC	--	--	470-480 and 570	Probably it is a mixture similar to that proposed for orange-yellow colour
Orange-yellow	Arsenic sulphides	4, 5, 8	(Double) Sigmoid	--	490-500 and 550-560	Probably a mixture of two synthetic arsenic sulphides
Yellow	Arsenic sulphide	1, 2, 3, 5, 6, 11	Sigmoid	--	500 (and 550?)	The use of an organic yellow (like gamboge) was not totally excluded
Ochre/Brown	Iron oxides / red earth	3, 4, 8, 10, 11			570-590	There is a limited use of these pigment in Shuntei's series
Pink	Eosin	1, 2, 4	440-450 (band)	530 and 500 (sh.)		Always used in small details of the design
Light pink	Eosin	1, 3, 4, 8, 11		530		Probably mixed with a white pigment to become lighter
Violet	Synthetic violets / Mixture of red (eosin?) and blue pigments	1, 2, 6, 8, 9, 10, 11	470	530-540 and 590		Specially used in kimono colours
Dark violet	Mixture of fuchsine (?) and black pigment	1, 3, 10	450	560 and 530 (sh.)		
Dark purple	Prussian blue + vermilion	1, 9	450	550 (band)	585-595	
Purple	Crystal violet	6	420	560 and 600 (broad band)		Some addition of blue pigment was not excluded

HIGHLIGHTS

- New analytical insights on Japanese pigments used in woodblocks prints in ukiyo-e style
- Reflectance Spectroscopy, a valuable tool to reduce complexity in the interpretation of hyperspectral imaging.

Figure 1

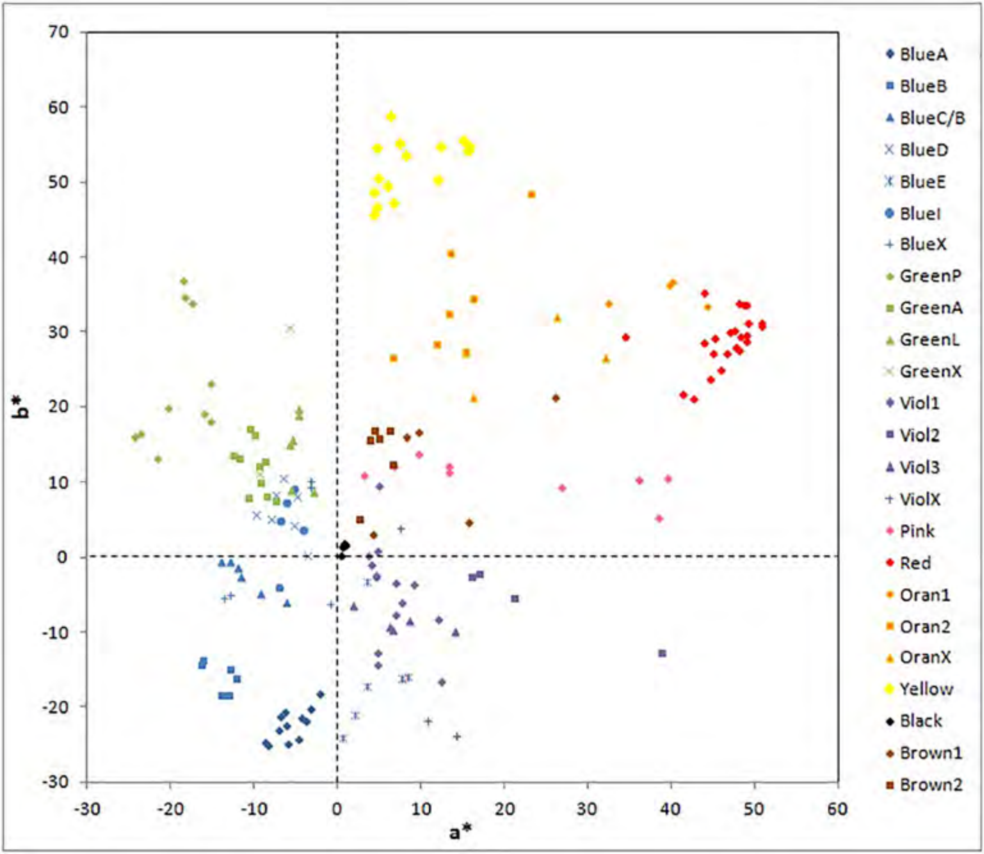
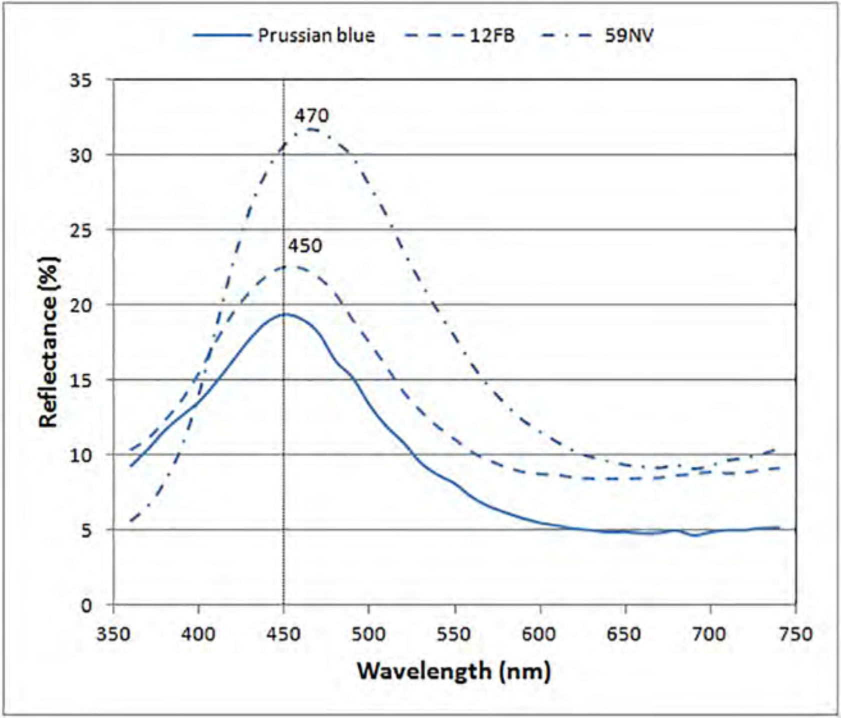

b*
a*
70
60
50
40
30
20
10
0
-10
-20
-30
-30
-20
-10
0
10
20
30
40
50
60
BlueA
BlueB
BlueC/B
BlueD
BlueE
BlueI
BlueX
GreenP
GreenA
GreenL
GreenX
Viol1
Viol2
Viol3
ViolX
Pink
Red
Oran1
Oran2
OranX
Yellow
Black
Brown1
Brown2

Figure 2

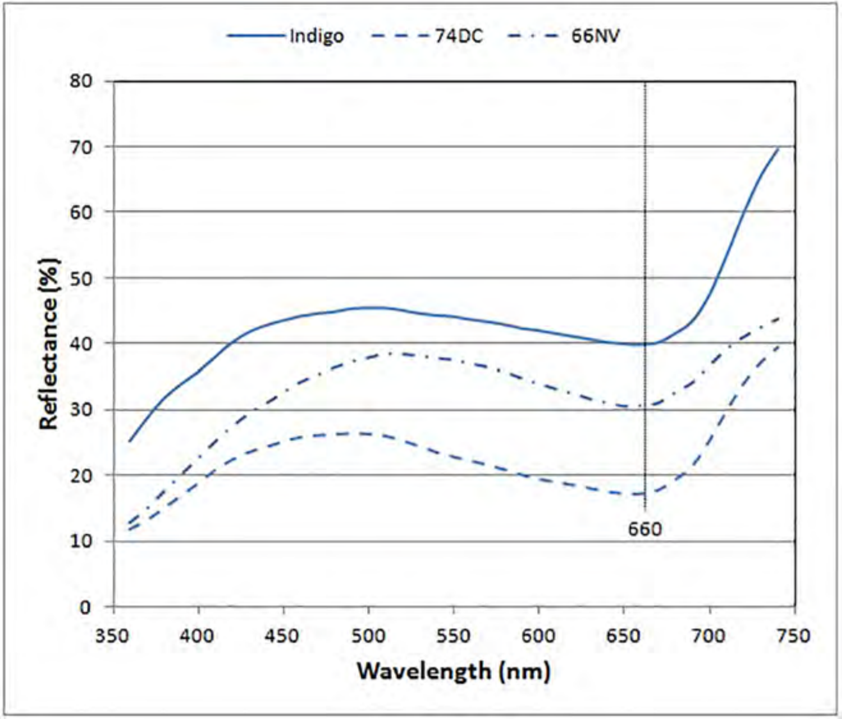
a b

Figure 3



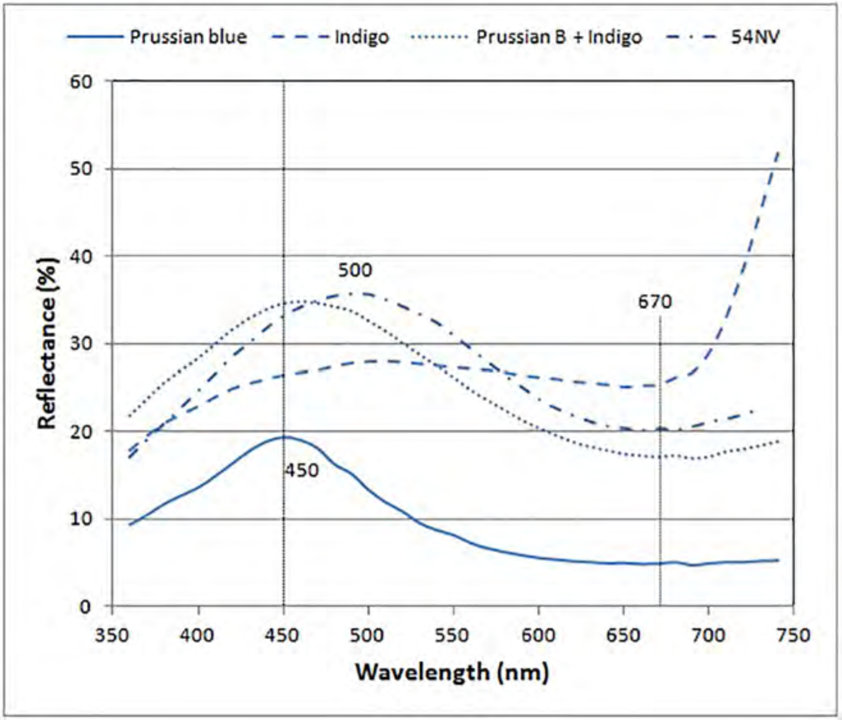
Prussian blue
12FB
59NV
470
450
Reflectance (%)
Wavelength (nm)
35
30
25
20
15
10
5
0
350
400
450
500
550
600
650
700
750

Figure 4



Indigo
74DC
66NV
Reflectance (%)
80
70
60
50
40
30
20
10
0
660
350
400
450
500
550
600
650
700
750
Wavelength (nm)

Figure 5



Prussian blue
Indigo
Prussian B + Indigo
54NV
Reflectance (%)
60
50
40
30
20
10
0
500
670
450
350
400
450
500
550
600
650
700
750
Wavelength (nm)

Figure 6

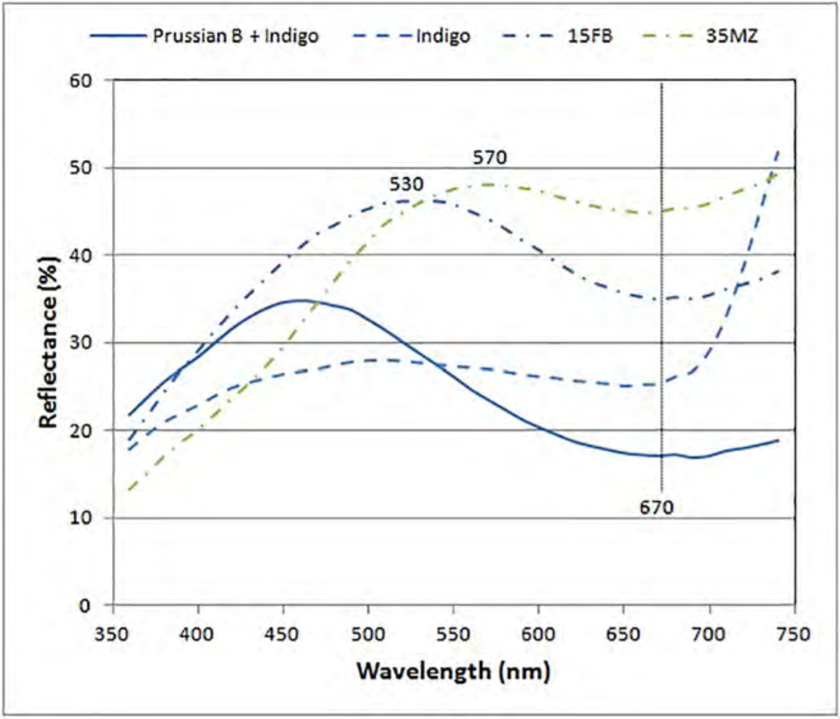
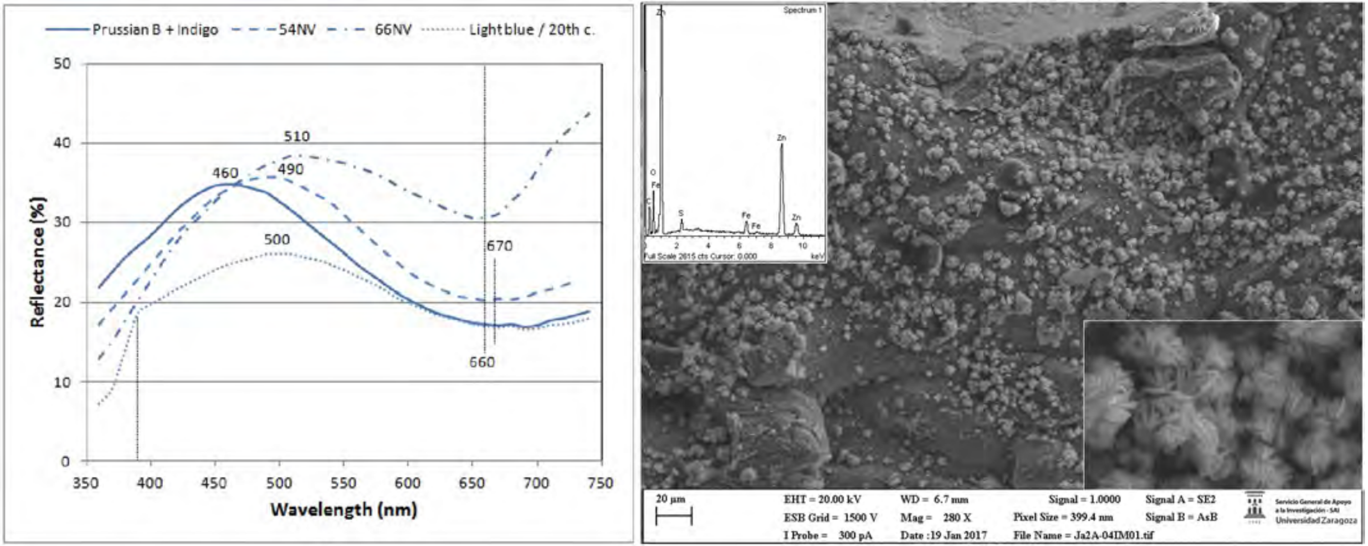

Prussian B + Indigo
Indigo
15FB
35MZ
570
530
670
Reflectance (%)
Wavelength (nm)
0
10
20
30
40
50
60
350
400
450
500
550
600
650
700
750

Figure 7


Prussian B + Indigo
54NV
66NV
Light blue / 20th c.
Reflectance (%)
Wavelength (nm)
510
460
490
500
670
660
50
40
30
20
10
0
350
400
450
500
550
600
650
700
750
Spectrum 1
Zn
O
Fe
C
S
Fe
Fe
Zn
Zn
Full Scale 2615 cts Cursor: 0.000
keV
20 µm
EHT = 20.00 kV
ESB Grid = 1500 V
I Probe = 300 pA
WD = 6.7 mm
Mag = 280 X
Date :19 Jan 2017
Signal = 1.0000
Pixel Size = 399.4 nm
File Name = Ja2A-04IM01.tif
Signal A = SE2
Signal B = AsB
Universidad Zaragoza

a b

Figure 8

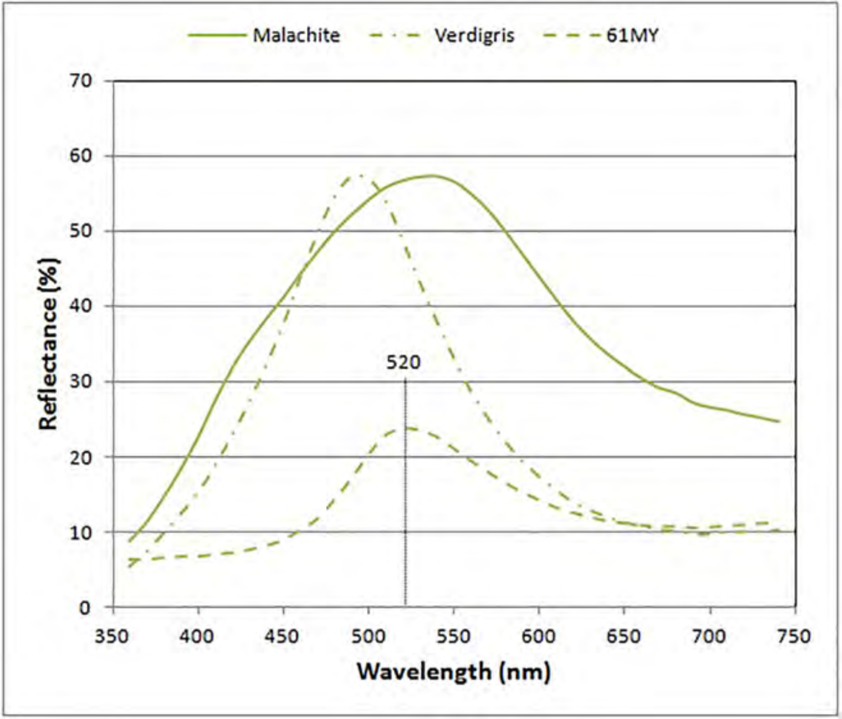

Malachite
Verdigris
61MY
Reflectance (%)
Wavelength (nm)
520
0
10
20
30
40
50
60
70
350
400
450
500
550
600
650
700
750

Figure 9

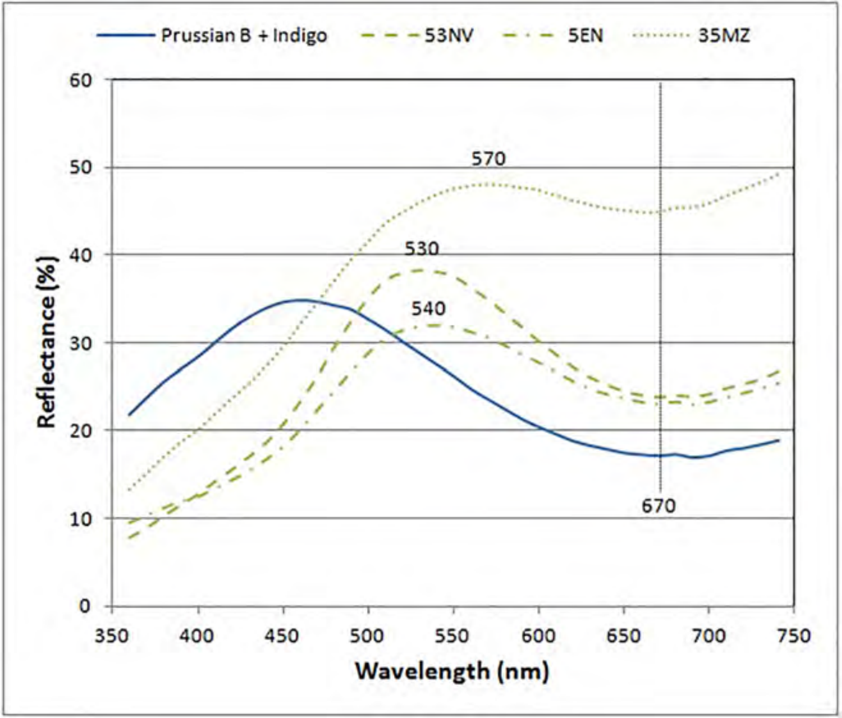
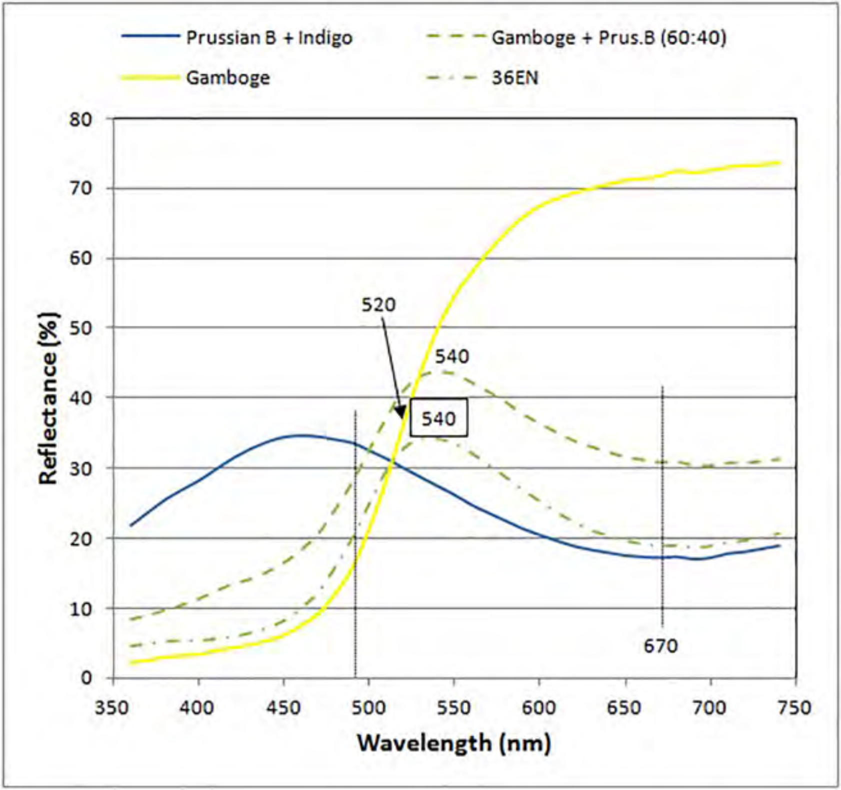

Prussian B + Indigo
53NV
5EN
35MZ
Reflectance (%)
Wavelength (nm)
60
50
40
30
20
10
0
350
400
450
500
550
600
650
700
750
570
530
540
670

Figure 10



Prussian B + Indigo
Gamboge + Prus.B (60:40)
Gamboge
36EN
Reflectance (%)
Wavelength (nm)
0
10
20
30
40
50
60
70
80
350
400
450
500
550
600
650
700
750
520
540
540
670

Figure 11

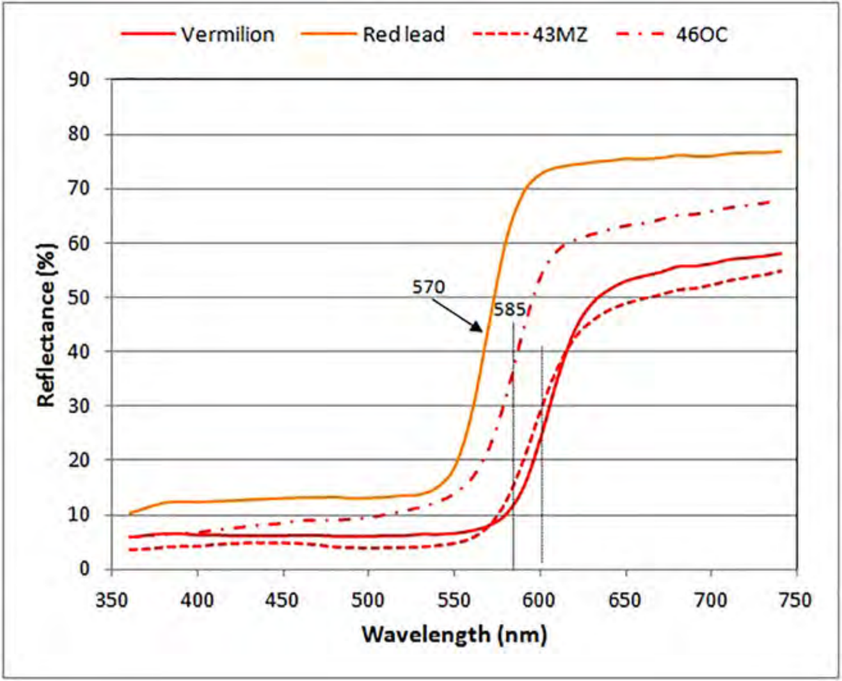
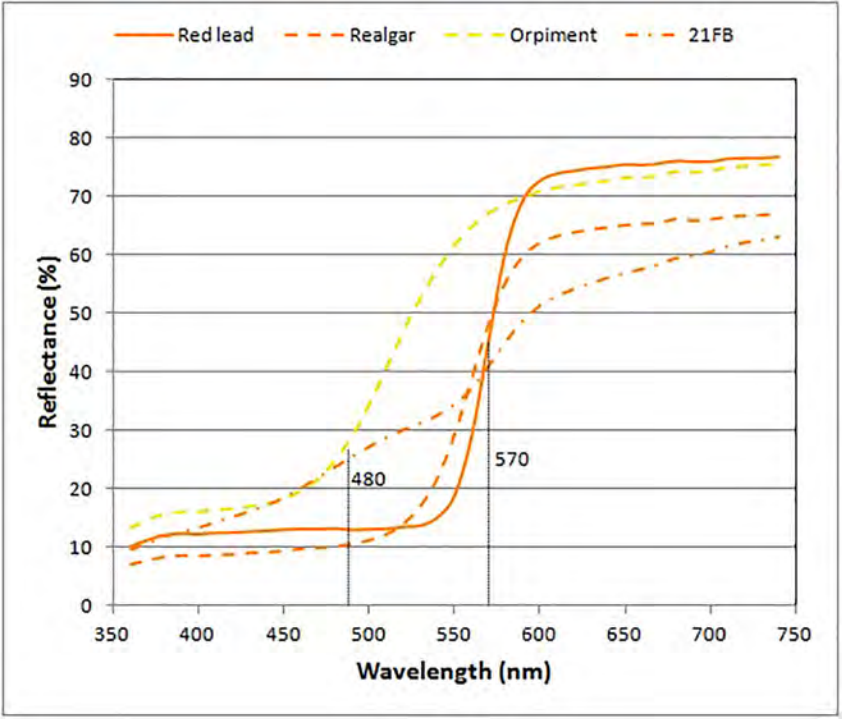

Vermilion
Red lead
43MZ
46OC
Reflectance (%)
Wavelength (nm)
570
585
0
10
20
30
40
50
60
70
80
90
350
400
450
500
550
600
650
700
750

Figure 12



Red lead
Realgar
Orpiment
21FB
90
80
70
60
50
40
30
20
10
0
Reflectance (%)
480
570
350
400
450
500
550
600
650
700
750
Wavelength (nm)

Figure 13

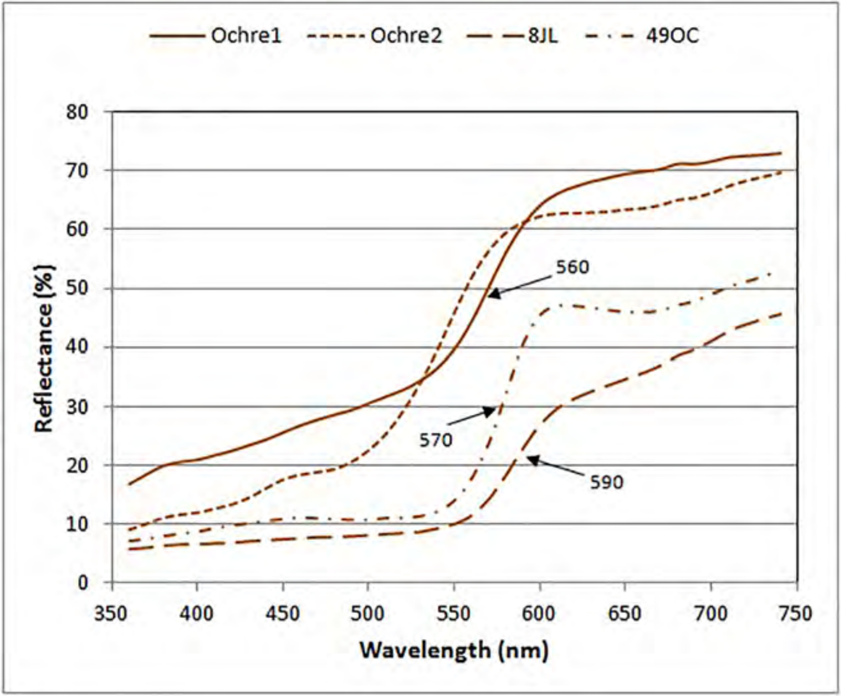

Ochre1
Ochre2
8JL
49OC
Reflectance (%)
80
70
60
50
40
30
20
10
0
560
570
590
350
400
450
500
550
600
650
700
750
Wavelength (nm)

Figure 14

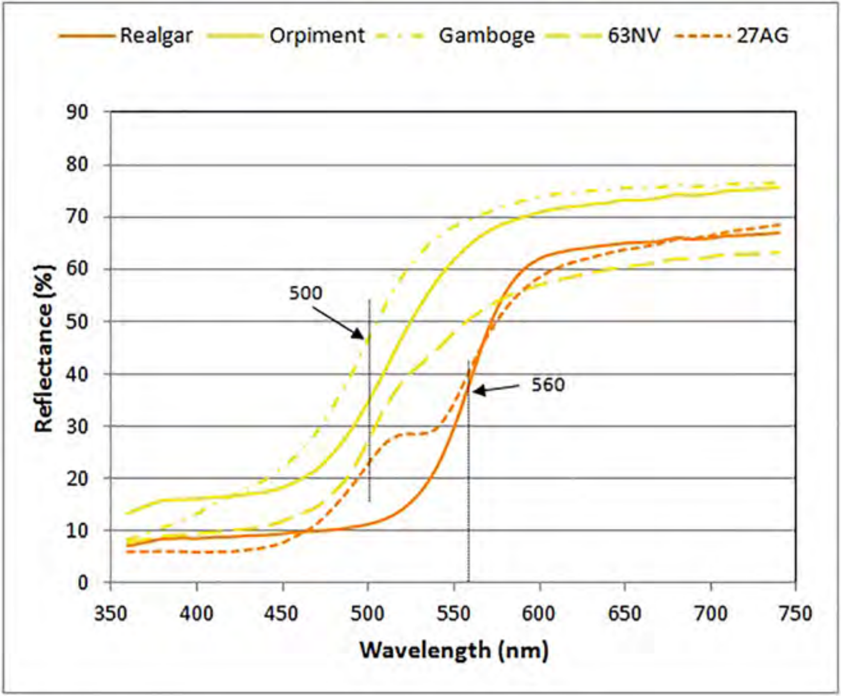
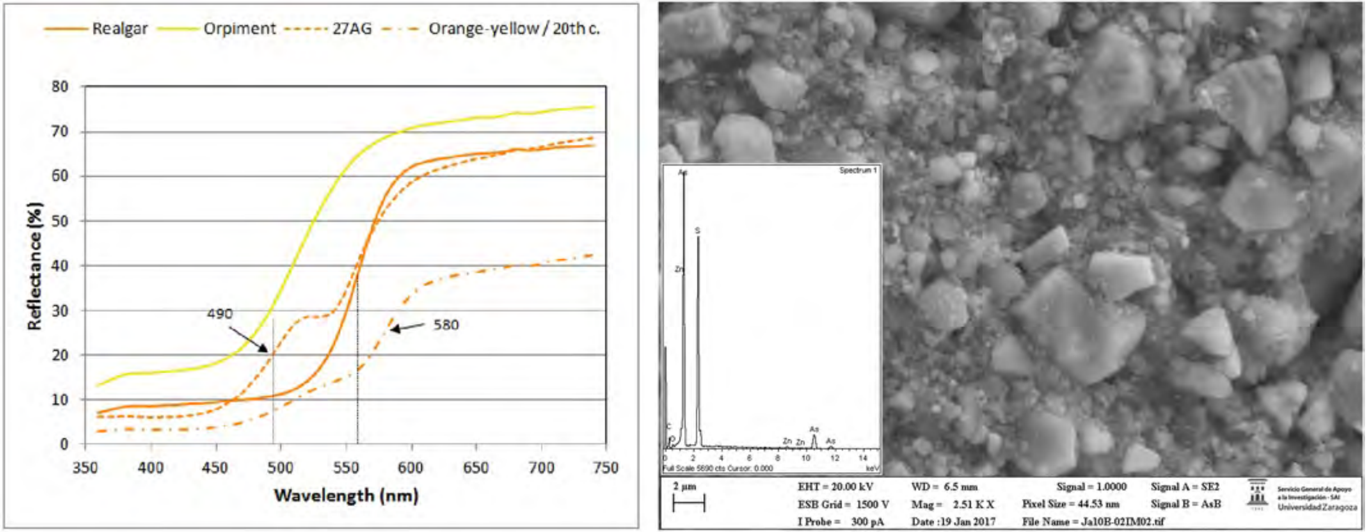

Realgar
Orpiment
Gamboge
63NV
27AG
90
80
70
60
50
40
30
20
10
0
Reflectance (%)
500
560
350
400
450
500
550
600
650
700
750
Wavelength (nm)

Figure 15


Realgar
Orpiment
27AG
Orange-yellow / 20th c.
Reflectance (%)
Wavelength (nm)
490
580
0
10
20
30
40
50
60
70
80
350
400
450
500
550
600
650
700
750
Spectrum 1
As
S
Zn
Full Scale 5690 cts Cursor: 0.000
keV
2 µm
EHT = 20.00 kV
ESB Grid = 1500 V
I Probe = 300 pA
WD = 6.5 mm
Mag = 2.51 K X
Date :19 Jan 2017
Signal = 1.0000
Pixel Size = 44.53 nm
File Name = Ja10B-02IM02.tif
Signal A = SE2
Signal B = AsB
Universidad Zaragoza

a b

Figure 16

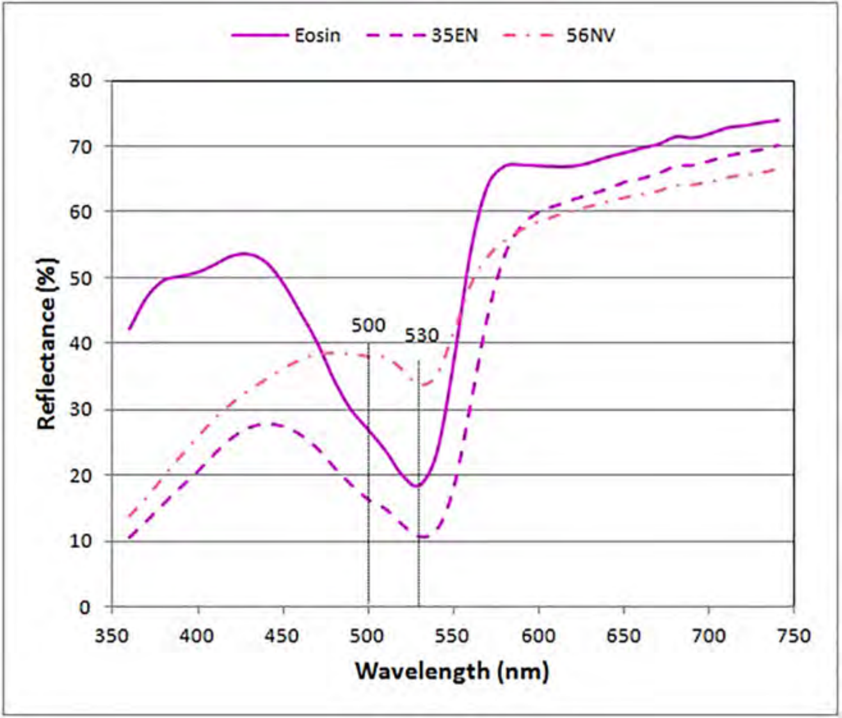
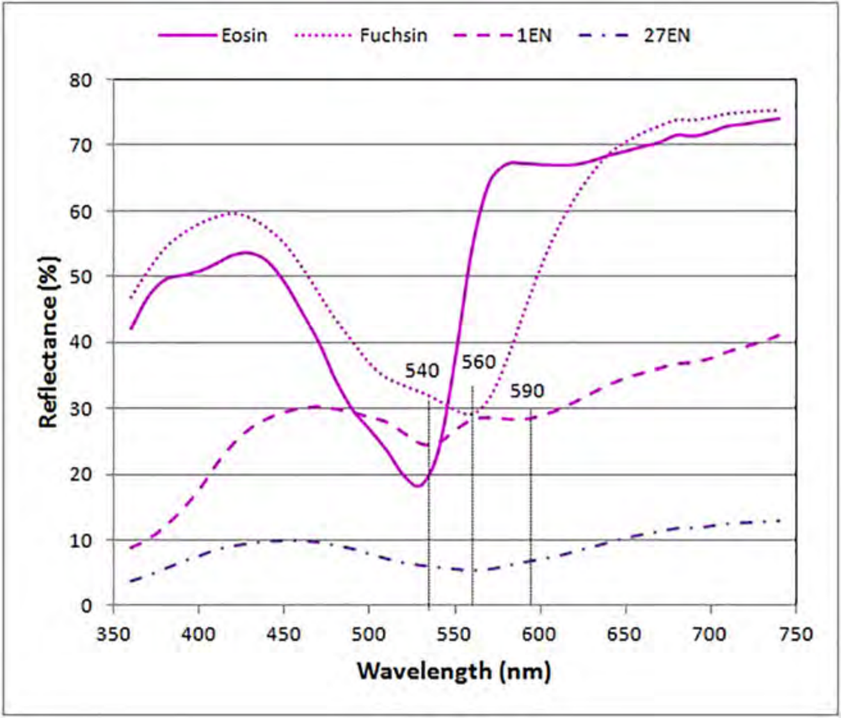

Eosin
35EN
56NV
Reflectance (%)
Wavelength (nm)
0
10
20
30
40
50
60
70
80
350
400
450
500
550
600
650
700
750
500
530

Figure 17



Eosin
Fuchsin
1EN
27EN
80
70
60
50
40
30
20
10
0
Reflectance (%)
540
560
590
350
400
450
500
550
600
650
700
750
Wavelength (nm)

Figure 18

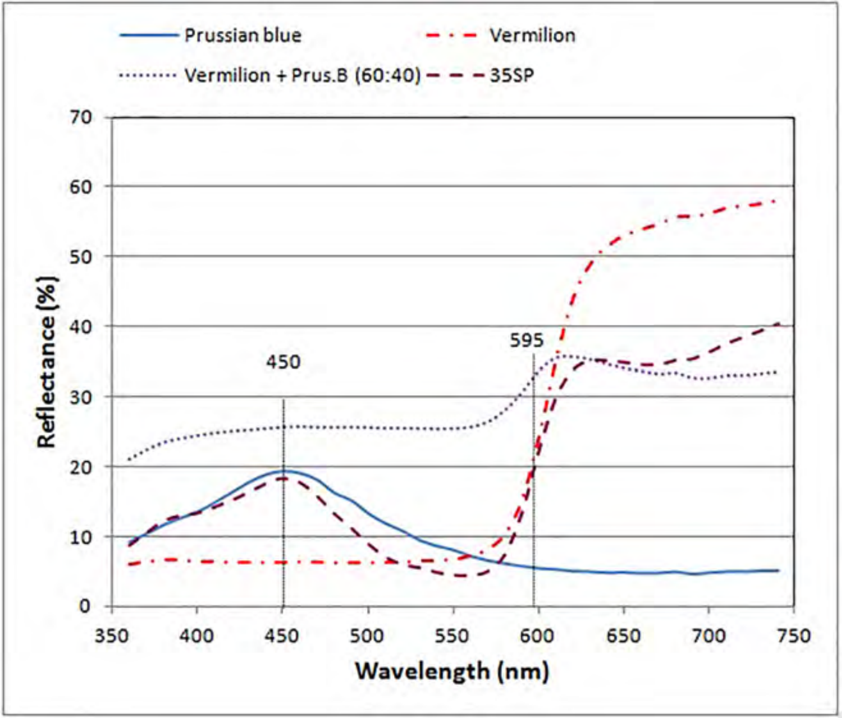

Prussian blue
Vermilion
Vermilion + Prus.B (60:40)
35SP
Reflectance (%)
Wavelength (nm)
450
595
0
10
20
30
40
50
60
70
350
400
450
500
550
600
650
700
750

Figure 19

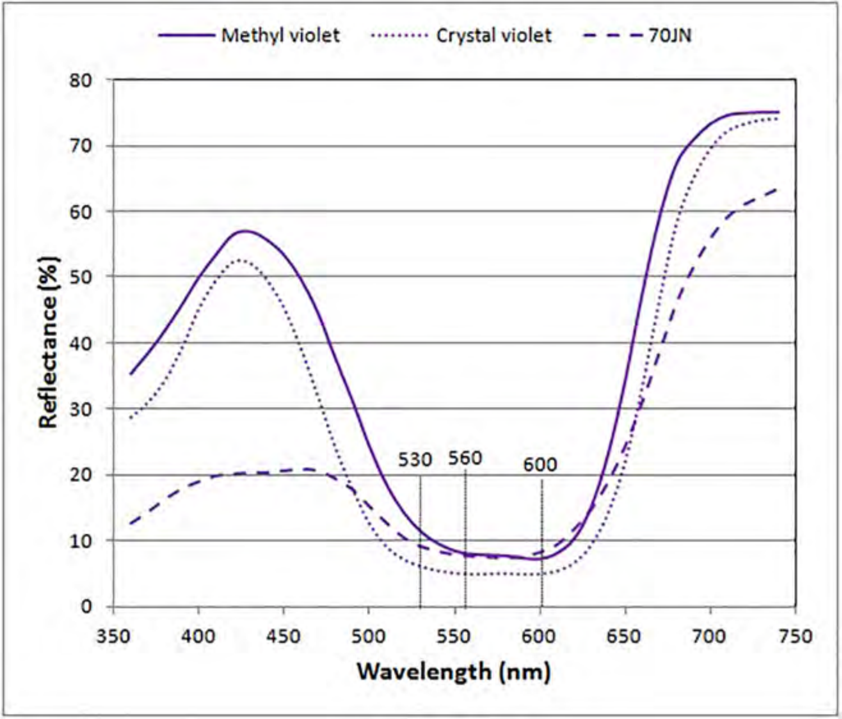
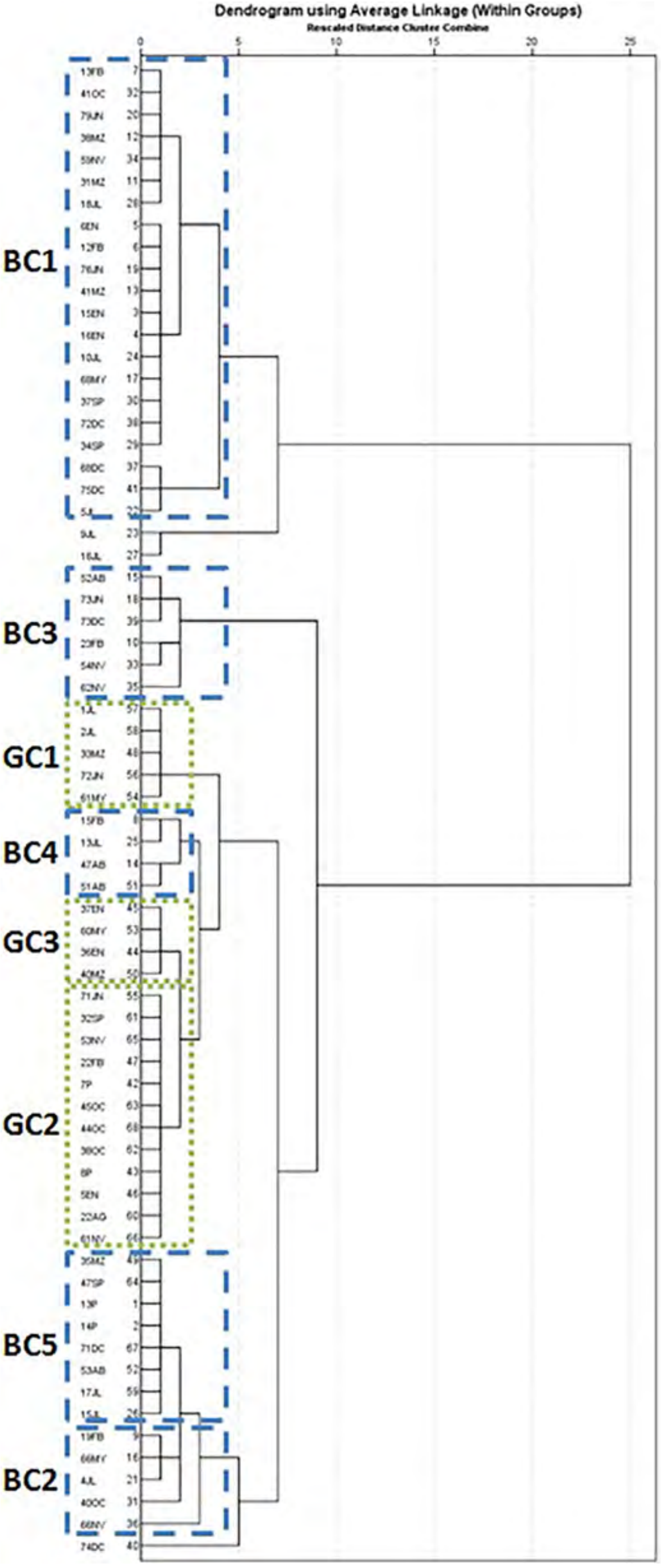
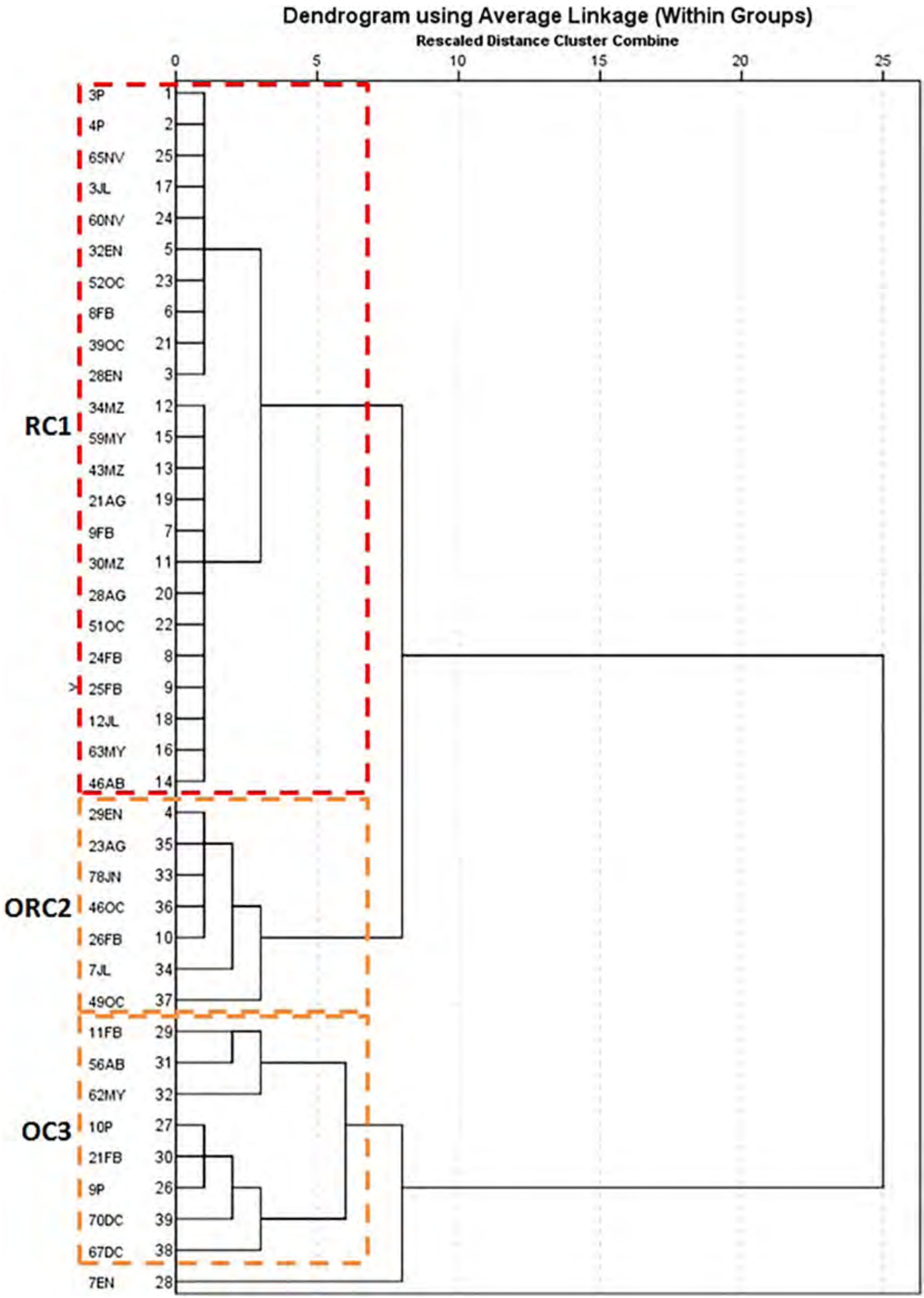

Methyl violet
Crystal violet
70JN
Reflectance (%)
80
70
60
50
40
30
20
10
0
530
560
600
350
400
450
500
550
600
650
700
750
Wavelength (nm)

Figure 20



Dendrogram using Average Linkage (Within Groups)
Rescaled Distance Cluster Combine
0
5
10
15
20
25
BC1
BC3
GC1
BC4
GC3
GC2
BC5
BC2

Figure 21



Dendrogram using Average Linkage (Within Groups)
Rescaled Distance Cluster Combine
0
5
10
15
20
25
RC1
ORC2
OC3
3P 1
4P 2
65NV 25
3JL 17
60NV 24
32EN 5
52OC 23
8FB 6
39OC 21
28EN 3
34MZ 12
59MY 15
43MZ 13
21AG 19
9FB 7
30MZ 11
28AG 20
51OC 22
24FB 8
25FB 9
12JL 18
63MY 16
46AB 14
29EN 4
23AG 35
78JN 33
46OC 36
26FB 10
7JL 34
49OC 37
11FB 29
56AB 31
62MY 32
10P 27
21FB 30
9P 26
70DC 39
67DC 38
7EN 28

Figure 22

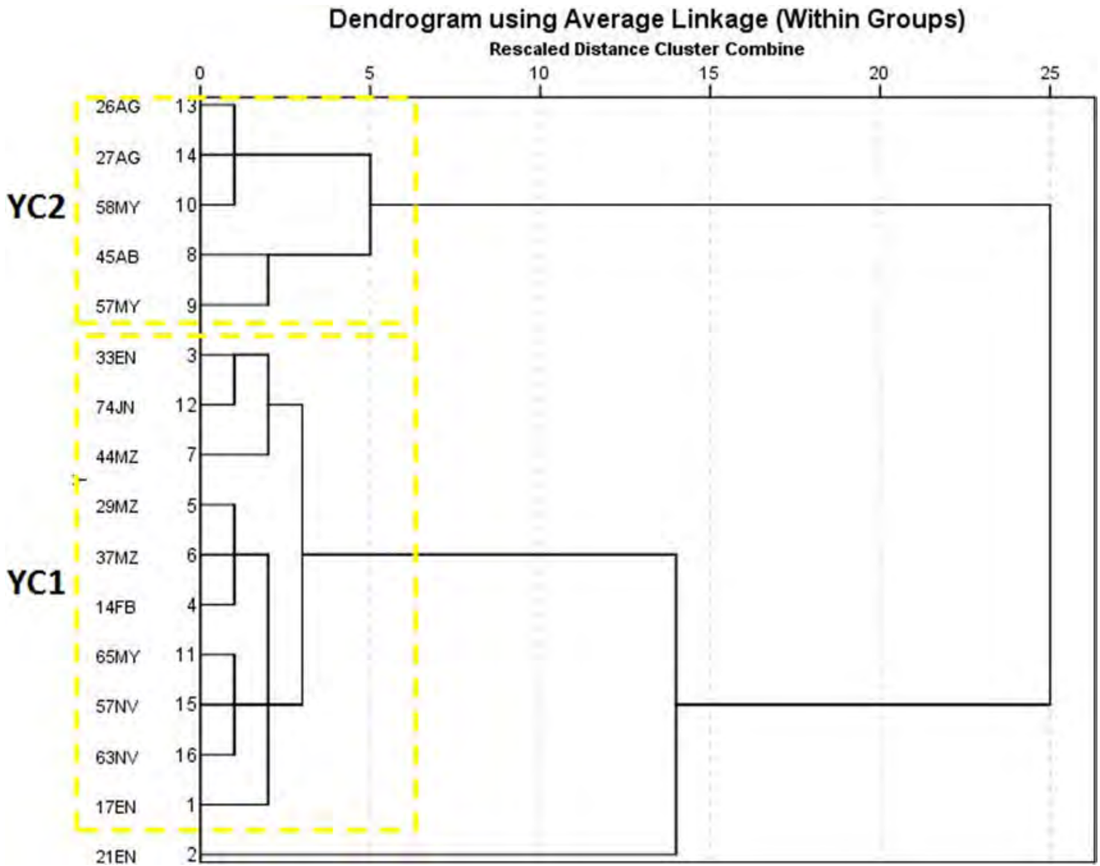
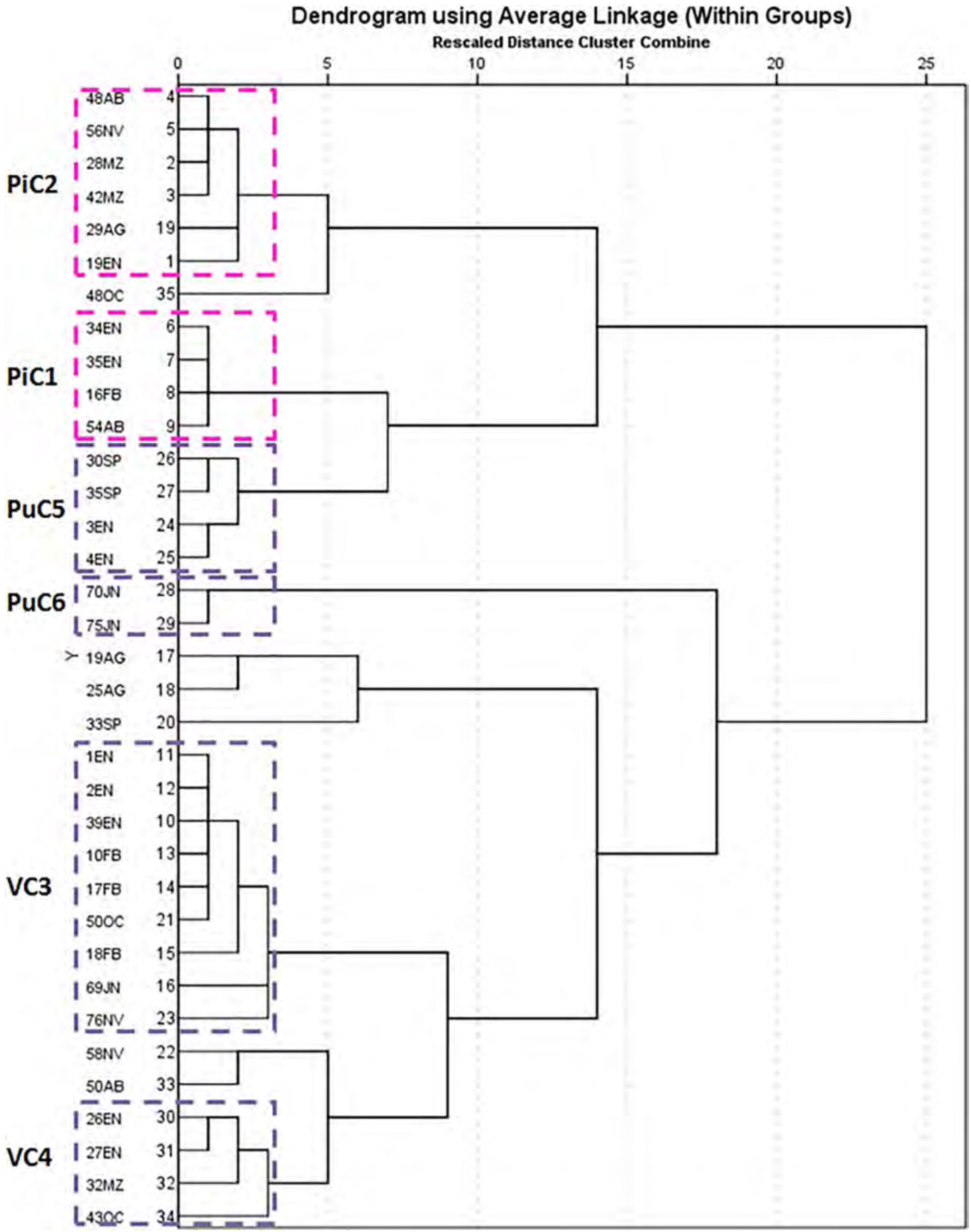

Dendrogram using Average Linkage (Within Groups)
Rescaled Distance Cluster Combine
0
5
10
15
20
25
YC2
YC1
26AG 13
27AG 14
58MY 10
45AB 8
57MY 9
33EN 3
74JN 12
44MZ 7
29MZ 5
37MZ 6
14FB 4
65MY 11
57NV 15
63NV 16
17EN 1
21EN 2

Figure 23


Dendrogram using Average Linkage (Within Groups)
Rescaled Distance Cluster Combine
0
5
10
15
20
25
PiC2
PiC1
PuC5
PuC6
VC3
VC4
48AB 4
56NV 5
28MZ 2
42MZ 3
29AG 19
19EN 1
48OC 35
34EN 6
35EN 7
16FB 8
54AB 9
30SP 26
35SP 27
3EN 24
4EN 25
70JN 28
75JN 29
19AG 17
25AG 18
33SP 20
1EN 11
2EN 12
39EN 10
10FB 13
17FB 14
50OC 21
18FB 15
69JN 16
76NV 23
58NV 22
50AB 33
26EN 30
27EN 31
32MZ 32
43OC 34
Figure 24